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IDENTIFICATION AND QUANTIFICATION OF CHEMICALS OF EMERGING CONCERN (PERSISTENCE ORGANIC AND INORGANIC POLLUTANTS) IN SOME SELECTED MARINE ENVIRONMENTS OF CAPE TOWN, SOUTH AFRICA

By

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KEYWORDS

Bioaccumulation

Cape Town

Chemicals of emerging concern

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Endocrine disrupting compounds

Fish

Gas chromatography-mass sectrometry

Herbicides

Human health risk

Hydrophilic-lipophilic balance

Inductively Coupled Plasma Optical Emission Spectrometry

Industrial chemicals

Liquid chromatography-mass sectrometry

Marine biota

Marine environment

Marine organisms

Metals

Perfluorinated compounds

Pharmaceuticals and personal care product

Pollutants

Risk assessment

Seawater

Seaweed

Sediment

Solid phase extraction

ABSTRACT

The increasing evidence of chemicals of emerging concern (CECs) in water bodies is causing major concern around the world because of their toxicological effects upon humans and aquatic organisms. The release of wastewater to the aquatic environment is most likely to introduce some trace levels of organic contaminants, some of which may be toxic, carcinogenic, or endocrine disruptors, as well as, persistent in the environment. These compounds are often persistent but not regularly monitored because they are mostly still excluded from environmental legislation. Their fate and persistence in the environment are not well understood.

Additionally, increasing contamination of marine ecosystem due to the inability of wastewater treatment plants to remove these contaminants have become a global issue. The presence of these pollutants in the marine ecosystem may have negative effects on marine biota and often pose potential human health risks through consumption of contaminated seafood.

Why this study focused on the identification and quantification of chemicals of emerging concern is because of the very large volumes of untreated sewage discharged into the marine in the marine environment of Cape Town including Kalk Bay, Green Point, Camps Bay and False Bay. Solid phase extraction (SPE) method based on Oasis HLB cartridges were used to concentrate and clean-up the samples for 16 target chemical compounds (pharmaceuticals and personal care products, perfluorinated compounds and industrial chemicals) using Liquid chromatography–mass spectrometry analysis. A miniature QuEChERS (**Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged and **S**afe) method was used to extract herbicides samples and analyse them using Gas chromatography–mass spectrometry

analysis. Metal extraction was carried out using acid digestion method followed by inductively coupled plasma - optical emission spectrometry. These analysis were done on selected commercially exploited, wild caught small and medium sized pelagic fish species (*Thyrsites atun, Sarda orientalis, Pachymetopon blochii* and *Pterogymnus laniarius*) obtained from Kalk Bay harbour only as well as on seawater, sediments and marine biota samples sea (*Ulva* sp., *Codium fragile, Gelidium pristoides, Bifurcaria brassicac formis, Caulerpa filiformis, Aeodes Orbitosa, Oxystele sinensis, Oxystele tigrina, Cymbula granatina, Marthasterias glacialis, Mytilus galloprovincialis* and *Parechinus angulosus*) sampled from Green Point, Camps Bay and False Bay.

The results revealed that perfluorodecanoic acid, perfluorononanoic acid and perfluoroheptanoic acid were the most predominant among the perfluorinated compounds. They were discovered at concentration ranges of 20.13-179.2 ng/g, 21.22 - 114.0 ng/g and 40.06 -138.3 ng/g respectively, measured from dry weight (dw) of fish species and their organs. Also diclofenac had the highest concentration in these edible fish species out of all the pharmaceuticals detected (range: 551.8 – 1812 ng/g). The concentration detected for herbicides in the fish samples ranged from atrazine: not detected (nd) to 65.87 ng/g dw, simazine: nd to 157.82 ng/g dw, alachlor: nd to 47.44 µg/g dw, metolachlor: nd to 94.30 ng/g dw and butachlor: nd to 8.52 ng/g dw. The heavy metal concentrations found in fish tissues varied for Cu: 18.0 – 131.0, Zn: 105.6 – 234.5, Mn: 2.12 – 10.3, Fe: 362.6 – 443.9, Cr: nd – 11.5, Co: 0.6 – 3.7, Ni: 9.9 – 26.5, Sr: 71.6 – 687.7 and Nb: 418.3 - 420.9 mg/kg dry weight. Cd was not detected in any tissues of the fish species all in dry weight.

The results observed from Green Point samples showed that all the PFCs were dominant in seawater (0.01 – 1.06 ng/ L), sediment (0.65 – 3.51 ng/g dry weight (dw)), benthic

organisms (0.15 – 12.72 ng/g dw) and seaweed samples (0.19 – 1.94 ng/g dw). Pharmaceuticals and personal care product ranged from: seawater (0.07 – 4.79 ng/L), sediments (0.79 - 4.48 ng/g dw), benthic organisms (0.38 - 10.72 ng/g dw) and seaweed (0.51- 6.60 ng/g dw). Bisphenol A was the most dominant compound out of the industrial chemical compounds, and ranged between: 0.07 – 0.20 ng/L, 3.14 -3.25 ng/g, 2.45 – 7.97 ng/g in seawater, sediment and benthic organisms, respectively and was 3.60 ng/g in seaweed.

The results revealed the presence of four of these sewage derived compounds in seawater samples, seven compounds in sediment samples, five compounds in seaweed and seven in benthic organisms from Camps Bay. The results showed that diclofenac was the dominant pharmaceutical in seawater (range: 0.73-2.86 ng/ L), sediments (range: 110.9-357.45 ng/g dry weight (dw)) and marine organisms (range: 67.47-314.04 ng/g dw) while perfluoroheptanoic acid was the dominant PFC in seawater (range: 0.21-0.46 ng/ L), sediments (range: 86.28-149.73 ng/g dw) and marine organisms (range: 258.97-282.58 ng/g dw). Especially, seaweed was an excellent accumulation matrix for perfluorodecanoic, perfluorononanoic and perfluorooctanoic acids, since their concentrations were 764 ng/g, 504.52 ng/g and 597.04 ng/g in dried sample, respectively. The average concentration of the herbicides were from their quantification limit concentrations up to 45.32 ng/g (dw) and 157 ng/g (dw) in sediment and benthic organisms, respectively, and at 12.25-87.04 ng/g (dw) level in seaweed samples. The toxic metal concentrations found in sediment and biota samples varied from Cu: 1.18 – 58.76, Zn: 2.40 – 821.50, Mn: 5.38 – 50.37, Fe: 291.94 – 9287.87, Cr: not detected – 12.73, Co: 0.03 – 11.09, Ni: 4.28 – 19.90, Sr: 250.32 – 5146.24, Pb: 2.03 – 233.17, As: 0.35 – 19.70, Ti:

4.90 – 97.44, Mo: 0.13 – 13.04 and Nb: 0.47 – 422.3 mg/kg dry weight while the detected metal concentration in seawater varied from Zn: not detected – 0.01, Sr: 5.67 – 5.97, As: 0.01 – 0.02, Mo: 0.01 mg/L.

The results observed from False Bay sample analysis showed that all the PFCs were dominant in seawater (range: 1.23-18.76 ng/ L), sediment (range: 43.85 -239.65 ng/g dry weight (dw)), benthic organisms (ranged: 36.48 – 2444.87 ng/g dw) and seaweed samples (range: 13.86 – 2309.23 ng/g dw). Pharmaceuticals ranged from: seawater (0.07 – 4.79 ng/L), sediments (8.89-171.89 ng/g (dw)), benthic organisms (14.02 -780.26 ng/g dw) and seaweed (8.46 - 309.11 ng/g dw). Nonylphenol was the most dominant compound out of the industrial chemical compounds, however it was not detected in seawater samples and its concentration ranged from: sediment (5.18 – 582.58 ng/g), marine organisms (339.20 – 2235.35 ng/g) and seaweed (41.57 – 1358.82 ng/g).

Out of the sampling locations, False Bay samples had the highest concentrations of these contaminants, this may be due to the very large volume of partially treated sewage discharged in that location because there are about five sewage plants situated around the Bay. Also, among the matrices, marine organisms including fish have highly accumulated the contaminants followed by sediment samples compared to concentrations found in seawater. This indicates and confirms the bioaccumulating nature of the contaminants in marine organisms. Furthermore, diclofenac, simazine and atrazine for pharmaceuticals and pesticides respectively were the predominant contaminants in the different environmental matrices across the different sampling locations/sites, an indication of the frequent use of these compounds by residents and industries in Cape Town.

Ecological risk assessment values for acute and chronic risk calculated following the US Environmental Protection Agency method were above acceptable limit, (that is) the assessment results were greater than 0.5 for acute risk and 1.0 chronic risk which show that these chemicals have a high health risk to the pelagic fish, aquatic organisms and to humans who consume them. The human risk evaluation (non-carcinogenic and carcinogenic risk) were also above the acceptable level, indicating that the concentration of these chemical contaminants in the selected fish samples and marine organisms were at levels where there is a possibility of developing cancers should the seafood and fish be consumed over a period of time. Therefore, it can be concluded that these contaminants in edible parts of the examined species could pose health problems for consumers, if agricultural and recreational practices in the surroundings of the bay increases.

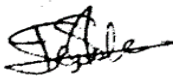
This study reveals the impact of the chemical load being discharged together with sewage, upon the local marine environment. The study confirms that selected pollutants are bioaccumulating in sessile organisms and that the purported high dilution of pollution by discharge of sewage into the oceanic environment is not operating effectively and poses high acute and chronic risk concerns.

Therefore, there is an urgent need for a precautionary approach and the adequate regulation of the use and disposal of synthetic chemicals that persist in aquatic/marine environments in this province and other parts of South Africa, to prevent impacts on the sustainability of our marine environment, livelihood and lives.

DECLARATION

I declare that "Identification and quantification of chemicals of emerging concern (persistent organic and inorganic pollutants) in some selected marine environments of Cape Town, South Africa" is my own work and that it has not been submitted before for any degree or assessment in any other university and that all the sources I have used or quoted have been indicated and acknowledged by means of complete referencing.

Cecilia Yejide Ojemaye



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DEDICATION

This thesis is dedicated to the Holy Trinity, God the Father, Son and the Holy Spirit for protection and guidance throughout my study. I also dedicate this thesis to my Late Father, Engr. C.O. Sanusi.

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My sincere appreciation goes to my Supervisor, Prof. Leslie Petrik for her faith in my ability and given me the opportunity to pursue my doctoral degree under her supervision at the Environmental and Nano Sceince Research Group (ENS). Her encouragement, unique way of mentoring, support and patience have gone a long way, in keeping me focus all through this study. You are not just a supervisor but also a friend and a mother I will forever be grateful. May God continue to shower you with his blessings.

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I sincerely want to thank my Knight in shining armor, my hearthrob, my husband, Dr. Mike Ojemaye for all his sacrifices, prayers, love and encouragement. I thank you for all you are to me; and may God Almighty bless and keep you. I love you wholeheartedly. To my daughter, Tryphena, you are my dream come true, May God continue to keep and bless you.

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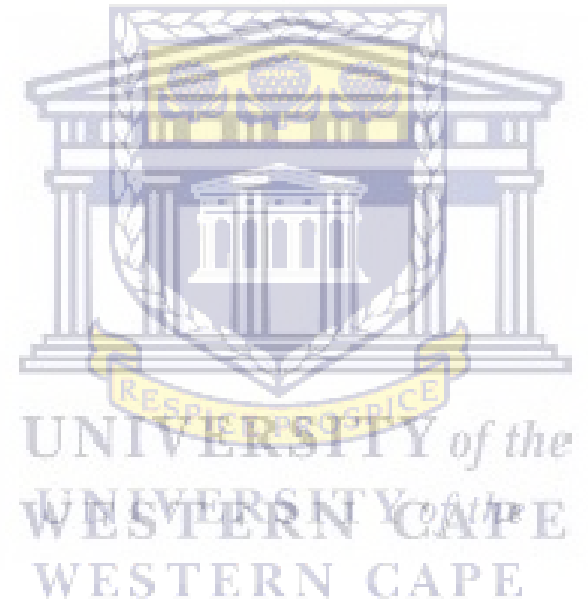

LIST OF ABBREVIATIONS

ACT:	Acetaminophen
BAF:	Bioaccumulation Factor
BPA:	Bisphenol-A
CAF:	Caffeine
CAR:	Carbamazepine
CEC:	Chemicals of emerging concern
DCF:	Diclofenac
EDC:	Endocrine disrupting compounds
GC-MS:	Gas Chromatography -Mass Spectrometry
HLB:	Hydrophilic-lipophilic balance
ICP-OES:	Inductively Coupled Plasma Optical Emission Spectrometry
LA:	Lamivudine
LOD:	Limit of detection
LOQ:	Limit of quantification
LC-MS:	Liquid Chromatography-Mass Spectrometry
NP:	Nonylphenol
na:	not available

nd:	not detected
PFCs:	Perfluorinated compounds
PFDA:	Perfluorodecanoic acid
PFHpA:	Perfluoroheptanoic acid
PFNA:	Perfluorononanoic acid
PFOA:	Perfluorooctanoic acid
PFUnDA:	Perfluoroundecanoic acid
PPCPs:	Pharmaceuticals and personal care products
PHE:	Phenytoin
QuEChERS	**Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged and **S**afe
SPE:	Solid phase extraction
SMX:	Sulfamethoxazole
TCS:	Triclosan
UNEP:	United Nations Environmental Programme
WHO:	World Health Organization
WWTP:	Wastewater treatment plants
2-N:	2-nitrophenol

LIST OF UNITS

L:	Litre
L/kg:	Litre per kilogram
µL:	Microlitre
mg/kg:	Milligram per kilogram
mg/L:	Milligram per litre
mL:	Millilitre
ng/g:	Nanogram per gram
ng/L:	Nanogram per litre

ACADEMIC OUTPUTS OF RESEARCH REPORTED IN THIS THESIS

The output outlined below emanated from this study:

Contributions to publications are given in details, which are part of research given in this thesis (this involves publications, submitted and *in press* with the detailed contributions of each author to the experimental work and writing of each manuscript for publication).

Journal Publications

Ojemaye, C.Y., Onwordi, C.T. and Petrik, L., 2020. Herbicides in the tissues and organs of different fish species (Kalk Bay harbour, South Africa): occurrence, levels and risk assessment. *International Journal of Environmental Science and Technology*, *17*(3), pp.1637-1648.

Ojemaye, C.Y., Onwordi, C.T, Pampanin D.M., Sydnes M.O. and Petrik, L., 2020. Presence and risk assessment of herbicides in the marine environment of Camps Bay (Cape Town, South Africa), *Science of the Total Environment*, 738, pp.140346.

Ojemaye, C.Y. and Petrik, L., 2019. Occurrences, levels and risk assessment studies of emerging pollutants (pharmaceuticals, perfluoroalkyl and endocrine disrupting compounds) in fish samples from Kalk Bay harbour, South Africa. *Environmental Pollution*, *252*, pp.562-572**.**

Ojemaye, C.Y. and Petrik, L., 2019. Pharmaceuticals in the marine environment: a review. *Environmental Reviews*, *27*(2), pp.151-165.

Petrik, L., Green, L., Abegunde, A.P., Zackon, M., **Sanusi, C.Y**. and Barnes, J., 2017. Desalination and seawater quality at Green Point, Cape Town: A study on the effects of marine sewage outfalls. *South African Journal of Science*, *113*(11-12), pp.1-10.

Press releases

Green L., Petrik L., Solomon N., **Ojemaye C.** and Romero S., 2018. Sewage flowing into Kuils River creates a health hazard for all of Cape Town. *Daily Maverick. 05.12.2018*

Workshops and seminars

Leslie Petrik, Lesley Green, Adeola P. Abegunde, Melissa Zackon, **Cecilia Y. Sanusi,** Jo Barnes. 2018. A study on the effects of marine sewage outfalls on water quality. WRC dialogue on Marine Sewage outfalls: impact on seawater quality and desalination. 28 February, 2018, Civic Centre, Cape Town. Invited speaker.

L.Petrik, Lesley Green, Adeola P. Abegunde, Melissa Zackon, **Cecilia Y. Sanusi,** Jo Barnes. 2018. The impact of the marine sewage outfall at Green Point, Cape Town on bio accumulation of persistent organic pollutants in marine organisms, 12 March 2018. MA-RE SANCOR seminar series. South African Network for Coastal and Oceanic Research (SANCOR). Invited speaker.

Leslie Petrik and **Cecilia Ojemaye,** 2020. Persistent organic pollutants in the marine environment. UWC, Research week, Global impact, local relevance. Economic and Environmental sustainability. 2nd October 2020

Under Review

Ojemaye C.Y., and Petrik, L., 2020. Pharmaceuticals and personal care product in the marine environment around False Bay, Cape Town, South Africa: Occurrence and risk assessment study. Submitted to *Environmental Toxicology and Chemistry*.

Manuscript under preparation

Ojemaye C.Y. Onwordi C.T. and Petrik L. Metal concentrations in marine invertebrate and seaweed inhabiting the marine water of Camps Bay, South Africa and human health implication.

Ojemaye C.Y. Omoniyi O.E and Petrik L. Metal profile and risk assessment in commercial fish from Kalk Bay, Cape Town, South Africa.

Ojemaye C.Y., Zackon, A.P., Green, L., and Petrik, L. Emerging contaminants (pharmaceuticals, perfluorinated and endocrine disrupting compounds) in the marine environment around Camps Bay, Cape Town, South Africa.

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Chapter 1

1.1. Background

Chemicals of emerging concerns are contaminants emerging in the environment and the adverse effect which they pose on natural ecosystems and humans have been one of the major concern globally. These chemicals are toxic, because of their ability to be transported either by water or wind; they tend to affect wild and aquatic organisms far from the place of use and release. As a result of their transport mechanisms from the site of their use or emission, they have been detected even in remote locations e.g., the Arctic and Antarctic areas and animals (Weber and Goerke 2003; Webster 2004).

These pollutants are not easily biodegradable (very long half-life), very lipophilic, accumulate in organisms and enter the food chain, thereby posing a serious threat to the health and safety of humans and aquatic species in the environment (Borja et al. 2005).

In view of these problems, some countries including South Africa agreed under the treaty of the Stockholm Convention to eliminate the use of these chemicals which were amongst the dirty dozen (Stockholm Convention 2009) (UNEP, 2011). Numerous studies have shown that these dirty dozens are not the only toxic pollutants in existence but a wide variety of persistent organic pollutants or chemicals of emerging concerns (CECs) have been reported to be present in wastewater effluents, surface water, groundwater and marine environments. According to the National Research Council ((NRC) 2012), different types of chemicals of emerging concern groups are known, these include; industrial chemicals, pesticides, natural chemicals, toxic metals, pharmaceuticals and metabolites, personal care products, household chemicals, food additives and transformation products ((NRC) 2012).

These pollutants find their way into the aquatic environments through incautious wastewater discharge, agricultural runoff, and municipal landfill leachates. Over ten thousand metric tons of

these chemicals are annually released directly or indirectly into marine environment by natural and human means (Lindholm-Lehto et al. 2015). The presence of these contaminants in the environment result in a growing menace which cannot be attributed to the activities of the chemical and pharmaceutical industries or climate change alone (Phillips et al. 2010). Some compounds can also be found in the environment through natural disasters like wide fires and volcanic eruptions (Freeman and De Tejada 2002).

Recently, a lot of attention has been given towards the determination of several of these toxic contaminants in marine water, sediments and biota in order to limit exposure of humans to these contaminants while boosting the advantages of using marine water and seafood consumption (James 2013). Recent studies have shown that ingestion is a major route for the exposure of human to micro organic pollutants through the consumption of food, unlike other exposure routes such as inhalation and dermal contact experienced in the case of marine water (Liem 1999; Sweetman et al. 2000; Falandysz et al. 2002). Risk evaluation of micro organic pollutants in the marine environment for human health is, therefore of great importance.

For instance, bivalves and fish are distinct indicators of different environmental areas in association with their habitat. Their food web position shows different rates of biotransformation and bioaccumulation regarding to xenobiotics (Porte and Albaigés 1994; Livingstone 2001; Scaps 2002).

The consumption of fish is one of the primary pathways through which these chemicals find their way into human tissues according to a population survey conducted in year 2000 (Sjödin et al. 2000). The risks and hazards associated with micro organic pollutant residues in tissues are a function of the compounds toxicity and an individual's exposure. Because of bioaccumulation of these compounds, the consumption of fish might become a serious problem as revealed in many studies (Corsolini et al. 2005).

Bivalves such as mussels have been identified as bio-indicators for the monitoring of trace levels of toxic organic pollutants in coastal waters because of their wide distribution, sessile lifestyle, their ability to tolerate a considerable range of salinity and turbid water, easy sampling, resistance to stress and high accumulation of a wide range of chemicals and also their filter feeding nature (Tanabe et al. 2000).

Studies have shown that these contaminants occur in ultra-trace levels in different environmental matrices, hence highly sensitive and selective instruments are needed to determine these substances in ng/L or ng/g level. Based on this analytical challenge gas chromatography coupled with a mass spectrometry detector (GC-MS) and High performance liquid chromatography coupled with mass spectrometry (HPLC-MS) are deemed to be the most useful analytical tools (Cloutier et al. 2017).

The following sections describe the statement of problem, aim and objectives of this research.

1.2. Problem statement

This research addresses a selection of the levels of the most important emerging environmental pollutants that are detrimental to humans and marine biota. Pharmaceuticals, which are normally produced to speed up the anatomical responses in humans and animals, are now considered a great threat due to their high polarity, low volatility and substantial use as well as their ubiquitous presence in the environment. Aside from the benefits they may have, these pollutants impose negative impacts on humans and non-target organisms. Likewise, herbicides and personal care products as well as toxic metals are problematic. Having gone through literature, research that documents the fate and occurrence of these contaminants in South Africa are scanty. To the best of my knowledge, no study has been carried out for the simultaneous determination of the levels of these contaminants (organic and inorganic) in seawater, sediments and biota in the marine environment in South Africa except in surface water, sludge wastewater influent and effluent

(Adeleye 2016; Swartz et al. 2016; Swartz, C.D., Genthe, B., Chamier, J., Petrik, L.F., Tijani, J.O., Adeleye, A., Coomans, C.J., Ohlin, A., Falk, D., and Menge 2018; Olisah et al. 2019a). This may be due to the complexity involved in extraction and clean-up of these analytes prior to analysis. Since the greater fraction of these substances are oil soluble and the halogenation of these substances determines their ability to accumulate in environmental matrices (Rahman et al. 2001), the fauna of the ecosystem must be taken into consideration in order to thoroughly monitor these pollutants. Owing to the fact that these substances are lipophilic, the marine environment (marine water, sediment and biota) should to be evaluated for possible sources of these pollutants and to gain insight for both research and regulatory needs (e.g. monitoring, control and management).

In the Western Cape region of South Africa, a region known to be one of the most industrialised provinces in South Africa (Figure 1.1), with some of the produce and end-products intended for international markets, the environmental matrices have been reported to be reservoirs for these contaminants, hence the need to adequately assess the level of these contaminants in marine organisms and fish tissues in this region (Tijani et al. 2016). The need to monitor these pollutants in the marine environment is paramount since most of them occur in our natural environment through effluent discharges from poorly or untreated municipal sewage or by-products from industrial processes (Freeman and De Tejada 2002). This research will, therefore help to track the fate of these compounds and to monitor the bioaccumulation of these endocrine disrupting chemicals in marine water and the food web. The study also provides baseline data for Cape Town in the Western Cape Province of South Africa.

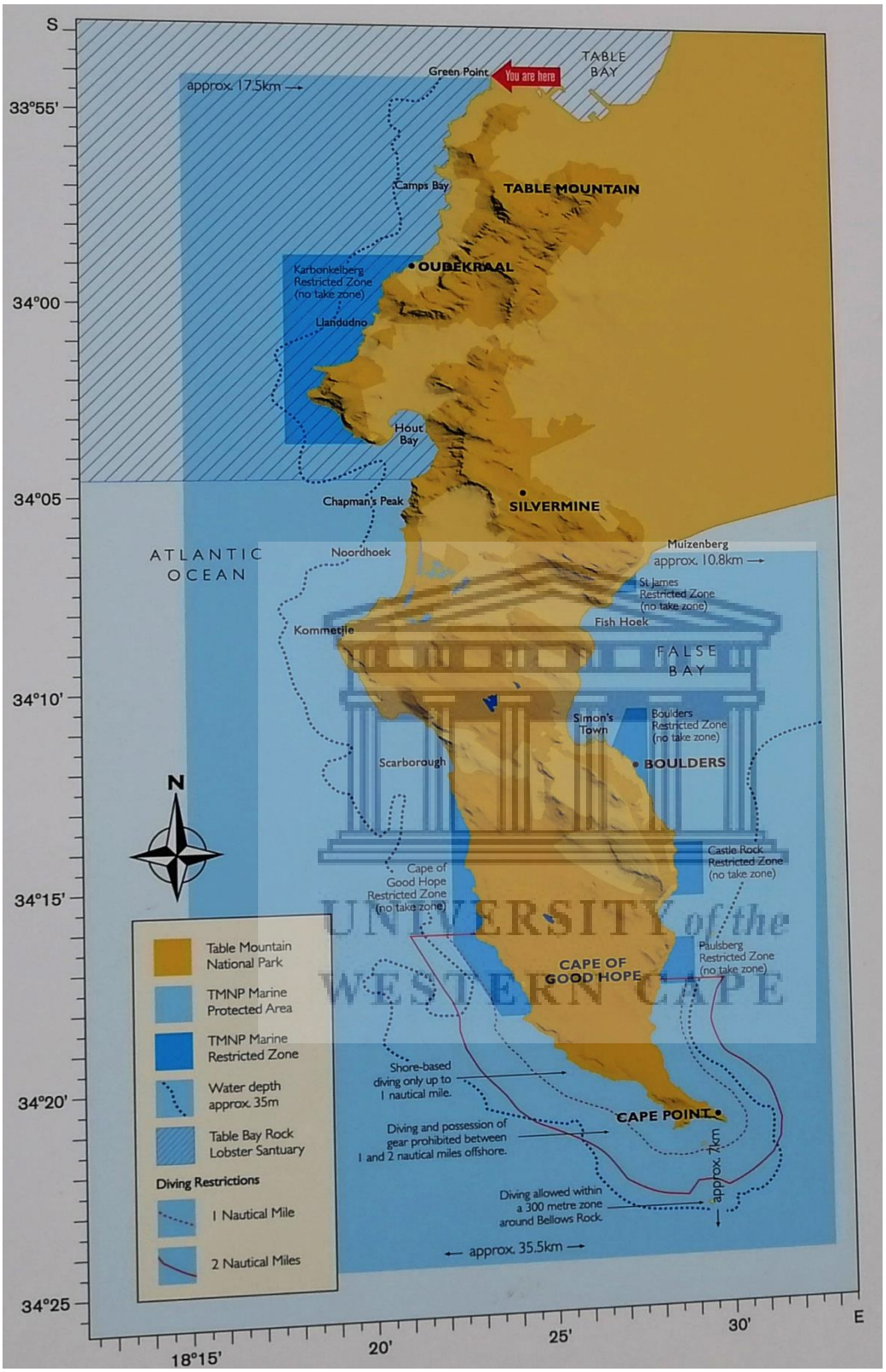


Figure 1. 1: Map of Cape Town showing the coastal line from Table Mountain to False Bay as well as National parks (https://www.sanparks.org/parks/table_mountain/tourism/map.php)

1.3. Aim and objectives of study

This study is aimed at investigating the occurrence of chemicals of emerging concern (CEC) in the marine environment of Cape Town in Western Cape, South Africa. To achieve this aim, the following objectives were employed:

I. To identify the presence and determine the concentrations of selected CECs compounds (perfluoroinated compounds, pharmaceuticals and personal care products, industrial chemicals, pesticides and metals) in the marine biota, seawater and sediment samples.

II. To modify an existing method for the determination of CECs using GC-MS and LC-MS.

III. To validate the method modified from number (ii) above by determining the limit of detection (LOD), limit of quantification (LOQ) and by carrying out recovery studies.

IV. To determine the metal concentration (toxic and beneficial) in the aforementioned matrices.

V. To identify the presence and determine the concentrations of these (metals and CECs) compounds in the marine samples.

VI. To compare the concentration of these pollutants from number (i), and (v) with other studies.

VII. To determine the lipid contents in the fish samples.

VIII. To carry out risk assessment studies in order to ascertain the level of risk upon exposure to these pollutants.

1.4. Research hypothesis

This study is premised on the null-hypothesis that chemicals of emerging concern are not present in some selected marine environment matrices in the Western Cape region of South Africa. Thus bioaccumulation of compounds in species will negate the premise.

1.5. Research questions

The following research questions are addressed:

I. Are perfluorinated compounds, pharmaceuticals and personal care product, herbicides, industrial chemicals and metals present in the marine environment and marine biota?

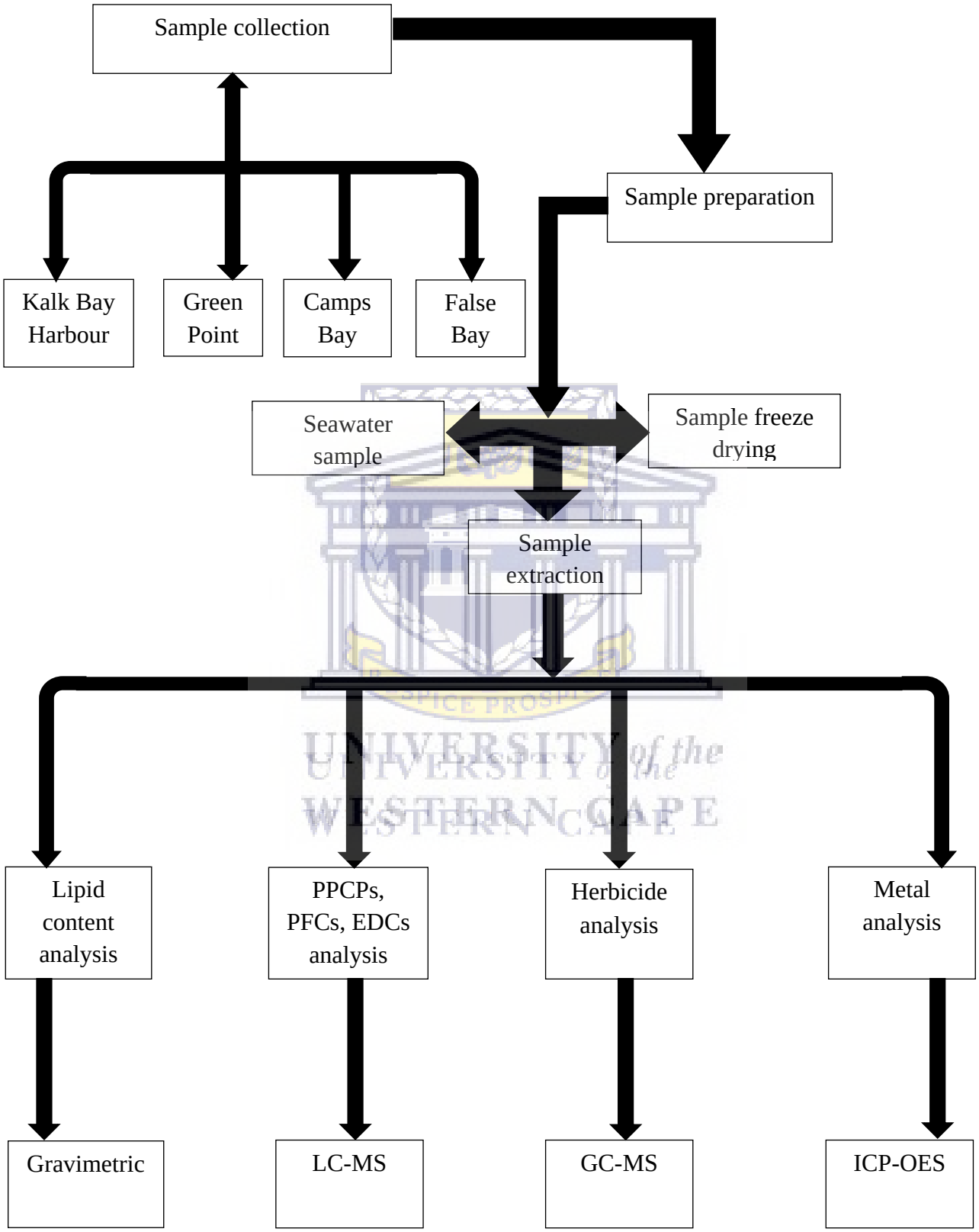
II. If present, at what level/concentration?

III. Is the concentration of these pollutants high enough to be detected in marine organisms?

IV. Are these compounds bioaccumulating in marine biota relative to background levels?

V. What are the risk factors?

1.6. Research approach



1.7. Scope and limitation

This research focuses on the occurrence of selected chemicals of emerging concern (CEC) in the marine environment of Cape Town, South Africa, although the marine environment may contain several other pollutants. This study is limited to the Western Cape, Peninsula and False Bay. It only analyses for a few compounds and considered specific marine organisms. The compounds selected in this study were based on their wide use in South Africa, their inclusion in the priority list of contamiannats to be monitored in South Africa, their occurrence in the environment, the time frame and resources available to complete this research. Furthermore, this study will not cover the following

- Analysis of pharmaceuticals metabolites
- Analysis of PFCs such as the sulfonamides, fluorotelomer alcohols, fluoropolymers and all other PFC precursors and their metabolites
- Effects of seasonal variation of the studied contaminants in the marine environment.
- Studies on occurrence of pollutants outside the marine environment of Cape Town, Western Cape.

1.8. Thesis structure

This thesis comprises novel and original work by assessing the occurrence, levels and risk of some selected persistent inorganic and organic pollutants (pharmaceuticals, personal care product, perfluorinated compounds, industrial chemicals, pesticides and metals) in the marine environment (seawater, sediment and marine biota) of Cape Town. This thesis is written in thesis format with each sampling survey (site) making upa separate chapters. In total, there are nine chapters in this thesis.

Chapter 1: In this chapter, a brief introduction is provided on persistent organic and inorganic pollutants and their pathways into the marine environment. Problems encountered with some

marine organisms if the marine environment is continuously polluted were reviewed briefly. Furthermore, the problem statement emphasising the need to protect the marine environment from pollution, and the aim and objectives of this study are provided in this chapter.

Chapter 2: This chapter provides a literature review of the background relevant to the study by providing information on the types of pollutants, their sources, and the effects of these persistent inorganic and organic pollutants. It also considered the marine matrices investigated in this study, as well as the instruments commonly used for the type of analysis employed in this study. **Part of this chapter has been published in a peer review journal (Environmental Reviews, 2018, volume 999, page 1-15).**

Chapter 3: The research methodology chapter provides detailed analytical techniques that were adopted to generate data needed to achieve the outlined aims and objectives of the study including materials and methods, reagent and equipment used in this study. Information on sampling sites as well as sample collection procedures are discussed. Methods for determination of the samples' physicochemical properties are also described.

Chapter 4: This chapter describes the investigation conducted on different oceanic fish species, the results, discussion as well as the risk involved in consuming such fish species as food in the Province. **This chapter has generated a total of three manuscripts, two of which has been published [Environmental Pollution (2019) 252, 562-572 and International Journal of Environmental Science and Technology (2020) 17(3), 1637-1648].**

Chapter 5: This chapter provides the result on the analysis conducted on different marine matrices obtained from the marine environment of Green Point. **The data from this chapter has been reported in a peer reviewed journal (South African Journal of Science, 2017, volume 113 (11/12) 10 pages).**

Chapter 6: This chapter presents the result and discussion of the assessment of chemicals of emerging concern in Camps Bay. The result on the level of the selected pollutants in the marine biota, sediments and water sampled from the region of Camps Bay, Cape Town as well as their risk assessment were discussed here. **A total of three manuscripts are expected from this chapter, one of which have been published in Science of the Total Environment and two others being prepared for submission to a peer review journal**.

Chapter 7: Here, the result and discussion of the occurrence of selected pollutants in marine water, biota and sediment of eight different sites in the marine environment of False Bay, Cape Town are presented. **This chapter is anticipated to generate three research papers in accredited journals.**

Chapter 8: This chapter provides the comparison of results obtained from different matrices among the different sites in this study in the form of an overall discussion and conclusions. It provides answers to the research questions highlighted in chapter one. This chapter also gives recommendation for future studies.

Chapter 2

Literature review

2.0. Introduction

The increasing evidence of persistent organic pollutants in water bodies is causing major concerns around the world because of their toxicological effects to man and aquatic organisms. This chapter deals with a review of the literature relevant to the study. An overview of emerging micropollutants and types, endocrine disrupting compounds, sources, effects, and environmental fate is provided. This chapter describes water, water pollution, sources and their environmental impact. A brief discussion of the instrumentation methods employed for this study was also highlighted in this chapter. Lastly, the knowledge gap that necessitated this study is also presented in this chapter.

2.1. Water and water pollution

Water is one of the essential natural resources which humans have misused instead of as a valuable assets for the sustenance of their lives. The greater part of the water on this planet is found in seas and ice caps which render these water sources hard to recoup for differing needs. The vast majority of our requirement for freshwater is satisfied by rain water which gets stored in surface and ground water assets. The nature of this utilisable water is especially constrained on the earth. However, water is ceaselessly purified by evaporation and precipitation, yet contamination of water emerged as one of the most critical ecological issues of the current era (Goel, 2006).

Water contamination is the pollution of water bodies (e.g. rivers, lakes, streams, ocean, aquifers, and groundwater). This type of natural debasement happens when pollutants (chemicals or microorganisms) are released into water bodies directly or indirectly without satisfactory

treatment to remove hazardous components, thus degrading the water quality and making it toxic to humans, animals and/or the environment (Tiwari et al. 2008; Melissa Denchak 2018). Water pollution influences the whole biosphere. In all cases, the impact is harmful to individual species and the population. It has been reported that about 80% of the population of the earth is at risk with regards to water quality and security (Vörösmarty et al. 2010). The quality of a water body is often a good indication of the way of life within a community through which it flows and all that happens in a catchment range is reflected in the quality of the water that flows through.

In South Africa, the scarcity of fresh water is accompanied by its decreasing quality because of an increase in pollution and the destruction of river catchments, caused by urbanization, deforestation, damming of rivers, destruction of wetlands, industry, mining, agriculture, energy use, and accidental water pollution. As the human population increases, there is an increase in pollution and catchment destruction. In the process of treating sewage, wastewater and drinking water, all these treatment waste eventually wash down into larger water bodies such as the ocean.

2.2. Persistent organic pollutants (Emerging micropollutants)

The expression “persistent organic pollutants" implies natural or mineral substances whose poisonous, and bioaccumulative properties may negatively affect the environment as well as humans and animals (Ritter et al. 1995). They are available in numerous items that we use daily (drugs, makeup, phytosanitary items, insecticides, and so forth), at home, public places or in industry. Progress in laboratory analysis is increasingly highlighting their presence in the marine environment at extremely low concentrations, in the order of one nanogram per litre or microgram per litre (hence the term micropollutants). Some of these substances are liable to have potentially chronic direct or indirect effects on the ecosystem (e.g. the feminisation of fish due to endocrine-effect substances in the aquatic environment), and even on human health.

Initially, the emphasis of environmental exposure research was on the so called 'priority pollutants' such as pesticides and industrial intermediates. As environmental interest grew and research progressed, so too did the technologies employed, resulting in the development of more advanced techniques and the discovery of a new group of emerging contaminants, collectively referred to as 'chemicals of emerging concern (CECs)' (Bhandari et al. 2009). There was no clear definition and comprehensive list for emerging micropollutants or chemicals of emerging concern. They have been referred to as a group of new chemicals found in the environment (Field et al., 2006). Kümmerer, (2011) characterized emerging contaminants as a pretty much approximately characterized sub-group of micro-pollutants existing in nature at low concentration with clear chemical properties, structures, application ranges, and impacts. The United States Geological Survey (USGS 2014) characterizes emerging micropollutants as any natural or synthetic occurring chemicals or microbial constituent that has not yet been recognized, or generally known, or thought to be a contaminant, which interferes with hormonal functions in charge of homeostasis, or development.

At the same time, these new groups of contaminants that are yet unregulated in most developing countries have attracted public attention. These groups of so-called "emerging contaminants (substances)" comprise various compounds used in everyday life, such as human and veterinary pharmaceuticals, plasticizers, and various industrial additives. Although often less persistent in the environment than conventional contaminants, their continuous introduction might lead to negative effects. Therefore, emerging contaminants belong to the most important chemical contaminants currently found in the environment (Gros et al. 2006; Field et al. 2006). Today, many emerging micropollutants have been distinguished and recognized in almost every ecological specimen, for example, soil, air, water, and even in human food. Due to the

unmanageable nature of these compounds, some bioaccumulate in living cells through the lipid layer and might be harmful to life, depending upon level of exposure.

2.3. Classes/ categories of emerging contaminants

Different classes of emerging contaminants can be identified depending on their chemical compositions, sources, effects in the ecosystem, mode of action and interaction. Although these contaminants are initially useful compounds, their original and metabolite forms cause deleterious effects to the environment and humans, thereby raising concerns about their fate and effects in the environment. The following section describes briefly the different categories of emerging contaminants. Houtman (2010) opined that rising contaminants don't just mean the recently created or existing compounds found in the environment, and classified them into three unique classes. The first class are the chemical compounds as of late discharged into the environment; the second class are compounds that have been in the environment for a more drawn out time yet have recently been identified because of advances in analytical methods. The third class are the compounds whose related adverse health effects are just showing. The US EPA (2007) classified emerging contaminants as new chemicals without an administrative status of which the effects on nature and human wellbeing are insufficiently comprehended or unknown.

2.3.1. Endocrine disrupting compounds

Physiological activities like growth, development, fertility, and reproduction in the body are controlled by hormones (endocrine system). Some synthetic and natural compounds do obstruct or mimic or block the action of these hormones (antagonize the endocrine system); these substances are called endocrine-disrupting chemicals or known as endocrine-disrupting compounds or endocrine-disruptors (EDCs) (Schug et al. 2011; Flint et al. 2012). They are on the other hand, called ecological hormones that cause antagonistic impacts on aquatic and

terrestrial organisms through changing the action of common hormones, or that alter hormone receptor in a cell, or stick to receptors of the endocrine framework (Jiao and Cheng 2010; Olujimi et al. 2010) however, they connect with the oestrogenic receptors and hinder the hormones from working appropriately (Jackson and Sutton 2008). EDCs can be synthetic (17α-ethinylestradiol, and phytoestrogens) or natural (17β-estradiol, estriol and estrone) (Jackson and Sutton 2008; Houtman 2010). Furthermore, various pesticides and industrial compounds, for example, alkylphenols, alkylphenolethoxylates, and bisphenol A, which are applied as surfactants, plasticizers, and raw materials for the generation of polycarbonate plastics, are estrogenic. Picogram to nanogram per litre concentrations of estrogenic activity have been found throughout the aquatic environment, e.g. in wastewater, surface water, and sediments (Bolz et al. 2001; López de Alda and Barceló 2001; Petrovic et al. 2002; Houtman et al. 2004, 2006; Peck et al. 2004; Céspedes et al. 2005; Morteani et al. 2006). The exposure of humans to endocrine disruptors as of late has drawn attention because of the high introduction rate, particularly among aquatic organisms. Human exposure to EDCs could be through dermal assimilation or sullied media, for example, water, sustenance, air, and soil. The human endocrine system is comparable to that of animal vertebrates like fish. Therefore, exposure to endocrine disrupting compounds might imply a certain health risk for humans also. A link between environmental contaminants and reproductive health of humans has been suggested in terms of declining sperm counts, increased incidences of other reproductive disorders related to male infertility, testicular cancer, and breast cancer (Nordkap et al. 2012; Thankamony et al. 2016; Katsikantami et al. 2016; Di Nisio and Foresta 2019). To date, no far-reaching rundown of EDCs exists, in light of the fact that the vast majority of new chemicals are being produced constantly. There is an exceptionally constrained and fragmented proof of endocrine disrupting effects since more than 87,000 new chemicals in the market have not been tested for their endocrine lethality (Snyder et al. 2007;

Kim et al. 2007). Directly, more than 38,000 chemicals and possibly poisonous components have been recognized as potential endocrine-disturbing pharmaceuticals. This means that more chemicals might be perceived as endocrine disrupters as numerous new compounds evoke unexpected impacts (Ferraz et al. 2007; Fatoki and Opeolu 2009).

2.3.2. Personal care products

Personal care products comprise a large group of active or inert ingredients of cosmetics, toiletries, and fragrances, and includes prescribed and non-prescribed pharmaceuticals used by humans in their day to day activities. They are applied as preservative or to alter odour, appearance, touch, or taste. In most cases, personal care products are not meant for ingestion, but are applied externally on the human body (Daughton and Ternes 1999; Jiang et al. 2013). One group of personal care products includes compounds used as fragrance, such as polycylic musks. A second group comprises preservatives like parabens applied in shampoos, creams, and toiletries to prevent bacterial decay. Not to mention, disinfectants like triclosan and chlorophene are used on a large scale for the manufacture of a wide variety of consumer products such as toothpaste, sportswear, medical disinfectant, mouthwash, and hand soap to toys and socks (Petrović et al. 2003; Fawell and Ong 2012). In addition, compounds such as benzophenone and alkylated siloxanes are included in sun screen lotions that block UV light, as well as in soaps and hair-care products. These micropollutants enter the marine environment directly or indirectly via sewage treatment effluent as a result of showering, bathing as well as washing of clothes, or by recreational activities such as swimming and sunbathing. Over the years these personal care products and their metabolites have been observed in effluents and surface waters (Kasprzyk-Hordern et al. 2008; Kuster et al. 2008), because of their lipophilic nature and non-biodegradability (Richardson 2009; Jiang et al. 2013). Some PCPs can accumulate in exposed

organisms for example, Houtman (2010) reported that triclosan and clorophene were observed in bile from bream in the Dutch River Dommel.

2.3.3. Pharmaceuticals

Pharmaceuticals are synthesised or natural chemical compounds used for diagnosis, treatment, or prevention of diseases in humans and animals as well as adding value to their lives. They are also administered to animals to accelerate their feeding efficiency and growth rate (Daghrir and Drogui 2013; Maletz et al. 2013). Pharmaceuticals have different chemical structures, behaviour, applications and metabolism in the human and animal body and hence the environment (Fawell and Ong 2012; Jiang et al. 2013).

Pharmaceuticals are classified based on their therapeutic uses into the following categories: antibiotics (e.g. ciprofloxacin), anti-diabetics (e.g. sulfonylurea), anti-epileptic (e.g. carbamazepine), antimicrobials (e.g. penicillins), anti-inflammatories and analgesics (e.g. ibuprofen, paracetamol diclofenac), antiulcer and antihistamine drugs (e.g. ranitidine and famotidine), antianxiety/hypnotic agents (e.g. diazepam), lipid regulators (e.g. clofibrate), antidepressants (e.g. benzodiazine-pines), β-blockers (e.g. atenolol, metoprolol), anticancer drugs (e.g. cyclophosphamide, ifosfamide), tranquilizers, antipyretics and stimulants (Ikehata et al. 2006; Esplugas et al. 2007; Richardson 2008; Bruce et al. 2010; Jiang et al. 2013; Rivera-Utrilla et al. 2013; Kanakaraju et al. 2014). Pharmaceuticals were first reported as environmental contaminants by Richardson and Bowron (1985) but, their negative ecological impact was just later recognized in the late nineties when they were described as ‘agents of subtle change’ (Daughton and Ternes 1999).

The use of pharmaceuticals still rises due to increasing use to prevent (instead of to cure) diseases by applying them as additives in food products and due to growth or aging of the population. As

observed for endocrine disruptors, inefficient municipal sewage treatment plants provide a direct route for release of pharmaceuticals in nature. The general public are mostly oblivious or not aware of the risk posed through introduction of these compounds into the environment as individuals carelessly discard unused or out of date drugs into sinks and toilets (Petrovic et al. 2004). A large portion of these medications can be administered orally or by infusion yet because of their incomplete metabolism in humans and animals, some portion of the medications might also be discharged in urine or faeces and in the long run end up escaping through wastewater treatment plants. Other means are landfill site, septic tanks, urban wastewater, showering and bathing, industrial effluent and agricultural practices (Rodil et al. 2012). Because of the extensive use of pharmaceuticals by humans and for animals, coupled with incomplete metabolism in the body, the original or partially metabolised medications have been detected in the environment. These contaminants are stable and not easily degradable by regular wastewater treatment plants because they are designed to be robust. Moreover, their polar and non-volatile nature causes their incomplete removal in wastewater treatment plants resulting in their release into the environment (Baker and Kasprzyk-Hordern 2013). These pharmaceutically active compounds have been detected in various environmental water samples, for example, surface water, groundwater and wastewaters in China, USA, Holland, Spain, Germany, Canada, Brazil and even in South Africa (Garric and Ferrari 2005; Fent et al. 2006; Chen et al. 2011b; Rivera-Utrilla et al. 2013; Yan et al. 2014). The increasing levels of human and veterinary pharmaceutical residues in the environment has become a cause of concern, since many of these emerging contaminants have been found in significant concentrations in surface waters, sewage treatment plant effluents, ground waters (Schwaiger et al. 2004) and drinking water (Kümmerer 2001; Martin-Diaz et al. 2009), which lead to their ubiquitous presence, as a result of their continuous use by human populations (Nunes et al. 2008), and their systematic introduction into marine ecosystems.

As far back as the mid-2000s, there has been broad research concentrating on the discovery of pharmaceuticals and pharmaceutical residue in water resources (Kanakaraju et al. 2014). Kleywegt et al. (2011) reported the identification of more than 30 unique pharmaceuticals in drinking water over the world. Exposure to pharmaceuticals and their metabolites by means of food or water may have short-and long term negative impacts on humans and marine species (Daghrir and Drogui 2013). Pharmaceuticals enter and persist within the soil depending on their capacity for sorption, resistance to photodegradation and affinity for water, which if high, will cause leaching from the solid into water systems (Díaz-Cruz et al. 2003). The unfavorable consequences for people and other biological species include disruption of endocrine function chronic lethality and resistance to antibiotic in various bacterial strains. For example, Daghrir and Drogui (2013) reported that the exposure of terrestrial and aquatic species to tetracycline residues resulted in slow growth which shows that tetracycline causes endocrine disruption; hence excessive consumption should be avoided. Therefore, over the counter utilization of antibiotic medication ought to be restricted. The fundamental worry is not about the intensely dangerous nature of the pharmaceuticals but rather their ceaseless poisonous quality on living creatures (Jiang et al. 2013).

Table 2. 1: Most prescribed drugs in public health sector in South Africa grouped according to the class of drug (Osunmakinde et al. 2013)

Drug	Drug Type
Paracetamol	Analgesic
Albendazole	Antihelmintic
Chlorphenoxamine hydrochloride	Anti-Allergic
Chloramphenicol; amoxycillin; ampicillin; ceftriaxone; furosemide	Antibiotics
Hydrocortisone acetate	Corticosteroid
Co-trimoxazole; lamivudine; efavirenz; stavudine; tenofovir disoproxil fumarate	ARV
Salbutamol Sulphate	Asthma

Simvastatin	Cholesterol
Levonorgestrel & ethinyloestradiol; norgestrel; norethisterone enantate	Contraceptive
Cocillana	Cough syrup
Metformin Hydrochloride; gliclazide; insulin	Diabetic
Hydrochlorothiazide; enalapril maleate & Hydrochlorothiazide; amlodipine; nifedipine; perindopril; Medroxyprogesterone	Hypertension
Methyl salicylate	NSAID
Atenolol	β-blocker

2.3.4. Pesticides

Pesticides are substances or mixture of substances that are intended for destroying, preventing, or controlling pest (vectors of human or animal disease), undesirable types of plants or animals. These compounds are associated with the production, processing, storage, transport of food, farm produce, animal feedstuffs, wood and wood commodities, or substances that may be given to animals for the control of insects and other pests in or on their bodies (United, Nations 2002). By their nature, pesticides are potentially toxic to humans and other organisms. Pesticides include herbicides, fungicides, insecticides, plant development controllers, bactericides, and defoliants, the most common of these are herbicides which account for approximately 80% of all pesticides in use (US EPA 2011b). It has been estimated that only 0.1% of pesticides reach the target pests, leaving the bulk of the pesticides (99.9%) to impact the environment (Horrigan et al. 2002). These compounds have been a topic of concern for surface water quality for decades. Their broad use in agrarian practice and from industrial emission during production are causes of pesticides and their residues being found in the marine environment. The major sources of pesticides are domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways and etc.) and agricultural runoff (Luo et al. 2014). Environmental impact of pesticides include loss of biodiversity and elimination of key species such as bees, water pollution, soil contamination,

pest resistance resulting in the need for increased application of pesticides or formulation of alternate pesticides (Bowler 2002; Charles Benbrook 2009; Dubrovsky and Pixie A. Hamilton 2010).

Table 2. 2: Types of pesticides

Type	Action
Algicides	Control algae in water tanks, lakes, swimming pools, canals, and other sites
Antifouling agents	Repel or kill organisms that attach to underwater surfaces, such as boat bottoms
Antimicrobials	Kill microorganisms (such as bacteria and viruses)
Attractants	*Attract* pests (for example, to lure an insect or rodent to a trap). (However, food is not considered a pesticide when used as an attractant.)
Biopesticides	Biopesticides are certain types of pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals
Biocides	Kill microorganisms
Disinfectants and sanitizers	Kill or inactivate disease-producing microorganisms on inanimate objects
Fungicides	Kill fungi (including blights, mildews, molds, and rusts)
Fumigants	Produce gas or vapour intended to destroy pests in buildings or soil
Herbicides	Kill weeds and other plants that grow where they are not wanted
Insecticides	Kill insects and other arthropods
Miticides	Kill mites that feed on plants and animals
Microbial pesticides	Microorganisms that kill, inhibit, or out compete pests, including insects or other microorganisms
Molluscicides	Kill slugs and snails
Nematicides	Kill nematodes (microscopic, worm-like organism that feed on plant roots)
Ovicides	Kill eggs of mites and insects
Pheromones	Biochemicals used to disrupt the mating behavior of insects

2.3.5. Illicit drugs, non-controlled drugs, and sweeteners

Utilising comparative approaches concerning pharmaceuticals, it was shown that our environment is additionally contaminated with drugs with transcendently non-medicinal applications. It is assessed that up to 5% of the total population utilises unlawful medications, similar to cocaine, heroin, cannabinoids (hashish, cannabis), and amphetamine-like stimulants, (such as ecstasy) (Castiglioni et al. 2008). In 2005, Zuccato et al., (2005) distributed a first precise review on the extent of cocaine and its degradation product (benzoylecgonine) in surface and wastewater samples from the Italian stream Po. The outcomes were intriguing from an ecological as well as from a societal-scientific perspective; in view of the deliberate focus, Zuccato *et al.* reported that cocaine utilisation was significantly higher than estimated. From that point forward, a few reviews have researched the occurance of cocaine and other illegal medications as cannabinoids, amphetamins in surface and wastewaters all through Europe. Furthermore, non-controlled stimulatory compounds such as caffeine from tea, espresso and sodas, also nicotine from tobacco smoking were regularly incorporated into these investigations. These illicit and non-controlled drugs were found in waste and surface water at a nanogram to low microgram per litre concentration. The most discovered compound was benzoylecgonine indicating the utilisation of cocaine (Kasprzyk-Hordern et al. 2008; Zuccato et al. 2008). One of the current groups of emerging contaminants are artificial sweeteners such as aspartame, saccharin, acesulfame, cyclamate and sucralose which are consumed daily in large quantities as a low calorie sugar alternatives in food and drinks (Richardson 2009). Some of these compounds are heat stable (acesulfame used for baking) and are very persistent in liquids (applied in soft drinks with long expiry dates). Some of these sweeteners are not degradable by the human body so it is excreted, thus ends up in surface water after use as indicated in German waste and surface waters (Scheurer et al. 2009). Several research groups have carried out an investigation on its occurrence

and fate in the environment including the Swedish Environmental Research Institute, the Norwegian Institute for Air Research, Linkcoping University (Sweden) together with the Swiss Federal Institute of Aquatic Science and Technology (EAWAG) and the Water Technology Center in Karlsruhe, Germany (Scheurer et al. 2009, 2010; Neset et al. 2010; Richardson 2012).

2.3.6. Nanomaterials

There remains a progressing research endeavour in the area of nanomaterials, with many organisations and colleges concentrating on this topic. Nanoparticles constitute a quickly developing exploration territory. These materials fall in the size range of 1 and 100 nm and have novel properties unlike smaller (atoms) or bigger (bulk materials) particles of the same composition (Wiesner et al. 2009). Other than inorganic compounds, for example, titanium dioxide and nanosilver, and furthermore organic compounds, for example, carbon nanotubes or "nano-C_{60}" are included in nanoparticles. They can be of natural origin as well as synthetically produced and are applied in a wide assortment of uses for instance, in medicine and the food industries. In the interim, inquiries regarding their ecological destiny and conceivable risk or danger emerge. Because of their tiny size, their surface area is enlarged and their synthetic reactivity and organic action concomittantly high. Nanoparticles can enter the body and cells more effortlessly than bigger particles. It is feared that they might cause untoward reactions and DNA harm. Nonetheless, next to no thought is given to the conceivable dangerous properties of nanoparticles (Wiesner et al. 2009). Lin et al. (2010) published a review on the fate and transport of engineered nanomaterials in the environment, which included collection and suspension conduct, and how variables, for example, pH, regular natural matter, normal colloids, and ionic strength can impact this behaviour. The review also indicated how few studies have investigated nanomaterials in the natural aquatic environment.

2.3.7. Flame retardants

Fire retardants are a class of chemicals that are broadly utilised as a part of plastics, textile, and outfitting froths, for example, PCs, TVs, garments, and couches to eliminate combustion in case of a fire. In that capacity, they should have contributed significantly to the decrease of flame dangers (Rahman et al. 2001; De Wit 2002; Olukunle et al. 2012). The level of these compounds in various products constitute up to 5% – 30% by weight. Chiefly, polybrominated biphenyl and polybrominated diphenyl ethers, tetrabromobisphenol A and hexabromocyclododecane are commonly utilised for this purpose. The use of these flame retardants is believed to have successfully reduced fire-related deaths, injuries, and property damage. Be that as it may, there is a concern about their general existence in the environment, in humans and other living creatures, and also their presence in areas a long way from where they were created or utilised. These compounds are basically like the traditional contaminants such as polychlorinated biphenyls, and are similar in the way they behave in the environment. Brominated fire retardants have been identified in tissues, blood and breast milk of human and wildlife (Rahman et al. 2001). This is alarming, as clear confirmation has been acquired years ago that these compounds and their degradation products have harmful properties, for example, the capacity to upset the thyroid, androgenic and estrogenic hormone systems (Legler 2008). Their harmfulness for the sensory system has been shown and they may likewise be cancer-causing (Richardson 2009). On account of their low solvency in water, they tend to sorb to silt in waterways (Rahman et al. 2001) rather than being attracted to water. Another class are organophosphate fire retardants, with tributylphosphate and tris(2-chloroethyl)phosphate as essential agents. Their far reaching use may indeed, surpass previous chemicals incremental since many brominated fire retardants have been restricted (Reemtsma et al. 2008). Organophosphate fire retardants, for which poisonous quality information still are rare, are persistent, albeit more dissolvable in water than brominated

compounds, and a few reviews have detailed their presence in surface and wastewaters (Stackelberg et al. 2007; Terzić et al. 2008; Focazio et al. 2008; Reemtsma et al. 2008; Yang et al. 2019; Chokwe and Mporetji 2019).

2.3.8. Perfluorinated compounds (PFCs)

Perfluorinated compounds, also referred to as fluorotelomer acids, alcohols, and sulfonates such as perfluoroctanoic acid and perfluoroctane sulphonic acid are compounds with uncommon chemical properties; they repulse water and in addition oil and lipids. They are utilized as soil, water, or oil repellent coatings and protect calfskin, texiles, or are applied in manufacturing of paints, adhesives, waxes, polishes, metals, electronics, fire-fighting foams, and in polytetrafluoroethylene (PTFE) and Teflon non-stick cookware, as well as grease-proof coatings for food packaging (e.g. hamburger wrappers, microwave popcorn bags, French fry boxes, etc.) (Clara et al. 2008). PFCs are both hydrophobic (water repulsive) and lipophobic (lipids/oil repulsive), and they contain one of the strongest chemical bonds known, the carbon-fluorine bond (C-F). As a result of these properties, they are exceedingly stable in the environment and have extraordinary profiles of dispersion in the body (Richardson 2009). Concerns about perfluorinated compounds is increasing as they give off an impression of being persistent; accumulating in creatures and having an extensive variety of dangerous properties, including formative impedance and cancer-causing tendencies (Skutlarek et al. 2006; McLachlan et al. 2007). These compounds are pervasive at low levels in humans, even in those living far from any obvious sources. Their presence is detected far from evident point-sources. For instance, Nakayama et al. measured PFCs in the Cape Fear drainage basin in North Carolina and discovered very high levels of 287, 194, 132, and 329 ng/L for PFOA, PFNA, PFOS, and PFHpA, respectively. Furthermore, perfluorinated compounds are found in a wide assortment of untamed life species worldwide and in explored human serum and tissues (Farré et al. 2008; Richardson

2009; Kwadijk et al. 2010). Water seems, by all accounts, to be the major repository in the earth and an essential medium for their transport (Prevedouros et al. 2006).

2.3.9. Organic solvents methyl tertiary butylether (MTBE) and ethyl tertiary butylether (ETBE)

A few mechanically utilised natural solvents, for example, diglyme, triglyme, and diisopropylether are consistently detected in surface waters (Houtman 2010). The organic solvents methyl tertiary butylether (MTBE) and ethyl tertiary butylether (ETBE) are utilized as fuel additive to advance ignition, lessen outflows, and as antiknock agent. MTBE and ETBE have some unfavorable properties: they scatter quickly in the environment because of high solvency, show poor biodegradability and are often detected in surface waters at the low mg/L levels. Of great concern is that, MTBE and ETBE are not effectively degraded during amid drinking water purification.

2.3.10. Complexing agents

Complexing compounds are natural molecule that can bind metals. They are utilised as a part of cleansers and toothpaste, for instance EDTA. Different molecules are 1Hbenzotriazoles, utilised as coating to ensure that metals that are in contact with liquids do not corrode, e.g. in motor coolants, air ship de-icers, or are used to prevent the solidification of detergents used to wash dishes. They are dispersed in water, impervious to biodegradation and ineffectively degraded in wastewater treatment (Weiss et al. 2006). One intricacy of complexing compounds is that, once transmitted, they can withdraw substantial amount of metals from sludge and keep the metals dispersed in the fluid phase. This hampers the removal of metals from drinking water and, besides, enhances their bioavailability in the marine environment.

2.4. Persistent inorganic pollutants

Inorganic substances that are stable in the environment, and thus liable to long-range transport, may bio-accumulate in human and animal tissues and may have significant impacts on human health and the environment.

These inorganic pollutants are non-biodegradable and persist in the environment. These pollutants include mineral acids, inorganic salts, trace elements, metals, metals compounds, complexes of metals with organic compounds, cyanides, sulphates, etc. They have adverse effect on aquatic flora and fauna and may constitute a public health problem.

2.4.1. Toxic metals

Recently, some toxic metals were classified as priority hazardous substances by a United State of America agency, Agency for Toxic Substances and Disease Control (ATSDR) as a result of the fact that continuous release of toxic metal ions into the environment has been causing adverse health problems (ATSDR 2015). This is so because metal ions are non biodegradable and exist in the environment for long periods. Their treatment is becoming necessary due to their continued persistent for long periods in the environment. Metals in high concentration can be toxic to biota e.g. Hg, Cu, Cd, Pb, As, and Se. Copper greater than 0.1 mg/L is toxic to microbes.

2.4.1.1. Copper

Copper (Cu) is one of the essential element for growth and development in living organisms. It is an important constituent of lipid digestion, blood pigment, the nervous system and respiratory enzyme complex. The importance of excess amount cannot be underestimated, as even at low amounts copper in the body causes symptoms like vomiting, fatigue and diarrhea. Despite its importance, a very high amount in the body causes anemia, lung and liver disorder and death (Johnson 2018). The major source of this toxic metal in the environment is from industries (such

as electrical, fertiliser, wood and pigment, electroplating, paint and metal finishing manufacturing companies) from which toxic wastes are flushed into the sewage system and out into the marine water.

2.4.1.2. Mercury

Mercury (Hg) is ranked as the third most toxic metal in relation to its intake (ATSDR 2015). Mercury is used in industries for the manufacture of battery, fertiliser, insecticides, paper and pulp in their production processes. The effects of mercury intake by upon humans are birth defects, lung and brain dysfunction, vomiting, headaches, skin rashes, disruption of the nervous system and sometimes death. The contamination of aquatic environments by mercury is mainly through the discharge of mercury containing effluents by chlor-alkali plants and combustion of fossil fuels.

2.4.1.3. Lead

Lead (Pb) is a trace metal commonly found in the environment as gases, liquid or solids from discharge industrial waste, dust particles and car exhausts (Tangahu et al. 2011). Pb is a very toxic metal and because it is not biodegradable, it stays in the environment for a very long time causing harm to humans and animals. Lead is used in insecticides, batteries, plumbing pipes and as alloy. Lead is a highly poisonous metal (inhaled or swallowed), affecting almost every organ and system in the human body by causing severe damage to the brain and kidneys and ultimately death (U. S. et al. 2014).

2.4.1.4. Arsenic

Arsenic (As) cause diseases such as cancer, neurological disorder, muscular weakness. It is used primarily in the production of alloys of lead, other uses include as pesticides treated wood products (Hughes et al. 2011).

2.5. Sources and effects of chemicals of emerging concern

The sources of emission of chemicals of emerging concern into the water cycle can be classified by the type of source and by the origin of the source (Figure 2.1). The type of source is classified as: (Schwarzenbach et al. 2006; Wuijts and Van Rijswijk 2008; Agunbiade and Moodley 2014)

- Accidental point spills: These are a result of a calamity or unforeseen event. Characteristic of this group of spills is that it is a single discharge that in most cases could not be prevented. The influence of the spill on the water quality can be enormous on local scale, but due to mixing, their concentration will dilute.
- Structural point spills: These are continuous discharges, which are sometimes licensed. The effect on the water quality of the receiving water body is more or less constant.
- Line sources: These are similar to point sources, but occur in a line.
- Diffuse sources: These are sources that spread over a wide area. Characteristic of this group of sources is the difficulty to trace the original sources of the spills and the seasonal variation of their occurrence in the water.

While origin of the source are:

- Domestic origin: Pharmaceuticals, personal care products and other chemicals used by humans. It concerns the discharge of chemical of emerging concern originating from residential areas, hospitals and health care centres. Their emission into water is mainly by sewage and wastewater treatment plants. But a small part of many houses is not connected to the sewer system and discharges its wastewater directly into the surface water.
- Agricultural origin: By leaching and runoff of pesticide remnants.
- Industrial origin: Direct point spills from industries or improper treatment.

In urban areas, these chemicals of emerging concern could also be introduced into the environment through sewer floods, run-off from farmlands, discharge of animal waste and septic tank effluents. Other routes through which chemicals of emerging concern enter the environment include incineration of solid waste, metal production, production of bricks and cement, tobacco smoking, illegal/ unlawful waste disposal, production of textiles, landfills and waste dumps, or from household use and disposal of personal care products, cleaning agents, recommended, illegal and unused medications into septic tanks or sewerage infrasture as well as partially metabolised drugs from humans and animals defecation (Labadie et al. 2007; Dougherty et al. 2010; Swartz, C.D., Genthe, B., Chamier, J., Petrik, L.F., Tijani, J.O., Adeleye, A., Coomans, C.J., Ohlin, A., Falk, D., and Menge 2018). All these have shown disastrous consequences on the aquatic environment.

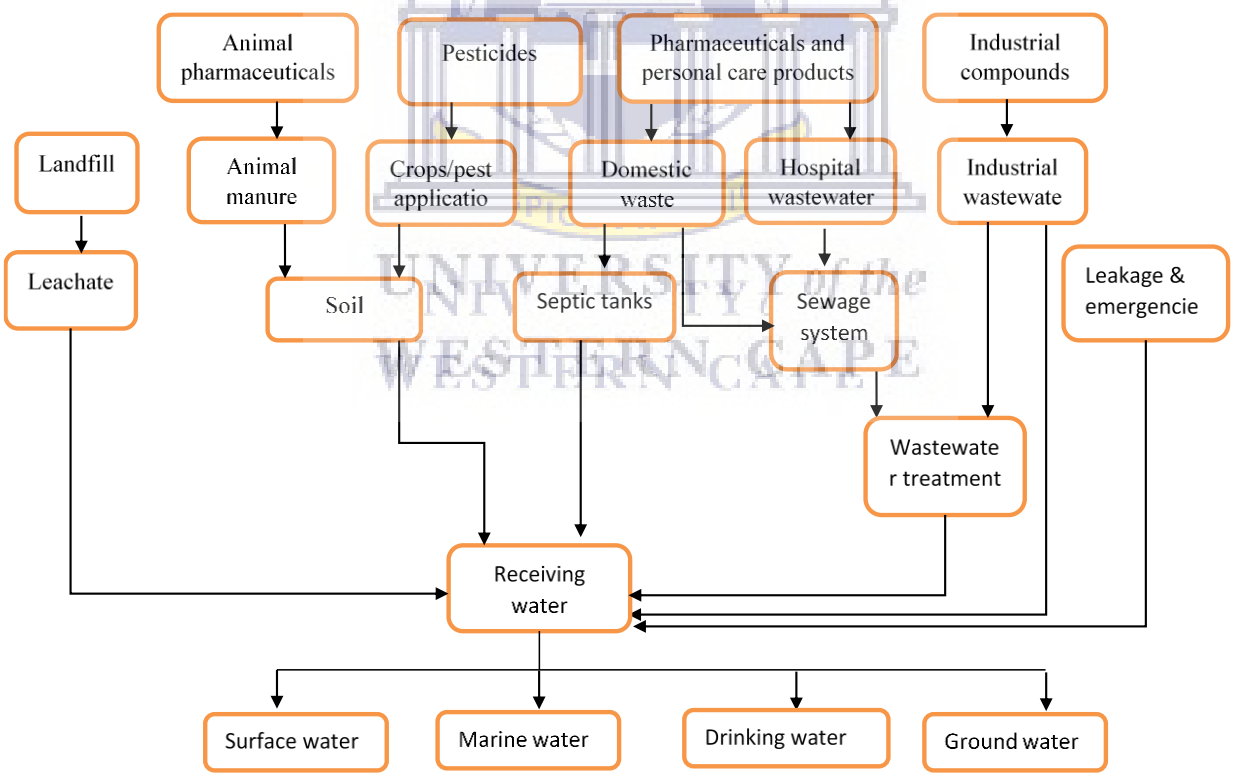


Figure 2. 1: Sources of CECs in the environment (Riwa 2007)

2.6. Selection of Emerging Contaminants in this Study

Globally, there is a huge number of emerging contaminants released to the environment. In addition, there is limited available information on their occurrence, fate, and impact on human and wildlife. ECs such as persistent compounds, pharmaceuticals, personal care products and industrial chemicals include a large number of compounds, which are extensively used in society. For example, there are many types of pharmaceuticals and each group consists of a wide range of compounds with different behaviours. Hence, it is necessary to choose specific compounds that represent various groups for investigation.

2.6.1. Occurrence in the marine environments

2.6.1.1. Occurrence of pharmaceuticals in the marine environments

Lately, studies have centred on the existence of pharmaceuticals in freshwater conditions with similarly little information with regards to the occurrence, dissemination and fate of pharmaceuticals in estuarine or marine environments. This might be because of the trouble of working with a more complicated matrix or the presumption that pharmaceutical remnants are in low concentration in the marine environment. The consequences of pharmaceuticals in the marine environments are of serious concern (Daughton and Ternes 1999; Ankley et al. 2007), because living organisms present are subjected to constant exposure with potential consequences for future generations. These pharmaceuticals are present at low (trace) concentrations (nanogram or microgram/L), depending on their sources (Brooks et al. 2005; Wen et al. 2006; Brown et al. 2007; Chu and Metcalfe 2007; Ramirez et al. 2007; Nakamura et al. 2008; Mottaleb et al. 2009; Huerta et al. 2013).

Practically every single industrial process involved in the manufacture of pharmaceuticals, results in discharging enormous amounts of emerging contaminants or pollutants into the aquatic ecosystem. The most continuous occurrence is the growing accumulation of pharmaceuticals and

endocrine-disrupting compounds that have over-burdened and polluted the different receiving water bodies.

One of the major issues resulting from the discharge of pharmaceuticals into marine waters is their capability to bioaccumulate in aquatic biota. The level of a chemical compound in an organism by exposure to water only is known as bioconcentration while the absorption or ingestion of chemical substances or compounds by an organism through the contribution from air, food, water, and sediment, as it occurs in the natural aquatic milieu is known as bioaccumulation (Arnot and Gobas 2006). Bioavailability in the marine system, the physicochemical nature of pharmaceuticals, biotic factors relating to the exposure of marine organisms and the pH, temperature, flow and quality of its marine waters are a few of the components that can impact the bioaccumulation of pharmaceuticals (Bremle et al. 1995; Nakamura et al. 2008; Rendal et al. 2011).

A few reviews have examined the presence of pharmaceuticals in wild aquatic organisms, concentrating basically on accumulation in wild fish species. Similar work was first done by Brooks et al. (2005) through which various antidepressants were examined in the tissues of undomesticated fish dwelling in two different effluent-influenced water bodies in North Texas, USA. Fluoxetine and sertraline, two antidepressants, and their corresponding metabolites, norfluoxetine and desmethylsertraline, were observed at concentrations higher than 0.1 ng/g wet weight in all tissues, with most elevated concentrations being detected in the cerebrum and liver. The corresponding values for trimethoprim ranged from 0.2 to 0.4 ng/g. McEneff et al. (2014) also determined the spatial occurrence of five targeted pharmaceuticals (trimethoprim, diclofenac, mefanamic acid, gemfibrozil and carbamazepine) in Ireland marine environment (marine surface water and *Mytilus spp*) observed for a period of 12 months. They observed the

presence of all five pharmaceuticals at high concentration (ng/L) in exposed marine surface water and marine mussels. The limit of quantification obtained was between 3 and 38 ng/L and between 4 and 29 ng/g dry weight respectively. Cages of rainbow trout were exposed at three different effluent outfall sites in Sweden for a duration of 14 days by Fick et al. (2010). Sixteen of twenty-five pharmaceuticals observed in the effluent were detected in the plasma of the fish. A similar study was carried out, where rainbow trout were exposed to a downstream of a Canadian wastewater treatment plant for 14 days and two antidepressants were present at a high concentration in ng/L in the bile of exposed rainbow trout (Togunde et al. 2012). With respect to exposure studies of pharmaceutical and the use of caged mussels, a recent study employed five cages of blue mussels off the Belgian coast for a period of six months. Five pharmaceuticals were present in tissues of the mussels including the residues of salicylic acid, with concentration up to 490 ng/g dry weight (Wille et al. 2011). The high concentration of chemical compounds in marine organisms is an evidence of bioaccumulation over time as the organisms have no way of escaping the pervasive presence of these chemicals in the seawater (Petrik et al. 2017).

2.6.1.2. Occurrence of endocrine-disrupting chemicals (EDCs) in the marine environment

Basheer and Lee (2004) determined the presence of alkylphenols, bisphenol A and chlorophenols using hollow fiber-protected liquid-phase microextraction coupled with injection port-derivatisation gas chromatography–mass spectrometry in seawater. Limits of quantification obtained were in the range of 10 – 30 ng/L. With respect to biota, only a few studies have been conducted. Tavazzi et al. (2002) described a accelerated solvent extraction (ASE) method followed by LC-MS analysis for the determination of octylphenol, nonylphenol, and bisphenol A in fish liver. After the authors compared the efficiency of accelerated solvent extraction with conventional Soxhlet extraction, they applied the developed procedure to the analysis of liver samples. The limits of detection (LOD) were 5 ng/g for 4-t-octylphenol, 15 ng/g for bisphenol A,

and 20 ng/g for nonylphenol. The distribution and behaviour of alkylphenol [i.e nonylphenol (NP) octylphenol (OP)], and nonylphenol monoethoxylate (NP1EO) was evaluated in wastewater effluents, river water and riverine and bay sediments as well as mussels in Tokyo metropolitan area (Isobe et al. 2001). The authors extracted their samples using solid-phase extraction, soxhlet extraction, followed by purification process prior to analysis using a GC-MS. A recent study carried out by Salgueiro-González et al. (2012) simultaneously detected the presence of alkylphenol (4-tert-octylphenol, 4-octylphenol, 4-n-nonylphenol, nonylphenol) in seawater collected from the Northwest of Spain at a concentration of 140 ng/L. Koniecko et al. (2014) determined the concentrations of alkylphenols, (4-nonylphenol and 4-*tert*-octylphenol), in surface sediments of the Gulf of Gdansk, Baltic sea. They observed that in summer, the concentrations of the alkylphenol (NP; 2.31 ng/g, OP; 13.09 ng/g) was very high compared to spring, which was related to tourism and recreational activity. A more recent study was reported by Chokwe et al. (2016) on alkylphenol ethoxylates (octylphenol penta ethoxylates, nonylphenol ethoxylates (mono- di) and nonylphenol penta ethoxylates) in the sediment samples collected from vaal river in South Africa with concentration ranging from not detected to $4.6*10^4$ ng/g, $2.0*10^4 – 1.2*10^5$ ng/g, $2.4*10^4$ - $38*10^4$ ng/g dw respectively.

2.6.1.3. Occurrence of pesticides in the marine environment

Most of the common pesticides reported in literatures are the organochlorine compounds such as hexachlorcyclohexane, DDT, hexachlorobenzene e.t.c. Kaczyński et al. (2017) investigated pesticides residue (atrazine, , DDT-pp', DDT-op', DDD-pp', DDE-pp', HCH-beta, S-metolachlor, heptachlor and methxychlor). These compounds were quantified in fish samples using one step extraction-cleanup strategy for simultaneous analysis of over 340 pesticides in a fatty fish and liver matrix, coupled with liquid-chromatography tandem mass spectrometry. The

method was employed in the analysis of 54 real fish and liver samples (Poland) in which 10 different pesticides with concentrations ranging from 5 to 47 ng/g were detected.

Teklit, (2016), conducted a study to assess the levels of organochlorine (OC) pesticide residues (namely DDT, DDE, lindane, endosulfan, heptachlor and chlordane) using water, sediment and fish samples (Ethiopian) as a case study to find out the extent of pesticide contamination and accumulation in the lake using liquid-liquid extraction (Soxhlet extraction) technique and gas chromatograph equipped with electron capture detector (GC-ECD). He found that DDE was the predominant residue in all the samples analyzed, at the mean concentrations of 52 ng/L, 9.80 ng/g and 4.81 ng/g in water, sediment and fish samples, respectively. The lowest levels of OC pesticides were related to heptachlor and chlordane which none of them were found in water samples indicates the less use of these pesticides in the area of study.

Thitiphuree et al. (2013) carried out an analysis on mussel (*Uniandra contradens*), sediment and water from an agricultural catchment in Nan Province, Thailand using GC-MS. The levels of atrazine were found in water and sediment from the catchment were ($2.0*10^5$ ng/L) and (230 ng/g) respectively. Mussel samples collected to monitor potential effects of atrazine on aquatic animals, the results showed that detectable levels of atrazine were found in the tissues of mussel with the highest level of 8.40 ng/g in late wet season when runoff from heavy rain was evidenced. Jacomini et al. (2006) reported the bioaccumulation of atrazine in freshwater bivalves ((*Anodontites trapesialis* and *Corbicula fluminea*) using high-performance liquid chromatography (HPLC). They expose the bivalve to atrazine (concentrations 60 to 340 ng/ml) during 48 h. The results obtained showed that both bivalve species were able to bioaccumulate atrazine in their tissues. Reindl et al. (2015) determined the concentration level as well as accumulation and magnification coefficients, of triazine derivatives in herring gulls and Baltic

grey seals 11 years after a ban on their use by the European Union, EU and eight after their exclusion in Poland using the sonification method in three 45-min cycles and HPLC system. They found out that 8 years after these herbicides were obsolete, the results obtained indicated constant presence of all the assayed triazines (atrazine, simazine, propazine, terbutrine, prometrone, prometrine and ametrine) in whole Baltic herring and their livers. However, ametrine and prometrone were not found in the muscles of herring while ametrine, terbutrine or propazine were not found in the muscles and liver of the grey seal which is a predator of herring. Studies showed no accumulation and magnification of simazine in herring gulls or seals. Atrazine accumulated in the livers of birds and mammals, while its magnification was determined in their muscles. The accumulation of ametrine was observed in seal muscles. Karagiannis et al. (2011), studied the effect of atrazine on the viability of the mussel *Myttilus galloprovincialis* and the formation of their byssus through exposure of six groups of mussels to five concentration of atrazine (10^6 – $1*10^7$ ng/L) for 21 days with one group as a control. They observed that from all the concentrations of atrazine to which the mussels were exposed only those mussels exposed to 10^6 ng/L and $2*10^6$ ng/L survived until the last day of the experiment, also survival rate in the control group was significantly higher than those of mussels that were exposed to atrazine.

Velisek et al. (2012) carried a study to assess the toxicity of simazine in different developmental stages of common carp (*Cyprinus carpio*) on the basis of mortality, early ontogeny, growth rate, and occurrences of morphological anomalies, and Fulton's condition factor during and at the conclusion of the test. They observed that concentration of simazine at 60 ng/L had no effect on the early life stages of carp, while at concentration of $6*10^5$ and $3*10^6$ ng/L there was a decrease in mass and total length of carp. They also observed that fish exposed to the three highest levels of simazine showed alteration of tubular system of caudal kidney.

2.7. Fate in the environment

After the release and escape of persistent environmental pollutants from sewage and wastewater treatment plants, the requirement for a better comprehension of their fate and effects on the environment cannot be disregarded. These toxins enter the environment amid manufacturing activities, processing, handling, and transportation among others (Gaw et al. 2014; Gogoi et al. 2018). The routes into the environment could be air, water, soil or sediment. The depletion of pharmaceutical compounds in the aquatic environment is controlled or limited by various processes (Baena-Nogueras et al. 2017). The fate and behaviour of the individual xenobiotic compounds rely on environmental conditions as well as hydrophobic and hydrophilic properties for example, pH, water solubility, salinity, bacterial communities, redox condition, adsorption coefficient, irradiance, bioaccumulation potential and temperature among others (Baena-Nogueras et al. 2017). The levels of residual pesticides, pharmaceuticals and endocrine disruptors in marine environments are as affected by variables, for example, the measure of wastewater created, the utilised treatment designs, land areas, lifestyle, suitable treatment methods etc (Rogers et al., 2013). Finally, these compounds are harmful in nature and it is just a matter of time before the levels develop to a point where human toxicity will be apparent. Hence, the precautionary approach standard might be a better approach and it is proposed that South Africa take after the examples of other advanced nations and control the sources containing these emerging pollutants by continuously monitoring these compounds before their release into the receiving environment.

2.8. Marine species used in this study

2.8.1. Mussels

The marine mussel of the species *Mytilus edulis* are bivalve molluscs found attached to hard surfaces in dense populations around the coastline. Estuarine mussel (*Arcuatula capensis*), ledge

mussel (*Septifer bilocularis*), ribbed mussel (*Aulacomya ater*) brown mussel (*Perna perna*), brack-water mussel (*Brachidontes virgiliae*), ear mussel (*Modiolus auriculatus*), black mussel (*Choromytilus meridionalis*), mediterranean mussel (*Mytilus galloprovincialis*), semistriated mussel (*Brachidontes semistriatus*) and half-hairy mussel (*Gregariella petagnae*) are examples of mussels found in South Africa marine water. *Mytilus galloprovincialis* are medium-sized were introduced into South African shores in the late 1970s. It is found occupying the mid- to high rocky shore and has spread rapidly along the coastline dominating nearly 2000 kilometers of our shoreline (Branch et al. 2010; Mead et al. 2011). Compared to the indigenous black mussel it is fat and usually has eroded shells (Picker and Griffiths 2011).They are a benthic animal type found in the littoral zone of the shoreline (Craeymeersch and Jansen 2018). They are predominantly a sessile species which attach themselves to a substrate by means of byssal threads, a proteineous material secreted from glands associated with the foot (Hennebert et al. 2015; Zhang et al. 2017). Inside this zone, the organism may encounter huge changes in temperature and salinity and are able to adapt and respond to these unstable conditions. The fact that some individuals spend extended periods of time exposed to air and thus potential desiccation, reduced oxygen intake and thermal shock, adaptations to these environmental stressors are related to the functional adaptation of the body of the organism, which is enclosed within two opposing shells and surrounding mantle tissue, forming the bivalve morphology (Brian Morton 2018). Bivalves such as mussels have been identified as bio-indicators for the monitoring of trace toxic organic pollutants in the coastal waters because of their wide distribution, sessile lifestyle, their ability to tolerate a considerable range of salinity and turbid water, easy sampling, resistance to stress and high accumulation of a wide range of chemicals and also their filter feeding nature (Tanabe et al. 2000; Richardson et al. 2001; Hellou and Law 2003; Fung et al. 2004). Mussels are distinctly suitable for culture in the coastal waters; they

occupy a low position in the food chain because of their filter feeding nature, hence making their exploitation a highly economic utilisation of the primary production available in coastal areas. Furthermore, mussels have a high protein content which averages 67% of their body weight (Tanabe et al. 2000). Moreover, the extensive knowledge of their metabolic pathways makes it possible to elucidate the links between internal doses of pollutants and the elicited biological effects (Cajaraville et al. 2006; Sureda et al. 2011; Brenner et al. 2012, 2014; Cuevas et al. 2015; Brooks et al. 2015; Strehse et al. 2017).

2.8.2. Fish

For the purpose of this research *Thyrsites atun* is discussed here. *Thyrsites atun* (Euphrasén, 1791), commonly referred to as snoek in Southern Africa, is a long, thin species of snake mackerel found in the seas of the Southern Hemisphere. They occur from Angola to Algoa Bay, on the southern coast of South Africa, but are mostly found along the South Western coast, i.e., in the Benguela ecosystem (Griffiths 2002, 2003). This fish can reach a length of 2000 mm (79 in) standard length with a maximum weight of 9 kg. It is also known in Australasia as barracouta. The ecological importance of snoek should not be underestimated; it is both a predator and prey in the Benguela ecosystem. Snoeks are capable of consuming over 300 000 tons of anchovy (*Engraulis capensis* Gilchrist, 1913) per annum and can have significant top-down effects on the lower levels of the food web (Crawford 1995; Verheye and Richardson 1998). Fish are sensitive indicators for substances that enter aquatic ecosystems.

2.8.3. Sea urchin

The sea urchin (*Echinoidea*) is commonly found along the ocean floors, but seldom in very low temperature regions. Sea urchins are found in both shallow and deeper water along the rocky ocean floor and found inhabiting coral reefs. Sea urchins eat both plant and animals matter, they mainly feed on algae on the coral and rocks, also decomposing matter such as dead fish,

periwinkle, mussels, kelp, sponges and barnacles (Kirwan et al. 2018). *Parechinus angulosus* are peculiar to the Southern Africa (Kroh and Mooi 2020).

Sea urchins are food for predators that inhabit their marine environment, but also those animals that don't. The main predators of the sea urchin are crabs, large fish, sea otters, birds, foxes, eels, and humans (Burnett and Burnett 1999).

Due to dredging on the ocean floor and pollution in the marine environment (water), the sea urchin populations are declining and thought to be threatened with extinction.

2.8.4. Limpet

Limpets a gastropod mollusc (most marine species) lives on the rocky coasts of ocean, clamp down on rocky substrates. It is near impossible to remove them in one piece from the rock using brute force alone (Rafferty 2020). Limpet will allow itself to be destroyed rather than stop clinging to its rock. Many species of limpets adhere to plants as substrate, including brown algae, red algae, and marine grasses.

They generally feed on algae that grow on rocks or other surfaces (Lindberg 2004). Limpets are prey to a variety of organisms, including starfish, predatory gastropods, shore-birds, fish, lizards, small mammals, seals, and humans. In some part of the world (Hawaii and Portugal), they form part of the local diet. Limpets also are used for biological monitoring of the health of ecosystems.

2.8.5. Starfish

Starfish occur on the seabed in all the world's oceans, from the tropics to frigid polar waters. They are found from the intertidal zone down to abyssal depths. They are opportunistic feeders and are mostly predators on benthic invertebrates.

Echinoderms, including starfish, maintain a delicate internal electrolyte balance that is in equilibrium with sea water which means that it is only possible for them to live in a marine environment and they are not found in any freshwater habitats (Dorit et al. 1991). Habitats range

from tropical coral reefs, rocky shores, tidal pools, mud, and sand to help forests, sea-grass meadows and the deep-sea floor.

2.8.6. Sea-snail

Sea snails refer to the kind of snails that exist in saltwater and are classified under the class Gastropoda. They belong to this taxonomic class together with other types of snails such as the land snails and freshwater snails. Sea snails can be found throughout the world's oceans. They are considered to be herbivorous since most of them usually feed on sea plants (seaweed and algae) while omnivorous sea snails feed on small sea animals (Heller and Kurz 2015). Sea snails can well be observed by the habitats they inhabit. Those may not be as various and also not as different on small distances, like on lands (which is the reason for the very large number of terrestrial snail species), but nevertheless sea snails of the coastal region (the littoral) differ noticeably from their relatives of the high sea (pelagic) and the sea floor (benthic).

2.9. Major analysis trends

These CECs are present in the environments at low concentrations (ng/L to µg/L) and (ng/g to µg/g) and thus their detection requires advanced analytical techniques particularly chromatography, which is a technique for identification, purification and separation of mixture by distributing its components between two phases (mobile phase which is the carrier, and a contiguous stationary phase) (Coskun 2016; Keller and Giddings 2020). Numerous methods have been published over the past 30 years relating to specific analytical techniques (chromotagraphic techniques) for the determination of these emerging contaminants in food and environmental matrices. Although, the following analytical equipment namely liquid chromatograph mass spectrometer {LC-MS}, or tandem mass spectrometer (LC-MS/MS), and liquid chromatograph equipped with other detectors, such as UV/Vis detectors and electrochemical detectors (ECD), capillary electrophoresis (CE), Gas chromatograph coupled with mass spectrometer (GC-MS) or

with tandem mass spectrometer (GS-MS/MS) have been widely used to quantify the concentration of chemicals of emerging concern in various environmental samples, GC and LC are the two most important techniques used for the analysis of emerging contaminants in different environmental matrices. HPLC method is a separation method based on the interaction of analytes with the stationary and solubility into the mobile phase. GC method relays on the separation of volatile analytes by interaction with the stationary phase stationary phase and carrier gas. Analytes with differing tendencies to interaction with the phases travel through the chromatographic system over different lengths of time. Because of its versatility, high selectivity and specificity of LC-MS/MS, it has become the preferable analytical technique for the determination of emerging contaminants in different environmental matrices (Wille et al. 2012). Although, occurrence of matrix effects is the major negative aspect for LC analysis of pharmaceuticals and other emerging contaminants, most of these methods usually require solid-phase extraction (Misra et al. 2015; French 2017; Stone 2017; Filigenzi 2018) and derivatization of samples in the case of GC-MS prior to analysis (Liebeke et al. 2010).

However, triple quadrupole (QqQ) MS is required to enhance the determination selectivity and unambiguous identification of the target analytes when highly complex matrices are investigated (Barceló and Petrovic 2007a, b). These instruments, "tandem MS" are able to isolate the molecular ion of the compound of under investigation in the first stage of the mass analyser and obtain selective precursor-product ion transitions when operated in selected reaction monitoring (SRM) mode and or multiple reaction monitoring (MRM). The most intensive fragment ion from the precursor ion is used for quantification. A less sensitive secondary transition is used as the second criterion for confirmation purposes. Recently, more advanced MS technologies, such as time-of-flight (TOF-MS) or linear ion trap (LIT-MS), have been introduced and represent a powerful new identification tool. New hybrid quadrupole-time-of-flight mass spectrometry (Qq-

TOF-MS) allows the acquisition of full-scan product-ion spectra, which provide the accurate mass of the product ion (Petrovic and Barceló 2013; Galindo-Miranda et al. 2019). Is now being utilized both for target analytes and also for identifying non-target analytes. (Comerton et al. 2009).

2.10. Chapter's summary and identified knowledge gaps

In this chapter, information on the classes, sources, occurrences, fate as well as the instruments used for detection and quantification of chemicals of emerging concern in the environment were discussed. It is noted that the rate at which these compounds are consumed daily has increased tremendously. Due to the inability of wastewater treatment plants to remove these pollutants, they have been detected in different environmental matrices such as surface water, wastewater effluent, sediment, freshwater, biota etc. Globally, little attention has been directed towards the marine environment, it is believed that the ocean is too large and wide to be polluted. Moreso, no study have been done in marine environment to assess the levels of these pollutants in Cape Town, South Africa.

Based on the gaps identified in the literature which have been highlighted above, the present study is conducted to know if these pollutants are present in the marine environment of Cape Town and to determine the level they present as well as the risk involved in consuming the foods from this environment.

Chapter 3

Materials and Methodology

3.1. Description of sites

3.1.1. Kalk Bay habour

The Kalk Bay harbour is one of the last working fishing harbours on the Cape Peninsula, situated in Kalk Bay, around 30 km (34°07'45.3"S 18°26'57.3"E) from Cape Town, it was once a fishing village on the coast of False Bay, South Africa and it is now a suburb of greater Cape Town. It lies between the ocean and sharply rising mountainous heights that are buttressed by crags of grey Table Mountain Sandston (Compton 2004). The community of fishers uses small trawlers and ply their trade in False Bay and environs, bringing their catches into the harbour daily from whence it is sold.

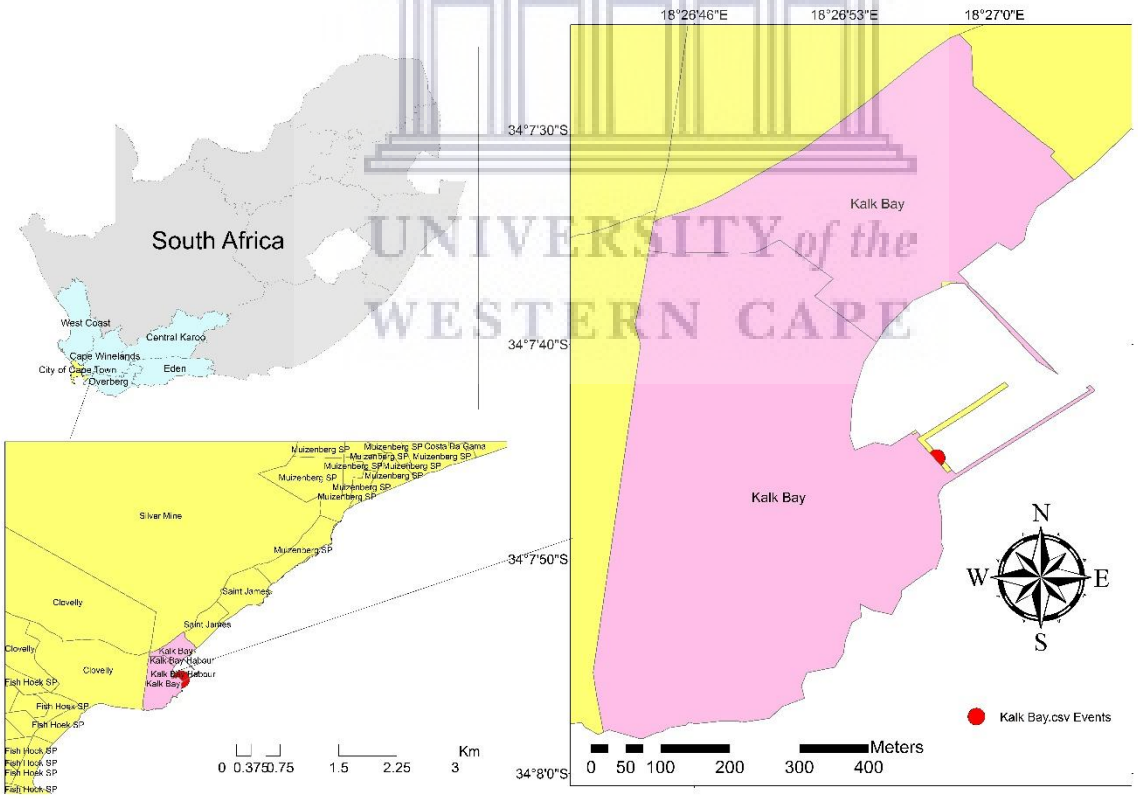


Figure 3. 1: Map of Kalk Bay Harbour sampling points

3.1.2. Green Point

Green Point is located at 33°54′S 18°24′E, an affluent suburb on the Atlantic Seaboard region of Cape Town, South Africa. It is located to the north west of the central business district. It is a popular residential area for young professionals. Green Point is a popular leisure district dominated by its namesake park. The park is also home to Cape Town Stadium and there are steakhouses and fish eateries along nearby Sea Point Promenade.

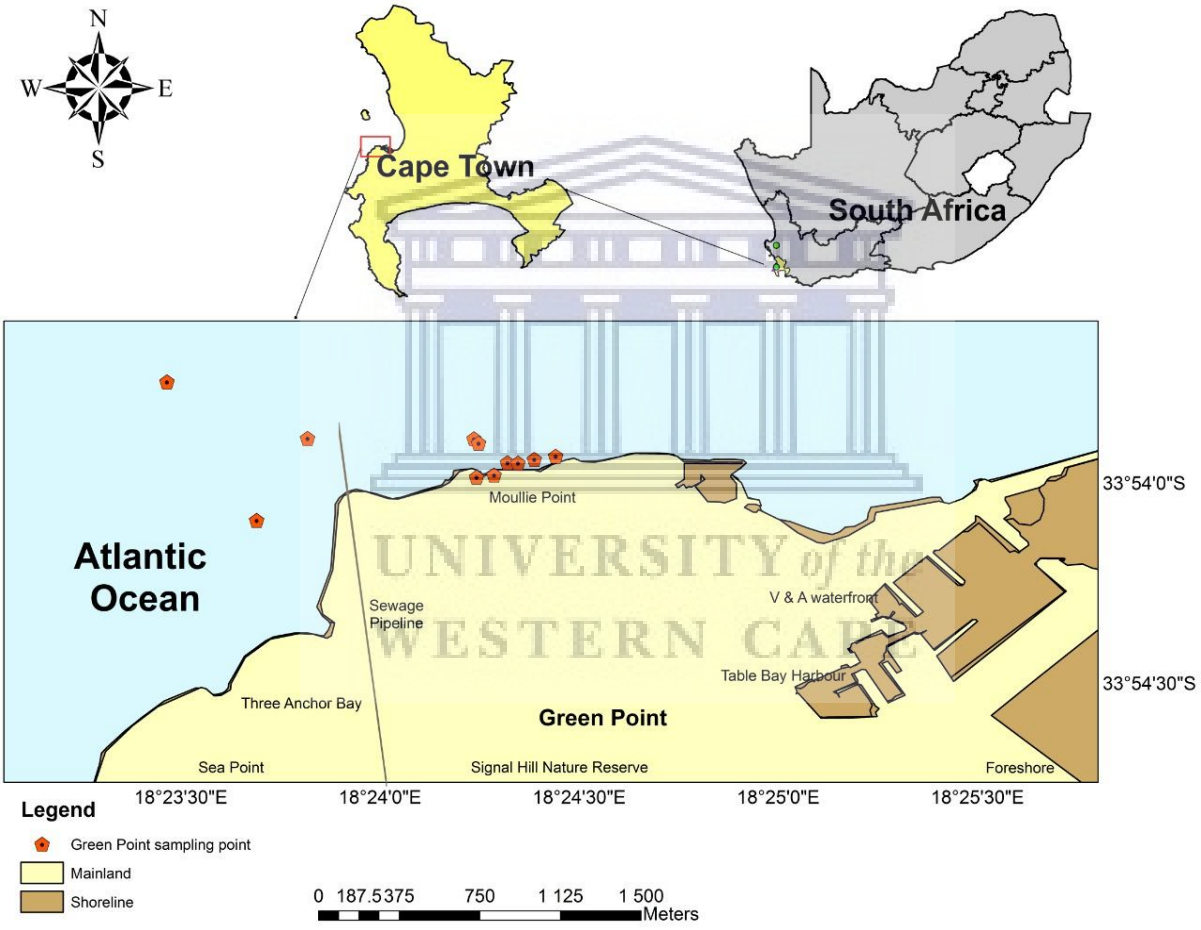


Figure 3. 2: Map of the sampling sites/points in Green points

3.1.3. Camps Bay

Camps Bay is a small, shallow bay, about 850 m wide, situated at 33°57′00″S 18°23′00″E of Cape Town (Figure 3.3). It is an enclosed bay and abuts a geographically isolated suburb

accommodating a community of wealthy citizens, with many popular eateries, hotels that cater for tourists and beachgoers, and no manufacturing industry. The bay ends with a rocky head at Maidens Cove and the beach runs adjacent to Camps Bay Drive. The seabed is a mixture of sand and exposed bedrock (CSIR 2017). Camps Bay hosts a Blue Flag beach, i.e. it meets the organization's standards of environmental management. These standards includes water quality, safety, and public environmental education (Lucrezi et al. 2015; Lucrezi and Saayman 2015; Saayman and Saayman 2017).

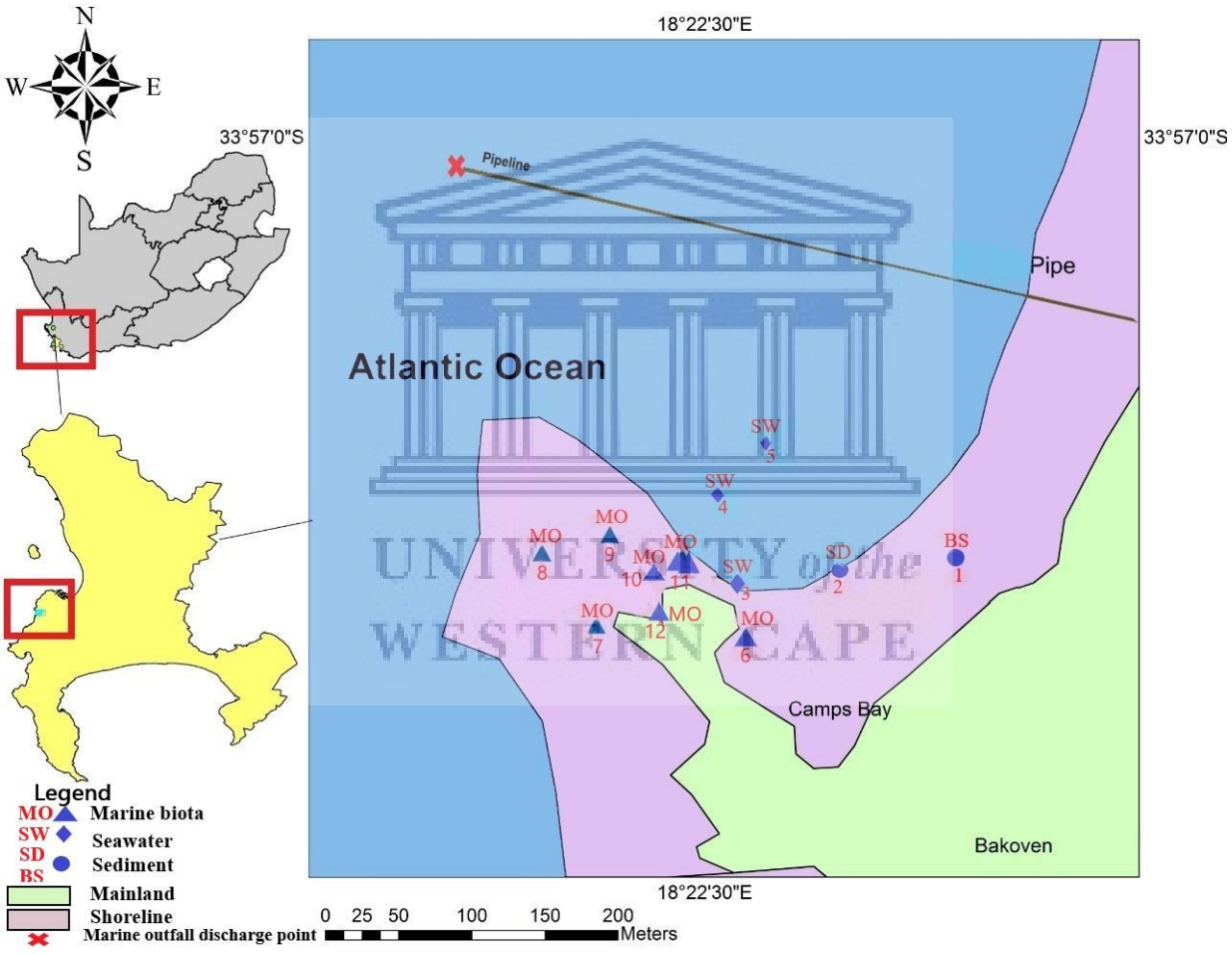


Figure 3. 3: Map of Camps Bay sampling points

The suburb of Camps Bay, with a population density of about 1,700/Km^2, discharges about 2.4 million litres of untreated sewage per day into the ocean via a marine outfall (1.5 km from the

coast) in close proximity to this study's sampling sites (CSIR 2017; Kretzmann 2019; Kretzmann and GROUNDUP 2019). There are no industries releasing effluent into this bay.

3.1.4. False Bay

False Bay is 30 kilometres wide at its widest point, located at 34°13.19′S 18°38.4′E of Cape Town, and is a body of water defined by Cape Hangklip and the Cape Peninsula south-west of South Africa. The eastern and western shores of the bay are very rocky and even mountainous; in places large cliffs plunge into deep water. Notable peaks associated with the bay include Koeëlberg (1289 m / 4229 feet), which rises from the water itself forming the highest point of the Kogelberg, as well as Somerset Sneeukop (1590 m / 5217 feet) and Wemmershoek Peak (1788 m / 5866 feet) which are clearly visible across the bay. The highest peak visible across False Bay is Du Toits Peak near Paarl (1995 m / 6545 feet). The northern shore, however, is defined by a very long, curving, sandy beach. This sandy, northern perimeter of the bay is the southern edge of the area known as the Cape Flats. The following sites are locations where samples were collected along the Bay.

3.1.4.1. Miller's Point (Site 1)

Miller's Point is located at 34°13'57.9"S 18°28'36.5"E of the bay, the site is very secluded and surrounded with plenty of vegetation. The shoreline has different size boulders with fine to medium sand sediments. As far as the site observation is concern, there are storm water pipes that discharge effluents into the ocean (Brown et al. 1991) which serves as one of the potential source of pollution to the bay. Another source of pollution is a slipway and restaurant near the site. Fishing boats could potentially leak oil and fuel when they enter the ocean via the slipway.

3.1.4.2. Simon's Town (Site 2)

Simon's Town is located at 34°10'22.87"S 18°25'42.73"E of False Bay. This sampling location is situated between Simon`s Town Station and Glencairn Station. A railway line separates the road and the shoreline of this location. This location is rocky with fine to medium size sediments between the rocks. The trademark of this site is the largest Naval Base in South Africa which is situated at this site.

3.1.4.3. Muizenberg (Site 3)

This site is located at 34° 6'38.12"S 18°28'5.09"E of False Bay. This site is located near Muizenberg train station. There was plenty of vegetation above this site in particular green grass. The shoreline consists of large boulders with fine to medium grain sand particles. The aquatic life in this area was very limited although empty shells of mussels were evident on the sandy side of the site. A small amount of limpets were collected from the rocks as far as the aquatic life is concerned. Along this location, was a large diameter pipe discharging effluent into the ocean. The discharge effluent looked murky and appeared to be orange/yellow in colour and possibly a source from a spring nearby.

3.1.4.4. Monwabisi beach (Site 4)

The resort is situated on an exposed stretch of coast, where limestone cliffs along the seafront provide protection from the wind. The site is located at 34°04'26.8"S 18°41'21.5"E of False Bay. The many picnic and braai sites are set out on terraced lawns in the bowl behind the cliffs, while an enormous tidal pool lies in the lee of a headland jutting out into the sea. There are also paddling pools and a pavilion, with kiosks and ablution facilities. Activities along the beach include picnics and braaing area, beach access, camping and caravanning, walking, swimming.

3.1.4.5. Strand (Site 5)

Strand is a seaside resort situated on (34° 7'3.71"S, 18°49'29.38"E) the eastern edge of False Bay and at the foot of the Hottentots Holland Mountains. Its geographical position is between Macassar and Gordon's Bay, and is about 50 km southeast of Cape Town. Strand is in the Western Cape province of South Africa, and has a population of approximately 50,000. Strand's main attraction is the beach; 5 km of white sandy beach off False Bay.

3.1.4.6. Gordon's Bay (Site 6)

Gordon bay is located at 34°9'57.55"S, 18°51'30.39"E of False Bay, a harbour town in the Western Cape Province of South Africa, close to Strand. It is situated on the north-eastern corner of False Bay about 50 km from Cape Town. Gordon's Bay consists of the old village, situated around the old harbour and Bikini Beach, the mountainside on the lower slopes of the Hottentots-Holland Mountains overlooking False Bay, and the low-lying suburbs close to the main beach, making up the most recent expansion of the town.

3.1.4.7. Klippies Baai Camp (Site 7)

Klippies Baai camp is situated on the GPS coordinate: 34°14'39.21"S, 18°51'6.77"E of False Bay. Klippies Bay is also a popular pinic, camping and braai spot.

3.1.4.8. Rooi Els (Site 8)

Rooi Els is located at 34°17'50.65"S 18°48'49.16"E, and is situated 5 km north of Pringle Bay, on the eastern shore of False Bay. Rooi Els does not boast of a long strip of sandy beach for its angular nature means that the little town is surrounded on three sides by water. To the east is the Rooi Els River estuary that drains into the sea after flowing under the bridge that carries Route 44 across it.

Worthy of mention is that four different wastewater treatment facilities are located within and around False Bay as shown in Figure 3.4.

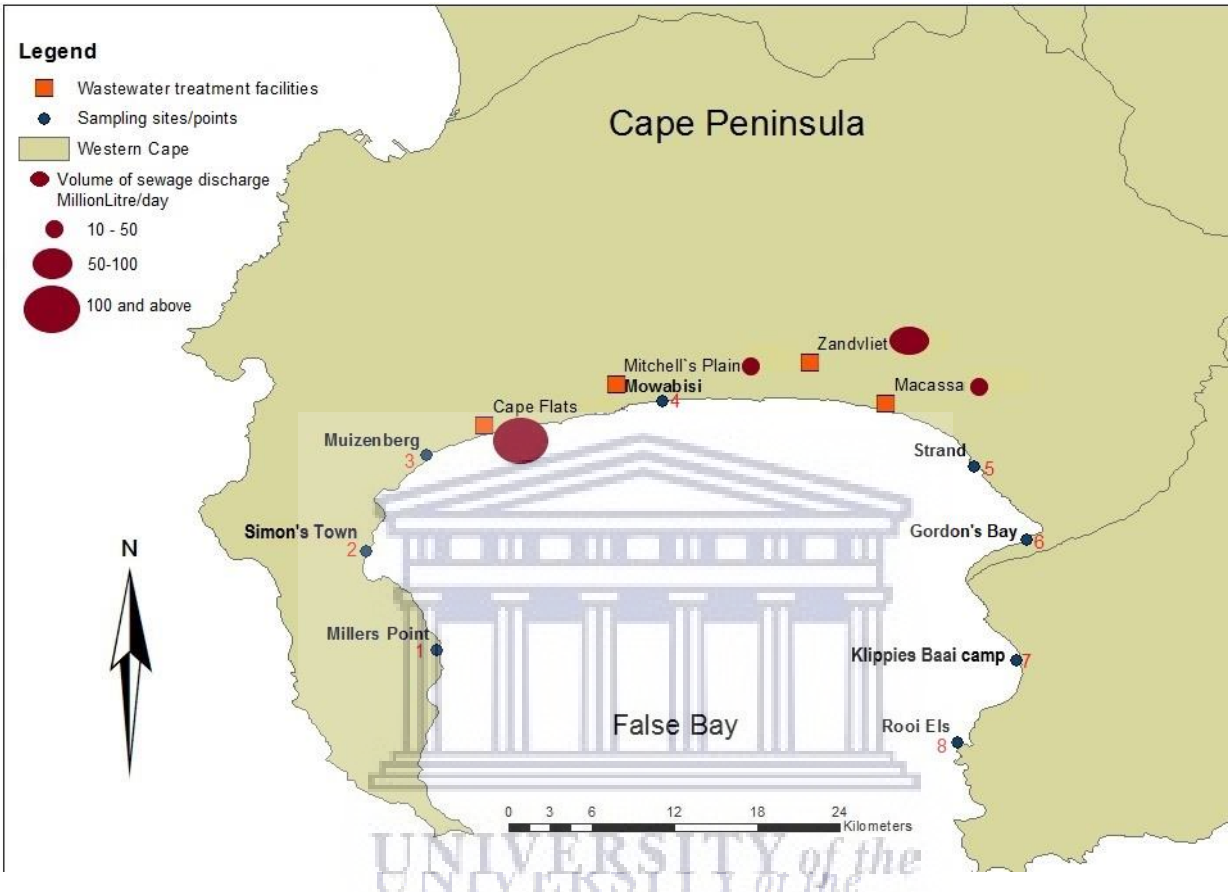


Figure 3. 4: Map of False Bay sampling sites/points

3.2. Materials and method

3.2.1. Labware

The following laboratory wares and equipment were used in this study: 2 L amber bottles, pipettes, measuring cylinders, polypropylene tube (50 and 15 mL), 6 cc, 200 mg Oasis Hydrophilic-lipophilic balance (HLB) solid phase extraction (SPE) cartridge (polymeric reversed-phase sorbent) (Waters, South Africa), beakers, 2 mL amber screw-caps septum vials, centrifuge, freeze dryer, heating mantle, soxhlet apparatus, rotary evaporator, vortex apparatus, drying oven, pH meter, refrigerator (+4° C and -20°C), vacuum manifold and pump (VAC ELUT

SPS 24 Port Agilent Varian,USA), 0.45 µm nitrocellulose membrane filter, digestion vessel, laboratory blender, 0.45 µm filter papers (GF/A, Whatman, UK), aluminium foil, Teflon container, polyethylene bags, ultrasonic bath and cooler bags. All sample bottles, extraction, and volumetric flasks used were washed in Milli-pore water, rinsed well with tap water and lastly methanol with prior to drying. The sample bottles were then air-dried.

3.2.2. Reagents

Methanol, acetone and acetonitrile purchased were HPLC grade from Sigma Aldrich (South Africa). The following list of standards was purchased: perfluorooctanoic acid (PFOA 96%), perfluoroheptanoic acid (PFHpA 99%), perfluorononanoic acid (PFNA 97%), perfluorodecanoic acid (PFDA 98%), perfluoroundecanoic acid (PFUnDA 95%), bisphenol A (BPA ≥99%) and acetaminophen (ACT ≥99%), caffeine (CAF), diclofenac (DCF), lamivudine (LA), triclosan (TS), phenytoin (PHE), sulfamethoxazole (SMX), carbamazepine (CAR), 2-nitrophenol, nonylphenol (NP) atrazine, simazine, alachlor, matolachlor, butachlor, magnesium sulphate (≥99.5%), sodium chloride (≥99%), acetic acid (≥99.7%), chloroform, from Sigma Aldrich (South Africa), internal standards: sulfamethoxazole-d_4 and acetaminophen-d_4, atrazine-d_5 and simazine-d_{10} were purchased from Sigma-Aldrich (Darmstadt, Germany). Water was purified by Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid (65%), hydrochloric acid (36%) and hydrogen peroxide (30%) were supplied by Kimix, South Africa.

3.2.3. Solutions

Primary stock solutions of individual analytes were prepared in methanol at a concentration of 1000 µg/mL. Working standard solutions were prepared by appropriate dilution of the stock solutions in methanol. All solutions were stored at 4°C in amber glassware to prevent light degradation. Working standard solutions were used for preparation of the calibration curves and for spiking samples in the validation study.

3.3. Sample collection, handling and preservation

3.3.1. Seawater

3.3.1.1. Sampling for LC-MS and GC-MS analysis

Before seawater collection, clean and new bottles (previously washed with a mild liquid soap, rinsed with Millipore water and methanol and dried at 105 °C overnight) were rinsed multiple times with ambient water before the sample collection. Seawater samples were collected using a kayak approximately 30 cm below the surface in 2 L amber glass bottles with screw caps, in triplicate. Samples were taken from under the surface to avoid floating debris. Replicates of three different seawater samples were collected for analyses of organic compounds. Samples were collected in pre-washed amber glass bottles with screw caps. Field blanks were also prepared by filling pre-washed bottles with ultrapure water that were transported to the sampling site, and subjected to all the field conditions. All seawater samples were kept on ice and transported back to the laboratory for analyses. Samples were pre-filtered using a 0.45 µm filter paper to remove debris and suspended material. Seawater samples and field blanks were stored at 4 °C until further analysis.

3.3.1.2. Sampling for ICP-OES analysis

Before seawater collection, bottles were rinsed three times with ambient water and samples were taken from under the surface of the water to avoid floating debris. Water samples were collected into acid washed 250 mL plastic bottles with screw caps from approximately 50 cm below the surface water in triplicate. Water samples were acidified with 10% HNO_3, brought to the laboratory and kept refrigerated until needed for analysis. The water samples were filtered using a 0.45 µm nitrocellulose membrane filter.

3.3.2. Marine organisms, seaweed and sediment

Marine biota samples were collected with a stainless steel tong and a knife from the intertidal zone in rock pools along the shore line in 2017 and 2018. The organisms and seaweeds were wrapped in aluminium foil and then placed in polyethylene bags upon collection. Sediment samples were collected with a stainless steel grab from where the organisms were found as well as collected at various points on the beach and placed in glass containers before placing all the samples in cooler bags on ice for transportation to the laboratory. All sediment and biota samples were then placed in cooler bags on ice during transportation to the laboratory. All seaweed samples as well as marine organisms that were removed from their shells upon arrival at the laboratory, were placed in polyethylene bags and immediately stored at -20 $^{\circ}$C until further analyses.

3.3.3. Fish

The fish species were selected from random daily commercial catches freshly landed and sold at Kalk Bay harbour, Cape Town (South Africa) in 2017. They were purchased whole from the flinching table and wrapped in aluminium foil, placed in polyethylene bags and stored on ice in cooler bags for transportation to the laboratory. The samples were washed with millipore water, dried, weighed, and dissected. The dissected organs and tissue parts were isolated, homogenised using a laboratory blender, packed separately in polyethylene bags and stored below -20 ^{0}C for further analysis. Four species of fish namely *Thyrsites atun* (snoek), *Sarda orientalis* (bonito), *Pachymetopon blochii* (panga) and *Pterogymnus laniarius* (hottentot) were chosen and used in this study according to their high commercial value and common human consumption.

3.4. Sample preparation for the extraction and clean-up of pharmaceuticals and personal care products, perfluorinated compounds and industrial chemicals for LC-MS analysis

3.4.1. Seawater

For water sample extraction, the method was based on that of Valdés et al., (2014) method with certain adjustment and modifications. Samples were extracted in triplicate. Solid-phase extraction (SPE) was applied by using a vacuum manifold. Up to twenty-four SPE (200 mg, 6 cc HLB) cartridges were connected to the manifold and the manifold was directly connected to a vacuum supply with tubes. 500 mL of each seawater sample was filtered through filter paper (particle retention 1.2 μm, GF/C diameter 47 mm) to avoid sorbent clogging. In order to avoid the analytes of interest being lost through filtration, the filter papers were then washed with 2 mL methanol. Prior to extraction, the methanol extract was collected and added to the filtered sample. The pH of the filtered solution was adjusted to 6 with 0.1 M of HCl and NaOH. SPE was carried out with each HLB cartridge preconditioned with 7 mL of methanol followed by 7 mL Milli-Q water, and care was taken not to dry the cartridges during the loading process. 500 mL of each filtered seawater sample was separately loaded in the preconditioned cartridges, with a flow rate of 5 mL/min and the cartridges were subsequently washed with 5 mL of 40 % v/v methanol. The cartridges were left to dry under a gentle stream of nitrogen. Analytes were eluted with 7 mL of methanol at a flow rate of 1 mL/min. The eluate was subsequently concentrated to 2 mL under a gentle stream of nitrogen and was further centrifuged for 25 mins prior to analysis.

3.4.2. Marine organisms, fish, sediment and seaweed

All marine organisms, fish and seaweed were freeze-dried and ground whole in a stainless steel industrial blender into a fine powder while sediment was air dried. Approximately 10 g of each dried sample was extracted using soxhlet extractor. The samples were extracted using 100 mL of

methanol/acetone 3:1 (v/v). The extract was concentrated to 10 mL using a rotary evaporator at reduced pressure, and the sample pH was adjusted to 6 by adding 1 M NaOH or 1 M HCl to allow the precipitation of lipids. The extract was centrifuged at 3000 rpm for 20 min. The supernatant was transferred to glass bottles and millipore water was added to make up to a volume of 100 mL. The SPE procedure followed thereafter was the same as that used for treating seawater samples.

3.4.3. Sample analysis and calibration chromatographs

3.4.3.1. Chromatographic conditions

Analyses were carried out using Waters ACQUITY UPLC™ system consisting of ACQUITY UPLC™ binary solvent manager and ACQUITY UPLC™ sample manager. Separation of the compounds of interest was achieved using an ACQUITY UPLC BEH C18 column (1.7 µm; 2.1 mm × 1000 mm) with an ACQUITY BEH C18 VanGuard™ precolumn (1.7 µm; 2.1 mm×5 mm) (Waters, Mildford, MA, USA). The column was kept at 50 ^{0}C. The mobile phase was a mixture of 2 mM ammonium acetate in milli-Q water (solvent A), and 2 mM ammonium acetate in methanol (solvent B). Linear gradient elution of 0.35 mL/min with a mixture of 90 % solvent A and 10 % solvent B was used for 9 min and at 10 min, the acetonitrile percentage was increased linearly from 90 to 100 % and was maintained at 90 % of solvent A and 10 % of solvent B. 5 µL of each sample was injected into the LC/MS system. Standards and the test samples were each subjected to 12 min chromatographic run.

3.4.3.2. Mass spectrometry (MS)

The UPLC was coupled to a triple quadrupole mass spectrometer (Xevo TQ-MS), with an electrospray ionisation (ESI) source. A multiple reaction monitoring (MRM) scan mode was generated for all analytes during optimisation. Source cone voltage, temperature, cone gas flows, capillary voltage and desolvation temperatures were used to obtain the maximum sensitivity. It

was achieved by direct injection of 10 µg/mL concentration of the stock solutions. The capillary voltage of 3.5 kV, desolvation gas (N_2) flow of 800 L/h, source temperature of 140 ^{0}C and desolvation temperature of 400 ^{0}C were applied. Masslynx software was used to collect and analyse the obtained data.

Table 3. 1: Gradient elution method

Time(min)	**Flow (mL/min)**	%A	%B	Curve
Initial	0.300	90.0	10.0	Initial
1.00	0.350	90.0	10.0	6
9.00	0.350	10. 0	90.0	6
10.00	0.350	0.0	100.0	6
10.10	0.350	90.0	10.0	6
12.00	0.350	90.0	10.0	6

Table 3. 2: Summary of instrumentation and analytical conditions

UPLC conditions	
LC System	Acquity Ultra Performance LC (Waters)
LC Column	Acquity UPLC BEH C18, 2.1x100 mm, 1.7µm (Waters)
Column temperature	60 ^{o}C
Eluent	(A) 2 mM ammonium acetate in milli-Q water
	(B) 2 mM ammonium acetate in methanol
Run time	12.00 min
MS condition	
MS System	Xevo TQ-MS
Ion Mode	ESI+
Desolvation Temperature	400 ^{o}C

Desolution gas (L/h)	800
R F lense (v)	1.0
Capillary Voltage (KV)	3.5

3.4.4. Method modification, validation, quality control and calibration

3.4.4.1. Determination of selectivity, linearity, precision, accuracy

Selectivity was evaluated by qualitative comparison of the retention time of the peaks obtained with those of a standard solution. Simultaneously, the identification of the analytes was confirmed by comparing the corresponding spectra of the peaks in the chromatograms of the sample and standard solutions. Linearity was assessed using calibration curves at six concentrations and peak area was plotted against concentration of each analyte. Precision was determined by replicate (5) injection of standards. Accuracy, expressed as recovery percentages, was determined by comparing the concentrations found in spiked samples with the added concentration.

3.4.4.2. Determination of LOD and LOQ

Limits of detection (LOD) and quantification (LOQ) was determined based on the standard deviation of blank-sample responses and the slope of the calibration curve for each analyte. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were determined for each compound. The limits of detection (LODs) and limit of quantification (LOQs) were calculated using the following formulas: LOD = 3.3 α/S and LOQ = 10 α/S, where α is the standard deviation of the response and S is the average slope of the calibration curves, with the same curves. Method was validated against a comprehensive set of quality control parameters including: laboratory and field blanks, matrix spikes and triplicate samples. Blank contamination

is the most common problem observed in the determination of emerging contaminants. Thus, precautions were taken to prevent contamination from personnel, organic solvents, equipment and glassware. Blank samples of MilliQ water were extracted and analysed along with the samples and laboratory spikes to monitor potential laboratory contamination of the studied compounds. Methanol blanks were also run between samples in order to monitor instrumental contamination and carryover. Signal noise, chromatographic peak area and height were used to characterize the analytes of interest; peak area was used to measure the optimal signal intensities for quantification. This provided the most reliable response among the chromatographic response choices such as the peak height and the signal-to-noise ratio

3.5. Preparation of samples for metal analysis with ICP-OES

3.5.1. Seawater samples

Seawater samples were acidified with 0.5 mL of 10% HNO_3, on site then brought to the laboratory and kept refrigerated until needed for analysis. The water samples were filtered using a 0.45 μm nitrocellulose membrane filter.

3.5.2. Biota samples

The samples were freeze dried by means of a freeze dryer, and then ground into a fine powder with a mortar and pestle. Digestion of the samples was performed by using high pressure decomposition vessels, known as digestion bomb. Each sample (0.65 g) was mixed with 8 mL of 68% nitric acid and 4 mL of 30% hydrogen peroxide in a Teflon container (triplicate). The system was heated up to 140 °C for 130 min. After cooling to ambient temperature, the solution was filtered through a 0.45 μm nitrocellulose membrane filter, followed by transfer to an acid-washed volumetric flask (25 mL) and made up to volume with milli pore water. Blank digest was also carried out in the same way (Fallah et al. 2011).

3.5.3. Sediment samples

Sediments were air-dried at room temperature, and sieved through a polyethylene sieve to remove very large particles in order to obtain a homogenous sample. In each case, 3 g of sediment sample was air dried, crushed, and screened through a 1-mm sieve. One gram of the sieved sediment was taken, and 15 mL of HCl and 5 mL of HNO_3 were added. The mixture was boiled on a hot plate. The digested samples were filtered and 100 mL of distilled water was added (Ahmad et al. 2014).

The analysis was performed by inductively-coupled plasma emission spectrometry (ICP-OES) (Varian 710 ES). It included the assessment of concentrations of the following 26 heavy metals and trace elements: Al, As, Si, Cd, Co, Cr, Ti, Li, Cu, Be, Fe, Mn, Mo, Ni, Pb, Ta, Se, Sr, Zn, Nb, Ce, Zr, Rb, Th, Y and P which were purchased from LGC standards (South Africa). The following wavelength lines of the ICP-OES analysis were used: Al 394.401 nm, As 193.697 nm, Si 250.690 nm, Zn 213.867 nm, Ta 268.517 nm, Cd 214.439 nm, Cr 267.716 nm, Cu 327.395 nm, Fe 238.204 nm, Mo 202.032 nm, Mn 259.373 nm, Co 238.892 nm, Ni 221.648 nm, Pb 217.000 nm, Se 203.985 nm, Sr 407.771 nm, Ti 336.122 nm, Be 313.042 nm, Li 670.783 nm, P 213.618 nm, Y 371.029 nm, Rb 780.026 nm, Th 269.242 nm, Zr 343.823 nm, Nb 313.078 nm and Ce 418.659 nm. All calibration standards were prepared by appropriate dilution of stock solutions (1 g/L) in 2% HNO_3. The calibration range was adjusted from 1 to 1000 mg/L, depending on the sensitivity of selected of the element.

3.6. Sample preparation for herbicides analysis with GC-MS

3.6.1. Sample preparation

The herbicides were extracted from all the samples using a miniature QuEChERS (**Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged and **S**afe) method. Marine organism, fish and seaweed samples were

freeze dried and ground into powder using a laboratory blender, while sediment and beach sand samples were air dried. 10.0 mL (seawater sample) and 3 g (sediment and biota (dry weight)) of sample were accurately weighed in a 50 mL centrifuge tube, 6 g of magnesium sulphate and 1.5 g of sodium chloride were added followed by the addition of 10.0 mL of Milli-Q water. Later, 10.0 mL of 1% acetic acid in acetonitrile (ACN), 2.0 mL of acetone and 50 µL of a 5 µg/mL mixture containing the internal standards were added. Samples were vortexed for 30 sec and sonicated in an ultrasonic bath for 60 min. Extracts were centrifuged for 2 min at 5000 g/min. Then, 250 µL of the ACN layer (containing the herbicides) was dried under a gentle stream of nitrogen. Dry extracts were then reconstituted with 150 µL acetone and injected into the gas chromatography-mass spectrometer (GC-MS) instrument.

3.6.2. Chromatographic separation

Chromatographic analyses were performed on a Thermo Scientific TSQ 8000 triple quadrupole MS operated in selected reaction monitoring (SRM) mode. Separation of the herbicides was performed on a ZB-Semi-volatile (30 m, 0.25 mm i.d., 0.25 µm film thickness) Zebron 7HG-G027-11-GGA capillary column. Helium was used as the carrier gas at a flow rate of 1 mL/min. The injector temperature was maintained at 280 °C. Then, 1.0 µL of each extracted sample was injected in splitless mode. The oven temperature was programmed as: 40 °C for 3 min, ramped to 180 °C at a rate of 25 °C/min for 9.6 min; followed by a ramping rate of 10 °C/min for 2 min until 300 °C. The ionisation source temperature was set at 250 °C and emission current of 50 µA was used with argon collision.

3.6.3. Quality assurance and quality control

Methods were evaluated through these parameters: linearity, limit of detection (LOD), limit of quantification (LOQ), recovery, and precision according to the EU guidelines (EU Commission

Decision, 2002; Mitchell, 2016). Concentrations were determined using an internal standard method. Seven concentrations (0.1 to 1000 ng/L) of the standard mix were used for the different matrices, and the linearity was qualified by linear correlation coefficient (r^2). To ensure that there was no external contamination, field blank and laboratory blanks were used as quality control parameters, and all equipment used was thoroughly cleaned. None of the target compounds were detected in blank samples. The LOD was calculated using 3.3 α/S, and LOQ using 10 α/S, where S is the average slope of the calibration curves and α is the standard deviation of the response. Recovery tests were done by spiking each of the sample matrices with 100 µL of 20 ng/L and 100 ng/L herbicides standard mix. Recovery was calculated by comparing spiked extract with the added concentration in each matrix. Recoveries of the studied compounds varied from 98.7% to 102.50%, precision was determined by replicate injection of standard and this was found to be below 20% for all the analysed compounds.

3.7. Lipid content determination of fish samples

The determination of lipid content in fish wet samples was carried out according to Bligh and Dyer's method. 5 g of fish sample was weighed in a 250 mL separating funnel, 20 mL methanol and 10 mL chloroform were added. The sample was homogenized for 2 min with an UltraTurrax mixer. Another 10 mL of chloroform was added and the mixture was shaken vigorously for 1 min. 15 mL of distilled water was added and the mixture was vortexed for 1 min. To prevent some tissue from forming an emulsion, 5 mL NaCl was added. The two layers were allowed to separate and the lower layer was transferred into a pre-weighed pear-shaped flask. The sample was extracted the second time with 20 mL of 10% (v/v) methanol in chloroform, the mixture was vortexed for 2 min. The mixture was allowed to separate and the lower chloroform phase was added to the first extract. The sample was evaporated to dryness using a rotary evaporator. The

residue was further dried at 104°C in the oven for 1 h. The dried extract weight was recorded and the lipid content was calculated using equation 3.1.

$$Lipid\ content = \frac{weight\ of\ the\ dried\ extract - weight\ of\ empty\ flask}{Weight\ of\ sample\ (which\ is\ 5\ g)} x\ 100 \quad (3.1)$$

3.8. Data analysis

Statistical analysis included the mean of samples and corresponding standard deviation, which was separated by Duncan New Multiple Range Test. One-way analysis of variance (ANOVA) was used to determine the differences in comtanimante residue among the various environmental matrices. All tests were regarded as statistically significant when $p < 0.05$. Analyses were performed using the Statistical Package for Social Sciences (SPSS, IBM version 20 software) (Ojemaye and Petrik 2019a).

3.9. Bioaccumulation factor

Bioaccumulation factors (BAFs) were calculated to determine the bioaccumulation of herbicides in marine biota (see equation 3.2). BAF is the ratio of the contaminant concentration in aquatic organism's tissue (C_T) to the contaminant concentration ratio in water (C_W). It includes uptake from all exposure routes as well, while the bioconcentration factors (BCFs) describes only the exposure from the abiotic environment, and uptake due to equilibrium partitioning of contaminants between the surrounding environment and the organic phase in biota (Borgå 2013; Speight 2017; Mackay et al. 2018).

$$BAF = {}^{C_T}/_{C_W} \quad (3.2)$$

3.10. Sorption coefficient

The sorption coefficient Kd is used to describe the reversible sorptive exchange of chemicals between water and sediment (Tolls 2001; Sheppard et al. 2009). Kd was calculated according to equation 3.3:

$$Kd = {}^{C_S}/_{C_W} \quad (3.3)$$

Where, Cw is the average concentration in water and Cs is the average concentration in sediment.

3.11. Risk assessment

3.11.1. Ecological risk assessment

Risk quotient (RQ) is the ratio of a point estimate of exposure and a point estimate of effects. It is commonly used by the US Environmental Protection Agency (EPA) to assess the ecological risk of chemicals of emerging concern (US EPA 2016a) and it is calculated using equations 3.4 and 3.5

$$RQ = \frac{exposure}{toxicity} \quad (3.4)$$

$$RQ = \frac{estimated\ environmental\ concentration\ (EEC)}{ecotoxicity\ endpoints} \quad (3.5)$$

Where exposure is the same as EEC (estimated environmental concentration) of contaminants and toxicity is the same as ecotoxicity endpoint. For acute risk LC_{50} (50% lethal concentration) values, i.e. concentration at which 50% of the animals is expected to die, and EC_{50} (effect concentration for the 50%) values, i.e. the concentration of test substance which results in a 50 % reduction in either algae growth/growth rate or Daphina immobilization were used. For chronic risk, no observed effect concentration (NOEC) values were used.

The RQ was calculated according to the EPA guidelines for each contaminant. Risk presumptions were obtained from the US EPA website (US EPA 2016a). According to US EPA, when a comparison of RQs to levels of concern (LOC) in these matrices is carried out, the risk presumption is said to be acute high risk when the calculated RQ is 0.5 and above LOC, and chronic risk when the calculated RQ is 1.0.

For combination effect of all types of herbicides only, the risk quotient of this combination (RQc) was determined by the addition of individual RQ values denoted as RQn as presented in equation determined by the addition of individual RQ values denoted as RQn as presented in equation 3.6.

$$RQc = \sum_{i=1}^{n} RQn \qquad (3.6)$$

The addition of risk quotients of each contaminant found gives a preliminary indication of the total ecological risk to the specific representative species. LC_{50} or EC_{50} and NOEC were used to determine the level of toxicity using the risk presumption (acute and chronic risk) and were compared to the levels of concern (LOC). Published LC_{50}, EC_{50} and NOEC values for algae, invertebrate and vertebrate, which were used as toxicity endpoint in this study, are reported in Table 3.3.

Table 3. 3: Acute toxicity data for available contaminants across the three trophic levels

Compounds	Class	Algae			Invertebrate			Fish		
		EC_{50} (mg L^{-1})	Species	Reference	EC_{50} (mg L^{-1})	Species	Reference	EC_{50}/LC_5 (mg L^{-1})	Species	Reference
Acetaminophen	Pharmaceutical	134	*S. subcapitata*	(Grung et al. 2008; Kosma et al. 2014)	9.2	*Daphnia magna*	(Kosma et al. 2014)	378 mg/l	*B. rerio*	(Kosma et al. 2014)
Caffeine	Stimulant	339.3	*S. capricornutum*	Valcárcel et al., 2011	46	*Daphnia magna*	Kuzmanovic et al., 2015	87	*Pimephales promelas*	(Sanderson and Thomsen 2009)
Carbamazepine	Pharmaceutical	31.6	*C. meneghiniana*	Ferrari et al., 2004	6.36	*Daphnia magna*	Santos et al., 2007	35.4	*Pimephales promelas*	Kuzmanovic et al., 2015
Diclofenac	Pharmaceutical	14.5	*S. leopoliensis*	Ferrari et al., 2004	20	*Daphnia magna*	Haap et al., 2008	532	*Pimephales promelas*	Kuzmanovic et al., 2015
Lamivudine	Pharmaceutical				1000	*Daphnia magna*	(Sanderson and Thomsen 2009)			
Sulfamethoxazole	Pharmaceutical	1.5	*S. vacuolatus*	Białk-Bielińska et al., 2011	10	*Daphnia magna*	(Sanderson and Thomsen 2009)	562.5	*Oryzias latipes*	Kim et al., 2007
Triclosan	Personal care product	0.56	*P. subcapitata*	(Brausch and Rand 2011)	0.39	*Daphnia magna*	(Brausch and Rand 2011)	0.26	*Lepomis macrochirus*	(Sanderson and Thomsen 2009)
Bisphenol A (BPA)	Industrial chemicals	2.7		Sanderson et al., 2003	7.750	*Daphnia magna*	Sanderson et al., 2003	1284		Sanderson et al., 2003
Nonylphenol (NP)	Industrial chemicals	0.197		(ECOTOX 2018)	140	*Daphnia magna*	(ECOTOX 2018)	170		(ECOTOX 2018)
PFHpA	Perfluorinated compound	1896.75	*Chlorella vulgaris*	(Latała et al. 2009)						
PFOA	Perfluorinated compound	977.21	*Chlorella vulgaris*	(Latała et al. 2009)	211.59	*Daphnia magna*	(Ding et al. 2012a)	1000	*Pimephales promelas*	(Hekster et al. 2003)
PFNA	Perfluorinated compound	481.632 496.57	*P. subcapitata) Chlorella vulgaris*	(Durjava et al. 2012)	92.800	*Daphnia magna*	(Durjava et al. 2012)	120.64		(Durjava et al. 2012)
PFDA	Perfluorinated compound	437.41	*P. subcapitata)*	(Durjava et al. 2012)	77.100	*Daphnia magna*	(Durjava et al. 2012)	35.980		(Durjava et al. 2012)
PFUnDA	Perfluorinated compound	318.66	*P. subcapitata)*	(Durjava et al. 2012)	56.4	*Daphnia magna*	(Durjava et al. 2012)	33.840		(Durjava et al. 2012)
Alachlor	Herbicide	0.966	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	10	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	1.8	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)

Metolachlor	Herbicide	57.1	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	23.5	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	3.9	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Atrazine	Herbicide	0.059	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	6.9	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	4.5	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Simazine	Herbicide	0.04	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	1.1	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	9.0	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
butachlor	Herbicide	0.2	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	2.4	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	0.44	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Mn	Metal	8.100		(Reimer 1999)	29	*Daphnia magna*	(Reimer 1999)			
Hg	Metal	0.7	*Selenastrum capricornutum*	(Kudłak et al. 2011)	9.63	*Daphnia magna*	(Kudłak et al. 2011)			
Co	Metal	100		(ECOTOX 2018)	4.400	*Daphnia magna*	(ECOTOX 2018)			
Ni	Metal	0.125		(ECOTOX 2018)	1.000	*Daphnia magna*	(ECOTOX 2018)			
Cu	Metal	0.021		(ECOTOX 2018)	0.0395	*Daphnia magna*	(ECOTOX 2018)			
Zn	Metal	0.067		(ECOTOX 2018)	1.670	*Daphnia magna*	(ECOTOX 2018)			
As	Metal	0.674	*Selenastrum capricornutum*	(Kudłak et al. 2011)	3.800	*Daphnia magna*	(Kudłak et al. 2011)			
Pb	Metal	1.8	*Selenastrum capricornutum*	(Kudłak et al. 2011)	4.400	*Daphnia magna*	(Kudłak et al. 2011)			
Cd	Metal	0.045	*Selenastrum capricornutum*	(Kudłak et al. 2011)	0.123	*Daphnia magna*	(Kudłak et al. 2011)			
Li	Metal				26.56	*Daphnia magna*	(Kudłak et al. 2011)			
Cr	Metal	0.0040	*Selenastrum capricornutum*	(Kudłak et al. 2011)	0.0083	*Daphnia magna*	(Kudłak et al. 2011)			
Fe	Metal				0.256	*Daphnia magna*	(Kudłak et al. 2011)			

Table 3. 4: Chronic toxicity data for available contaminants across the three trophic levels

	Algae			Invertebrate			Fish		
Compounds	NOEC (mg L^{-1})	Species	Reference	NOEC (mg L^{-1})	Species	Reference	NOEC (mg L^{-1})	Species	Reference
Acetaminophen	46.0	*Chlorella vulgaris*	(ECHA)	5.72	*Daphnia magna*	(ECHA)	9.5	*Oryzias latipes*	(ECHA)
Diclofenac	10	*P. subcapitata*	(Kosma et al. 2014)	1	*C. dubia*	(Kosma et al. 2014)	0.5	*D. rerio*	(Kosma et al. 2014)
Caffeine									
Carbamazepine	10	*P. subcapitata*	(Kosma et al. 2014)	0.025	*C. dubia*	(Kosma et al. 2014)	25	*D. rerio*	(Kosma et al. 2014)
Sulfamethoxazole	0.09	*P. subcapitata*	Ferrari et al., 2004	0.25	*C. dubia*	Ferrari et al., 2004	>8	*D. rerio*	Ferrari et al., 2004
Triclosan	0.2	*P. subcapitata*	(Brausch and Rand 2011)	200	*Daphnia magna*	(Brausch and Rand 2011)	71.3 0.034	*O. mykiss*	(Brausch and Rand 2011) Ramaswamy et al 2011
Lamivudine				100mg/l	*Daphnia magna*	(Sanderson and Thomsen 2009)			
PFOA	74000	*P. subcapitata*	(Delamore; Verbruggen et al. 2002)	414.07	*Daphnia magna*	(Ding et al. 2012a)	40	*Oncorhynchus mykiss*	(Delamore; Verbruggen et al. 2002)
PFNA	464.08	*P. subcapitata*	(Ding et al. 2012b)	0.008	*Daphnia magna*	(Lu et al. 2015)			
PFDA	514.09	*P. subcapitata*	(Ding et al. 2012b)	102.82	*Daphnia magna*	(Ding et al. 2012a)			

PFUnDA				84.61	*Daphnia magna*	(Ding et al. 2012a)			
Alachlor	0.02	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	0.02	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	0.19	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Metolachlor	3.0	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	3.0	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	1.0	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Atrazine	0.1	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	0.1	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	2	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
Simazine	0.6	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	0.6	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	0.7	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)
butachlor	na	*P. subcapitata*	(Köck-Schulmeyer et al. 2012)	na	*Daphnia magna*	(Köck-Schulmeyer et al. 2012)	0.025	*Oncorhynchus mykiss*	(Köck-Schulmeyer et al. 2012)

3.11.2. Human health risk assessment

In this study, the potential risk of the contaminants to human health was evaluated by calculating the risks associated with cancer and non-cancer health effects due to exposure over a certain period of time to the selected compounds separately. This assessment was estimated using the method reported by the US EPA (US EPA 1991). The parameter of exposure are given thus: exposure duration = 30 years, average bodyweight = 70 kg, life expectancy = 70 years. It is assumed that humans with an average body weight of 70 kg consume 54 g of seafood on a daily basis in South Africa (Zokwana 2018).

3.11.2.1. Non-carcinogenic risk (hazard quotient)

The hazard quotient (HQ) was calculated in accordance to US EPA, using Equations 3.7 -3.9 (US EPA 1992) and represent the non-carcinogenic effect due to long term exposure. The HQ is assumed to be the threshold value below which no adverse health effects would be expected to occur. This was calculated by comparing the individual exposure to the contaminant with an oral reference dose (RfD). If HQ is > 1, this indicates that the compounds pose a potential threat to the ecosystem and/or harmful ecological effect may arise; conversely, if HQ is < 1, the risk is relatively low (Kamunda et al. 2016).

$$HQ = \frac{ADD}{RfD} \tag{3.7}$$

Where HQ = Hazard Quotient; ADD (average daily dose) = is the level of intake of the contaminant per day ($mgkg^{-1}$ per day) (US EPA 1989; Pawełczyk 2013) RfD is the estimate of a daily exposure to humans that is likely to be without an appreciable risk of deleterious (non-cancer) effects during a lifetime. The unit is mg/kg-day. The Rfd values used for this evaluation are given in Table 3.5 which were obtained using an integrated risk information system (IRIS) reported by the US EPA (U.S. EPA IRIS 2011; US EPA 2016b). Hazard index (HI) which is the

total hazard ratio, was also determined as the sum of HQs for the four compounds in each studied biota samples (Equation 3.7). No adverse human health effects would be expected to occur if HI value is equal to or less than 1.0, but any value above 1.0 suggests a significant risk level (Yahaya et al. 2017; Titilawo et al. 2018).

$$HI_i = \sum HQ_i \tag{3.8}$$

$$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT} \ (mgkg^{-1} per\ day) \tag{3.9}$$

Where C = concentration of contaminant (mg/kg); IR = ingestion rate (kg/d); EF = exposure frequency (365 days per year); ED = exposure duration; BW = body weight (70 kg); AT = averaging time (equal to exposure duration for non-carcinogens (i.e. ED x 365 days); LT = lifetime (70 years for carcinogen (70 years x 365 days)). The lifetime average daily dose (LADD) or concentration that would yield an equivalent exposure if exposure continued for the entire lifetime was calculated as follows (Equation 3.10): (Barnhoorn et al. 2015; Yao et al. 2018).

$$LADD = \frac{ADD}{ED} \tag{3.10}$$

3.11.2.2. Carcinogenic risk

The carcinogenic risk was evaluated by multiplying the cancer slope factor (CSF) also referred to as carcinogen potency factor by lifetime average daily dose (LADD) of the compound in the biota samples (Equation 3.11), carcinogenic risk estimates the risk of a person developing cancer due to exposure to carcinogenic compounds over a lifetime by comparing the level exposure of individual to the slope factor (Titilawo et al. 2018).

$$Carcinogenic\ risk = LADD \times CSF \tag{3.11}$$

Where CSF is the cancer slope factor which is a measure of the incremental lifetime risk of cancer by oral intake of the chemical, and is usually expressed per mg/kg-day. CSF values are given in Table 3.5 (US EPA 1989, 2005; ECETOC 2001; Hamilton et al. 2003). The risk value is considered very low when it is $\leq 10^{-6}$ and significant if it is $\geq 10^{-4}$. The cancer risk is high when it $\geq 10^{-3}$ and very high when it is $\geq 10^{-1}$ (Man et al. 2013). Carcinogenic risk assessment was evaluated for all the herbicides and metals whose CSF values were available.

Table 3. 5: Reference doses (RfD) in (mg/kg-day) and Cancer Slope Factors (CSF) for the different herbicides and metals

Compounds	RfD	Cancer slope factor
Alachlor	$1*10^{-2}$	$5.6E^{-2}$
Atrazine	$3.5*10^{-2}$	$2.3E^{-1}$
Metolachlor	$1.5*10^{-1}$	0.0092
Butachlor	na	na
Simazine	$5*10^{-3}$	0.092
Zn	0.3	na
Pb	0.0035	0.0085
As	0.0003	1.8
Mn	0.14	na
Ni	0.02	9.1
Mo	0.005	na
Co	0.0003	na
Cr	0.0035	4.6
Cd	0.001	1.5
Cu	0.037	na
Se	0.005	na
Li	0.002	na
Be	0.002	8.4

Sr	0.6	na
Rb	0.004	na
Zr	0.00008	na
Al	1	na
Fe	0.3	na

(CA-OEHHA 2001; OEHHA 2001; U.S. EPA IRIS 2011; US EPA 2016b)

Chapter 4

Levels and risk assessment studies of chemicals of emerging concern in different fish species from Kalk Bay harbour

4.0. Introduction

The presence of chemicals of emerging concern such as endocrine disrupting chemicals (EDCs), pesticides, flame retardants, perfluorinated compounds (PFCs), pharmaceuticals and personal care products (PPCPs) in the marine environment is of environmental and public concern (Daughton and Ternes 1999; Jin and Peldszus 2012). They enter the marine environment continuously through sewage effluents, wastewater discharge, agricultural runoff, inappropriate cleaning and run-off from yards, lawns and roadways through local wastewater and municipal landfill leachates raising concerns for regulatory agencies worldwide (Gaw et al. 2014; Luo et al. 2014). As a result of the continuous discharge of these compounds into the environment, marine organisms such as fish, which are sensitive indicators for substances that enter aquatic ecosystems can accumulate significant amounts of these compounds to levels several times higher than the surrounding water via diffusion across the gills and skin, regardless of these compounds soluble properties in water (Mottaleb et al. 2009; Togunde et al. 2012; Wang and Gardinali 2012). The levels found are usually in the low ng/g but depending on the compound they can reach up to a few hundreds of ng/g. Fish consumption is regarded to be a unique part of a balanced human diet, which has led to an increase in consumption of fish in the last few decades globally (Nácher-Mestre et al. 2010; Kalachova et al. 2013).

The term ‘pesticide’ is a universal term that includes herbicides, insect sprays, fungicides, plant development controllers, bactericides, and defoliants (Houtman 2010). The most common of these are herbicides which account for approximately 80% of all pesticide used (US EPA 2011b).

Atrazine (6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine) and simazine (6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine) are herbicides of the triazine class. Atrazine is applied as pre and post emergence herbicides to prevent broadleaf weed and grasses in crops (Du Preez et al. 2005) while simazine is used as a residual nonselective herbicide to control broadleaved weeds and plants (Stara et al. 2012). Alachlor, 2-chloro-*N*-(2,6-diethyl phenyl)-*N*-(methoxymethyl) acetamide is employed to avoid the growth of grasses and broadleaf weeds in crops (Ramesh and Maheswari 2004; Peebua et al. 2007), N-(butoxymethyl)-2-chloro-N-(2,6-diethylphenyl)acetamide, butachlor, is a selective pre-emergent herbicide employed for rice in form of granules as post emergence herbicides (Yu et al. 2003; Chang et al. 2013), while metolachlor, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide is a derivative of aniline used to control grass and broadleaf weed in cotton, corn, peanuts, soybean, and sorghum. It is also used in combination with other herbicides (Jin et al. 2011). Alachlor, butachlor and metolachlor are members of the chloroacetanilide family of herbicides.

Due to the enormous global application of these compounds and their metabolite, they spread through the environment contaminating the aquatic environment, soil and atmosphere, putting humans and our environment at risk. Moreover, due to the contribution of municipal run-off to the sewage system, the existence of these contaminants in effluent wastewaters cannot be overemphasized (Singer et al. 2010; Campo et al. 2013; Köck-Schulmeyer et al. 2013). Because these compounds by nature are not the target of most conventional wastewater treatment plants, they escape the treatment plant and enter into the aquatic environment.

The continuous release of chemicals of emerging concerns into the marine environment may cause long term toxicity to marine biota and humans through exposure to contaminated air, ingestion of water and foods. For years, chemicals of emerging concerns have been broadly used

all over the world (Pempkowiak et al. 2000; Wang et al. 2011b; Velisek et al. 2012), however because of the toxic nature and harmful effects of atrazine and simazine on plants and animals, European Union member states banned the use of these herbicides from 2004 (EU Commission Decision 2004).

Toxic metal contamination of the aquatic environment is not left out of this discussion. Toxic metals can enter into the environment by natural means such as weathering and/or by human activities including mining, agriculture, municipal waste disposal, industrial activities, burning of fossil fuels and so on (Alloway, 1990; Raskin *et al*., 1994; Shen *et al*., 2002). They have a very huge tendency to enter and accumulate in food chains. Even though these metals are needed in the body at minute levels for growth and development, a large amount of these metals in the body is dangerous for living species and can sometimes cause death (Adongo *et al*., 2012).

Fish can bioaccumulate contaminants straight from water through dispersion across the gills and skin, thus, the level of contaminants in the gills of fish shows their levels in the water which the fish inhabit, while the levels of contaminants in liver reflect the storage of these compounds in the water (Quinn et al. 2011). The route of uptake of contaminants in fish varies with location and accumulation of contaminants within fish. From the human health perspective, the use of fish as bio monitor for pollution from chemical contaminants is therefore significant in order to assess the bioaccumulation and magnification within the ecosystem (Deb and Fukushima 1999; Botelho et al. 2015). Fish act as nonpolar media that can adsorb hydrophobic organic chemicals within the water column. Since birds and humans consume fish, this makes fish good biomonitors for xenobiotic pollutants. The ingestion of foods contaminated with persistent lipophilic chemicals can result in the accumulation of these chemicals in humans. The potential for chemical residues to cross the placental barrier (Waliszewski et al. 2000) even if it were in trace

concentrations, may cause serious damage in newborns and therefore raises great concern. Medium pelagic fish are the major source of food for many and thus contamination for both top marine predators and human consumers.

This chapter reports on the occurrence, levels and risk associated with chemicals of emerging concern in different parts of various fish species obtained from Kalk bay harbour, Cape Town, South Africa. In this chapter, the aim was to accurately measure the concentrations of PPCPs, PFCs, EDCs (inductrial chemicals), herbicides and toxic metals in the different part of selected fish samples. The compounds were mainly chosen according to their high annual consumption, previous studies about their occurrence in marine biota (Wang and Gardinali 2012; Klosterhaus et al. 2013; Álvarez-Muñoz et al. 2015; Moreno-González et al. 2016; Petrik et al. 2017), their stability and poor elimination in wastewater treatment plants (WWTPs) as well as their concern about their possible effects on human and aquatic organisms (Pampanin et al. 2016). In addition, the fact that some of these compounds have been included in the priority list of contaminants to be monitored in South Africa (Osunmakinde et al. 2013), there is an urgent need to evaluate their presence in fish samples regularly consumed by humans in Cape Town.

4.1. Results and discussion

The assessment of the occurrence and levels of contaminants under study in organs (fillet, liver, gills and intestine) of four different fish species namely: [Hottentot (*Pachymetopon blochii)*, Bonito (*Sarda orientalis)*, Snoek (*Thyrsites atun)* and Panga (*Pterogymnus laniarius)*] purchased in September 2017 from Kalk Bay Harbour were determined using solid liquid extraction, QuEChERs and acid digestion methods described previously in Chapter 3 of this thesis followed by LC-MS, GC-MS and ICP-OES analysis. The results of analysis are presented in this chapter

while the size and weight of the fish species as well as the lipid content are presented in Table 4.1.

Table 4. 1: Information on the average size, weight, length as well as lipid content of the different fish species

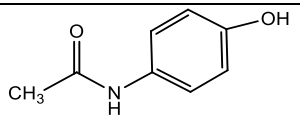
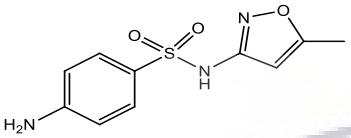
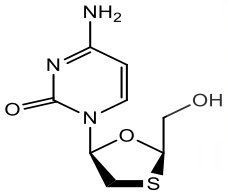
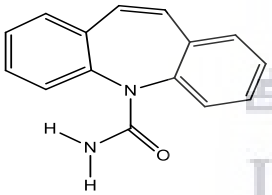
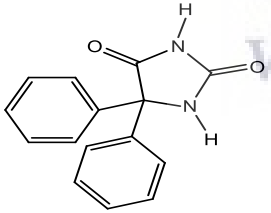
Species of fish	**N**	**Lipid content (%) Mean ± SD**	**Length (cm) Mean ± SD**	**Weight (kg) Mean ± SD**	**Main food**
Hottentot (*Pachymetopon blochii)*	5	5.91± 0.12	20±2.83	0.26±0.025	Seaweeds, algae, crustaceans, worms, molluscs, sea urchins, and sometimes small fish
Bonito (*Sarda orientalis)*	6	11.13±0.40	52±4.24	2.33±0.04	Mackerel, sand lances, menhaden, silversides, alewives, other fishes and squid.
Snoek (*Thyrsites atun)*	5	6.59±0.16	68±3.54	3.85±0.07	Crustaceans, cephalopods and small fish like anchovy and pilchard.
Panga (*Pterogymnus laniarius)*	4	9.02±0.02	20±1.41	0.30±0.00	Amphipods, fishes and crabs with polychaetes, ophiuroids

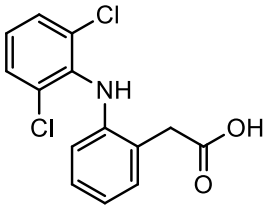
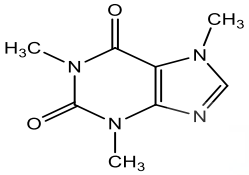
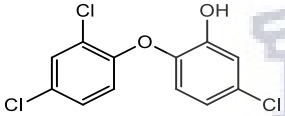
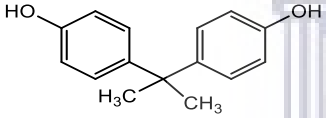
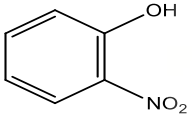
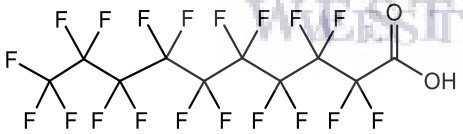
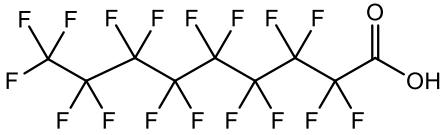
4.2. Occurrence in fish

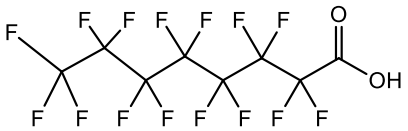
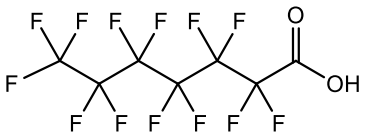
4.2.1. Pharmaceuticals and personal care product, perfluorinated compounds and endocrine disrupting compounds (industrial chemicals)

Table 4.2 provides the LC–MS retention time, transition and collision energy, limit of detection (LOD), and limit of quantification (LOQ) while Table 4.3 presents the percentage recoveries of each fish species. Appendix I, Table I.1 provides a summary of analytical concentrations of the pharmaceuticals and personal care products (PPCPs) and EDC compounds detected in fish fillet, intestines, gills and liver tissues respectively. The calibration curves and chromatograms for the target analytes are showed in Appendix I, Figure I.1. Seven PPCPs compounds, 5 perfluorinated compounds and 2 industrial chemical compounds were analysed in this study. The target compounds were selected based on the results of previous study conducted on marine biota (Petrik et al. 2017). According to the results, all the selected compounds were detected in all the marine biota samples. Four different parts of the fish samples were analysed namely; fillet, liver, gills and intestine. Samples were analysed in triplicates, following the analytical procedure described in Chapter 3. Nine chemical compounds were found in panga fillets, five compounds in bonito fillets, seven compounds in hottentot fillet and eight compounds in snoek fillet samples. The fillets of these fish are consumed whereas the gills, intestine and livers are discarded but may form part of fish meal products. From the results of this study, triclosan and bisphenol A were below quantification limit while 2-nitrophenol was not detected in any of the fish parts.

Table 4. 2: Chemical structures and instrumental parameters for target compounds using LC–MS (Quantitation ions in bold)

Compounds	Family	Molecular structure	Polarity (ESI)	Retention time (min)	m/z ions	Collision energy (eV)	LOD (ng/g)	LOQ (ng/g)
Acetaminophen	Analgesics/anti inflammatory		+	2.01	**152**, 110	15	0.023	0.077
Sulfamethoxazole	Antibiotic		+	3.23	**254**, 156	25	0.019	0.058
Lamivudine	Antiretroviral		+	1.74	**237**, 194	15	0.025	0.09
Carbamazepine	Psychiatric-antiepileptic		+	6.43	**230**, 112	20	0.010	0.025
Phenytoin	Anti-epileptic		+	6.18	**253**, 182	15	0.034	0.098

Diclofenac	Analgesics/anti inflammatory		+	6..72	**294**, 250	15	0.025	0.089
Caffeine	Psychomotor Stimulant		+	3.41	**195**, 138	20	0.027	0.083
Triclosan	Disinfectants		-	9.09	**287**, 36.8	10	0.023	0.075
Bisphenol A	Industrial chemical		-	5.87	**227**, 212	28	0.014	0.047
2-nitrophenol	Industrial chemical		+	-	**139**, 121	15	-	-
Perfluoroundecanoic acid	Industrial chemical		-	8.57	**563**, 563	15	0.036	0.114
Perfluorodecanoic acid	Industrial chemical		-	8.24	**513**, 469	15	0.021	0.055
Perfluorononanoic acid	Industrial chemical		-	7.88	**463**, 419	15	0.010	0.02

Perfluorooctanoic acid	Industrial chemical		-	7.39	**413**, 369	15	0.023	0.075
Perfluoroheptanoic acid	Industrial chemical		-	6.82	**363,** 319	15	0.025	0.08

LOD= Limit of Detection; LOQ= Limit of quantification

Table 4. 3: Correlation coefficients (r^2) and recoveries (%) of analytes

Compounds		Recovery (%)			
	r^2	Panga	Bonito	Hottentot	Snoek
PFUnDA	0.997	107.5 ± 1.3	85.3 ± 4.0	69.2 ± 2.6	89.2 ± 2.3
PFDA	0.994	95.1 ± 2.7	90.6 ± 3.4	101.9 ± 1.8	98.2 ± 2.7
PFNA	0.991	100.6 ± 0.5	99.7 ± 1.8	99.2 ± 3.5	102.7 ± 3.2
PFOA	0.999	100.5 ± 1.2	99.5 ± 0.9	103.2 ± 0.2	101.9 ± 4.0
PFHpA	0.992	96.8 ± 1.6	93.6 ± 0.6	99.6 ± 3.4	100.2 ± 0.8
diclofenac	0.999	94.1 ± 3.0	92.7 ± 1.5	88.9 ± 2.9	98.5 ± 0.8
Sulfamethoxazole	0.996	90.5 ± 2.9	87.3 ± 0.3	86.4 ± 0.8	83.9 ± 2.4
Phenytoin	0.998	70.5 ± 0.9	78.0 ± 2.1	71.2 ± 1.6	74.3 ± 2.3
carbamazepine	0.989	84.1 ± 0.4	78.7 ± 3.6	74.9 ± 2.2	89.5 ± 3.1
Lamivudine	0.998	81.9 ± 2.5	90.8 ± 4.1	78.9 ± 1.9	89.9 ± 0.5
Caffeine	0.989	79.3 ± 1.4	89.7 ± 2.9	75.6 ± 0.3	68.8 ± 0.9
acetaminophen	0.998	89.2 ± 2.0	78.2 ± 2.3	92.5 ± 0.1	79.5 ± 3.9
Triclosan	0.999	70.8 ± 3.1	77.5 ± 1.3	88.5 ± 3.3	85.2 ± 2.5
Bisphenol A	0.993	71.3 ± 2.3	69.5 ± 0.4	74.4 ± 2.6	72.6 ± 0.2
2-nitrophenol	-	nd	nd	nd	nd

4.2.1.1. Perfluorinated compounds

The result of perfluorinated compounds in the selected fish species are shown in Figures 4.1- 4.4. Their mean values and standard deviations are presented in Appendix I, Table I.1.

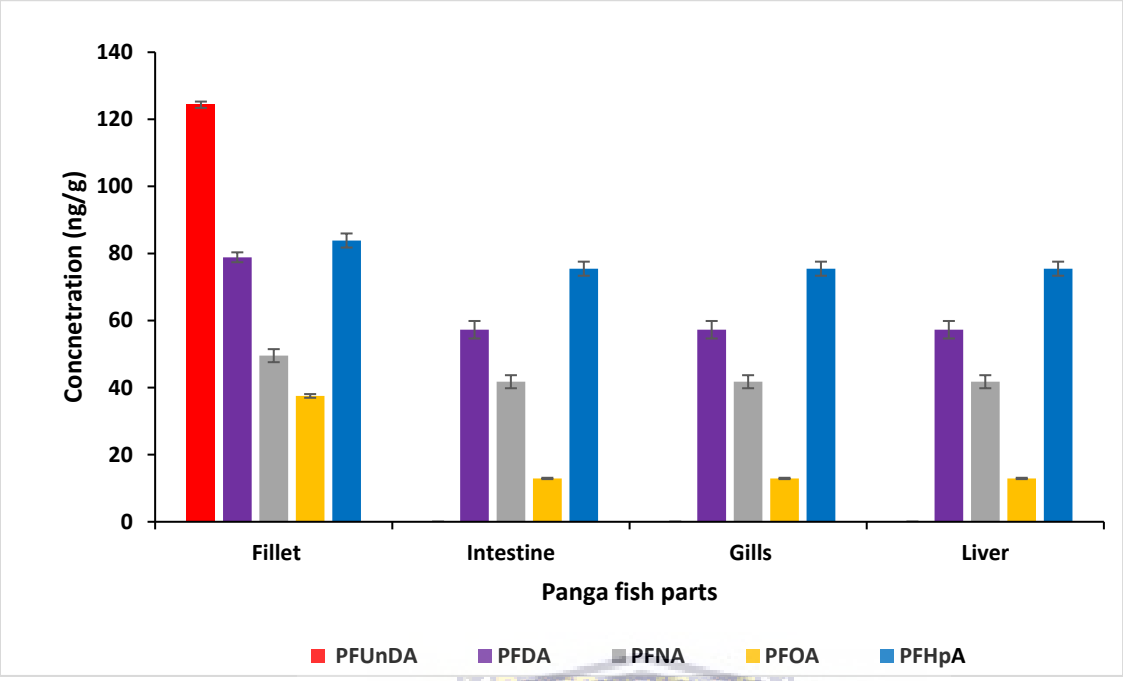


Figure 4. 1: Perfluorinated compounds in panga fish parts

PFUnDA was detected in the fillet of panga fish at a concentration of 124.4 ng/g while it was not detected in any of the other part of the fish. PFDA, PFNA, PFHpA and PFOA were detected in all the part of panga fish. Fillets had the highest concentration of 78.86 ng/g, 49.53 ng/g, 83.86 ng/g and 37.52 ng/g respectively, while the intestine, liver and gills ranged from 27.26 - 57.26 ng/g, 21.76 - 41.76 ng/g, 65.56 – 75.64 ng/g and 10.91 – 13.91 ng/g respectively (Appendix I, Table I.1). The overall distribution of PFCs in panga fish followed the order fillet > gills > intestine > liver (Figure 4.1).

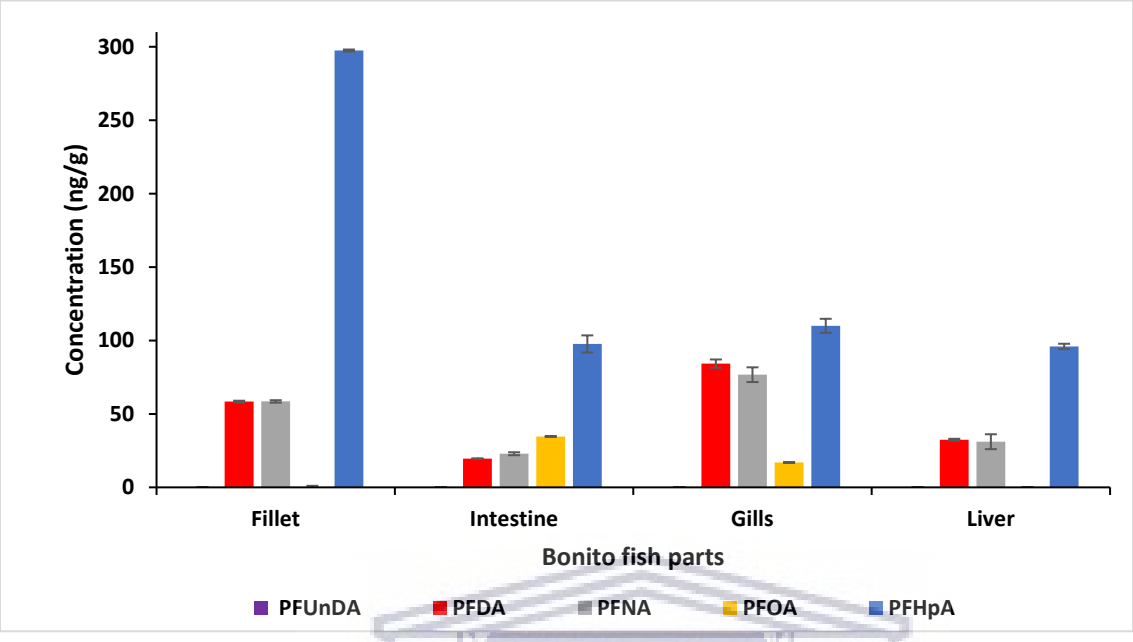


Figure 4. 2: Perfluorinated compounds in different parts of bonito fish species

As shown in Figure 4.2, in bonito fish, PFDA and PFNA were found in all the fish parts with gills having the highest concentration of 84.24 ng/g and 76.72 ng/g respectively while the concentration in other parts of the fish ranged from 19.52 – 58.41 ng/g and 22.89 – 58.52 ng/g respectively. PFHpA was detected in all the parts with the fillet having the highest concentration of 297.5 ng/g while other parts ranged from 95.95 – 110.0 ng/g. PFOA was detected in just the intestine and gills with a concentration of 34.65 ng/g and 19.91 ng/g respectively (Appendix I, Table I.1). PFUnDA was not detected in any of the fish parts. Furthermore, out of the perfluorinated compounds, PFHpA had the highest concentration in all the parts of the fish. The overall distribution of PFCs in bonito fish varied from part to part.

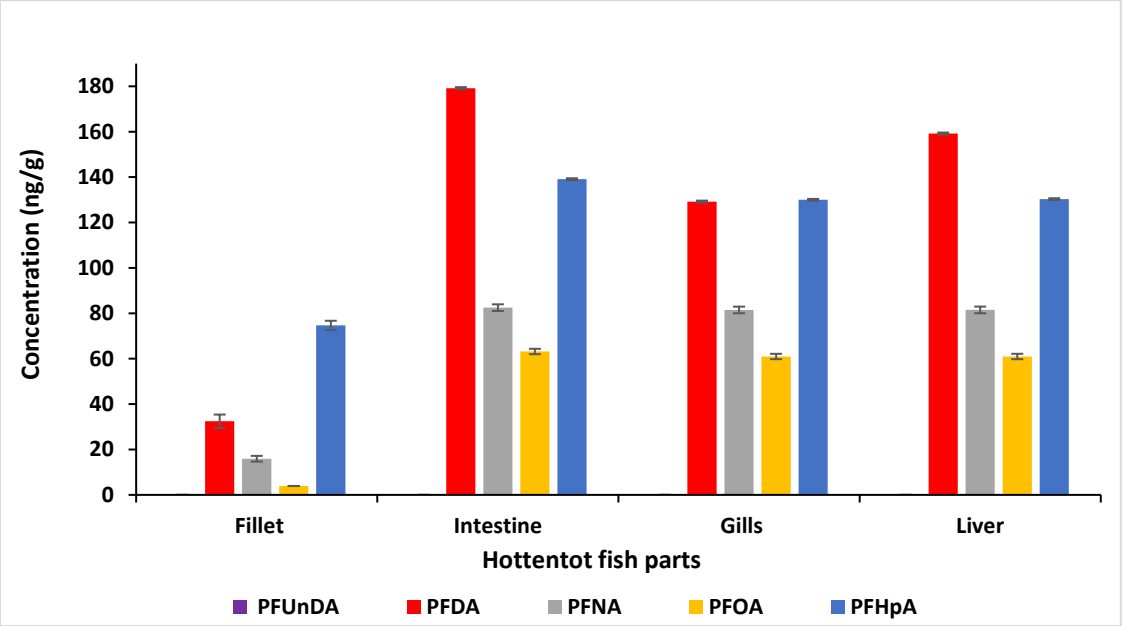


Figure 4. 3: Perfluorinated compounds in the different parts of hottentot fish species

In hottentot fish (Figure 4.3), PFDA, PFNA, PFOA and PFHpA were detected in all the parts. The intestine of hottentot fish part had the highest concentration of 179.2 ng/g, 82.49 ng/g, 63.17 ng/g and 139.1 ng/g respectively while the concentration in other parts ranged from 32.44 – 159.2 ng/g, 15.92 – 81.49 ng/g, 3.900 – 61.27 ng/g and 74.67 – 130.0 ng/g. However, Quinete et al., (2009) evaluated PFOA in the muscles of mullet from Guanabara Bay, Brazil and the concentration of (3.4 ng/g) were quite lower compared to our result in this study. The fillet has the lowest concentration of all the compounds; PFUnDA was not detected in any of the fish parts. The overall distribution of PFCs in hottentot fish followed the order: intestine > liver > gills > fillet (Figure 4.30).

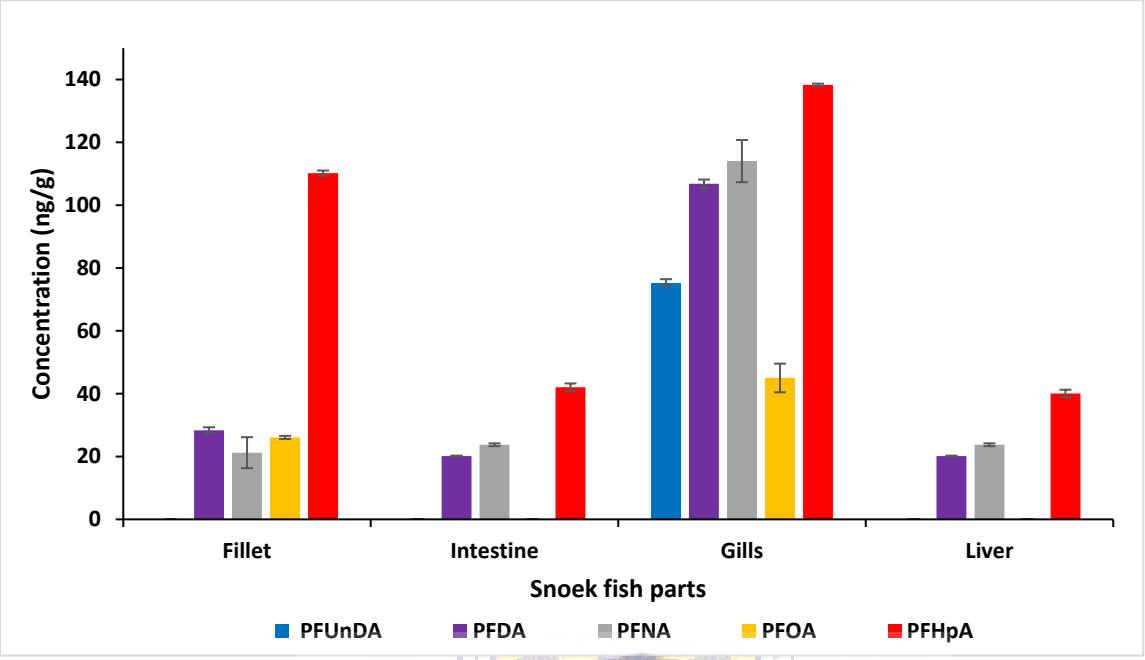


Figure 4. 4: Perfluorinated compounds concentration in snoek fish parts

In snoek fish (Figure 4.4), PFUnDA was only found in the gills with a concentration of 75.18 ng/g. PFDA, PFNA and PFHpA were detected in all the parts with gills having the highest concentration of 106.8 ng/g, 114.0 ng/g, 138.3 ng/g respectively while the concentration in other parts ranged from 20.13-28.33 ng/g, 21.22 – 23.74 ng/g and 40.06 – 110.2 ng/g respectively (Appendix I, Table I.1). PFOA was only detected in the fillet and gills with a concentration of 26.07 ng/g and 45.01 ng/g respectively. The overall distribution of PFCs in snoek fish followed the order gills > fillet > intestine > liver (Figure 4.4).

Overall, hottentot had the highest concentration of PFDA and PFOA of 179.2 ng/g and 63.17 ng/g respectively, snoek had the highest concentration of PFNA of 114.0 ng/g, bonito had the highest concentration of PFHpA of 297.5 ng/g. In a study conducted in Xiamen and Hong Kong, PFDA, PFNA, PFUnDA, and PFOA were determine in three marine fish and three fresh water fish, the concentration obtained from the study (0.33-0.71 ng/g) were considerably lower than the concentration from this present study (Zhao et al. 2011) (Table 4.4). These showed that

perfluorinated compounds levels might be higher in fish species around the marine environment of Cape Town, South Africa compared to the marine environments in other part of the world. This shows that marine water in Cape Town, South Africa contains high levels of perfluorinated compounds as a result of the possible high use of these compounds in the city.

Table 4. 4: Comparison of PFAs compounds (ng/g) in fish samples obtained in this study with others in previously published studies

Location/Country	PFUnDA	PFDA	PFNA	PFOA	PFHpA	Reference
Hong kong	0.71	-	0.65	-	-	(Zhao et al. 2011)
Xiamen	0.59	0.60	0.86	1.0	-	(Zhao et al. 2011)
Brazil	<3.0	<1.19	<1.41	1.63	2.34	(Quinete et al. 2009)
West coast of Korea	0.04	0.05	0.02	0.06	0.23	(Naile et al. 2013a)
North Carolina, USA	6.72	15.0	-	-	-	(Delinsky et al. 2010)
Greece	1.05	0.65	0.60	-	-	(Vassiliadou et al. 2015)
China	1.85	1.22	-	<0.5	-	(Shi et al. 2010)
New York, USA	-	-	-	5.2	-	(Sinclair et al. 2006)
Spain	0.71	<0.06	0.51	0.09	<0.08	(Domingo et al. 2012)
Ohio, USA	3.50	1.79	0.74	<0.20	0.64	(Ye et al. 2008)
Germany	nd	Nd	nd	2.3	nd	(Hölzer et al. 2011)
Cape Town, South Africa	124.4	78.86	49.53	37.52	83.86	This study

Moreover, PFUnDA was found only in panga fish, whereas hottentot fish had the highest concentration of PFDA and PFOA, in addition PFOA had the lowest concentration across the fish species. Snoek fish had the highest concentration of PFNA, and bonito fish had the highest concentration of PFHpA. Although, there was no specific trend in the concentration of perfluorinated compounds in each fish part of all fish species tested in this study, there were significant amounts of these contaminants in all fish parts. the health implication of these compounds to humans have been extensively highlighted in Chapter 7 of this thesis and the results on the levels of perfluorinated compounds in fish parts indicate that these compounds bioaccumulate in all fish parts which compliments the concentration of these compounds in seawater samples from False Bay-region where the fish were caught (Chapter 7).

4.2.1.2. Pharmaceutical compounds

The result of pharmaceutical compounds in the selected fish species are shown in Figures 4.5 - 4.8 with their average concentrations and standard deviations presented in Appendix I, Table I.1.

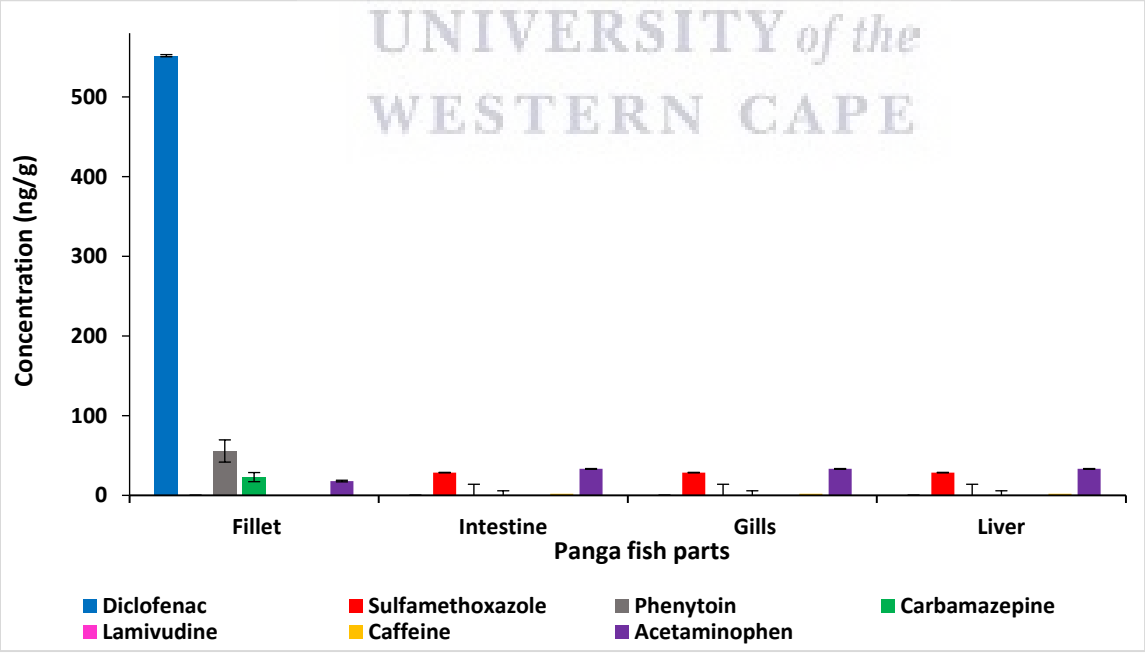


Figure 4. 5: Pharmaceutical compounds concentrations in panga fish parts

In the panga fish result (Figure 4.5), diclofenac, phenytoin and carbamazepine were only detected in the fillet with a concentration of 551.76 ng/g, 55.67 ng/g and 22.90 ng/g respectively while sulfamethoxazole and caffeine were only detected in the intestine, gills and liver with a concentration of 28.55 ng/g and 2.03 ng/g respectively. Acetaminophen was detected in all the parts with liver having the highest concentration of 33.26 ng/g and other parts ranging from 17.95 – 30.26 ng/g.

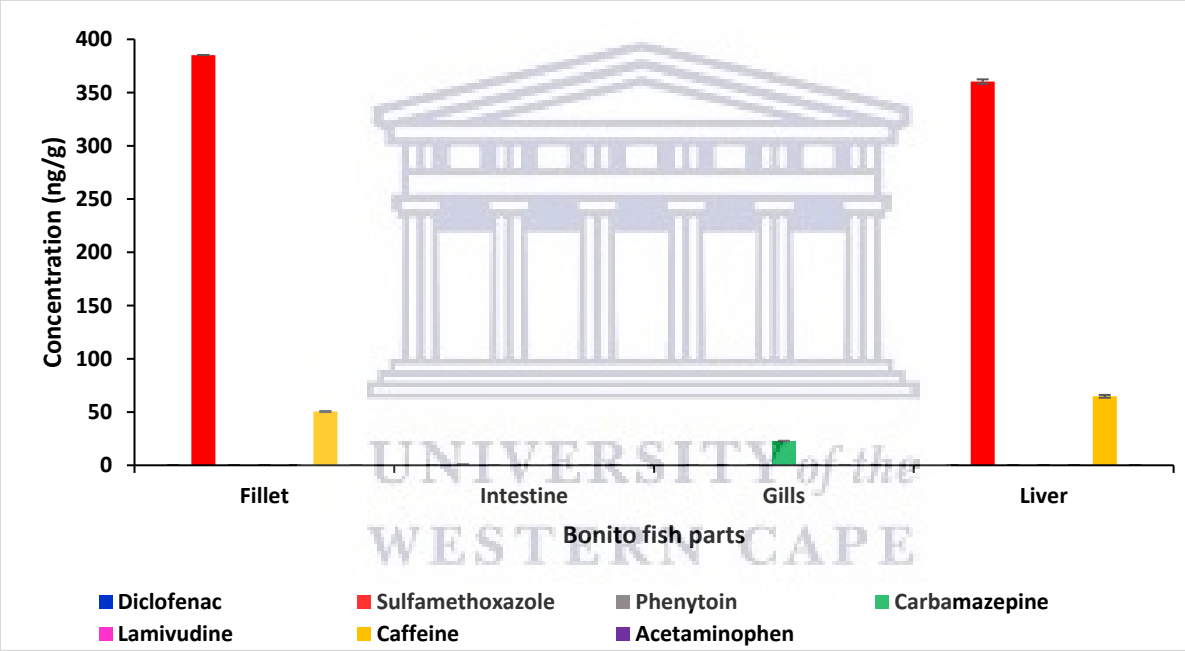


Figure 4. 6: The concentrations of pharmaceutical compounds found in bonito fish parts

In bonito fish (Figure 4.6), diclofenac, phenytoin and acetaminophen were not detected in any of the fish parts, whereas sulfamethoxazole and caffeine were detected in the fillet and liver with a concentration of 385.17 ng/g and 50.49 ng/g, 36.34 ng/g and 64.78 ng/g respectively. Caffeine was only detected in the gills with a concentration of 22.83 ng/g.

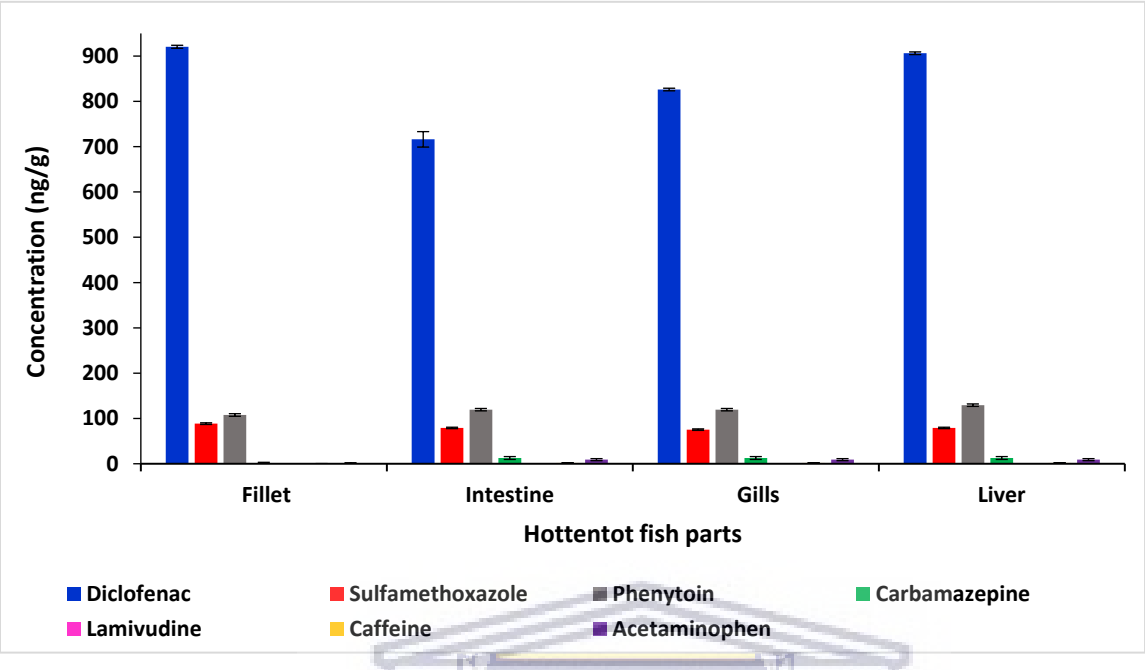


Figure 4. 7: Pharmaceutical compounds concentration in different parts of Hottentot fish

In hottentot fish (Figure 4.7), diclofenac and sulfamethoxazole were detected in all the fish parts with the fillet having the highest concentration of 920.52 ng/g and 88.53 ng/g respectively while phenytoin was detected in all parts but with liver having the highest concentration of 129.38 ng/g. The concentration in other parts ranged from 716.19 – 906.19 ng/g, 75.25 - 79.12 ng/g and 107.65 – 119.35 ng/g for diclofenac, sulfamethoxazole and phenytoin respectively.

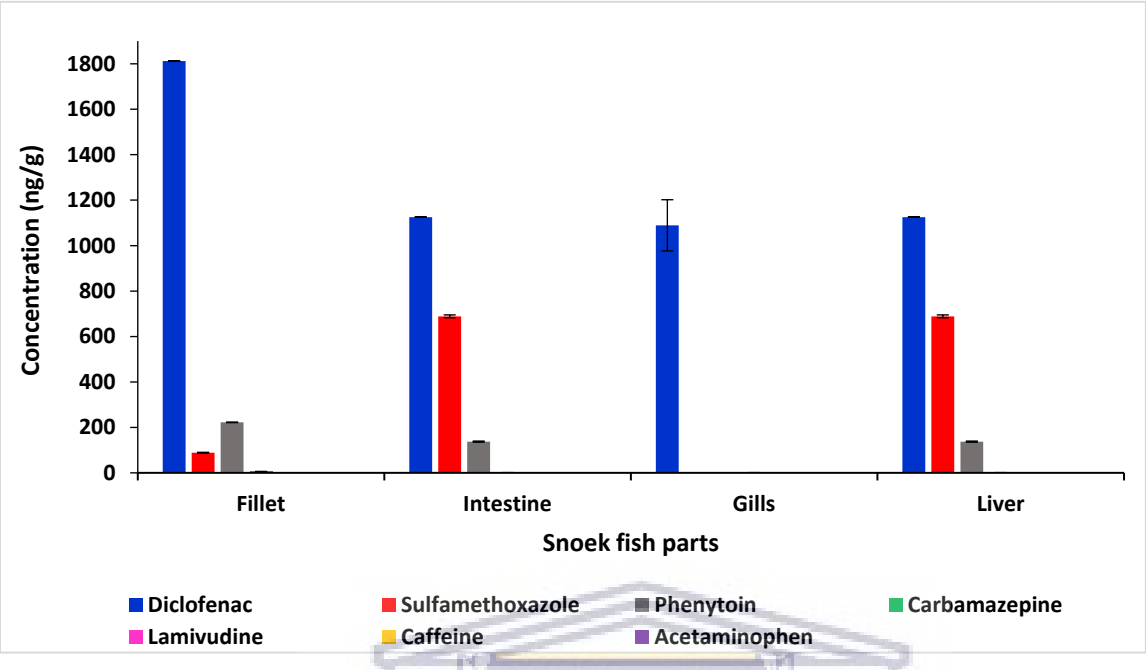


Figure 4. 8: The concentration of pharmaceutical compounds in Snoek fish parts

In snoek fish (Figure 4.8), diclofenac was detected in all the parts with the fillet having the highest concentration of 1812.32 ng/g and the concentrations in other parts ranged from 1089.07 – 1125.30 ng/g. Caffeine and acetaminophen were not detected in any of the fish part while carbamazepine was only detected in the fillet with a concentration of 5.16 ng/g. Sulfamethoxazole and phenytoin were detected in snoek fillet, intestine and liver with a concentration range of 88.63 – 688.55 ng/g and 137.44 – 222.24 ng/g respectively.

Overall diclofenac had the highest concentration out of all the pharmaceuticals compounds while sulfamethoxazole was the most dominant in all the fish samples, and was detected in at least in one part of all the fish species. Acetaminophen was only detected in panga fish and hottentot fish while caffeine was detected only in panga fish, bonito fish and hottentot fish. Carbamazepine was detected in at least in one part of all of the fish samples while phenytoin was detected in only panga fish, hottentot fish and snoek fish (Appendix I, Table I.1).

Although, there is no specific trend in the concentration of pharmaceutical compounds in each fish part of all the fish species in this study, there was a significant amount of these diverse contaminants in all fish parts. Also, worthy of note is that the concentration of these contaminants in the different parts/organs of panga and hottentot fish were the same, this could be attributed to the similarities observed in the size of these two fish species and the fact that these are reef fish found locally (Appendix I, Table I.1) compared to that of snoek and bonito fish species which are pelagic fish with a wider range of movement. A previous study has reported that pharmaceuticals in fish can reach significantly higher concentrations in plasma than in ambient water (Fent et al. 2006). These results indicate that pharmaceutical compounds bioaccumulate in all fish parts. Other fish species have shown similar bioaccumulation of diverse compound (Wang and Gardinali 2012; Álvarez-Muñoz et al. 2015; Moreno-González et al. 2016; Kim et al. 2017). However, maximum concentrations found in this study were considerably higher than those in the aforementioned studies.

By comparison, the highest concentration of sulfamethoxazole in this study was higher than that (0.95 ng/g) reported in the tissue of hake fish in Spain (Fernandez-Torres et al. 2010) and in a study reported by Li et al. (2012b) in North China (2.15 ng/g) while in a study from Laizhou Bay, North China the concentration of sulfamethoxazole (40-110 ng/g) in some fish organs were similar and others were lower compared to our study (Liu et al. 2018). The concentration of carbamazepine, acetaminophen and diclofenac reported in a study conducted by Dasenaki et al. (2015) in fish (20 ng/g for each compound) were also lower compared to this study.

Furthermore, several publications report PPCPs in freshwater fish species (Chu and Metcalfe 2007; Ramirez et al. 2007; Togunde et al. 2012; Garcia et al. 2012; Huerta et al. 2013; Du et al. 2014; Tanoue et al. 2014) and fish from brackish water, or contaminated rivers (Kolpin et al. 2002; Fick

et al. 2010; Gelsleichter and Szabo 2013). These prove the existence of these compounds in different water bodies worldwide.

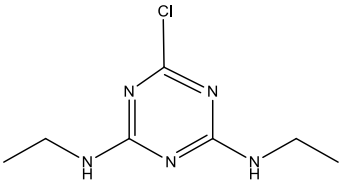
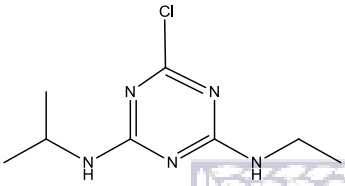
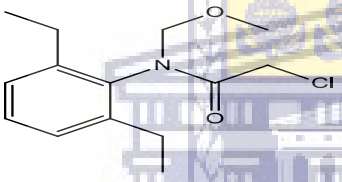
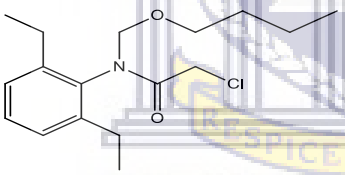
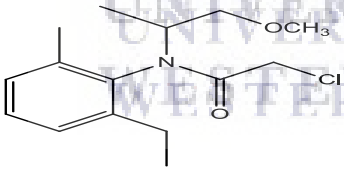
Bioaccumulation in fish can be achieved from water through the gills, skin, and food, resulting in enhanced levels of pollutants in fish tissue. Generally, feeding preference, general behaviour, amount of body lipid, and trophic level of fish are considered as factors affecting bioaccumulation. Moreover, the ecological characteristics of fish play a significant role in the bioaccumulation of these pollutants.

To sum up, exposure of organisms to biologically active chemicals in urban sewage effluents does not solely affect vertebrates. In some cases there is greater sensitivity in invertebrates, microbes, and plants than in fish, which can change the entire community structure (Waiser et al. 2011). Nevertheless, more complete experimental design, such as laboratory and field controls should be employed to determine the impacts of persistent organic pollutants upon fish in future work.

4.2.1.3. Herbicides

The experimental protocols have been discussed in Chapter 3 of this thesis. Table 4.5 provides the chemical parameters and instrumental conditions for the target compounds including GC-MS retention time, transition and collision energy, limit of detection (LOD), and limit of quantification (LOQ). Appendix I, Table I.2 shows the analysis of the compounds concentration in ppb according to each fish type and fish part, and compared the concentrations of the contaminants (Simazine, Atrazine, Alachlor, Metolachlor, and Butachlor). Their corresponding chromatograms and calibration curves are shown in Appendix I, Figure I.2.

Table 4. 5: Molecular mass (g/mol), retention time (min), quantification and diagnostic ions used in GC-MS/MS analysis and LODs and LOQs of analyzed pesticides.

Compounds	Molecular mass (g/mol)	Molecular structure	RT (Min)	m/z ions	CE (V)	R^2	LOD (ng/g)	LOQ (ng/g)
Simazine	201.6		12.38	**201**, 186, 174	1.45	0.9979	62.43	208.10
Atrazine	215.7		12.32	**200,** 122, 132	1.50	0.9995	29.15	97.17
Alachlor	269.8		13.42	**160,** 132, 130	1.05	0.9991	44.94	149.80
Butachlor	311.85		15.37	**176,** 160, 146	1.05	0.9999	16.22	54.08
Metolachlor	283.8		14.21	**162,** 132, 133	1.05	1.0000	14.96	49.87

Quantitation ions in bold RT - retention time, CE - collision energy (V), LOD – limit of detection, LOQ – limit of quantification,.

The concentration of herbicides in the muscle and organs of each fish species are shown in Figures 4.9 - 4.12 and are presented in Appendix I, Table I.2.

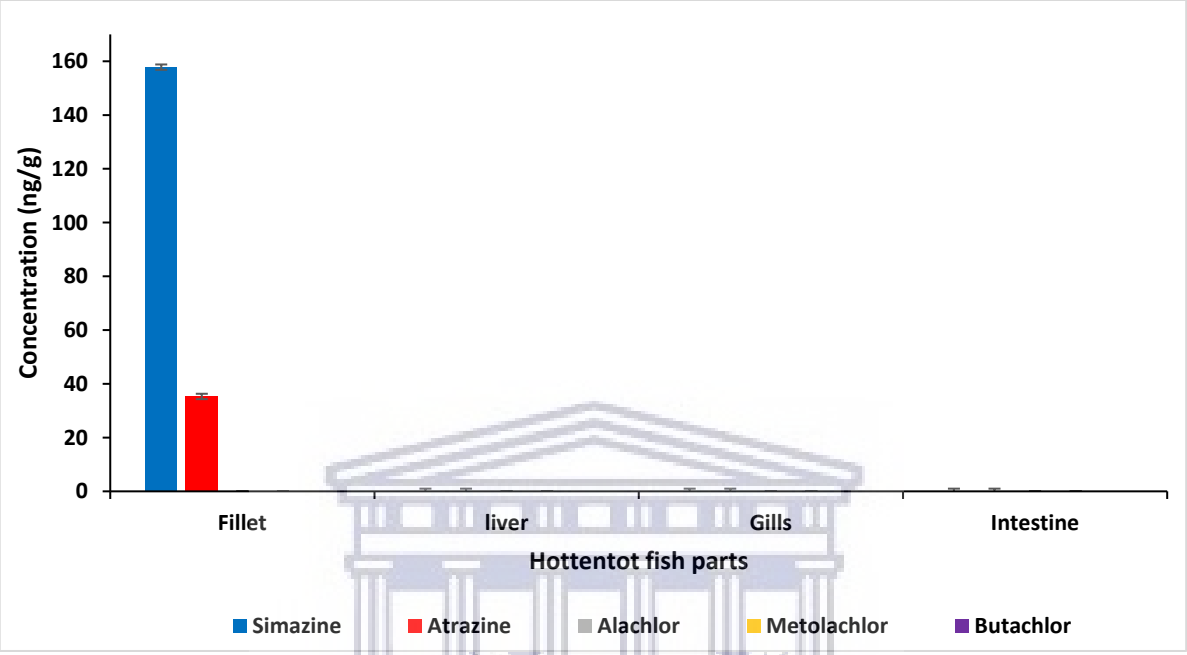


Figure 4. 9: Herbicide concentrations in hottentot fish parts

In hottentot fish (Figure 4.9), simazine and atrazine were detected mainly in the fillet sample with a concentration of 157.82 ng/g dw and 35.31 ng/g dw respectively, whereas alachlor, metolachlor and butachlor were below detection limit in all of the hottentot fish parts.

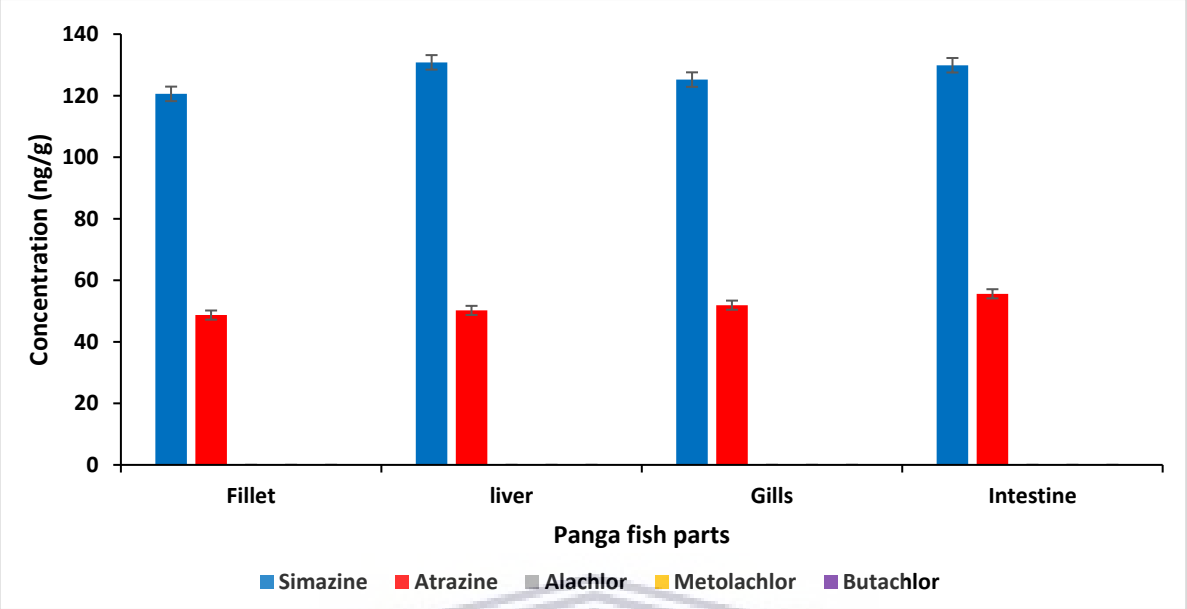


Figure 4. 10: Herbicide levels in panga fish parts

In panga fish (Figure 4.10), simazine was found to be present in all the fish organs and tissues, while the highest concentration was found in the liver (130.82 ng/g) and the observed concentration in other organs and tissues were found to range from 120.58 ng/g dw– 129.88 ng/g dw. The order of distribution of simazine in panga fish sample followed liver > intestine > gills > fillet. Atrazine was also found in all the fish organs and tissues and the highest concentration of 55.61 µg/g was found in the intestine and the concentration of atrazine in other organs was found to range from 48.69 ng/g dw – 51.91 ng/g dw. The distribution of atrazine in panga fish was in the order of intestine > gills > liver > fillet. However, alachlor, metolachlor and butachlor were below the limit of detection in all the panga fish organs and tissues. In a recent study conducted by Cruzeiro et al. (2016b) the concentration of alachlor, atrazine and simazine were considerably lower compared to this study.

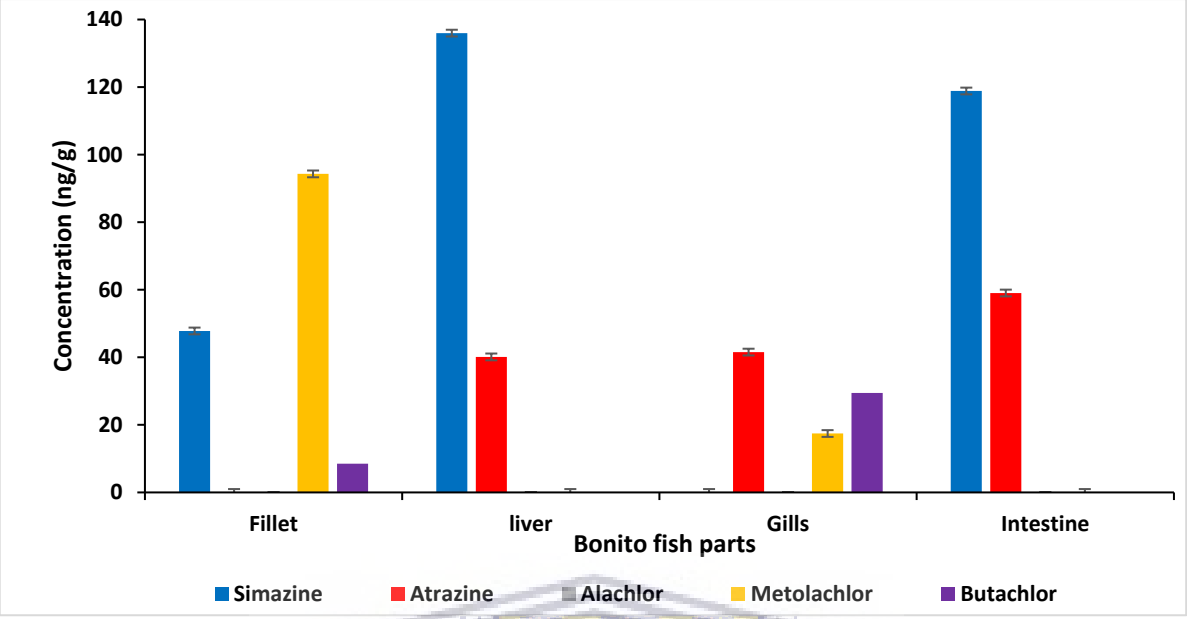


Figure 4. 11: Herbicide concentrations detected in different parts of bonito fish species

In bonito fish (Figures 4.11), simazine was detected in the fillet, liver and intestine only and the highest concentration of simazine was found in the liver (135.97 ng/g) while the simazine concentration in fillet and intestine were 47.79 ng/g dw and 118.84 ng/g dw respectively. The overall distribution of simazine in bonito fish sample followed the order liver > intestine > fillet > gills. Atrazine was detected in the liver, gills and intestine a concentration of 59.04 ng/g dw was detected in the intestine which was the highest concentration observed in the fish sample while the detected concentration of gills and liver were 41.55 ng/g dw and 40.12 ng/g dw respectively. The observed distribution of atrazine in bonito fish sample was found to followed this order intestine > gills > liver > fillet. Metolachlor, alachlor and butachlor were below the limit of detection in any of the bonito fish parts. The concentration of metolachlor found in fish in a study reported by Belenguer et al. (2014) was higher compared to the concentrations obtained in this study. Also in a study conducted on *Tilapia zilli* and *Clarias gariepinus* by Lawrence et al. (2015) the observed

concentration of atrazine in this fish species were lower compared to the concentration of atrazine found in this study.

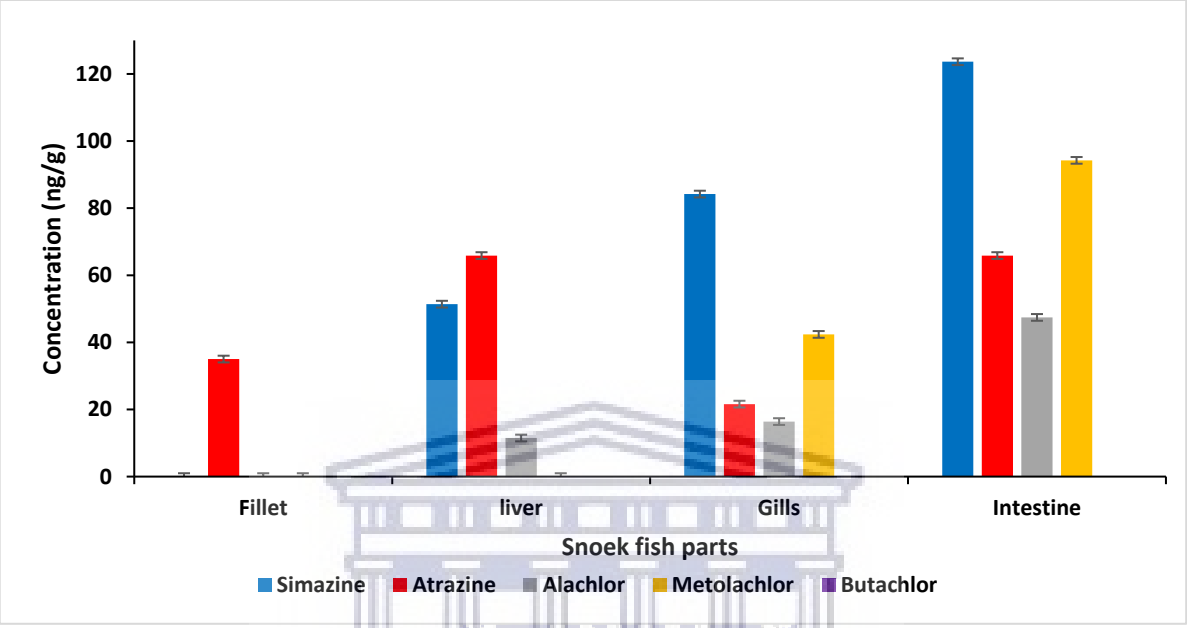


Figure 4. 12: The concentration of the detected herbicides in snoek fish parts

In snoek fish (Figure 4.12), simazine was detected only in the liver, gills and intestine, the highest levels of simazine was found in the intestine and liver (123.64 ng/g dw) while the levels of simazine found in the liver and gills were 51.38 ng/g and 84.20 ng/g respectively. Similarly, alachlor was found only in the gills and intestine with the intestine having greater amount of 47.43 ng/g dw. The concentration of alachlor in gills was 16.39 ng/g dw. The general distribution of simazine and alachlor in snoek fish was in this order: intestine > gills > liver > fillet. Atrazine was found to be present in all the fish organs and tissues and the highest amount was found in liver and intestine (65.87 ng/g) while the observed concentration in the remaining parts of the fish was from 21.59 ng/g dw – 35.03 ng/g dw. The overall occurrence of atrazine in snoek fish was liver = intestine > gills > fillet. Metolachlor was found only in the gills (42.38 ng/g). The concentration of metolachlor found in the liver and muscle of fish analysed by Kaczyński et al. (2017) were higher compared to

this study. Butachlor was found to be below the detection limit hence not detected in any of the snoek fish parts.

Generally, simazine and atrazine were the most dominant compounds detected in the fish species. Simazine had the highest significant mean concentration 157.8 ng/g followed by atrazine with a significant mean 35.31 ng/g across the fish species, while alachlor was detected only in snoek fish and butachlor was detected only in bonito fish (Appendix I, Table I.2). Metolachlor was found to be present only in snoek fish. Reindl et al. (2015), reported atrazine and simazine in fish but their results were found to be lower compared to the results observed in this study. Other studies that have reported similar levels of these herbicides include (Manirakiza et al. 2002; Masiá et al. 2013; Belenguer et al. 2014; Lawrence et al. 2015; Kaczyński et al. 2017).

Atrazine, simazine and metolachlor according to USEPA belong to Group C which are possible human carcinogens while alachlor belongs to Group B2 which indicates sufficient evidence in animals but inadequate or no evidence in humans (US EPA 2000). Generally, herbicides use is a reality in South Africa, it does not only impact the farmer but also the produce and natural resources end-user of the fish or water. Thus, the application of herbicides and its use must be considered as an important matter and not only at agricultural level, but, also at municipal level. Cities such as Cape Town rely on herbicides for weed control on pavements, golf course and parks instead of weeding by hand. Given that the city seasonally applies weed killers, it is highly likely that such herbicides would leach out into storm water drains and out into the oceans during rainfall event. Moreover, many homeowner apply herbicides to curb unwanted growth in gardens. Thus urban use as well as agricultural application may contribute to this pollution at sea. This is particularly the case in Camps Bay (Chapter 6) which has no agricultural activities.

4.2.2. Metal accumulation in fish species

The method of analysis for the determination of metals have been highlighted in Chapter 3. The toxic metals analysed in this study include arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), aluminium (Al), Thorium (Th), yttrium (Y), rubidium (Rb), niobium and (Nb) (Masindi and Muedi 2018; Zhuang 2019), while the non-toxic include titanium (Ti), silicon (Si), strontium (Sr), cerium (Ce), selenium (Se), zinc (Zn), iron (Fe), copper (Cu), cobalt (Co), molybdenum (Mo), manganese (Mn), zirconium (Zr). However, some of these non-toxic metals may become toxic when consumed at higher concentrations. For instance, selelnium, zinc, iron and copper but to mention a few are known to become toxic when consumed or exposed to much higher concentrations (Abdallah 2008). Comparative analysis of metal content in the different fish species are presented in Appendix I, Table I.3 and the concentration in each fish species are shown in Figures 4.13- 4.16. As and Cr were not detected in bonito fish and Th was not detected in snoek fish while Cd and Be were not detected in any of the fish species. This may be as a result of the fact that these elements are not significantly present in these fish environment or they do not bio-accumulate in these fish species. Similar results have been reported for these metals in previously published papers (Tüzen 2003; Uysal et al. 2008; Elnabris et al. 2013; Baharom and Ishak 2015).

The levels of contamination of the different fish species were observed to be highest from Sr > Fe > Al > Si > Zn > Cu > Pb > Ni while Y > Rb > Co > Zr > Cr accumulated lowest in all fish species. Although there were great variations in the sequence of metal concentrations in all fish species, the level of concentration of all metals (except Nb and Th) varied significantly across all fish samples ($p < 0.05$). This variation in metal concentrations in all fish species can be ascribed to the different

levels of metal binding proteins like metallothioneins in these fishes (Canli and Atli, 2003; Al-Yousuf *et al*., 2000; Usero *et al*., 2004). Cd was not detected in any of the fish species.

The accumulation orders of metals in the tissues were nearly similar. In other words, while Sr, Zn, Nb, Si, Al and Fe accumulated at highest concentrations in all tissues of the species, Y, Co, Zr and Rb were also accumulated at the lowest levels. On the other hand, there were great variations among metal accumulation amounts in the investigated tissues of the species.

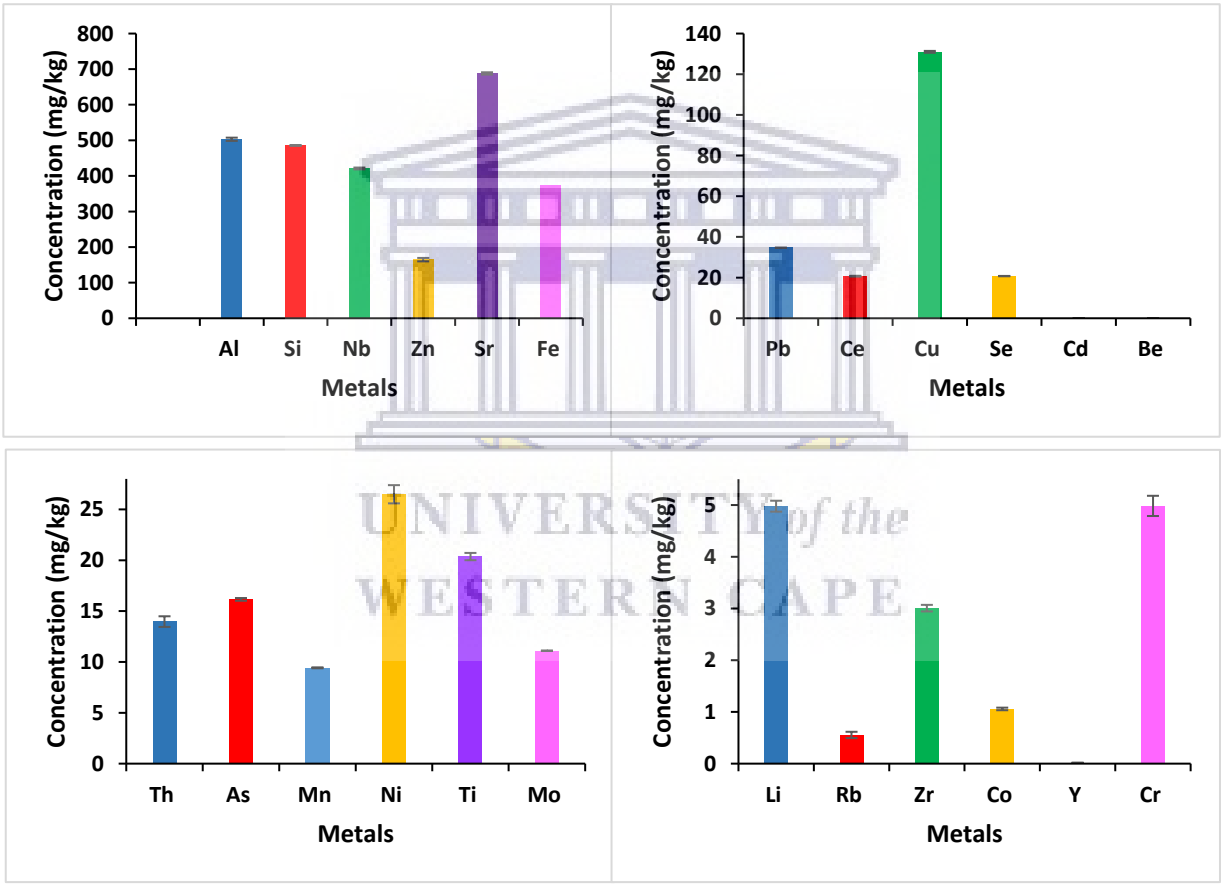


Figure 4. 13: The concentration of metals in panga fish species

In panga fish (Figure 4.13), Sr had the highest concentration 687.7 mg/kg while Y had the lowest concentration of 0.02 mg/kg. The distribution of metals in panga fish was Sr > Al > Si > Nb > Fe > Zn> Cu > Pb > Ni > Se > Ce > Ti > As > Th > Mo > Mn > Cr = Li > Zr > Co > Rb > Y.

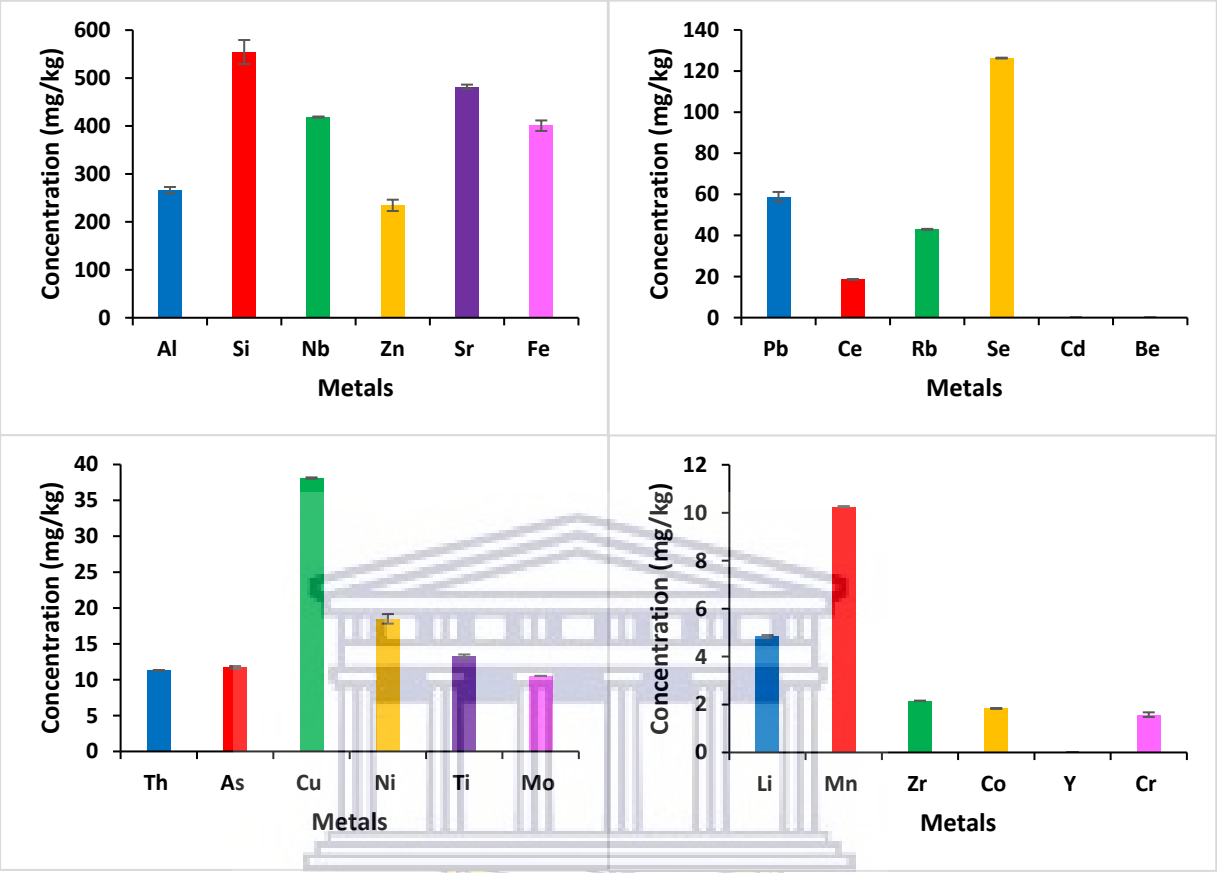


Figure 4. 14: Metal concentrations in Hottentot fish species

In hottentot fish (Figure 4.14), Si had the highest concentration of 554.30 mg/kg while Y also had the lowest concentration of 0.01 mg/kg. The distribution of metals in panga fish was Si > Sr > Nb > Fe > Al > Zn > Se > Pb > Rb > Cu > Ce > Ni > Ti > As > Th > Mo > Mn > Li > Zr > Co > Cr > Y.

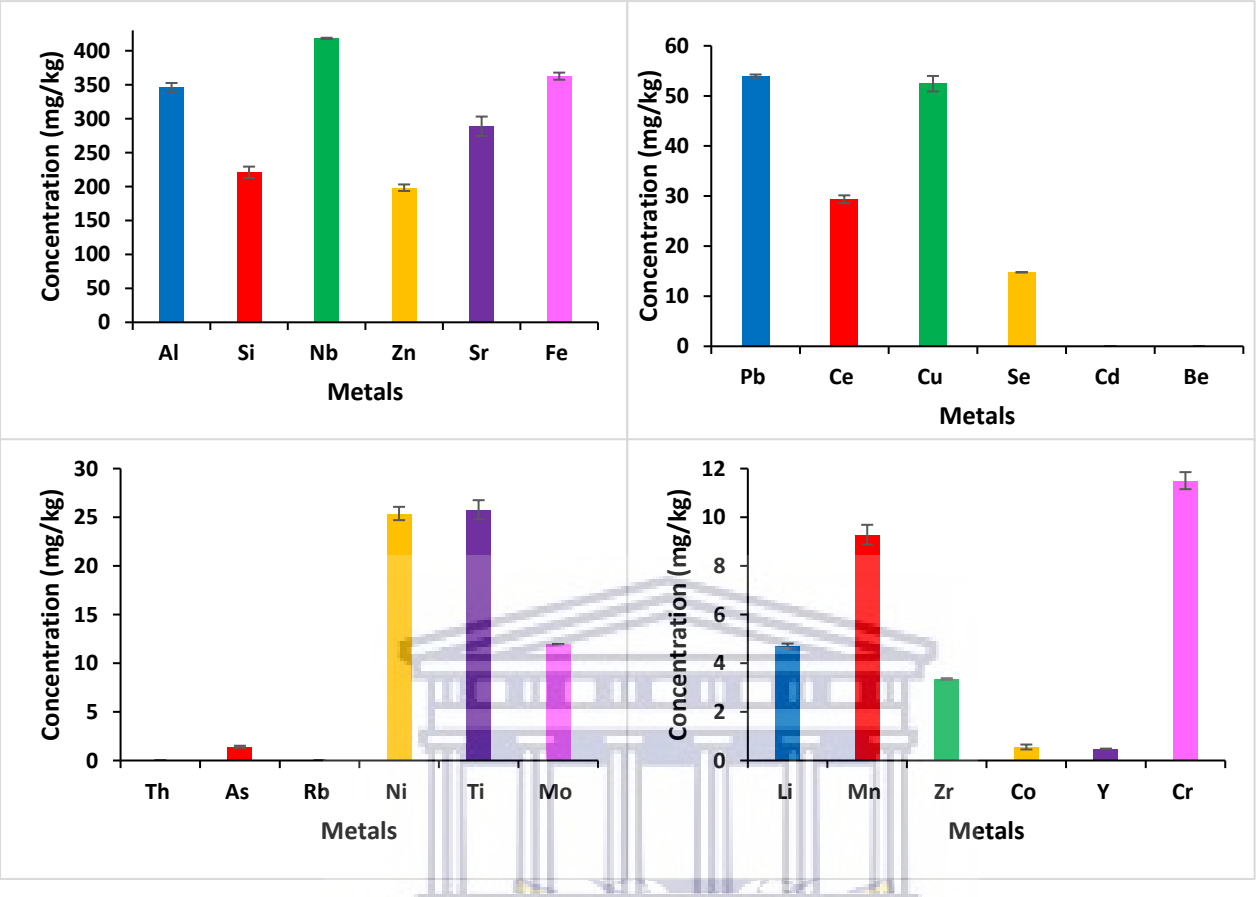


Figure 4. 15: The metal concentration in snoek fish samples

In snoek fish (Figure 4.15), Nb had the highest concentration of 418.3 mg/kg while Y had the lowest concentration of 0.48 mg/kg whereas Th and Rb were below detection limit. The distribution of metals in panga fish was Nb > Fe > Al > Sr > Si > Zn > Pb > Cu > Ce > Ti > Ni > Se > Mo > Cr > Mn > Li > Zr > As > Co > Y.

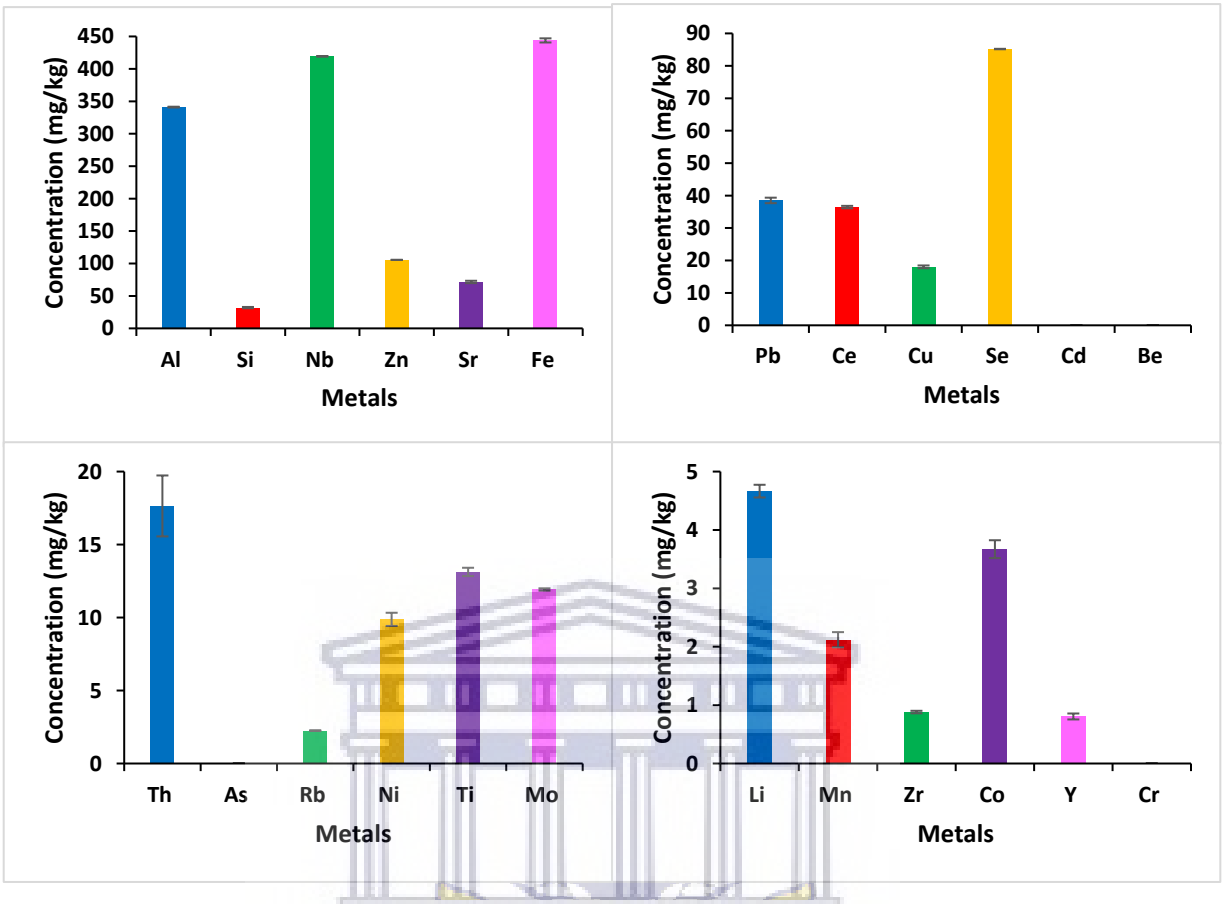


Figure 4. 16: The concentration of metals in bonito fish

In bonito fish (Figure 4.16), Fe had the highest concentration of 443.9 mg/kg while Y had the lowest concentration of 0.81 mg/kg whereas As and Cr were not detected. The distribution of metals in panga fish was Fe > Nb > Al > Zn > Se > Sr > Pb > Ce > Si > Cu > Th > Ti > Mo > Ni > Co > Rb > Mn > Zr > Y.

Comparing our study with other studies, the level of metals found in *Acipenser ruthenus* (Jaric et al. 2011) and in fishes from Palestine (Elnabris et al. 2013) were lower compared to the levels observed in this study. Similarly in a study conducted on *Alosa immaculata* Bennet 1835 the concentrations found were also lower compared to this study (Visnjic-Jeftic et al. 2010). Türkmen et al. (2009) reported a lower concentration of metals in fish species from Aegean and Mediterranean Seas. In a study by Fallah et al. (2011) conducted on farmed and wild *Oncorhynchus*

mykiss the observed concentration were considerably lower to this study. Similar results to this study were found in fish analysed from the Red Sea by (El-Moselhy et al. 2014) and fish from Saudi Arabian markets (Alturiqi and Albedair 2012).

It was determined that the mean concentration of heavy metals in tissues was quite different among species (Appendix I, Table I.3). Some researchers indicated that different fish species from the same area contained different metal levels in their tissues. Metal bioaccumulation in fish is species-dependent. Feeding habits and life style of species are strongly related to accumulation levels (Andres et al. 2000; Canli and Atli 2003). The fact that toxic metals are present in high concentrations in South Africa marine fish species is of particular concern.

Cu and Zn are important for human nutrition and good health but intakes at a very high concentration can cause health problems (Abdallah 2008). Food and Agricultural Organization's limits for Cu and Zn is 30 mg/kg (FAO 1983). The levels of Cu and Zn determined in the tissues of the fish species were higher than the levels issued by FAO and Turkish legislation. According to European Commission Regulation (1881/2006/EC), the maximum acceptable concentrations (MAC) for Cd and Pb in fish meat are 0.05 µg/g and 0.3 µg/g wet weight, respectively. National regulation of the Republic of Serbia prescribed 1.0, 0.1 and 2 µg/g wet weight as MAC for Pb, Cd and As in fresh fish meat, respectively (Baltic et al. 1979). The metal levels in tissues of fish species in the current study was compared with the maximum permissible limits for human consumption (MPL) established by many different organizations (Appendix I, Table I.3). The levels of the metals exceeded the maximum acceptable concentrations (MAC), indicating that the different fish in this area are heavily contaminated with metals which will pose serious health complications to the fish and consequently to humans when the fish are consumed. The presence of these metals

could be as a result of anthropogenic activites, sewage discharge and industrial activies around these sites. Similar observations were reported in previously published studies (Aktar et al. 2011; Qadir and Malik 2011; Authman et al. 2012) where metal concentrations exceeded acceptable limits or where they were lower (Tabari et al. 2010) with industrial and man-made pollution reported for their presence in fish parts.

4.3. Risk assessment studies

4.3.1. Ecological risk assessment

The impact of PPCPs, PFCs and herbicides in different fish species was evaluated using risk quotient method highlighted in Chapter 3, section 3.11.1; LC50 and NOEC were use to determine the level of toxicity from the acute and chronic ecotoxicity testing. For chronic risk, when RQ < 1.0, this shows no chronic risk concern but if higher, there is a chronic risk. Also, for acute risk, when RQ < 0.5, this shows no high acute risk concern (US EPA 2016a). Therefore, the levels of concern for both acute and chronic risk are values above 0.5 and 1.0 respectively.

4.3.1.1. Risk assessment for PPCPs and PFCs

Table 4.6 shows the respective risk quotients of the results obtained for the PPCPs and PFCs in fish. From Appendix I, Table 1.1, triclosan, bisphenol A and 2-nitrophenol were not detected in any of the fish species therefore their risk quotient were not calculated.

Table 4. 6: Values for acute and chronic risk in fish species for PPCPs, PFCs and EDCs

	Panga fish				Bonito Fish				Hottentot fish				Snoek fish			
	Fillet	Intestine	Liver	Gills	Fillet	Intestine	Gills	Liver	Fillet	Intestine	Liver	Gills	Intestine	Liver	Gills	Fillet
PFUnDA																
Acute	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0
Chronic	6.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6	0.0
PFDA																
Acute	1.3	1.0	1.0	1.0	1.0	0.3	1.4	0.5	0.5	3.0	3.0	3.0	0.3	0.3	1.8	0.5
Chronic	3.9	2.9	2.9	2.9	2.9	1.0	4.2	1.6	1.6	9.0	9.0	9.0	1.0	1.0	5.3	1.4
PFNA																
Acute	0.8	0.7	0.7	0.7	1.0	0.4	1.3	0.5	0.3	1.4	1.4	1.4	0.3	0.4	1.9	0.4
Chronic	2.5	2.1	2.1	2.1	2.9	1.1	3.8	1.6	0.8	4.1	4.1	4.1	1.1	1.2	5.7	1.1
PFOA																
Acute	0.6	0.2	0.2	0.2	0.0	0.6	0.3	0.0	0.1	1.0	1.0	1.0	0.0	0.0	0.8	0.4
Chronic	1.9	0.6	0.6	0.6	0.0	1.7	0.8	0.0	0.2	3.0	3.0	3.0	0.0	0.0	2.3	1.3
PFHpA																
Acute	1.4	1.3	1.3	1.3	5.0	1.6	1.8	1.6	1.2	2.2	2.2	2.2	0.7	0.6	2.3	1.8
Chronic	4.2	3.8	3.8	3.8	14.9	4.9	5.5	4.8	3.7	6.5	6.5	6.5	2.0	2.0	6.9	5.5
DCF																
Acute	14.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.3	11.9	15.1	13.8	18.8	18.7	18.2	30.2
Chronic	42.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	46.0	35.8	45.3	41.3	56.3	56.2	54.5	90.6
SMX																
Acute	0.0	0.5	0.5	0.5	6.4	0.0	0.0	6.0	1.5	1.3	1.3	1.3	11.5	11.4	0.0	1.5
Chronic	0.0	1.4	1.4	1.4	19.3	0.0	0.0	18.0	4.4	4.0	4.0	4.0	34.4	34.4	0.0	4.4
PHE																
Acute	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	2.0	2.0	2.0	2.3	2.2	0.0	3.7
Chronic	2.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.4	6.0	6.0	6.0	6.9	6.8	0.0	11.1
CAR																
Acute	0.4	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.2	0.2	0.2	0.0	0.0	0.0	0.1
Chronic	1.1	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.6	0.6	0.6	0.0	0.0	0.0	0.3
CAF																
Acute	0.0	0.0	0.0	0.0	0.8	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chronic	0.0	0.1	0.1	0.1	2.5	0.0	0.0	3.2	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
ACT																
Acute	0.3	0.6	0.6	0.6	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.0	0.0	0.0	0.0
Chronic	1.0	1.7	1.7	1.7	0.0	0.0	0.0	0.0	0.0	0.5	0.5	0.5	0.0	0.0	0.0	0.0

The risk quotients for perfluorinated compounds in panga fish type, PFUnDA shows high acute and chronic risk with high values of 2.07 and 6.22 respectively in the fillet which had the highest values out of all the compounds while it was not detected in other organs (gills, liver and intestine). PFDA, PFHpA and PFNA were observed to be of high acute and chronic risk concern in all parts of the fish while PFOA showed a high acute and chronic risk in the fillet, and low risk in liver, intestine and gills of the fish. All the compounds showed a high risk, both acute and chronic, in the fillet parts of the fish which is the part humans consume. For pharmaceutical compounds, diclofenac showed a very high acute and chronic risk in the fillet with values of 14.20 and 42.59 respectively while sulfamethoxazole showed low acute and high chronic risk in the gills, liver and intestine but was not detected in the fillet of the fish. Phenytoin was observed to be of high acute and chronic risk concern only in the fillet of the fish while carbamazepine showed low acute and high chronic risk in the fillet but was not detected in other organs of the fish. Caffeine showed low acute and chronic risk in the gills, liver and intestine but was not detected in the fillet of the fish while acetaminophen showed low acute and chronic risk in the fillet but high acute and chronic risk in the gills, liver and intestine of the fish.

For perfluorinated compounds in bonito fish: PFUnDA was not detected in any of the fish organs. PFDA showed high acute and chronic risk in the fillet, gills and liver and low acute and chronic risk in the intestine of the fish. PFNA was observed to be of high acute and chronic risk concern in the fillet, gills and liver and low acute and high chronic risk in the intestine of the fish. PFOA showed a high acute and chronic risk in the intestine, and low risk in gills of the fish but was not detected in the fillet and liver of the fish. PFHpA showed high acute and chronic risk in all the fish organs (fillet, gills, intestine and liver). For pharmaceutical compounds, diclofenac, phenytoin, acetaminophen and lamivudine were not detected in bonito fish so their risk quotient were not

determined. Sulfamethoxazole showed a very high acute and chronic risk in the bonita fillet and liver with values of 6.42 and 19.26, 6.01 and 18.02 respectively while carbamazepine showed a low acute but high chronic risk in the gills of the fish. Caffeine was observed to be of high acute and chronic risk concern in the fillet and liver of the fish while it was not detected in the gills and intestine of the fish.

For perfluorinated compounds in hottentot fish: PFUnDA was not detected in any of the fish organs. PFDA and PFHpA were observed to be of high acute and chronic risk concern in all organs of the fish while PFOA and PFNA showed a high acute and chronic risk in the intestine, gills and liver of the fish and low risk in the fillet of the fish. For pharmaceutical compounds, diclofenac showed a very high acute and chronic risk in all the fish organs with values ranging from 11.94 - 15.34 and 35.81- 46.03 respectively while sulfamethoxazole and phenytoin were observed to be of high acute and chronic risk concern in all the fish organs. Carbamazepine, acetaminophen and caffeine showed low acute and chronic risk in the gills, liver and intestine and were not detected in the fillet of the fish, while lamivudine was not detected in any of the fish organs.

For perfluorinated compounds in snoek fish: PFUnDA showed a high acute and chronic risk with values of 1.25 and 3.76 respectively in the gills while it was not detected in other organs (fillet, liver and intestine). PFDA and PFNA showed high acute and chronic risk only in the gills with low acute but high chronic risk in the intestine, liver and fillet of the fish. PFOA showed a high acute and chronic risk in the gills as well as a low acute and high chronic risk in the fillet of the fish but was not detected in the intestine and liver of the fish. PFHpA was observed to be of high acute and chronic risk concern in all the fish organs (fillet, gills, intestine and liver). For pharmaceutical compounds, diclofenac showed a very high acute and chronic risk in all the snoek fish parts with values that ranged from 18.2 – 30.2 and 54.5 – 90.6 respectively with the fillet

having the highest values. Sulfamethoxazole and phenytoin showed a very high acute and chronic risk in the fillet, intestine and liver but were not detected in the gills of the fish, while carbamazepine showed a low acute and chronic risk in the fillet and was not detected in the remaining organs of the fish. Results from screening the risk level characterization in the fish samples showed high acute and chronic risk for some of the investigated compounds, implying that significant impacts on seawater fish species are likely and so is the associated risk. Hence, further perfluorinated compounds and PPCP occurrence, exposure and toxicological input (especially for long-term (chronic) effects on organisms and possible effects of combined exposure to multiple compounds) are required for better understanding of their possible adverse effects to non-target organisms and in order to provide a more comprehensive picture of their combined risk and impact upon the oceanic environment. These fish are wild caught by small commercial fishing vessels that are stationed at Kalk Bay harbour. The high degree of contamination found in fish that are free swimming in the pelagic zone around the coastal waters of the Western Cape should be a cause for alarm since the pollution can only be due to the poor sewage disposal practiced by the city as these compounds are all due to human excretion and effluents being discharged into the marine environment (CSIR 2017; Petrik et al. 2017).

4.3.1.2. Risk assessment for herbicides

The impact of herbicides in different fish species was evaluated using the risk quotient method, and Table 4.7 shows the results obtained for the herbicides in fish with their respective risk quotients.

Table 4. 7: Risk quotient values for acute and chronic risk for fish species for pesticides

Fish type	Fish part	Simazine		Atrazine		Alachlor		Metolachlor		Butachlor	
		Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute	Chronic
Hottentot	Fillet	2.6	7.9	0.6	1.8	nd	nd	nd	nd	nd	nd
	Liver	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Gills	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Intestine	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Panga	Fillet	2.0	6.0	0.8	2.4	nd	nd	nd	nd	nd	nd
	Liver	2.2	6.5	0.8	2.5	nd	nd	nd	nd	nd	nd
	Gills	2.1	6.3	0.9	2.6	nd	nd	nd	nd	nd	nd
	Intestine	2.2	6.5	0.9	2.8	nd	nd	nd	nd	nd	nd
Bonito	Fillet	0.8	2.4	nd	nd	nd	nd	nd	nd	nd	nd
	Liver	2.3	6.8	0.7	2.0	nd	nd	nd	nd	nd	nd
	Gills	nd	nd	0.6	2.1	nd	nd	nd	nd	nd	nd
	Intestine	2.0	5.9	1.0	3.0	nd	nd	nd	nd	nd	nd
Snoek	Fillet	nd	nd	0.6	1.8	nd	nd	nd	nd	nd	nd
	Liver	2.1	6.2	1.1	3.3	nd	nd	nd	nd	nd	nd
	Gills	1.4	4.2	0.4	1.1	0.3	0.8	0.7	2.1	nd	nd
	Intestine	2.1	6.2	1.1	3.3	0.8	2.4	nd	nd	nd	nd

From Table 4.7, the risk quotients of Hottentot fish type, showed that the risk factor of simazine and atrazine in fillet parts of the fish were 2.63 and 7.89, 0.58 and 1.76 for acute and chronic respectively, while these compounds were not detected in liver, gills and intestine. Alachlor, metolachlor and butachlor were not detected. For panga fish, all the fish parts were observed to be of high acute and chronic risk concerns while alachlor, metolachlor and butachlor were not detected.

The risk quotients of bonito fish, showed a high acute and chronic risk for simazine in the fillet, liver and intestine of the fish but not in the gills where it was not detected. While in atrazine a high acute and chronic risk factor was noted in the gills, liver and intestine of the fish except in the fillet where atrazine was not detected. Metolachlor showed a high acute and chronic risk in bonito fillet and low acute and chronic risk in the gills of the fish. It was not detected in the liver and intestine of the fish. Butachlor shows no acute or chronic risk in any of the detected fish part. Alachlor was not detected in any part of the fish.

The risk quotients of snoek fish showed a high acute and chronic risk from simazine in the liver, gills and intestine of the snoek fish except in the fillet where it was not detected, unlike atrazine which showed a high acute and chronic risk in all the part of the fish. Alachlor showed high acute and chronic risk in the intestine and low acute and chronic risk in the liver and gills of the snoek fish. Metolachlor showed a high acute and chronic risk in the gills and intestine of the fish but was not detected in the other fish parts while butachlor was not detected in any of the fish parts.

These herbicides are commonly used in South Africa, especially simazine and atrazine which are used for apples, grapes, maize, pears, sorghum, (Quinn et al. 2011) commonly grown in Cape

Town as well as cottonseed and sugar cane. This could be the reason why these compounds showed the highest acute and chronic risks to fish because of their day to day use in this region.

4.3.2. Health risk assessment to humans

In this chapter, the cancinogenic (cancer risk) and non-carcinogenic risk (hazard quotient) to humans were evaluated for herbicides and metals. These were calculated based on exposure duration, the number and sizes of consumed meals and body weight assumption as highlighted in Chapter 3, section 3.11.2 of this thesis. In this study, only compounds that were found to be present in each fish samples were used for the assessment. Oral ingestion of fish was deduced using default ingestion values from US EPA (1991). The results are presented in Tables 4.8 and 4.9.

Table 4. 8: Hazard Quotient (HQ), cancer risk and average and lifetime daily dose (ADD & LADD) values of herbicides in fish species

	Hottentot				Panga				Bonito				Snoek			
	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ
Simazine	0.044	0.019	0.002	**8.89**	0.034	0.015	0.158	**6.79**	0.013	0.019	0.207	**2.69**	0.035	0.015	0.162	**6.96**
Atrazine	0.010	0.004	0.019	0.28	0,014	0,006	0.026	0.39	0.011	0.048	0.210	0.32	0.010	0.004	0.018	0.28
Alachlor	0	0	0	0	0	0	0	0	0	0	0	0	0.005	0.002	0.035	0.46
Metolachlor	0	0	0	0	0	0	0	0	0	0	0	0	0.012	0.005	0.556	0.08

4.3.2.1. Cancer risk

This assessment was done on the contaminants using Equations 3.10 and 3.11 in Chapter 3 with available cancer slope factor (CSF) values and these can be found in Table 3.5. If a cancer risk value is $\leq 10^{-6}$ this indicates that the cancer risk is low, significant; if it is $\geq 10^{-4}$, if the value is $\geq 10^{-3}$, the cancer risk is high, hence this needs protective measures and very high when it is $\geq 10^{-1}$.

4.3.2.1.1. Herbicides

From the results in Table 4.8, it showed that all the risk values calculated for compounds that were detected in fish species in this study were considerably higher than the recommended risk value, and should one consume these fish samples there is a possibility of developing cancer (US EPA 2011a). The highest calculated cancer risk was observed in bonito fish and lowest in the hottentot fish. The cancer risk calculated for snoek fish is associated with atrazine, simazine, alachlor and metolachlor only, while for hottentot, bonito and panga is associated with simazime and atrazine. Herbicides use is a reality in South Africa, it does not only impact the farmers but also the produce, consumer, exporter and end-user of natural resources such as water. Therefore, the use of pesticides must be regarded as a serious management issue and not only at agricultural level, but, also at municipal level. Cities such as Cape Town rely on herbicides for weed control on pavements, golf course and parks instead of weed by hand. Given that the city seasonally applies weed killers, it is highly likely that such herbicides would leach out into storm water drains and out into the oceans during rainfall event. Moreover, many homeowner apply herbicides to curb unwanted growth in gardens. Thus urban use as well as agricultural application may contribute to this pollution at sea. Although, pesticides have been detected in most environmental matrices, there is still a lack of knowledge of background levels. These levels are needed to make realistic impact and health assessments when studying highly impacted areas. The serious health risks associated with certain pesticides are not only from occupational exposure, but also from end-user exposures.

4.3.2.1.2. Metals

Carcinogenic risk was evaluated for As, Cr, Ni and Pb. From Table 4.9, the risk values obtained for all these metals in the different fish species were very high i.e. values were greater than 10^{-1}. This implies that there are chances that human may develop cancer risk for a lifetime consumption

of these contaminanted fish. Hence, the regulatory bodies in this province are thus strongly advised to do everything possible to reduce the level of these comtaminants in the environments in order to preserve the health of citizens who consume these fish produce.

4.3.2.2. Hazard Quotient

The hazard quotient (HQ) is assumed to be the threshold value below which no adverse health effects would be expected to occur (Equation 3.8 and 3.9). If HQ is > 1.0, this points out that the compound is ecosystem threatening and/or harmful effects may arise; if HQ is < 1.0, the risk is quite low. Similarly if the hazard index (HI) which is the sum of all the HQs is greater than 1, there are chances of human contracting any non-carcinogenic diseases. The reference dose values (RfD) used are presented in Table 3.5.

4.3.2.2.1. Herbicides

From the result obtained in this study (Table 4.8), all the HQ values for simazine in all the different fish samples were greater than 1.0 indicating that there are chances of humans contracting any non-carcinogenic diseases. While all HQ values for atrazine, alachlor and metolachlor in all the fish samples were less than 1.0, hence, the chances of humans contracting any non-carcinogenic diseases or other health-related issues by consuming the contaminated fish is unlikely.

4.3.2.2.2. Metals

In panga fish, (Table 4.9) the HQ values for As, Co, Cu, Ni, Pb, Se, Mo, Li, Zr, Ti, and Fe were greater than 1 while other metals were less than 1. In hottentot fish, the HQ values for As, Co, Pb, Se, Mo, Li, Zr, Ti, Rb, and Fe were greater than 1. In snoek fish, with the exception of Cr, Mn, Zn, Sr, Rb, Al and Fe the HQ values for all other metals were greater 1. In bonito fish, the HQ values for Co, Pb, Se, Mo, Li, Zr, Ti, and Fe were greater than 1. These show that there are chances

of human contracting any non-carcinogenic diseases. Owing to the fact that the involved fish were exposed to a mixture of metals, therefore the evaluation of the cumulative health risk (hazard index) of metals was done by summing the HQs of the individual metal in each fish species. The values for each fish species were also greater than 1, indicating a potential significant health risk.

Table 4. 9: Hazard Quotient (HQ), cancer risk and average and lifetime daily dose (ADD & LADD) values of metals in fish species

	Panga			Hottentot fish			Snoek fish			Bonito fish		
	EDI	HQ	Cancer risk	EDI	HQ	Cancer risk	EDI	HQ	Cancer risk	EDI	HQ	Cancer risk
As	0.0125	41.5	120.39	0.0090	30.2	165.82	0.0010	3.6	1378.01	0.0	0.0	0
Co	0.0008	2.7		0.0014	4.7		0.0004	1.4		0.0028	9.4	
Cr	0.0038	0.0	11965.36	0.0012	0.0	37831.66	0.0089	0.0	5183.61	0	0	0
Cu	0.1011	2.5		0.0294	0.7		0.0405	1.0		0.0139	0.3	
Mn	0.0073	0.1		0.0079	0.1		0.0072	0.1		0.0016	0.0	
Ni	0.0204	1.0	445.32	0.0143	0.7	638.25	0.0196	1.0	464.7232	0.0076	0.4	1194.56
Pb	0.0268	6.7	0.3176	0.0454	11.3	0.1874	0.0416	10.4	0.204108	0.0297	7.4	0.28611
Se	0.0160	3.2		0.0974	19.5		0.0114	2.3		0.0657	13.1	
Zn	0.1271	0.4		0.1809	0.6		0.1530	0.5		0.0814	0.3	
Mo	0.0086	1.7		0.0081	1.6		0.0092	1.8		0.0092	1.8	
Li	0.0038	1.9		0.0037	1.9		0.0036	1.8		0.0036	1.8	
Zr	0.0023	29.0		0.0017	20.8		0.0026	32.3		0.0007	8.5	
Ti	0.0157	4.5		0.0103	2.9		0.0199	5.7		0.0101	2.9	
Sr	0.5305	0.9		0.3715	0.6		0.2228	0.4		0.0552	0.1	
Rb	0.0004	0.1		0.0331	8.3		0.0	0.0		0.0017	0.4	
Al	0.3880	0.4		0.2054	0.2		0.2670	0.3		0.2631	0.3	
Fe	0.2876	1.0		0.3091	1,0		0.2797	0.9		0.3425	1.1	
	HI	97.6			105.1			63.5			48.0	

This study demonstrates that the existence of several herbicides and metals in different fish species could have detrimental effects upon these marine fish species, and may also pose a risk to

human health because these fish are consumed by humans. The risk is further increased as atrazine and other herbicides as well as metals in this study have been identified as potential endocrine disruptor. The risk assessment for these fish underpins that these diverse herbicides and metals are a threat to fish, higher predators and humans. Hence, the stringent control of the levels of these contaminants in the ocean is significant in the preservation of the health of the marine ecosystem. Their presence points to many other contaminants that may also be contaminating the ocean. These results have significant implications for understanding the intricacy of ecotoxicological impacts of chemicals of emerging concerns in the ocean where some toxic contaminants may act on the environment or food quality of an organism and other chemicals may react on the organism itself, which in due course may increase the total ecotoxicological effect on the oceanic ecosystem structure and function.

4.4. Conclusion

This study showed that the methods used are capable of detecting low parts per billion concentrations in different fish species, which was also the case in our previous study (Petrik et al. 2017). Application of these methods indicated that diverse chemicals including (PFCs), herbicides and several PPCPs as well as metals are present in fish samples and significantly accumulated in them. This study showed that these chemical concentrations are greatly related to anthropogenic activities, including sewage discharge which all contribute to these chemicals finding their way into the oceanic environment, thereby accumulating in various edible fish species inhabiting the oceanic environment.

Risk assessment of these pollutants on aquatic organisms suggested that higher animals and humans who consume these species of fish could be at risk of ingesting diverse compounds. In addition, a risk assessment based on the calculated risk quotient (RQ) showed that those

compounds present in all the fish species could pose high (RQ>1) risks to sensitive aquatic organisms and humans who consume these contaminated seafood would be at risk. The implication of these results indicates that chemical compounds and drugs can remain bioavailable for aquatic organisms for long time or period (weeks to months to years) and even re-enter the food web at a later time. As such, for an understanding of accumulation and dispersion of these contaminants in aquatic food webs, detailed ecological knowledge is required. Information on PFCs, herbicieds, metals and PPCPs in fish to date indicate that an additional understanding of PFCs, EDCs, PPCP and metal accumulation in aquatic life at a broad scale and in pelagic fish is necessary to support future efforts in characterizing ecological and human health risks of diverse chemical compounds in the oceanic environment. The study of the oceanic environment has become a crucial concern and this study presents more evidence of this increasing trend in fish.

The study demonstrates that the simultaneous presence of several pesticides, pharmaceuticals, perfluorinated compounds and metals in different fish species may have adverse effects upon these aquatic species, and also poses a human health risk since these fish are all edible species and considered of economic interest. Thus, the strict control of these contaminants and other persistent compounds concentrations in the ocean is important to preserve the aquatic ecosystems health. Their presence points to many other contaminants that may also be impacting the ocean.

The results from this study have important implications for understanding the complexity of ecotoxicological effects of diverse hazardous persistent contaminants in the ocean where some toxic compounds may act on the habitat or food choice of an organism and other compounds may act on the organism itself, which eventually may increase the total ecotoxicological effect on the oceanic ecosystem structure and function.

Although the need and usefulness of these compounds cannot be denied, the hazards of introducing these chemicals into the environment needs to be considered due to their many negative effects. Therefore, critical consideration should be given to educating the public, farmers as well as municipal officer and encouraging the use of less harmful and toxic alternatives and banning their use as has been done elsewhere due to their well-known adverse effect. There is a need for either banning or setting up of an appropriate guideline and monitoring of the use, storage and disposal of chemicals in South Africa generally and Western Cape Province specifically. These findings also suggest the need for increased monitoring programmes, with a wider scope for both currently used chemical compounds.

Chapter 5

Chemicals of emerging concerns in different environmental matrices from Green Point marine environment

5.0. Introduction

Due to the increase in anthropogenic activities, the marine environment worldwide has been subjected to continuous pollution through the release of various types of emerging contaminants (Van De Vijver et al. 2003). As a result, the emerging more polar anthropogenic contaminants, such as pharmaceuticals, perfluorinated compounds (PFCs), and herbicides have recently gained more attention. When these emerging contaminants enter aquatic ecosystems through human excretion into sewage systems, improper disposal, and agricultural runoff associated with therapeutic treatment of livestock (Gaw et al. 2014) they potentially pose harmful effects both to aquatic organisms as well as to humans via indirect exposures (Stackelberg et al., 2004). Almost every chemical compound that is used by humans daily has been detected in water. The levels and occurrence of such emerging contaminants in benthic organisms like seaweeds and aquatic plants, bivalve other than mussels, snails or amphipod crustaceans are rarely determined (Du et al. 2015; Huerta et al. 2016; Xie et al. 2017) and such matrices may be a potential source of contamination to higher organisms and humans (Lagesson et al. 2016). In this study, the occurrence of 15 compounds in seawater, sediment and marine organisms was investigated in the marine environment of Green Point, Cape Town, South Africa.

5.1. Results and discussion

This chapter discusses the contaminants analysed in different environmental matrices collected from the marine environment of Green Point in July 2017. The experimental procedures used to carry out the analysis of the samples obtained are described in Chapter 3 of this thesis. Table 5.1

provides the information about the LC-MS parameters obtained for each compound, while Appendix II, Table II.1 and II.2 summarizes the PPCPs, PFCs and EDCs compounds detected in the marine environment of Green Point (Granger Bay). In this study, only 2-nitrophenol was not detected in any of the samples.

Table 5. 1: Compounds analyzed ordered by elution times (min), parent ion, and MRM transitions monitored and optimized cone voltages and collision energies for each PFCs

Compound Name	Retention Time (min)	Ion transition (m/z)	Product ion (m/z)	Collision energy (eV)	LOD			LOQ			Recoveries (%)		
					Seawater (ng/L)	Sediment (ng/g)	Organism (ng/g)	Seawater (ng/L)	Sediment (ng/g)	Organism (ng/g)	Seawater	Sediment	Organism
PFHpA - C7	7.00	363	319	15	0.01	0.03	0.04	0.05	0.08	0.11	99.0	98.5	98.0
PFOA - C8	7.56	413	369	15	0.02	0.09	0.10	0.08	0.28	0.30	98.7	99.2	99.7
PFNA - C9	8.03	463	419	15	0.01	0.56	0.79	0.02	1.76	2.39	99.6	98.9	101.0
PFDA - C10	8.41	513	469	15	0.02	0.79	1.55	0.06	2.39	4.71	99.5	99.3	99.9
PFUnDA - C11	8.74	563	523	15	0.04	0.90	1.69	0.11	2.74	5.11	100.2	99.9	100.5
Bisphenol A	6.71	227	212	28	0.01	0.93	1.45	0.05	2.83	4.39	99.1	101.3	100.2
Acetaminophen	1.78	152	110	15	0.02	0.43	0.36	0.08	1.31	1.10	99.7	99.1	99.5
Caffeine	3.25	195	138	20	0.03	0.62	0.46	0.08	1.89	1.41	100.3	99.9	100.1
Lamivudine	1.32	230	112	15	0.03	0.18	0.38	0.09	0.55	1.14	98.6	99.0	98.9
Carbamazepine	6.24	237	194	20	0.01	0.08	0.08	0.03	0.25	0.25	99.1	98.9	99.6
Phenytoin	5.96	253	182	15	0.03	0.30	0.30	0.10	0.91	0.91	100.9	101.5	101.1
Sulfamethoxazole	2.71	254	188	25	0.02	0.50	0.17	0.06	1.51	0.53	99.8	99.0	99.4
Diclofenac	6.80	296	250	15	0.03	0.17	0.24	0.09	0.53	0.73	98.5	98.1	98.8
Triclosan	9.09	288	36.8	10	0.02	0.66	0.92	0.08	1.99	2.81	101.1	100.4	99.9
2 nitrophenol	na	139	121	15	-	-	-	-	-	-	-	-	-

na= not available

5.1.1. Seawater

The concentration of emerging pollutants in seawater from Green Point marine area are summarized in Appendix II, Table II.1. A total of 14 out of the 15 target compounds were detected in the water samples. Point 1 to point 8 were sampling points located away from the beach, further into the ocean as pointed out in the map area of the studied area (Figure 3.2), these were sampled using a kayak.

5.1.1.1. Perfluorinated compounds

The levels of perfluorinated compounds in seawater samples from points 1 to 8 are shown in Figure 5.1.

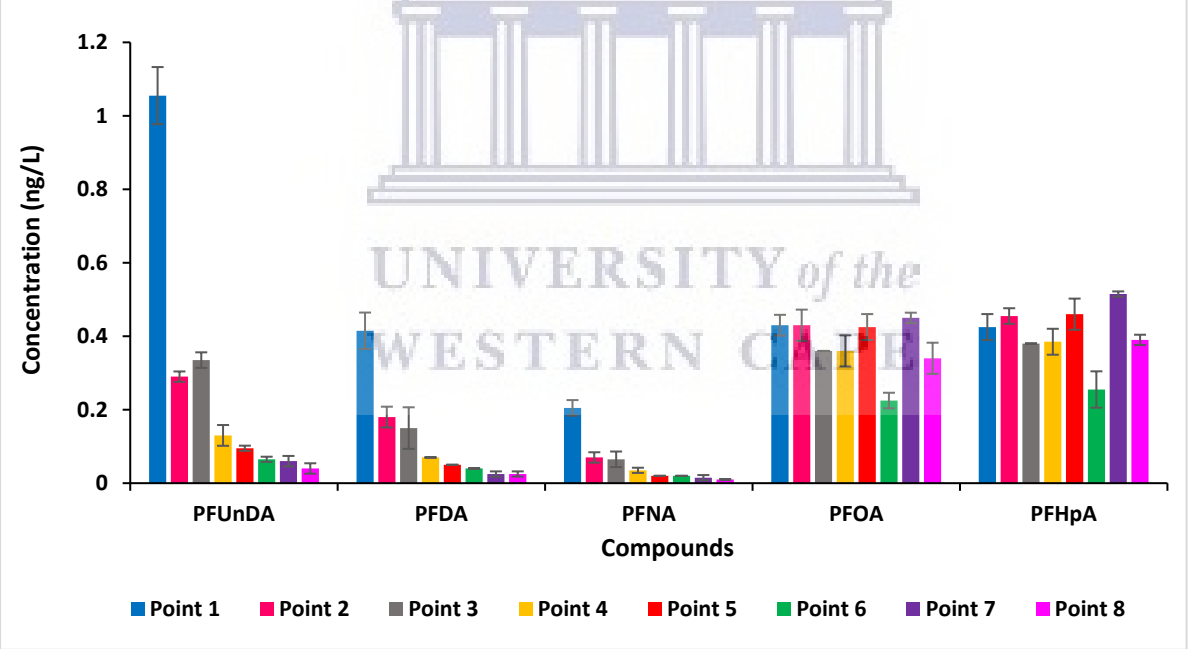


Figure 5. 1: PFCs levels in seawater samples from various points in Green Point

The composition and distribution of compounds in the water samples showed that PFCs were the predominant compounds in all the seawater samples with the highest concentrations, and sampling points 1 and 2 were the most impacted by sewage. PFOA and PFHpA showed similar

concentration across the points. While point 1 seems to have high levels of the compounds in higher concentration than the other points. This might be due to incomplete dispersion of the sewage plume and the concentration reduces as the sampling extended further into the ocean. Lower levels of compounds in the seawater samples were found in some cases further away from the coast line showing the effect of dilution by ocean currents but not all compounds disperse uniformly. PFOA and PFHpA did not show dilution further away from the coast. The levels of the PFCs ranged as follows: PFUnDA (0.04 – 1.06 ng/L), PFDA (0.03 – 0.42 ng/L), PFNA (0.01 – 0.21 ng/L), PFOA (0.23 – 0.45 ng/L), and PFHpA (0.26 – 0.52 ng/L). The concentrations of PFCs in this study are lower compared to the concentration found in samples from the suceeding chapters (Camps Bay and False Bay). The beach area (point 1) was most impacted by sewage constituent, highlighting the hazards to bathers and surfers as these chemicals point to microbial contamination as was discussed in one of the publication from this chapter (Petrik et al. 2017).

The concentration (2.46 – 20.6 ng/L) of perfluorinated compounds in water collected along the western coast of Korea (Naile et al. 2010) and the concentration of PFOA (0.17 – 37.55 ng/L) from Dalian coastal waters (Ju et al. 2008) were significantly higher compared to this study. Similar concentrations of PFOA and PFNA were observed in water samples from Northern Spain (0.05 – 0.31 ng/L and 0.04 – 0.20 ng/L respectively) (Gómez et al. 2011). Also, a study from South Korea revealed similar concentration for PFNA compounds (0.02 – 0.59 ng/L) while the concentration of PFOA was higher in samples from South Korea than Green Point samples (0.24 – 320 ng/L) (So et al. 2004). In another study, the concentration of PFOA (0.94 – 120 ng/L) were also higher compared to this study (Pico et al. 2012).

5.1.1.2. Pharmaceuticals and personal care product

PPCPs concentrations in seawater samples from various points in the study area are shown in Figure 5.2.

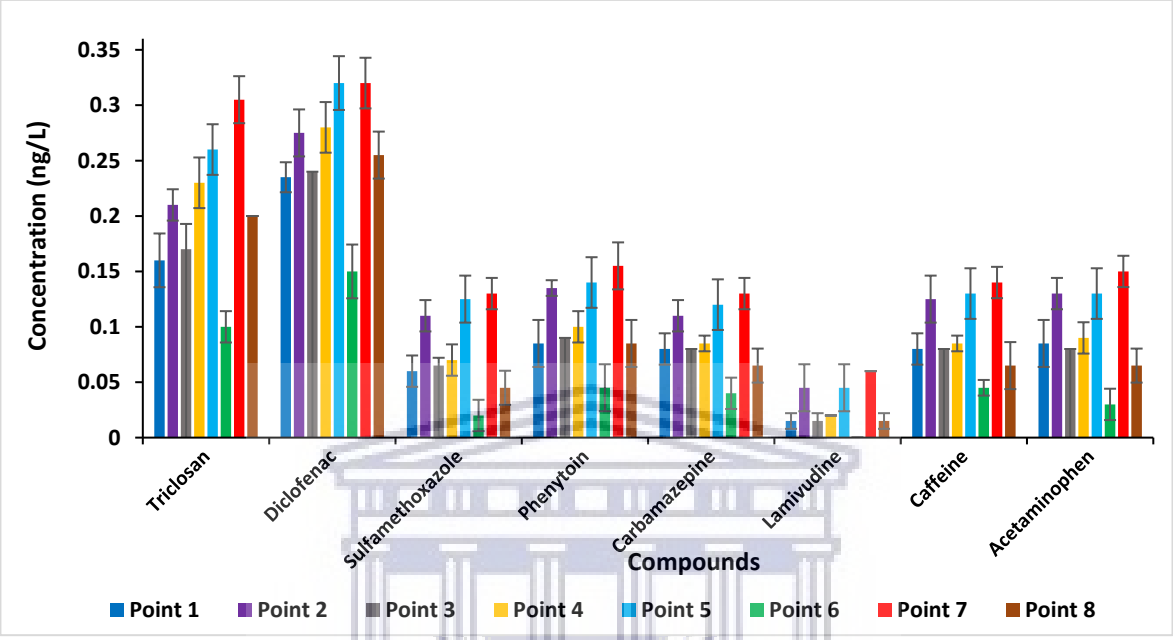


Figure 5. 2: PPCPs concentrations in seawater samples from Green Point

The PPCPs had no specific pattern relative to sampling points distance from the coast. Triclosan and diclofenac seems to be the dominant compounds with the highest concentration at all the seawater sampling points (0.10 – 0.26 ng/L and 0.15 – 0.32 ng/L respectively) while lamivudine and acetaminophen had the lowest seawater concentrations (nd – 0.02 ng/L and 0.03 – 0.15 ng/L respectively) in all the samples.

The concentration of caffeine in a study conducted in Boston Harbour (Siegener and Chen 2002) and (Weigel et al. 2002) (140 – 1600 ng/L) and (2.0 – 16.1 ng/L) respectively were considerably higher to the levels found in this study. Similar concentrations of sulfamethoxazole was observed in seawaters from Victoria Harbour Hong Kong (Minh et al. 2009) while higher concentrations (nd – 48.1 ng/L) were found in seawater samples from South Yellow sea in China (Du et al. 2017).

The concentration of carbamazepine (2.7 ng/L) and acetaminophen (paracetamol) (67.1 ng/L) in the water from Sydney estuary (Birch et al. 2015) were higher compared to the concentration detected in this study. A similar concentration for diclofenac was observed in a study by McEneff et al. (2014) while the concentration of carbamazepine was higher compared to this study.

5.1.1.3. Industrial chemicals

The concentration of the analysed industrial chemicals in various seawater samples from different points are presented in Figure 5.3.

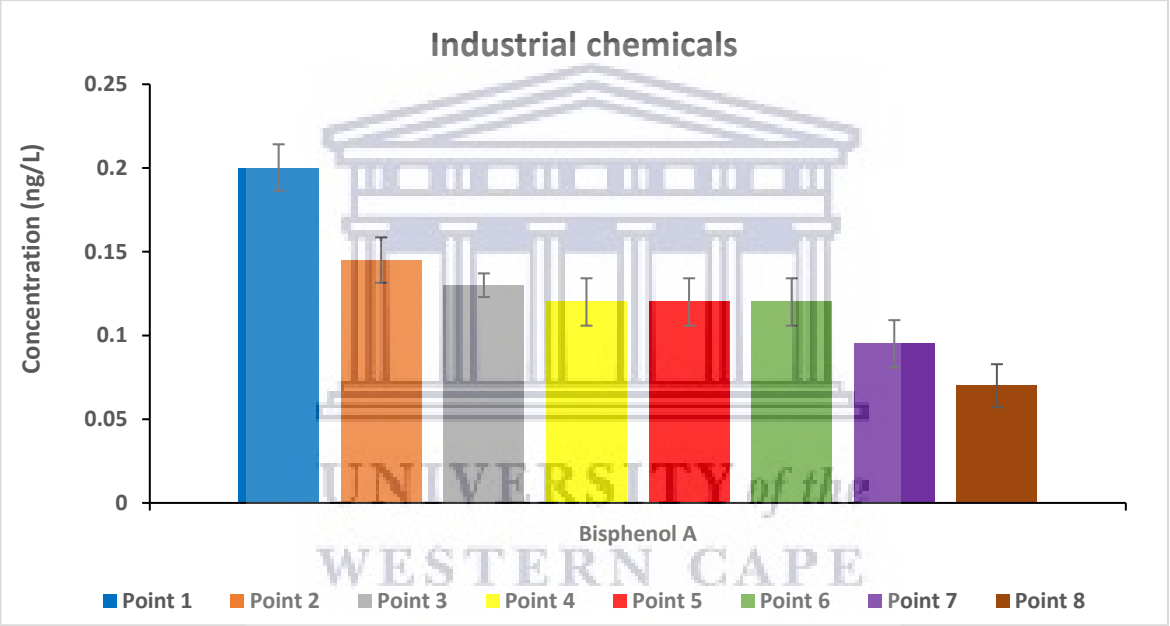


Figure 5. 3: Industrial chemicals concentrations in seawater samples from Green Point

Bisphenol A displayed a similar trend to the PFCs, the concentration ranged from 0.20 – 0.07 ng/L with point 1 having the highest concentration and point 8 having the lowest concentration. A similar concentration of bisphenol A was detected in seawater sample from Spain (Salgueiro-González et al. 2012).

Generally, the level of contaminants in the water sample were not very high compared to other sample matrices, City of Cape Town officials claim that the concentrations in water are so low that

these compounds pose no hazard, yet low levels in water are misleading as these compounds bioaccumulate significantly, as shown in the following sections indicating that using seawater concentrations to determine impacts of pollution is not a suitable approach.

5.1.2. Sediment and beach sand

Fourteen out of fifteen target compounds were found to be present in the beach sand and sediment from Green Point coastal environment. The levels/concentrations detected in the samples analysed are shown in Appendix II, Table II.2. All fourteen compounds were detected in the beach sand and sediment samples.

5.1.2.1. Perfluorinated compounds

The concentration of perfluorinated compounds detected in sediment samples are shown in Figure 5.4.

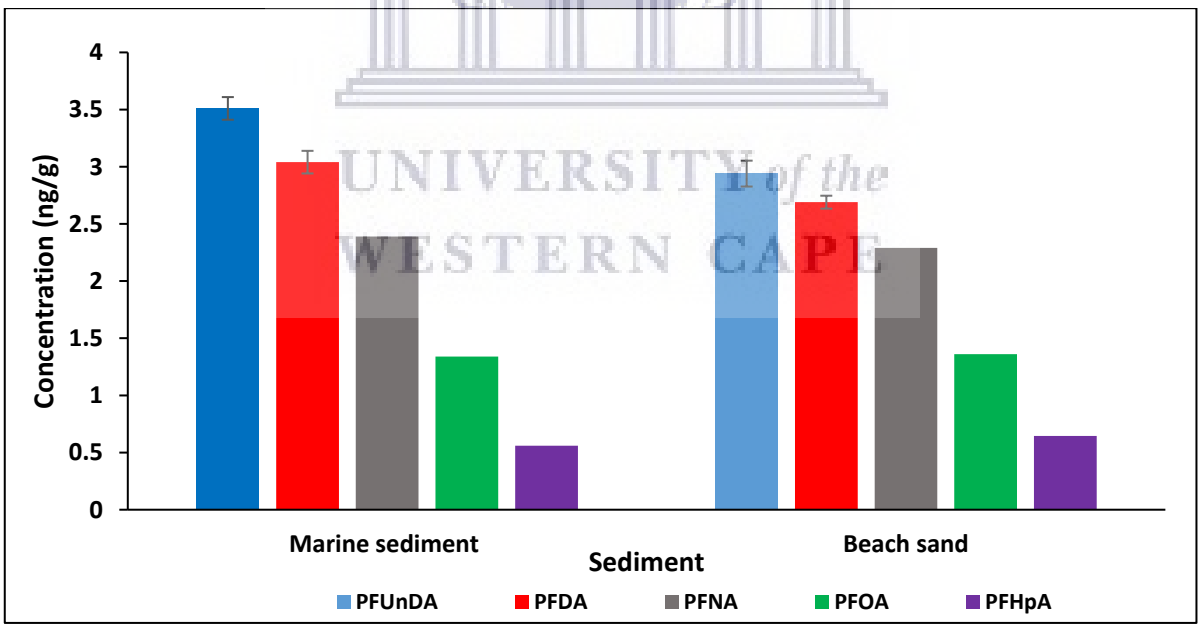


Figure 5. 4: PFCs concentration in sediment samples from Green Point

Out of the perfluorinated compounds, PFUnDA had the highest concentration in both samples: 2.94 ng/g and 3.51 ng/g respectively which is an order of magnitude higher than in the seawater.

Interestingly, the concentration of perfluorinated compounds in the sediment samples decrease as the molecular weight (Carbon chain: C_{11} to C_7) of the compounds decreases. A similar trend was observed in all other sample matrices collected from this location.

In a study from coastal areas of the East China Sea (Yan et al. 2015) and Baltic sea (Theobald et al. 2012), the concentration of perfluorinated compounds in sediment (nd – 2.70 ng/g) and (<0.03 – 1.58 ng/g) respectively were lower to the concentration of these compounds in this study. This observation is also similar when compared with a recent study conducted by Dong et al. (2018) (<0.02 - <0.032 ng/g). The concentration of perfluorinated compounds in this study was similar to a study from Tianjin coast (0.42 – 4.3 ng/g) (Wang et al. 2012b).

5.1.2.2. Pharmaceuticals and personal care products (PPCPs)

The concentrations of the detected compounds from PPCPs class of contaminants are shown in Figure 5.5.

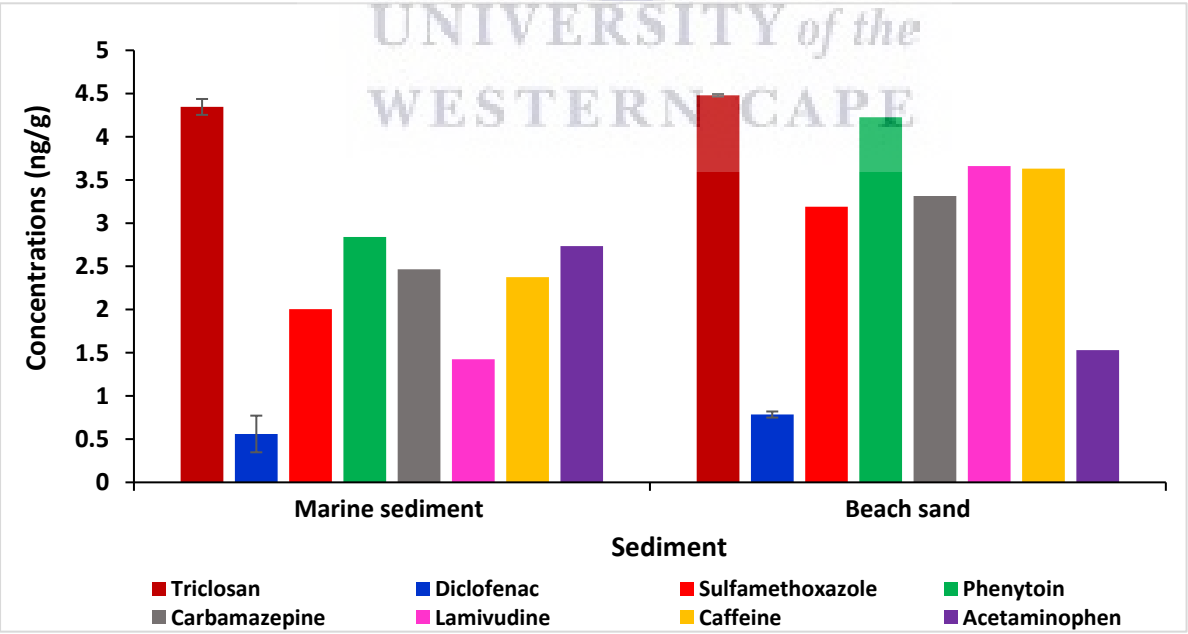


Figure 5. 5: Concentration of PPCPs in sediment samples from Green Point

Out of the PPCPs, the antiseptic triclosan had the highest concentration in beach sand and sediment samples (4.48 and 4.35 ng/g respectively). Almost all the concentration of PPCPs in beach sand were higher than that of the sediment except for acetaminophen whose concentration is higher in sediment than beach sand. This result reveals that beach sand tend to retain more of these sewage related contaminants and this is where children play most often when they are at the beach. The concentration of diclofenac (52.1 ng/g), caffeine (25.4 ng/g) and carbamazepine (40.3 ng/g) in sediment from Donana Park (Camacho-Muñoz et al. 2013) were very high compared to concentrations of these compounds found in this study. Also the concentration of sulfamethoxazole (2.64 – 50.73 ng/g) and acetaminophen (6.43 - 8.96 ng/g) were higher, while carbamazepine (1.02 – 2.32 ng/g) found in sediment samples from KwaZulu-Natal (Matongo et al. 2015), and sulfamethoxazole (0.7 ng/g) from San Francisco Bay (Klosterhaus et al. 2013) was lower compared to this study. The concentrations of diclofenac (0.9 -2.0 ng/g) and carbamazepine (1.3 - 2.7 ng/g) found by Aminot et al. (2015) were similar to the concentration of this study. In a study from Bahia, Brazil (Beretta et al. 2014), the concentration of caffeine (23.4 ng/g), carbamazepine (4.81 ng/g) and diclofenac (1.06 ng/g) in marine sediment were higher compared to this study. None of these compounds should naturally occur in sediments or beach sand and can only derive from the sewage released by the marine outfall, showing that the plume makes landfall and contaminates the intertidal zone significantly.

5.1.2.3. Industrial chemicals

The levels of industrial chemicals in this sample matrix are shown in Figure 5.6.

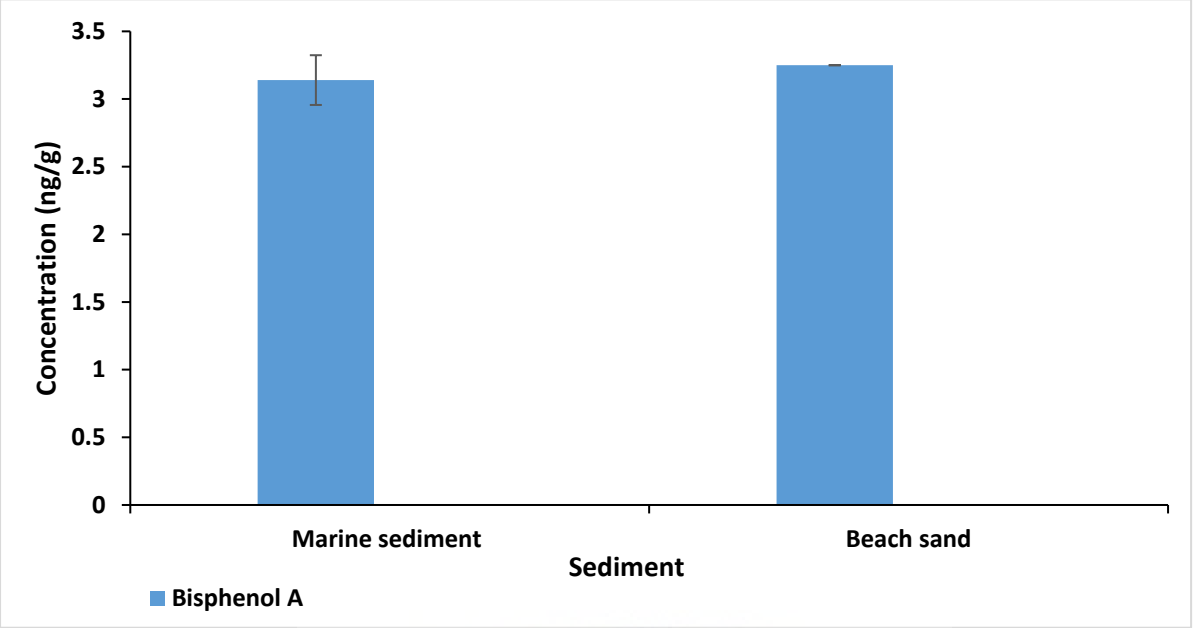


Figure 5. 6: Industrial chemical concentration in sediment samples from Green Point

The concentration of bisphenol A in both samples (beach sand and sediment) were 3.25 and 3.14 ng/g respectively.

5.1.2.4. The sorption coefficient in sediment

The sorption coefficient Kd is used to describe the reversible sorptive exchange of chemicals between water and sediment. This was calculated according to Equation 3.3 in Chapter 3 section 3.10. The Kds values for sediment and beach sand are presented in Table 5.2.

Table 5. 2: Kd values for detected compounds sediment samples

	Kd (L/Kg)	
	Marine sediment	Beach sand
PFUnDA	3.311	2.773
PFDA	7.238	6.404
PFNA	11.38	10.90
PFOA	2.978	3.022
PFHpA	1.077	1.250
TS	16.73	17.23

BPA	15.70	16.25
DCF	1.750	2.469
SMX	0.154	0.245
PHE	6.173	9.195
CAR	19.00	25.54
LA	23.833	61.00
CAF	17.00	25.93
ACT	18.00	10.20

Kd measures the mobility of a substance in soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil. A very low value means it is highly mobile in soil. From the results, shown in Table 5.2, the Kd values of detected compounds in sediment sample were low which implies that all the compounds are mobile, which indicates that these compound can easily leach permitting their uptake from sediment. Mobility of these compounds was demonstrated in the bioaccumulation of these compunds in the marine organism and seaweed samples as is shown in the next section.

5.1.3. Marine biota

Seafood is a major food source not only for humans but also for higher animals (mammals) in the ocean due to their nutritional benefits. However, consumption of seafood is an important exposure pathway to pollutant/contaminant for humans. In this study, five marine organisms: limpets (*Cymbula granatina* and *C. oculus*) n=15, mussels (*Mytilus galloprovincialis*) n=12, sea urchin (*Parechinus angulosus*) n=7, starfish (*Marthasterias africana*) n=5 and seaweed (*Ulva* sp.) were investigated. The dry-weight based concentration of compounds detected in marine biota are summarized in Appendix II, Table II.2.

5.1.3.1. Perfluorinated compounds

The perfluorinated compounds in marine biota samples (different species) are shown in Figure 5.7.

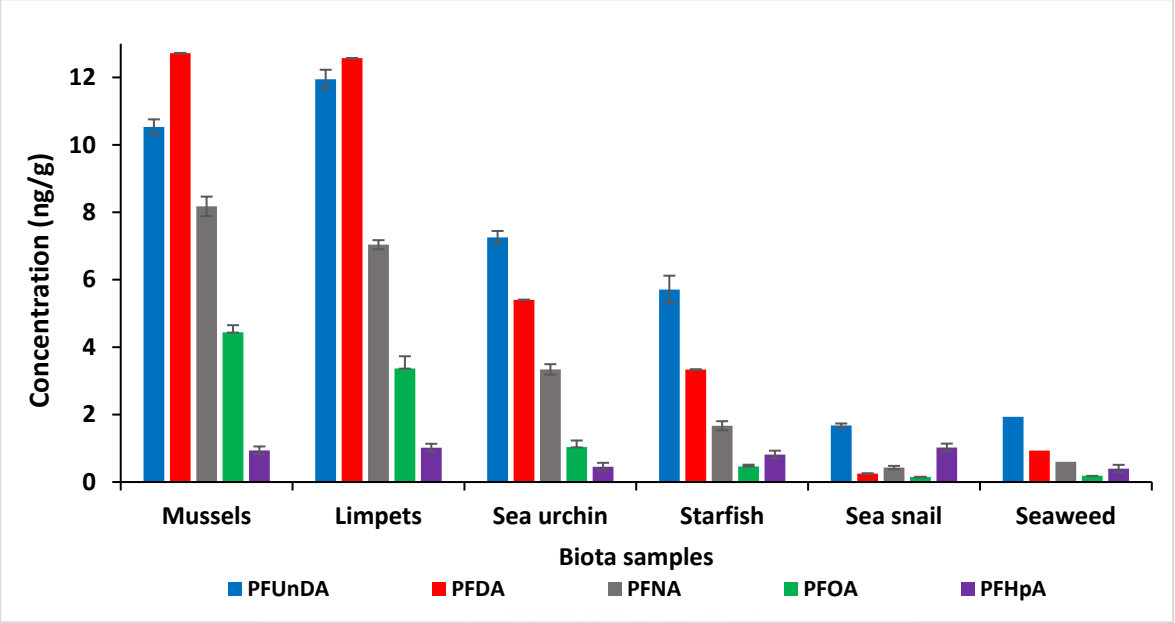


Figure 5. 7: Concentration of PFCs in marine biota samples from Green Point

Fourteen out of fifteen of the target compounds were found in all the biota samples. Of all the perfluorinated compounds, PFUnDA and PFDA were observed to have the highest concentration in all the biota. Mussels and limpets had almost the highest concentration of all the perfluorinated compound which ranged between (0.94 – 12.72 ng/g) and (1.02 – 12.57 ng/g) respectively. The sea snail and seaweed had the lowest concentration of the perfluorinated compounds which ranged between (0.25 – 1.68 ng/g) and (0.19 – 1.94 ng/g). The concentrations of PFCs were in two orders of magnitude higher than the concentration in seawater.

In addition, PFCs biomagnified through the food webs, since several studies have reported their occurrence in wildlife (Olivero-Verbel et al. 2006). The concentration of PFHpA (0.5 ng/g), PFNA (3.1 ng/g) PFUnDA (8.1 ng/g) in mussels collected on the Northern coast of Spain were lower than this study (Villaverde-De-Sáa et al. 2012). In another study on molluscs, the concentration of PFHpA (<0.5 – 3.32), PFUnDA (<0.5 – 1.74 ng/g) and PFDA (<0.5 – 0.97 ng/g) were also lower than the concentration found in this study, except PFOA (<0.5 – 12.2 ng/g) which was higher (Pan

et al. 2010). The levels of PFCs (PFOA; 1.65 - 10.4 ng/g, PFNA; 0.66 – 10.6 ng/g, PFDA; 0.53 – 3.84 ng/g) in floating plants were higher compared to this study except for (PFUnDA; 0.12 – 1.41 ng/g) which was lower (Shi et al. 2012). In another study the concentration of PFNA (8.5 – 12.01 ng/g), and PFOA (6.56 – 45.15 ng/g) in aquatic plant were higher compared to this study (Wilkinson et al. 2018).

5.1.3.2. Industrial chemicals

The levels of the analysed industrial chemicals in the marine biota samples are shown in Figure 5.8.

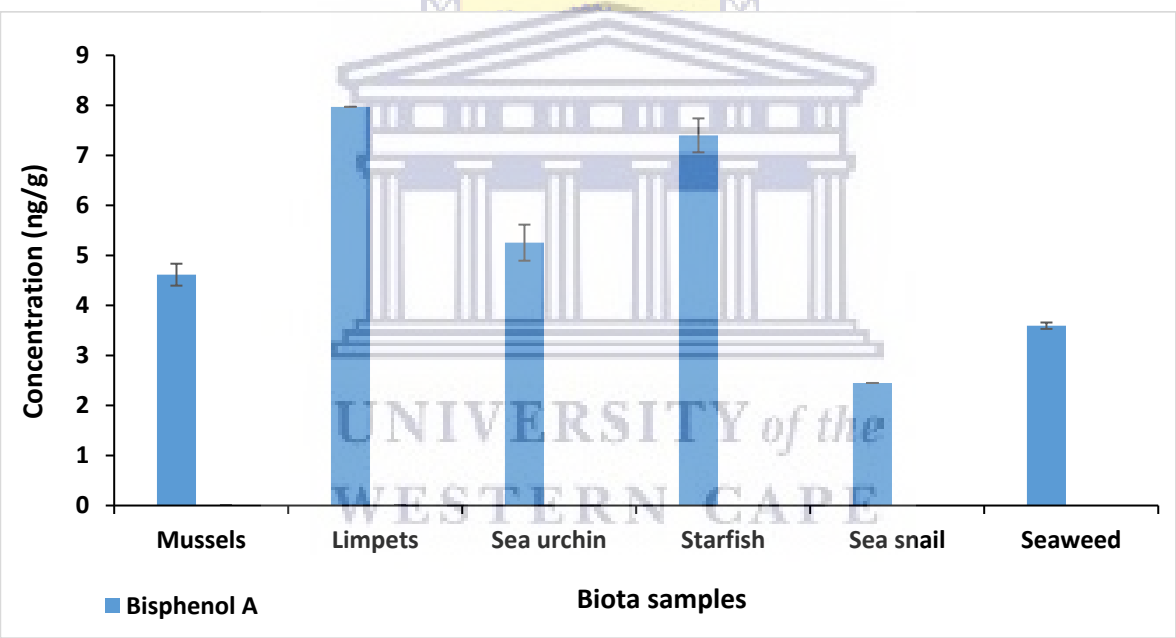


Figure 5. 8: Concentration of industrial chemicals in biota samples from Green Point

Limpets and starfish had the highest concentration of bisphenol A (7.97 ng/g and 7.40 ng/g respectively), but 2-nitrophenol was not detected in any of the biota samples. It might be either the sample preparation method would need more sample (due to its low concentration) or 2-nitrophenol is complexes with metals or organic matter and do not appear in the final analyses. 2-

nitrophenol is not very hydrophilic, and probably need 1.5 L water sample before detected with LC-MS. This was observed althrough the thesis.

5.1.3.3. Pharmaceuticals and personal care products

The concentration of PPCPs in different species of the marine biota samples are shown in Figure 5.9.

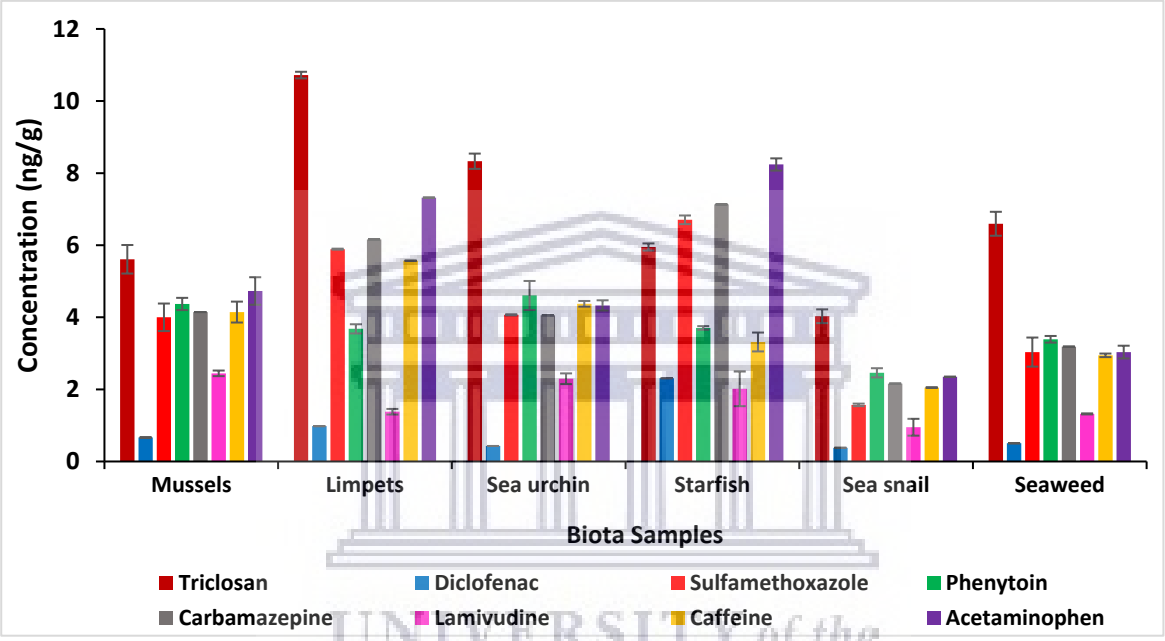


Figure 5. 9: The levels of PPCPs in different species of biota samples from Green Point

Limpets had the highest concentration of triclosan and caffeine compared to other biota (10.72 ng/g and 5.57 ng/g respectively) while starfish had the highest concentration of sulfamethoxazole (6.71 ng/g), acetaminophen (8.24 ng/g), carbamazepine (7.13 ng/g) and diclofenac (2.31 ng/g). Sea urchin had the highest concentration of phenytoin (4.61 ng/g) while mussels had the highest concentration of lamivudine (2.45 ng/g). There is no specific pattern to how these compounds are detected in the biota. The concentration of compounds detected in seawater was relatively low whereas the selected compounds found in biota samples were present at a considerably higher

concentration than the background ocean levels. The levels observed were order of magnitude higher than the observed levels in seawater.

A study conducted on mussels in Balgian coastal zone showed that the concentration of PFCs (1 ng/g) and carbamazepine (nd) was lower compared to this study while acetaminophen was higher (96 ng/g) compared to this study (Wille et al. 2011). Diclofenac detected in this study in mussels was similar to a study conducted by (Cunha et al. 2017) while the concentration of caffeine in a mussel watch study in California was higher than the concentration in this study area (Maruya et al. 2014). In a study conducted on aquatic plants, the concentration of acetaminophen (0.38 ng/g) and diclofenac (0.42) were lower compared to the seaweed analysed in this study (Wilkinson et al. 2018). The levels of sulfamethoxazole found in mussels in this study was higher compared to the levels found in mussels from Bohai Sea (Li et al. 2012b). The concentration of phenytoin (5 ng/g), acetaminophen (20 ng/g), caffeine (5 ng/g), diclofenac (1 ng/g) in a study conducted on mussels were higher while carbamazepine (0.7 ng/g), PFOA (2 ng/g) and sulfamethoxazole (0.4 ng/g) were lower compared to this study (Mijangos et al. 2019).

The continuous discharge of sewage containing these compounds will lead to the increase in their levels in the environment, posing serious health effect to humans consuming these seafoods.

5.1.4. Bioaccumulation of PFCs, PPCPs and industrial chemicals in marine biota

Bioaccumulation Factor (BAF) is the ratio of the concentration of a contaminant in an organism to the concentration in the ambient environment (water) (Equation 5.1) at a steady state, where the organisms can take in the contaminant through ingestion with its food as well as through direct content and it is usually expressed in the unit L/kg (Karlsson et al. 2002; Kinney et al. 2008).

$$BAF = [C]_{organism}/[C]_{water} \quad 5.1$$

When the BAF of a contaminant in an organism is greater than 5000 L/kg, the contaminant is presumed to be bioaccumulative. When the BAF is between the range of 2000 – 5000 L/kg in an organism then it is presumed to be potentially bioaccumulative (Arnot and Gobas 2006; Na et al. 2013).

Based on the concentrations of compounds measured in seawater and biota samples collected from the marine environment of Green Point, the observed BAFs of the contaminants were calculated for different aquatic species (Table 5.3).

Table 5. 3: BAF values of marine organisms and seaweed

	BAF(L/Kg)					
	Mussel	Limpets	Seaurchin	Starfish	Sea snail	Seaweed
PFUnDA	9933.96	11273.6	6849.06	5386.79	1584.91	1830.19
PFDA	30285.7	29928.6	12881.0	7952.38	595.240	2238.10
PFNA	38952.4	33523.8	15904.8	7952.38	2047.62	2857.14
PFOA	9866.67	7488.89	2311.11	1044.44	333.330	422.220
PFHpA	1807.69	1961.54	884.620	1576.92	1980.77	769.230
TCS	21576.9	41230.8	32038.5	22884.6	15500.0	25384.6
BPA	23100.0	39850.0	26300.0	37000.0	12250.0	18000.0
DCF	2093.75	3062.50	1343.75	7218.75	1187.50	1593.75
SMX	307.690	453.080	313.080	516.150	120.770	233.850
PHE	9500.00	8000.00	10021.7	8065.22	5347.83	7369.57
CAR	31923.1	47384.6	31230.8	54846.2	16615.4	24538.5
LA	40833.3	23000.0	38333.3	33666.7	15833.3	22000.0
CAF	29642.9	39785.7	31285.7	23714.3	14642.9	21071.4
ACT	31533.3	48800.0	28866.7	54933.3	15666.7	20266.7

PFUnDA= perfluoroundecanoic acid, PFDA= perfluorodecanoic acid, PFNA= perfluorononanoic acid, PFOA= perfluorooctanoic acid, PFHpA= perfluoroheptanoic acid, BPA= bisphenol A, DCF= diclofenac, SMX= sulfamethoxazole, PHE= phenytoin, CAR= carbamazepine, CAF=caffeine, LA=lamivudine, ACT= acetaminophen, TCS= triclosan.

All the perfluorinated compounds and BPA (except PFHpA which was not bioaccumulative) are bioaccumulative in mussels and limpets. SMX was not bioaccumulative and DCF was potentially

bioaccumulative while the other PPCPs were bioaccumulative in mussel and limpet. DCF, SMX and PFHpA were not bioaccumulative in sea urchin, PFOA was potentially bioaccumulative while other contaminants were bioaccumulative in sea urchin. PFOA, PFHpA and SMX were not bioaccumulative in starfish while all other contaminants were bioaccumulative in starfish. In Sea snail, PFUnDA, PFDA, PFOA, SMX and DCF are not bioaccumulative, PFNA is potentially bioaccumulative while all other contaminants were bioaccumulative. In seaweed, PFDA, PFNA are potentially bioaccumulative, PFUnDA, PFOA, PFHpA, DCF are not bioaccumulative while other contaminants are bioaccumulative. The result suggest that almost all the compounds tested for in this study area bioaccumulative in the marine biota.

Contaminants with too high accumulation in the body can be very harmful and are temporarily stored in fat tissues. When fat is burnt for energy, they are released for storage. If these chemicals are not completely metabolized, or are not excreted through faeces and urine or through the consumption of seafood by humans, they tend to be very harmful. These chemicals that are either synthetic or natural can affect the immune, nervous and reproductive systems of animals. The result of the bioaccumulation of these chemicals result in birth defects in offspring or reproductive failure. (Biegel et al. 2001; Berthiaume and Wallace 2002; Milnes et al. 2006; Crain et al. 2008). These chemicals affect the whole ecosystem and not just the individual organisms especially when keystone species are involved. Keystone species are species that can greatly affect population numbers and the health of an ecosystem.

5.1.5. Risk assessment

5.1.5.1. Ecological risk assessment

In this section, the risk of PPCPs, PFCs and industrial chemicals were evaluated using Equations 3.4 and 3.5 in Chapter 3 in different seawater point in Green Point marine environment. The risk

quotient method was used to assess the impact of these emerging contaminants found in seawater samples from Green Point, the results are presented in Figure 5.10 for acute risk and Figure 5.11 for chronic risk. The concentrations of compounds detected in the seawater samples were divided by an effect level reported in literature (Tables 3.4 and 3.5). For acute risk, if the RQ < 0.5, it shows no high acute risk concern while for chronic risk if RQ < 1.0 it shows no chronic risk concern (US EPA 2016a).

For acute risk (Figure 5.10) results obtained for contaminants exhibit low to high risk, as calculated from the corresponding RQs for algae, invertebrate and fish. For algae, all compounds pose low risk except for triclosan (TCS) in point 5 and 7 that poses high risk (RQ > 0.5). For the case of invertebrate, all compounds pose low risk (RQ < 0.5) except for triclosan which poses high risk. While for fish all compounds pose low risk.

Similarly for chronic risk (Figure 5.11), in algae all contaminants pose low risk except for triclosan which pose high risk (RQ > 1) in points 2, 4 and 7, and sulmathoxazole which pose high risk in 2, 5 and 7. In invertebrate, PFNA and carbamazepine poses high risk across the points and other compounds pose low risk. Finally in fish, triclosan and diclofenac poses high risk while other compounds pose low risk.

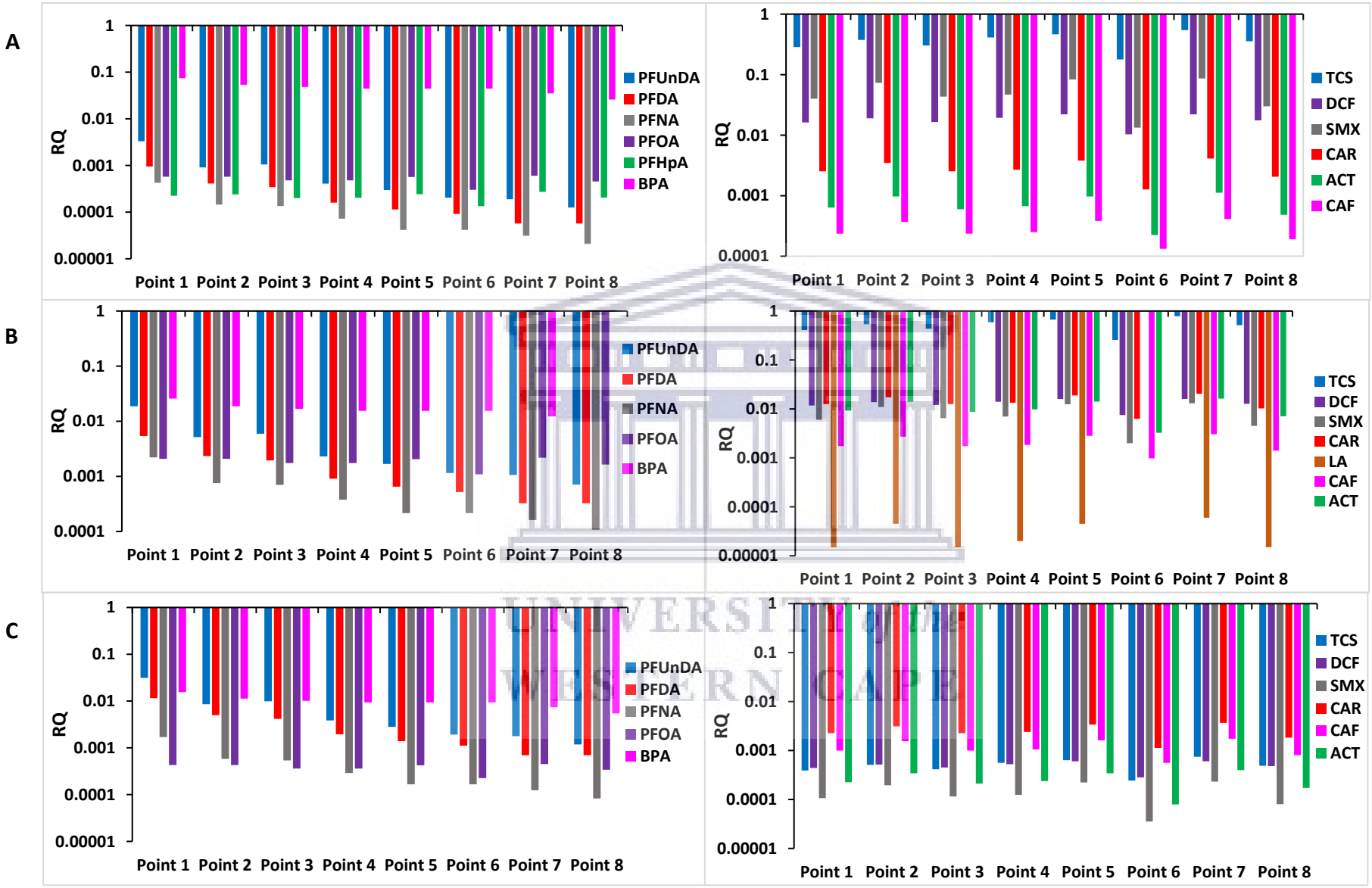


Figure 5. 10: Risk quotients (acute risk) for contaminants estimated for (A) algae (B) daphnia and (C) fish

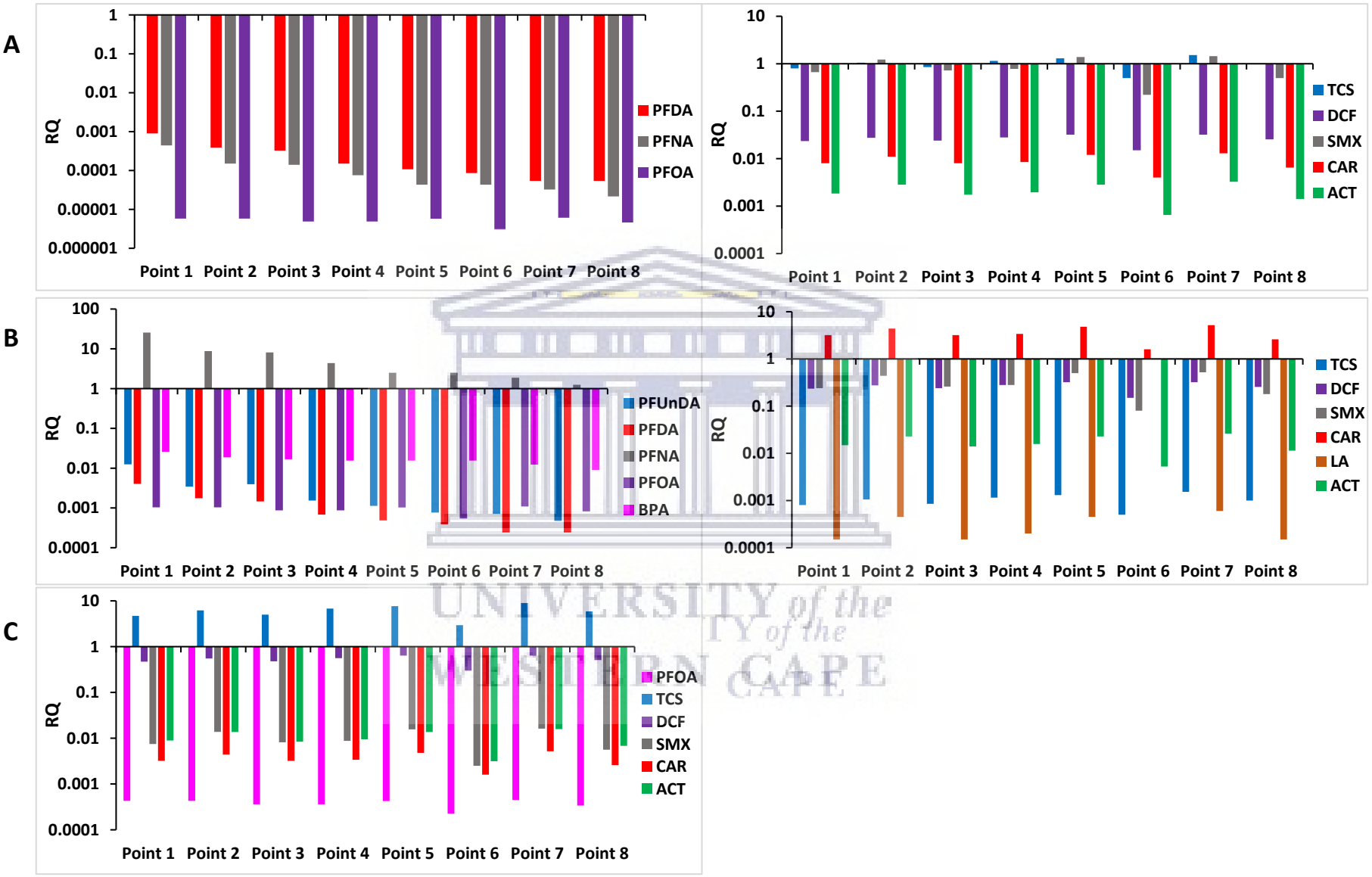


Figure 5. 11: Risk quotients (chronic risk) for contaminants estimated for (A) algae (B) daphnia and (C) fish

From the results obtained from this study area it showed that these compounds pose a low to high ecotoxicological risk for marine organisms. Furthermore, the values are much lower compared to the values found in samples from other sites (Camps Bay and False Bay) because the levels of these contaminants were much higher than the levels found in Green Point. This may be due to the near shore environment in Green Point that provides greater ocean current circulation.

5.2. Conclusion

In the case of Green Point study area, 15 emerging contaminants were investigated, 14 out of 15 of the PPCPs, PCFs and EDC extracted were detected in all sediment and biota samples indicating that these emerging contaminants are ever present in the local marine environment and can have serious long-term impacts upon the aquatic ecosystems (seawater). The concentration of these compounds in seawater were lower compared to the biota inhibiting the water and the sediment samples showing that their dilution in seawater does not prevent their bioaccumulation. Many marine organisms are at the base of the tropic chain and thus may be a source of contaminants to higher trophic levels, although the underlying mechanisms and biomagnification factors still need to be studied. This revealed that almost all these contaminants are either bioaccumulative or potentially bioaccumulative. The result showed that PFCs, EDCs and PPCPs are widely present in the marine environment of Green Point, but at lower levels than at Camps Bay or False Bay.

Chapter 6

Chemicals of emerging concern in some environmental matrices in Camps Bay: Occurrence and risk assessment study

6.0. Introduction

The increasing evidence of emerging contaminants (ECs) in water bodies is causing major concern around the world because of their toxicological effects upon humans and aquatic organisms (Jiang et al. 2013). Emerging contaminants are natural or synthetic chemical substances that are increasingly being discharged into water bodies or have potential to enter into the environment or have been in the environment for a while, in significant quantities with a consequent risk for aquatic ecosystems and the food chain globally (Li et al. 2012a; Álvarez-Muñoz et al. 2015; Geissen et al. 2015). These compounds are often persistent and not regularly monitored because they are mostly still excluded from environmental legislation. Their fate and persistence in the environment are not well understood (Zenker et al. 2014; Sauvé and Desrosiers 2014; Geissen et al. 2015).

In recent years, the number of studies reporting the occurrence of emerging contaminants in the marine environment has increased globally. The impact of these persistent organic pollutants are greater in coastal areas than in the rest of the marine environment, since that is where direct and indirect discharges occur due to human activities (Sánchez-Bayo et al. 2011; van Dam et al. 2011).

Pharmaceutical and personal care products (PPCPs), perfluorinated compounds (PFCs) and endocrine disrupting compounds (EDCs) are among the contaminants of emerging concern (CEC) (Álvarez-Muñoz et al. 2015; Birch et al. 2015; Geissen et al. 2015). Such EDCs (natural or fabricated) include, among others, flame retardants, pesticides, surfactants, fungicides, plasticisers, synthetic birth control pills, and phenolic products (Jackson and Sutton 2008). PFCs are used in

the manufacture of Teflon, stain, oil and water-resistant products, and are also applied in fire-fighting foams, cleaners, motor oil additives, cosmetics, paints and ink, adhesives, medical equipment and insecticides (Posner 2012). Pharmaceuticals include anti-diabetics, β-blockers, antibiotics, lipid regulators, anti-ulcer and antihistamine drugs, anti-inflammatories and analgesics, antipyretics and stimulants (Jiang et al. 2013; Rivera-Utrilla et al. 2013; Ojemaye and Petrik 2019b). Personal care products include compounds such as triclosan (Wyllie 2015; Weatherly and Gosse 2017) and pharmaceutically active compounds (PhACs) such as hormones (Álvarez-Muñoz et al. 2015). The associated risks of exposure to PPCPs, PFCs and EDC includes reproductive disorders in women (Crain et al. 2008), feminisation of male fish due to estrogen exposure (Sumpter 1995; Jakimska et al. 2013), or the development of antimicrobial resistance in aquatic and terrestrial animals, human health and the environment. (Cabello 2006; Sapkota et al. 2008), alteration in development of male characters (Milnes et al. 2006), as well as tumour promotion (Biegel et al. 2001). Potent peroxisome proliferation and mutagenicity in toxicity tests (Berthiaume and Wallace 2002) need to be taken into consideration, not only at the species level, but also at the consumer level through the possible ingestion of contaminated seafood (Álvarez-Muñoz et al. 2015).

The main sources of pollutants in marine environments are sewage effluents, waste disposal, aquaculture, animal husbandry and agriculture (Gaw et al. 2014; Ojemaye and Petrik 2019b). There is a ceaseless discharge of these compounds into the marine system, especially through marine outfalls and as a result these compounds have been detected at ng/L to low mg/L in marine waters (Arditsoglou and Voutsa 2012; Baker and Kasprzyk-Hordern 2013; Bayen et al. 2013a, 2014; Álvarez-Muñoz et al. 2015; Lolić et al. 2015; Du et al. 2017; Kim et al. 2017), ng/g to mg/g range in sediment (Klosterhaus et al. 2013; Na et al. 2013; Beretta et al. 2014; Moreno-González et al. 2015; Xie et al. 2017). However, the number of papers published reporting the occurrence

and levels of PPCPs in marine biota (Wang and Gardinali 2012; Li et al. 2012b; Klosterhaus et al. 2013; Dodder et al. 2014; Franzellitti et al. 2014; McEneff et al. 2014; Álvarez-Muñoz et al. 2015; Moreno-González et al. 2016; Hallmann et al. 2016; Núñez et al. 2016; Teixeira et al. 2017; Gilroy et al. 2017; Silva et al. 2017) is quite limited and such studies that exist focused mainly on molluscs. Due to the continuous exposure of marine organisms in the marine environment to these chemical compounds, one of the major issues is their transfer between the neighbouring media and the marine biota, and accordingly their potential bioaccumulation (Álvarez-Muñoz et al. 2015). These compounds are considered as pseudo-persistent contaminants due to the fact that their degradation rate is lower than their access rate (Daughton 2002, 2003). Endocrine disrupting compounds, in particular, have attracted a lot of attention in the last decade and the number of published studies, describing EDCs levels in marine organisms, is considerable (Álvarez-Muñoz et al. 2015; Petrik et al. 2017).

Similarly, pesticides are a group of semi-volatile POPs, which are often classified according to their use as biocides, fungicides, insecticides, and herbicides (McCance et al. 2018) and are of worldwide concern due to their persistence, bioaccumulation, and negative effects on humans, animals, plant life and the environment at large (Aigner et al. 1998; Jones and De Voogt 1998; Afful et al. 2010; Calderón-Preciado et al. 2011; Plaza et al. 2019). Due to their volatility and persistence, pesticides are also subject to global dispersion throughout the environment (Wang et al. 2019). Herbicides are potentially hazardous to living organisms because of their lipophilic properties, which causes them to bioaccumulate in the lipid compartment of biota, as well as their resistance to degradation (Ying and Williams 2000; Wyss et al. 2006; Jurado et al. 2011; Aparecida et al. 2013; Yu et al. 2016). Generally, the majority of herbicide monitoring studies have been concentrated on surface freshwater, such as lakes, rivers and reservoirs with a particular focus on organochlorine compounds (Tadeo et al. 2008; Masiá et al. 2013; Palma et al. 2014; Papadakis et

al. 2015; Ccanccapa et al. 2016b; Miller et al. 2019). It is well known that a large portion of herbicide residues reach the ocean through agricultural runoff, atmospheric transportations, and sewage discharge (Pandit et al. 2006; Stamatis et al. 2010; Campo et al. 2013; Knopp et al. 2016; Münze et al. 2017). When these chemicals are discharged into the ocean, they are dispersed into the water, and may accumulate in sediments and marine organisms. The exposure to these chemical compounds such as atrazine has been associated with severe health problems in humans, such as low weight of the fetus and heart, birth defects, neurologic diseases, cancers, urinary defects, limb defects, dermatologic diseases, and respiratory disorders (ATSDR 2003; Ochoa-Acuña et al. 2009; Pathak and Dikshit 2012; Rinsky et al. 2012). Therefore, it is desirable to fully understand their distribution and concentration in all matrices of the marine environment (Tiemann 2008; Amdany et al. 2014).

The monitoring of marine environment for all classes of persistent pollutants is of great importance because oceans are considered to be the largest sink of POPs (Iwata et al. 1993; Dachs et al. 2002; Lohmann et al. 2006), which may be changed into a secondary source of specific POPs.

Also, toxic metals have been identified as a serious cause of pollution in studies of degradation of coastal sites and the environment. Because of the toxicity and non-degradability of these metals, great attention has been placed on monitoring to ensure their presence in the environment is controlled.

Pollution of the aquatic/marine environment by toxic metals has long been recognized as a serious environment concern (Tüzen 2003). In the marine environment, pollutants including toxic metals are bioaccumulated in organisms and sediments and find their way to humans. Because of this, the knowledge, level and fate of heavy metals in marine organisms and environment need to be

determined in order to ascertain their risk to humans upon the consumption of these organisms (Pérez Cid et al. 2001).

Humans may be contaminated by organic and inorganic pollutants associated with aquatic systems by consumption of contaminated fish and other aquatic foods from this contaminated environment. This is due to the capacity of some marine organisms to concentrate heavy metals up to 10^5 times the concentration present in water (Aderinola et al. 2009).

In most studies of environmental degradation of coastal areas, metals are recognised as a cause of serious pollution. Special attention is usually paid to toxic metals because of their toxicity and non-degradability in the environment. Bioaccumulation of metals in marine organism's tissues was recorded in a number of monitoring projects of the status of the marine environment. Several studies have been conducted on aquatic biota and sediment from different locations in the world to determine metal levels in rivers and lakes (Binning and Baird 2001; Visnjic-Jeftic et al. 2010; Fallah et al. 2011; Jaric et al. 2011; Alturiqi and Albedair 2012; Benzer et al. 2013; Edward 2013; Hashim et al. 2014; Baharom and Ishak 2015; Adebayo 2017) however, few papers have been published reporting the occurrence and levels of metals in marine biota and environment (Khalifa et al. 2010; Meche et al. 2010; Olowu et al. 2010; Rončević et al. 2010; Sen et al. 2011; El-Moselhy et al. 2014).

Sediments are important sinks for various pollutants like herbicides, pharmaceuticals and toxic metals and also play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions and in interactions between water and sediments (Gilroy et al. 2012). The biota that inhabit contaminated sites is generally exposed to very high concentrations of these pollutants because many of them process sediment as a food source and many are filter feeders, thus can be susceptible to bioaccumulation and therefore biomagnify and potentially threaten the

health of many species at the top of the food chain, especially those who feed on them (Edward 2013). Heavy and trace metals including both essential and non-essential elements have a specific importance in ecotoxicology since they are very persistent and all have the potential to be toxic to living organisms (Storelli et al. 2005).

The present chapter aims to determine the distribution and abundance of selected emerging pollutants in the marine reserve at Camps Bay, and to quantify selected pollutants originating from the marine outfall that could cause stress to the marine ecosystem. Thus the study aims to determine any impacts that the sewage outfall system has (in the absence of any manufacturing industry), and whether the purported high dilution of pollution when sewage is discharged into the ocean environment is operating as effectively as is claimed by city officials. Furthermore, it is necessary to verify whether the selected pollutants are bioaccumulating in sessile organisms (mussels, limpet and sea urchin) and sea weeds. The selection of PPCPs, PFCs, EDCs, herbicides and toxic metals for this study was based on one criterion: that their source could only be from sewage.

6.1. Results and discussion

Samples were collected in September 2017 and the analytical protocols earlier described in recently published articles (Ojemaye and Petrik 2019a; Ojemaye et al. 2020) were employed for the determination of the levels of these contaminants in these samples. In the following sections, the results of analysis carried out on the different environmental matrices are presented and discussed. The discussion is on the basis of the class of contaminants in each of the matrices.

6.2. Occurrence in Camps Bay

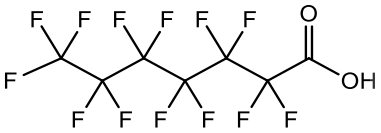
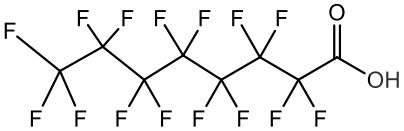
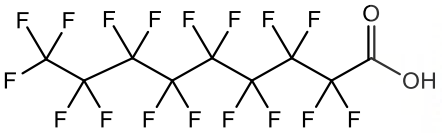
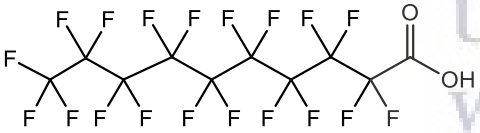
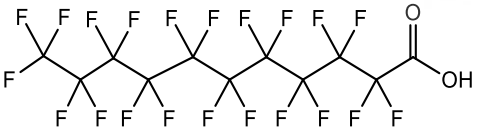
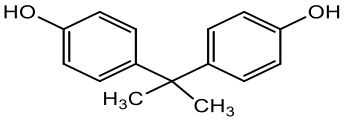
In this section, five classes of contaminants were evaluated namely: pharmaceuticals and personal care product, perfluorinated compounds, industrial chemicals, herbicides and metals in seawater,

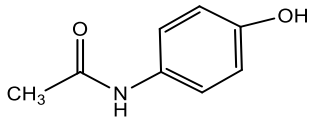
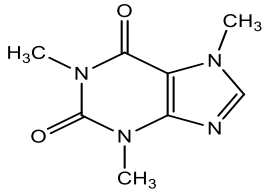
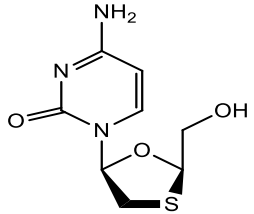
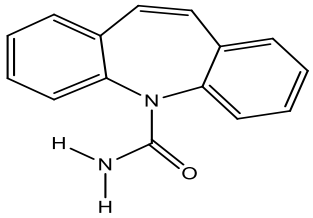
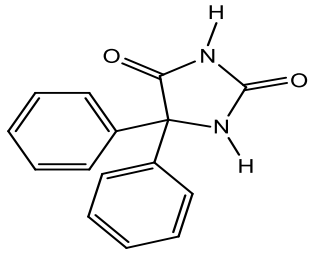
sediment, marine organisms and seaweeds. Industrial chemicals in this chapter are referred to as endocrine disrupting compounds (EDCs).

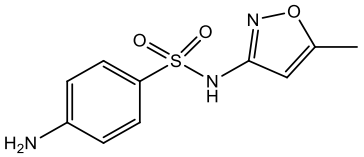
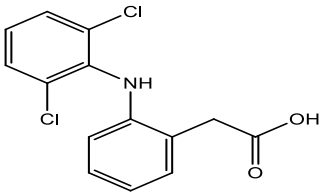
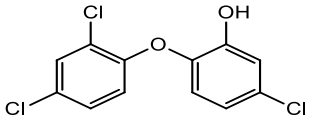
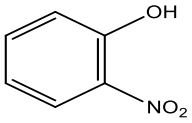
6.2.1. Pharmaceutical and personal care product, perfluorinated compounds and industrial chemicals (EDC)

Table 6.1 provides the LC–MS retention time, transition and collision energy, limit of detection (LOD), and limit of quantification (LOQ) while Figure 6.1 provides a summary of the PPCPs, PFCs and industrial chemical compounds detected in samples collected at Camps Bay. The analysis of variance conducted on all data obtained showed that the level of all contaminants varies significantly ($p<0.05$) across all environmental samples assessed in this study. Furthermore, statistical analysis of all data obtained in this study (Figure 6.1) showed that the result obtained for the quantification of PPCPs, PFCs and ECDs in the environmental samples reported in this study are replicated. The calibration curve and chromatograms of these compounds are shown in Appendix III, Figures III.1 and III.2.

Table 6. 1: LC–MS retention time, transition and collision energy, limit of detection (LOD), and limit of quantification (LOQ)

Compound Name	Molecular weight (g/mol)	Molecular structure	Retention Time (min)	Ion transition (m/z)	Collision energy (eV)	LOD			LOQ			% Recovery		
						Seawater (ng/L)	Sediment (ng/g)	Organism (ng/g)	Seawater (ng/L)	Sediment (ng/g)	Organism (ng/g)	Seawater	Sediment	Organisms
PFHpA	364.06		6.82	363 to 319	15	0.03	0.04	0.06	0.08	0.13	0.18	96.5	97.5	99.8
PFOA	414.07		7.39	413 to 369	15	0.003	0.02	0.08	0.01	0.08	0.24	97.3	99.1	98.2
PFNA	464.08		7.88	463 to 419	15	0.01	0.05	0.08	0.02	0.14	0.23	98.0	98.9	100.4
PFDA	514.09		8.24	513 to 469	15	0.02	0.34	0.44	0.06	1.03	1.35	99.6	100.9	101.2
PFUnDA	564.09		8.57	563 to 523	15	0.04	0.53	0.84	0.11	1.61	2.55	97.0	98.5	98.3
Bisphenol A	228.29		5.87	227 to 212	28	0.01	0.03	0.44	0.05	0.08	1.35	96.2	96.9	97.0

Acetaminophen	151.16		2.01	152 to 110	15	0.02	0.32	0.32	0.07	0.98	0.98	98.1	99.3	99.8
Caffeine	194.19		3.41	195 to 138	20	0.03	0.20	0.34	0.08	0.59	1.04	97.8	98.7	98.0
Lamivudine	229.26		1.74	230 to 112	15	0.03	0.20	0.29	0.09	0.60	0.88	96.0	97.0	99.5
Carbamazepine	236.27		6.43	237 to 194	20	0.01	0.03	0.07	0.03	0.10	0.22	99.3	99.9	100.9
Phenytoin	252.27		6.18	253 to 182	15	0.27	0.37	0.37	0.81	1.12	1.12	99.0	98.4	98.9

Sulfamethoxazole	253.28		3.23	254 to 188	25	0.02	0.02	0.15	0.06	0.06	0.46	96.0	96.5	98.2
Diclofenac	296.15		6.72	296 to 250	15	0.03	0.23	0.33	0.09	0.71	1.01	98.6	99.4	101.3
Triclosan	289.54		9.09	288 to 36.80	10	0.02	0.07	0.27	0.08	0.22	0.81	95.9	96.7	95.5
2 nitrophenol	139.11		-	139 to 121	15	-	-	-	-	-	-	-	-	-

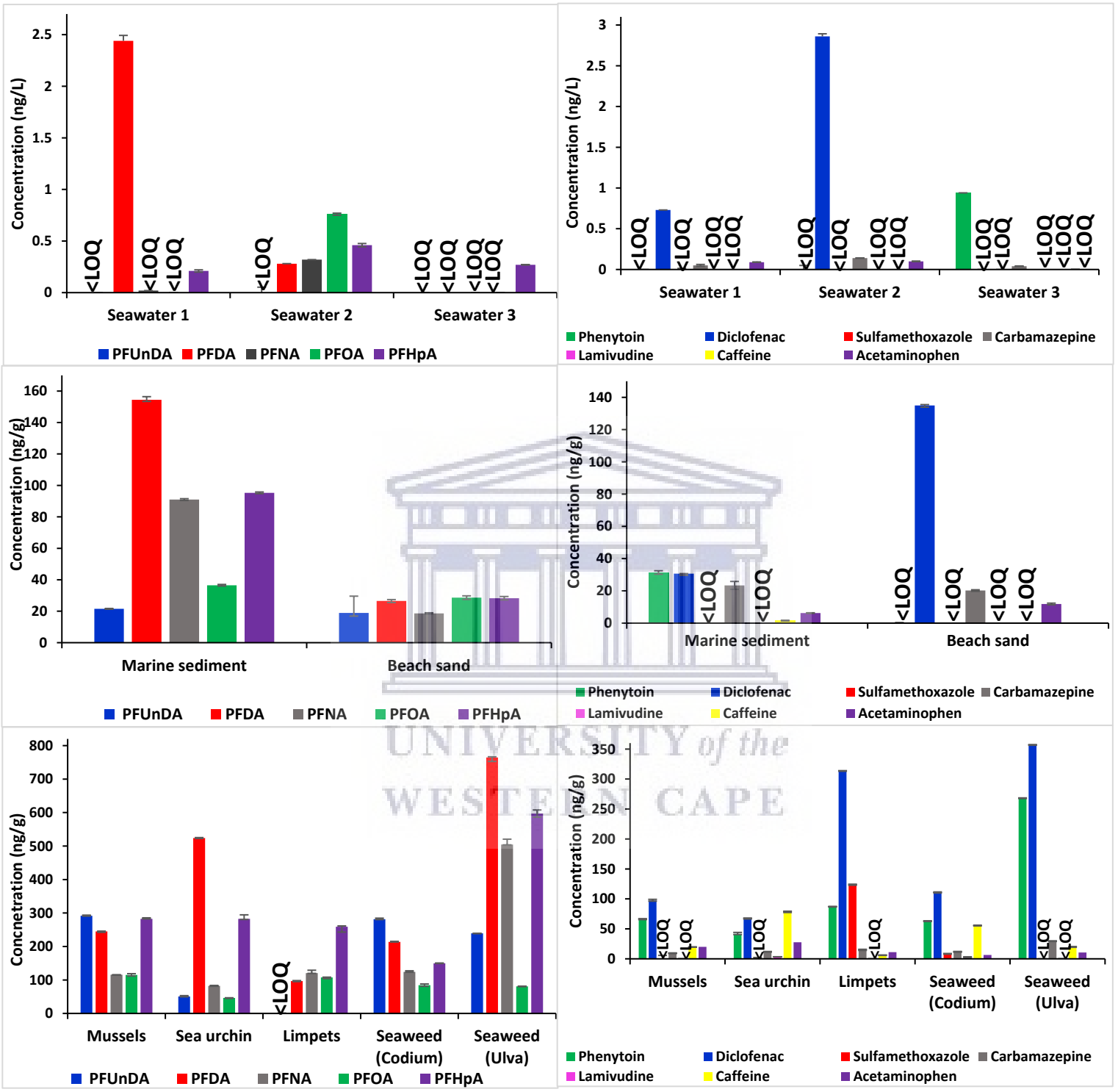


Figure 6. 1: Concentration of PFCs, EDCs and PPCPs in sea water (top), sediment (middle) and biota (bottom) collected from Camps Bay (n=4, replicate samples taken at the same time), <LOQ= below limit of quantification.

6.2.2. Sea waters

Of the fifteen target compounds, eight were detected in at least one of the sea water samples and two of these compounds were detected in all the samples (Figue 6.1). The compounds detected in the highest concentrations were among those most frequently detected. The detected compounds represent a variety of chemical types and therapeutic uses, and most have been frequently observed in other marine/sea water studies (Liu et al. 2011; Fang et al. 2012; Jiang et al. 2014; Birch et al. 2015; Kim et al. 2017). PFDA and diclofenac were the two compounds detected in the highest concentration in seawater samples (2.44 and 2.86 ng/L respectively), and both carbamazepine and PFHpA were detected in all water samples in this study. Only a few studies have previously investigated their occurrence in the environment (Naile et al. 2010; Yang et al. 2011; Munaron et al. 2012; Petrik et al. 2017). Several other compounds that have been suggested as tracers of wastewater contamination due to incomplete metabolism in humans, low removal efficiency during wastewater treatment, and persistence in the environment (Boxall et al. 2012; Rodil et al. 2012; Verlicchi et al. 2012; Lambropoulou and Nollet 2014) were also detected in the Camps Bay seawater samples, these include acetaminophen and diclofenac.

The concentrations of the various compounds detected in all the sea water samples were less than 5 ng/L as can been seen in Figue 6.1. These concentrations are lower than those typically reported for sites in freshwater systems, which are often located near wastewater outfalls (So et al. 2007; Fernández et al. 2010; Yang et al. 2011; Gorga et al. 2013; Klosterhaus et al. 2013; Rodríguez-Navas et al. 2013; Zhou and Broodbank 2014; Xie et al. 2015) and are similar to concentrations reported for other marine and estuarine environments, where wastewater discharges are also common but dilution occurs to a greater extent (Togola and Budzinski 2008; Knee et al. 2010; Fang et al. 2012; Zhang et al. 2013b; Birch et al. 2015). The levels of these compounds in seawater

samples from this site were higher compared to the levels reported in Green Point (Chapter 5) but lower to the levels of seawater samples reported in False Bay (Chapter 7).

The presence of pharmaceuticals had also been reported in the Mediterranean Sea, (Gros et al. 2012; Rodríguez-Navas et al. 2013), Marine Bay (Singapore) (Bayen et al. 2013b), Baltic Sea (Björlenius et al. 2018), and North Sea though the detected pharmaceuticals were at higher levels than those reported in this study, while Zhao et al. (2017) found similar concentrations of PFHpA, PFNA and PFDA in seawater from Bohai Sea and Yellow Sea. On the other hand, the PFCs selected in this study were higher in seawater samples from coastal regions of Shandong peninsula (Wan et al. 2017), Bay of Marseille (Schmidt et al. 2019), Osaka Bay, the Pacific Ocean, and Kagoshima Bay (Beškoski et al. 2017).

Recently, the CSIR report (CSIR 2017) published in 2017 detected the following pollutants carbamazepine, diclofenac and paracetamol (acetaminophen) with concentrations shown in Table 6.2 in Camps Bay sewage effluent discharge at the pump station before discharge to the ocean. Hence, the dilution factor can be assumed to range between 16 to above 1000 times for carbamazepine, diclofenac and paracetamol as shown in Table 6.2, considering the concentration difference between the concentrated sewage at the pump station and the diluted sewage in the ocean surrounding the discharge.

Table 6. 2: Dilution factor of diverse compounds discharged into the marine environment in Camps Bay

Compounds	Sewage at pump station (ng/L)	Seawater (ng/L)	Dilution factor
Carbamazepine	280 – 580	0.05 – 0.14	4142x
Diclofenac	630 – 1500	0.73 – 2.86	524x
Paracetamol	250000 – 950000	0.09 – 0.10	9700000x

Despite the purported adequate dilution of the chemicals and sewage by the ocean according to the City and the outfall design criteria (CSIR 2017), these compounds were shown to be present in measurable amounts in the ocean water, albeit not equally dispersed, which points to the uneven and slow dilution and dispersion of contaminants in a concentrated sewage plume released into the marine environment. It also shows that the dispersion rate of chemical compounds is related to the type of chemical, since these compounds are not all equally hydrophilic. In addition, changes in pH and salt concentration greatly influence the electrostatic properties of these chemicals, which may have multiple ionizable functional groups with substantially different acid dissociation constant (pK_a) values thus influencing their environmental partition in seawater (Fabbri and Franzellitti 2016).

6.2.3. Sediment and beach sand

Twelve of the fifteen target analytes were detected in one or more of the Camps Bay sediment samples (Figue 6.1). Compounds detected in the highest concentrations were diclofenac (maximum 134.94 ng/g dw), PFHpA (maximum 95.30 ng/g dw), PFDA (154.45 ng/g dw), phenytoin (maximum 31.34 ng/g dw) and PFNA (maximum 91.00 ng/g dw). In contrast to the other compounds detected in Camps Bay sediments, lamivudine was not detected in any sea water or other sample except sea urchins in this study. Nine of the compounds were detected in all of the sediment samples (acetaminophen, diclofenac, caffeine, PFNA, PFHpA, PFDA, PFUnDA, phenytoin and PFOA). These high levels in an inorganic matrix such as sediment and beach sand shows that the sewage plume must make frequent landfall, causing a buildup of chemical contaminants along the shoreline, as the chemicals are not flushed away by clean sea water frequently enough to prevent accumulation. The levels of these compounds in sediment samples reported in this chapter were higher compared to the levels reported in Green Point (Chapter 5) but lower to the levels of sediment samples reported in False Bay (Chapter 7). The presence of

PFCs also have been reported in the Pacific Ocean and Kagoshima Bay though at higher levels than those reported herein (Beškoski et al. 2017). Compared with the results obtained from other studies the concentrations of PFCs in the sediment of this study were much higher than those in Bohai Sea and East China Sea (Gao et al. 2014), Laizhou Bay (Zhao et al. 2013) and Jiaozhou Bay (Wan et al. 2017).

6.2.4. Marine organisms and seaweeds

The biota tested from Camps Bay were namely: [limpet (*Cymbula granatina* and *C. oculus*), mussels (*Mytilus galloprovincialis*), sea urchin (*Parechinus angulosus*) and seaweeds (*Ulva* sp. and *Codium fragile*). Twelve of the fifteen target compounds (Figue 6.1) were detected in at least one or more of the marine biota and seaweed samples collected from rock pools along the Camps Bay shoreline. The compounds detected in the highest concentrations in the marine organisms were PFHpA (597.04 ng/g dw), PFNA (504.52 ng/g dw), PFDA (523.93 ng/g dw), PFUnDA (291.81 ng/g dw), caffeine (78.38 ng/g dw), diclofenac (357.45 ng/g dw) and phenytoin (226.63 ng/g dw). Six of the compounds were detected in all the samples (PFNA, PFHpA, PFDA, diclofenac, acetaminophen and PFOA). Some compounds that were not detected in biota were also not detected in Camps Bay sea water nor in the sediment samples (bisphenol A, 2-nitrophenol and triclosan). Among the selected PPCPs tested for and detected in marine biota in this study, only diclofenac, acetaminophen, carbamazepine, caffeine and sulfamethoxazole have been previously detected in aquatic organisms (Wille et al. 2011; Li et al. 2012a, b; Dodder et al. 2014; McEneff et al. 2014; Álvarez-Ruiz and Picó 2019). Similar levels of caffeine were also found in other studies (Maruya et al. 2014; Alvarez-Muñoz et al. 2015; López-García et al. 2019), triclosan (Krogh et al. 2017) in mussels from other studies were higher than levels found in this study.

The concentration of compounds detected in seawater was relatively low (Figue 6.1) whereas the selected compounds found in biota samples were present at a considerably higher concentration than the background ocean levels. None of these synthetic compounds would of themselves be found in seawater and should definitely not be present in these marine organisms. With the exception of caffeine, all are manufactured substances. Considering the fact that some of the selected compounds that were investigated, were found in every organisms, this is an indication that a vast array of other chemical substances could also be present in the marine environment. The occurrence of phenytoin, PFNA, PFHpA, PFDA, diclofenac, acetaminophen, PFOA, lamivudine, sulfamethoxazole, PFUnDA, caffeine, 2-nitrophenol, bisphenol A, triclosan and carbamazepine in marine organisms collected from the field has not been reported previously in South Africa apart from the study in Green Point (Petrik et al. 2017). This is particularly of concern since these compounds clearly derive from the sewage being pumped into the ocean via the marine outfall discharge point. The high levels detected in the marine biota show that the dilution of the sewage by the ocean does not adequately prevent bioaccumulation by the marine organisms and that the sewage plume must make frequent landfall.

Some of these compounds were reported to be present in the Camps Bay pump station sample marine sewage discharge and were also found at Green Point. Comparing the results obtained (Camps Bay) with that of a previous publication (Green Point) (Petrik et al. 2017), shows that these pollutants are present in Cape Town marine water. Currently Camps Bay sewage discharge volume is 2.4 million liter per day, although daily discharge volumes differ by an order of magnitude, and fewer compounds were detected in Camps Bay marine biota, the levels detected were much higher than that of Green Point showing that dilution of the sewage in Camps Bay was completely inadequate. Thus, it is incontrovertible that raw sewage discharge into a designated marine reserve is having a significant impact upon the marine biota due to bioaccumulation in their

tissues. Furthermore, to dispose of raw sewage into a marine protected zone is shown to be a highly questionable practice. The well-known adverse effects of these compounds upon living organisms including endocrine disruption, genotoxicity feminisation, cancer etc., point to the urgent necessity to prevent marine discharge of sewage to avoid destroying the marine environment.

6.2.5. Bioaccumulation in marine biota and sorption coefficient in sediment samples

Bioaccumulation factors (BAFs) is the ratio of the contaminant concentration in aquatic organism tissue and plant (C_{biota}) to the contaminant concentration ratio in water (C_w). These were calculated to evaluate the bioaccumulation of the contaminants analysed in aquatic organisms (Kinney et al. 2008). Chemicals are said to be ‘‘bioaccumulative’’ If the BAF in aquatic organisms is greater than 5000 L/kg and ‘‘potentially bioaccumulative’’ if the BAF is in the range from 2000 L/kg to 5000 L/kg in aquatic organisms (Arnot and Gobas 2006; Na et al. 2013). Based on the concentrations of compounds measured in Camps Bay seawater and biota samples, the observed BAFs of the eight most widespread compounds were calculated for different aquatic species from Camps Bay (Table 6.3).

Table 6. 3: BAFs and Kd,s values of samples

	BAF(L/Kg)					$K_{d,s}$ (L/Kg)	
Compounds	Mussel	Urchin	Limpets	*Codium*	*Ulva* sp	Marine sediment	Beach sand
PFHpA	614130	614304	562978	325000	129791	20717.0	61478.0
PFOA	151394	61000.0	141328	111184	106421	48066.0	37697.0
PFNA	361031	256781	376156	387187	1576625	284375	58187.0
PFDA	100393	214725	39582.0	87631.0	313377	63299.0	10868.0
DCF	34003.0	23591.0	109804	38776.0	124983	10727.0	47181.0
PHE	70691.0	44159.0	93117.0	67383.0	28265.0	33340.0	0
CAR	70142.0	87428.0	107642	86785.0	214357	167142	144428
ACT	200400	275900	111000	65000.0	105000	62000.0	118000

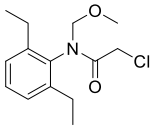
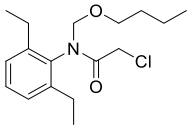
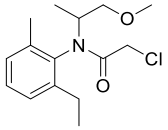
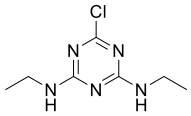
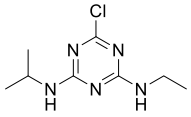
The BAFs observed in mussels, urchin, limpets, seaweeds ranged from 325000 – 614000 for PFHpA, 61000 – 151000 for PFOA, 256000 – 1577000 for PFNA, 39000 – 313000 for PFDA, 23000 – 125000 for DCF, 28000 – 93000 for PHE, 70000 – 214000 for CAR and 65000 – 275000 for ACT (Table 6.3). These result suggested that all compounds are highly bioaccumulative. The interspecies differences of the BAFs found in organisms from Camps Bay marine environment might reflect their species habitats, lifestyles and different contaminant metabolic capacities. BAF assessments assume that the organisms sampled exist at steady state with the ambient water, but the compounds' concentrations in the natural marine environment might be very dynamic and mostly inconsistent. In addition, organisms that move about can be exposed to a wide range of chemical compounds in the water. The sorption coefficient K_d defined as the ratio of concentration of contaminant in sediment to that in water (K_d = Cs/Cw, L/kg) is used to describe the reversible sorptive exchange of chemicals between water and sediment. PFHpA, PFNA, CAR and ACT had

the highest sorption capacities among the other compounds. Furthermore, the Kd values of all the compounds are high which could imply a benefit because they would absorb upon the sediment but the higher BAFs values in organisms and seaweed samples shows otherwise because even these compounds are actually highly bioaccumulating in the marine species. For perfluorinated compounds, findings shows that Kd and BAF increase with each increase in chain length (Kwadijk et al. 2010; Labadie and Chevreuil 2011) which is not the case in this study.

6.2.6. Herbicides

The experimental protocols to determine herbicide compounds in the above listed sample matrices are described in Chapter 3 of this thesis. The GC–MS retention time, transition and collision energy, LOD and LOQ are outlined in Table 6.4, and Figure 6.2 reports a summary of the concentration of compounds detected in samples collected in the marine environment of Camps Bay as well as Appendix III, Table III.1. The analysis of variance conducted on all data from seawater, sediment, and biota showed that the level of all analysed contaminants varied significantly across environmental samples. Three samples of seawater were collected, sample 1 was collected from water extracted from a site dug very close to the beach, sample 3 was collected where most activities takes place on the beach, while sample 2 was collected further into the ocean. The calibration curves and chromatograms of each herbicide compounds are shown in Appendix III, Figure III.4.

Table 6. 4: Molecular mass and structure and GC-MS parameters of the analysed herbicide compounds

Compounds	Molecular mass (g/mol)	Molecular structure	RT (Min)	Log kow	Log koc	GUS index	Quantification ion *m/z*	Qualifier ion	CE (V)	Recoveries (%)			LOD			LOQ		
										Seawater	Organism	Sediment	Seawater (ng/L)	Organism (ng/g)	Sediment (ng/g)	Seawater (ng/L)	Organism (ng/g)	Sediment (ng/g)
Alachlor	269.8		13.42	3.52	2.49	1.07	237 /**160**	237/146	1.05	102.5	98.9	94.6	0.5	1.9	0.9	1.5	5.7	2.8
Butachlor	311.85		15.37	4.15	2.99	2.02	176 /**146**	160/132	1.05	97.2	95.2	98.7	0.2	2.8	1.1	0.5	8.4	3.4
Metolachlor	283.8		14.2	3.13	2.34	2.00	238 /**162**	162/133	1.05	101.3	99.2	96.1	0.3	4.0	6.8	1.1	12.2	20.6
Simazine	201.6		12.38	2.18	2.11	2.20	**201** /186	201/172	1.45	98.8	97.3	96.9	0.3	3.3	1.8	0.8	10.1	5.6
Atrazine	215.7		12.32	2.61	2.00	3.86	**215** /**200**	200/173	1.50	101.0	98.5	99.9	0.2	0.6	0.4	0.5	1.9	1.2

RT - retention time, CE - collision energy (V), LOD – limit of detection, LOQ – limit of quantification, Quantitation ions in bold

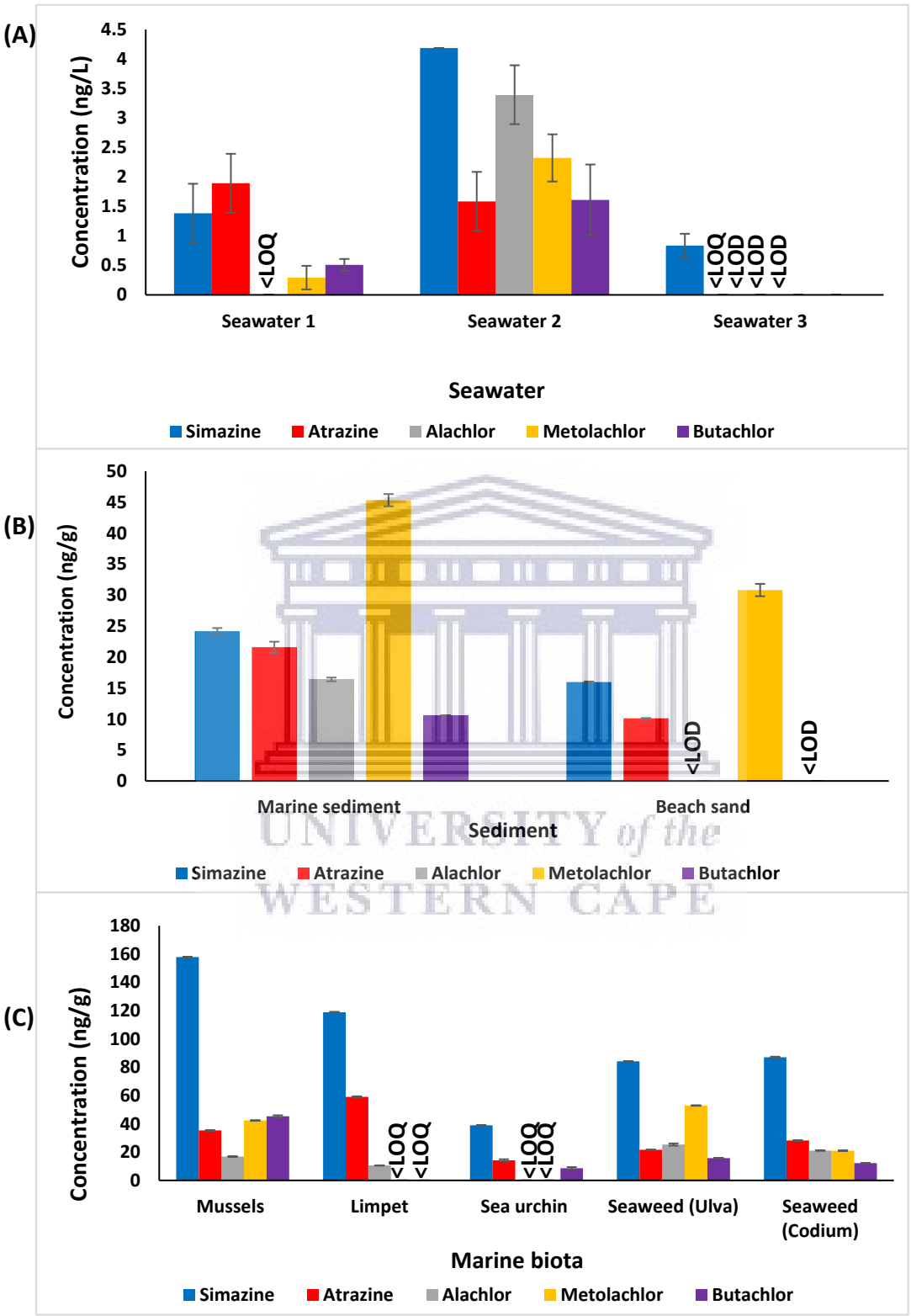


Figure 6. 2: Concentration (ng/L and ng/g dry weight) of compounds detected in different matrices of Camps Bay marine environment. (< LOD = below limit of detection < LOQ = below limit of quantification).

6.2.7. Seawater

Herbicides were detected in seawater samples, at a very low concentration (Figure 6.2). The concentration of herbicides in seawater sample 1 (near shore) ranged from <LOQ to 1.9 ng/L, with atrazine having the highest concentration. Simazine had the highest concentration in seawater samples 2 and 3 (near outfall and open ocean respectively), the concentration of herbicides ranged from 4.2 ng/L to 1.6 ng/L and <LOD to 0.8 ng/L, respectively.

The concentration of all analysed compounds in seawater sample 2 was higher compared to the other seawater samples. This might be due to the impact of the uneven dispersion and the landfall of the sewage effluent released by a marine outfall present in the area, which discharges essentially untreated sewage from the suburb into the marine environment near the seawater sampling points at Camps Bay (Feiter 2015; Webwolly 2015; Hirsch 2017; Chothia 2019; Kretzmann 2019; Kretzmann and GROUNDUP 2019; Mbane 2019). Also, considering the fact that agricultural areas are some kilometers away from Camps Bay, the atmospheric deposition is not likely to be a large source of these contaminants, due to both distances from agricultural areas and prevailing wind direction (Williams 2019). Comparing our findings with studies in other geographical areas, seawater sample levels of simazine and atrazine in this study were lower compared to what was found in the Sydney estuary (1.6 – 8.0 ng/L) (Birch et al. 2015), a coastal lagoon in Spain (16.3 and 7.9 ng/L) (Moreno-González et al. 2013), and in Singapore (<7.0-366 ng/L) (Bayen et al., 2016). In addition, levels of atrazine in seawater samples collected from Aegean, Darganelles, Adriatic, and the Mediterranean seas ranged from 1.5 – 33 ng/L (Nödler et al. 2014) and were also higher than those found in this study.

6.2.8. Sediment and beach sand

Concentrations of all compounds in the marine sediment (Figure 6.2) were higher than the ones found in the beach sand. Metolachlor had the highest concentration in both sediment and beach sand samples, with concentrations of 45.3 ng/g dry weight (dw) and 30.8 ng/g dw, respectively. The concentration of other compounds ranged from 10.6 – 24.2 ng/g and <LOD – 16.0 ng/g, respectively. It is important to consider the fact that some herbicides tend to accumulate in sediment and marine biota (Jurado et al. 2011; Aparecida et al. 2013; Masiá et al. 2015; Ccanccapa et al. 2016b). Much higher concentrations are expected in these matrices, potentially posing an environmental risk for the Camps Bay marine organisms and human risk via consumption of contaminated sea food (Ccanccapa et al. 2016a). The results reported herein show that the concentration of herbicides in the sediment and sand were much higher than in the seawater. This could be associated with the fact that the marine sediment acts as a sink for these pollutants as it is constantly wet (Gilroy et al. 2012). Moreover, the high concentration of herbicides in the beach sand indicated that polluted water is affecting the Blue Flag beach facilities (Blue Flag Criteria: industrial, waste-water or sewage-related discharges must not affect the beach area), and that microbial monitoring is not sufficient to ensure public health (Blue Flag 2020). Available data on the levels of these compounds in sediment samples indicates that the level of simazine from this study is higher than in the report published by Villaverde et al. (2008) (7.01-15.7 ng/g) from Portugal, as well as the level of alachlor (0.01-0.24 ng/g) and metolachlor (0.38-0.63 ng/g) reported by Xue et al. (2008) from Northern Beijing, China.

6.2.9. Marine biota and seaweeds

Data regarding the concentration of herbicides in marine organisms are reported in Figure 6.2. Mussel tissue had the highest concentration of all the studied compounds compared to other invertebrates, except atrazine. Simazine levels were the highest in mussels, with a concentration of

157.8 ng/g dry weight. Alachlor had the lowest concentration (16.9 ng/g dw) in mussels, and the concentration of atrazine, metolachlor, and butachlor ranged from 35.3 ng/g dw - 45.3 ng/g dw. Metolachlor and butachlor were below detection limit in limpets, and the compound with the highest concentration in limpets was simazine (118.9 ng/g dw). The concentration of atrazine and alachlor were 59.0 ng/g dw and 10.6 ng/g dw, respectively. Alachlor and metolachlor were below limit of quantification in sea urchins while simazine had the highest concentration (39.0 ng/g dw) out of all the detected compounds. The concentration of atrazine, alachlor, metolachlor, and butachlor ranged from 1.8 ng/g dw to 14.3 ng/g dw.

In seaweed (*Ulva*), all herbicides were detected and simazine had the highest concentration (84.2 ng/g dw), followed by metolachlor (52.9 ng/g dw), while the other compounds' concentration ranged from 15.8 ng/g dw to 25.4 ng/g dw. Simazine also had the highest concentration in the seaweed species *Codium fragile* (87.0 ng/g dw), while other compounds ranged from 12.3 ng/g dw to 28.2 ng/g dw.

Since Cape Town and Camps Bay are geographically remote from Northern Hemisphere pollution, it is unlikely that herbicides are being transported by ocean currents from elsewhere, thus the source has to be local. Sea urchins seemed to accumulate the studied herbicides less than other organisms. Mussel species are one of the most commonly used organisms for environmental monitoring, for instance in the Mussel Watch Program (USA) or the ROCCH network (French chemical monitoring network), due to several characteristics such as wide distribution, sessile lifestyle, resistance to stress and high accumulation of a wide range of chemicals and also their filter feeding nature (Viarengo and Canesi 1991; Farrington et al. 2016; Beyer et al. 2017). In a study conducted on mussels from Belgian coastal zone by Wille et al. (2011), the concentration of metolachlor (1 ng/g) reported were lower than the concentration observed in this study. Simazine and atrazine

were the most frequently detected in all the tested sample matrices, with simazine having the highest concentration in all cases. In general, the concentration of herbicides were higher in sediments and biota, indicating that these compounds are bioaccumulated in marine biota and adsorbed to inorganic solid matrices, as also reported by Thitiphuree et al. (2013). In a study conducted on mussels from Vilaine estuary, France and Nantong of Southeast China respectively, the concentration of simazine and atrazine found were 0.02 ng/g (Farcy et al. 2013) while the concentration of metolachlor was 0.07 ng/g (Farcy et al. 2013) and 0.34 ng/g (Wang et al. 2012a). In a recent study on macroalgae from Saudi Arabian Red Sea, the concentration of atrazine ranged from not detected to below limit of quantification (Ali et al. 2018). In a study conducted by Cruzeiro et al. (2016) on the bivalve *Scrobicularia plana* from Portugal (4.5 – 56.9 ng/g) and de Souza et al. (2016) on *P. perna* from Santa Catarina, Brazil (<LOD), the concentration of atrazine were considerably lower compared to values found in this study, as well as the concentrations of alachlor and simazine found in *Scrobicularia plana* (3.9 – 7.0 ng/g) and (11.9 – 72.2 ng/g), respectively (Cruzeiro et al. 2016).

The comparison of our results with data from other studies indicates that if no urgent regulation is put in place to mitigate the release of effluents harbouring these chemicals into the marine environment of an isolated suburban community like Camps Bay, the health impact of those chemicals will be deleterious to the marine biota and inhabitats of this region. It is clear that there is a worrying tendency of bioaccumulation. If not halted, the continuous discharge of effluents containing these hazardous chemicals via the marine sewage outfall will result in an increase in levels of these chemicals in marine waters and species in Camp Bay, which will have a negative impact on the viability of the associated Marine Protected Area. It is evident that these herbicides enter the environment of Camps Bay primarily through urban resident's raw sewage discharged through the marine sewage outfall since there was no storm water runoff in this urban setting during

the severe drought of 2015- 2018. Moreover, the detected herbicide levels in beach sand, sediments and marine biota located in rock pools along the shore show that the sewage plume makes frequent landfall, which indicates that dilution of the sewage by the ocean is inadequate and that the outfall location is too close to the shore to prevent contamination, which clearly contradicts the Blue Flag criteria used by the City to establish safe bathing or water use.

6.2.10. Bioaccumulation factors

Bioaccumulation factors (BAFs) were calculated from the results to determine the bioaccumulation of these herbicides in marine biota. Simazine and atrazine were found to be bioaccumulative in all the analysed species (Table 6.5). While, alachor was bioaccumulative in seaweeds and potentially bioaccumulative in mussels and limpets. Metolachor and butachlor were bioaccumulative in mussels and seaweeds, while they were potentially bioaccumulative in sea urchins.

Table 6. 5: Bioaccumulation factor (BAF) values of herbicides detected in marine biota, reported as L/Kg dry weight. BAF > 5000 L/kg = bioaccumulative and 2000 L/kg - 5000 L/kg = potentially bioaccumulative.

	Mussels	Limpet	Sea urchin	Seaweed Ulva	Seaweed codium
Simazine	37758	28435	9320.0	20141	20822
Atrazine	18682	31232	7539.0	11423	14899
Alachlor	4970.0	3115.0	525.00	7480.0	6227.0
Metolachlor	18262	0	2262.0	22814	9060.0
Butachlor	28149	0	4242.0	9788.0	7608.0

The BAF results showed that low levels of herbicides in seawater can be translated into considerable bioaccumulative effects in the marine organisms, highlighting the importance that it is inadequate to merely monitor levels in seawater. Thus, the dilution factor and dispersion in seawater of such herbicides is not sufficient to prevent negative impacts on associated benthic

communities. These results confirm and compliment the data regarding the concentrations of these pollutants in marine biota (Figure 6.2). These results are in agreement with the study of Jacomini et al. (2006), where they reported that bivalve species when exposed to low concentrations of atrazine can bioaccumulate. In addition, a recent study confirmed the bioaccumulation of atrazine in shellfish (Ali et al. 2018).

6.2.11. Herbicide regulation

Herbicides are widely used in South Africa and there are thousands of different products registered for use on agricultural crops (Olisah et al. 2019a). In South Africa, the public health significance of water source pollution by pesticides, particularly herbicides, has attracted little attention from government and regulatory agencies, unlike microbiological quality of potable water, which is of a high priority to legislative bodies. This abnormality is reflected in the current drinking water, effluent discharge limits and aquatic ecosystem guidelines in South Africa (DWAF 1996a, b; CSIR 2017) with few standards for organic contaminants, and only one standard for a herbicide, atrazine (0-0.002 mg/L), but with detailed standards for coliform content and inorganics. Since South Africa is a major market in Africa for pesticides (Quinn et al. 2011; Dabrowski 2015), this is a serious gap that needs to be closed very urgently. Atrazine was withdrawn for use on heavy clay soils (Springbok Flats) in 1977 and its industrial use withdrawn on 31 March 1995 (DAFF 2017). The maximal residue levels (MRL) of herbicide in their associated crops are: alachlor 0.05-0.1 mg/kg, metolachlor 0.05 mg/kg, simazine 0.2 and 10 mg/kg and atrazine 0.05 mg/kg (Quinn et al. 2011). Most countries have developed their pesticide laws and regulatory authorities, while in South Africa; herbicides are managed under Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies Act, governed by the Department of Agriculture, Forestry and Fisheries. This study and other studies in South Africa showed the presence of herbicides (Ojemaye et al. 2020) and pesticides (Ansara-Ross et al. 2012; Yahaya et al. 2017; Verhaert et al. 2017; Olisah et al. 2019a,

b) in the aquatic ecosystem. Hence, the regulation of this class of compounds in marine and freshwater ecosystem needs to be put in place, also considering that people might be the end user of contaminated seafood.

6.3. Occurrence of Metals

Table 6.6 summaries the average concentration of all element detected in seawater, sediment and marine biota.

Table 6. 6: Concentrations of metals in (mg/L for water and mg/kg for sediment and biota) from Camps Bay

Element (ppm)	Mussels	Sea urchin	Limpets	Seaweed	Sediment	Beach sand	Seawater 1	Seawater 2	Seawater 3
Al	526.59±2.8	432.65±7.4	326.14±18	1331.73±3.4	1228.14±2.2	252.59±2.4	0.03±0.4	0.03±0.1	0.01±0.2
Si	131.57±6.3	2.52±0.0	67.03±2.5	64.01±5.1	112.36±2.4	106.28±2.9	0.55±0.9	0.11±0.5	0.33±0.5
Ce	53.41±0.0	54.15±1.9	32.88±0.2	48.62±0.0	2.23±0.2	2.20±0.0	nd	0.01±1.0	nd
Pb	114.71±2.5	233.17±0.9	145.19±0.3	118.34±1.5	19.13±0.1	2.03±0.0	nd	nd	nd
Nb	419.79±0.1	419.81±2.0	422.28±0.8	422.39±1.1	1.82±0.0	0.47±0.0	$2.8*10^{-4}$	$2.7*10^{-4}$	nd
Th	nd	55.62±0.1	18.55±1.9	nd	nd	0.36±0.0	0.08±1.3	0.08±0.8	0.09±0.6
Y	0.82±0.6	0.79±0.1	0.94±0.1	1.38±0.1	0.99±0.1	0.81±0.0	$1.8*10^{-4}$	$3.7*10^{-4}$	nd
Rb	nd	2.51±0.0	0.69±0.4	24.00±0.2	2.01±0.1	0.08±0.0	0.09±0.5	0.08±0.4	0.08±0.3
Cu	28.92±1.6	22.94±0.1	58.76±0.1	15.44±0.0	18.74±0.0	1.18±0.0	nd	nd	nd
As	4.39±0.6	3.21±0.1	19.70±0.2	16.77±0.1	3.52±0.1	0.35±0.0	0.02±0.0	0.01±0.1	0.01±0.3
Zn	821.50±9.9	84.12±1.5	230.56±0.1	28.49±0.31	20.42±0.7	2.40±0.0	nd	0.01±0.3	nd
Mo	13.04±0.0	11.33±0.1	12.77±0.0	10.14±0.0	0.40±0.3	0.13±0.0	0.01±0.6	0.01±0.4	0.01±0.2
Co	5.76±0.3	11.09±0.0	2.21±0.5	8.07±0.1	0.57±0.0	0.03±0.0	$3.5*10^{-4}$	$3.5*10^{-4}$	$6.8*10^{-4}$
Cr	8.23±0.9	1.91±0.1	nd	12.73±0.7	5.62±0.2	2.06±0.0	nd	nd	nd
Ni	19.90±0.4	12.11±0.5	10.69±0.4	13.01±0.1	4.28±0.1	0.40±0.0	nd	nd	nd
Se	13.48±0.1	24.47±0.1	29.05±0.4	39.03±0.2	nd	1.03±0.0	nd	nd	$4.2*10^{-4}$
P	19497.87±9.9	3585.52±4.3	14878.38±8.1	4483.00±6.7	199.57±0.6	162.58±2.2	0.04±0.8	0.02±0.0	nd
Cd	nd	nd	12.40±0.3	nd	0.17±0.0	0.05±0.0	$1.2*10^{-4}$	$10*10^{-3}$	nd
Li	4.98±0.1	6.86±0.0	5.06±0.1	6.36±0.0	5.94±0.1	1.95±0.0	0.12±0.7	0.11±0.3	0.12±0.5
Be	nd	0.29±0.11	0.55±0.0	1.22±0.0	0.12±0.0	0.02±0.0	nd	nd	nd
Mn	5.74±0.2	7.29±0.6	5.38±0.1	35.13±1.6	50.37±0.0	6.37±0.0	nd	nd	nd

Zr	3.29±0.1	6.14±0.1	3.88±0.0	4.45±0.2	0.42±0.1	0.10±0.0	$1.0*10^{-3}$	$6.2*10^{-4}$	nd
Ti	13.31±0.5	4.90±0.1	7.04±0.3	97.44±0.1	80.94±0.0	26.26±0.1	nd	nd	nd
Sr	700.68±0.7	5146.24±2.4	250.32±0.5	913.91±11	387.67±0.1	695.22±4.5	5.97±0.9	5.67±0.4	5.79±0.3
Fe	615.79±9.5	291.94±7.5	835.05±1.6	2233.66±1.6	9287.87±9.5	511.30±0.8	nd	nd	nd
Ta	nd	nd	6.20±0.0	nd	nd	nd	0.68±0.2	0.14±0.3	0.54±0.0

nd = not detected

6.3.1. Seawater

The result obtained for the seawater samples from three different points in Camps Bay marine environment are presented in Table 6.6. Pb, Cu, Cr, Ni, Fe, Ti, Mn and Be were below detection limit in all of the seawater samples. The concentration of Cd, Zr, Co, Nb, Y and Se were low i.e 10^{-4}. Sr had the highest concentration in all the water samples (5.67 – 5.97 mg/L) while As (0.01 – 0.02 mg/L) and Mo (0.01 mg/L) had the lowest concentration in all the seawater samples. Ce and Zn were detected in only one seawater sample while P was detected in just two water samples. Ta was detected in all the water samples but for biota, in the limpet sample only in this study. Generally the metal concentration detected in all the water samples were relatively low. The result of Co (0.08 mg/L), Cu (0.09 mg/L), Fe (0.15 mg/L), Ni (0.4 mg/L) and Zn (0.13 mg/L) obtained from water sample from Tigris, Turkey were higher compared to the concentration obtained in this study (Karadede-Akin and Ünlü 2007). The concentrations of Cu (0.0024 mg/L), Pb (0.0026 mg/L, Cr (0.0116 mg/L) and Cd ($7.0*10^{-5}$ mg/L) in seawater from Guangdong Province, South China were higher with exception of Zn (0.00085 mg/L) and As (0.0014 mg/L) which were lower to this study (Zhang et al. 2016). The concentration of analysed metal in samples from Pearl River Estuary (Zhang et al. 2013a), Eastern Black Sea, Turkey (Baltas et al. 2017), Belgian coastal zone (Gao et al. 2013) and Málaga Bay, Mediterranean (Alonso Castillo et al. 2013) were also higher compared to this study.

6.3.2. Sediment and beach sand

Th and Se were not detected in sediment sample while Ta was not detected in both the sediment and beach sand. Fe had the highest concentration (9287.87 mg/L) in the sediment sample while Sr had the highest concentration (695.22 mg/L) beach sand sample. The distribution of metal in sediment was Fe > Al > Sr > P > Si > Ti > Mn > Zn > Cu > Pb > Li > Cr > Ni > As > Ce > Rb >

Nb > Y > Co > Zr > Mo > Cd > Be while the distribution of metal in beach sand was was Sr > Fe > Al > P > Si > Ti > Mn > Zn > Ce > Cr > Pb > Li > Cu > Se > Y >Nb > Ni > Th > As > Mo > Zr > Rb > Cd > Co > Be. Comparing the result of this study to others, the concentration Cu, Pb, Cr, Cd and Zn in sediment from Southern Taiwan (Lin et al. 2013) and Shuangtaizi estuary, China (Li et al. 2015) were significantly high compared to this study. In a study conducted on sediment from South China (Zhang et al. 2016), the concentration of Cu (21.3 mg/kg), Pb (41.6 mg/kg), Zn (99.1 mg/kg) Cr (63.2 mg/kg) and As (8.44 mg/kg) were quite higher that our values while the concentration of Cd (0.19 mg/kg) is similar to the concentration obtained from this study. Metal concentration in sediment samples from Montenegrin coast (Joksimović et al. 2018) and Eastern Black Sea (Baltas et al. 2017) and Ujere, (Adebayo 2017) were higher than the concentration found in samples from this study

In sediments, the permissible limits of Ni, Cd, Pb, Cu, Cr and Zn are 35, 0.8, 85, 36, 100 and 140 mg/kg, respectively, as recommended by Dutch Target Limits (Tabinda et al. 2013a, b). In the present study, Ni, Cd, Pb, Cu and Zn concentrations were all below the recommended limit

6.3.3. Marine biota

The mean metal concentration in different biota are presented in Table 6.6. In mussels, P had the highest concentration of 19497.87 mg/kg and Zr with the lowest concentration of 3.29 mg/kg. Th, Rb, Cd, Be and Ta were not detected in the mussel sample. The distribution of metal in mussels follows P > Zn > Sr > Fe > Al > Nb > Si > Pb > Ce > Cu > Ni > Se > Ti > Mo > Cr > Co > Mn > Li > As > Zr > Y. In sea urchin, Cd and Ta were below detection limit. Sr had the highest value of 5146.24 mg/kg while Be had the lowest concentration (0.29 mg/kg). The distribution of metal in seaurchin Sr > P > Al > Nb > Fe > Pb > Zn > Th > Ce > Se > Cu > Ni > Co > Mo > Mn > Li > Zr > Ti > As > Si > Rb > Cr > Y > Be. In limpets, P had the highest concentration of 14878.38 mg/kg

and Be the lowest concentration of 0.55 mg/kg. Cr was not detected in the limpet sample. The distribution of metal in limpets follows P > Fe > Nb > Al > Sr > Zn > Pb > Si > Cu > Ce > Se > As > Th > Mo > Cd > Ni > Ti > Ta > Mn > Li > Zr > Co > Y > Rb > Be. In seaweed, P had the highest concentration of 4483.00 mg/kg and Be with the lowest concentration of 1.22 mg/kg. Th, Cd and Ta were not detected in the seaweed sample. The distribution of metal in seaweed follows P > Fe > Al > Sr > Nb > Pb > Ti > Si > Ce > Se > Mn > Zn > Rb > As > Cu > Ni > Cr > Mo > Co > Li > Zr > Y > Be.

The concentration of Co (0.002 mg/kg), Cr (0.027 mg/kg), Cu (0.098 mg/kg), Fe (6.799 mg/kg), Ni (0.016 mg/kg), Pb (0.010 mg/kg) and Zn (0.911 mg/kg) in mussel from Gőlbaşi, Turkey were lower compared to this study while Cd (0.006 mg/kg), Mn (10.67 mg/kg), were higher (Türkmen and Ciminli 2007). The concentration of Cu (5.61 mg/kg), Ni (0.83 mg/kg), Zn (10.29 mg/kg) and Fe (204.86 mg/kg) in mussels from a study by (Karadede-Akin and Ünlü 2007) were lower while Mn (224.36 mg/kg) was higher compared to this study. The mean metal concentrations in molluscs (Zhang et al. 2016), were 44.1, 1.71, 111.1, 0.55, 4.18, and 9.93 mg/kg for Cu, Pb, Zn, Cr, Cd, and As, respectively were lower compared to this study with exception to As and Cd which were higher. The levels of metals in *Mytilus galloprovincialis* from Adriatic coastal area (Jovicá et al. 2014), Algerian West Coast (Rouane-Hacene et al. 2015), Montenegrin coast (Joksimović et al. 2018), Montenegrin coast (Azizi et al. 2018), Eastern Aegean coast (Kucuksezgin et al. 2013), Coastal areas of Casablanca (Mejdoub et al. 2018), Boka Kotorska Bay, Montenegro (Perošević et al. 2018) were lower compared to this study. However, the levels of metals in *Rapana venosa* from Eastern Black Sea, Turkey (Baltas et al. 2017) were higher compared to the levels found in this study. This comparison shows that if the pollution of this marine environment is not abated, the consequences of the continuous pollution will be huge to the inhabitant of Camps Bay.

6.4. Risk assessment of study

6.4.1. Ecological risk assessment

The impact of emerging contaminants in Camps Bay marine environment was assessed using the RQ method. The concentrations of compounds detected in the seawater samples were divided by an effect level reported in the literature (Tables 3.3 and 3.4, Chapter 3). Figures 6.3- 6.5 shows results obtained for contaminants exhibiting low to high risk at either average or extreme conditions, as calculated from the corresponding RQs. The level of concern for both acute and chronic risk are 0.5 and 1.0 respectively (US EPA 2016a). For chronic risk, RQ < 1.0 represents the limit for no chronic risk concern, and for acute risk, RQ < 0.5 is the limit for no high acute risk concern.

6.4.1.1.Perfluorinated and pharmaceutical compounds

Figure 6.3 showed the RQ values obtained for acute and chronic risk assessment. This evaluation was done based on the availability of the toxicity endpoint values obtained from literature.

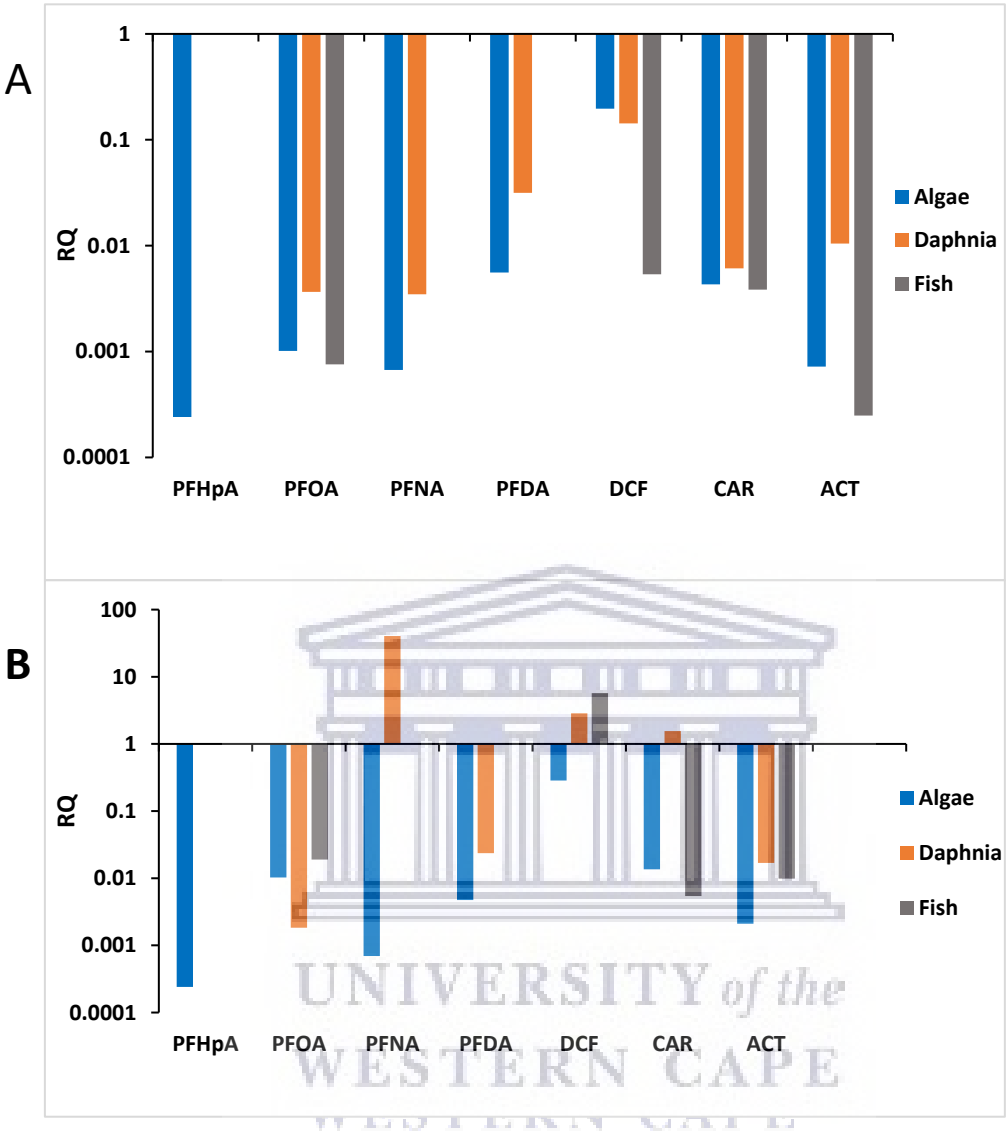


Figure 6. 3: Risk quotients for PFCs and pharmaceuticals estimated for algae, invertebrate and fish (A) acute risk (B) chronic risk.

For acute risk, algae, invertebrate and fish from this site are not likely to be at risk because their RQ values are significantly less than 0.5 (i.e RQ < 0.5). Worthy of note, there is no variation in the risk level posed by these contaminants, as all contaminants pose similar risk level in this site. For chronic risk, in algae all compounds pose low risk (RQ < 1) while in invertebrate, PFNA, DCF and CAR poses high risk (RQ > 1) which indicates that these compounds might present a significant environmental risk to the invetebrate in the seawater in Camps Bay. Similarly in fish,

DCF pose a high risk while other compounds pose low risk. Chronic toxicity evaluation indicates that contaminants from two trophic levels (invertebrate and fish) showed the high risk could cause changes in fish and invertebrate communities and enhancement of the more resistant ones or the decrease of the most sensitive species, with a consequent loss of biodiversity.

6.4.1.2. Herbicides

Figure 6.4 and 6.5 show results obtained for herbicides exhibiting low to high risk at either average or extreme conditions, as calculated from the corresponding RQs for algae, *Daphnia magna* and fish. The result of acute toxicity obtained for the three levels of aquatic life (i.e algae, daphnia and fish) is presented in Figure 6.4. For algae, all compounds pose high risk (RQ > 0.5) except for metolachlor that poses low risk (RQ < 0.5). Regarding daphnia, all compounds pose low risk (RQ < 0.5) except for simazine that poses high risk (RQ > 0.5). For fish, butachlor and alachlor poses high risk while metolachlor, simazine and atrazine poses low risk.

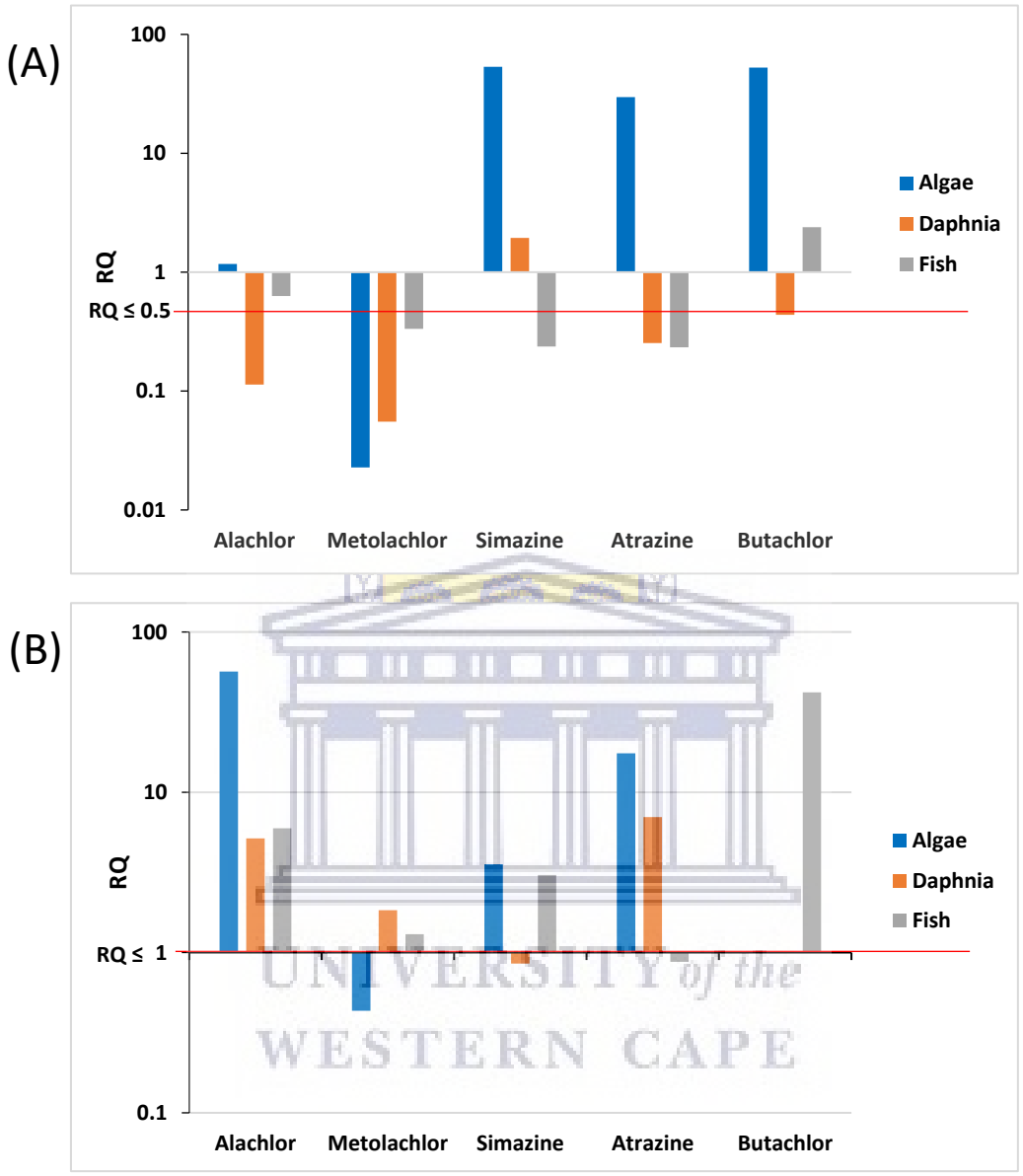


Figure 6. 4: Risk quotients for herbicides estimated for algae, daphnia and fish (A) acute risk (B) chronic risk

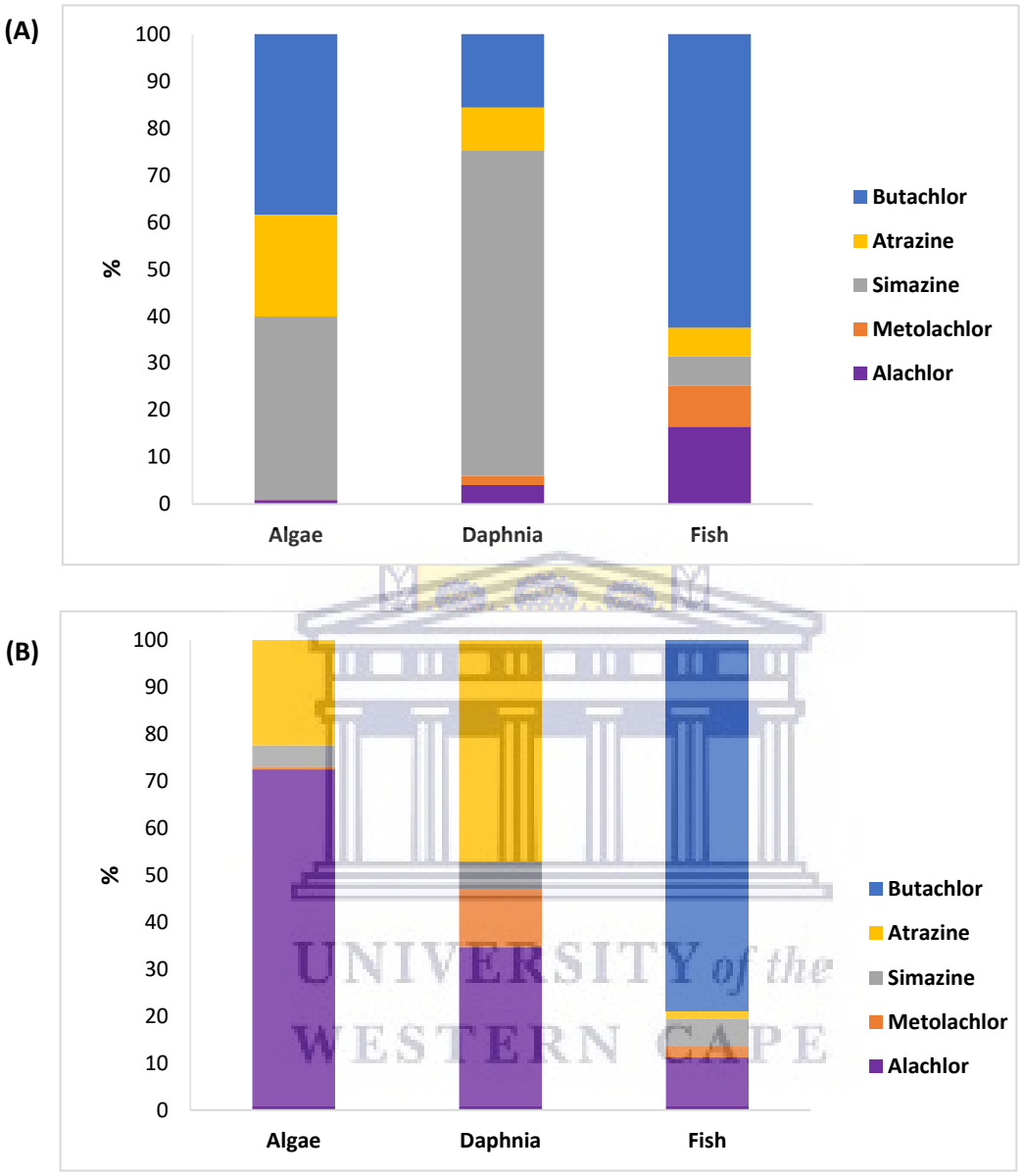


Figure 6. 5: The contribution of detected compounds in total (A) acute and (B) chronic toxicity estimated for algae, daphnia, and fish

Figure 6.5 illustrates the % contribution of all compounds regarding the three selected species at three environmental levels. The percentage contribution of each compound to the total toxicity is thus: for algae it is apparent that simazine contributes 39%, butachlor 38% and atrazine 23%. In daphnia, the relative contribution of the herbicides detected shows that simazine and butachlor contributed 69% and 15% respectively to the total toxicity.

Finally, in fish, butachlor contributed 62% to the total toxicity. Similarly, for chronic risk, for algae all compounds posed high risk (RQ > 1) except for metolachlor that posed low risk (RQ < 1). For daphnia, all compounds posed high risk except for simazine that posed low risk while for fish all compounds posed high risk except for atrazine which poses low risk. The percentage contribution of each herbicide to the total toxicity follows: for algae, alachlor and atrazine contributed 72% and 22% respectively to the total toxicity, for daphnia, alachlor and atrazine also contributed 34% and 47%, respectively, and for fish, butachlor contributed 78% to the total toxicity. Note NOEC values for algae and daphnia were not available, so this was not estimated.

6.4.2. Human health risk assessment

Individual ADD and HQs linked to the consumption of the sampled marine biota and seaweed contaminated with herbicides are outlined in Table 6.7. If HQ is > 1, it indicates that the compounds pose a potential threat to the ecosystem and/or harmful ecological effect may arise; if HQ is < 1, the non-carcinogenic risk is relatively low while the cancer risk value is considered very low when it is $\leq 10^{-6}$ and significant if it is $\geq 10^{-4}$. The cancer risk is high when it is $\geq 10^{-3}$ and very high when it is $\geq 10^{-1}$.

In this study, carcinogenic and non-carcinogenic risks were determined for compounds whose Rfd and CSF values were available. Only HQ values for simazine in all the species were greater than 1.0, while HQ values for the other compounds were less than 1.0, also the HI which is the sum of all the HQ values of each compound in the different species were also greater than 1. For the carcinogenic risk, the risk values for simazine are as follows: it was high in mussels, sea urchin, and *Ulva* sp seaweed while it was very high in limpets and *Codium fragile* seaweed.

Table 6. 7: Hazard Quotient (HQ), cancer risk and average and lifetime daily dose (ADD & LADD) values of herbicides in marine organisms from Camps Bay.

	Mussels				Limpet				Sea urchin				*Ulva sp*				*Codium fragile*			
	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ	ADD	LADD	Cancer risk	HQ
Simazine	0.044	0.019	**0.002**	**8.9**	0.033	0.014	**0.156**	**6.7**	0.011	0.005	**0.051**	**2.2**	0.024	0.010	**0.110**	**4.7**	0.025	0.011	**0.114**	**4.9**
Atrazine	0.010	0.004	**0.019**	0.3	0.017	0.007	**0.031**	0.5	0.004	0.002	**0.007**	0.1	0.006	0.003	**0.011**	0.2	0.008	0.003	**0.015**	0.2
Alachlor	0.005	0.002	**0.036**	0.5	0.003	0.001	**0.023**	0.3	0.0005	0.0002	**0.004**	0.1	0.007	0.003	**0.055**	0.7	0.006	0.003	**0.045**	0.6
Metolachlor	0.011	0.005	**0.556**	0.1	-	-	-	-	0.001	0.001	**0.069**	0.0	0.015	0.006	**0.694**	0.1	0.006	0.003	**0.276**	0.0
HI Values				12.8				7.5				2.4				5.7				5.7

Numbers in bold are above limit for non-carcinogenic and carcinogen risk

For atrazine and alachlor, the risk values were high in all the different species, while metolachlor risk values was very high in mussels, *Ulva* sp, and *Codium fragile* seaweed and high in sea urchin.

6.4.3. Ecological and human health implication

Results from ecological and human health risk assessments are important in other to understand the risk that contaminants pose to the marine environment. The estimation of RQs in this study have taken into account calculations based on each one of the contaminants separately. Since in the marine environment, herbicides and other contaminants are present in a large number of classes, toxicity risks may not be visible in single compound evaluations. RQ values showed that these compounds pose a low to high ecotoxicological risk for marine organisms.

Since the values of HQ (Table 6.7) for three herbicides were below 1 (atrazine, alachlor, and metolachlor), there is no health issue arising from non-carcinogenic diseases associated with the consumption of the seafood except for simazine with HQ value greater than 1, which shows that an harmful ecological effect may arise. However, the carcinogenic risk assessment of the analysed herbicides was very much higher than the recommended levels (Man et al. 2013). Indeed, these results indicated that an average sized human (70 kg) might suffer significant health risks should any of the seafood analysed herein be consumed on a daily basis (54 g) over a lifetime period (life expectancy of 70 years). Even though all compounds were found in at least one of the marine biota in the present study, the assessment and the evaluation of joint risks of the herbicide mixture were considered as the HI values of the herbicide mixtures in each species was found to be greater than 1 (Table 6.7). This suggests that non-carcinogenic health implication may arise as a result of exposure to a mixture of these contaminants. It should be noted that these calculated values pertain to humans with greater risks and health implications may be experienced by diverse organisms that live in the same marine environment or feed on these biota. Furthermore, herbicides undergo

degradation processes such as physical, chemical and biological processes that give rise to one or more complex transformation product (metabolites) that could be persistent or be more toxic than the parent compound (de Castro-Català et al. 2016; Ccanccapa et al. 2016b), so then the sources, pathways, and routes of chemical exposure as well as the metabolites of these chemicals need to be evaluated further. Herbicides entering the environment of Camps Bay via the sewage marine outfall represent an ecological threat to this environment. The marine outfall is a potential source for these contaminants, as very little storm water was discharged during the study period in 2017 due to the extended drought that prevailed in Cape Town that period (Williams 2019). It may be that the local aquifer is contaminated by ground leachates discharged into the marine environment, and this aspect therefore requires further investigation.

6.5. Conclusion

This study has demonstrated that Camps Bay marine environment habours a variety of chemicals of emerging concern and the method employed herein satisfies the detection of these compounds in part per billion. However, pharmaceuticals are fashioned to respond at low physiological doses, can perform best at ng/kg concentrations and can interact even at low doses with multiple non-therapeutic receptors. Synergistic effects of multiple components cannot be ruled out and it is difficult to know exposure rate vs. actual dose. The acute limits in typical guidelines given for human consumption of contaminated marine foods such as mussels give no guidance in terms of the impacts of chronic exposure to low nanogram quantities of a plethora of persistent organic chemicals. Also, the acute exposure limits for humans that are set in guidelines for safety and risk, clearly do not apply to other species such as the marine organisms in question. The exposure to these compounds via seafood ingestion as well as via contact or accidental ingestion of seawater is probable, and the difference between acute toxicity and chronic toxicity is not known for humans

or for marine organisms. The risk, which depends on the hazard of the chemical, its concentration, the exposure over time, the volume or quantity ingested, and metabolism or elimination rate etc. is hard to determine.

Generally, total concentrations of the chemicals of emerging concern in marine biota inhabiting the Camps Bay marine ecosystem were significantly higher than the concentration of these compounds in the seawater showing that these compounds are bioaccumulated by benthic organisms and pose a potential risk to human health through food consumption (e.g. biomagnification). The high concentration of atrazine (59 ng/g) and simazine (157.8 ng/g) showed high use of this chemicals in this area such as application to curb unwanted growth in garden, application of herbicides to golf course, pavement and parks e.t.c.

The RQ assessment evaluation revealed that these compounds pose low and high (acute and chronic) risk to the marine organisms. The carcinogenic risk of Camps Bay edible species were above acceptable levels, while only simazine levels showed a non-carcinogenic risk. Even though the selected contaminants levels in seawater were relatively low, the chemical compounds are not sufficiently diluted by the ocean and are shown to be bio-accumulating in marine biota, thus building up to levels that will have significant impacts on the near shore marine environment and the Marine Protected Area adjacent to the suburb of Camps Bay. Moreover, the detected contaminants well levels in beach sand, sediments, and marine biota show that the sewage plume makes frequent landfall, which indicates that dilution of the raw sewage by the ocean is inadequate and that the marine sewage outfall is located too close to the shore. Based on these results, stricter legislation and regulatory controls on maximum permitted levels of herbicides are crucial. Treatment of the sewage before its release into the marine environment should be mandatory to protect and maintain marine biodiversity and human health. Legislative controls contained in

existing instruments such as the National Environmental Act and the Marine Living Resources Act should be implemented, enforced and monitored by the South African Department of Environment, Forestry and Fisheries to reduce the negative impact on the ecosystem and upon humans. Lastly, this study clearly showed that most chemicals of emerging concerns examine in this chapter specifically herbicides, banned in other countries, but still in use in suburban environments in South Africa, require urgent action to educate the public about the associated environmental and human risks of their choices.

Chapter 7

Occurrence of chemicals of emerging concern (pharmaceuticals, perfluorinated, endocrine disrupting compounds and metals) in the marine environment around False Bay, Cape Town, South Africa

7.0. Introduction

False Bay is a water body in the Atlantic Ocean which lies between Hottentots Holland Mountains and the Cape Peninsula. Recreational fishing is the largest and most economically important activity in the bay. It also contains small fishing harbours at Kalk and Gordon's Bays. Other invertebrates that are harvested in the bay under the permit system include mussels, octopus, clams, whelks, giant turban shells, crabs and various limpets. Sailing, swimming, scuba diving, surfing and free diving are all popular recreational activities in the Bay (Pfaff et al. 2019). The major increase of the human population from about 1.6 million inhabitants in 1980 to almost 4 million in 2018 (Statistics South Africa 2007), along with the inadequate development of infrastructure, review the backlog in service provision by City of Cape Town have increased anthropogenic pressures such as human interference (bait collecting, off-road vehicles, trampling, ecotourism mining and beach cleaning) on False Bay including pollution, eutrophication, introductions of invasive alien species, modification of habitat and over-utilization of marine living resources (Theron et al. 1992; Compton 2004) also the fact that a minmum of four different wastewater treatment plants (Mitchell's Plain, Macassar, Zandvliet and Cape Flats) are suitated around this bay with great concern for the discharge of improperly treated or untreated effluents into the marine water of this bay requires urgent assessment of the marine environment.

For years, chemicals of emerging concern (CECs) such as pharmaceuticals and personal care products, various endocrine disrupting chemicals, perfluorinated compounds, and flame retardants e.t.c. have been a major issue all over the world due to their huge consumption (extensive and long

term use). As a result, most of these compounds have become pseudo-persistent in the ecosystem (Hernando et al. 2006; Daughton 2016; Comber et al. 2017; Ojemaye and Petrik 2019b) and potentially harmful concentrations may build up in the coastal and marine environment. The discharge of these emerging pollutants into the environment is mostly associated with household, municipal and industrial wastewater (Phillips et al. 2010; Michael et al. 2013; Melvin and Leusch 2016). Other sources include human excretion into sewage systems, improper disposal of chemicals, and agricultural runoff associated with therapeutic treatment of livestock (Gaw et al. 2014; Klatte et al. 2017; Yang et al. 2017). Even though almost every chemical compound that is used daily by humans have been detected in different water bodies (Vidal-Dorsch et al. 2012; Tran et al. 2013; Hughes et al. 2013; Luo et al. 2014; Yi et al. 2015; Montesdeoca-Esponda et al. 2018; Álvarez-Ruiz and Picó 2019), the levels and occurrence of such emerging contaminants in seaweeds or aquatic plants, benthic organisms bivalve other than mussels (Mezzelani et al. 2018), snails, amphipod, crustaceans are rarely determined (Du et al. 2015; Huerta et al. 2016; Xie et al. 2017) and such contaminated organisms may be a potential source of contamination to higher organisms and humans (Lagesson et al. 2016).

Given that a generous fraction of the total population lives in coastal cities (Gaw et al. 2014), there is a need to better understand the exposure risks and fate of these contaminants (PPCP, PFC and EDC) in coastal marine ecosystems. Organisms in receiving waters experience more direct exposure to contaminants through wastewater discharge. PPCPs, PFCs and EDCs residues in the environment may pose a greater risks to wildlife and ecological health, compared to human health (Morley 2009).

Despite the fact that CECs are usually found at low environmental concentrations, many are of toxicological concern, particularly when they occur with the combined effects of

multiple contaminants (Schwarzenbach et al. 2006; Hoerger et al. 2014); hence, the potential environmental risk caused by these CECs should not be underestimated. There is a paucity of information about the occurrence of these classes of emerging contaminants in the False Bay region (Pfaff et al. 2019).

Similarly, in many regions, the increase in agricultural activities and industrialization has contributed to the increase in the discharge of chemicals into the ecosystem, which has led to a significant rise in the level of metals in the aquatic environment thereby damaging the freshwater and marine habitats (Bai et al. 2011; Aly Salem et al. 2013; Hu et al. 2013).

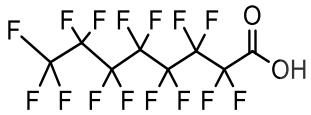
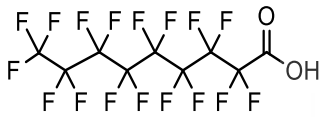
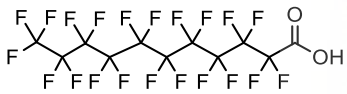
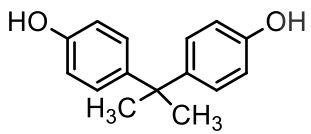
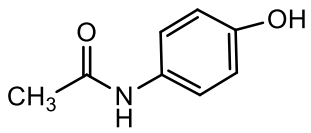
The objectives of the present chapter is to conduct a field study to generate a comprehensive dataset for those substances in the False Bay marine environment. Chemicals such as perfluorinated compounds, bisphenol A, 2-nitrophenol and nonylphenol, were included in the study due to their endocrine disruption potentials. Also, the study was designed to investigate for the first time these classes of contaminants (perflourinated compounds, pharmaceuticals and personal care products and industrial chemiclas) in the seawater, sediment and biota from the marine environment of False Bay, by determining and quantifying the presence of these contaminants in the selected matrices. This study will help to evaluate the efficiency and impact of the different WWTPs to the marine environment and its surroundings by assessing the level of accumulation of these contaminants to assist in acquiring information about their risk level in order to ascertain the safety of biota in this area for consumption.

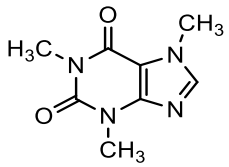
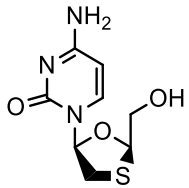
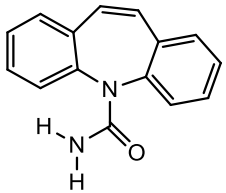
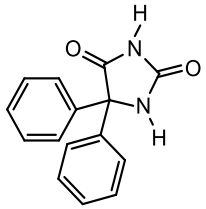
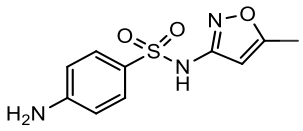
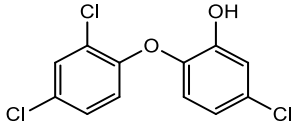
7.1. Results and discussion

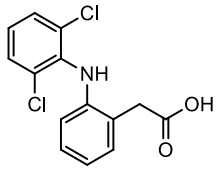
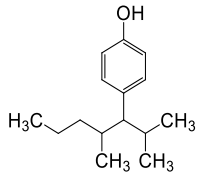
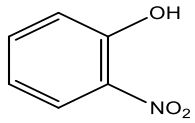
The assessment of the levels of perfluorinated compounds, pharmaceuticals and personal care product and industrial chemicals in False Bay were carried out as described in Chapter 3 of this thesis. Samples were obtained in May 2018 from eight different sites around the Bay and these

different sites are denoted in this chapter as follows: site 1 – Miller's Point; site 2 – Simon's Town; site 3 – Muizeigburg; site 4 – Monwabisi; site 5 – Strand; site 6 – Gordon's Bay; site 7 – Klippies Baai camp site; site 8 – Rooi-Els, the sites were shown in Chapter 3 Figure 3.4. Table 7.1 provides the LC–MS retention time, percentage recoveries, transition and collision energy, limit of detection (LOD) and limit of quantification (LOQ) in this study for the analysis of each contaminant. The calibration curves and chromatograms of the analysed compounds are shown in Appendix IV, Figure IV.1. The results of analysis and discussion are presented in each section of this chapter in relation to the contaminants against each environmental matrices.

Table 7. 1: LC–MS retention time, transition and collision energy, limit of detection (LOD), and limit of quantification (LOQ)

Compound Name	Molecular weight (g/mol)	Molecular structure	Retention Time (min)	Ion transition (m/z)	Collision energy (eV)	LOD			LOQ			Recovery (%)		
						Seawater (ng/L)	Sediment (ng/g)	Biota (ng/g)	Seawater (ng/L)	Sediment (ng/g)	Biota (ng/g)	Seawater	Sediment	Biota
PFHpA	364.06		7.00	363 to 319	15	0.01	0.38	0.38	0.03	1.15	1.15	100.9	96.7	98.3
PFOA	414.07		7.56	413 to 369	15	0.02	0.45	0.45	0.07	1.37	1.37	99.9	99.7	98.9
PFNA	464.08		8.03	463 to 419	15	0.01	0.81	0.81	0.02	2.46	2.46	101.2	100.8	99.0
PFDA	514.09		8.41	513 to 469	15	0.002	0.45	0.45	0.01	1.37	1.37	100.7	99.4	98.2
PFUnDA	564.09		8.74	563 to 523	15	0.002	0.47	0.47	0.01	1.42	1.42	99.6	99.8	98.9
Bisphenol A	228.29		6.71	227 to 212	28	1.25	3.92	3.92	3.80	11.9	11.9	101.2	102.3	99.2
Acetaminophen	151.16		1.78	152 to 112.2	15	0.002	0.99	0.99	0.005	3.00	3.00	98.1	96.5	97.9

Caffeine	194.19		3.25	195 to 138	20	0.001	1.05	1.05	0.002	3.19	3.19	95.5	96.1	95.0
Lamivudine	229.26		1.32	230 to 112	15	0.001	0.82	0.82	0.003	2.50	2.50	99.0	99.8	98.3
Carbamazepine	236.27		6.24	237 to 194	20	0.20	0.79	0.79	0.60	2.40	2.40	99.6	98.9	97.8
Phenytoin	252.27		5.96	253 to 182	15	0.003	0.62	0.62	0.01	1.89	1.89	98.5	98.2	98.4
Sulfamethoxazole	253.28		2.71	254 to 188	25	0.57	0.81	0.81	1.72	2.45	2.45	98.2	99.4	97.9
Triclosan	289.54		9.09	288 to 36.80	10	0.90	0.90	0.90	2.72	2.72	2.72	97.3	97.9	96.8

Diclofenac	296.15		6.80	296 to 250	15	0.001	0.87	0.87	0.01	2.64	2.64	102.9	100.5	99.1
Nonylphenol	220.35		8.03	219 to 133.2	25	1.40	1.40	1.40	4.24	4.24	4.24	98.9	99.2	98.5
2 nitrophenol	139.11		-	139 to 121	15	-	-	-	-	-	-	-	-	-

7.1.1. Occurrence in Seawater

This section gives an account of the levels of the different contaminants in seawater samples collected from sites 1 to 8 in May 2018 in the marine environment of False Bay. The sampling protocols and experimental methods described in Chapter 3 were employed for the quantification of these contaminants in the different samples.

7.1.1.1. Perfluorinated compounds

The target compounds' concentrations in seawater samples from sites 1 to 8 of False Bay are shown in Figure 7.1. The average concentrations and the standard deviation of the different contaminants across the various sites are presented in Appendix IV, Table IV.1. All five perfluorinated compounds were detected in all the seawater samples from all the eight sites.

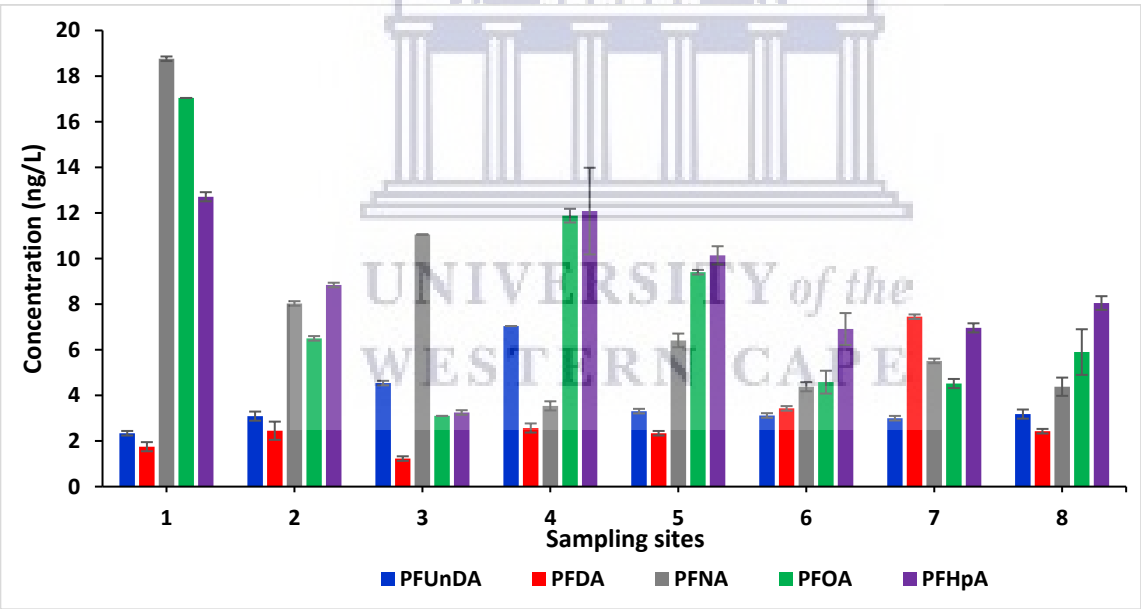


Figure 7. 1: Concentration of perfluorinated compounds in seawater samples from all the eight sites in False Bay

The concentration of PFCs in seawater samples varied among areas and locations. From the result observed in seawater samples from site 1, PFNA had the highest concentration (18.76 ng/L) while PFDA had the lowest concentration (1.75 ng/L). From site 2, PFHpA had the highest concentration

(8.84 ng/L) while PFDA had the lowest concentration (2.45 ng/L); site 3, PFNA also had the highest concentration (11.05 ng/L) while PFDA had the lowest concentration (1.23 ng/L), from site 4 PFHpA had the highest concentration (12.08 ng/L) while PFDA had the lowest concentration (2.57 ng/L); for site 5, PFHpA had the highest concentration of 10.14 ng/L while the PFAs with the lowest concentration is PFDA (2.34 ng/L). The observation in site 6 showed that PFHpA had the highest concentration (6.91 ng/L) and PFDA had the lowest concentration (3.43 ng/L) while site 7 showed a contrasting observation with PFDA having the highest concentration (7.45 ng/L) compared to other sites in which it was the lowest and PFUnDA had the lowest concentration (3.00 ng/L). In site 8, PFHpA had the highest concentration (8.05 ng/L) while PFDA had the lowest concentration (2.43 ng/L). Generally, comparing the concentration of PFCs in this study across the different sites, it was observed that the concentration of these compounds decreases from site 1 to site 8 even though all the sites were found to have a considerable amount of all these contaminants. Worthy of note, the concentration of PFUnDA increases from sites 1 to 4 and remained steady from sites 5 to 8 with little or no increase. This could be as a result of high volume of anthropogenic acvities around the location of the former than in the latter. Also the levels of PFCs in this location were higher compared to the levels in samples from Green Point and Camps Bay, this could also be linked to the volumes of sewage discharge into this Bay which is quite higher (about 100 ML per day from four different plants) than the level discharged into the other Bays (5 ML and 2 ML per day) respectively. The detection of PFCs in this region has been reported in wastewater effluents (Swartz, C.D., Genthe, B., Chamier, J., Petrik, L.F., Tijani, J.O., Adeleye, A., Coomans, C.J., Ohlin, A., Falk, D., and Menge 2018), drinking and raw water in addition to their presence in so many products used by humans in this environment and since these PFCs are not degradable in the environment, there is likelihood for their occurrence in the marine water in this region and consequently their bioaccumulation in the marine biota.

According to DEAT (2005), Cape Town coastline is threatened by multiple drivers and pressures, from coastal development and mining, to storm water runoff and effluent discharges. Interesetingly, the levels of the detected contaminants in this study corresponds to the observation of Department of Environmental Affairs and Tourism (DEAT) on marine waters Cape Town.

Comparing the concentration of PFCs in this study to other reports, similar results were observed in water samples from South Korea (PFHpA: 0.10-10 ng/L, PFOA: 0.43-29, PFDA:0.10-8.3 ng/L, PFNA: 0.17 -4.8 ng/L and PFUnDA: 0.10- 3.6 ng/L) (Hong et al. 2015). The concentration of PFCs in water samples collected from the west coast of Korea PFHpA: <1.0-110 ng/L, PFOA: 0.54-31, PFDA:<0.20-9.3 ng/L, PFNA: <0.20-5.9 ng/L were higher and PFUnDA: 0.22- 1.3 ng/L) were lower than the concentration observed in this study (Naile et al. 2013b). The highest levels of PFC found in seawater from Osaka Bay and coastal waters of Western Japan was 7.0 ng/L which is lower to the levels found in this study (Beškoski et al. 2017). Highest level of PFOA observed in the Bohai Sea was 106 ng/L and Yellow Sea (14 ng/L) (Zhao et al. 2017) which were quite higher while samples also from Bohai sea (9.9 ng/L) were lower compared to the present study (Chen et al. 2016).

7.1.1.2. Pharmaceuticals and personal care product (PPCPs)

The observed concentrations of PPCP compounds in seawater samples are shown in Figure 7.2, while a comprehensive data including the standard deviation of the different contaminants across the various sites are summarized in Appendix IV, Table A-IV.1.

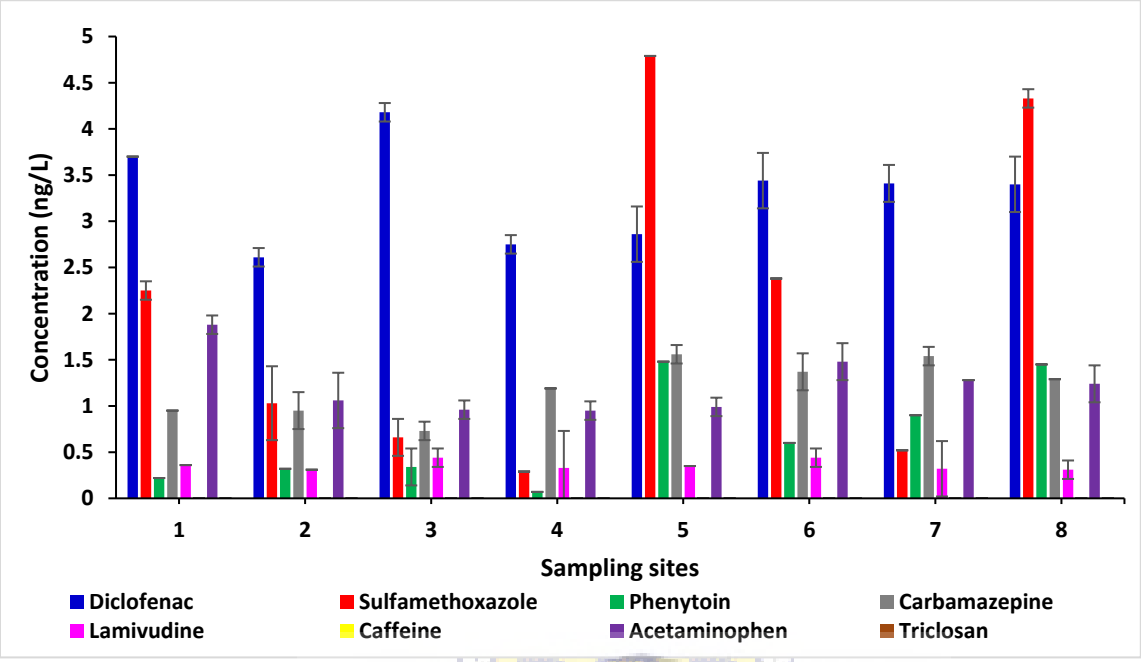


Figure 7. 2: Concentration of target analytes in seawater samples from sites 1 to 8 of False Bay

Six out of seven pharmaceuticals were detected in all the seawater samples collected from all the sites. Diclofenac had the highest concentration (3.70 ng/L) followed by sulfamethoxazole (2.25 ng/L) while phenytoin had the lowest concentration (0.22 ng/L) in seawater samples from site 1. In seawater samples from sites 2 and 6, diclofenac had the highest concentration (2.61 and 3.44 ng/L) followed by sulfamethoxazole (1.03 and 2.38 ng/L) and lamivudine had the lowest concentration (0.31 and 0.44 ng/L) respectively. The highest concentration observed in site 3 was found to be diclofenac (4.18 ng/L) also and the lowest was phenytoin (0.34 ng/L). The compound with the highest concentration in seawater from sites 4 and 7 is diclofenac (2.75 and 3.41 ng/L respectively), followed by carbamazepine (1.19 and 1.54 ng/L) and the lowest in site 4 phenytoin (0.07 ng/L) and site 7 was lamivudine (0.32 ng/L) while the highest levels from sites 5 and 8 were also sulfamethoxazole (4.79 and 4.33 ng/L respectively) and the lowest was lamivudine (0.35 and 0.31 ng/L respectively).

Generally the highest concentration of diclofenac was found in samples from site 3 while high sulfamethoxazole, carbamazepine and phenytoin were found in samples from site 5. The concentration of acetaminophen was found to be highest in samples from site 1 and lamivudine in sites 3 and 6. Out of the detected compounds, diclofenac was the dominant pharmaceutical in all the sites. The concentration of lamivudine was lower compared to other compounds in all the samples from the different sites. This observation could not come as a surprise because of the high prescription of diclofenac as an inflammatory drug around this region (Osunmakinde et al. 2013). Triclosan, which was the only personal care product tested and caffeine (a stimulant) were below the detection limit in all of the seawater samples from the different sites investigated in this study. The presence of these compounds in this matrix could be as a result of the frequent use of these compounds by humans in this Province as well as their unchanged metabolism even after excretion from the body. Furthermore, the occurrence of these compounds in this matrix could be linked to the discharge of partially untreated effluent from the WWTPs around these sites. In 2017, CSIR reported the detection and levels of these compounds in the final effluent from the WWTPs in Cape Town (CSIR 2017), this is an indication of a possible pollution of this marine environment with these compounds.

The concentration of carbamazepine and caffeine (0.06-4.63 and 5-1389 ng/L respectively), in water from Singapore were higher while diclofenac, sulfamethoxazole were <0.04-1.7, <0.06-6.26 ng/L respectively and were lower compared to the levels found in this study (Bayen et al. 2016). The concentration of acetaminophen, diclofenac, caffeine, carbamazepine and sulfamethoxazole in ocean water from the Gulf of Cadiz (that ranged from nd – 2.8, nd – 2.5, 4.3 – 96.6, nd – 0.1 ng/L and nd) were lower except for caffeine which was higher compared to this study (Biel-Maeso et al. 2018). The level of acetaminophen and caffeine in coastal water of the Red sea ranged from < LOQ-2379 ng/L and 62 - >3000 ng/L respectively (Ali et al. 2017) and the concentration of

acetaminophen 16.7, carbamazepine 3.83, and caffeine 16.92 ng/L in seawater (Jiang et al. 2014) were higher than the concentration found in this study. The concentration of caffeine, carbamazepine, diclofenac and triclosan in eight locations in Singapore ranged from <59-655, <0.3-10.9, <1.5-11.6 and <0.55-10.5 ng/L respectively (Bayen et al. 2013b) and the concentration of caffeine (8.4-3068 ng/L), carbamazepine (8.8- 157 ng/L), diclofenac (6.1- 9.7 ng/L), acetaminophen (12 – 2983 ng/L) and sulfamethoxazole (4.1 -61 ng/L) from Baltic sea, Aegean sea, Adriatic sea and pacific ocean (Nödler et al. 2014) were higher compared to the result obtained in this study. The concentrations of carbamazepine 0.57–3.2 ng/L in seawater from Baltic Sea (Björlenius et al. 2018) and the levels of caffeine (0.32 – 0.89 ng/gL), carbamazepine (0.0038-0.0133 ng/L), acetaminophen (0.03 – 0.111 ng/L), triclosan (0.02 – 00305 ng/L) (Brumovský et al. 2017) were comparable to this study while sulfamethoxazole and diclofenac found in Baltic Sea water samples (5.4 – 70.1 ng/L and nd – 92.6 ng/L) were higher (Borecka et al. 2015).

The concentrations of sulfamethoxazole detected in Yellow Sea (Du et al. 2017) and Bohai Bay (Zou et al. 2011) water samples, (7.7 ng/L) and (2.3 – 140 ng/L) respectively were higher compared to this study. In Brazilian coastal zone, the level of diclofenac (19.4 ng/L), caffeine (89 - 648.9 ng/L) and acetaminophen (17.4 – 34.6 ng/L) (Pereira et al. 2016) as well as samples from Antarctica which had concentrations of acetaminophen (48.74 µg/L), diclofenac (15.09 µg/L) and caffeine (71.33 µg/L (González-Alonso et al. 2017) were also higher than the levels found in this study.

These results and comparisons shows that there are many regions globally that are impacted by the listed pollutants. False Bay is very remote from the listed locations yet is showing measurable traces of many of these synthetic compounds which are indicative of the presence of many other persistent compounds and of the impact of the sewage effluents released into False Bay. This shows that the level of pollution in this marine environment is comparably higher to most other

marine environments from more different advanced countries of the world. Therefore, precautions must be taken by habitat of this marine environment, government agencies and industry players to prevent the release of harzardous compounds (including the ones reported in this study) into the marine ecosystem of Cape Town.

7.1.1.3. Industrial chemicals

Figure 7.3 presents the observed concentrations of industrial chemical compounds analysed in seawater samples and Appendix IV, Table IV.1, summarises the concentrations and the standard deviation of the these contaminants across the different sites.

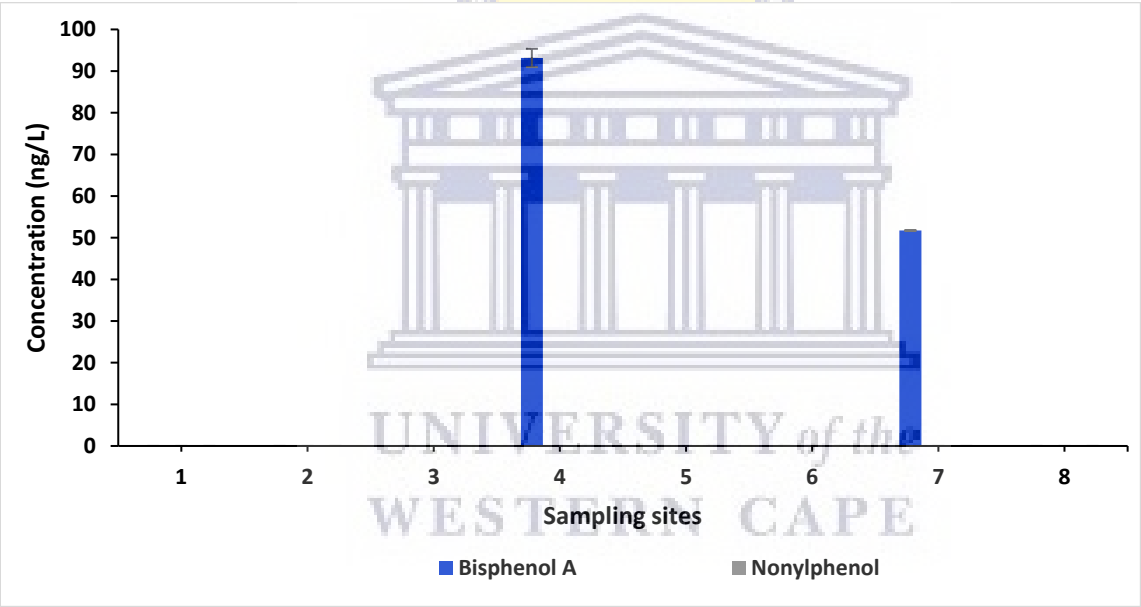


Figure 7. 3: Concentration of industrial chemicals in seawater samples from sites 1 to 8 from False Bay

Bisphenol A was only detected in seawater samples from sites 4 and 7 with concentration of 93.16 ng/L and 51.73 ng/L respectively. Nonylphenol was below the limit of detection contrary to the levels detected in marine organisms and seaweeds while 2-nitrophenol was not detected in any of the seawater samples from all the sites. The high level of bisphenol A is expected since Cape Town is one of the industrial cities in South Africa with huge number of canned food and plastic

manufacturing companies, (as epoxyresin to protect the inside of the cans and as plasticizers respectively) knowing fully well that bisphenol A is a major chemical in the production line of these companies. Worty of note is that 2-nitrophenol was not detected in any of the environmental matrices at this location and in samples from the preceeding Chapters (Chapters 4, 5 and 6) this could be that the method employed in this study is not appropriate for its detection or the instrument used is not sensitive enough for its detection.

The concentration of bisphenol A (5-1918 ng/L) in water were higher than the levels found in this study (Bayen et al. 2016). The concentration of bisphenol A in eight locations in Singapore ranged from < 96-694 ng/L (Bayen et al. 2013b).

7.1.2. Sediment

This section discusses the results of the selected contaminants found in sediment samples obtained from the marine environment of False Bay (sites 1 to 8) in May 2018. They were quantified according to the experimental protocol described in Chapter 3, section 3.4.2 and 3.4.3. Sediment plays a vital role in the movement of contaminants across the marine environment because it affects the amount of contaminants that are present in the water column and above all the bioavailabilty to filter-feeding organisms (Taleb et al. 2007). In False Bay specifically, the dynamics of the marine water of the bay is influenced by its shape (Taljaard et al. 2000) and this may be responsible for the similar concentrations of contaminants across the bay.

7.1.2.1. Perfluorinated compounds

The concentrations of contaminants in sediment samples from the study areas are presented in Figure 7.4 while data are summarized in Appendix IV, Table IV.3.

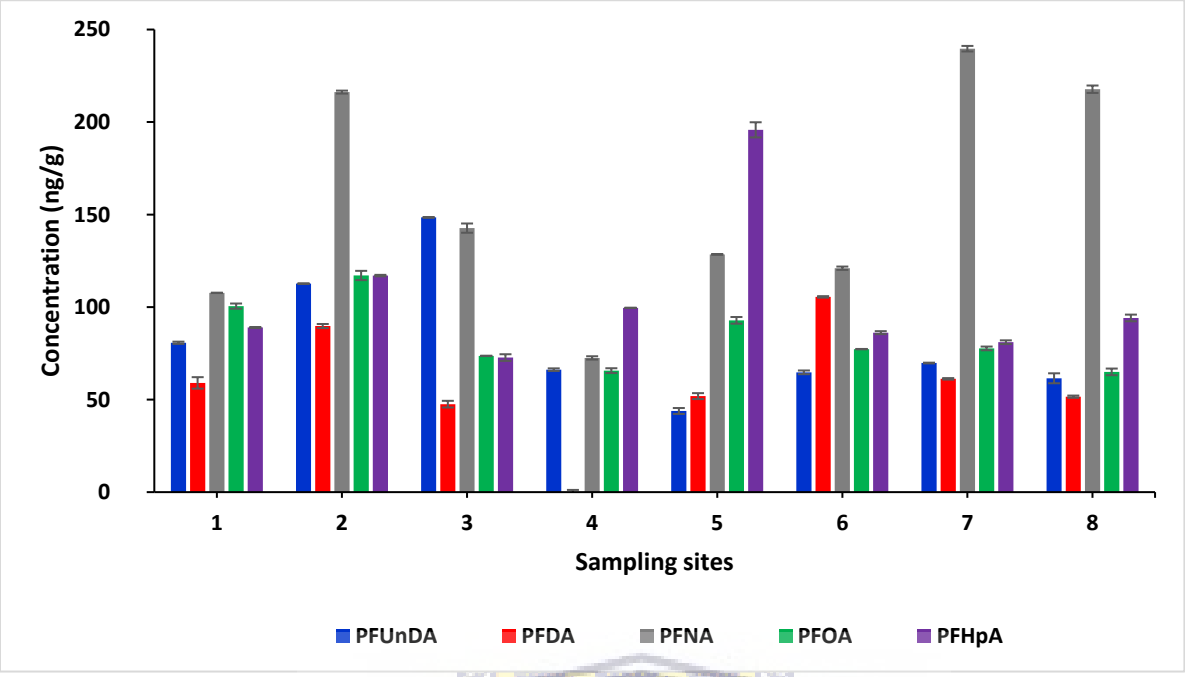


Figure 7. 4: Perfluorinated compound concentrations in sediment samples all the sites in False Bay

Perfluoroalkyl compounds (PFCs), have been widely produced and used as surfactants, lubricants, paints, polishes, fire-retardants and water repellents for leather, paper, and textiles. Their continuous use have made them persistent in the environment (Clara et al. 2008), their concentration was higher in sediment compared to what was found in False Bay seawater samples. Similar observation was also found in the studies conducted on PFCs in samples obtained from Green Point (Chaper 5) and Camps Bay (Chapter 6). Furthermore, recent published reports also showed that the level of PFCs are higher in sediment samples that in seawater samples. This is due to the fact that sediment acts as a sink/reservoir for all these chemicals (Shi et al. 2010; Lin et al. 2020) making it unsurprising to detect higher levels of these chemicals in sediment than in seawater samples in this study. Also according to the report by (Arvaniti et al. 2015), the concentrations of PFCs found in surface water and ground water samples, range up to some hundreds µg/L while concentrations in the range of some hundreds µg kg^{-1} to few thousands mg

kg^{-1} have been found in sediments. This is in line with the results found in this location and other locations in this study.

Concentrations of PFCs: PFUnDA, PFDA, PFNA, PFOA and PFHpA ranged from 43.85 to 148.46 ng/g, 47.54 to 105.51 ng/g, 72.52 to 239.65 ng/g, 64.98 to 117.09 ng/g and 72.72 to 195.79 ng/g respectively all in dry weight. All the perfluoroalkyl compounds investigated in this study were detected in all the sediment samples from the studied areas, this suggests that long-chain PFCs are prone to partition as they are less soluble resulting in their high adsorption onto the sediment unlike the short chain PFCs which are highly soluble and adsorb less onto the sediment. Site 3 had the highest concentration and site 5 had the lowest concentration of PFUnDA, site 3 had the lowest concentration while site 6 had the highest concentration of PFDA. Site 4 had the lowest concentration and site 7 had the highest concentration of PFNA, site 8 had the lowest concentration and site 2 had the highest concentration of PFOA while site 3 had the lowest concentration and site 5 had the highest concentration of PFHpA. The concentration of PFNA was much higher (Figure 7.4) than that of the other four PFCs across the sites from the area of study although in site 4, PFHpA had the highest concentration (99.59 ng/g) and in site 3, PFUnDA had the highest concentration (148.46 ng/g). From the sediment samples collected from Osaka Bay (Beškoski et al. 2017) the concentration of PFCs found (31 – 9500 ng/g) in the samples were quite higher than the result obtained from this study. The total PFCs concentration range in False Bay investigated in this study was higher compared to those in previous reports from the East China Sea (0.03 – 1.77 ng/g dw) and Chinese Bohai Sea (0.06–2.98 ng/g dw) (Gao et al. 2014), northern Bohai Sea in China (ND-4.3 ng/g dw (Chen et al. 2011a), Cantabrian Sea in North Spain (0.01–0.13 ng/g dw,(Gómez et al. 2011) and Hong Kong (0.10–1.59 ng/g dw) (Loi et al. 2013). In addition, the levels of these PFCs in sediment samples from this location were much higher than the levels found in the preceding Chapters (Green Point and Camps Bay). These high levels may be as a

result of increased level of sewage/wastewater discharged from a minimum of 4 different WWTP suitated within and around this location as well as heavily polluted stormwater in relation to fast urban development and local water circulation processes. Some studies in humans have shown that certain PFCs may have an impact on the developing fetus and child as well as decreased fertility, interfere with the natural hormones of the body, increase cholesterol, affect the immune system, and increase cancer risk (Starling et al. 2017; Olsen et al. 2017). PFCs are not produced in South Africa, they are imported from other countries and report has it that the rate of importation is increasing year in year out. Chemical industries in this region consume large amounts in the production of texile, paper and food packaging, synthetic carpets, leather and apparel, coatings, paint and varnishes e.t.c. This is an indication of the possible presence of these chemicals in the effluent of the WWTPs around this region. This suggestion that the WWTPs may harbour these compound was comfirmed by (Adeleye 2016).

7.1.2.2. Pharmaceuticals and personal care product

The levels of these contaminants are shown in Figure 7.6, data are also summarised in Appendix IV, Table IV.3

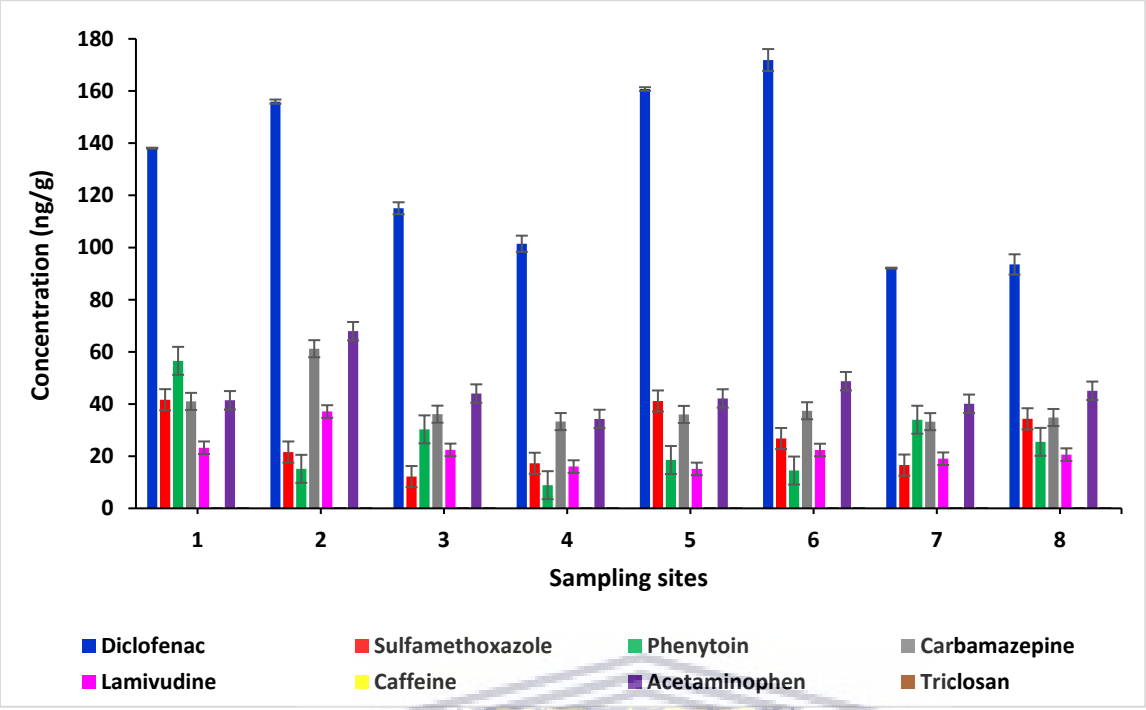


Figure 7. 5: The levels of PPCPs in sediment samples from the different sites in False Bay

Triclosan and caffeine were below limit of quantification in any of the sediment samples. Among the seven target pharmaceutical compounds, five of them (sulfamethoxazole, diclofenac, carbamazepine, lamivudine and acetaminophen) were detected in the sediment samples. Diclofenac had the highest concentration across the sites and ranged from 92.08 – 171.89 ng/g followed by acetaminophen (34.28 – 67.92 ng/g) and carbamazepine (33.27 – 61.20 ng/g) while phenytoin had the lowest concentration in almost all the sites (8.89 – 56.55 ng/g). From sites 1, 5 and 8, lamivudine had the lowest concentration, in sites 2, 4 and 6 phenytoin had the lowest concentration and in sites 3 and 7, sulfamethoxazole had the lowest concentration. The high concentration of diclofenac among the other pharmaceuticals can be attributed to the fact it is one of the drugs available over the counter used to treat inflammation and pain (Martinez-Sena et al. 2016) and as a result the public comsumption are not been regulated by government. Due to the high consumption of this drug and the fact that it is easily excreted from the body into the sewage plants, and since the sewage plants are not designed to remove these pharmaceuticals they are

easily detected in the effluent of these plants. Diclofenac, because of its high polarity and hydrophilicity are readily transported from these plants into other water bodies including the marine environment. In addition, diclofenac's high mobility in the sediment was attributed to its interaction between the solid phase and dissolved phase i.e octanol-water distribution coefficient ($logK_{ow}$) (Čelić et al. 2019). Furthermore, the high value ($logK_{ow} > 4$) of diclofenac made its sorption on suspended matter possible and its presence in sediment to some extent (Mandaric et al. 2019). These reasons account for the high values of diclofenac not only in this location but also in Green Point and Camps Bay marine environments, (Chapters 5 and 6) of this study. Although the concentration of diclofenac in False Bay marine environment is higher than the result from Green Point and Camps Bay (Chapters 5 and 6), the reason highlighted above for the high level of diclofenac accounts for their high concentration in Green Point and Camp Bays studies. Overall the detection of these pharmaceuticals in solid samples such as sediment serves as an indication that regardless of their high solubility in water, they can partition between water and solids. Also, poor system of sanitation in some parts of South Africa (this region) and some developing countries result in the spread of pharmaceuticals in the environment (Segura et al. 2015; Madikizela et al. 2017). In general, the levels of these pharmaceutical compounds were higher in sediment samples from False Bay than in samples from Green Point and Camps Bay this reason could be linked to the volume of sewage discharge as highlighted in previous sections.

Comparing the levels in this study with other studies, showed that the concentration of triclosan (15.14 ng/g) in sediment samples from Santos bay were higher than the level found from all these sites from the study area (Pusceddu et al. 2018), similarly, the concentrations of triclosan in sediment collected from Greenwich Bay ranged from less than 1 ng/g to 32 ng/g (Katz et al. 2013). The levels of sulfamethoxazole from sites 3, 4 and 7 were similar to the levels (18.5 ng/g) found in sediment samples from Baltic Sea (Siedlewicz et al. 2018) while the levels of sulfamethoxazole

and carbamazepine found in another study in sediment samples (1.76 ng/g and 1.3 ng/g respectively) from Baltic Sea (Siedlewicz et al. 2016; Bayen et al. 2016) were lower compared to the levels obsereved in this location.

7.1.2.3. Industrial chemicals

The levels of these class of contaminants are shown in Figure 7.7 and the detailed data are summarised in Appendix IV, Table IV.3.

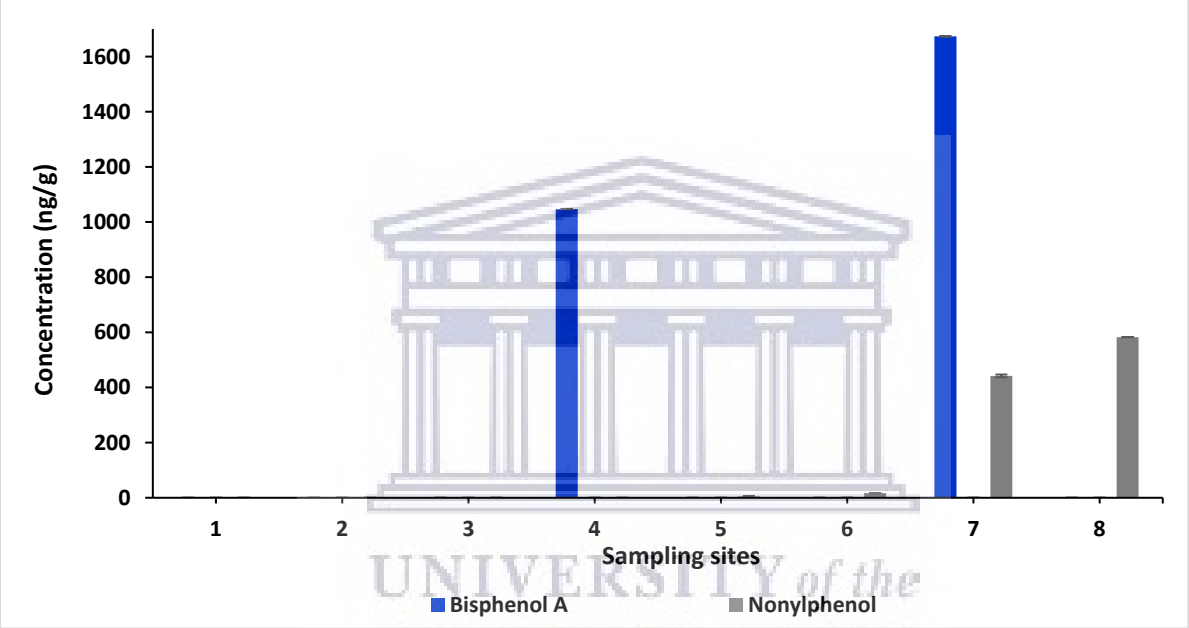


Figure 7. 6: Levels of industrial chemicals in sediment samples from eight sites in False Bay

Bisphenol A was only detected in sediment from sites 4 and 7 with a very high concentration of 1046.94 and 1673.13 ng/g respectively, the high concentration of this compound could be linked to the reasons highlighted in section 7.1.1.3, and in addition it could also be from industrial discharge from plastic companies around these two sites (about 4 plastic companies). Bisphenol A enter the marine environment majorly through the wasterwater effluents, and little amount enter through landfill leachate, WWTP is presumed to remove this chemical effectively by sorption to solid and biodegradation, however BPA bound with particulate and are discharged with effluents

and settles onto sediments. While nonylphenol was quantified in sites 5, 6, 7 and 8 with site 5 having the lowest concentration (5.18 ng/g) and site 8 the highest concentration (582.58 ng/g), the samples from other sites were below limit of quantification and 2-nitrophenol was not detected. The reason for high concentration of nonylphenol were highlighted in the following sections 7.1.3.1.3, 7.1.3.2.2 and 7.1.3.3.2. The concentration of bisphenol A in sediment <0.4-81 ng/g was lower (Bayen et al. 2016) compared to the levels found in this study. The mass of all detected compounds in the sediments of the False Bay is expected to be several orders of magnitude higher than that in the water column, where the concentrations of the compounds were only at the ng/L level. Recently the City of Cape Town declared that the water quality around the coast of Cape Town is bad (COCT 2019) i.e it failed the good water quality for reacreational purposes in which False Bay, Camps Bay and Green point are inclusive, this confirms the findings in this reasearch.

7.1.2.4. The sorption coefficients

The sorption coefficients of contaminants between sediment and seawater were estimated using the concentration of the compounds in the sediment and in the overlaying water at the same sampling sites. This is a very essential parameter used to estimate the potential of dissolved contaminants adsorption in contact with sediment. The sorption coefficient (Kd) describes the reversible sorptive exchange of chemicals between water and sediment (Kozerski et al., 2014), this was calculated using Equation 7.1.

$$K_d = {}^{Cs}/_{Cw} \qquad (7.1)$$

Where, Cs and Cw are the concentrations of compounds in sediment and in water.

Except for the null values, the Kd values in the sampling sites are presented in Table 7.2. The Kd values of perfluorinated compounds ranged from PFUnDA (9.40 to 36.47 L/kg), PFDA (8.22 – 38.76 L/kg), PFNA (5.71 – 49.72 L/kg), PFOA (5.33 – 23.72 L/kg), PFHpA (7.00 – 22.38 L/kg),

BPA (17.96 – 20.24 L/kg) while for pharmaceuticals ranged DCF (26.99 – 59.75 L/kg), SMX (8.58 – 59.34 L/kg), PHE (17.58 – 262.27 L/kg), CAR (21.54 – 79.10 L/kg), LA (42.68 – 120.00 L/kg) and ACT (31.37 – 64.00 L/kg). The Kd values of BPA for sites 4 and 7 were 20.24 and 17.96 L/kg respectively. PHE had the highest sorption capacity among the selected compounds (Kd = 262.27 L/kg). High values of Kd (of the order of 100 or more) indicate that, at any given time, the majority of the chemicals are adsorbed to the sediment surface and hence they do not move throughout the soil however the Kd values does not indicate the strength (reversibility) of that sorption. A very low Kd value means contaminants are highly mobile in sediments (Lewis et al. 2016). From the result of this study, LA and PHE are less likely to move in soil while other compounds may be mobile in the soil which makes them to leach or occur as runoffs to contaminate ground water, in addition marine organisms can easily take up these contaminants and plants into their foliage through transpiration which has direct connection to potential human health impact (Doucette et al. 2005a, b; Bagheri et al. 2019). However, the fact that compounds with high Kd values are less likey to leach into groundwater, the potential advese effects of these compounds on sediment dwelling organisms cannot be ignored.

Table 7. 2: Kd values for sediment from sites 1 to 8

	1	2	3	4	5	6	7	8
PFUnDA	34.57	36.47	32.74	9.40	15.27	20.87	23.47	19.33
PFDA	33.73	36.66	38.76	20.25	22.18	30.73	8.22	21.22
PFNA	5.71	26.93	12.91	20.49	20.03	17.29	43.52	49.72
PFOA	5.90	18.01	23.72	5.53	9.88	17.10	17.19	11.01
PFHpA	7.00	13.24	22.38	8.25	19.30	12.46	11.64	11.70
TS	0	0	0	0	0	0	0	0
BPA	0	0	0	20.24	0	0	17.96	0
DCF	37.33	59.75	27.51	36.95	56.23	49.93	26.99	27.54
SMX	18.54	20.90	18.50	59.34	8.58	11.24	31.93	7.94
PHE	262.27	46.65	87.96	132.22	39.90	24.07	37.80	17.58
CAR	43.20	64.19	79.10	28.06	23.13	27.75	21.54	27.00
LA	65.08	120.00	50.68	48.49	42.68	51.03	58.60	66.02
CAF	0	0	0	0	0	0	0	0

ACT	48.27	64.00	54.01	35.90	42.63	33.04	31.37	36.34
2-N	0	0	0	0	0	0	0	0
NP	0	0	0	0	0	0	0	0

7.1.3. Marine organisms

In this study, five different marine organisms namely limpet, mussels, sea urchin, seasnail and starfish, were examined for the levels of PCFs, PPCPs, and EDCs (industrial chemicals) from the eight sites in False Bay study area. The selection of species was based on their abundance (samples found it each sites) in various sites and they were analysed in accordance to the experimental protocol reported in Chapter 3 of this thesis. Since Taljaard et al. (2006) reported that the wastewater treatment plants and sewage outfalls from urban industrial areas releases sewage directly into False Bay in the company of pollutants like chemicals of emerging concern, it is important to carry out an evaluation of the levels of these contaminants in the marine organisms from this bay. Generally the levels of contaminants in organisms are orders of magnitude higher than in seawater and sediment samples. This is the first time, the levels of chemicals of emerging concern will be evaluated in the marine organisms from this Bay. All biota samples are reported in dry weight (dw). Because of the complexity of the data (huge amount of data) under this section, the reporting of the comparison of the results obtained in this section with other studies in literature will be done at the end of the discussion of the last seaweed specie.

7.1.3.1. Limpet (*Cymbula oculus and Cymbula granatina*)

Limpet samples were present and thus collected from all the eight sites of False Bay in May 2018 and results are presented in Appendix IV, Table IV.3 and in Figures 7.7 to 7.9.

7.1.3.1.1. Perfluorinated compounds

The levels of perfluorinated compounds in these species of organism are shown in Figure 7.7.

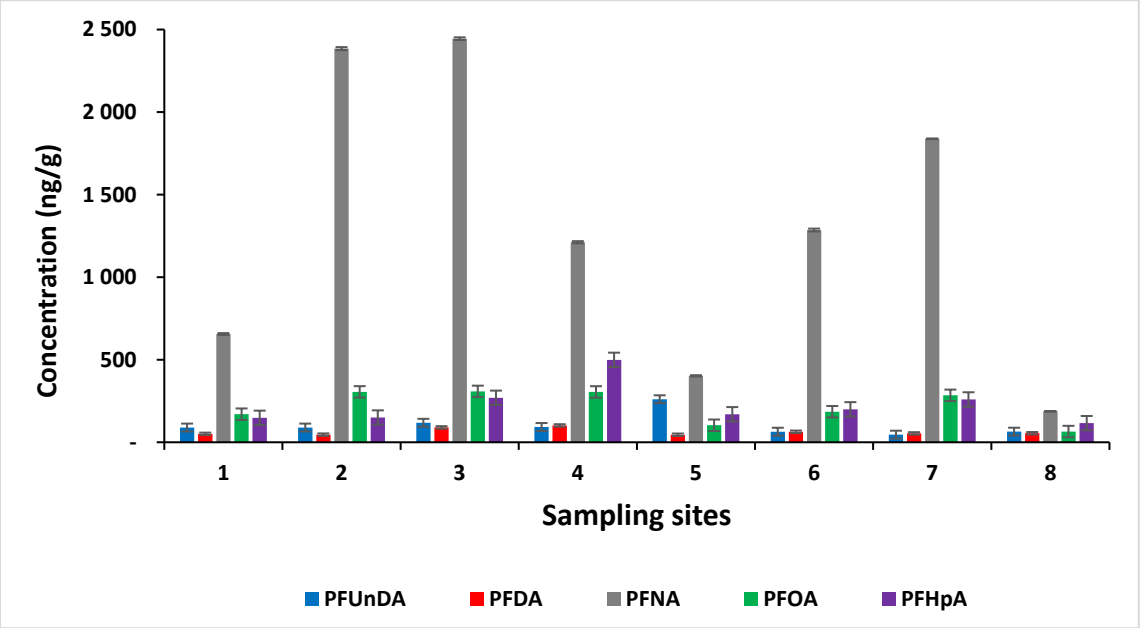


Figure 7. 7: PFCs concentration in Limpet samples from all the studied sites in False Bay

The concentrations of PFCs ranged as follows: PFUnDA (46.30 – 260.75 ng/g dw), PFDA (45.62 – 101.94 ng/g dw), PFNA (187.38 – 2444.87 ng/g dw), PFOA (64.96 – 308.23 ng/g dw) and PFHpA (115.77 – 269.48 ng/g dw). It can be observed from Figure 7.7 that the highest concentration of PFUnDA was found in samples from site 5, PFDA and PFHpA from site 4, PFNA and PFOA from site 3. PFNA was found to be the compound with the highest concentration of all the PFCs across the sites. These compounds were present in all samples from all sites showing the widespread impacts of sewage effluents reaching the oceanic environment. However, PFCs including perfluorononanoic acid (PFNA) are unaffected by environmental biodegradation processes such as oxidation, reductive halogenation and hydrolysis as well as metabolism due to the strength of the bond between carbon and fluorine. In laboratory experiment with animanl PFNA are associated with toxicity related to reproduction and growth (Butenhoff et al. 2004) and evidence of human exposure are known (Olsen et al. 2005). As a result of their presence in the ecosystem and their effect, they are of serious concerns to the environment and humans (Martin et al. 2002; Stock et al. 2004; Taniyasu et al. 2005). In addition, the high levels of PFCs in False Bay

compared to Green Point and Camps Bay could also be as a result of the fire training activites which uses fire fighting foams in which one of their major composition is PFCs on the naval base in (site 2) and around this location (Viberg and Eriksson 2017). Some of the impact due to exposure to these PFCs are highlighted in section 7.1.2.1.

7.1.3.1.2. Pharmaceuticals and personal care product

Pharmaceutical compounds concentrations in limpet samples collected from sites 1 to 8 are shown in Figure 7.8. Given that PPCPs tend not to be found in isolation but rather are found in complex mixtures (Kolpin et al. 2002), marine organisms are likely to be exposed to a wide range of PPCPs at the same time in waters receiving WWTP effluents, some of which may have the potential to accumulate.

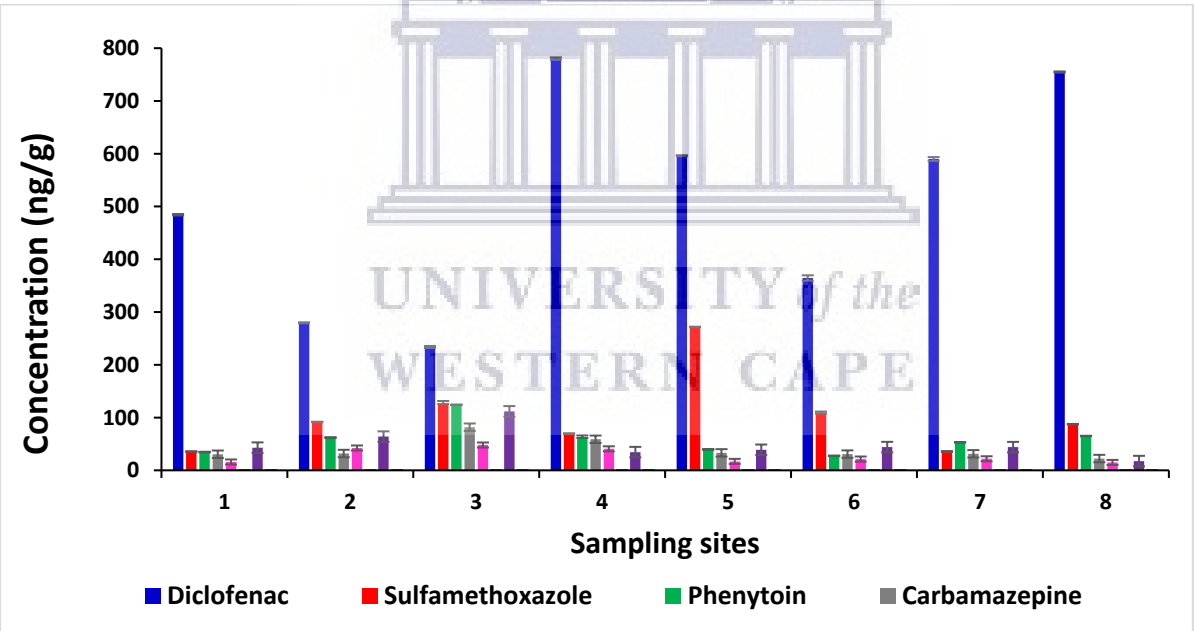


Figure 7. 8: PPCPs in limpet samples from sites 1 to 8 from False Bay

The concentration of pharmaceuticals in limpet ranged as follows: diclofenac (233.81 – 780.26 ng/g), sulfamethoxazole (35.85 – 272.09 ng/g), phenytoin (28.06 – 124.78 ng/g), carbamazepine (22.32 – 81.76 ng/g), lamivudine (14.97 – 47.98 ng/g) and acetaminophen (17.53 – 111.77 ng/g).

The highest concentration of pharmaceuticals in limpet samples was observed as follows: diclofenac found in limpet from site 4, sulfamethoxazole in samples from site 5, phenytoin, carbamazepine, lamivudine and acetaminophen in site 3 while the lowest concentration of pharmaceuticals found in limpet samples are as follows: diclofenac found in site 3, sulfamethoxazole in site 1, phenytoin in site 6, carbamazepine, acetaminophen and lamivudine in site 8. From the results, it was noticed that diclofenac had the highest concentration of all the pharmaceuticals across all the sites and was present in all biota. Caffeine and triclosan were below the limit of quantification because the concentrations found were below the limit set on the instrument for quantification of these compounds. High concentration of diclofenac across the sites could be linked to reasons previously mentioned in section 7.1.2.2. However the presence of antibiotics such as sulfamethoxazole found in all the sites can disrupt a number of vital ecological processes in the marine environment as they become toxic to non-target organisms or aquatic organisms in this environment thereby developing resistance to this antibiotic (Szymańska et al. 2019). This antibiotic has been reported to enter the marine ecosystem from incomplete biodegraded sewage waste from WWTPs as well as indiscriminate use of antibiotics by humans (Enachi et al. 2019). As a result, the high level of sulfamethoxazole in this study could be ascribed to the effect of the discharge of untreated sewage from a minimum four WWTPs around this location. Although, this study did not consider the levels of other antibiotics, previously published studies reported that among all antibiotic groups, the most persistent in the marine environment is the sulfonamides (in which sulfamethoxazole is a member) while β-lactams and aminoglycosides are the least persistent (Kumar et al. 2019; Szymańska et al. 2019). Overall, if these species continue to bioaccumulate contaminants, they will not be effiecent in treatement of diseases they are used for (bladder cancer and development of vaccines) (Glow-worm 2013) as well as they been hazardous to humans.

7.1.3.1.3. Industrial chemicals

The presence of the detected industrial chemicals in limpet samples are presented in Figure 7.9.

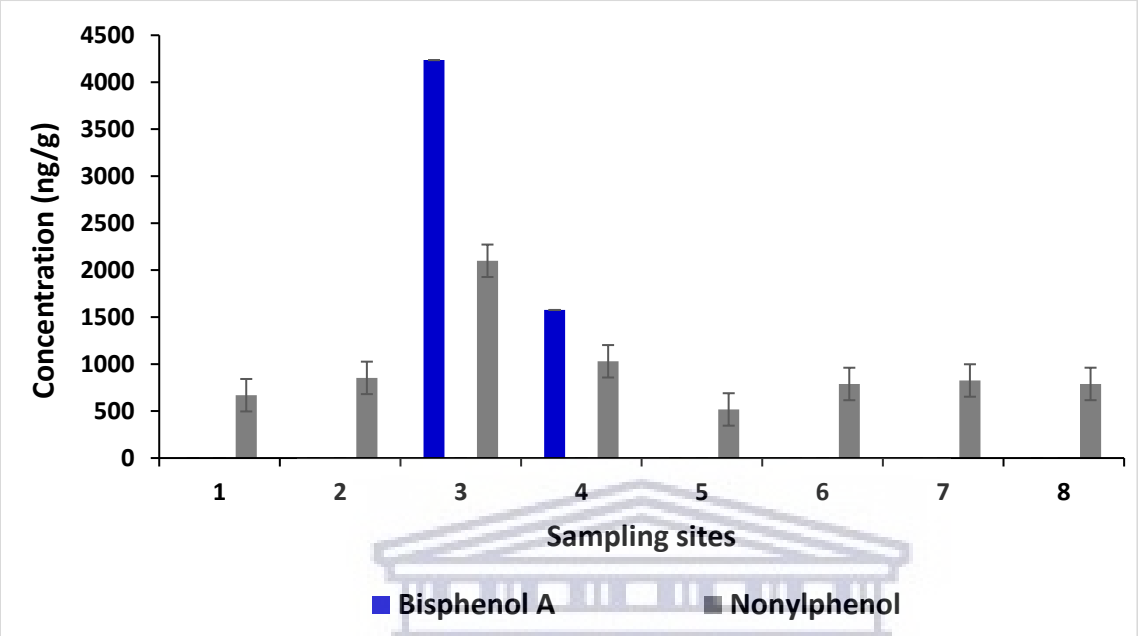


Figure 7. 9: Concentration of Industrial chemicals in limpet samples from sites 1 to 8 of False Bay

2-nitrophenol was not detected in any of the limpet samples, bisphenol A was only detected in samples from sites 3 and 4 with high concentrations of 1576.34 ng/g and 4236.20 ng/g respectively. The reasons given in sections 7.1.1.3 and 7.1.2.3 also account for the high levels of this compound in these two sites. However, the effect of the high concentration of bisphenol A is such that they distort hormonal balance when they act on the hormonal level (Ohore and Songhe 2019). Furthermore, they cause obesity, early sexual characteristics, feminization of the male fetuses in males and alteration of sperm quality. While in female, some of their effect include irregulaties in menstration and early puberty (Hines et al. 2017; Toner et al. 2018; Ohore and Songhe 2019).

The concentration of nonylphenol ranged from 517.10 – 2099.50 ng/g, with site 3 having the highest and site 5 having the lowest concentration but this compound was found in marine

organisms from all the sites at high to very high levels. These compounds are usually employed in the production of lubricating oil, detergents, paints, solubilizers, plastics, antioxidants and emulsifiers (Soares et al. 2008; Miyagawa et al. 2016; Anadón et al. 2017). Even so, they bioaccumulate and are persistent in marine environments since they are not readily biodegradable (Mao et al. 2012). Because of its application for the production of many "down the drainage" products including dish and laundry detergents, they are usually found in water milieu and due to their bioaccumulation and persistence in the environment, they have the history of travelling long distances from their site of contamination to other locations. Generally, in this study, it is observed that bioaccumulation is a very important contamination indicator in water dwelling organisms.

7.1.3.2. Mussels (*Mytilus galloprovincialis*)

Mussel samples were only found and sampled in five different False Bay sites (2, 4, 6, 7 and 8) in May 2018 and the results are summarised in Appendix IV, Tables IV. 3 and Figure 7.10 – 7.12. Bivalves such as mussels in marine and coastal waters have specific characteristics (filter feeding) which allows bioaccumulation of contaminants from water and food. Mussels are considered as pollution sentinel or as sentinel organisms and are used globally for bio monitoring of the quality of coastal marine environments (Edward 2013; Silva et al. 2017; Krishnakumar et al. 2018). However, other organisms such as limpet have demonstrated in this study that they can also be used to monitor pollution within a location. Generally the levels of all the contaminants detected in mussels from this location were higher than the levels of contaminants detected in mussel samples from Green Point and Camps Bay with the exception of caffeine and triclosan in Green Point and Camp Bay.

7.1.3.2.1. Perfluorinated compounds

The graphical presentation of the levels of PFCs detected in mussel samples are shown in Figure 7.10.

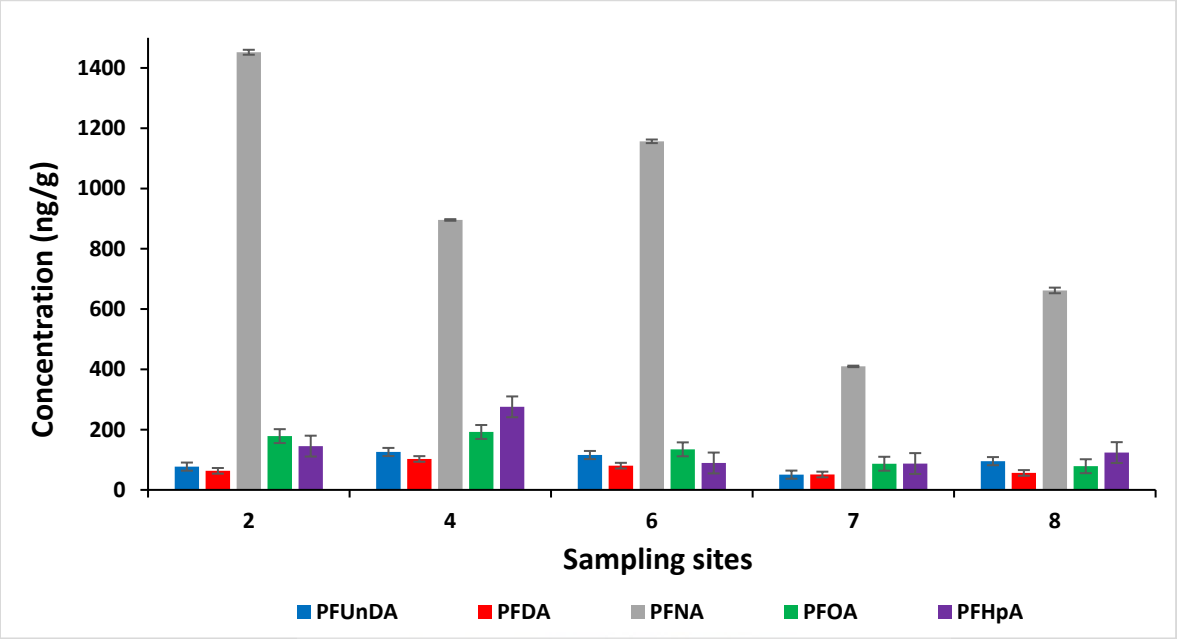


Figure 7. 10: PFCs levels in mussel samples from five sites in False Bay

The concentrations of PFCs in the mussel samples ranged as follows: PFUnDA (50.60 – 125.78 ng/g dw), PFDA (51.12 – 102.64 ng/g dw), PFNA (409.78 – 1452.07 ng/g dw), PFOA (78.61 – 192.20 ng/g dw) and PFHpA (87.48 – 275.61 ng/g dw). It can be observed from Figure 7.10 that the highest concentrations of PFUnDA, PFDA, PFHpA and PFOA were found in samples from site 4, PFNA from site 2. It was also observed that the concentration of PFNA was high across the samples from all the sites. A comparison of the levels of these PFCs in mussel and limpet samples indicates that they follow similar pattern (PFNA > PFOA > PFHpA > PFUnDA > PFDA) with PFNA having the highest concentration across the sites followed by PFOA and PFHpA, however the trend found in mussels samples from Camps Bay (PFUnDA > PFHpA > PFDA > PFNA > PFOA) were different as PFUnDA levels was found to be the highest. The high levels of PFNA found in the mussel samples can also be attributed to the reasons previously highlighted in section 7.1.3.1.1. These high levels can also be attributed to the fact that sewage plume makes frequent landfall, causing an increase of chemical contaminants along the shoreline, as the frequent flushing by sea water is not enough to prevent bioaccumulation of these contaminants in marine organisms.

Since none of these chemicals would of themselves be found in the marine environment talkless of them been present in the marine biota.

7.1.3.2.2. Industrial chemicals

The Figure 7.11 showed the concentrations of industrial chemical compounds detected in mussel samples from various sites in False Bay.

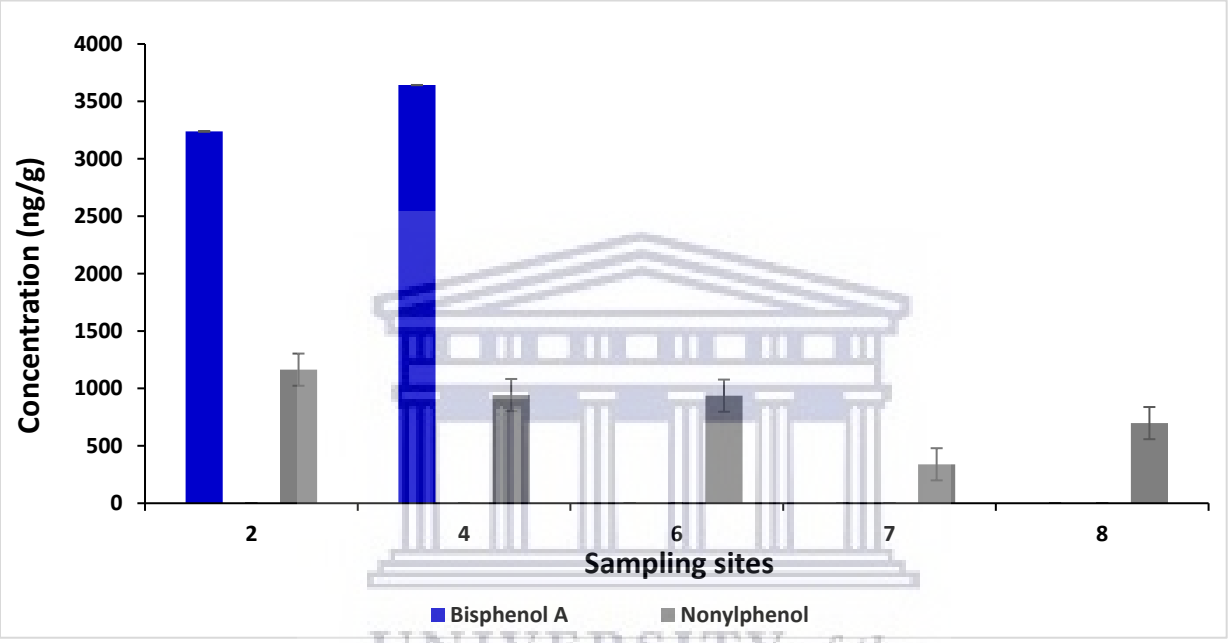


Figure 7. 11: The levels of industrial chemicals in mussel samples from five sites in False Bay

2-nitrophenol was not detected in any of the mussel samples, bisphenol A was only detected in samples from site 2 and 4 with very high concentrations of 3642.11 ng/g and 3238.80 ng/g respectively and 3 times higher than in sediment samples. South Africa is regarded as the 11th biggest global contributor per capital of marine plastic pollution, a huge and continuously deleterious problem affecting human health and the environment. According to a news article, the volume of plastic pollution in False Bay is alarming (Jeranji 2018), this accounts for the high levels of bisphenol A in marine organisms in this study. Furthermore in this article, Patrick Dowling reported that there is an overwhelming evidence showing that chemical constituents, such as

bisphenol A, of many plastics have disruptive effects on human health. This is worrysome as many resturants, cafes, fast food eatries, food packaging from stores in Cape Town all make use of one form of plastic material or the other.

The concentration of nonylphenol ranged from 339.20 – 1163.33 ng/g, with site 2 having the highest and site 7 having the lowest concentration. The presence of this contaminant in this organism could be ascribed to the primary degradation of alkylphenol ethoxylate (APEs) from wastewater treatment plants which result to a more persistent metabolite of APEs and alkylphenols (APs), such as Nonylphenol (Giger et al. 1984; Ying et al. 2002; Langford et al. 2005). Also, recently, nonylphenol was detected (9.83 µg/L) (Olujimi et al., 2013) in effluent samples collected from Cape Town, South Africa, an indication that this compound might be present in the marine environment of Cape Town including False Bay since there are evidence of indiscrimate discharge of sewage from WWTPs around this bay into the oceanic environment.

7.1.3.2.3. Pharmaceuticals and personal care product

The levels of the detected pharmaceutical compounds in mussel samples are shown in Figure 7.12.

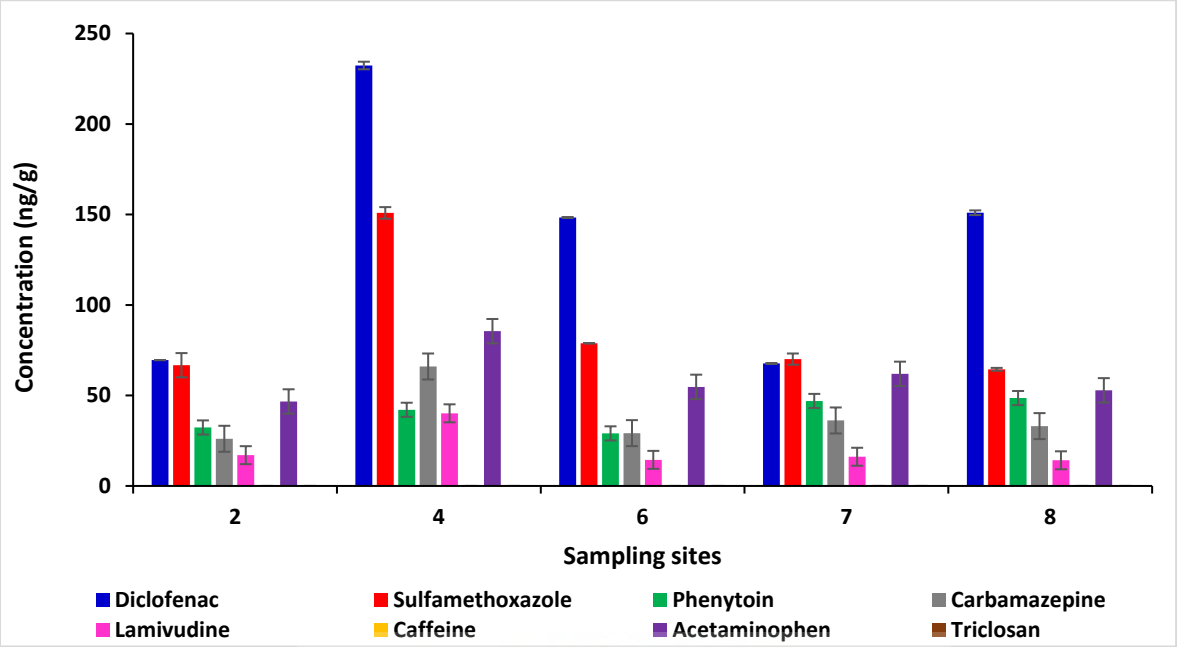


Figure 7. 12: PPCPs concentrations in mussel samples from five sites in False Bay

The concentration of pharmaceuticals ranged as follows: diclofenac (67.67 – 232.33 ng/g), sulfamethoxazole (64.44 – 150.88 ng/g), phenytoin (29.04 – 48.56 ng/g), carbamazepine (26.06 – 66.00 ng/g), lamivudine (14.17 – 40.13 ng/g) and acetaminophen (46.67 – 85.51 ng/g). The highest concentration of pharmaceuticals in the mussel samples was observed in samples from site 4 except for phenytoin which was observed to be high in samples from site 8. Caffeine and triclosan were below the limit of quantification in mussel samples from all the sites.

Marine environments are under great dangers due to the enhanced pressures of industrialization and urbanization. The marine environment in South Africa is regarded been in its original condition i.e clean in terms of world standards (Sparks et al. 2014). However, considering the numerous use of areas and increased population growth and development, anthropogenic activities in local communities along coastal areas may be increasing the destruction of organisms and loss of vulnerable ecosystems.

To limit these effects, marine environments are closed and considered marine protected areas. Although restricted to the populace, a key question is whether declaration of marine protected areas are really protecting the ecosystems and organisms that are proposed to be protected. The continous release of chemicals of emerging concerns into the marine environment may have negative impacts on the physicochemical composition of biota, diversity, productivity and abundance (Jose et al. 2011) this may explain the reason why some marine organisms were not found in some sites in this study.

False Bay's coastal, terrestrial and surrounding areas of the bay based sources of pollution are the major contributors of contamination in the area (Ngwenya 2006) with coastal ecosystems under considerable stress caused by non-point (maritime transportation) and point source contamination (sewage effluent, agricultural, commercial and urban development) (Harris 1978; Taljaard et al. 2006), these are the main reason for the high concentration of these pharmaceuticals and other contaminants in the bay as they accumulate in the organisms. Also, anthropogenic activities contribute largely to the loss of sensitive invertebrate species and poor water quality along False Bay (DWAF 1995; Bredenhand and Samways 2005) which may be responsible for the inability to obtain some species in some sites in False Bay observed in this study as some species were not found in some sites.

7.1.3.3. Sea snail (*Oxystele sinensis and Oxystele tigrina*)

Sea snail samples were present, therefore were collected from six False Bay sites (1, 2, 5, 6, 7 and 8) and the results are presented in Appendix IV, Table IV.3 as well as Figure 7.13 – 7.15.

7.1.3.3.1. Perfluorinated compounds

The results of perfluorinated compounds detected in sea snail samples from various sites in False Bay are shown in Figure 7.13.

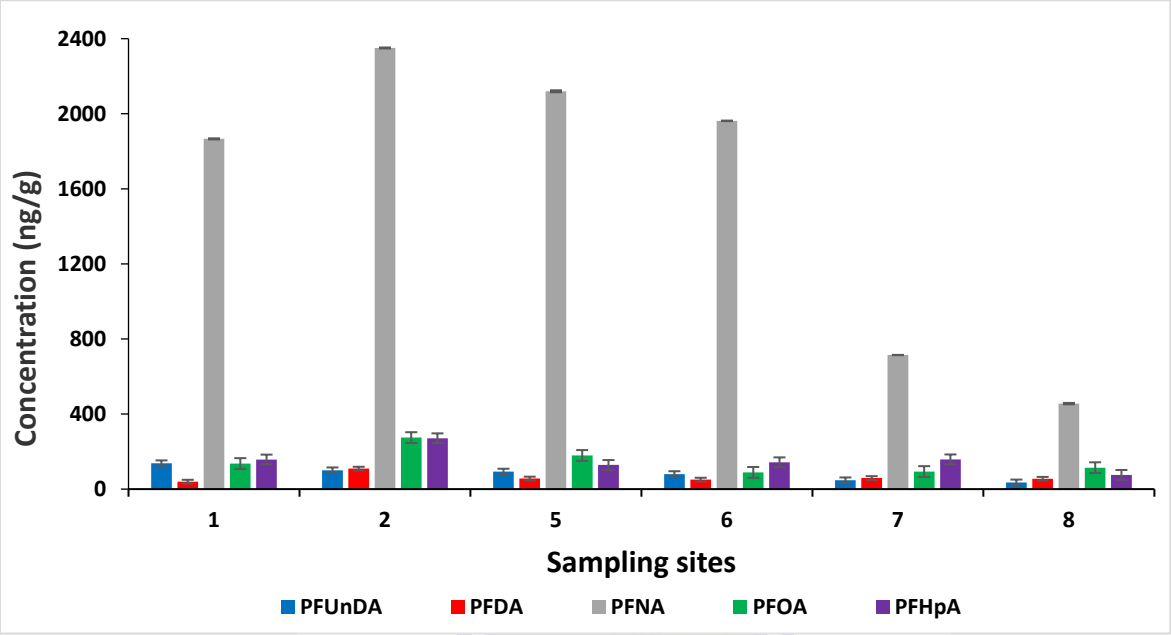


Figure 7. 13: Concentration of perfluorinated compounds in sea snail samples from five sites in False Bay

The concentrations of PFCs in sea snail samples ranged as follows: PFUnDA (35.59 – 137.79 ng/g dw), PFDA (39.80 – 109.12 ng/g dw), PFNA (455.43 – 2350.42 ng/g dw), PFOA (89.07 – 274.47 ng/g dw) and PFHpA (75.68 – 270.89 ng/g dw). It can be observed from Figure 7.13 that the highest concentration of PFUnDA was found in samples from site 1, PFDA, PFHpA, PFOA and PFNA from site 2. Out of the PFCs, the levels of PFNA was found to be the highest across the samples from the different sites. It is not clear why the concentration of all these contaminants became so high in site 2 as there are no major manufacturing and commercial activites going on in Simon's Town order than the wastewater treatment plants and the Naval harbour (which is the largest in South Africa) in this location. It is suggested that the high levels of PFCs in site 2 could come from the presence of these compounds in the finished products used by residence in this area which are transported ito WWTPs in this location. Generally, False Bay have been subjected to anthropogenic influences from rapid urbanization and industrialisation. Overall, they seemed to be influenced primarily by municipal and domestic sewage from the nearby areas of very urbanized

areas. Organic pollutant levels in biota may be affected by physiological factor of a specific species such as diet choice, growth, respiration and egestion rates as well as metabolic capability of organisms (Tomy et al. 2004; Falk et al. 2015) which may explain the remarkable variation in the levels of PFCs, PPCPs and industrial chemicals among various marine biotas from the study area.

7.1.3.3.2. Industrial chemicals

The result of the three industrial chemicals analysed in sea snail samples in the study area are presented in Figure 7.14.

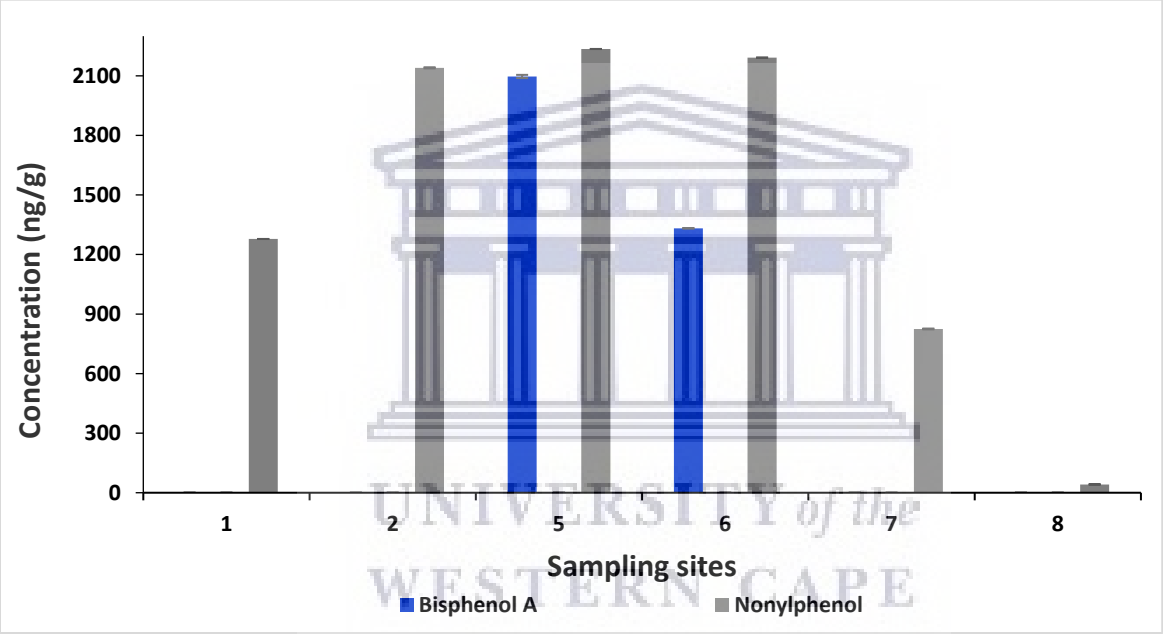


Figure 7. 14: The levels of industrial chemicals in sea snail samples from five sites in False Bay

2-nitrophenol was not detected in any of the sea snail samples, bisphenol A was only detected in samples from sites 5 and 6 with concentrations of 1576.34 ng/g and 4236.20 ng/g respectively. The concentration of nonylphenol ranged from 41.57 – 2235.35 ng/g, with site 5 having the highest concentration. Surprisingly, the detection of bisphenol A in all the marine organisms were not in any order across the sites. This indicates different variation in bioavailability and exposure pattern of contaminants between seawater and to organisms and the way the organisms process these

contaminants. The high levels of bisphenol A and nonylphenol can also be attributed to the suggestions hightighted in the previous sections. However nonlyphenol was below quantification limit in all the seawater samples (Figure 7.3), this may be due to its physio- chemical properties like low solubility in water, yet accumulate in other enivironmental matrices and can move up the food chain. According to literature, nonylphenol is very harmful and toxic to marine organisms (US EPA 2010), but does not biomanify to any great extent (Raju et al. 2018). Comparing the levels of all contaminants in sea snail from False Bay to Green Point, the levels in False Bay were higher than Green Point samples, while sea snails were not found in Camps Bay. Specifically in site 5 high amounts of these chemicals were found compared to other sites, this could be due to large numbers of industrial activities going in Strand (Pfaff et al. 2019; Helderberg 2020) where this site is located.

7.1.3.3.3. Pharmaceuticals and personal care product

Figure 7.15 shows the levels of PPCPs detected in sea snail samples collected from the various sites in False Bay.

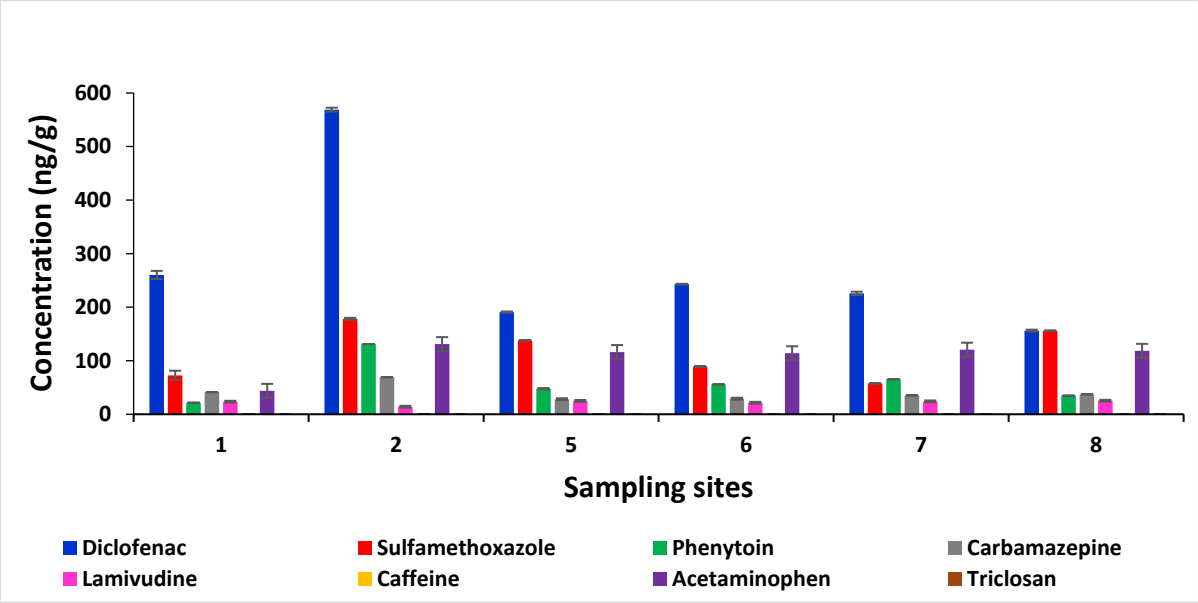


Figure 7. 15: Concentration of PPCPs in sea snail samples from six sites in False Bay

The concentration of pharmaceuticals in the sea snail samples ranged as follows: diclofenac (156.23 – 568.95 ng/g), sulfamethoxazole (57.47 – 178.36 ng/g), phenytoin (21.51 – 131.22 ng/g), carbamazepine (28.12 – 69.25 ng/g), lamivudine (14.02 – 25.23 ng/g) and acetaminophen (43.85 – 131.08 ng/g). The highest concentration of pharmaceuticals in sea snail sample was observed as follows diclofenac, sulfamethoxazole, carbamazepine, phenytoin, and acetaminophen found in site 2, lamivudine in site 8. From the results it was noticed that diclofenac had the highest concentration out of the pharmaceuticals across all the sites in the sea snails. Generally these compounds are more in samples from site 2 than samples from other sites. Caffeine and triclosan were below the limit of quantification, the fact that they are not quantified in samples from this site does not mean they are not present moreover, they have been detected in samples from Green Point (Petrik et al. 2017). Furthermore, the level of the quantified pharmaceutical compounds in sea snail samples from False Bay were higher than the levels found in samples from Green Point, once again this point out to the level of pollution which is higher in False Bay compared to Green Point. In addition, the volume of sewage discharged in False Bay is more than the volume been discharged

from the marine outfall of Green Point. Pharmaceuticals are regarded as pseudo-persistent contaminants because their rate of degradation is lower than their access rate (Daughton 2002). Arpin-Pont et al. (2016) reported that hydrodynamic conditions and site conformation determines the spatial distribution of the concentration of pharmaceutical compounds in the marine environment.

7.1.3.4. Sea urchin (*Parechinus angulosus*)

The collection of sea urchin samples were based on their abundance in each site thus they were found and collected from four False Bay sites (2, 6, 7 and 8) in May 2018. The results of contaminants in this specie are presented in Appendix IV, Tables IV.3 and Figure 7.16 - 7.18.

7.1.3.4.1. Perfluorinated Compounds

The concentration of PFCs in sea urchin samples from four different sites in False Bay are shown in Figure 7.16.

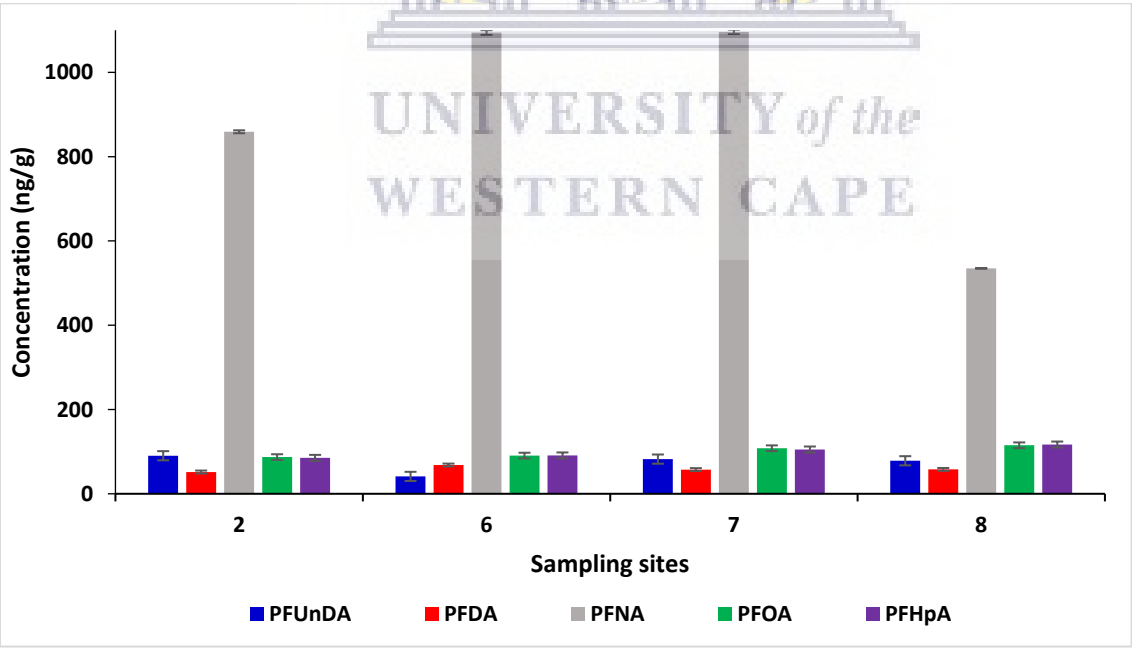


Figure 7. 16: Levels of PFCs in sea urchin samples from four sites in False Bay

The concentrations of PFCs ranged as follows: PFUnDA (41.25 – 90.30 ng/g dw), PFDA (57.40 – 68.22 ng/g dw), PFNA (534.84 – 1096.18 ng/g dw), PFOA (87.09 – 115.14 ng/g dw) and PFHpA (85.19 – 270.89 ng/g dw). It can be observed from Table 7.5 that the highest concentration of PFUnDA was found in samples from site 2, PFDA from site 6, PFNA from site 7, PFHpA and PFOA from site 8 while the lowest concentration of PFCs found in sea urchin samples were as follows: PFUnDA from site 6, PFNA from site 8, PFDA from site 7, PFHpA and PFOA from site 2. Once again PFNA was the highest PFCs across, the sites the reason for the high concentration of this compound have been discussed in previous sections (volume of sewage discharged, the high usuage of the chemical in consumer products as well as the persistent nature of the chemical in the environment). The levels of PFCs in sea urchin were not as high as the levels in mussels, limpets and sea snail from the study area in False Bay, however these levels were higher compared to sea urchin samples from Green Point and Camps Bay (Chapters 5 and 6 respectively).

7.1.3.4.2. Industrial chemicals

The concentration of industrial chemicals in sea urchin samples are shown in Figure 7.17.

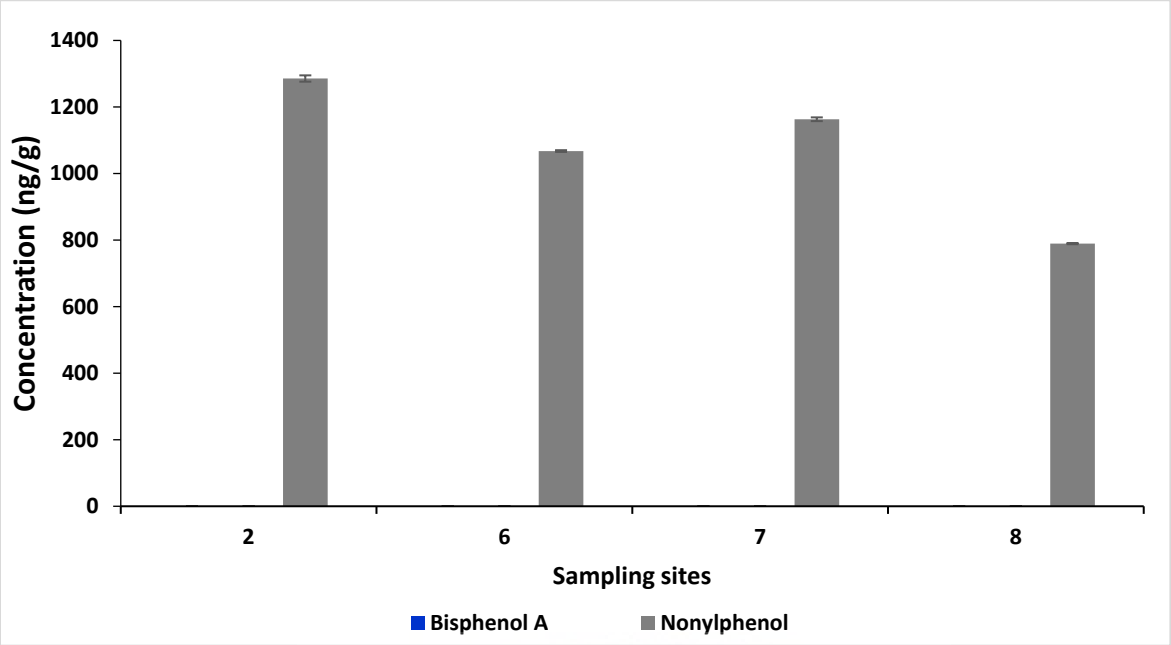


Figure 7. 17: Concentrations of industrial chemical compound in sea urchin samples from various sites in False Bay.

Sea urchins, because of their sedentary sensitivity and habit to a wide range of contaminants as well as their adaptation to changes in environmental conditions enables them to be regarded as an ideal biological-biochemical indicator of local pollution (Bayed et al. 2005; Soualili et al. 2008) specifically in protected marine areas (Angioni et al. 2012). 2-nitrophenol and bisphenol A was not detected in any of the sea urchin samples. The concentration of nonylphenol in sea urchin samples ranged from 789.42 – 1285.60 ng/g, with site 2 having the highest and site 8 having the lowest concentration. Interestingly bisphenol A was detected in at least some of the other organisms, thus it is present in the environment yet sea urchin did not bioaccumulate bisphenol A, this is as a result of the differences in physiological factor of this species. Compared to the other organisms the levels of nonylphenol in sea urchin samples was the second highest and the reason for this high concentration was discussed in sections 7.1.3.1.3, 7.1.3.2.3 and 7.1.3.3.2.

7.1.3.4.3. Pharmaceuticals and personal care product

The levels of PPCPs in sea urchin samples collected from the four studied areas in False Bay are shown in Figure 7.18 and Appendix IV, Table IV.3.

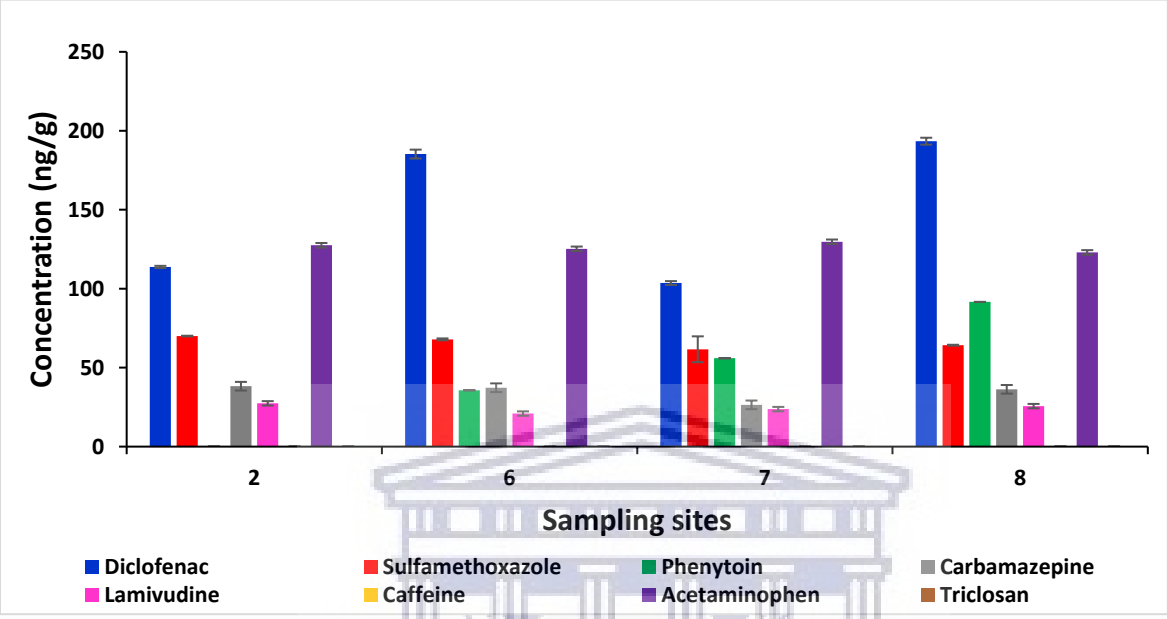


Figure 7. 18: Concentration of PPCPs in sea urchin samples from four sites in False Bay

The concentration of pharmaceuticals ranged as follows: diclofenac (103.60 – 193.41 ng/g), sulfamethoxazole (61.63 – 70.01 ng/g), phenytoin (nd – 91.63 ng/g), carbamazepine (26.44 – 38.24 ng/g), lamivudine (20.92 – 27.40 ng/g) and acetaminophen (122.97 – 129.69 ng/g) at the different sites. The highest concentration of pharmaceuticals in sea urchin samples was observed to be as follows: diclofenac and phenytoin in samples from site 8, sulfamethoxazole, lamivudine and carbamazepine in sea urchin samples from site 2 and acetaminophen found in samples from site 7, while the lowest concentration of diclofenac, sulfamethoxazole, carbamazepine was found in sea urchins from site 7, phenytoin in samples from site 2, acetaminophen in sea urchin samples from site 8 and lamivudine from site 6. From the result it was noticed that diclofenac had the highest concentration of the pharmaceutical detected across all the sites. Caffeine and triclosan were below

the limit of quantification. Discussions/reasons for the presence and high concentrations of these compounds have been earlier presented in sections 7.1.1.2, 7.1.2.2, 7.1.3.1.3 and 7.1.3.2.3.

7.1.3.5. Starfish (*Marthasterias glacialis*)

Starfish samples were collected from only two False Bay sites, sites 2 and 6 in May 2018, results are shown in Figure 7.19 – 7.21 and data provided in Appendix IV, Tables IV.3.

7.1.3.5.1. Perfluorinated compounds

The concentrations of PFCs found in starfish samples from the two False Bay sites are shown in Figure 7.19.

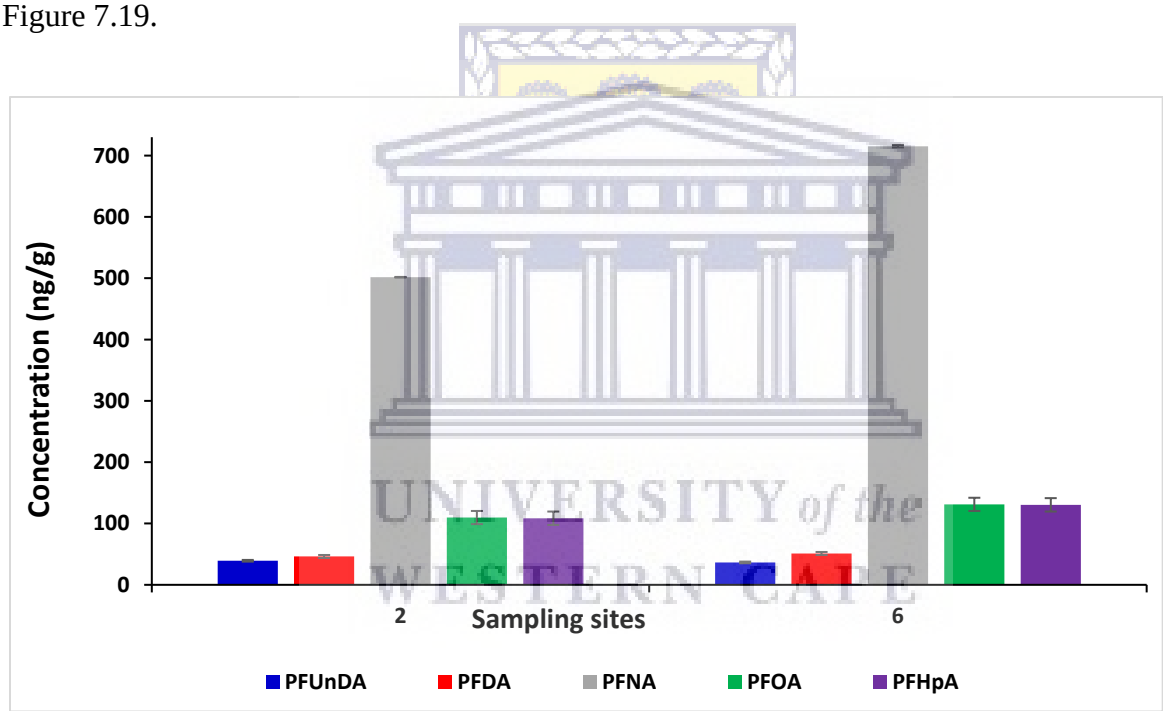


Figure 7. 19: PFCs concentration in starfish samples from two sites in False Bay

The concentration of PFNA was found to be the highest of the PFCs in starfish in both sites (501.61 and 716.15 ng/g) but lower than the concentration in other marine organisms as well as the other PFCs compounds. All the concentrations of the PFCs analysed were higher in samples from site 6 and all perfluorinated compounds were present in all starfish samples analysed.

Generally, the abundance of PFNA, PFUnDA, PFOA and PFHpA between the different species followed this order: limpets > sea snail > mussel > sea urchin > starfish while PFDA followed this order: sea snail = mussels > limpet > sea urchin > starfish. This trend was arrived at based on the total number of sites the contaminants were dominant in each species. The relative concentrations of PFCs in different marine organisms showed that bioaccumulation of PFCs was compound and species related, thus their fate in water and biological systems differ based on species and compounds.

7.1.3.5.2. Industrial chemicals

The result of the detected compounds in starfish samples from sites 2 and 6 in False Bay are shown in Figure 7.20.

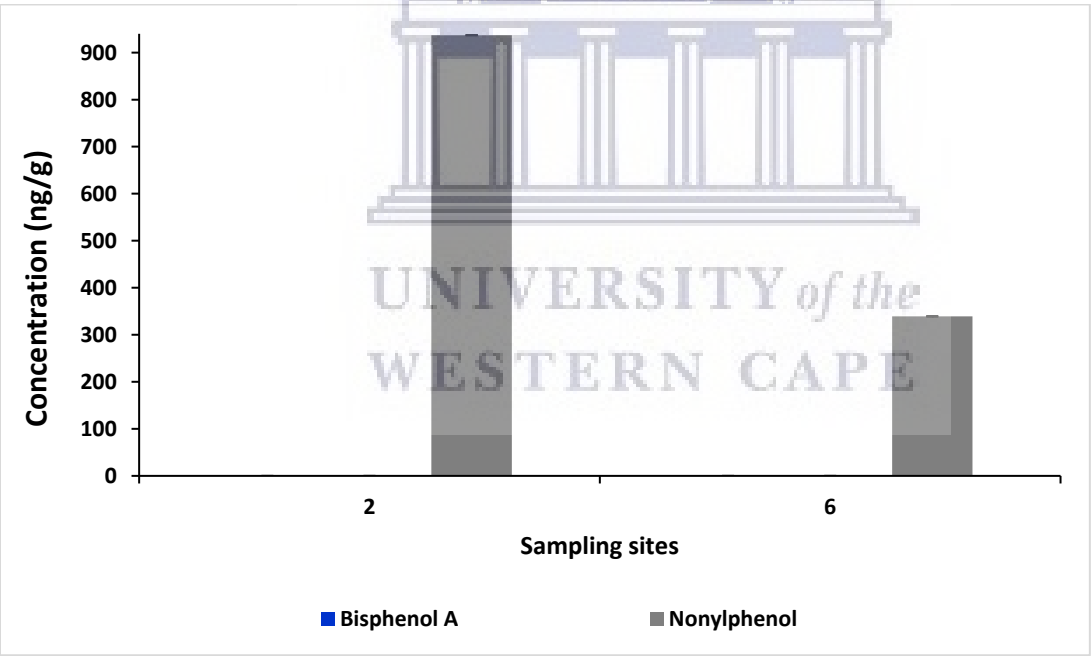


Figure 7. 20: Concentration of industrial chemicals in starfish samples collected from two sites in False Bay

2-nitrophenol was not detected in any of the starfish samples while bisphenol A was below quantification limit in the samples collected from the two sites which is also the case in sea urchin.

However, the concentration of nonylphenol in starfish samples from sites 2 and 6 were 937.02 and 339.10 ng/g respectively, the discussion of the presence on their high values have been presented in the previous sections under seawater, sediment and other marine organisms.

Generally, the abundance of nonylphenol between the different species followed this order: sea snail > sea urchin > limpets > mussel > starfish while bisphenol A followed this order: mussels > limpet > sea snail > sea urchin.

7.1.3.5.3. Pharmaceuticals and personal care product

The Levels of PPCPs in starfish samples from two sites in False Bay are shown in Figure 7.21.

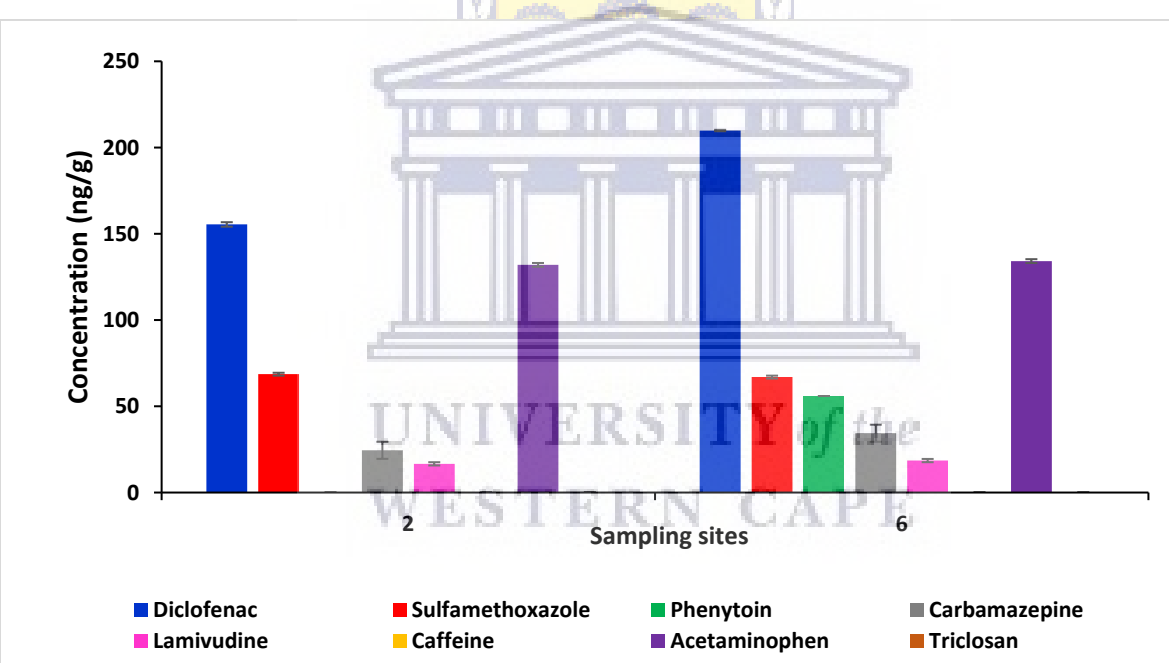


Figure 7. 21: Concentration of PPCPs in starfish samples from two sites in False Bay

Diclofenac had the highest concentration out of pharmaceuticals in the starfish samples followed by acetaminophene and the lowest was lamivudine. Sulfamethoxazole was only detected in sample from site 6. All the pharmaceutical compounds detected in starfish samples were higher in site 6 than 2. Generally, the abundance of PPCPs between the different species followed this order: for diclofenac and lamivudine; limpets > sea snail > sea urchin > mussel > starfish; sulfamethoxazole

follows limpet = sea snail > mussels > sea urchin > starfish; Acetaminophen - sea snail > limpets > mussel > sea urchin > starfish; Carbamazepine - sea snail > limpets = mussel > sea urchin > starfish and phenytoin follows this order: sea snail > limpets > sea urchin > mussel > starfish. Furthermore sea snail and limpet can also be used to monitor PPCPs contamination in an area. Although a study conducted in Italy (Capolupo et al. 2017) reported that sedimentation and sorption process limits the uptake of diclofenac by organisms, this study and other studies (Liu et al. 2015; Lagesson et al. 2016; Cunha et al. 2017; Grabicova et al. 2017; Ali et al. 2018; Huerta et al. 2018) found in literature showed that accumulation of diclofenac could result and be favoured by its hydrophilicity nature. Generally, the concentration and high level of diclofenac has become a great threat to non-target and target organisms as revealed by the continous exposure to diclofenac by species living in the marine environment, and this could represent an increased ecological risk (Mezzelani et al. 2018; Lindim et al. 2019).

7.1.4. Seaweeds

As the world population is growing and challenges of scarcity of food increases as well as seeking alternatives for animal proteins, seaweed should play a major role since it is a source of protein. For centuries seaweed are consumed and used in animal feed in various parts of the world. Recently considering its versatile use in various industries such as cosmetics, food, feed and pharmaceuticals, its exploration and exploitation is expected to increase (Synytsya et al. 2015; Delaney et al. 2016; Buschmann et al. 2017). There is a growing evidence on the health and nutritional importance of the consumption of seaweeds (algal and feed products) (Wells et al. 2017), however various questions about the effect of emerging contaminants that may arise through the consumption of seaweed remain unanswered. In this section, five different types of seaweeds species (*Ulva* sp, *Gelidium pristoides, Bifurcaria brassicac formis, Caulerpa filiformis* and *Aeodes Orbitosa*) were analysed from eight different sites in False Bay area. The abundance

of each species of seaweed varied among the False Bay sites. The results of contaminants in the different seaweed species are summarized in Appendix IV, Table IV.4 in accordance with determination using the experimental protocols described in Chapter 3 and presented in Figures 7.22 – 7.36.

7.1.4.1. *Ulva* sp

Ulva sp is known also by the common name sea lettuce, and is an edible green alga belonging to the family of Ulvaceae. This species of seaweed was found only at, and collected from sites 2, 4 and 7 in May 2018, the results of the contaminants analysed are as follows.

7.1.4.1.1. Perfluorinated Compounds

The result of PFCs in these *Ulva* sp sample in False Bay at three sites are shown in Figure 7.22, and presented in Appendix IV, Table IV.4.

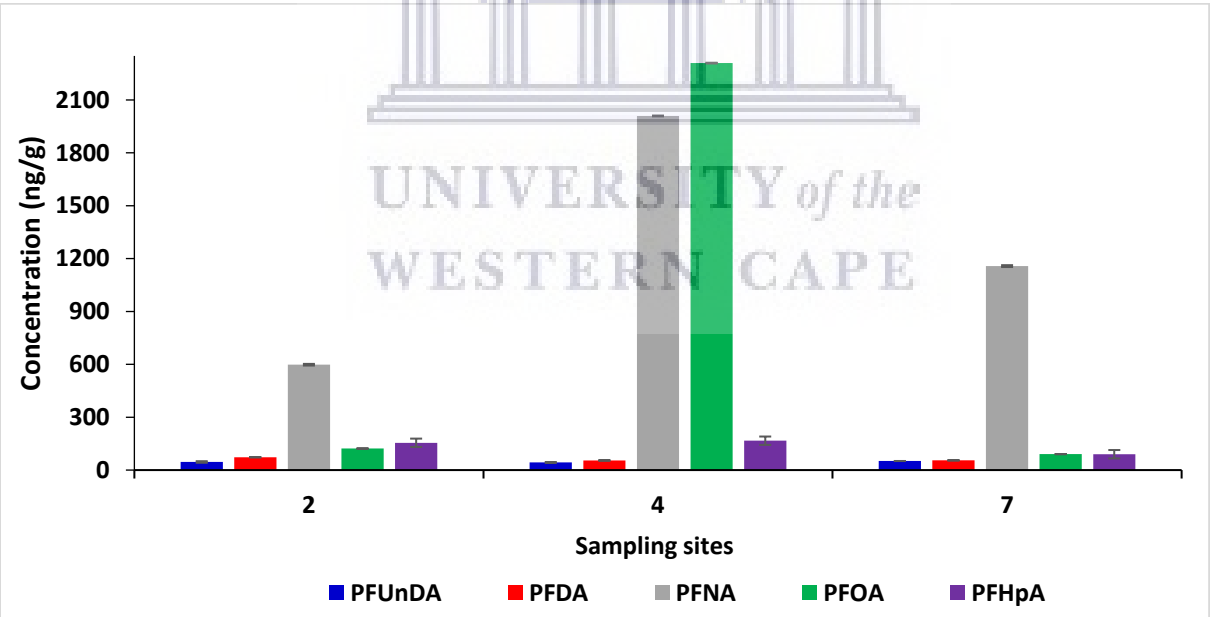


Figure 7. 22: Concentration of PFCs in *Ulva* sp samples from three sites in False Bay

Seaweeds, because of their abundance in several environmental bodies and ability to accumulate pollutants, they are regarded as one of the most suitable organisms for contamination monitoring

in marine environment (Anastasakis et al. 2011). The concentrations of PFCs in *Ulva* sp ranged as follows: PFUnDA (43.19 – 51.40 ng/g dw), PFDA (54.62 – 72.76 ng/g dw), PFNA (597.84 – 2009.24 ng/g dw), PFOA (90.39 – 2309.23 ng/g dw) and PFHpA (90.00 – 166.57 ng/g dw). It can be observed from Figure 7.22 that the highest concentration of PFUnDA was found in samples from site 7, PFDA from site 2, PFNA from site 4, PFHpA and PFOA from site 4. All these perfluorinated compounds were found in all the *Ulva* sp seaweeds samples gathered from all the sites, showing the widespread impact of sewage in False Bay. Overall, PFNA showed the highest concentration across the sites which is also the highest PFCs observed in other environmental matrices. These high concentrations can be attributed to the reasons highlighted in the previous sections about the characteristics of this compound including being stable to biodegradation, the high usage in consumer products and their presence in the effluent and the volume of the effluent discharged into the marine environment. One thing comes to mind, with these high levels in seaweed that attention has been drawn to for medicinal purposes and food, what will be the health impact of using contaminated seaweeds for these purposes? To answer this question, the risk associated with exposure to these compounds among others include increase cancer risk, decrease fertility, and effect of the immune system (Starling et al. 2017; Olsen et al. 2017). The levels of PFCs in these species of seaweed from False Bay were higher than the observed levels in *Ulva* sp samples from Green Point and Camps Bay.

7.1.4.1.2. Industrial chemicals

The levels of analysed industrial chemicals in *Ulva sp* samples are shown in Figure 7.23.

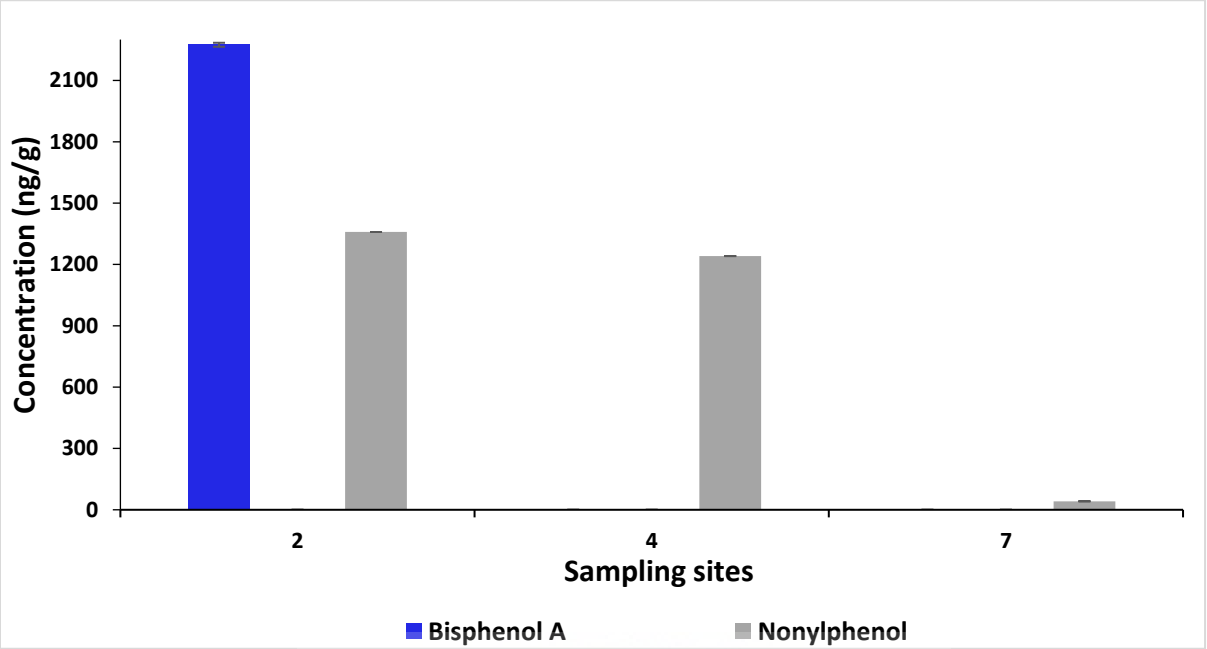


Figure 7. 23: Industrial chemical concentrations in *Ulva* sp samples from three sites in False Bay

2-nitrophenol was not detected in any of the *Ulva* sp samples while high levels of bisphenol A was detected in *Ulva* sp samples from site 2 (2274.54 ng/g). The concentration of nonylphenol ranged from 41.57 – 1358.82 ng/g, with site 2 having the highest concentration in *Ulva* sp (Appendix IV, Table IV.4.). Recall, 2-nitrophenol was not also detected in any sample (all environmental matrices) from all the locations in this study, this may be that the method used for extraction is not suitable or the instrument is not sensitive enough to detect this compound. Nonylphenol was analysed for only False Bay samples, so comparison cannot be done with previous chapters, however, higher levels of bisphenol A was observed in this particular location (False Bay) compared to other locations in previous chapters (Green Point and Camps Bay). Reasons for this observed high levels has been established in previous sections of this chapter (section 7.1.1.3, 7.1.2.3, 7.1.3.1.3, 7.1.3.2.3 and 7.1.3.3.2).

7.1.4.1.3. Pharmaceuticals and personal care product

The levels of analysed pharmaceuticals and personal care product in *Ulva sp* of seaweed samples found at three sites in False Bay are shown in Figure 7.24.

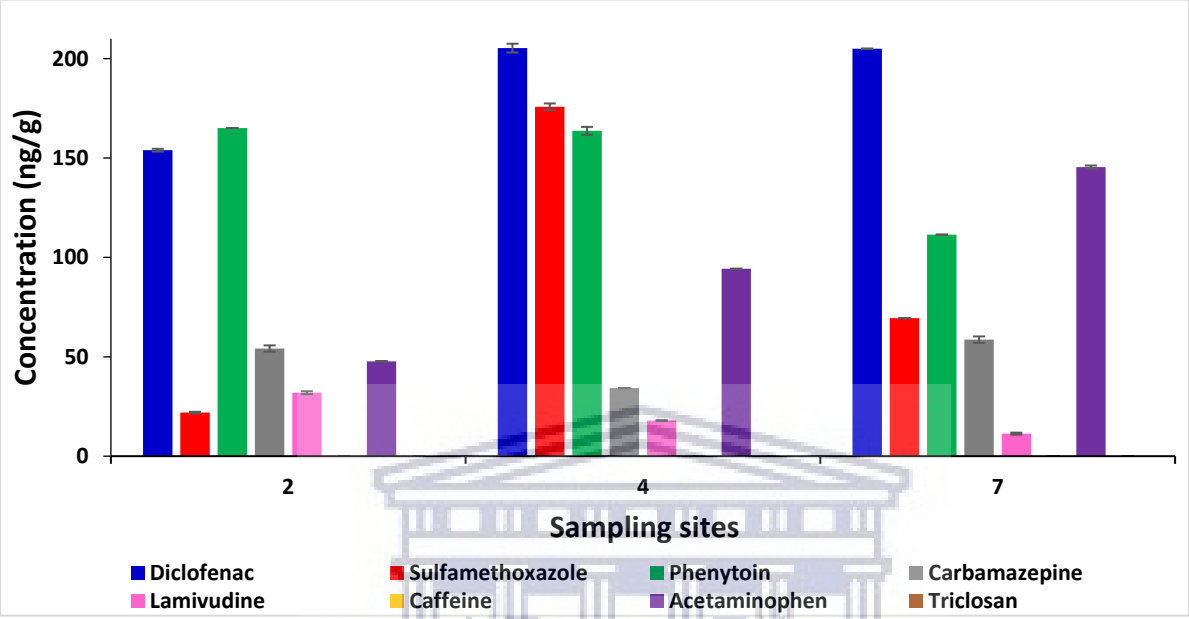


Figure 7. 24: Levels of pharmaceuticals and personal care product in *Ulva* sp samples from three sites in False Bay.

The concentration of pharmaceuticals in this species of seaweed ranged as follows: diclofenac (153.94 – 205.31 ng/g), sulfamethoxazole (21.93 – 175.76 ng/g), phenytoin (111.42 – 165.10 ng/g), carbamazepine (34.24 – 58.65 ng/g), lamivudine (20.92 – 27.40 ng/g) and acetaminophen (122.97 – 129.69 ng/g). The highest concentrations of pharmaceuticals in *Ulva* sp samples were observed as follows diclofenac, sulfamethoxazole found in site 4, phenytoin and lamivudine found in site 2, acetaminophen and carbamazepine found in site 7. From the result it was noticed that diclofenac and phenytoin had the higher concentration in most of the sites compared to the other pharmaceutical compounds. Similar results were found in *Ulva* sp samples from Camps Bay (Chapter 6), while lower level was found in samples from Green Point. Caffeine and triclosan were below the limit of quantification.

7.1.4.2. *Gelidium pristoides*

Gelidium pristoides belongs to the family of Gelidiaceae. Agar extracts from this seaweed are used in the manufacture of gelling agents used in food (jellies, sweet) as well bacteriological culture base (Bolton and Stegenga 2002). This species of seaweed was found and collected from seven False Bay sites (1, 2, 4 5, 6, 7 and 8) in May 2018. The results are presented in Appendix IV, Table IV.4 and in Figures 7.25 – 7.27.

7.1.4.2.1. Perfluorinated compounds

The distribution of PFCs in *Gelidium pristoides* species of seaweed are shown in Figure 7.25 and Appendix IV, Table IV.

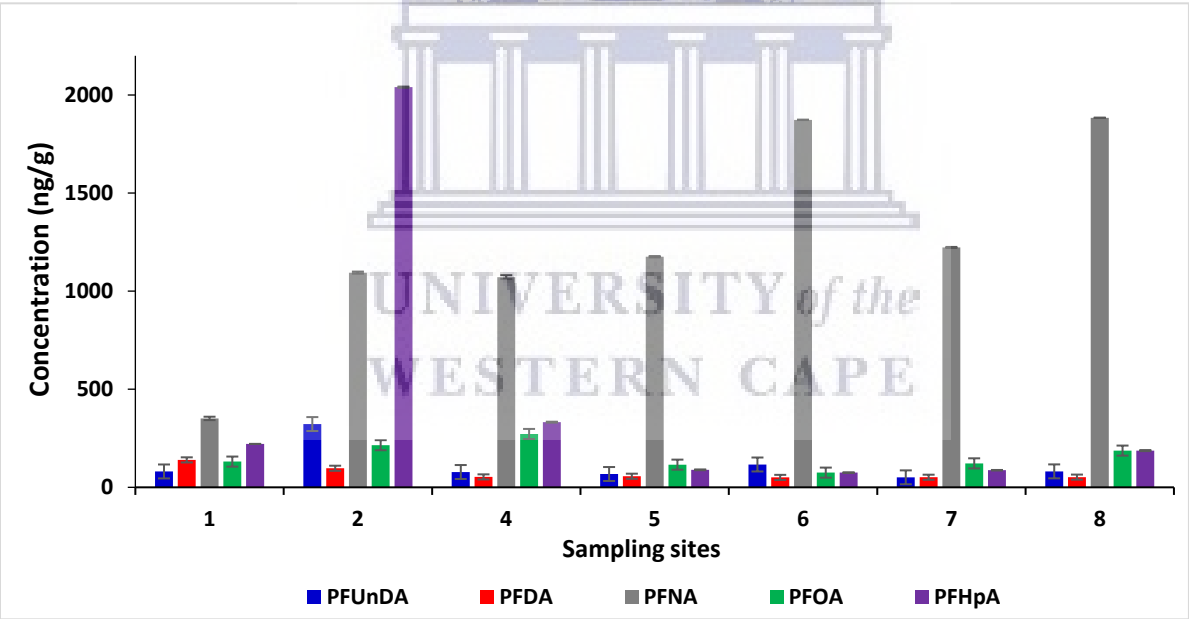


Figure 7. 25: PFCs concentrations in *Gelidium pristoides* from seven sites in False Bay

The concentrations of PFCs ranged as follows: PFUnDA (50.93 – 322.54 ng/g dw), PFDA (13.86 – 97.12 ng/g dw), PFNA (351.29 – 1883.85 ng/g dw), PFOA (115.47 – 271.91 ng/g dw) and PFHpA (87.11– 2040 ng/g dw). It can be observed from Figure 7.25 that the highest concentration

of PFUnDA was found in samples from site 2, PFDA from site 2, PFNA from site 8, PFHpA from site 2 and PFOA from site 4. Interestingly, the level of PFHpA was observed to be exponentially higher in *Gelidium pristoides* species from site 2 compared to other sites, this could be as a result of the less abundance of this specie in this site compared to the other sites. Also, PFNA was found to be the dorminant compound in this species. This therefore compliments and affirm the results obtained in this study on seawater, sediment and marine organisms where higher levels of PFNA were obtained across all the eight sites in False Bay.

7.1.4.2.2. Industrial chemicals

The levels of industrial chemicals in *Gelidium pristoides* seaweed species are presented in Appendix IV, Table IV.4 and Figure 7.26.

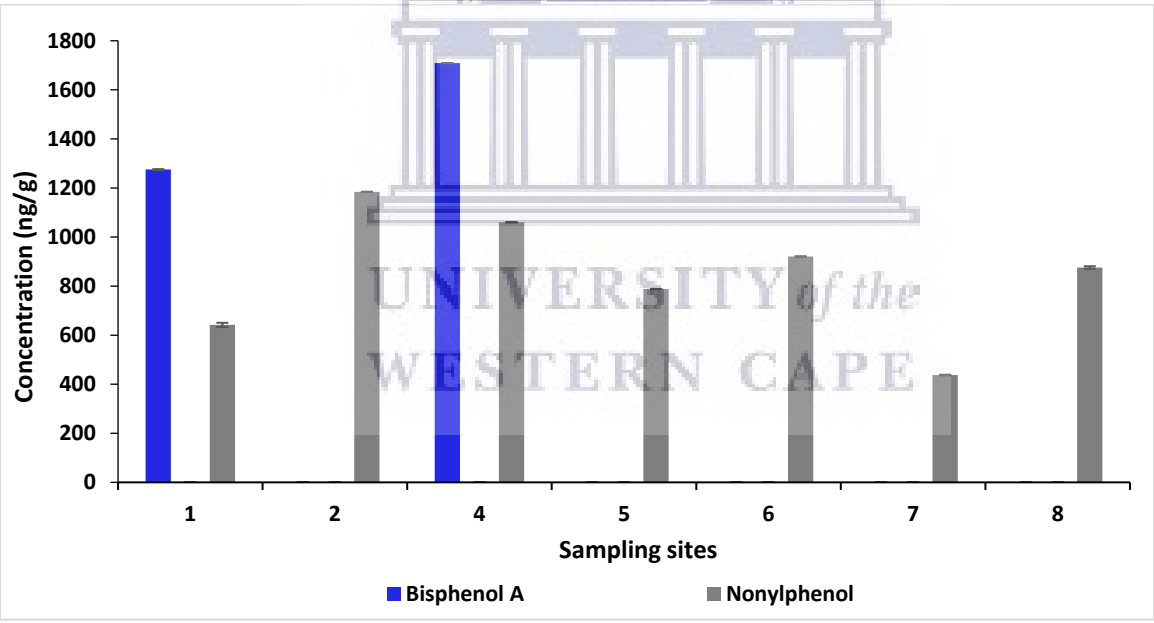


Figure 7. 26: The levels of selected industrial chemicals in *Gelidium pristoides* samples from seven sites in False Bay

2-nitrophenol was not detected in any of the *Gelidium pristoides* samples while bisphenol A was detected in samples from sites 1 and 4 at high concentrations (1275.09 – 1709.02 ng/g respectively). The concentration of nonylphenol ranged from 437.38 – 1184.17 ng/g, with site 2

having the highest concentration thus this compound was found in *Gelidium pristoides* seaweed species collected from all the sites. Again, in this specie as was found in other biota, nonylphenol was found in all sites indicating the usage of finished products made of this compound in most homes around this bay which inturn ends up in sewage plants and eventually into the marine environment.

7.1.4.2.3. Pharmaceuticals and personal care product

The concentrations of PPCPs in this specie of seaweed at seven sites in False Bay are shown in Figure 7.27.

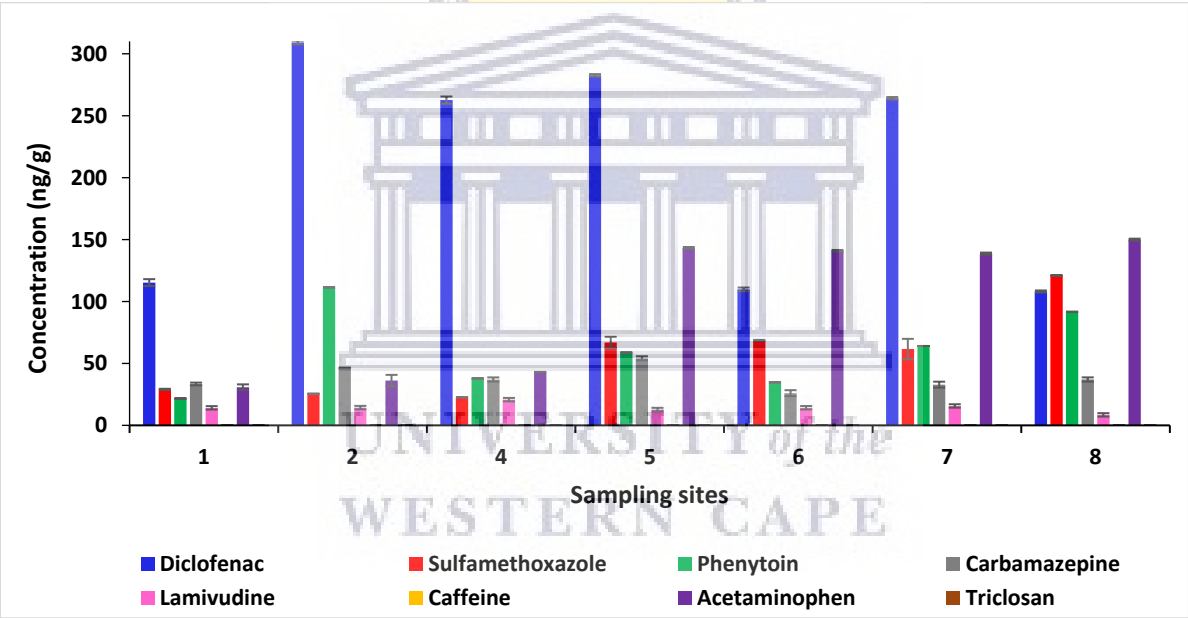


Figure 7. 27: PPCPs concentrations in *Gelidium pristoides* at seven sites in False Bay

The concentration of pharmaceuticals in *Gelidium pristoides* ranged as follows: diclofenac (108.11 – 309.11 ng/g), sulfamethoxazole (22.66 – 66.97 ng/g), phenytoin (21.68 – 111.36 ng/g), carbamazepine (32.85 – 54.16 ng/g), lamivudine (8.46 – 20.77 ng/g) and acetaminophen (30.78 – 149.93 ng/g). The highest concentration of pharmaceuticals in *Gelidium pristoides* sample was observed as follows diclofenac and phenytoin found in site 2, sulfamethoxazole found in site 5 and

lamivudine found in site 4, acetaminophen found in site 8 and carbamazepine found in site 5. From the results it was noticed that diclofenac had the highest concentration of all the pharmaceutical compounds across all the site compared to the other pharmaceutical compounds. Caffeine and triclosan were below the limit of quantification. This result is not a surprise as diclofenac has been observed to be very high in other marine matrices in False Bay samples. Also acetaminophen like diclofenac was observed to be dorminant in this specie and other marine samples. These may be due to the availability of these compounds as drugs on the counter of most pharmaceutical retailing shops and their incomplete metabolism in the body after comsumption. These compounds are excreted as part of human waste and transported into municipal wastewater treatment plants. Since City of Cape Town wastewater treatment plants are not designed to remove these compounds (COCT 2018), they are released back into the environment when reclaimed water are used as irrigation in agriculture, washing of cars etc. and there after deposited in the marine environment through stormwater drains (Brown et al. 1991).

7.1.4.3. *Bifurcaria brassicae formis*

This is a genus of brown algae seaweeds, used in so many edible food dishes and *Bifurcaria brassicae formis* species of seaweed was only found and collected from four sites (1, 2, 3 and 8) in False Bay in May 2018. The results of the selected contaminants analysed in this study are presented in Appendix IV, Table IV.4 as well as Figure 7.28 – 7.30.

7.1.4.3.1. Perfluorinated compounds

The selected PFCs detected in *Bifurcaria brassicae formis* species of seaweed are shown in Figure 7.28 and Appendix IV, Table IV.4.

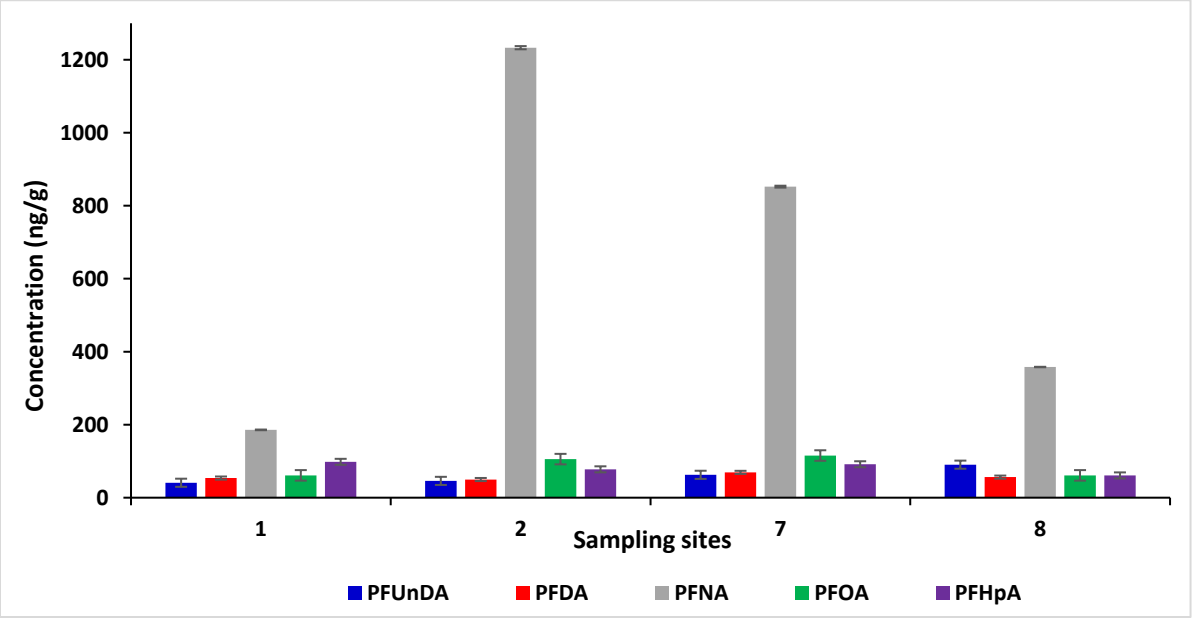


Figure 7. 28: PFCs concentrations in *Bifurcaria brassicae formis* samples from four sites in False Bay

The concentrations of PFCs in *Bifurcaria brassicae formis* ranged as follows: PFUnDA (40.85 – 90.40 ng/g dw), PFDA (49.70 – 69.29 ng/g dw), PFNA (185.76 – 1233.04 ng/g dw), PFOA (61.07 – 115.49 ng/g dw) and PFHpA (61.00 – 91.55 ng/g dw). It can be observed from Figure 7.28 that the highest concentration of PFUnDA was found in samples from site 8, PFDA from site 7, PFNA from site 2, PFHpA from site 1 and PFOA from site 7. Once again these compounds were found in all the sites for *Gelidium pristoide* seaweed. Worthy of note, PFNA was also the dominant contaminant with this specie however, the concentration of this contaminant found in this specie was less than the concentration obtained from *Ulva* sp and *Gelidium pristoide*. The high levels of PFNA compared to the other PFCs in *Gelidium pristoides* could be attributed to the reasons discussed in previous sections. A comparison of these species in relation to their sampling sites and sample locations (False Bay, Camps Bay and Green Point) could not be done as some of these species of seaweed were not found in similar sites/locations.

7.1.4.3.2. Industrial chemicals

The concentration of these class of contaminants in the species of seaweed samples are shown in Figure 7.29 and in Appendix IV, Table IV.4.

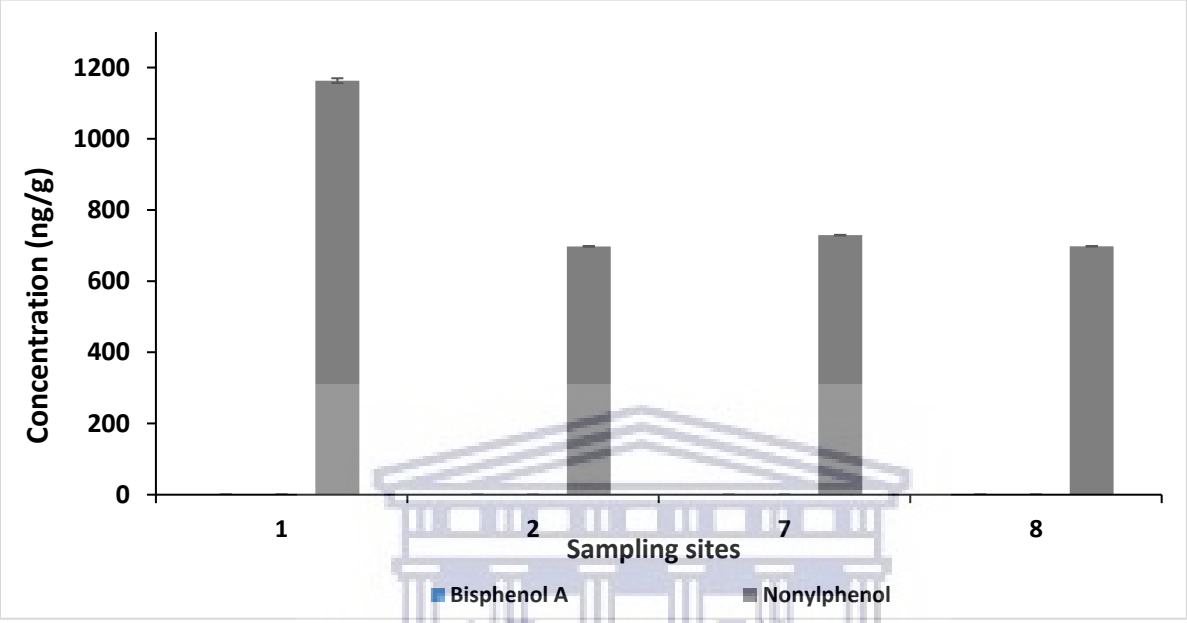


Figure 7. 29: Concentration of industrial chemicals in *Bifurcaria brassicae formis* at four sites in False Bay

2-nitrophenol was not detected while bisphenol A was below limit of quantification in any of the *Bifurcaria brassicae formis* samples, bisphenol A was quantified in some of the other species of seaweed in at least one site as well as in sediment, seawater and marine organisms. The concentration of nonylphenol ranged from 697.82 – 1163.21 ng/g, with site 1 having the highest concentration. Furthermore the concentration of nonylphenol in *Bifurcaria brassicae formis* was the second highest compared to other species of seaweeds. Generally the levels of accumulation of contaminants in the different species of seaweeds varies significantly, this could be as a result of their pattern in the uptake of chemicals and the availability of these chemicals in seawater and sediment. The presence of these chemicals in seaweed shows that these chemicals are present in

the surrounding media even at a low concentration, hence bioaccumulating in the seaweed samples.

7.1.4.3.3. Pharmaceuticals and personal care product

The concentration of this class of contaminants in *Bifurcaria brassicae formis* seaweed samples at four sites in False Bay are shown in Figure 7.30 and in Appendix IV, Table IV.4.

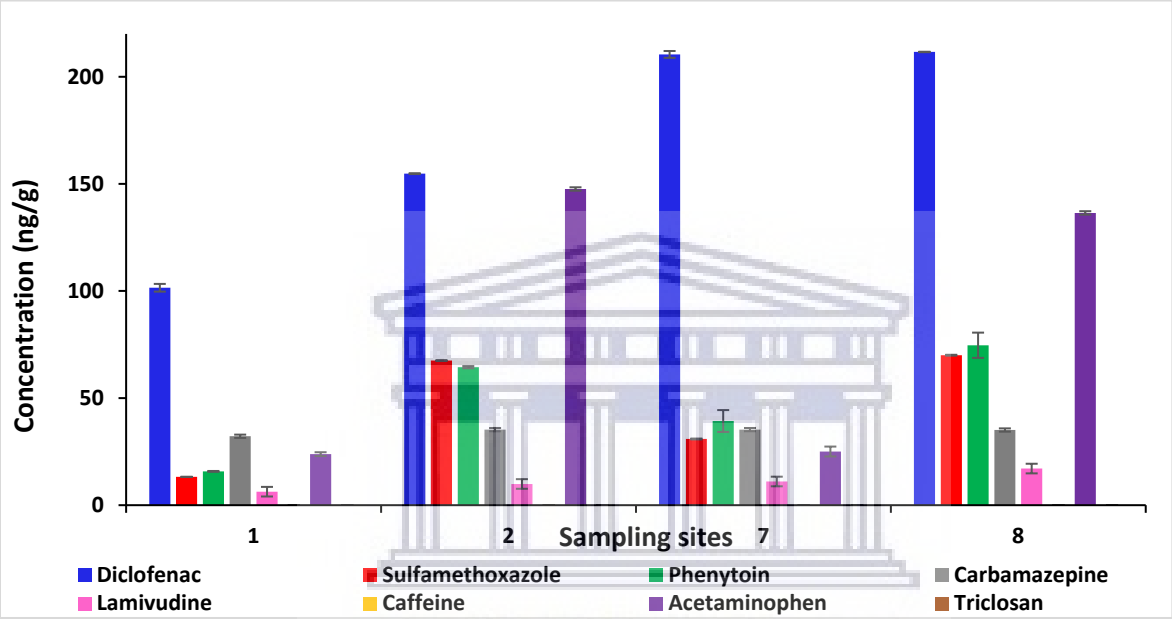


Figure 7. 30: PPCPs concentrations in *Bifurcaria brassicac formis* samples

The concentration of pharmaceuticals in *Bifurcaria brassicae formis* ranged as follows: diclofenac (101.50 – 211.59 ng/g), sulfamethoxazole (13.22 – 70.01 ng/g), phenytoin (15.77 – 74.66 ng/g), carbamazepine (32.18 – 35.28 ng/g), lamivudine (6.30 – 17.10 ng/g) and acetaminophen (23.82 – 147.61 ng/g). The highest concentration of pharmaceuticals in *Bifurcaria brassicac formis* sample was observed as follows diclofenac found in site 2, sulfamethoxazole, lamivudine, acetaminophen and phenytoin found in site 8, and carbamazepine found in site 7. Caffeine and triclosan were below the limit of quantification. From the result it was noticed that diclofenac had the highest concentration in *Bifurcaria brassicae formis* out of the pharmaceuticals, across all the four sites followed by acetaminophen which is similar to the trend found in *Ulva* sp and *Gelidium pristoides*.

The sewage plumes in different parts of the city discharged into the marine environment have their own unique compositions directly connected to lifestyle practices with relation to certain medications (Petrik et al. 2017). These may be responsible for the presence of these pharmaceuticals in the seaweeds samples.

7.1.4.4. *Caulerpa filiformis*

Caulerpa filiformis are bright green seaweed, usually forming grass-like beds in sandy gulleys, a genus of seaweeds in the family Caulerpacea. This species of seaweed was only found and collected from site 5. The reason why some species were not found in some sites has been stated in section 7.1.3.2.3 since anthropogenic activities have been identified to alter the water quality indices of the marine environment theerby leading to the absence of some species along this bay (DWAF 1995; Bredenhand and Samways 2005). Furthermore, a survey of the population of white sharks and whales off the coast of Cape Town has shown the second-lowest incidence of the aquatic mammals in 24 years (Marsili et al. 2016; Bloomberg 2019; Staff 2019) followed by the disappearance of these marine animals. These could also be due to the heavy pollution of chemicals of emerging concern around the Bay from the results observed in this study. The result of analysis are presented in Figures 7.31 – 7.33 as well as data in Appendix IV, Table IV.4.

7.1.4.4.1. Perfluorinated compounds

The concentration of PFCs in *Caulerpa filiformis* samples collected from site 5 are shown in Figure 7.31 and presented in Appendix IV, Table IV.4.

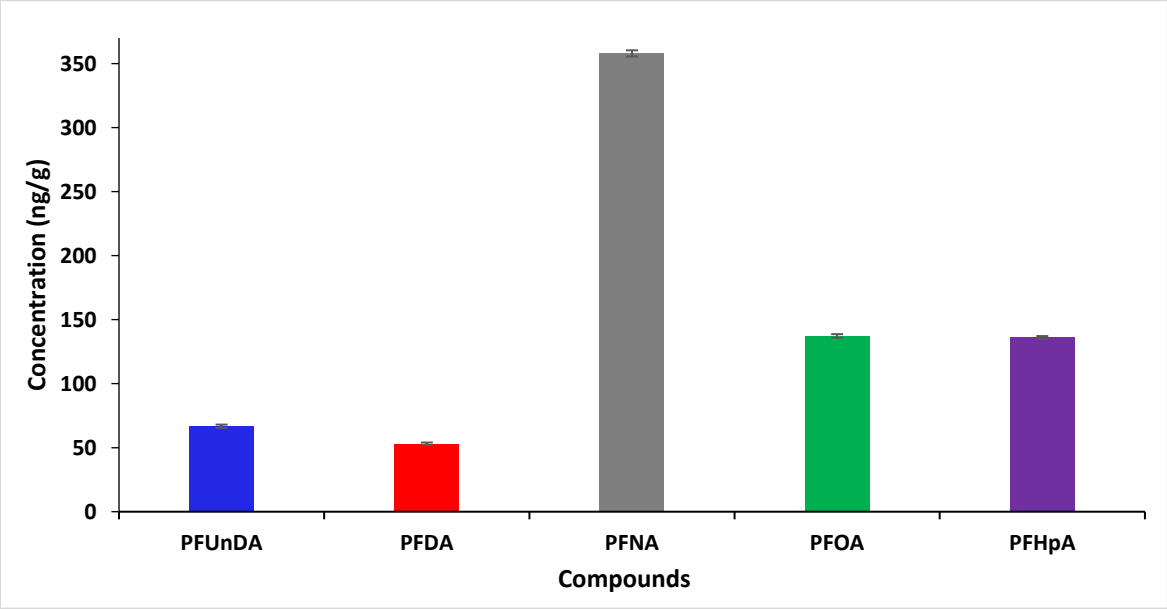


Figure 7. 31: PFCs concentration in *Caulerpa filiformis* from site 5 in False Bay

The concentration of PFNA (357.98 ng/g) was found to be the highest out of the PFCs at site 5 as was the case for all samples at all locations (sediment, marine oraganisms and seaweeds). The possible reason for the high level of PFNA in this species of seaweed as been discussed in several sections of this chapter. All perfluorinated compounds were present in the samples at site 5. The levels of PFCs in *Caulerpa filiformis* seaweed is comparable to the levels in other species of seaweeds from sites in False Bay.

7.1.4.4.2. Industrial chemicals

The levels of industrial chemicals in *Caulerpa filiformis* at site 5 are shown in Figure 7.32 and presented as a function of their mean values in Appendix IV, Table IV.4.

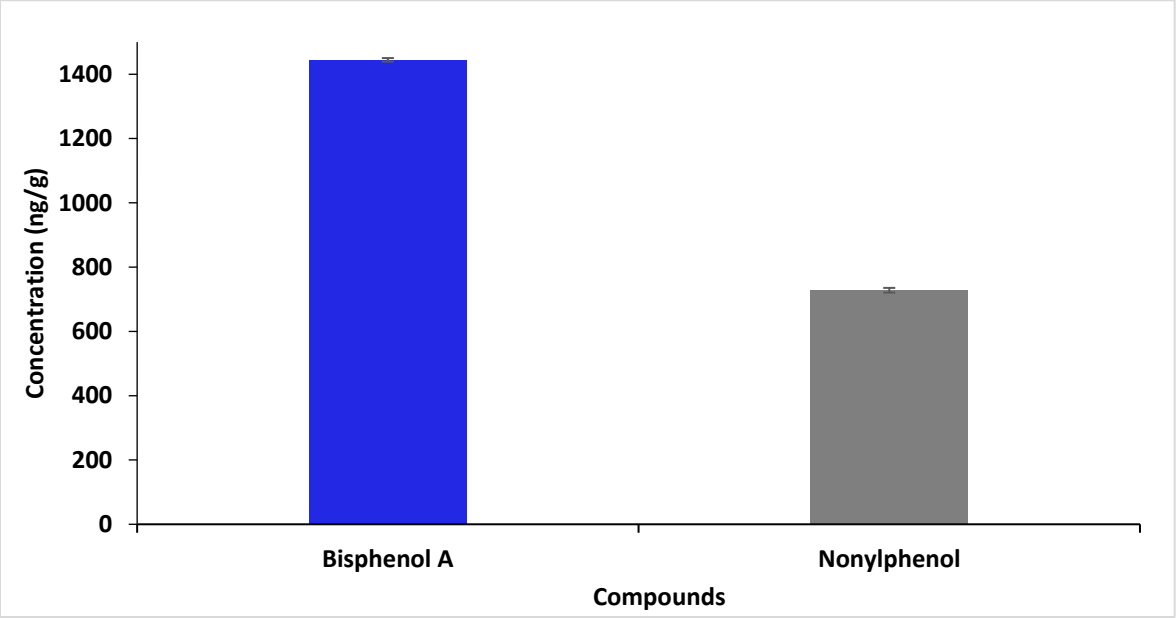


Figure 7. 32: The levels of industrial chemical compounds in *Caulerpa filiformis*

2-nitrophenol was not detected in this sample. The concentration of nonylphenol and bisphenol A were 728.13 and 1444.92 ng/g respectively in *Caulerpa filiformis* at site 5. The detection of these two compounds at high levels in this sample showed that this site and its environs harbour waste generated from humans, living in and around this site that might have been released from the sewage outlet from the popular WWTPs in Strand since these compounds could only result from the finished products of most household items as there are no industrial activities in this location.

7.1.4.4.3. Pharmaceuticals and personal care product

The levels of PPCPs in *Caulerpa filiformis* seaweeds are presented in Figure 7.33.

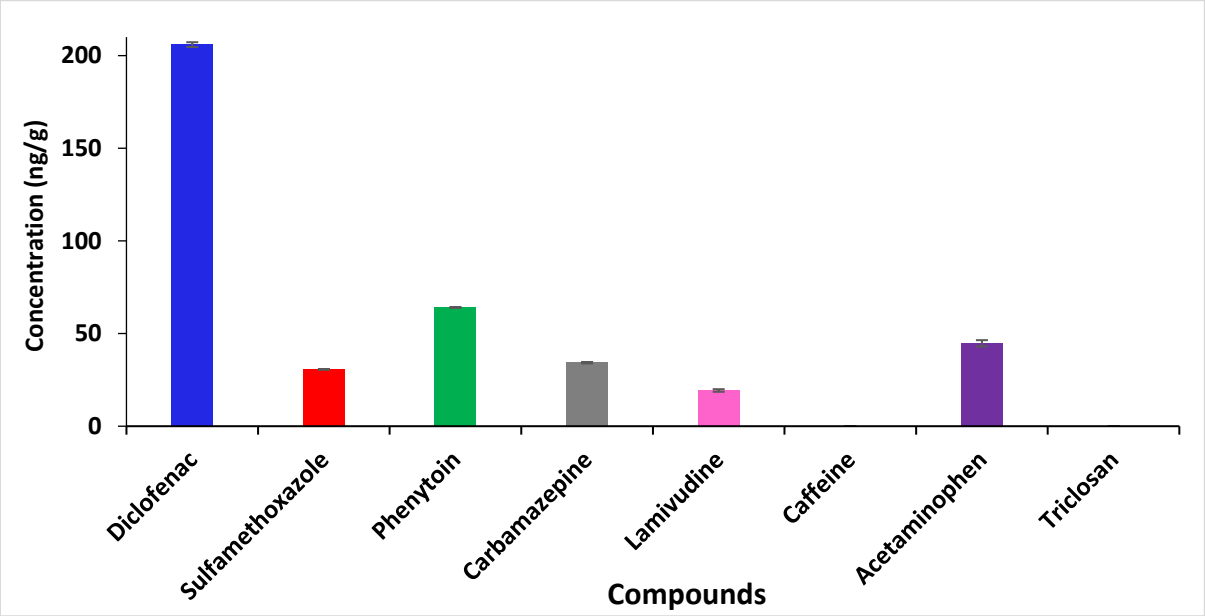


Figure 7. 33: PPCPs concentrations in *Caulerpa filiformis* samples from site 5 in False Bay

The concentration of pharmaceuticals in *Caulerpa filiformis* sampled at site 5 in False Bay ranged between 19.28 – 205.94 ng/g with diclofenac having the highest concentration out of the pharmaceuticals followed by phenytoin. Caffeine and triclosan were below the limits of quantification. The fact that sulfamethoxazole attained a level close to 31 ng/g means that this could result to the development of antibiotic resistance by humans and other marine organisms who consume this seaweed and many others as food since these seaweeds are edible.

7.1.4.5. *Aeodes orbitosa*

Aeodes orbitosa species of seaweed belongs to the family of Halymeniaceae. This edible species of seaweed was only found and collected from two False Bay sites (4 and 8) in May 2018. The results are presented in Appendix IV, Table IV.4 and in Figure 7.34 – 7.36.

7.1.4.5.1. Perfluorinated compounds

The levels of PFCs in *Aeodes orbitosa* seaweed samples are presented in Appendix IV.7 and also shown in Figure 7.36.

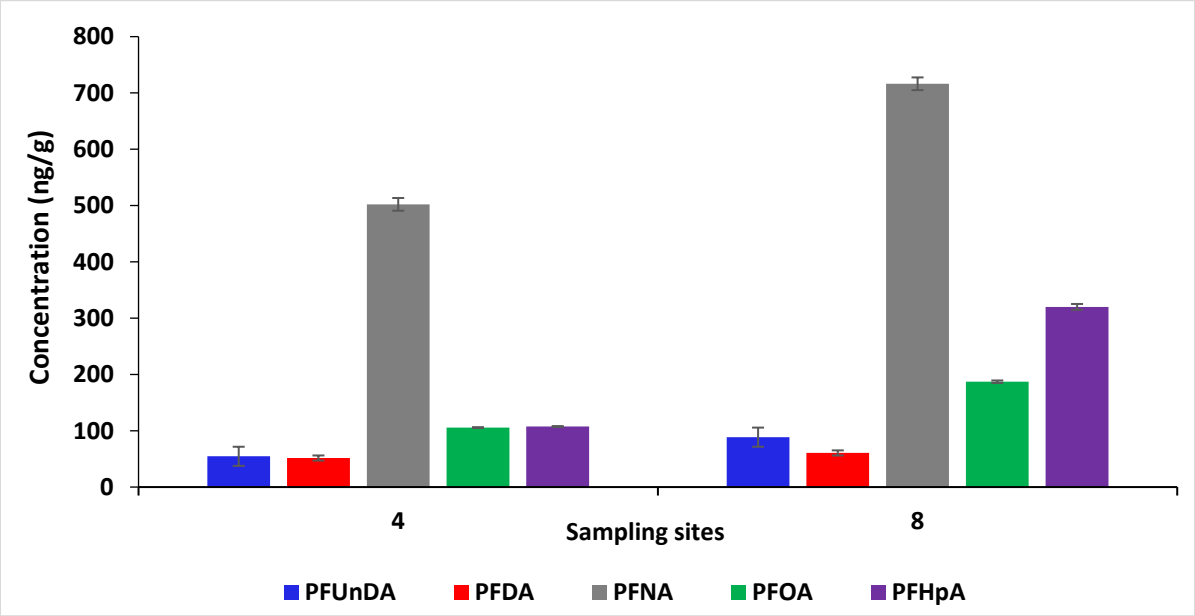


Figure 7. 34: PFCs concentration in *Aeodes orbitosa* seaweed found at site 4 and 8 in False Bay

The concentration of PFNA in *Aeodes orbitosa* was found to be the highest out of the PFCs in samples from both sites (502.15 ng/g and 716.28 ng/g). The concentration of all the PFCs analysed were higher in *Aeodes orbitosa* samples from site 8 compared to site 4, but all the PFCs were present in samples from both sites as in other samples. The levels of PFCs in both samples of *Aeodes orbitosa* are comparable to the levels in other species of seaweeds.

7.1.4.5.2. Industrial chemicals

The concentration of industrial chemical of contaminants in *Aeodes orbitosa* at sites 4 and 8 from False Bay are shown in Figure 7.35 and also presented in Appendix IV, Table IV.4.

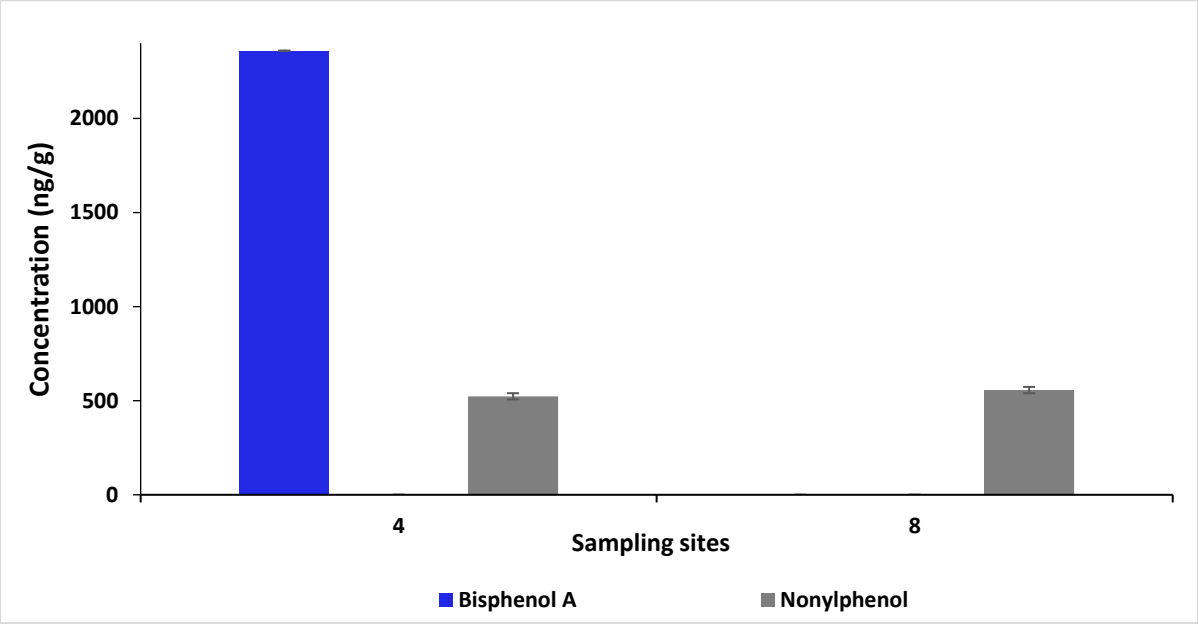


Figure 7. 35: Industrial chemicals concentration in *Aeodes Orbitosa* seaweed from 2 sites in False Bay

2-nitrophenol was not detected in *Aeodes orbitosa* samples at sites 4 and 8 while bisphenol A was detected at high levels in *Aeodes Orbitosa* samples from site 4 (2359.72 ng/g). The concentration of nonylphenol in samples from site 4 and 8 were 523.25 and 556.64 ng/g respectively. Interestingly all marine organisms (limpets and mussels) and two out of three seaweeds samples sampled and collected from site 4 were found to accumulate bisphenol A at a very high concentration. This could be due to the activies in this location as the tidal pool and beach of Monwabisi (site 4) are very important areas for recreational activities (bathing, surf angling, beach activities and recreational fishing) for Khayelisha people and its environs (Laird 2017) as well as the population growth of this location including the impact of tourism in this areas. Also, according to a new article, the Monwabisi beach is littered with a lot of plastics (Sukaina 2019) in which bisphenol A is a major component.

7.1.4.5.3. Pharmaceuticals and personal care product

The levels of PPCPs in *Aeodes orbitosa* species of seaweed from sites 4 and 8 in False Bay are presented in Figure 7.36.

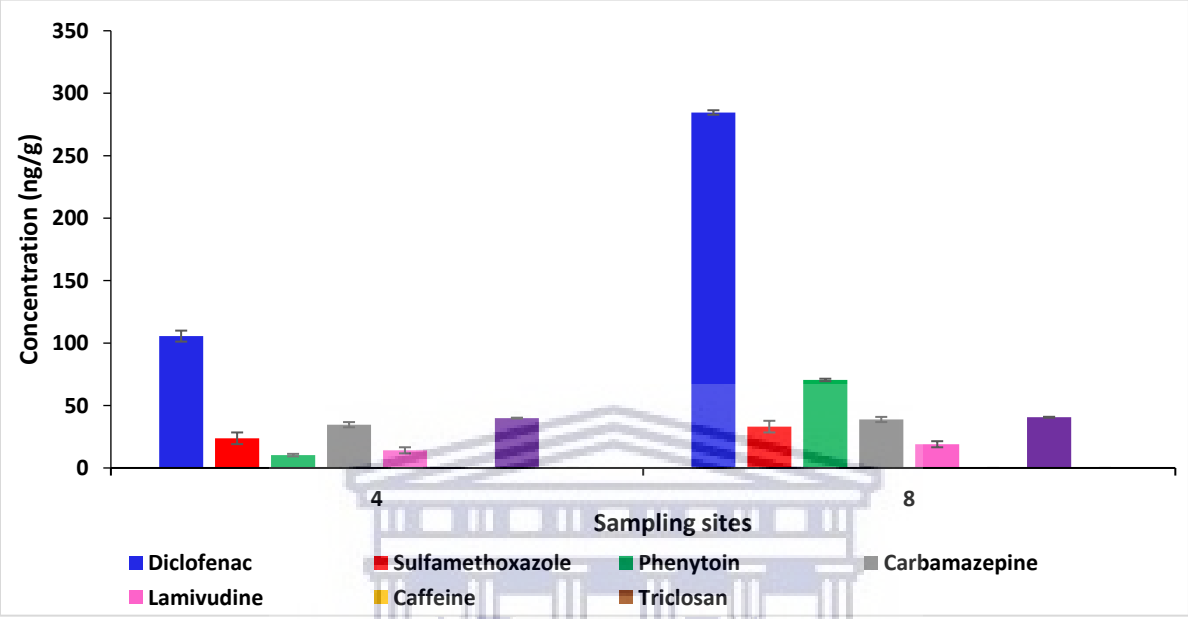


Figure 7. 36: PPCPs concentration in seaweed samples from sites 4 and 8 in False Bay

From the results, diclofenac had the highest concentration of the pharmaceuticals tested in *Aeodes orbitosa* sampled at sites 4 and 8 in False Bay, followed by acetaminophen as this was the case of other species of seaweeds collected from these two sites. All the pharmaceutical compounds detected in the samples were higher in site 8 than in samples from site 4. The levels of pharmaceuticals found in *Aeodes orbitosa* seaweed are comparable to the levels found in other species of seaweeds. Caffeine and triclosan were below the limit of quantification.

Overall, this study showed that perfluorinated compounds are present in all the seaweed samples with PFNA been the dominant compound. Also, diclofenac was observed to be high in level in the seaweed samples among the pharmaceuticals studied from False Bay. Nonephenol was detected in all the samples compared to bisphenol which was predominants in seaweeds from site 4. The

result of the level of these contaminants in these species of seaweed show that the seaweeds in False Bay are contaminated.

The question is whether the levels of contamination of these seaweeds are comparable to those found in marine organisms in this study as attentions have closely been drawn to contamination in marine organisms (e.g bivalves) thereby neglecting the potential pollution and by extention the harmful effect of seaweed species. It is evident that from this study, the levels of contamination of these seaweeds can be compared to those found in marine organisms. Given that the utilization of seaweeds is now on the increase for food and medicinal purposes (Chen et al. 2018), knowledge of the contamination of this type of marine biota should be of great concern forthwith as these seaweeds may cause harm to both humans and marine animals when consumed. Also, regular surveys on all these pollutants in seaweeds and the estimation of their health risk should be considered to protect consumers.

Comparing the levels found in this study with other studies from literature, it was found that the concentration of PFCs in bivalve, gastropod and starfish collected from the west coast of Korea were quite lower than the concentration found in samples from False Bay (PFHpA: 0.26-2.7, 0.12-3.4 and 0.47-0.60 ng/g, PFOA: 0.08-10.8, 0.10-7.8 and 0.06-1.9 ng/g, PFDA:0.11-0.98, 0.11-4.2 and 0.10 ng/g, PFNA: 0.16-8.2, 0.19-4.6 ng/g and <DL, and PFUnDA: 0.26-3.1, 0.31-2.5 and <DL-0.35 ng/g,) (Hong et al. 2015) similarly the concentration of PFCs in bivalve and gastropod collected from the west coast of Korea (Naile et al. 2013b) as well as in zoobenthos (snail and bivalve) (nd – 0.22 ng/g) collected in Taihu China (Xu et al. 2014) and snail (<0.11 – 1.1 ng/g) from Ariake Sea, Japan (Kobayashi et al. 2018) and Vietnam (< 0.06 – 0.04 ng/g) (Lam et al. 2017) were quite lower than the concentration found in this study. Also, the level found in biological samples (bivalve and snails) (nd- 2.26 ng/ g) from Northern Bohai Sea (Wang et al. 2011a) were

lower compared to the levels found in this study but similar to the levels found in samples from Green Point.

The concentration of diclofenac (0.5 – 4.5 ng/g) found in mussels from Portuguese coast (Cunha et al. 2017), carbamazepine (1.5 – 3.5 ng/g) in mussels from Mediterranean sea (Martínez Bueno et al. 2013), acetaminophen (< LOD) and diclofenac (<LOD – 16.11 ng/g) found in mussels from Adriatic coast (Mezzelani et al. 2016), carbamazepine in algae from Saudi Arabian coastal water (nd – 1.7), (Ali et al. 2018), bisphenol A, carbamazepine, caffeine, diclofenac, sulfamethoxazole and triclosan in mussel are <0.4-63, <0.003-0.05, <0.1-0.8, nd, <0.1-3.0 and nd respectively (Bayen et al. 2016), as well as acetaminophen (<1 ng/g) and carbamazepine (<2 ng/g) in sea urchin from Portuguese Atlantic coast (Rocha et al. 2018) were lower compared the levels found in this study. The concentration of acetaminophen 115 ng/g in *Mytilus edulis* from Belgian coast (Wille et al. 2011), caffeine reported in algae from Saudi Arabian coastal water (2.2- 41.2 ng/g) (Ali et al. 2018) were higher compared the this study.

However, the difference in the concentrations of the compounds reported in this study and the previously mentioned studies are most probably caused by local specific differences in the PFCs, PPCP and industrial chemical release patterns from primary sources, the resulting water concentrations as well as biota sample species and age. The various profiles of pollution between sites indicated that emerging contaminants levels vary with geographical regions globally. However, the results from the False Bay study generally show a much higher concentration of numerous compounds in different biota and seaweeds than the cited studies. The fact that the concentrations of these contaminants were observed to be preferentially higher in this study compared to some studies in literature indicates that if no urgent action is put in place to restrict the discharge of sewage containing these contaminants into the marine environment, there will be grievious consequence of the side effects of these contaminants to the marine organisms and

humans living around this bay and consuming these seafood. Also, strict measures needs to be set as huge tendencies of these contaminants getting to the top of the food chain as well as bioaccumulating if the release of sewage from various wastewater treatment plants around this study site is not halted. Furthermore, the populace needs to be sensitized on the need to continuously protect the marine environment from harzadous chemicals by a way of the modification and changes in the life style of humans living around this bay in other to avert the continuous pollution of this environment.

7.1.5. Bioaccumulation of perfluorinated compounds, pharmaceuticals and personal care products, industrial chemicals in organisms sampled in False Bay

Bioaccumulation is the continuous accumulation of substances, such as PPCPs, or other chemicals in an organism from the ambient environment. Bioaccumulation occurs when an organism absorbs a substance at a rate faster than that at which the substance is lost by catabolism and excretion (Borgå 2013; Wang 2016; Bindschedler et al. 2017).

The bioaccumulation factor (BAFs) is the ratio of the contaminant concentration in the aquatic organism tissue and plant (C_{biota}) to the contaminant concentration ratio in water (C_w). It is an important issue in the environmental assessment of contaminants (Vetter 2012). These values are calculated to evaluate the bioaccumulation of the contaminants analysed in aquatic organisms (Kinney et al. 2008). When BAF in aquatic organisms is greater than 5000 L/kg the compounds or chemicals are said to be ‘‘bioaccumulative’’ and it is ‘‘potentially bioaccumulative’’ if the BAF is in the range from 2000 L/kg to 5000 L/kg in aquatic organisms (Arnot and Gobas 2006; Na et al. 2013). In the present study, compounds that were below quantification limit (nonylphenol, triclosan and caffeine) in water and not detected in any of the environmental matrices (2-nitrophenol) were not evaluated. Based on the concentrations of compounds measured in seawater and organisms, the observed BAFs of the most widespread compounds were calculated for five

different marine species from the different sites along False Bay (Table 7.3). All the compounds detected in different species of organisms collected from individual site were bioaccumulative because their BAF values were greater than 5000 L/kg. Furthermore, in view of the long term and large scale usage of the compounds, their impacts on these organisms, as well as humans and the environment could not be neglected.

Table 7. 3: Bioaccumulation factors (dry weight) for marine species

		Limpet (L/kg)								Mussels (L/kg)				
	Log kow	1	2	3	4	5	6	7	8	2	4	6	7	8
PFUnDA	10.42	38129.78	28897.68	26035.40	13157.56	78777.77	20530.74	15433.83	20265.08	25007.53	17866.52	37083.07	16865.55	29989.42
PFDA	9.53	29118.78	18858.55	73296.15	39664.46	19494.11	18521.94	7206.165	22468.69	25843.20	39937.00	23470.33	6861.930	23178.59
PFNA	8.64	34964.91	296947.9	221254.9	342259.7	62803.44	293511.2	333637.3	42781.13	180830.3	253003.9	264057.6	74369.56	151093.2
PFOA	7.75	9979.666	46953.99	99429.38	25653.46	10963.49	40384.06	62902.37	11009.95	27452.04	16178.59	29386.87	19213.95	13323.40
PFHpA	6.86	11659.63	16969.70	82918.04	41335.27	16731.92	28913.41	37275.22	14381.00	16437.90	22815.52	12925.79	12568.81	15384.33
BPA	3.43	0	0	0	16920.80	0	0	0	0	0	39095.17	0	0	0
DCF	4.06	130895.5	107112.4	55936.27	283731.8	208447.6	105947.4	173036.9	222002.3	26644.62	84485.00	43122.5	19845.18	44398.79
SMX	1.31	15933.55	89443.59	191808.6	238925.0	56803.45	45493.95	69456.33	20312.49	64765.54	520289.4	33119.27	134781.3	14882.26
PHE	2.52	158346.4	194226.4	366985.8	890839.6	27087.27	46761.60	59495.54	45215.50	101008.0	601285.4	48397.46	52175.06	33488.05
CAR	2.67	32104.25	33540.18	112001.8	49520.99	21190.88	22445.23	20339.42	17302.92	27432.58	55463.17	21298.18	23493.79	25627.19
LA	-0.71	43915.14	136519.4	109044.8	123433.6	48375.00	48579.93	68244.91	48302.30	54841.49	121612.5	32760.01	50408.43	45704.83
ACT	1.10	22864.64	60317.6	116423.0	36319.05	39328.35	29732.23	34341.28	14140.85	44023.81	90009.18	36988.24	48388.24	42601.38

	Sea snail (L/kg)					Sea urchin (L/kg)			Starfish (L/kg)		
	1	5	6	7	8	2	6	7	8	2	6
PFUnDA	58884.25	28185.59	25476.48	15659.08	11190.28	29224.69	13219.55	27432.87	24636.60	12694.63	11693.81
PFDA	22741.59	24142.96	15340.50	7921.069	22707.60	21092.83	19888.35	7704.122	23791.76	18867.29	14899.91
PFNA	99470.16	330670.7	448211.3	129669.4	103980.1	106977.3	249921.1	198944.5	122109.6	62467.57	163505.4
PFOA	7989.748	19068.31	19616.22	20694.26	19351.35	13413.9	19790.63	23918.36	19514.96	16877.05	28648.79
PFHpA	12403.83	12691.80	20981.06	22762.59	9401.705	9863.163	13117.38	15533.19	14302.89	12409.6	18988.63
DCF	70312.14	66720.66	70499.46	66196.21	45950.33	43594.38	53857.66	30380.95	56886.06	59553.93	61012.32
SMX	32283.25	28817.28	37748.85	110525.3	36008.41	67972.04	28530.30	118515.3	15056.28	66621.28	28131.69
PHE	97762.43	32262.88	92944.30	72681.89	23938.13	0	59471.16	62179.63	63196.51	0	93281.1
CAR	43475.53	18028.72	22165.87	22919.05	28805.87	40254.74	27194.86	17170.05	28115.71	25783.83	25099.12
LA	65086.50	71162.10	52477.96	75208.20	81379.83	88373.15	47545.37	74214.81	82698.94	53673.1	42143.21
ACT	23326.97	117451.2	76684.01	94338.15	95602.31	120279.9	84621.16	101321.2	99171.55	124519.7	90665.56

In limpet samples, it was observed that BAF of PFUnDA was the highest in sample from site 5 and lowest in samples from site 4. PFDA had the highest BAF value in samples from site 3 and lowest value in site 7 samples. PFNA bioacumulated most in site 4 samples and least in site 1 samples while the bioaccumulation of PFOA was found to be the highest in site 3 samples and lowest in site 1 samples. Samples from site 3 had the highest BAF value of PFHpA and site 1 had the lowest BAF value. Although, all the PFCs bioaccumulated in this specie, overall the bioaccumulation of PFNA was the highest across all the sites. Bisphenol bioaccumulated in limpet sample from site 4 as it was only quantified in this sample. Diclofenac (DCF), sulfamethoxazole (SMX) and phenytoin (PHE) bioaccumulated the highest in samples from 4 and lowest in site 3 samples, site 1 samples and site 5 respectively. Carbamazepine had the highest BAF value in samples from site 3 and lowest in samples from site 8 while lamivudine bioaccumulated the highest in site 2 samples and lowest in site 1 samples. Site 3 had the highest BAF of acetaminophen BAF value and site 8 had the lowest.

The bioaccumulation in mussel samples is as follows, PFUnDA bioaccumulated most in samples from site 6 and least in samples from site 7; PFDA bioaccumulated most in samples from sites 4 and least in site 7; the highest BAF value of PFNA was found in samples from sites 6 and lowest from site 7 samples; samples from site 6 bioaccumulated PFOA the most while samples from site 8; PFHpA was found to bioaccumulate most in site 4 samples and least in site 7 samples. PFCs with seven or more carbon atom backbones are known to be bioaccumulative (Ahrens et al. 2011; Bertin et al. 2014; Wilkinson et al. 2018; Martín et al. 2019). The result obtained for mussel samples is in agreement with previously published studies with seven or more carbon chains. Bisphenol A bioaccumulated in samples from site 4; DCF had highest BAF value in samples from site 4 and lowest in samples from site 7. SMX and PHE also had the highest BAF values in samples

from site 4 while lowest value in samples from site 8; CAR, LA and ACT had highest BAF value in samples from site 4 and lowest in samples from site 6.

PFCs bioaccumulation in sea snail across the five sites in False Bay follows thus: PFUnDA bioaccummulated most in samples from site 1 and least in samples from site 8; PFDA had the highest bioaccumulation in samples from site 5 and lowest from site 7 samples; PFOA had the highest BAF value in samples from site 7 and lowest from site 1 sample; samples from site 6 bioaccumulated PFNA most while samples from site 1 bioaccumulated the least; and PFHpA bioaccumulated most in samples from site 7 and least in samples from site 8. Across all the sites the BAF values of PFNA were the highest among the PCFs. This was not suprising as PFNA was found to have the highest concentration in all the sites. The highest bioaccumulation of DCF was observed in samples from site 6 and lowest in samples from site 8, SMX had the highest bioaccumulation in samples from site 7 and lowest bioaccumulation in samples from site 5. Samples from site 1 bioaccumulated PHE and CAR the most while samples from site 8 bioaccumulated the least, LA had the highest BAF values in samples from site 8 and the lowest in samples from site 6. Samples from site 5 had the highest BAF values of ACT and samples from site 6 had the lowest BAF values of ACT.

The bioaccumulation of contaminants in sea urchin samples from four sites in False Bay were as follows: PFUnDA was found to bioaccumulate the most in site 2 samples and least bioaccumulation was found in samples from site 6 while PFDA had the highest bioaccumulation in samples from site 8 and lowest bioaccumulation in samples from site 7; PFNA and PFHpA bioaccumulated most in samples from site 6 and least in samples from site 2; PFOA was observed to have the highest bioaccumulation in samples from site 7 and lowest in site 2 samples. DCF bioaccumulated most in site 8 sample and least in site 7 samples while SMX bioaccumulated most

in sample from site 8 and least in samples from site 7; the highest bioaccumulation observed for PHE was in sample from site 8 while the lowest in site 6 samples while CAR bioaccumulated most in samples from site 2 and least in samples from site 7; bioaccumulation of LA and ACT was found to be highest in samples from site 2 and lowest in samples from site 6.

In starfish, the bioaccumulation in samples from the two sites in False Bay is as follows: PFUnDA, PFDA, ACT, LA, CAR, SMX bioaccumulated the most in site 2 samples while PFNA, PFOA, PFHpA, DCF bioaccumulated the most in site 6 samples.

Generally, in this study, marine organisms were found to bioaccumulate pharmaceuticals more than perfluorinated compounds across all the sampling sites. This indicates that pharmaceuticals usage by humans around these sites and their release into the oceanic environment is high as well as differences in capacities of the organisms to accumulate and metabolise these compounds. Similarly, limpets were observed to bioaccumulate the most, among all the species reported in this chapter across the sites. This is as a result of the feeding guild, food sources, metabolism, uptake and excretion rates of the organisms (Naile et al. 2010, 2013a). The high accumulation of contaminants in limpets coupled with the fact that they were the only specie found across all the sites in this bay indicates that they could serve as the ideal sentinel species in monitoring pollution in False Bay.

Furthermore, the bioaccumulation of chemical compounds is influenced by different factors including octanol–water partition coefficient (Kow) and lipid solubility. Compounds with logKow > 1 tend to accumulate in organisms (Kümmerer 2009). In this study (Table 7.3), the log Kow of all the contaminants except for lamivudine were greater than 1, this means that with their high log Kow values, the compounds tend to accumulate in organisms. This is in agreement with the report

of Kümmerer (2009) hence complimenting the previously reported result that these compounds are bioaccumulating in the marine organisms in False Bay.

Finally, contaminants seems to be differentially bioaccumulative in different marine organisms, showing that species-specific BAF classification system may be required. In addition, the most likely reason for the high levels of contaminants in marine organisms (zoobenthos) in False Bay is that exposure via contact with contaminated sediment can contribute to compounds accumulation in zoobenthos. However, in view of the long term and large scale use of pharmaceuticlas and products with PFCs, their impact on organisms and environment could not be neglected.

7.2. Ecological risk assessment

Previous studies have reported that contaminants in the aquatic environment may cause adverse ecological and health impacts (Hernando et al., 2006; Jiang et al., 2011). In the present study, PPCPs, PFCs, and industrial chemicals were frequently found in samples collected from False Bay. Therefore, it is necessary to estimate the ecological risk of these chemical compounds. In this section, the risk of PPCPs, PFCs and industrial chemicals were evaluated using Equations 3.4 and 3.5 in Chapter 3 in seawater samples from sites 1 to 8 of False Bay marine environment. The risk quotient method was used to assess the impact of these emerging contaminants and the results are presented in Figures 7.37 and 7.38 for acute risk and chronic risk. The concentrations of contaminants detected in the seawater samples were divided by an ecotoxicity endpoint values (LC50 or EC50 and NOEC) previously reported in literature (Tables 3.3 and 3.4). For acute risk, if the RQ < 0.5, it shows no high acute risk concern while for chronic risk if RQ < 1.0 it shows no chronic risk concern (US EPA 2016a). When selected contaminants for particular species of the

marine ecosystem at three environmental levels (e.g. algae, invertebrate and fish) are combined toxicologically, this is said to be toxicity assessment.

All samples below detection and quantification were treated as zeros for this evaluation. According to the results obtained for the three levels of aquatic life, for acute risk (Figure 7.37): for algae, all compounds pose low risk (RQ < 0.5) at all the eight sites with the exception of sulfamethoxazole (SMX) in sites 1, 2, 5, 6 and 8 that showed high risk (RQ > 0.5) and bisphenol A (BPA) in sites 4 and 7 that showed high risk. Regarding invertebrates, all compounds pose low risk (RQ < 0.5) except for bisphenol A which poses high risk. While for fish all compounds pose low risk. Figure 7.37 demostrates the risks that is posed from the compounds in all the sites.

Similarly for chronic risk (Figure 7.38), in algae all contaminants pose low risk except for sulfamethoxazole (SMX) which pose high risk (RQ > 1) at all the eight sites in False Bay. In invertebrate, PFNA, sulfamethozaxole, diclofenac and carbamazepine poses high risk across all the eight sites and other compounds pose low risk. Of a particular importance is the antibiotics (sulfamethozaxole), which can disrupt many vital ecosystem processes in the marine environment. Report has it that that any kind of antibiotic can become harmful to non-targeted organisms, or to pose a potential ecological risk to marine organisms considering the recent usage patterns (Carvalho and Santos 2016; Szymańska et al. 2019) as well as the spread of antibiotic resistance gene among microorganism ecosystem that may pose health threats to human and animals. Finally in fish, diclofenac poses high risk across all the eight sites while other compounds pose low risk. Studies have shown that diclofenac could have influence on the lipid peroxidation and cause tissue damage in organisms (Schmidt et al. 2011; Praskova et al. 2014).

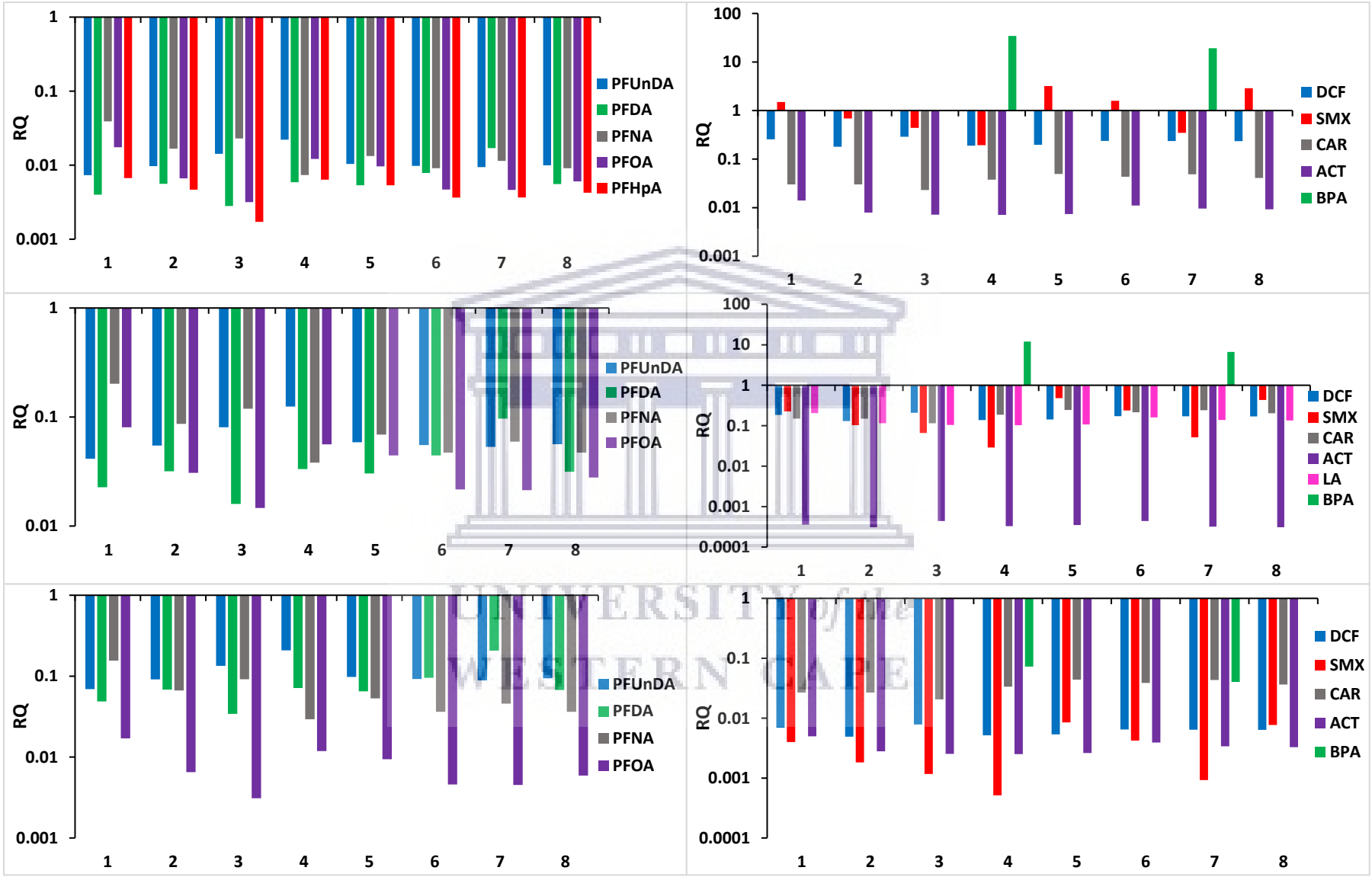


Figure 7. 37: Risk quotients (acute risk) for contaminants estimated for (A) algae (B) invertebrate (C) fish

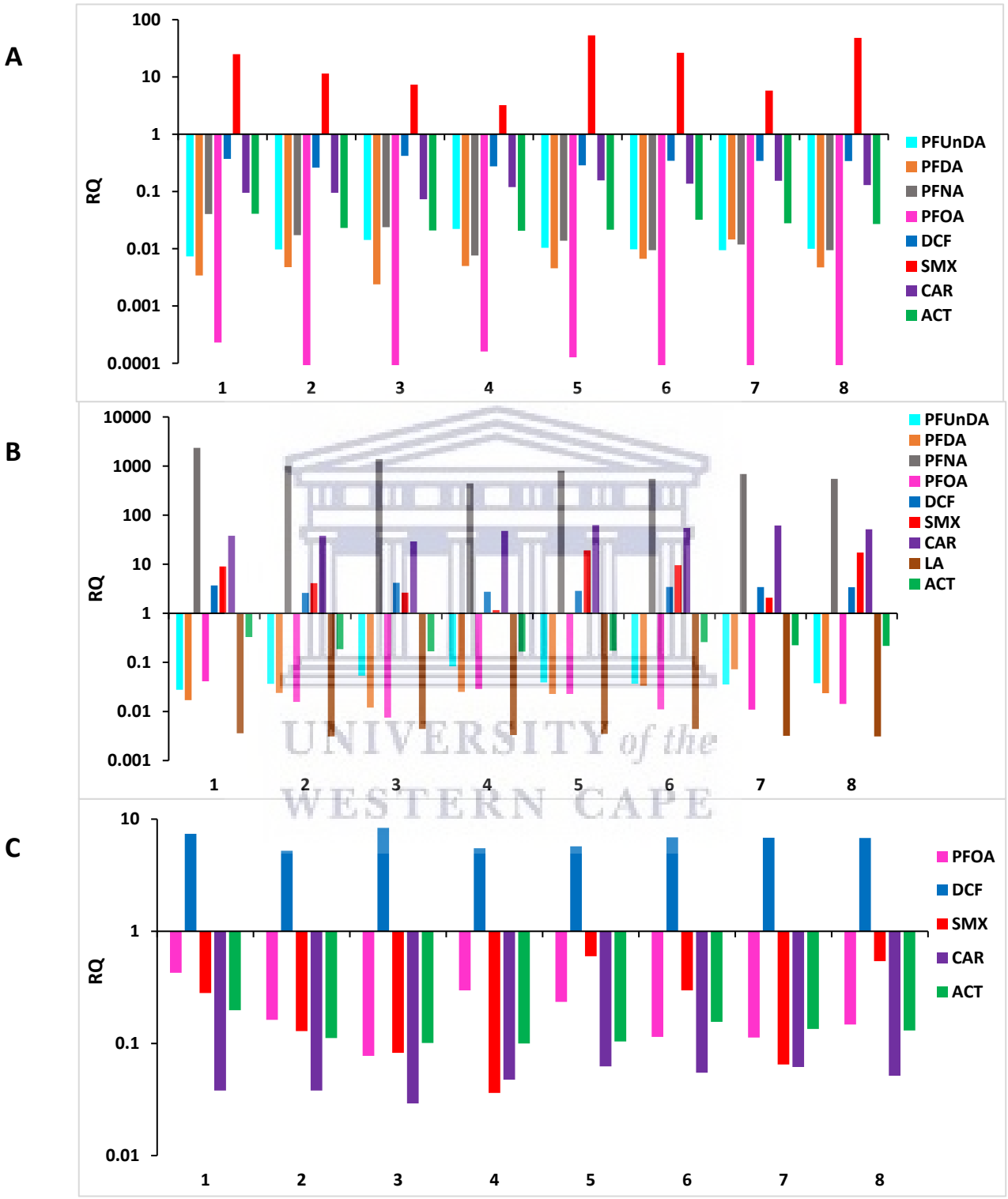


Figure 7. 38: Risk quotients (chronic risk) for contaminants estimated for (A) algae (B) invertebrate (C) fish

7.3. Conclusion

This result presents the first comprehensive survey of PFCs, PPCPs and industrial chemicals pollution in seawater, sediment and biota from the marine environment of False Bay, which is a rapidly urbanized and semi enclosed sea for Cape Town. Overall PFASs concentrations in this study region were high based on the comparison with those from other areas including Green Point and Camps Bay. The presented results underline the presence of chemicals of emerging concerns from various contamination sources in coastal environments and the potential temporal and spatial complexity of occurring emerging contaminants in coastal marine ecosystems. The highest individual concentration was observed for PFCs, bisphenol A, nonylphenol, diclofenac. Its high detection frequency demonstrates the widespread and direct impact of untreated wastewater and clearly highlights the significance of non-riverine inputs of raw sewage into coastal environments. Although, eight different sampling sites were examined for the presence of these contaminants in this study location, there were variations in the levels of these contaminants among the different sites with respect to the matrices. However, site 2 was observed to harbour vast majority of these contaminants in all the matrices.

Worthy of mention, the concentration of these contaminants is in the order: marine biota > sediments > seawater. However, seaweed among the biota were observed to accumulate contaminants in a similar pattern as was observed in other marine invertebrates. This is an indication that these species could also serve as pollution sentinel the in marine environment.

The ecological risk assessment for acute and chronic risks in this study showed that the contaminants in seawater from False Bay poses low to high risk to the three trophic levels (algae, invertebrates and fish). The implication of these results is that the marine environment of False Bay is heavily polluted and this could arise from the discharge of effluents from the wastewater treatments plants in False Bay. Consequently, anthropogenic activities could be said to also

contribute largely to the pollution of this bay. This explains the reason for the loss of sensitive invertebrate species and poor water quality along False Bay (DWAF 1995; Bredenhand and Samways 2005) which is responsible for the inability to obtain some species in some sites in False Bay (as some species were not found in some sites). The results obtained from this study therefore compliments and confirms the recent report released by the City of Cape Town on the poor water quality of False Bay (COCT 2019).

To conclude, the treatment of wastewaters will considerably decrease the input of contaminants into the marine environment. The wastewaters have to be collected and treated separately since the conventional methods for the sewage wastewater treatment do not remove these contaminants. To sustain a good and healthy marine ecosystem and prevent health problem to the locals, levels of contaminants should be monitored regular.

Chapter 8

General discussion, conclusion and recommendation

Some selected pharmaceutical compounds belonging to several therapeutic groups, perfluorinated compounds, industrial chemicals, herbicides and metals were investigated in fish, seawater, sediment, marine organisms and seaweed from some selected marine environment of Cape Town, South Africa. The present study is the largest in terms of number of evaluated analytes and the first one analyzing samples in different matrices from these locations. This study constitutes the first evidence of the presence of the substances in these marine environments. The analytical methods validated to support the present study allowed for the low-level analysis of selected EDCs, PFCs, PPCPs, herbicides and metals in marine waters, sediments, and biota samples using relatively small sample volumes. The methods are capable of detecting low parts per trillion concentrations in water samples and low parts per billion concentrations in sediment and tissue samples. Application of these methods indicated that EDCs, PFCs, PPCPs, herbicides and metals are present in Cape Town marine waters and sediments and significantly accumulated in marine organisms including seaweed. The results from this study which have been presented in previous chapters of this thesis indicate that the objectives of this study have been achieved and therefore requires that the research questions that were set at the beginning of this study needs to be answered. Below are the answers to the set research questions:

I. Are perfluorinated compounds, pharmaceuticals and personal care product, herbicides, industrial chemicals and metals present in the marine environment and marine biota?

   Seawater, sediment, fish and different species of marine biota were sampled from different location from the marine environment of Cape Town, South Africa, using the experimental protocols described in Chapter 3 of this thesis, the selected classes of chemicals of

emerging concern were present in the marine environment of Cape Town. These compounds were detected in each of the environmental matrix analysed in this study from the different selected location.

II. If present, at what level/concentration?

The levels/ concentrations of these contaminant were detected in ng/L to mg/L in seawater for all the contaminants. In sediment and biota samples, the contaminants were all detected in ng/g to mg/kg. Although, the concentration of these contaminants varies among the sites, in general, metals were found to be in higher concentrations among the contaminants examined in this study, perflouorinated compounds were next followed by pharmaceuticals, herbicides and lastly, industrial chemicals. False Bay marine environment had the highest level of these contaminants except for herbicides and metals that were not reported from this location. Camps Bay, fish samples from Kalk Bay habour and Green Point complete the order for the levels of these contaminants in the marine environment of Cape Town.

III. Is the concentration of these pollutants high enough to be detected in marine organisms?

The concentration/ level of contaminants were high enough to be detected in marine organisms as reported in previous chapters.

IV. Are these compounds bioaccumulating in marine biota relative to background levels?

The selected compounds are bioaccumulating in the marine biota as their concentration were higher than the concentration in the seawater these biota inhabit. The calculated bioaccumulation factor for the marine biota were above 5000 L/kg, which shows these compounds are bioaccumulative.

V. What are the risk factors?

These classes of chemicals of emerging concern poses low to high risk to the marine environments as well as humans feeding on some of the edible seafood from the studied areas.

The significant findings from this study include the following:

All through the analysis, 2-nitrophenol was not detected in any of the matrices from all the sample locations, this could be that the method is not efficient to extract this compound from the samples or the instrument is not sensitive to detect the compound or that this compound is not present in the environment of Cape Town. The results obtained from the different survey indicate varying levels of the other contaminants across the different locations/sites. For instance, the levels of contamination in the four fish samples from Kalk Bay harbour indicate that the fish are well contaminated, with the fillet parts of all fish species accounting for most of the pollution. Also, PFHpA, diclofenac as well as Al, Fe, Sr, Nb, simazine and atrazine were observed to be dominant in the fish samples from this site. While in Green Point samples, PFUnDA, PFHpA, triclosan and acetaminophen were the prevalent contaminants across the different matrices, in False Bay, PFNA, PFHpA, nonylphenol, diclofenac, sulfamethoxazole and Bisphenol A were very high in the different matrices. In Camps Bay, PFDA, Al, P, Nb, Sr, Fe, simazine, atrazine and diclofenac were higher among the contaminants. Although, conclusions could not be arrived at on the trend of the level of these contaminants with respect to the different species as pollutant levels in biota samples from these locations did not follow any particular pattern. This may be as a result of differences in the physiological factor of each specific specie such as diet choice, growth, respiration and egestion rates as well as metabolic capability of organisms (Tomy et al. 2004; Falk et al. 2015). Also, even though, published reports indicate that mussels are good setinnel organisms in marine

environments (Edward 2013; Silva et al. 2017; Krishnakumar et al. 2018), this study showed that organisms such as limpets, sea snail and sea urchins as well as sea weeds can also be used to monitor pollution as all contaminants bioaccumulated in high amounts in these species.

The distribution of contaminants among the different matrices indicates that the concentration of contaminants in biota were order of magnitude compared to seawater and sediment (i.e. biota > sediment > seawater) across the different sampling locations. Also, the degree of contamination across the bays goes in the order: False Bay > Camps Bay > Green Point. The levels of the contaminants in samples from False Bay were very high compared to the levels found in samples from other locations. This could be as a result of the total number (four) of sewage plants discharging waste into the marine environment of False Bay. The presence of these chemicals of emerging concern in the marine environment of Cape Town points to improper discharge of untreated sewage into the ocean and life style of the people in and around this environment.

In addition, this study confirms that selected pollutants are bioaccumulating in sessile organisms and that the purported high dilution of pollution by discharge of sewage into the oceanic environment is not operating effectively, despite claims to the contrary by city officials. High levels of chemicals in sessile organisms and in inorganic matrix such as sediment and beach sand shows that the sewage plume must make frequent landfall, causing a buildup of chemical contaminants along the shoreline, as these persistent chemicals are not flushed away by clean seawater frequently enough to prevent accumulation. The detection of EDCs, PFCs, PPCPs, herbicides and metals in the selected studied area biota and in the ambient environment highlights the importance of continuous monitoring of coastal environments, particularly given the paucity of data on the effects of long-term exposure and potential toxicity impacts. The RQ assessment evaluation revealed that these compounds pose low and high (acute and chronic) risk to the marine organisms. The carcinogenic risk of Camps Bay edible species and fish were above acceptable

levels, while only simazine levels showed a non-carcinogenic risk. Even though the selected contaminants levels in seawater were relatively low, the chemical compounds are not sufficiently diluted by the ocean and are shown to be bio-accumulating in marine biota, thus building up to levels that will have significant impacts on the near shore marine environment and the Marine Protected Area of Cape Town. This shows that high bioaccumulation potential in living organisms that are not adapted to cope with the continuous discharge of multiple chemicals into their ecology, and which may in turn produce additional metabolites. These chemical compounds could cause far more harm than the sewage itself, since many studies show that individually they may causes feminization or sterility of fish populations, cancers, growth deformities, fetal abnormalities, hormonal disturbances, etc. Moreover, the detected contaminants well levels in beach sand, sediments, and marine biota show that the sewage plume in the marine environment of Cape Town makes frequent landfall, which indicates that dilution of the raw sewage by the ocean is inadequate and that the marine sewage outfall is located too close to the shore.

Based on these results, stricter legislation and regulatory controls on maximum permitted levels of these contaminants are crucial as the treatment of sewage before its release into the marine environment should be mandatory to protect and maintain marine biodiversity and human health. With regard to environmental management, both the duty of care and the precautionary principle should apply to the bays, in addition to the laws governing Marine Protected Areas, because the synergistic effects of simultaneous exposure to multiple chemical compounds is not known nor is it known how much of the diverse compounds are being passed up the food chain to humans who eat fish and mussels etc. These chemicals and pharmaceuticals have high levels of toxicity because they are designed to withstand powerful gastric acids and be effective at low dose. It is therefore important to monitor the level of the most frequently used EDCs, PFCs, PPCPs, herbicides and metals in sewage and to develop efficient treatment methods that will remove all these persistent

chemical pollutants before discharging sewage into the receiving marine water. Finally, since it is evident from available literature, that there is very limited laboratory ecotoxicology data for the effect of these compounds on marine organisms and a marked lack of field data, further research is needed on the effects of continuous discharge of sewage that is loaded with complex chemical compounds into a marine reserve.

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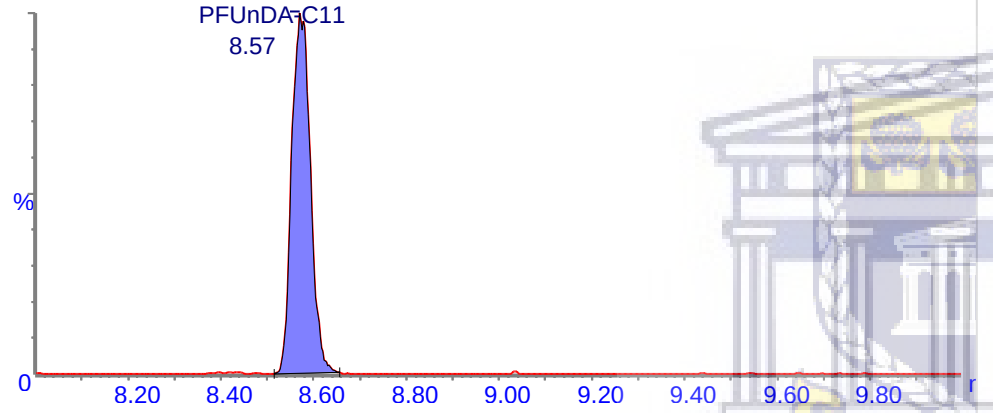
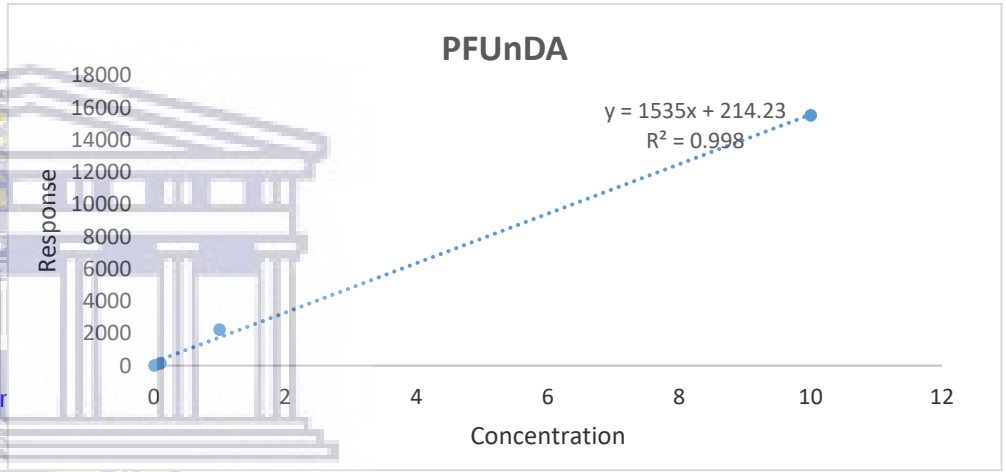
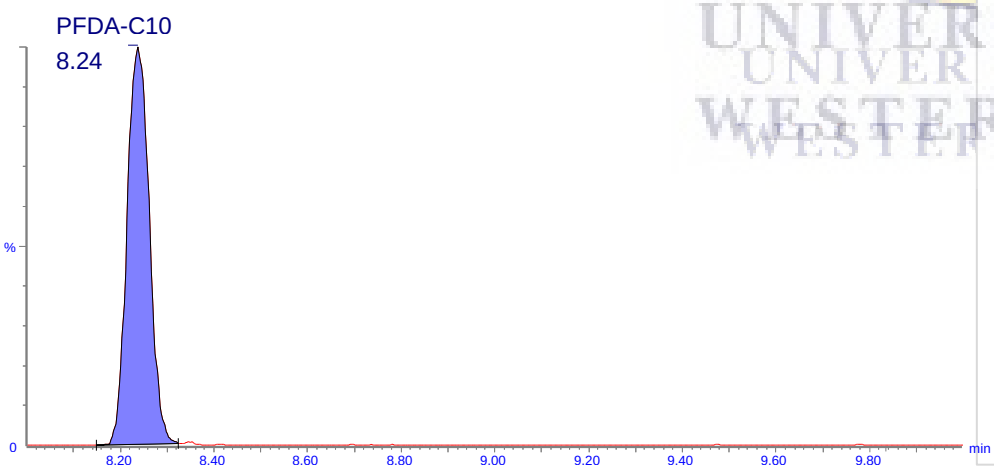
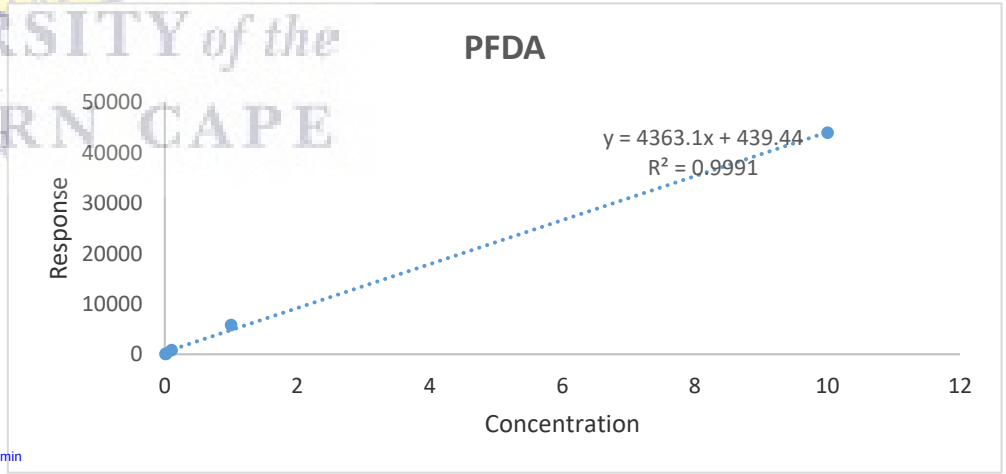
APPENDICES

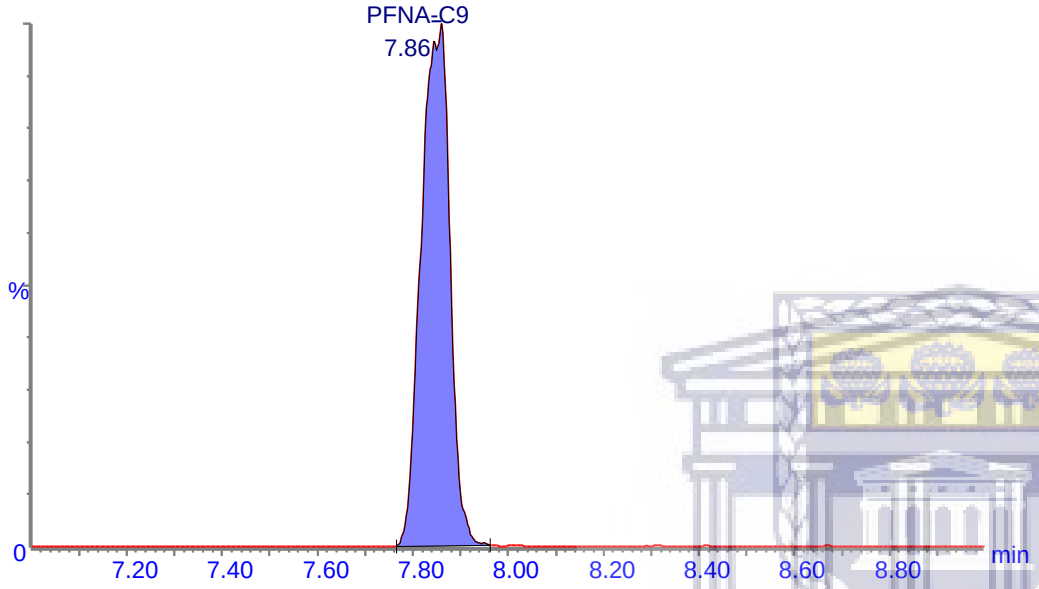
APPENDIX I

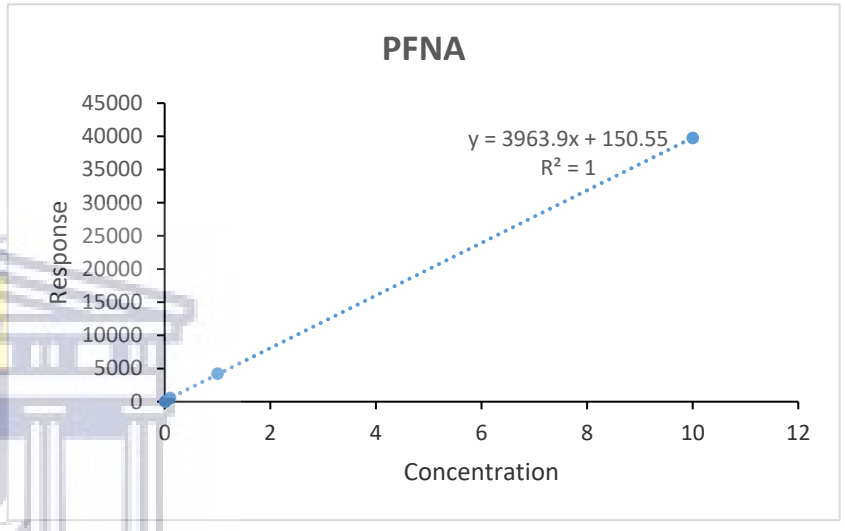


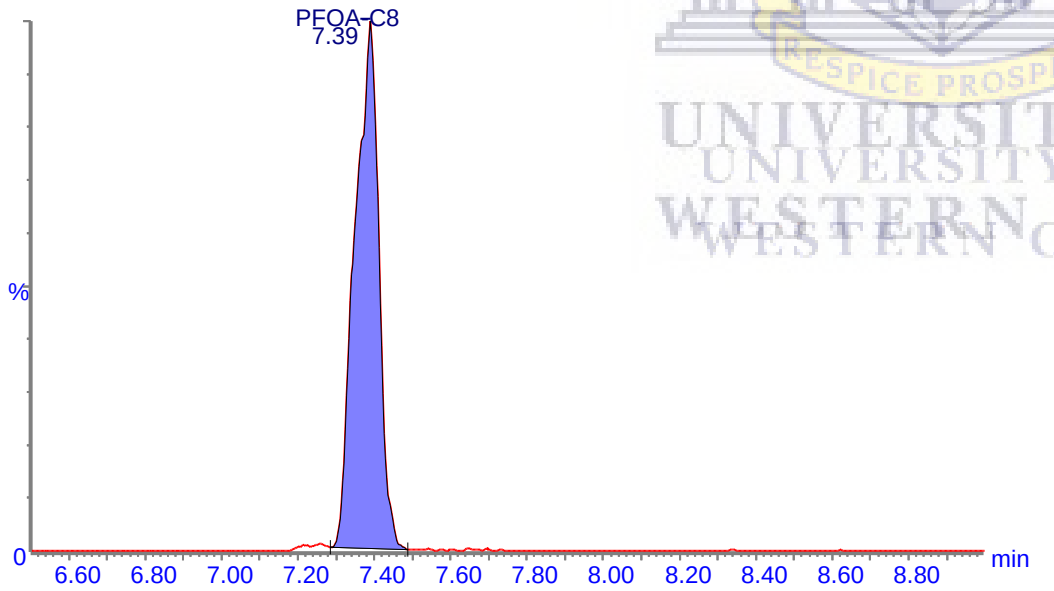


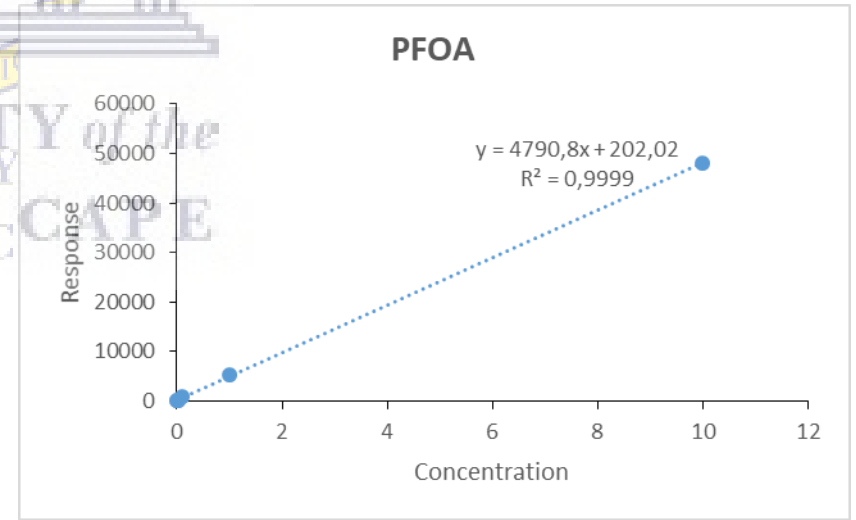


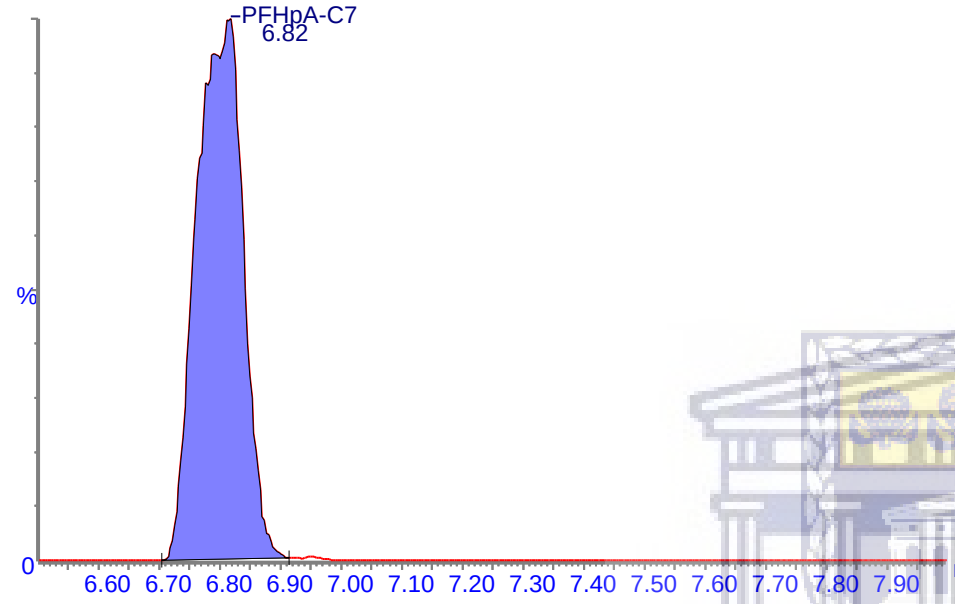


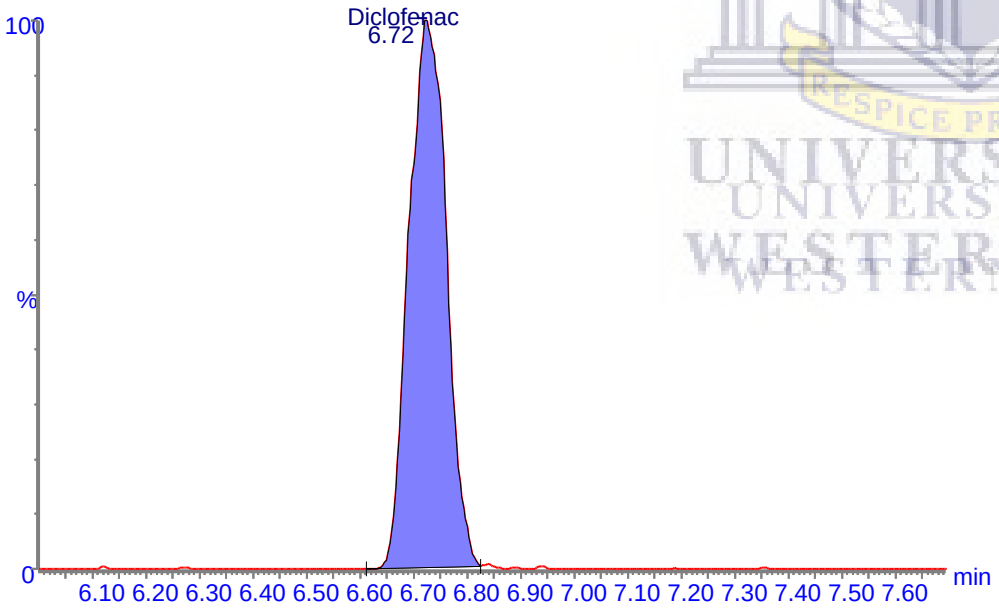


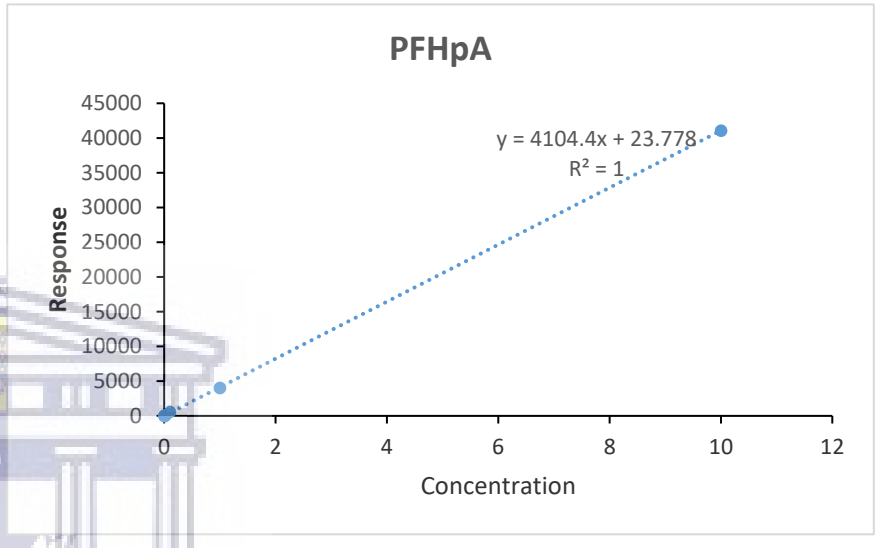


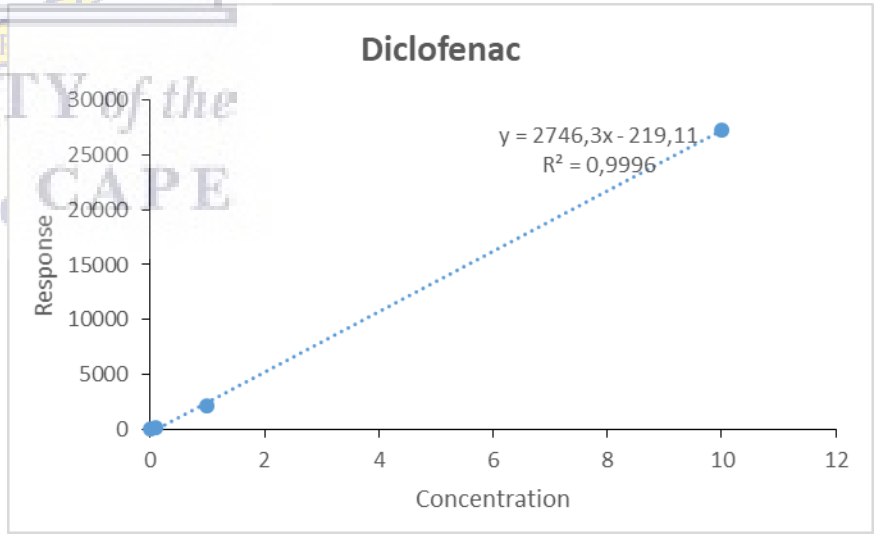


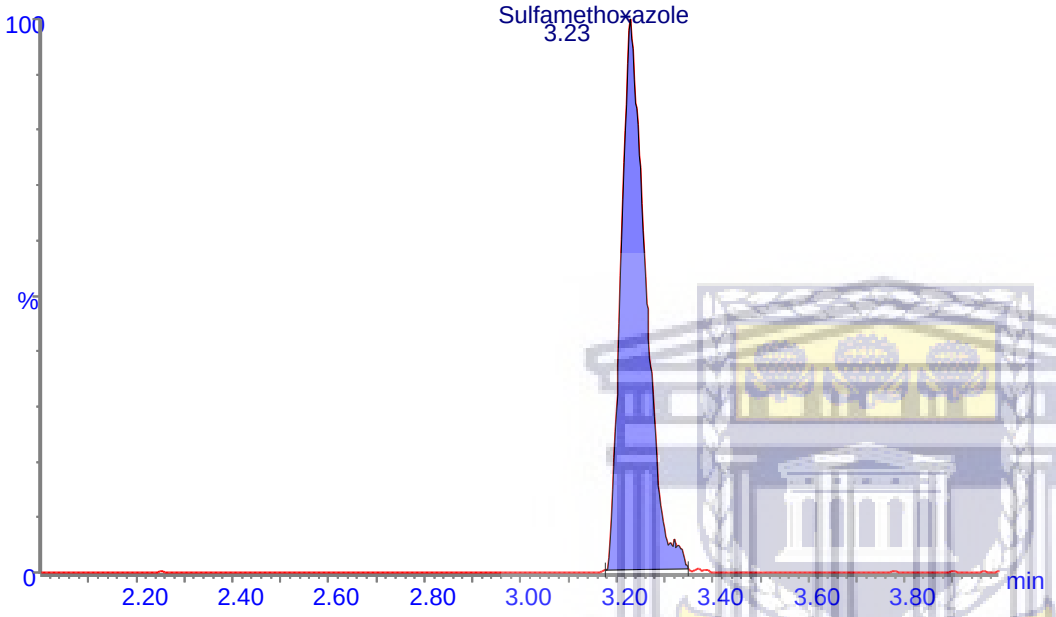


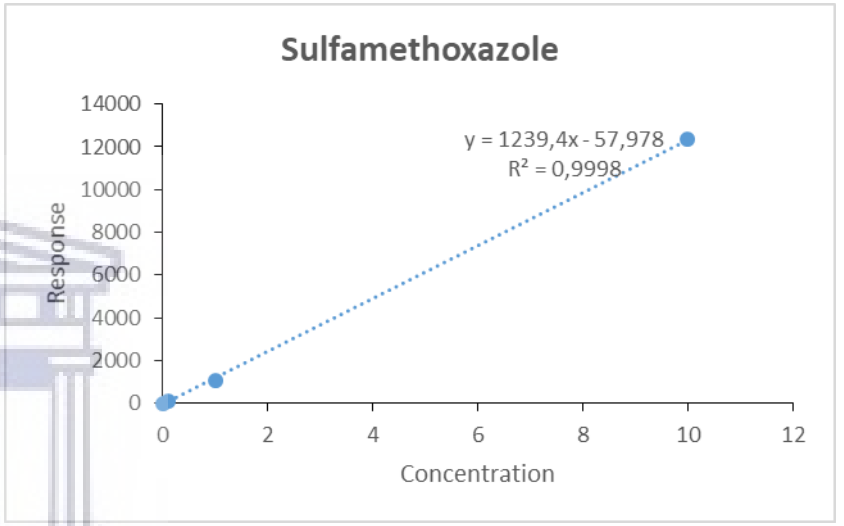


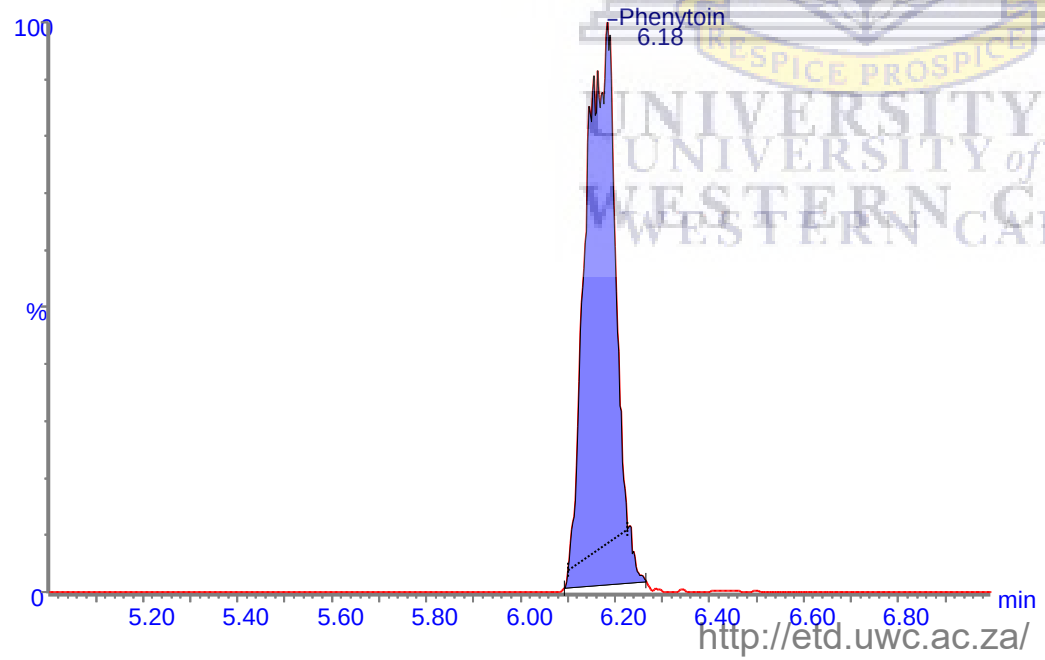


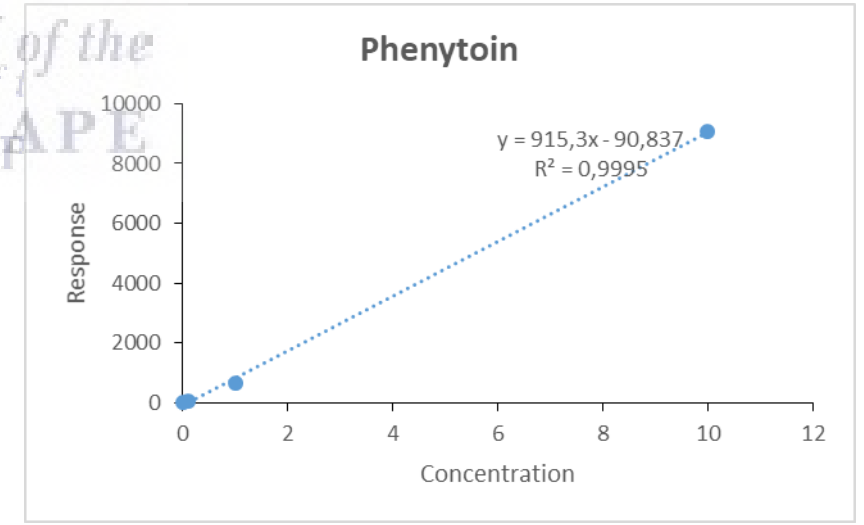


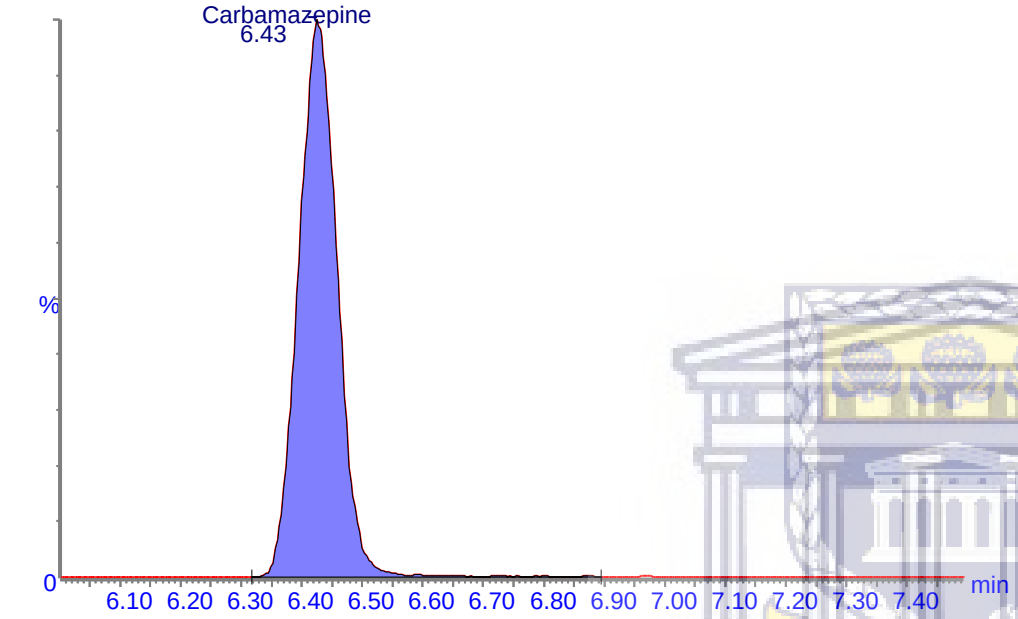


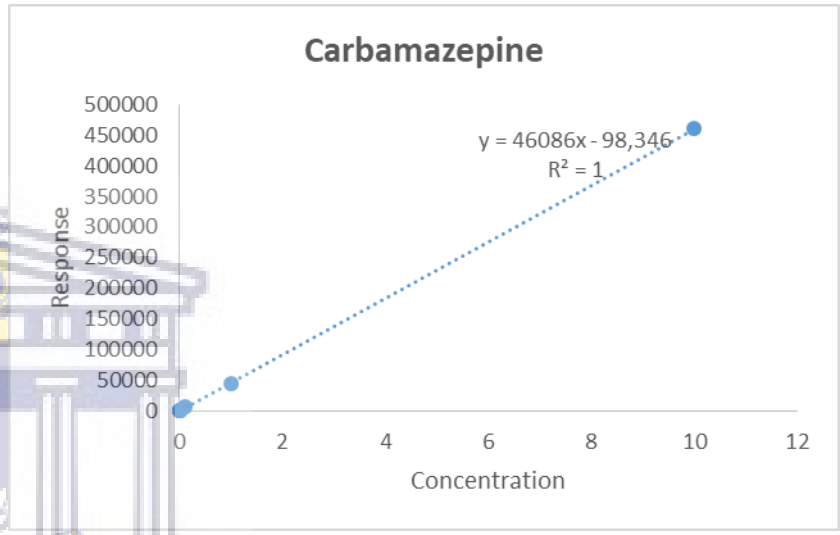


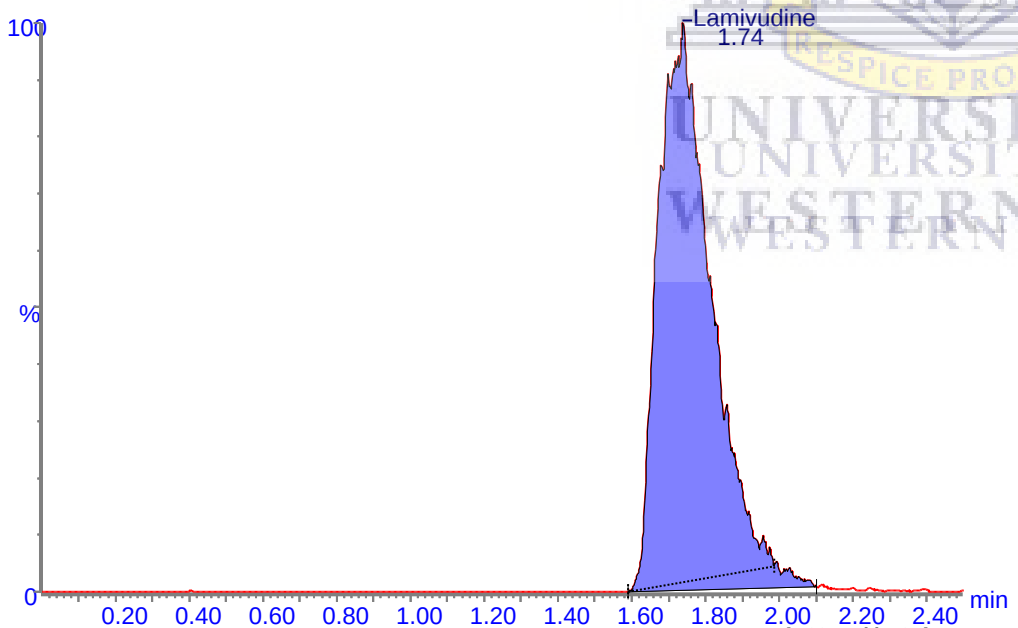


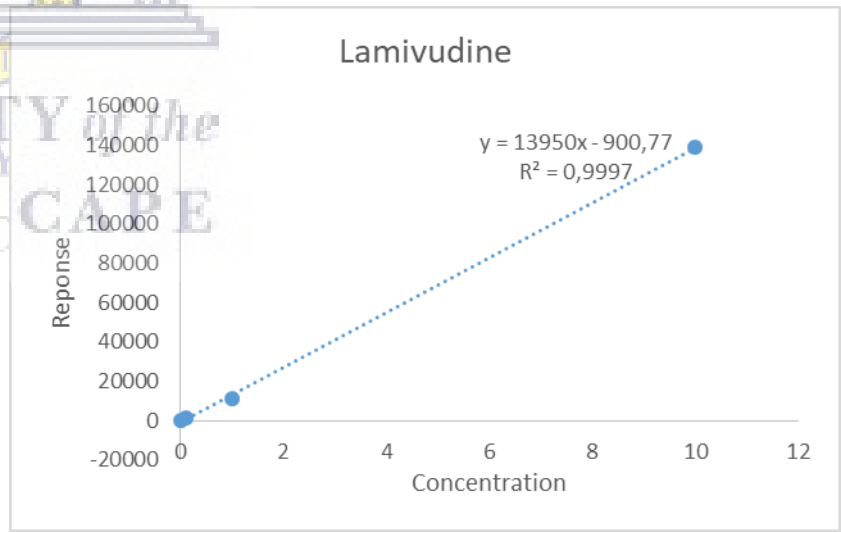












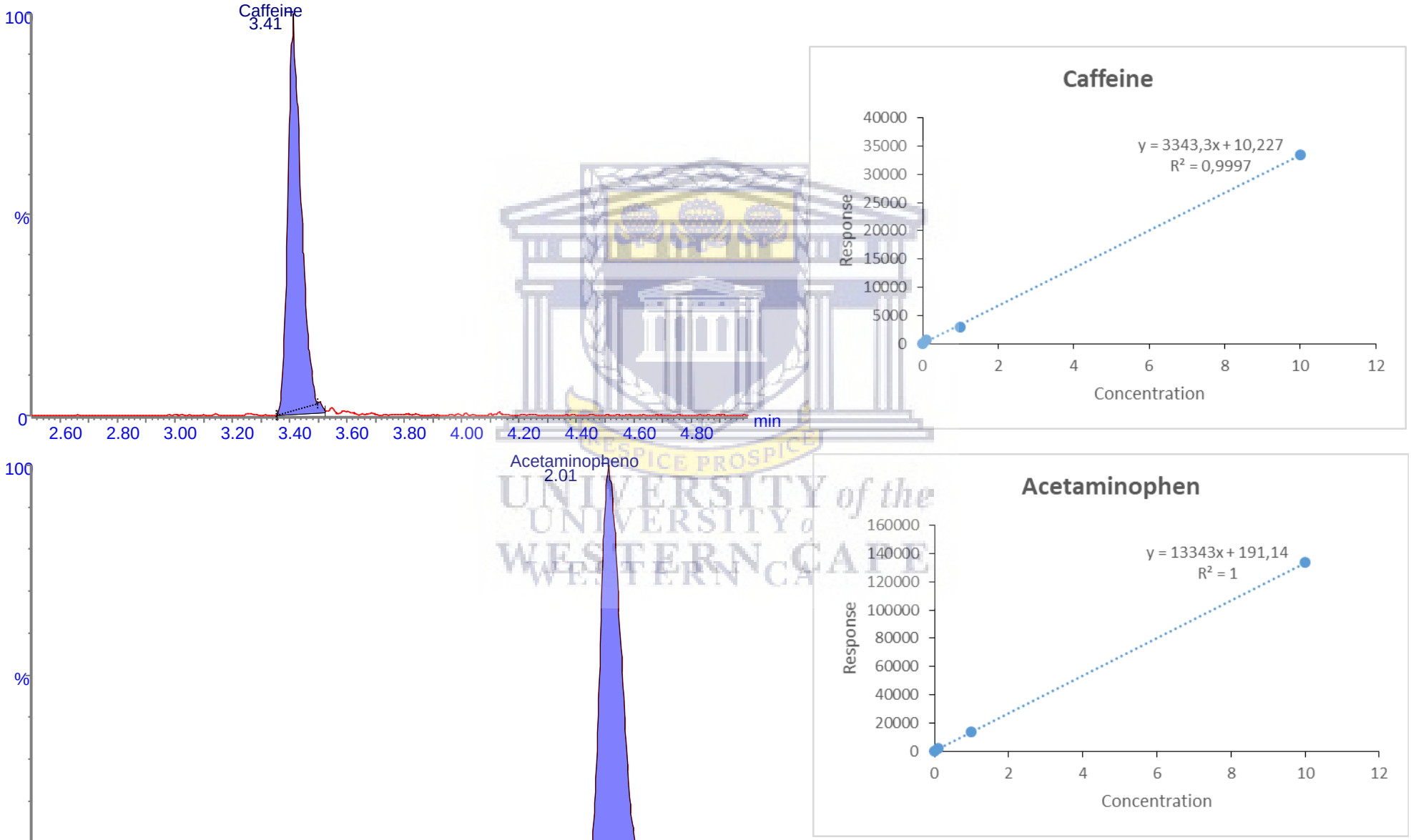
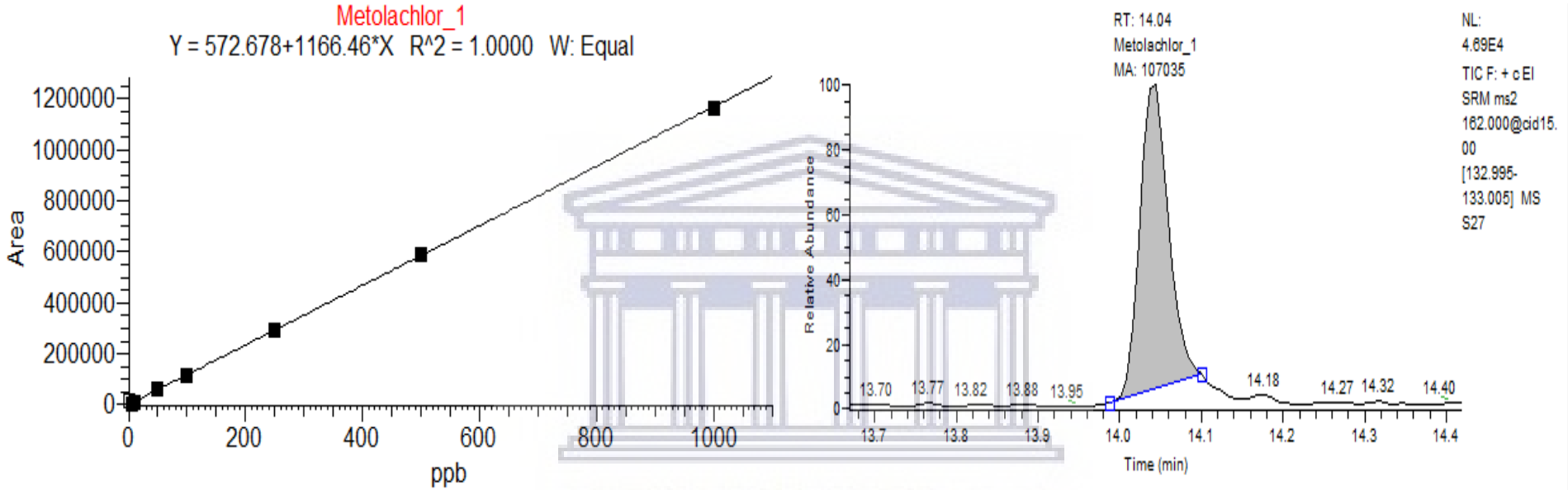
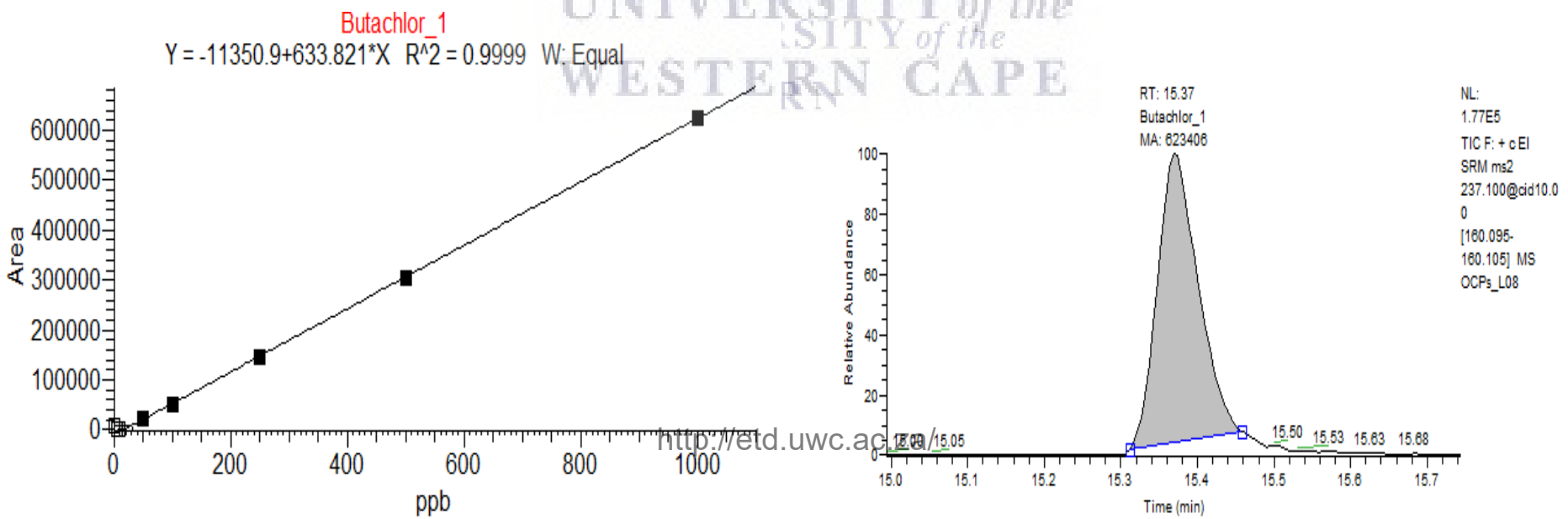


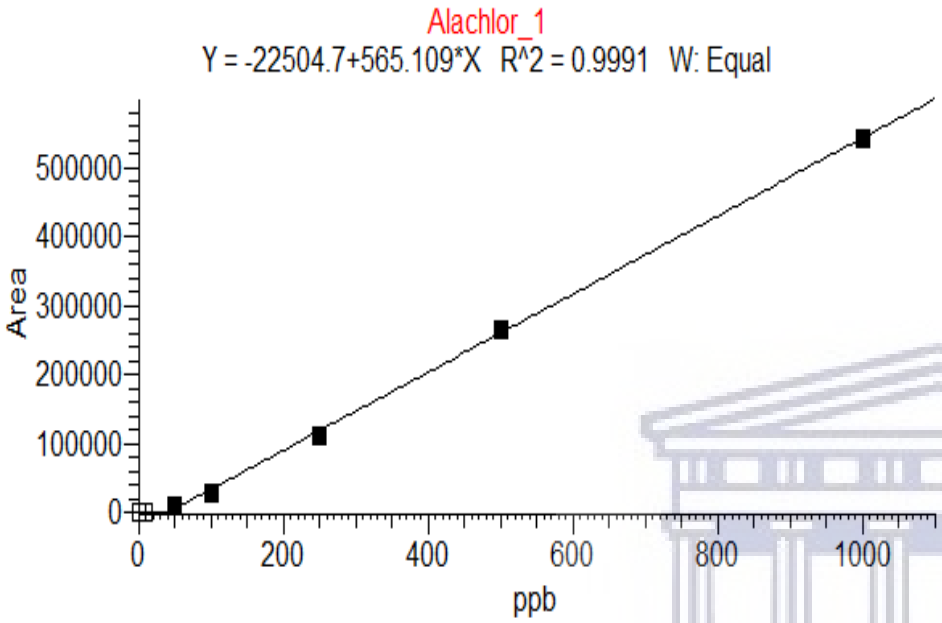
Figure I. 1: Calibration curves and chromatograms for PPCPs and PFCs for fish analysis

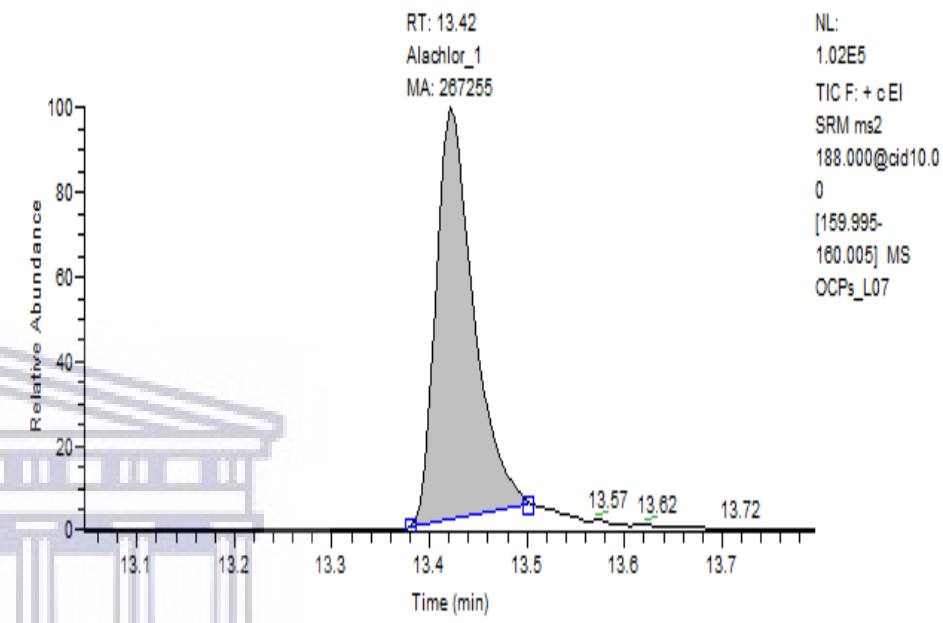
Table I. 1: Concentrations (ng/g dw) of PPCPs, PFCs and EDCs in different fish species

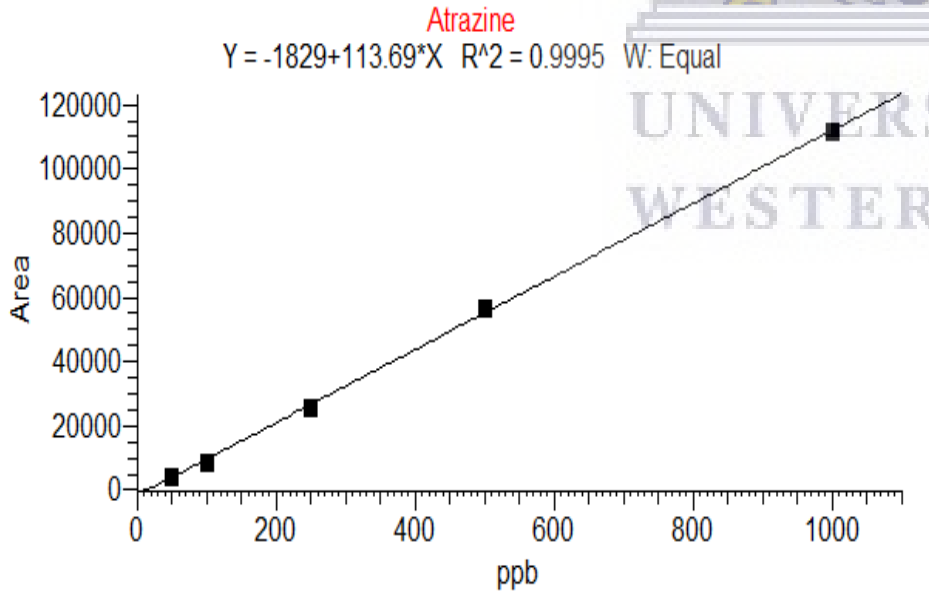
	Panga (*Pterogymnus laniarius)*				**Bonito (*Sarda orientalis)***				**Hottentot (*Pachymetopon blochii)***				**Snoek (*Thyrsites atun)***			
Compounds	Fillet	Intestine	Gills	Liver	Fillet	Intestine	Gills	Liver	Fillet	Intestine	Gills	Liver	Fillet	Intestine	Gills	Liver
PFUnDA	124.4±1.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	75.18±1.3	nd
PFDA	78.86±1.5	57.26±2.6	27.26±2.6	37.26±2.6	58.41±0.0	19.52±0.6	84.24±2.8	32.39±0.7	32.44±3.0	179.2±0.5	129.2±0.5	159.2±0.5	28.33±1.0	20.83±0.1	106.8±1.4	20.13±0.1
PFNA	49.53±3.4	41.76±0.7	41.76±0.7	41.76±0.7	58.52±1.0	22.89±0.8	76.72±5.0	31.08±5.1	15.92±1.3	82.49±1.5	81.47±1.5	81.49±1.4	21.22±4.9	23.74±0.5	114.0±6.7	23.14±0.5
PFOA	37.52±0.6	13.91±0.2	12.91±0.2	10.91±0.2	nd	34.63±1.0	16.91±0.1	nd	3.900±0.0	63.17±1.2	60.97±1.2	60.97±1.1	26.07±0.5	nd	45.01±4.6	nd
PFHpA	83.86±3.2	75.56±0.8	65.96±0.8	75.36±0.8	297.5±5.9	97.63±0.7	110.0±4.8	95.95±1.8	74.67±2.0	139.1±0.4	130.0±0.4	130.3±0.3	110.2±0.9	42.06±1.2	138.3±0.4	40.06±1.2
DCF	551.8±1.3	nd	nd	nd	nd	nd	nd	nd	920.5±3.3	716.2±7.0	826.2±2.9	906.1±2.8	1812±0.2	1125±0.3	1089±11	1125±0.3
SMX	nd	28.55±0.3	28.55±0.3	28.55±0.3	385.2±1.0	nd	nd	360.3±2.1	88.53±1.8	79.12±1.6	75.25±1.6	79.12±1.5	88.63±1.8	688.6±6.2	nd	688.6±6.2
PHE	55.67±0.2	nd	nd	nd	nd	nd	nd	nd	107.7±2.9	119.4±2.6	119.4±2.6	129.3±2.6	222.2±1.4	137.4±2.4	nd	137.4±2.3
CAR	22.90±2.2	nd	nd	nd	nd	nd	22.83±0.2	nd	nd	12.67±0.1	12.67±0.1	12.67±0.1	5.160±0.1	nd	nd	nd
LA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CAF	nd	2.030±0.1	2.030±0.1	2.030±0.1	50.49±0.1	nd	nd	64.78±1.3	nd	1.760±0.1	1.765±0.1	1.768±0.1	nd	nd	nd	nd
ACT	17.95±1.0	33.26±0.4	33.26±0.4	33.26±0.4	nd	nd	nd	nd	nd	9.030±0.2	9.035±0.2	9.039±0.2	nd	nd	nd	nd
TS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BPA	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-N	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

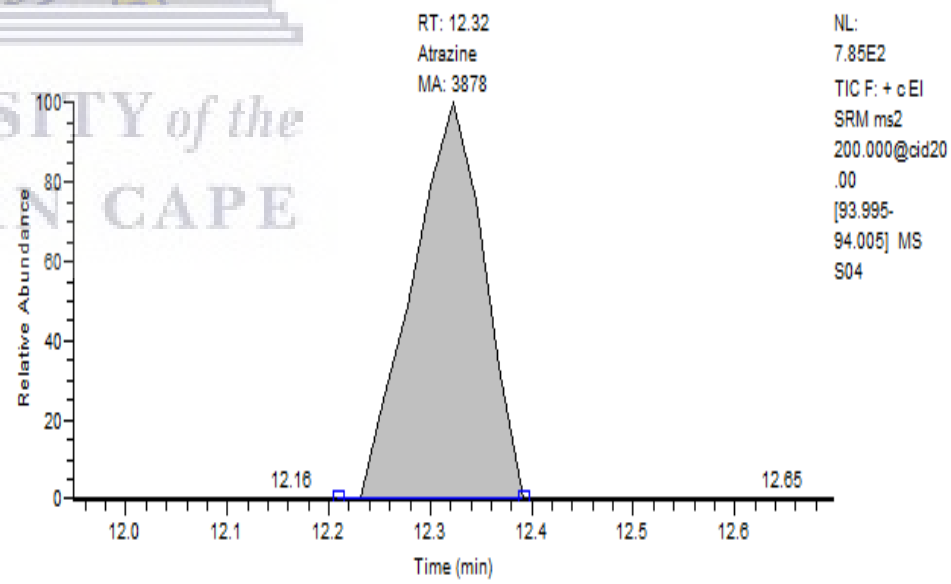












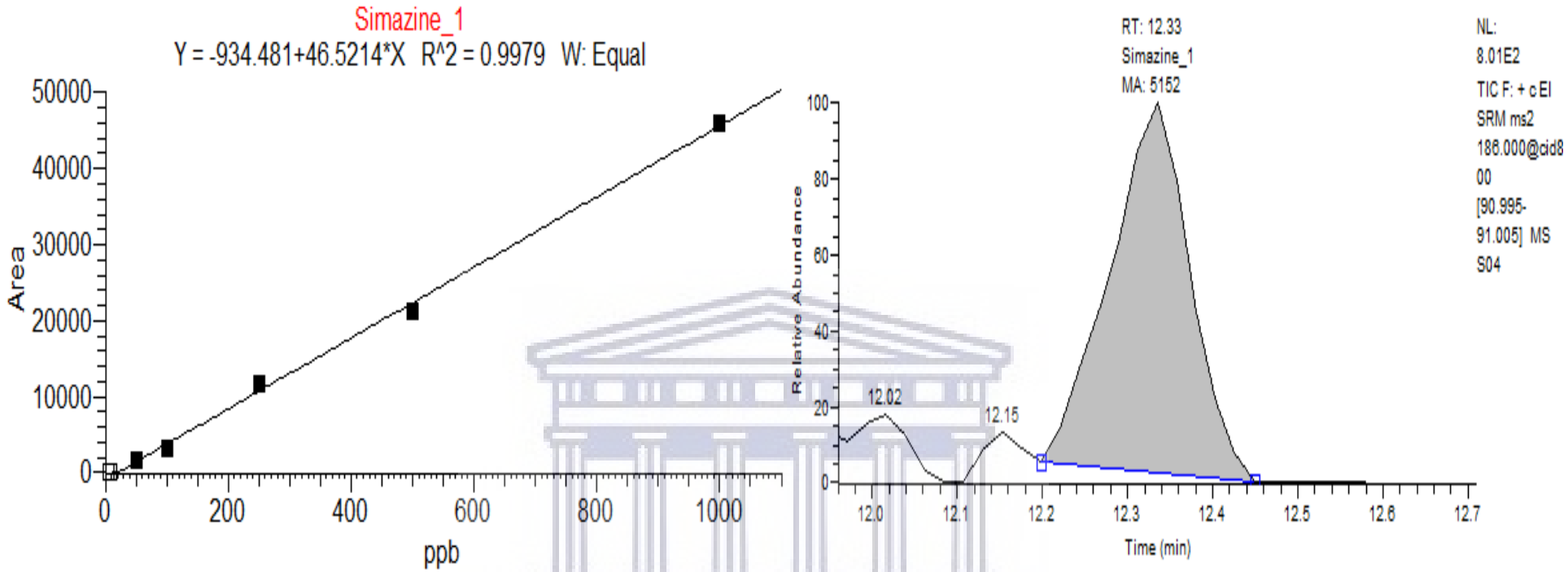


Figure I. 2: Calibration curves and chromatograms of herbicides compounds for fish samples

Table I. 2: Concentration (ng/g dw) of herbicides in different fish species.

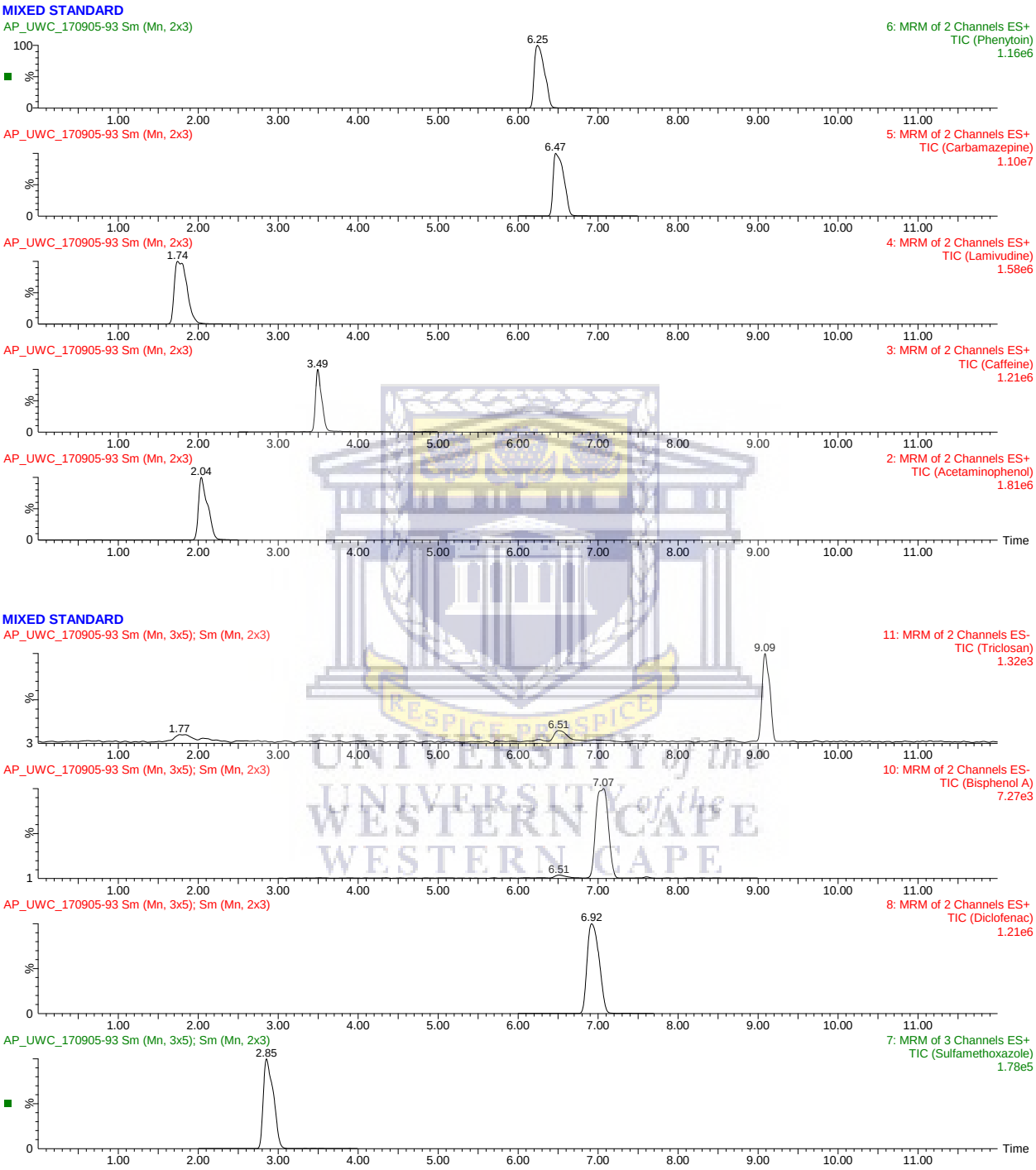
Fish type	Fish part	Simazine	Atrazine	Alachlor	Metolachlor	Butachlor
Hottentot	Fillet	157.82	35.31	nd	nd	nd
	Liver	nd	nd	nd	nd	nd
	Gills	nd	nd	nd	nd	nd
	Intestine	nd	nd	nd	nd	nd
Panga	Fillet	120.58	48.69	nd	nd	nd
	Liver	130.82	50.20	nd	nd	nd
	Gills	125.22	51.91	nd	nd	nd
	Intestine	129.88	55.61	nd	nd	nd
Bonito	Fillet	47.79	nd	nd	nd	nd
	Liver	135.97	40.12	nd	nd	nd
	Gills	nd	41.54	nd	nd	nd
	Intestine	118.84	59.03	nd	nd	nd
Snoek	Fillet	nd	35.03	nd	nd	nd
	Liver	123.64	65.87	nd	nd	nd
	Gills	84.19	21.59	16.39	42.37	nd
	Intestine	123.64	65.87	47.43	nd	nd

Table I. 3: Average levels of metal contaminants (mg/kg dry content)

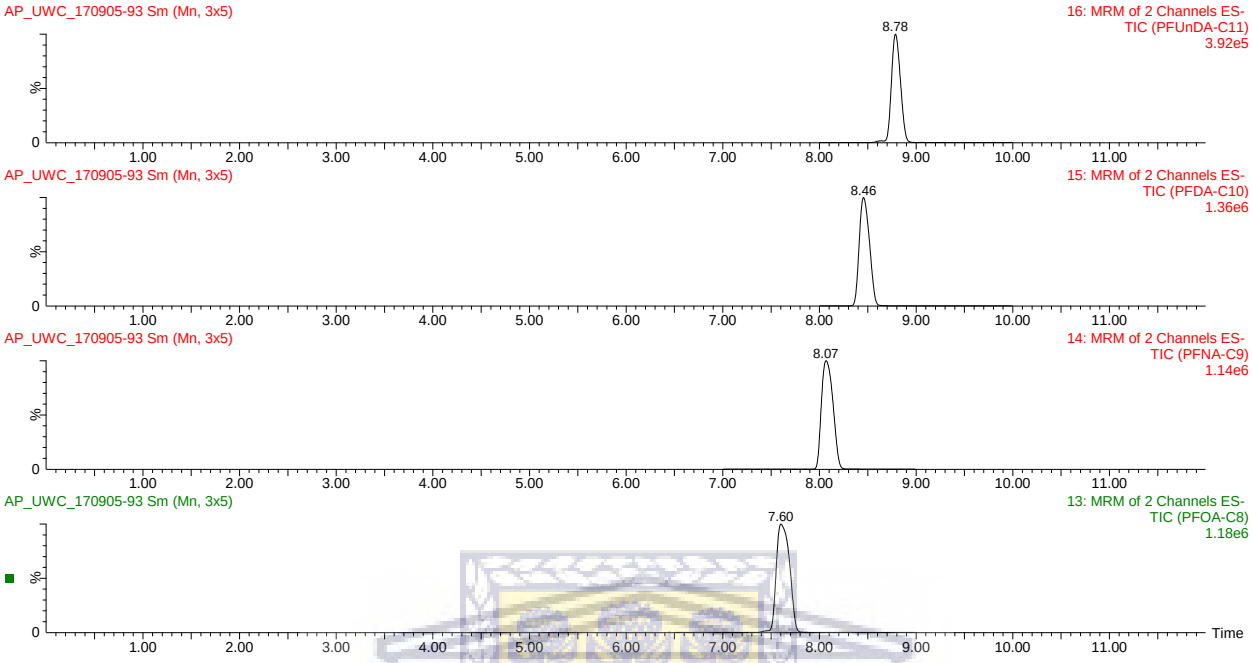
					Standards			
Element	**Panga fish**	**Hottentot fish**	**Snoek fish**	**Bonito fish**	**FAO/WHO**	**FAO**	**WHO**	**England**
Pb	34.69±0.11	58.79 ±2.38	53.79 ±0.29	38.51 ±0.85	0.5	0.5	2	2
Cu	131.00 ±0.26	38.11 ±0.10	52.44 ±1.54	18.04 ±0.42	30	30	30	20
As	16.15 ±0.13	11.73 ±0.19	1.41 ±0.11	nd				
Zn	164.73 ±2.57	234.48 ±11.80	198.29 ±4.81	105.58 ±0.04	40	30	100	50
Fe	372.82 ±3.05	400.62 ±10.97	362.56 ±5.26	443.93 ±3.19	-	-	100	-
Al	502.93±5.64	266.21±6.53	346.06±6.50	341.07±.62				
Si	485.64±4.59	554.29±2.50	220.95±4.23	32.01±0.99				
Mo	11.10 ±0.00	10.53 ±0.02	11.95 ±0.00	11.92 ±0.08				
Co	1.06 ±0.03	1.84 ±0.00	0.56 ±0.10	3.67 ±0.15				
Cr	4.98 ±0.20	1.58 ±0.10	11.50 ±0.35	nd				
Ni	26.49 ±0.90	18.48 ±0.67	25.38 ±0.68	9.88 ±0.45				
Se	20.74 ±0.09	126.31 ±0.20	14.78 ±0.05	85.18 ±0.07				
Mn	9.42 ±0.05	10.26 ±0.02	9.29 ±0.40	2.12 ±0.13			1	
Zr	3.01 ±0.06	2.16 ±0.00	3.35 ±0.03	0.88 ±0.02				
Ti	20.36 ±0.36	13.29 ±0.23	25.77 ±0.98	13.13 ±0.29				
Sr	687.71 ±4.85	481.52 ±4.82	288.79 ±14.3	71.56 ±1.82				
Ce	20.70 ±0.20	18.59 ±0.04	29.36 ±0.78	36.56 ±0.37				
Nb	420.97±0.36	418.71±1.03	418.25±0.89	419.34±0.48				
Th	13.97±0.52	11.30±0.02	nd	17.65±2.69				
Y	0.02±0.00	0.01±0.00	0.48±0.01	0.81±0.05				
Li	5.00±0.05	10.26±0.02	9.29±0.40	2.12±0.13				
Cd	nd	nd	nd	nd	0.5	0.05	1	2
Rb	0.56±0.06	42.96±0.25	nd	2.25±0.02				

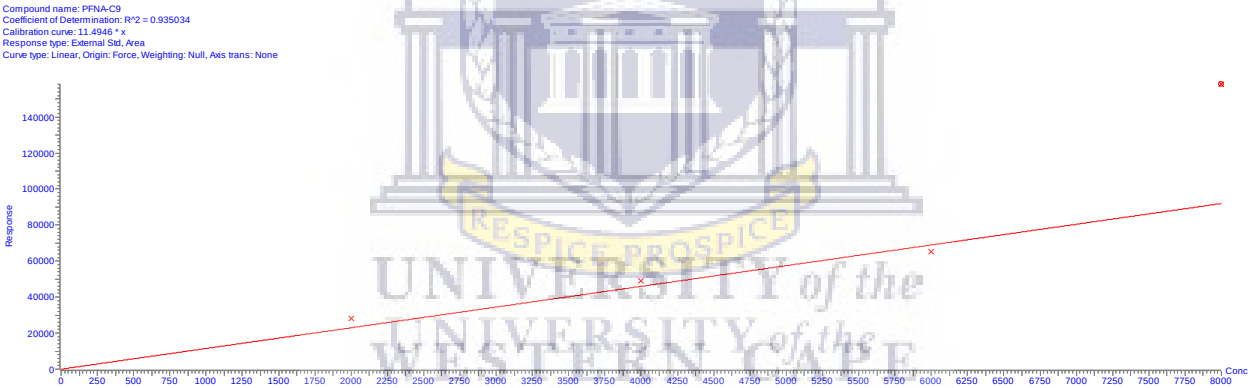
nd= not detected

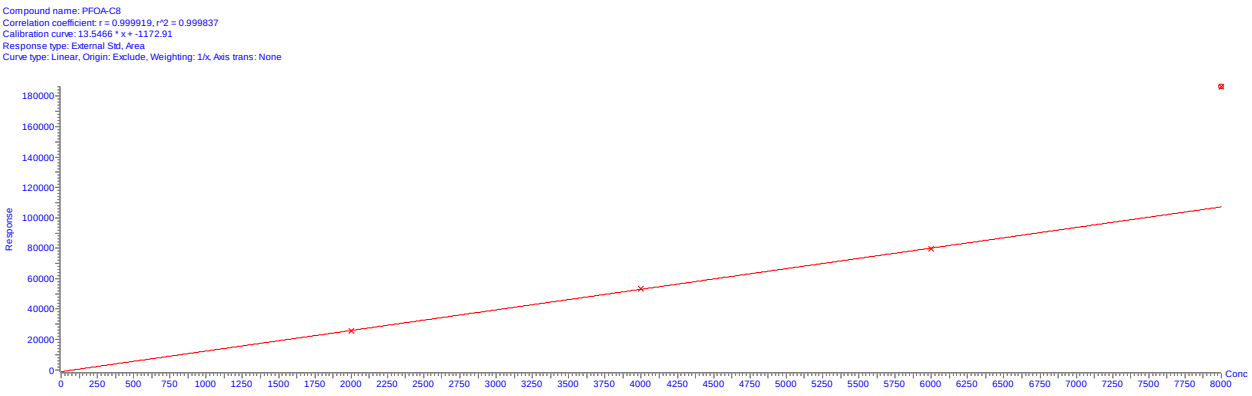
APPENDIX II



MIXED STANDARD







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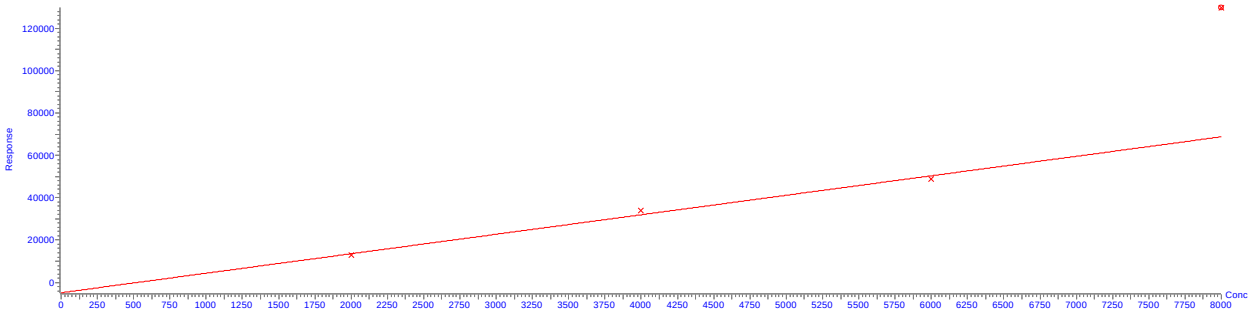
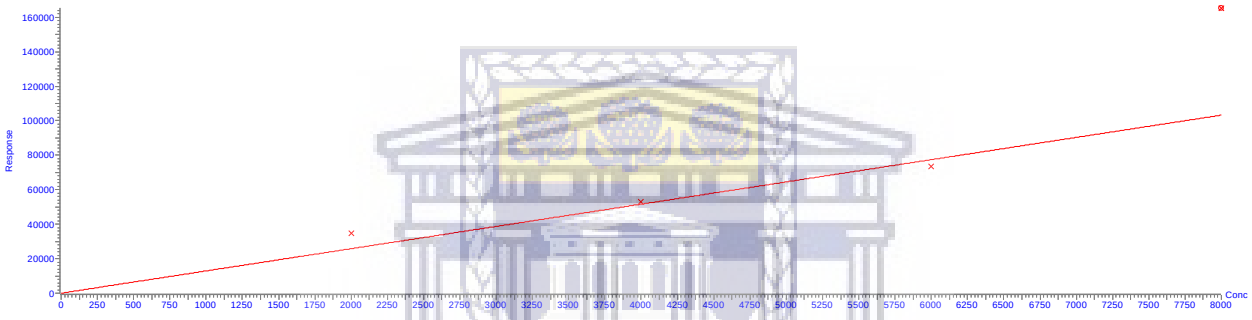
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Compound name: PFDA-C10
Coefficient of Determination: R^2 = 0.876502
Calibration curve: 12.9025 * x
Response type: External Std, Area
Curve type: Linear, Origin: Force, Weighting: Null, Axis trans: None



Compound name: Triclosan
Correlation coefficient: r = 0.999789, r^2 = 0.999577
Calibration curve: 0.0116867 * x + -11.8185
Response type: External Std, Area
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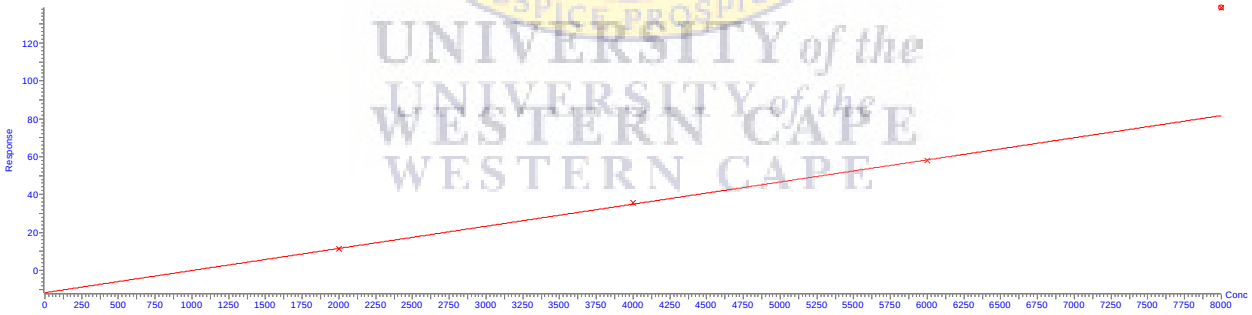

Compound name: Bisphenol A
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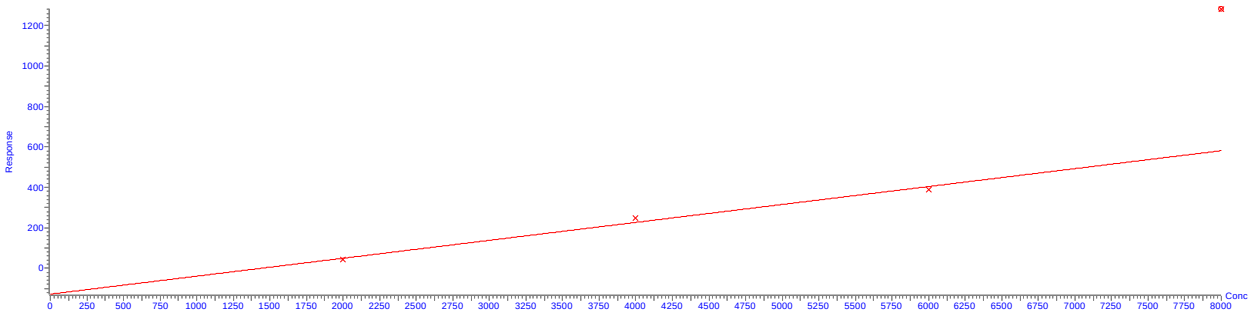

Compound name: Diclofenac
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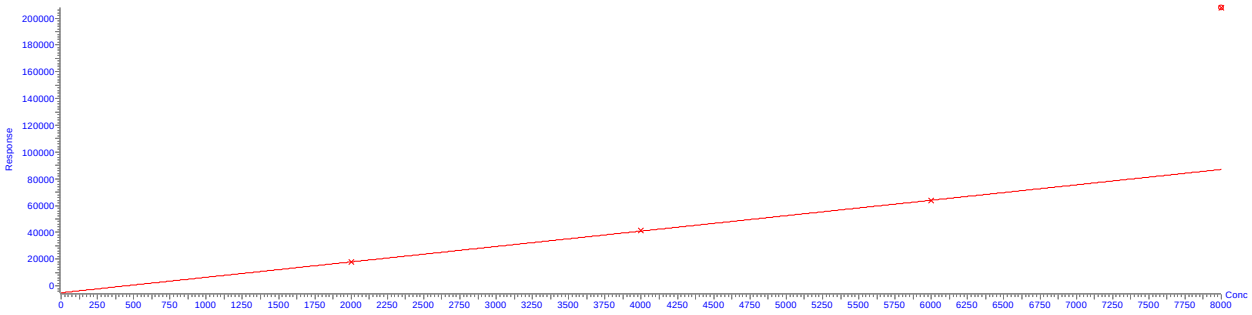
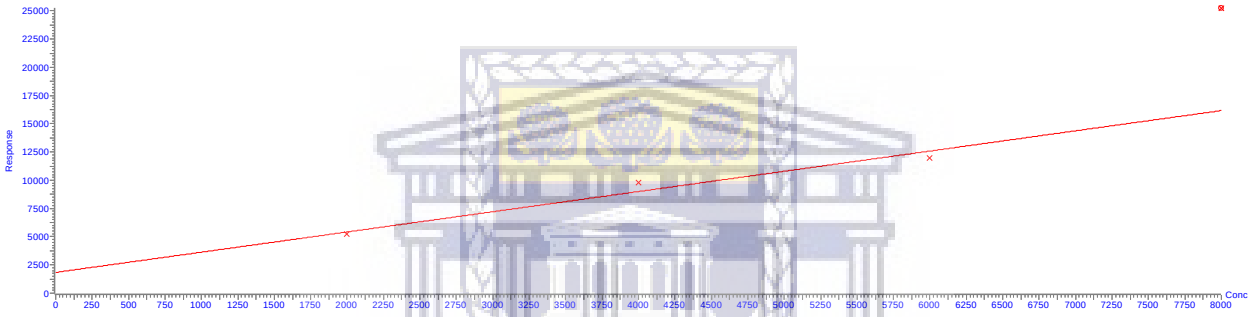
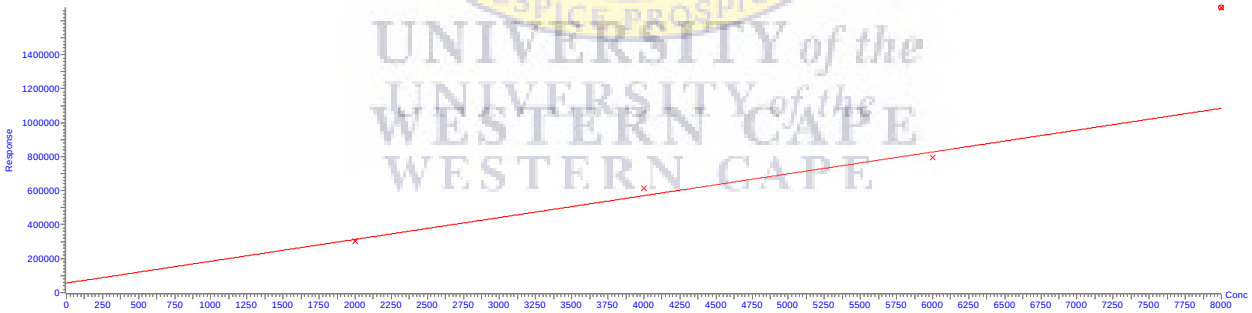
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Compound name: Sulfamethoxazole
Correlation coefficient: r = 0.984065, r^2 = 0.968383
Calibration curve: 1.79108 * x + 1837.91
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Compound name: Carbamazepine
Correlation coefficient: r = 0.990720, r^2 = 0.981527
Calibration curve: 128.595 * x + 56412.7
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



Compound name: Phenytoin
Correlation coefficient: r = 0.992926, r^2 = 0.985902
Calibration curve: 10.397 * x + 6934.19
Response type: External Std, Area
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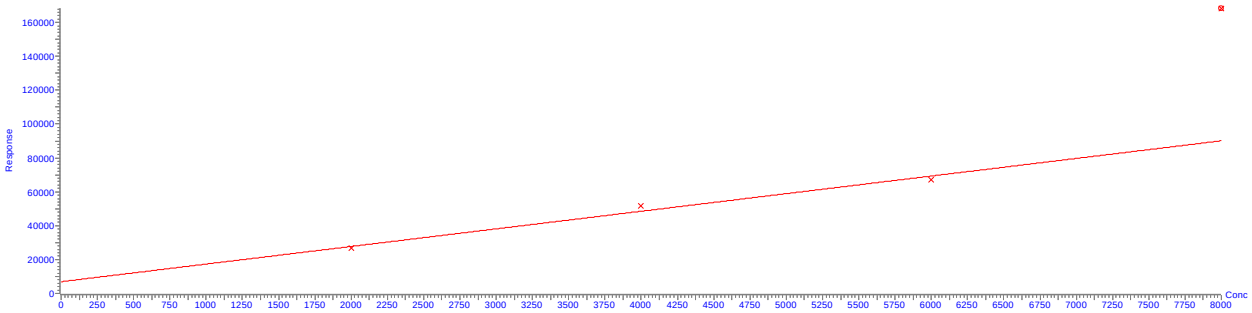


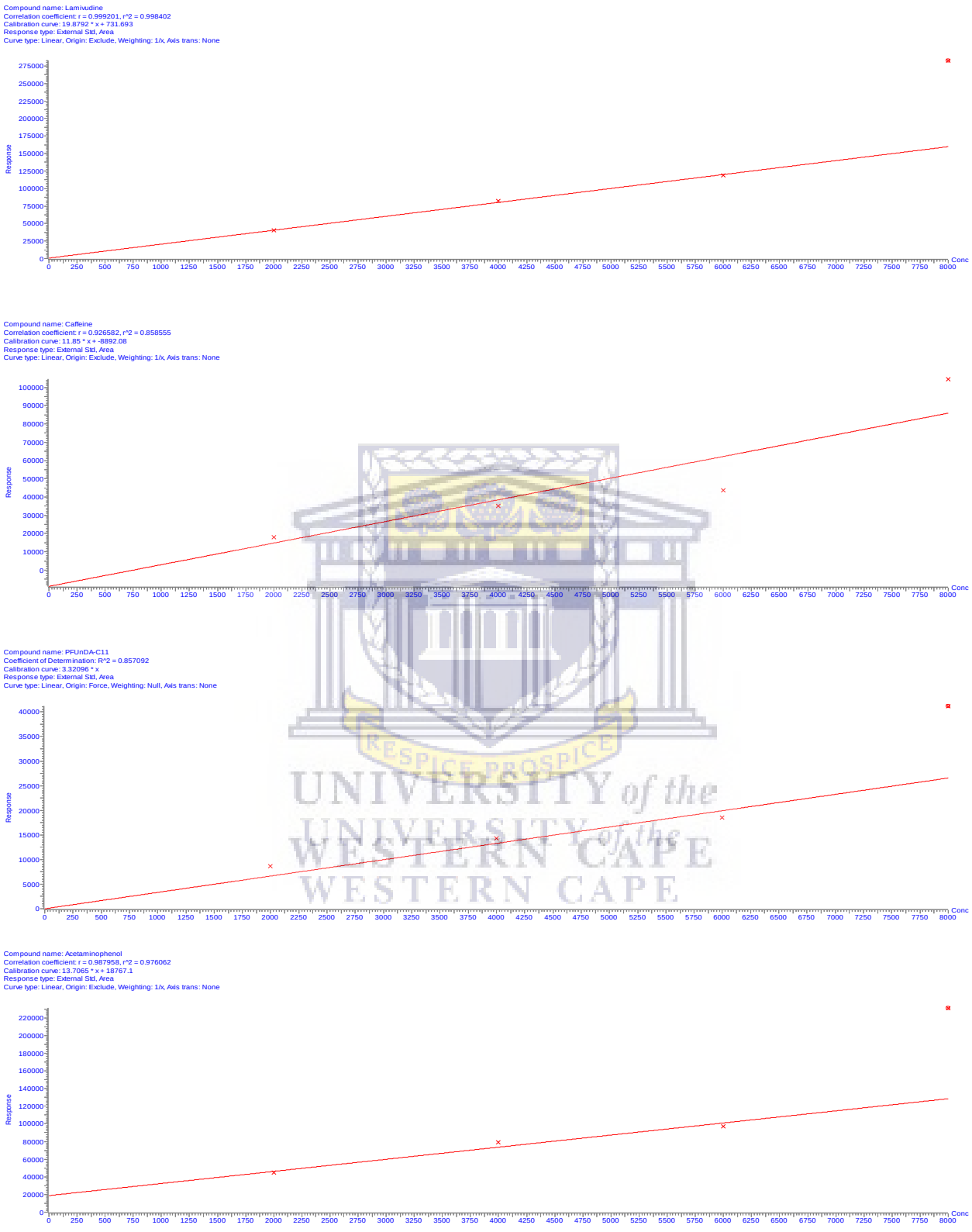


Figure II. 1: Calibration curves and chromatograms of target compounds in Green Point samples analysis

Table II. 1: Concentration of compounds (ng/L) in seawater collected from Green Point

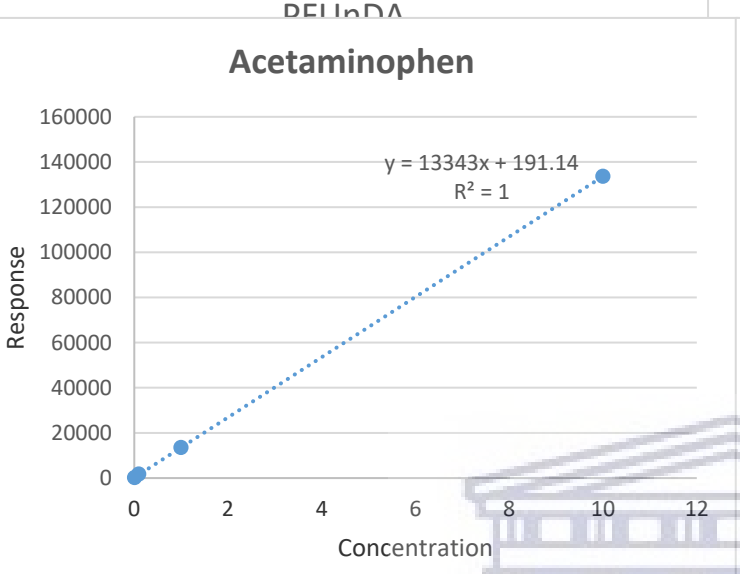
Compounds	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8
PFUnDA	1.06±0.08	0.29±0.01	0.34±0.02	0.13±0.03	0.10±0.01	0.07±0.01	0.06±0.01	0.04±0.01
PFDA	0.42±0.05	0.18±0.03	0.15±0.06	0.07±0.00	0.05±0.00	0.04±0.00	0.03±0.01	0.03±0.01
PFNA	0.21±0.02	0.07±0.01	0.07±0.02	0.04±0.01	0.02±0.00	0.02±0.00	0.02±0.01	0.01±0.00
PFOA	0.45±0.01	0.43±0.04	0.43±0.04	0.43±0.03	0.36±0.00	0.36±0.04	0.34±0.04	0.23±0.02
PFHpA	0.52±0.01	0.46±0.02	0.46±0.04	0.430.04	0.39±0.04	0.39±0.01	0.38±0.00	0.26±0.05
Triclosan	0.16±0.04	0.21±0.01	0.17±0.03	0.23±0.03	0.26±0.03	0.10±0.01	0.31±0.02	0.20±0.00
Bisphenol A	0.20±0.01	0.15±0.04	0.13±0.01	0.12±0.01	0.12±0.01	0.12±0.03	0.10±0.01	0.07±0.01
Diclofenac	0.24±0.04	0.28±0.02	0.24±0.00	0.28±0.03	0.32±0.04	0.15±0.04	0.32±0.03	0.26±0.02
Sulfamethoxazole	0.06±0.01	0.11±0.01	0.07±0.01	0.07±0.01	0.13±0.02	0.02±0.01	0.13±0.01	0.05±0.04
Phenytoin	0.09±0.02	0.14±0.01	0.09±0.00	0.10±0.01	0.14±0.03	0.05±0.02	0.16±0.02	0.09±0.02
Carbamazepine	0.08±0.01	0.11±0.01	0.08±0.00	0.09±0.01	0.12±0.03	0.04±0.01	0.13±0.01	0.07±0.04
Lamivudine	0.02±0.01	0.05±0.02	0.02±0.01	0.02±0.00	0.05±0.02	nd	0.06±0.00	0.02±0.01
Caffeine	0.08±0.01	0.13±0.02	0.08±0.00	0.09±0.01	0.13±0.03	0.05±0.01	0.14±0.01	0.07±0.02
Acetaminophen	0.09±0.02	0.13±0.01	0.08±0.00	0.09±0.01	0.13±0.03	0.03±0.01	0.15±0.01	0.07±0.04
2-nitrophenol	nd	nd	nd	nd	nd	nd	nd	nd

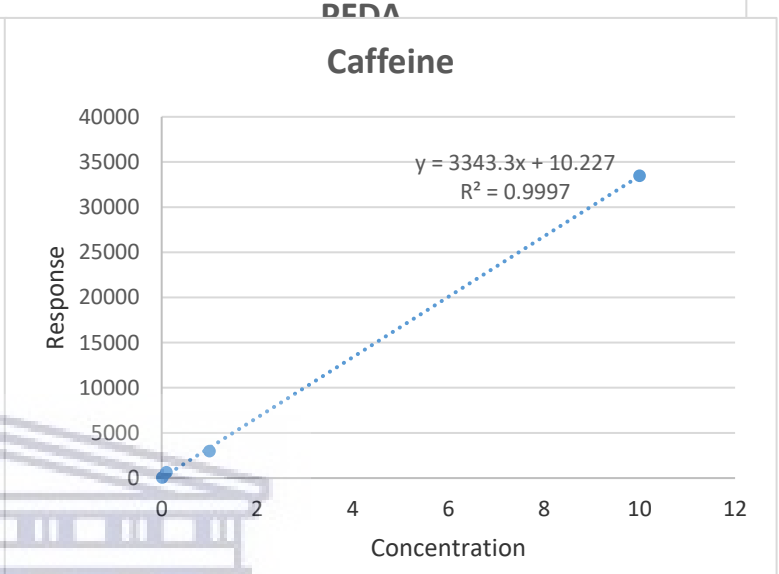
Table II. 2: Concentration of compounds (ng/g) in biota, sediment and seaweed collected from Green Point.

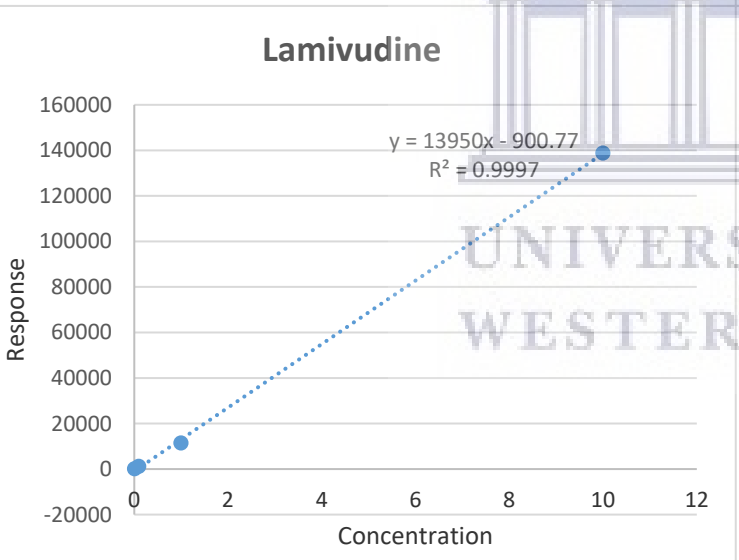
Compounds	Beach sand	Sediment	Mussels	Limpets	Sea urchin	Star fish	Sea snail	Sea weed
PFUnDA	2.94±0.10	3.51±0.10	10.53±0.23	11.95±0.01	7.26±0.29	5.71±0.21	1.68±0.00	1.94±0.09
PFDA	2.69±0.05	3.04±0.11	12.72±0.28	12.57±0.00	5.41±0.13	3.34±0.36	0.25±0.00	0.94±0.04
PFNA	2.29±0.11	2.39±0.17	8.18±0.19	7.04±0.00	3.34±0.16	1.67±0.20	0.43±0.00	0.60±0.06
PFOA	1.36±0.06	1.34±0.07	4.44±0.41	3.37±0.00	1.04±0.13	0.47±0.05	0.15±0.00	0.19±0.00
PFHpA	0.65±0.05	0.56±0.01	0.94±0.06	1.02±0.00	0.46±0.05	0.82±0.01	1.03±0.01	0.40±0.01
Triclosan	4.48±0.21	4.35±0.09	5.61±0.40	10.72±0.00	8.33±0.38	5.95±0.17	4.03±0.00	6.60±0.08
Bisphenol A	3.25±0.34	3.14±0.18	4.62±0.22	7.97±0.00	5.26±0.36	7.40±0.34	2.45±0.00	3.60±0.06
Diclofenac	0.79±0.04	0.56±0.01	0.67±0.09	0.98±0.00	0.43±0.01	2.31±0.13	0.38±0.00	0.51±0.08
Sulfamethoxazole	3.19±0.35	2.01±0.01	4.00±0.21	5.89±0.00	4.07±0.01	6.71±0.40	1.57±0.00	3.04±0.15
Phenytoin	4.23±0.09	2.84±0.11	4.37±0.10	3.68±0.00	4.61±0.12	3.71±0.05	2.46±0.00	3.39±0.48
Carbamazepine	3.32±0.32	2.47±0.13	4.15±0.19	6.16±0.00	4.06±0.04	7.13±0.13	2.16±0.00	3.19±0.23
Lamivudine	3.66±0.03	1.43±0.08	2.45±0.33	1.38±0.00	2.30±0.40	2.02±0.09	0.95±0.00	1.32±0.01
Caffeine	3.63±0.08	2.38±0.42	4.15±0.29	5.57±0.00	4.38±0.08	3.32±0.26	2.05±0.00	2.95±0.05
Acetaminophen	1.53±0.01	2.74±0.02	4.73±0.38	7.32±0.00	4.33±0.14	8.24±0.17	2.35±0.00	3.04±0.18
2-nitrophenol	nd	nd	nd	nd	nd	nd	nd	nd

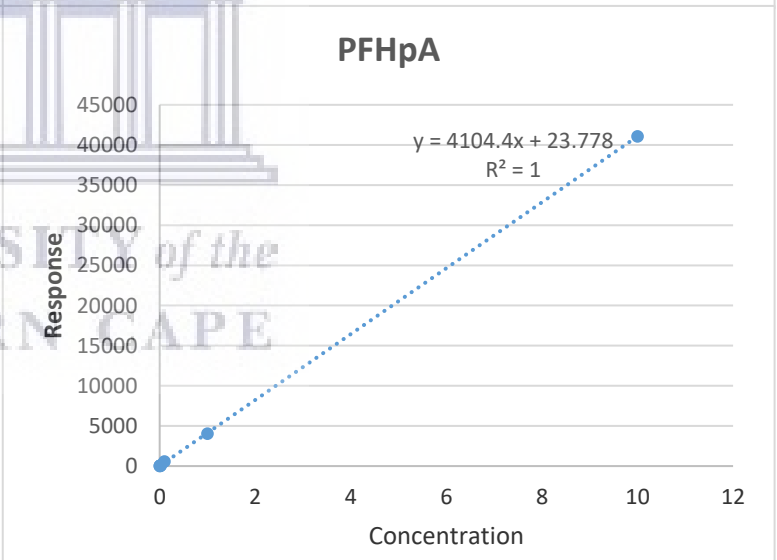
Mean±standard deviation (n=3, replicate samples taken at the same time) nd= not detected

APPENDIX III









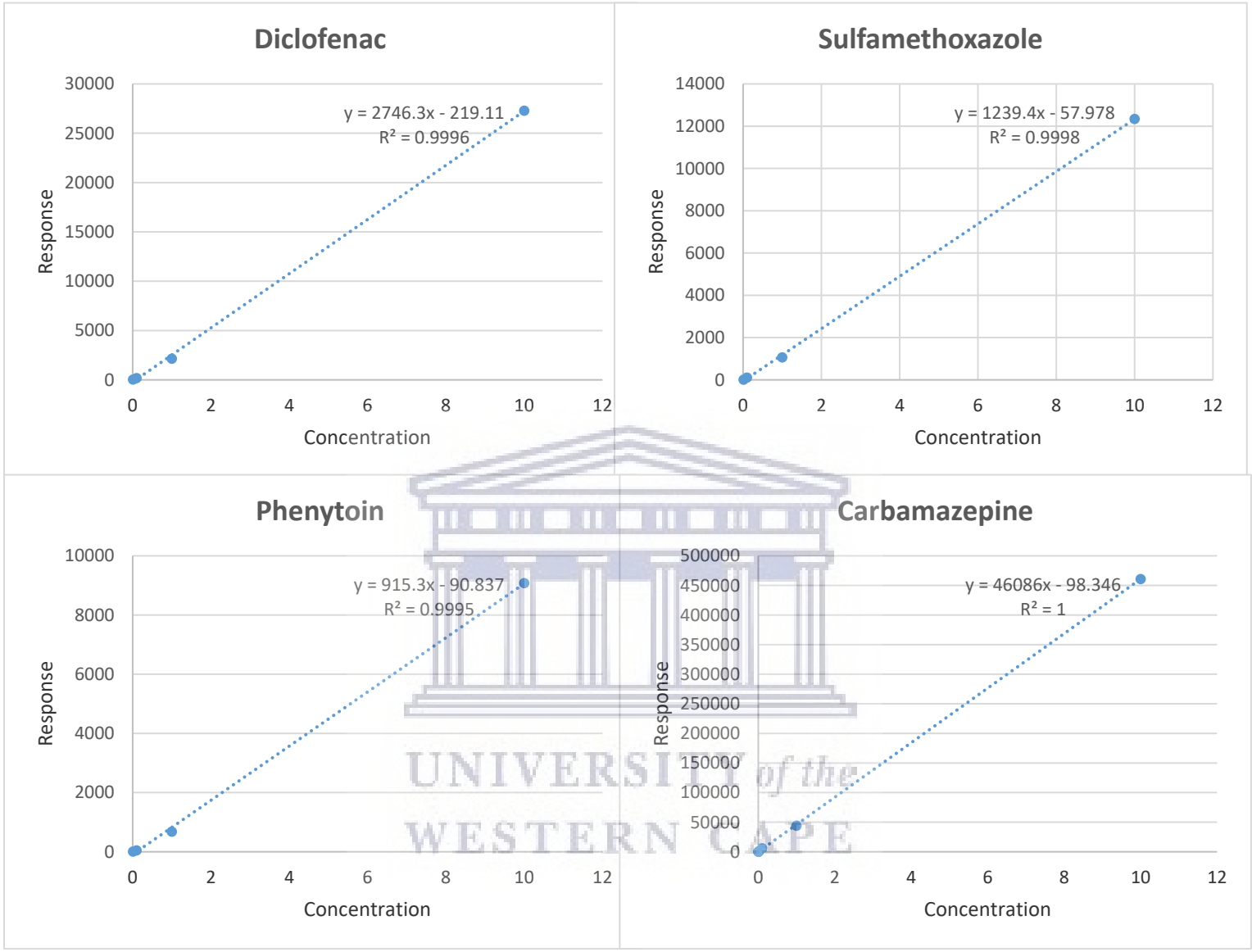
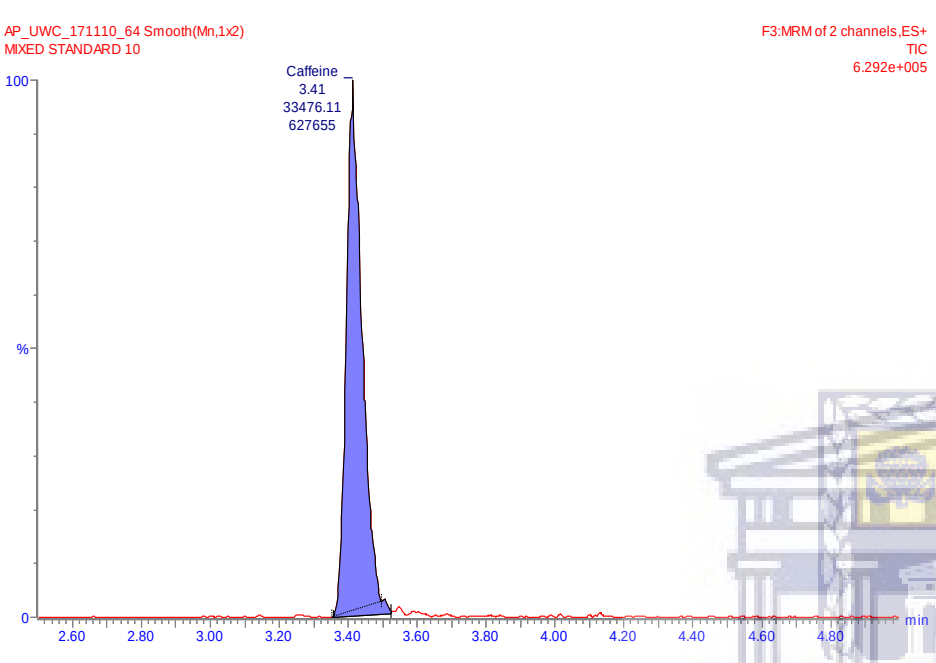
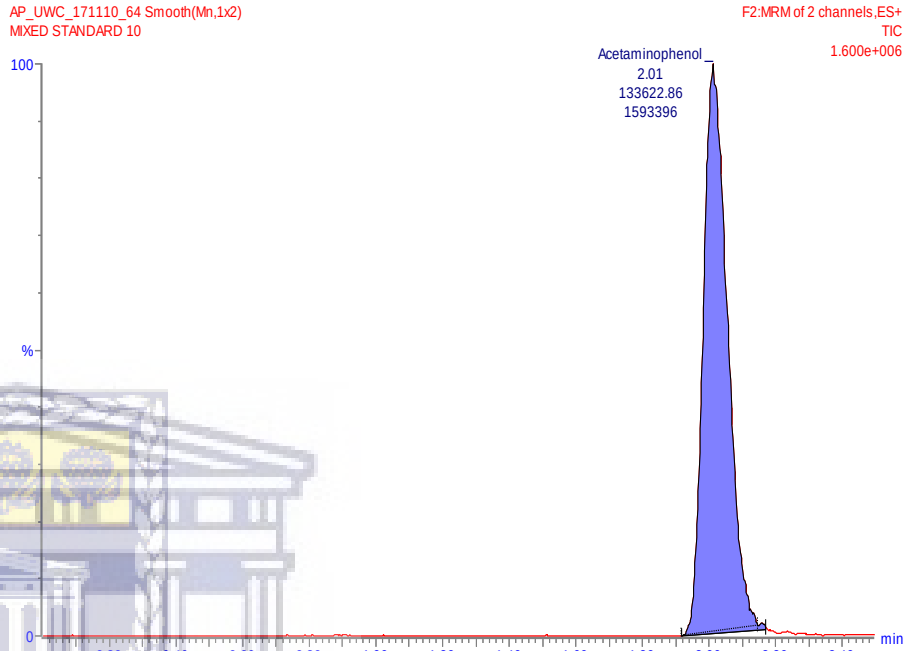
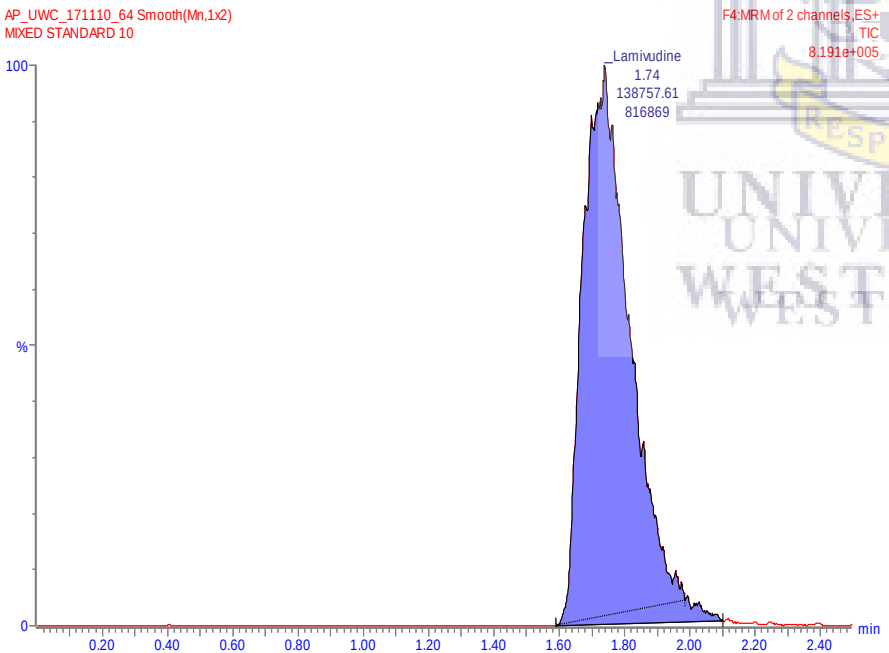
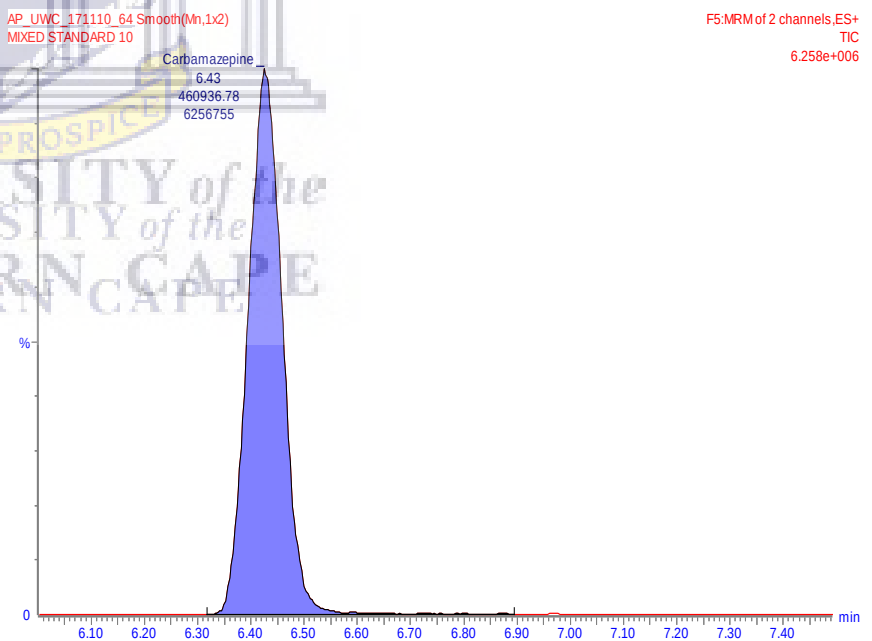


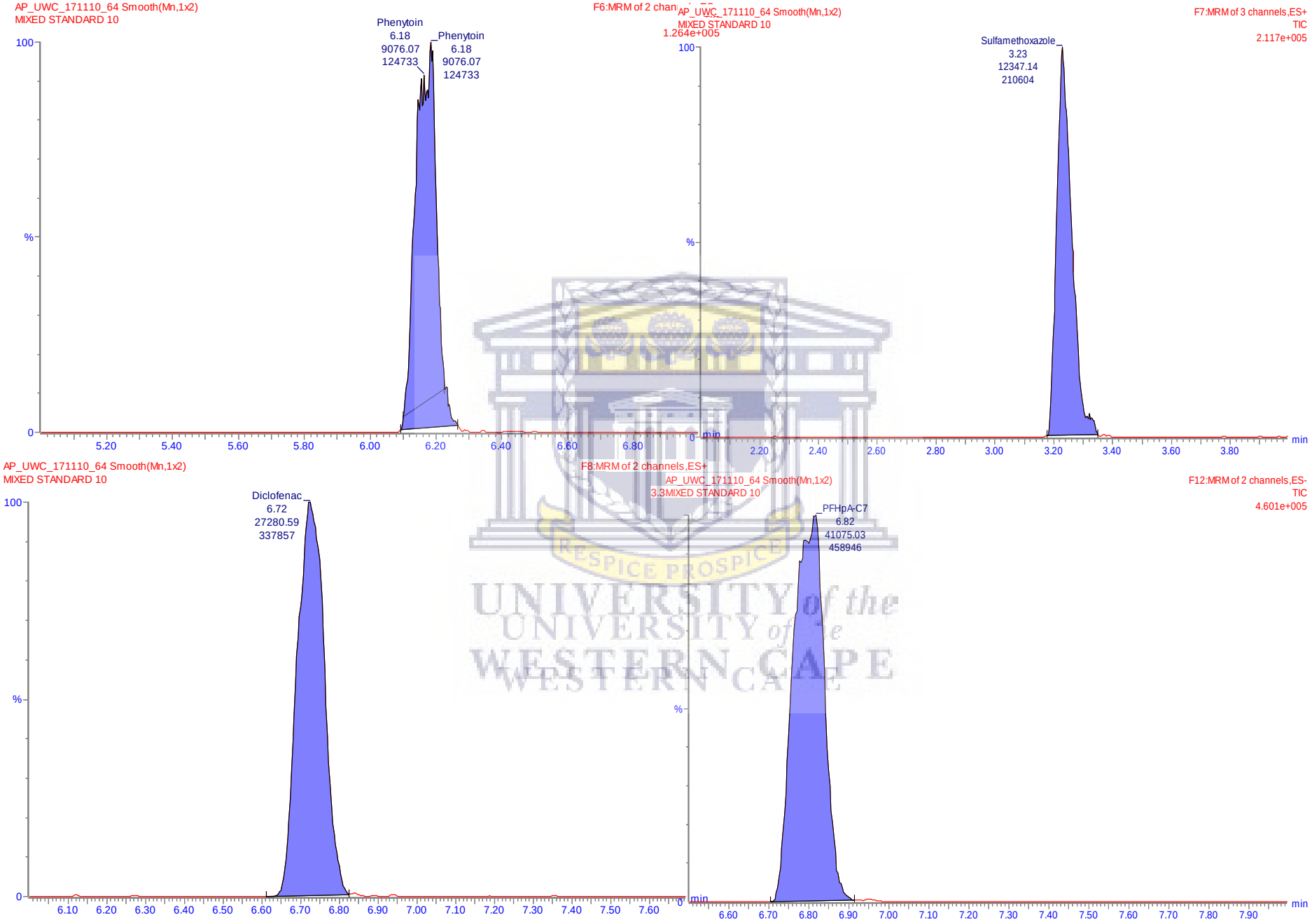
Figure III. 1: Calibration curves of analysed compounds for samples from Camps Bay











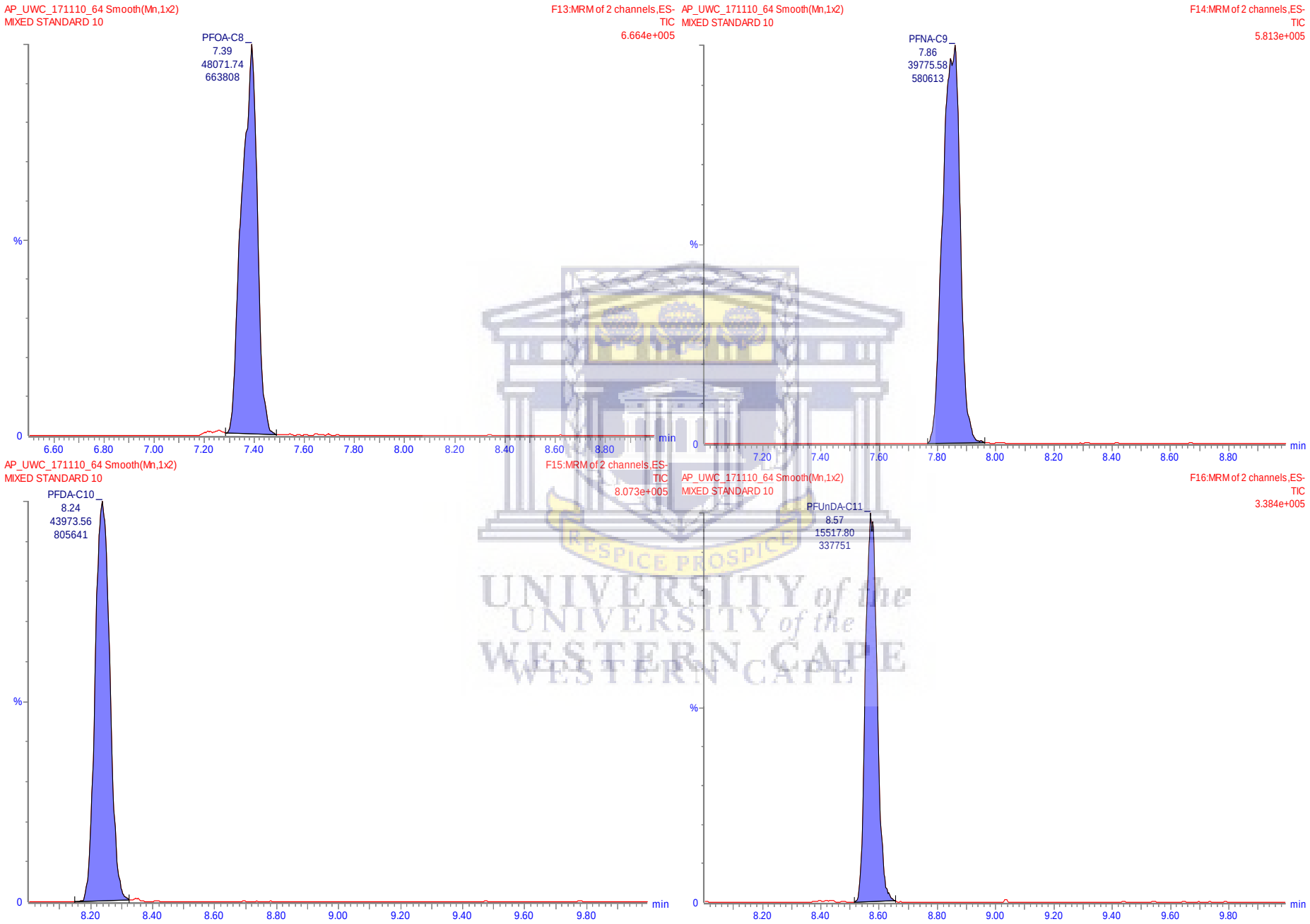
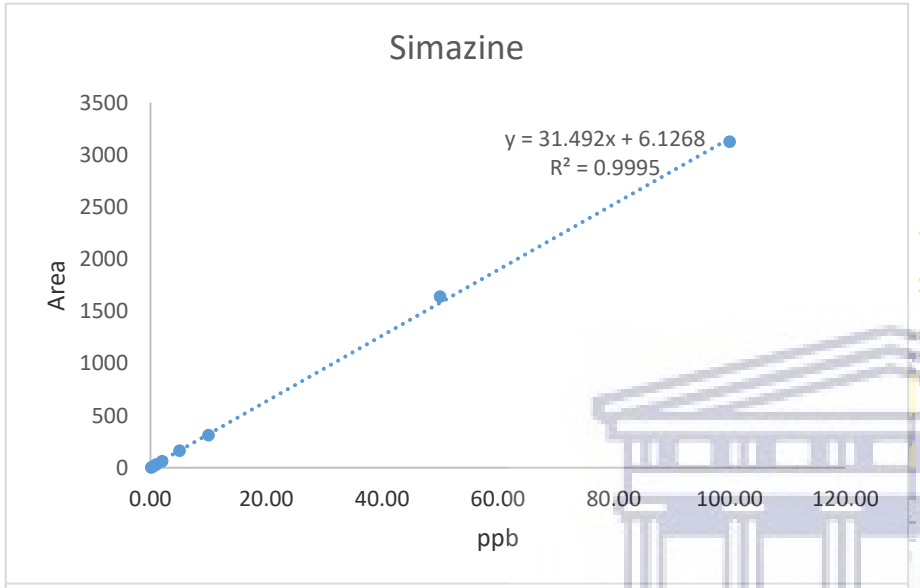
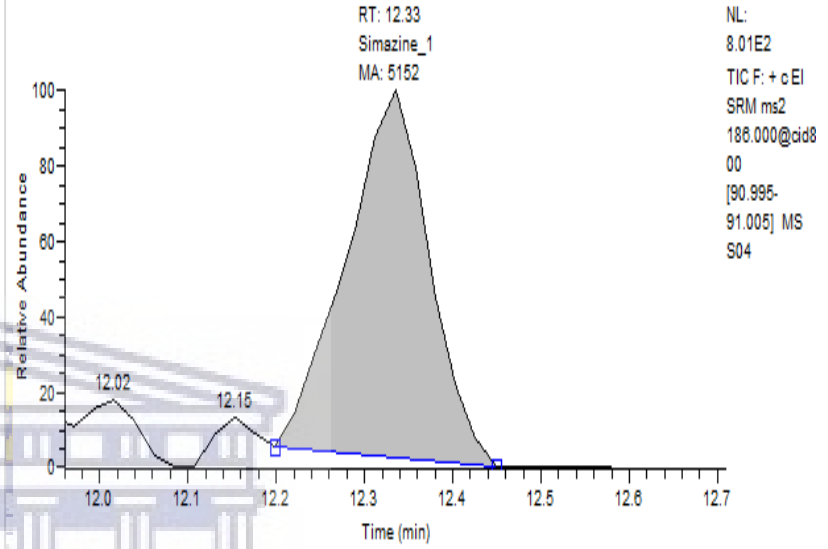
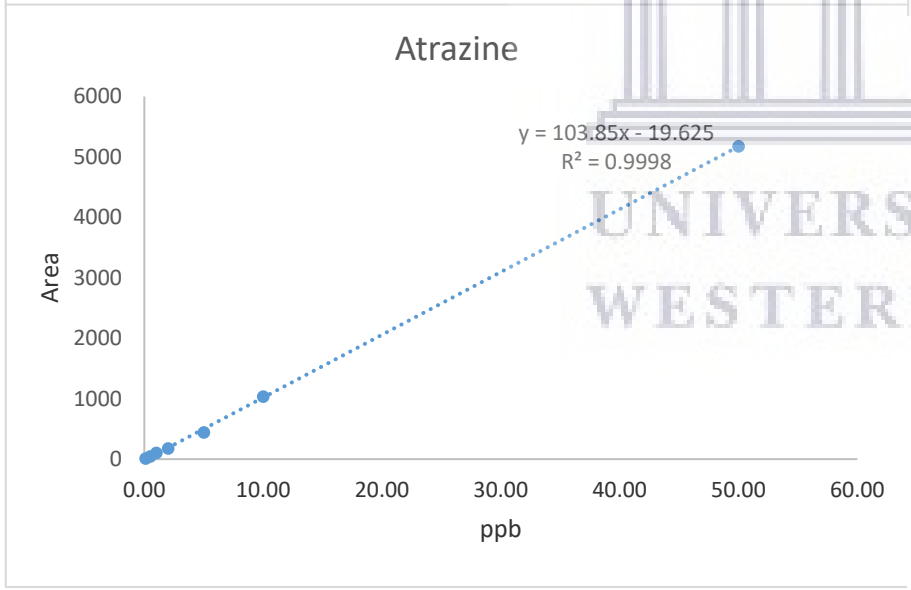
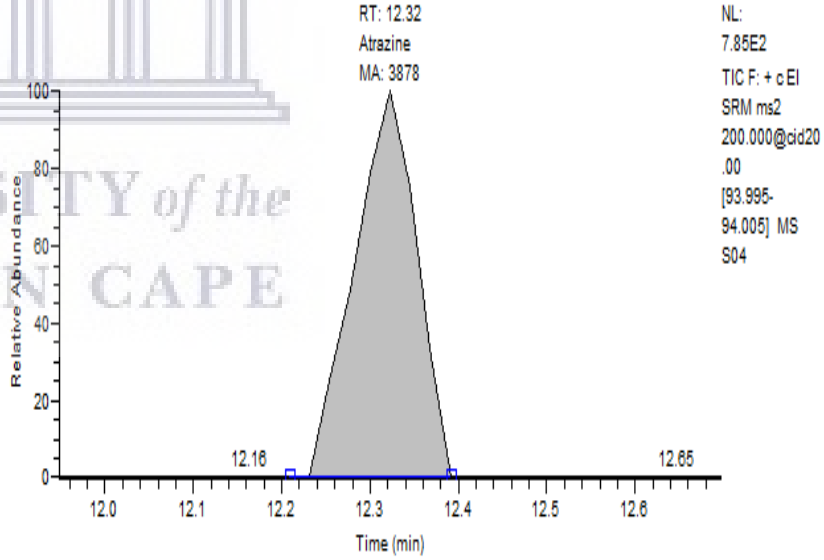


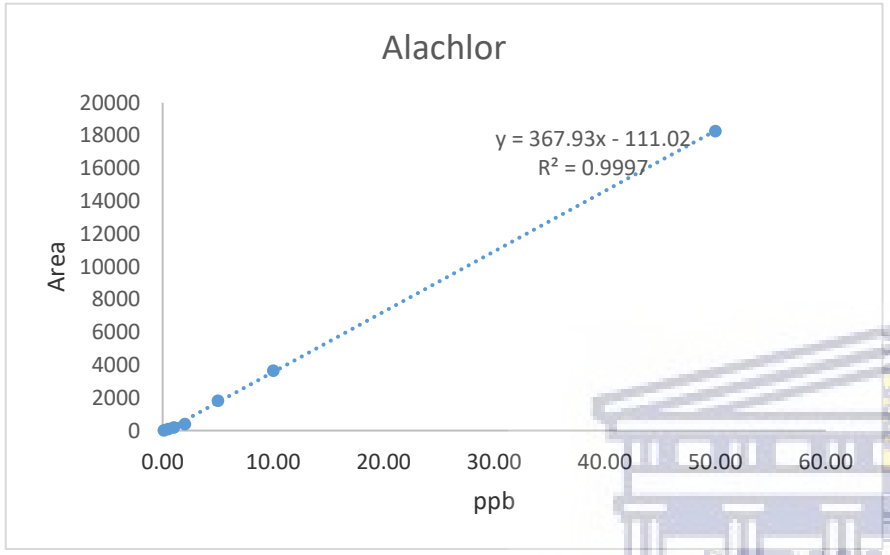
Figure III. 2: Chromatograms of analysed compounds for samples from Camps Bay

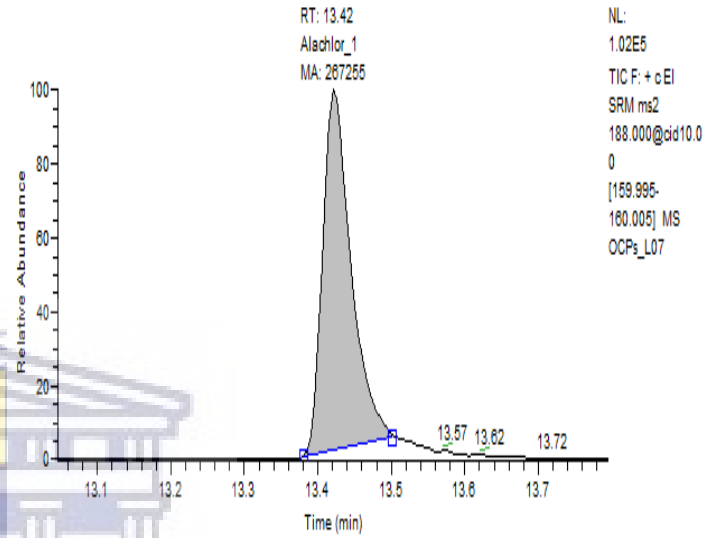


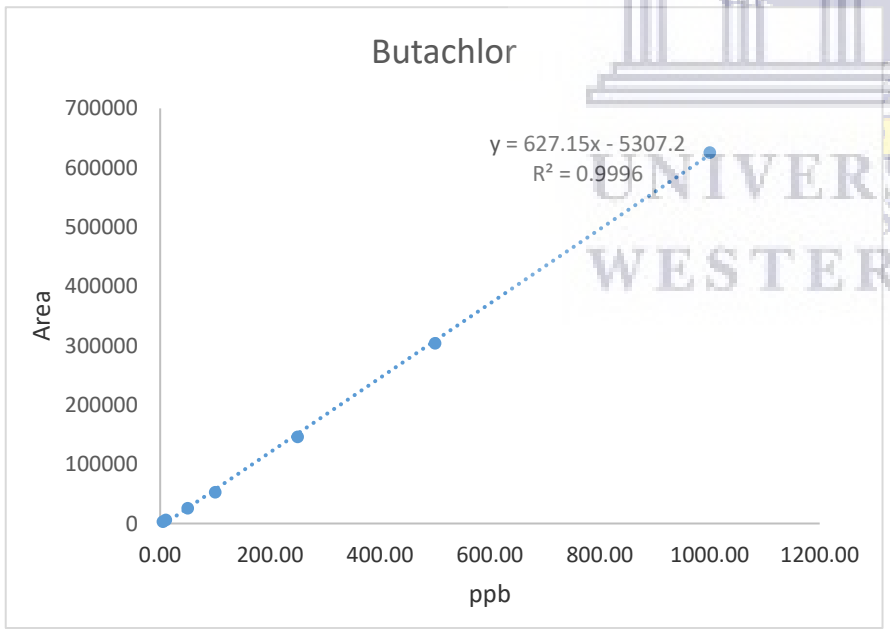


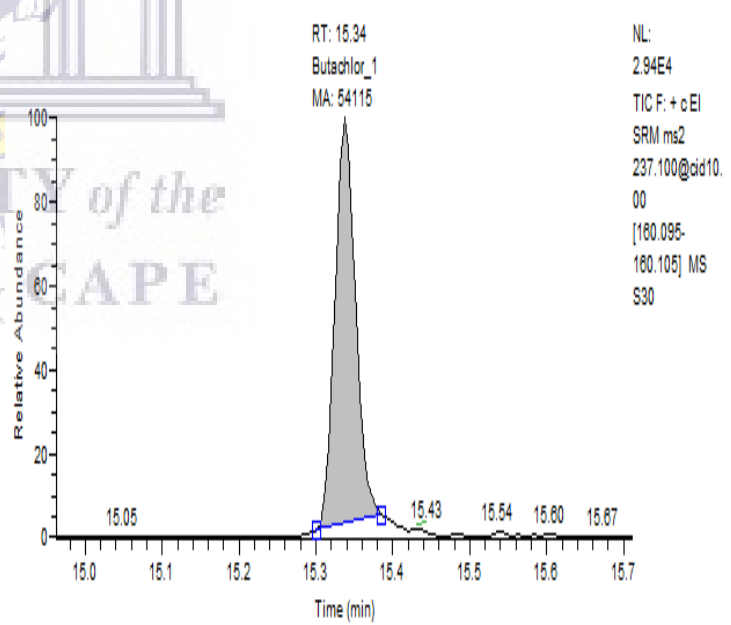












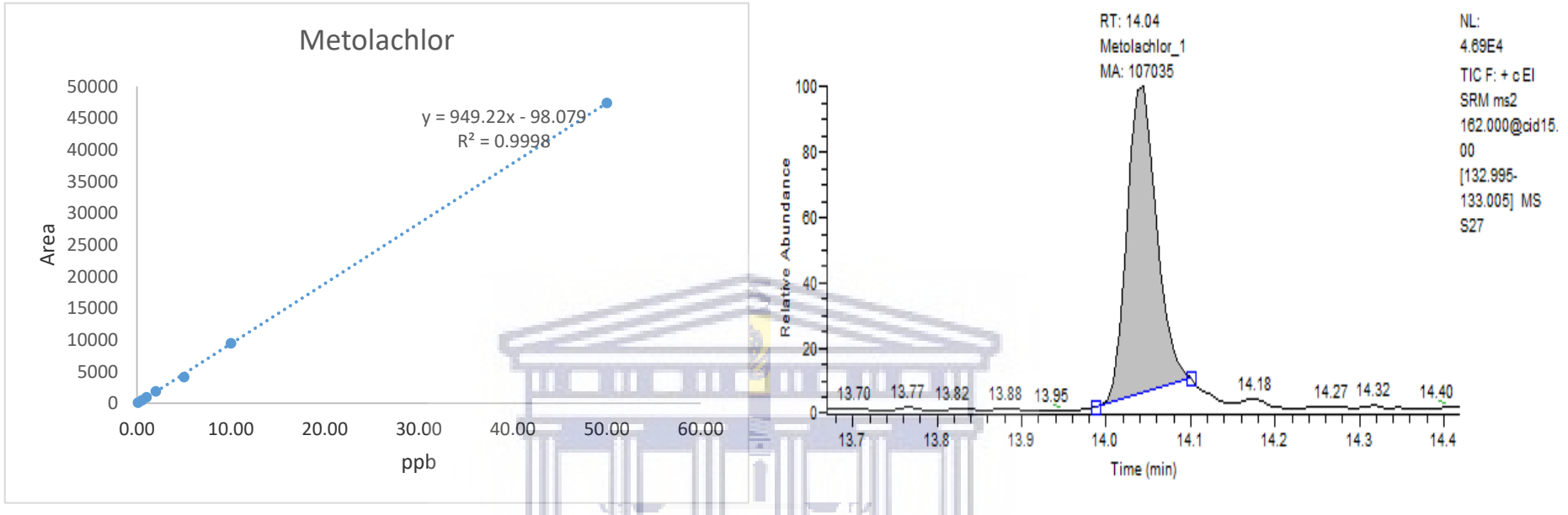


Figure III. 3: Calibration curves and chromatograms for herbicides compounds analysed in samples from Camps Bay

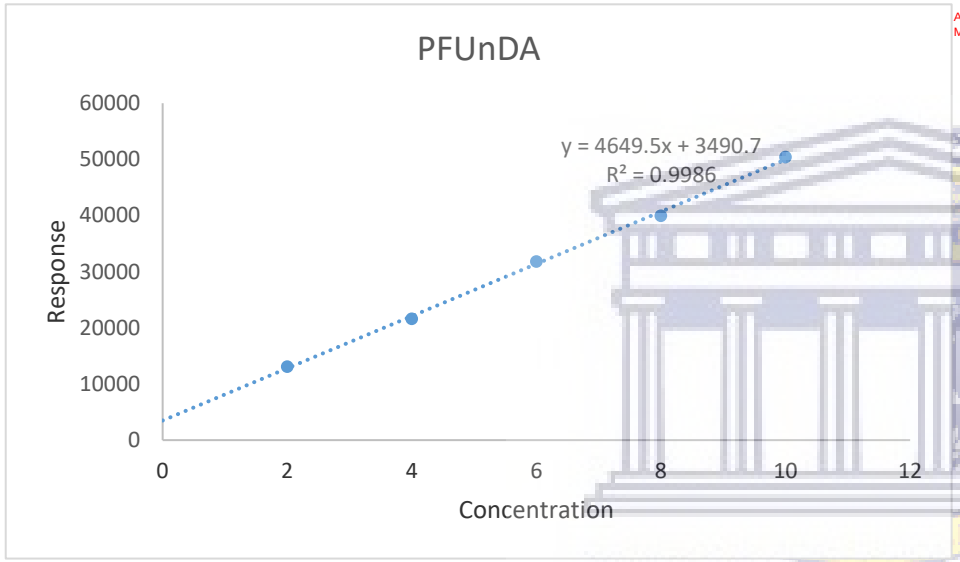
Table III. 1: Concentration of PFCs, EDCs and PPCPs in sea water, biota, sediment and seaweed collected from Camps Bay

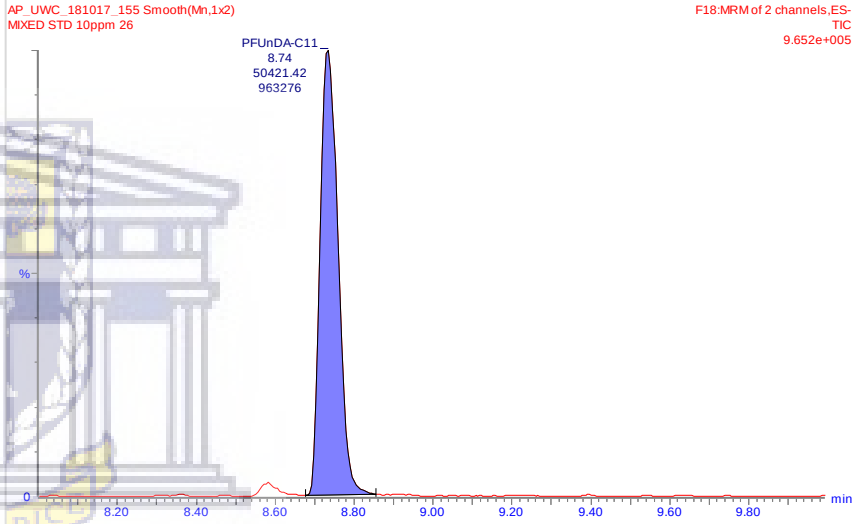
	Seawater 1	Seawater 2	Seawater 3	Mussels	Urchin	Limpets	Seaweed (*Codium fragile*)	Seaweed (*Ulva* spp.)	Marine sediment	Beach sand
Perfluorinated compounds										
PFHpA	0.21±0.01	0.46±0.02	0.27±0.00	282.50±0.11	282.58±2.01	258.97±6.04	149.73±0.56	597.04±10.7	95.30±0.52	28.28±1.08
PFOA	<LOQ	0.76±0.01	<LOQ	115.06±3.29	46.36±1.57	107.41±3.48	84.50±3.50	80.88±0.90	36.53±0.50	28.65±1.12
PFNA	0.02±0.00	0.32±0.00	<LOQ	115.53±1.08	82.17±1.50	120.67±8.38	123.90±0.98	504.52±2.42	91.00±0.56	18.62±0.37
PFDA	2.44±0.05	0.28±0.00	<LOQ	244.96±2.59	523.93±1.37	96.58±1.48	213.82±0.43	764.64±1.95	154.45±10.7	26.52±0.89
PFUnDA	<LOQ	<LOQ	<LOQ	291.81±1.82	50.58±0.91	<LOQ	281.36±3.67	239.39±3.12	21.52±0.11	18.89±1.99
Industrial Chemicals										
2-N	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BPA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Pharmaceuticals and personal care product										
TS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DCF	0.73±0.05	2.86±0.03	<LOQ	97.25±2.55	67.47±0.64	314.04±2.19	110.90±0.82	357.45±2.86	30.68±0.37	134.94±0.55
SUL	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	123.82±0.73	8.87±0.05	<LOQ	<LOQ	<LOQ
PHE	<LOQ	<LOQ	0.94±0.01	66.45±0.58	41.51±2.04	87.53±5.57	63.34±0.20	268.57±2.11	31.34±1.15	<LOQ
CAR	0.05±0.01	0.14±0.00	0.04±0.00	9.82±0.18	12.24±0.77	15.07±0.05	12.15±0.03	30.01±0.45	23.40±2.44	20.22±0.45
LA	<LOQ	<LOQ	<LOQ	<LOQ	3.41±0.06	<LOQ	2.84±0.10	<LOQ	<LOQ	<LOQ
CAF	<LOQ	<LOQ	<LOQ	19.70±0.22	78.38±1.07	6.03±0.41	55.53±1.59	19.87±0.66	1.56±0.06	<LOQ
ACT	0.09±0.00	0.10±0.00	<LOQ	20.04±1.50	27.59±0.35	11.10±0.07	6.56±0.09	10.50±1.02	6.22±0.18	11.86±0.52

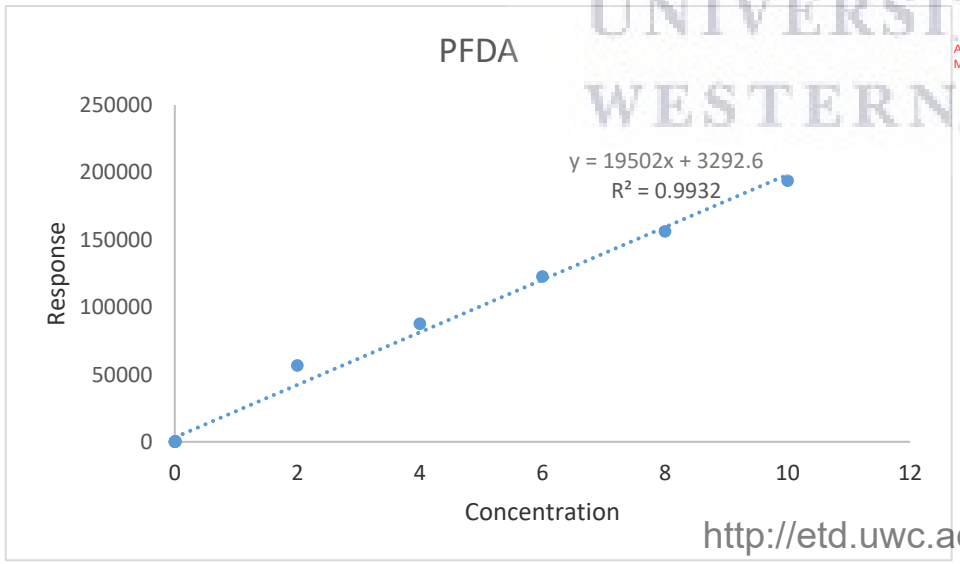
Table III. 2: Concentration (ng/L and ng/g dry weight) of compounds detected in different matrices of Camps Bay marine environment.

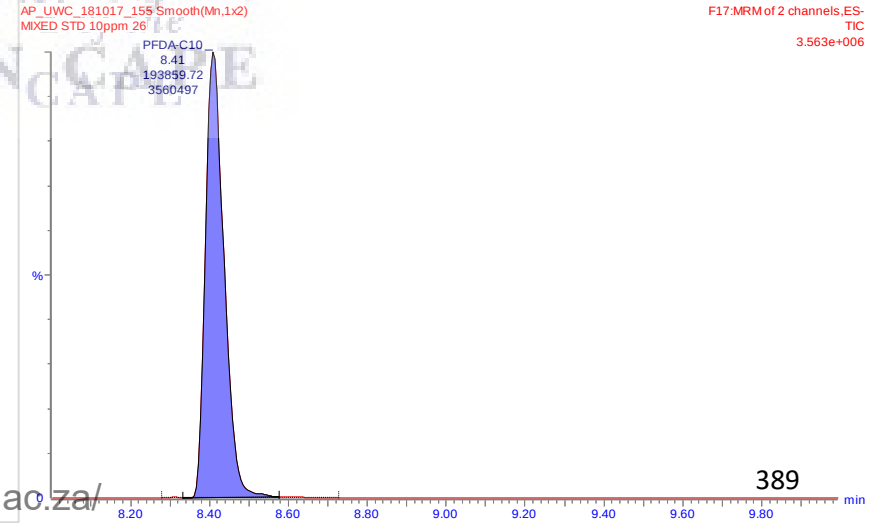
	Alachlor	Metolachlor	Butachlor	Simazine	Atrazine
Matrix	**Mean ± S.D**	**Mean ± S.D**	**Mean ± S.D**	**Mean ± S.D**	**Mean ± S.D**
Seawater 1	<LOQ	0.3 ± 0.2	0.5 ± 0.1	1.4 ± 0.9	1.9 ± 0.5
Seawater 2	3.4 ± 1.0	2.3 ± 0.4	1.6 ± 0.6	4.2 ± 0.0	1.6 ± 0.8
Seawater 3	<LOD	<LOD	<LOD	0.8 ± 0.2	<LOQ
Marine sediment	16.4 ± 0.0	45.3 ± 0.0	10.6 ± 0.0	24.2 ± 0.0	21.6 ± 0.9
Beach sand	<LOD	30.8 ± 0.0	<LOD	16.0 ± 0.1	10.1 ± 0.0
Mussels (*Mytilus galloprovincialis)*	16.9 ± 0.1	42.4 ± 0.1	45.3 ± 0.7	157.8 ± 0.1	35.3 ± 0.1
Limpet (*Cymbula granatina)*	10.6 ± 0.1	<LOD	<LOD	118.9 ± 0.3	59.0 ± 0.4
Sea urchin (*Parechinus angulosus)*	<LOQ	<LOQ	8.6 ± 0.8	39.0 ± 0.1	14.3 ± 0.7
Seaweed (*Ulva* spp)	25.4 ± 0.8	52.9 ± 0.2	15.8 ± 0.2	84.2 ± 0.1	21.6 ± 0.2
Seaweed (*Codium fragile*)	21.1 ± 0.0	21.0 ± 0.1	12.3 ± 0.1	87.0 ± 0.4	28.2 ± 0.1

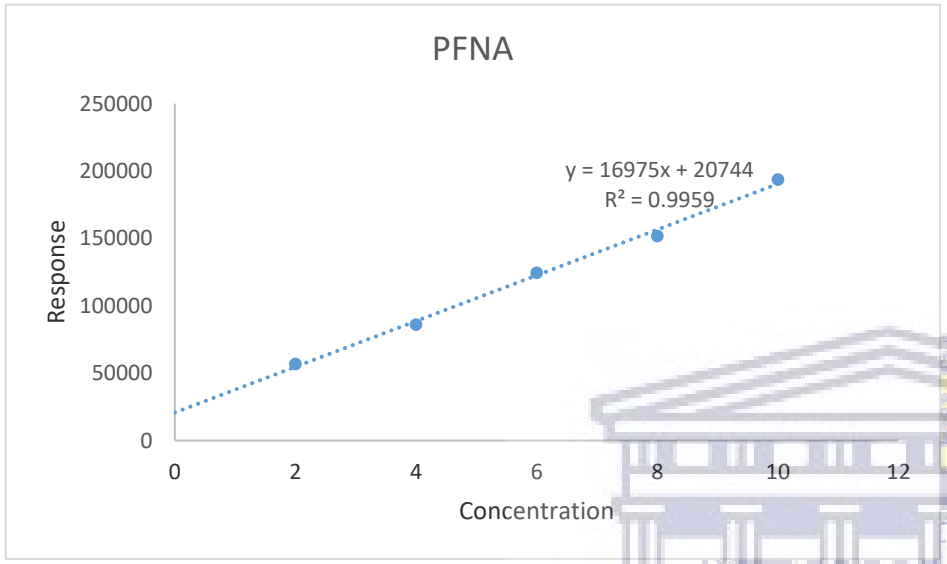
APPENDIX IV

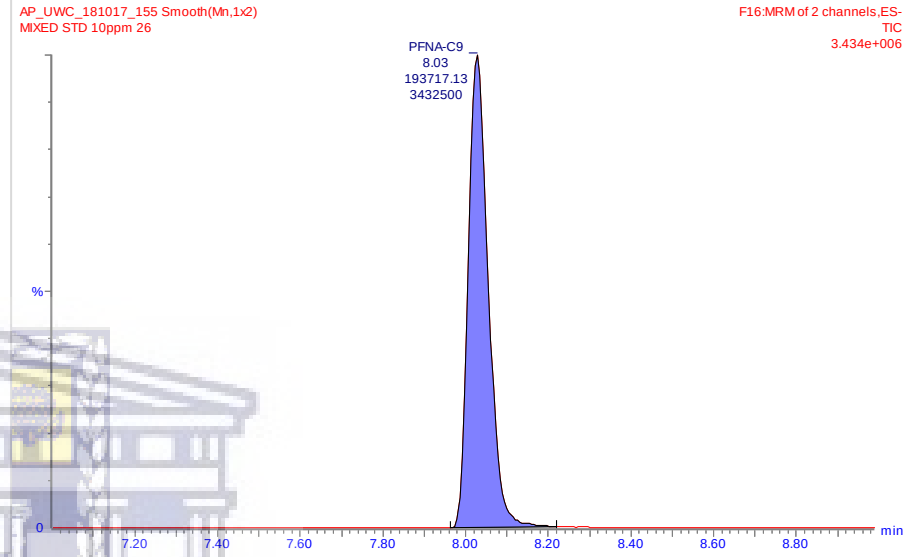


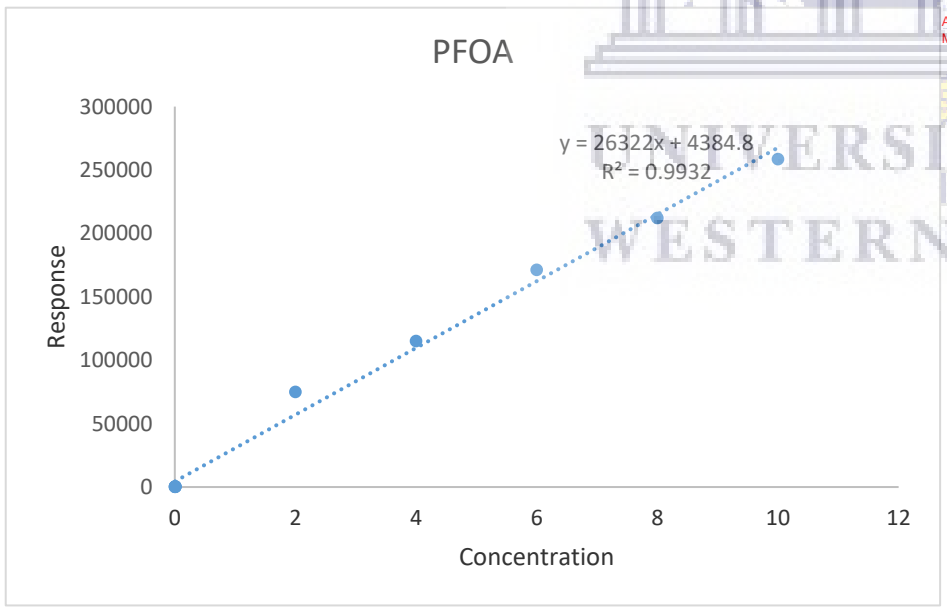


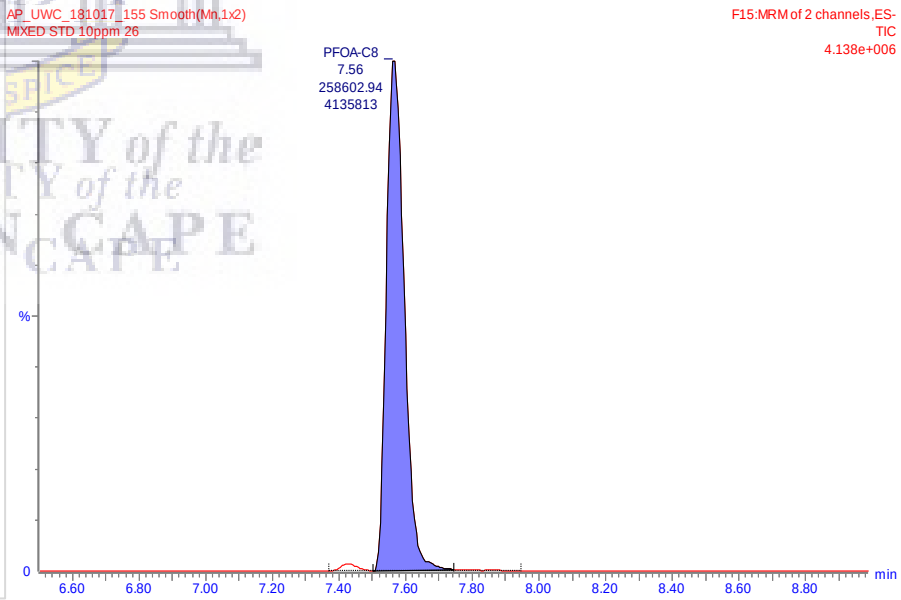


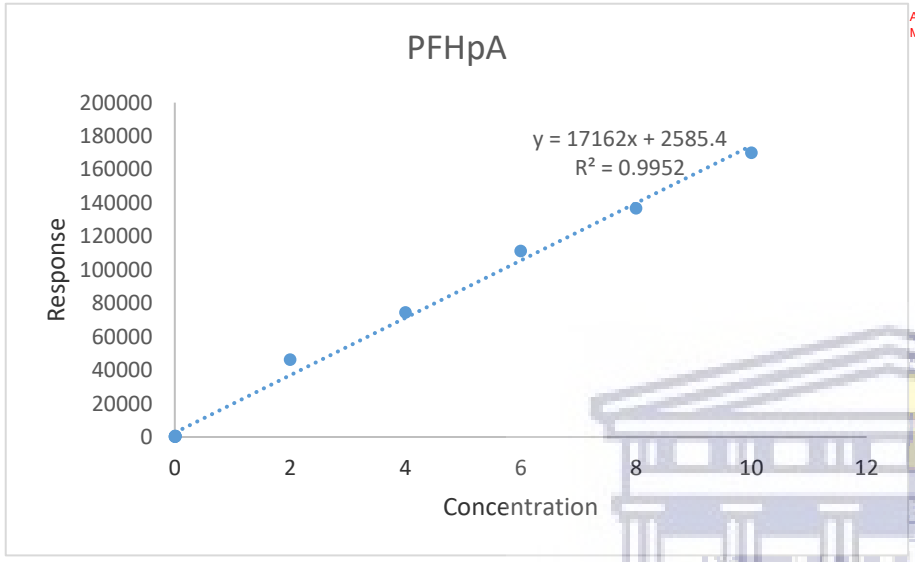


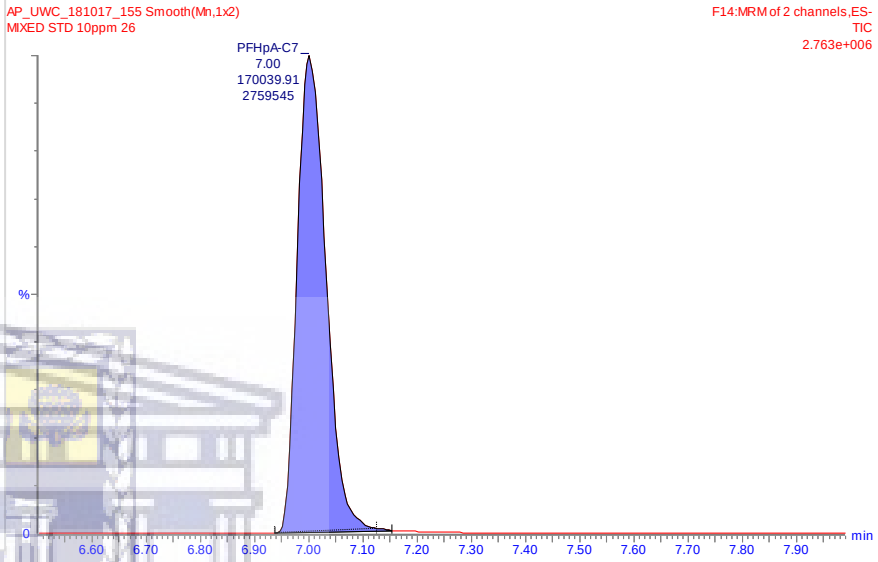


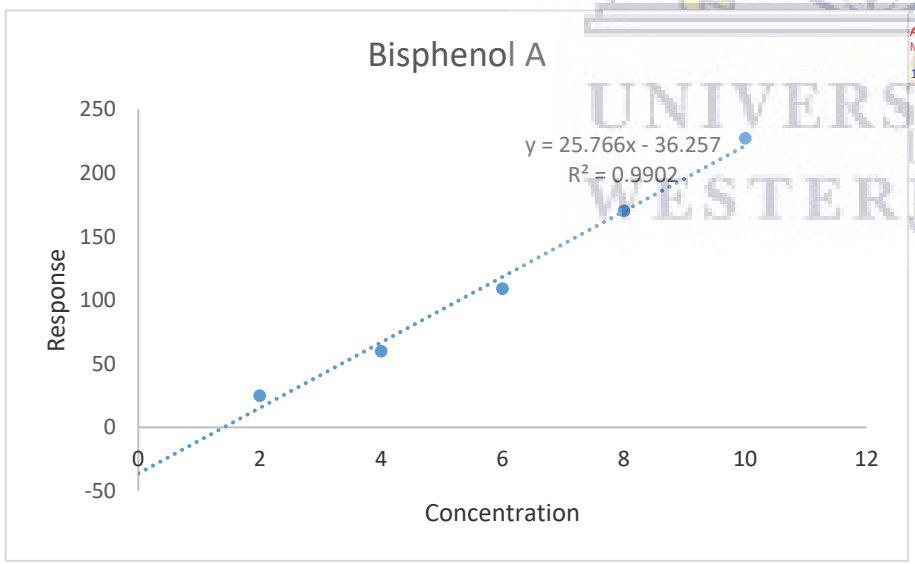


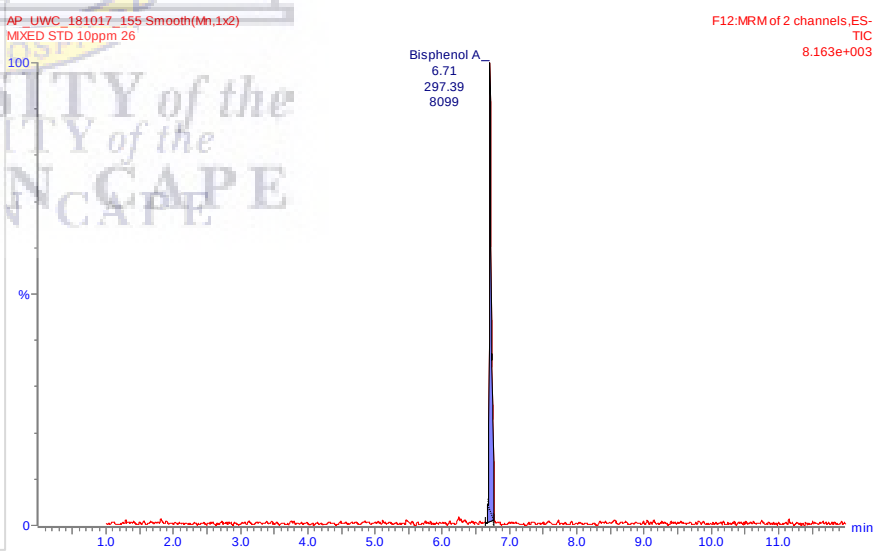


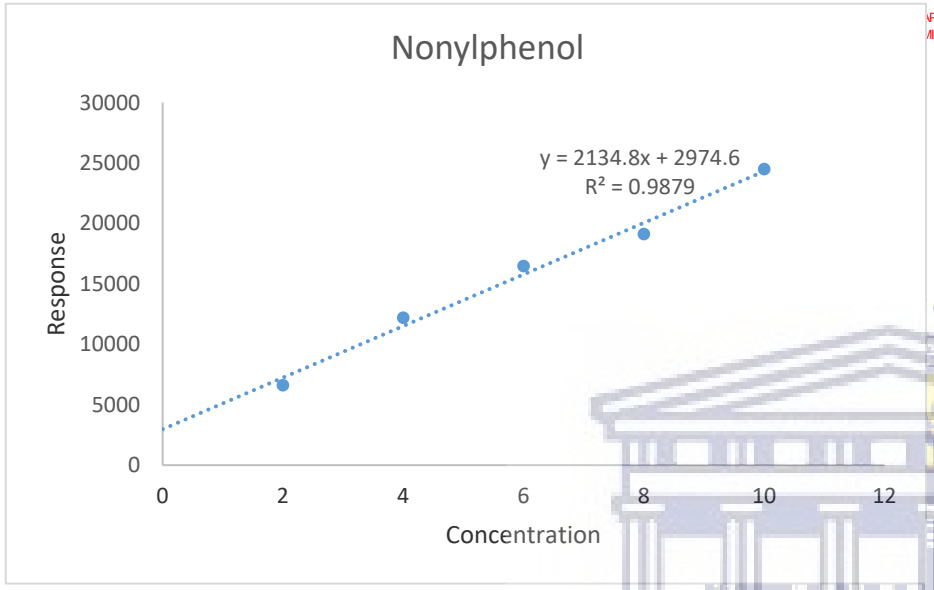


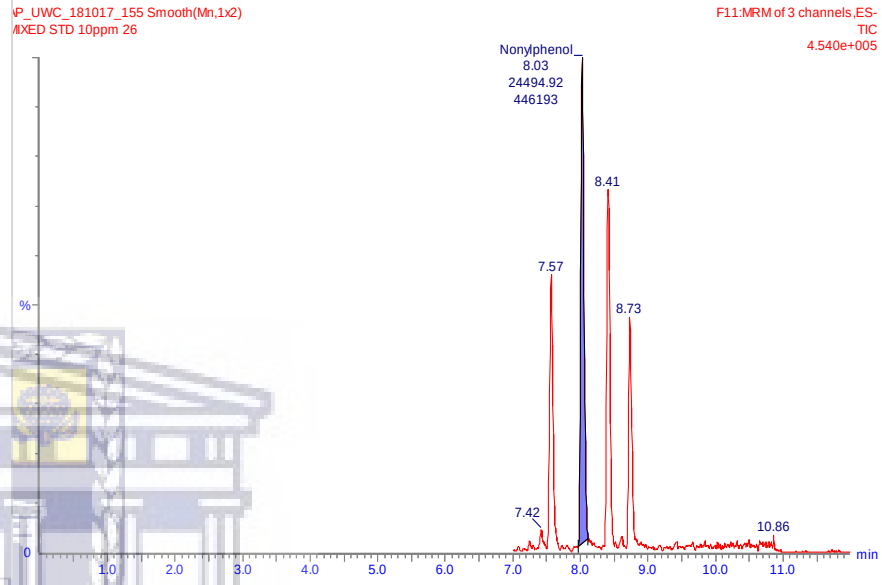


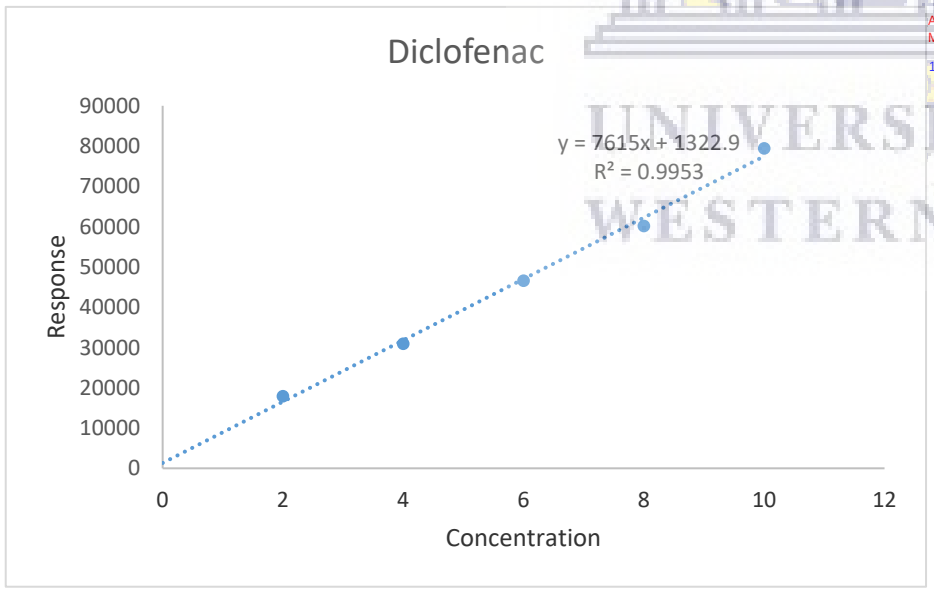


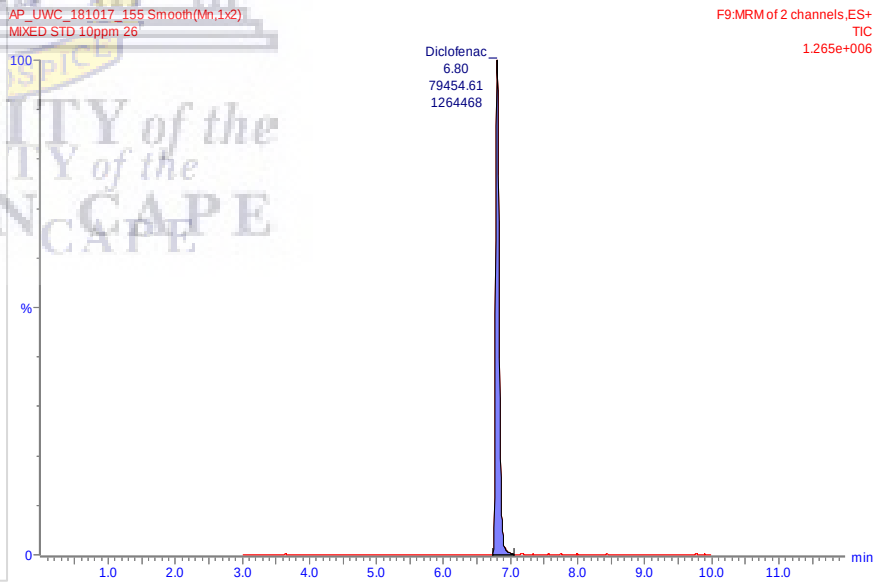


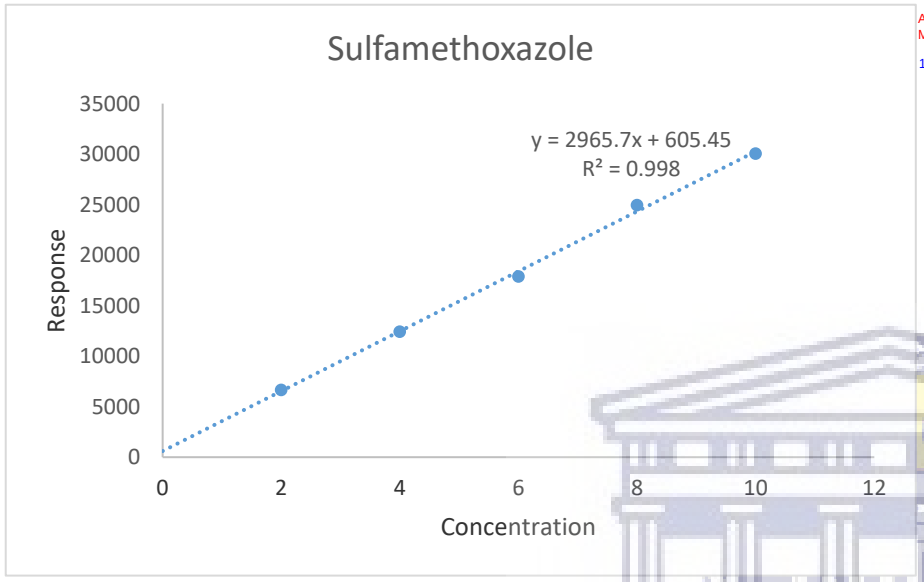


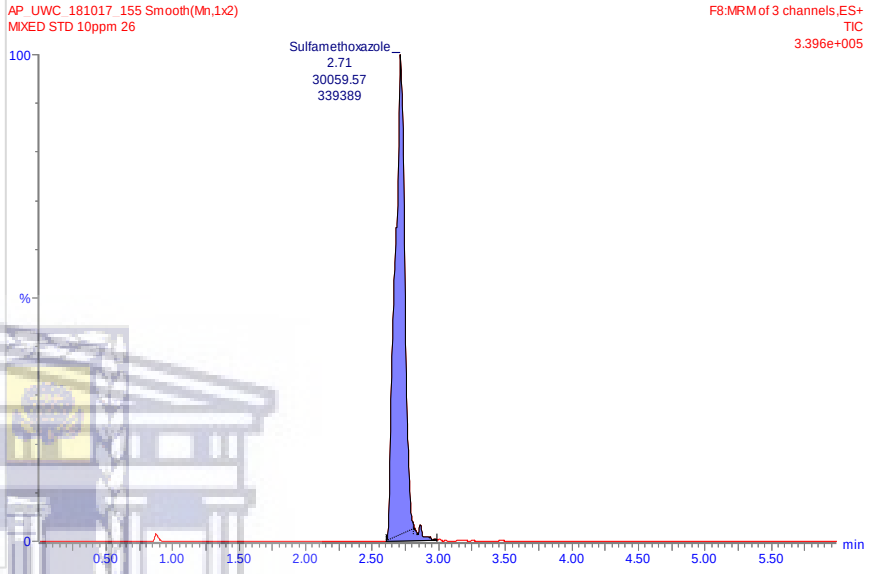


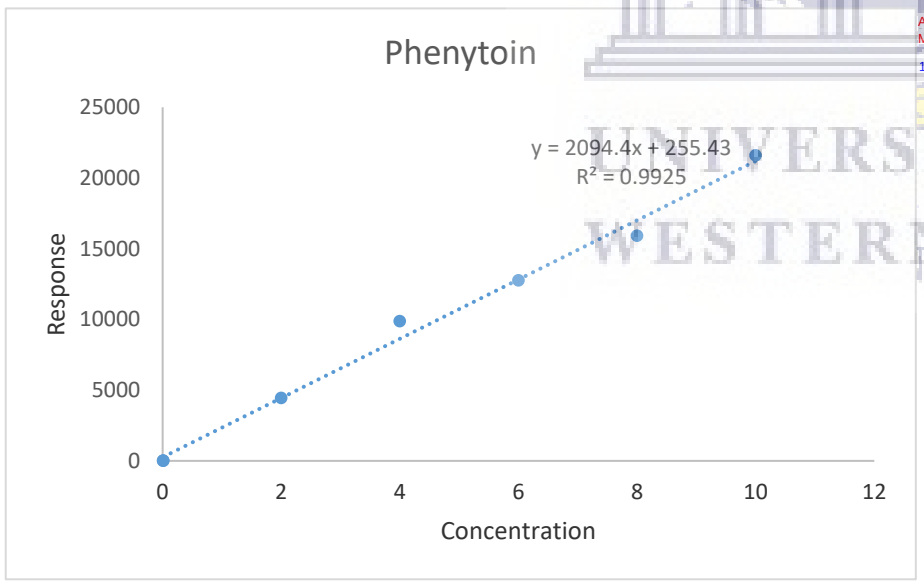


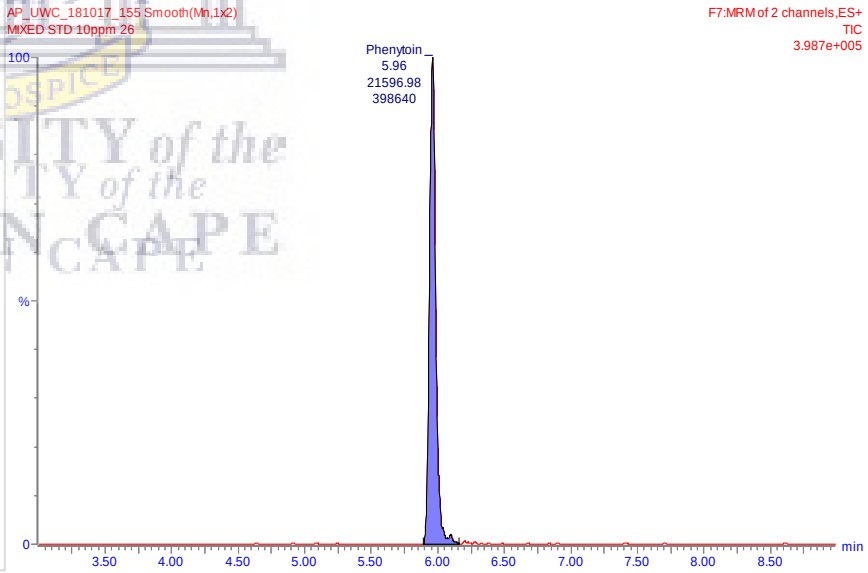


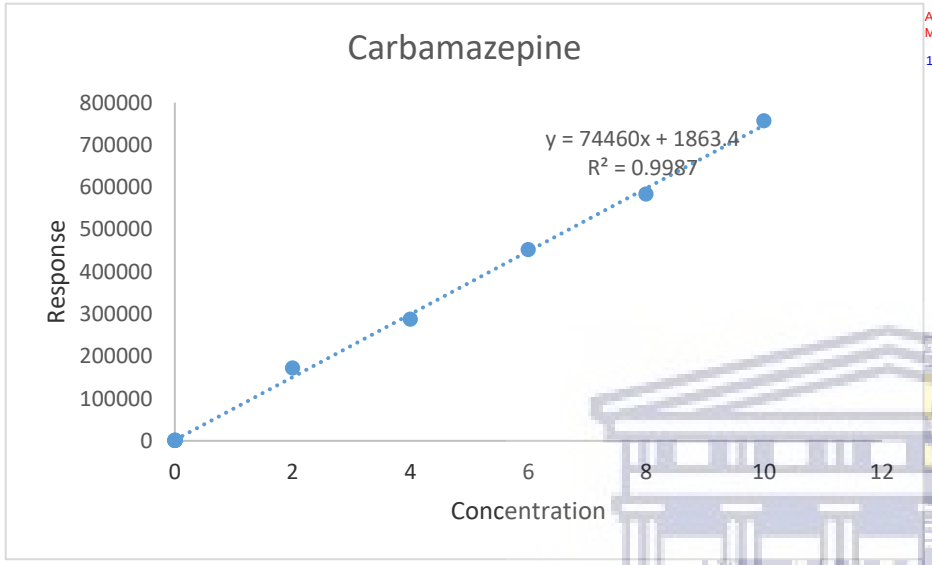


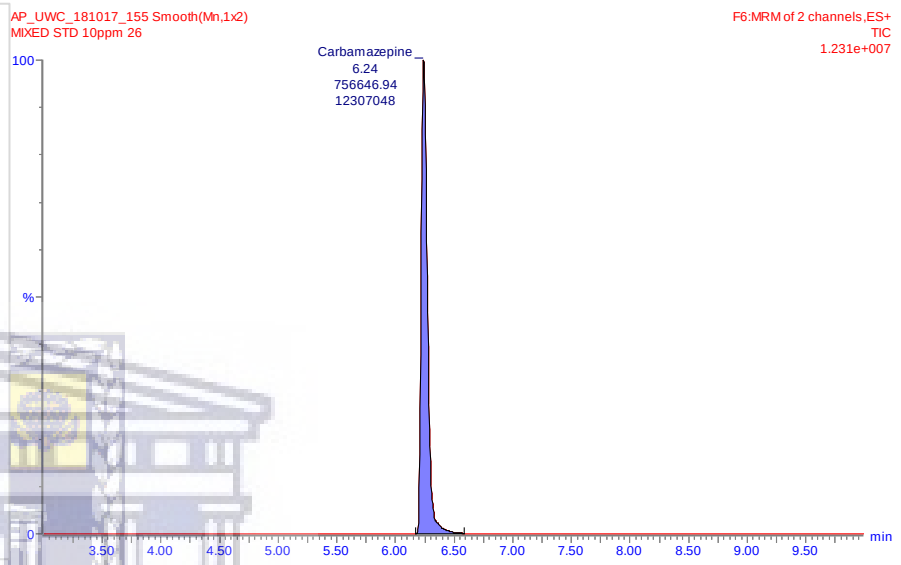


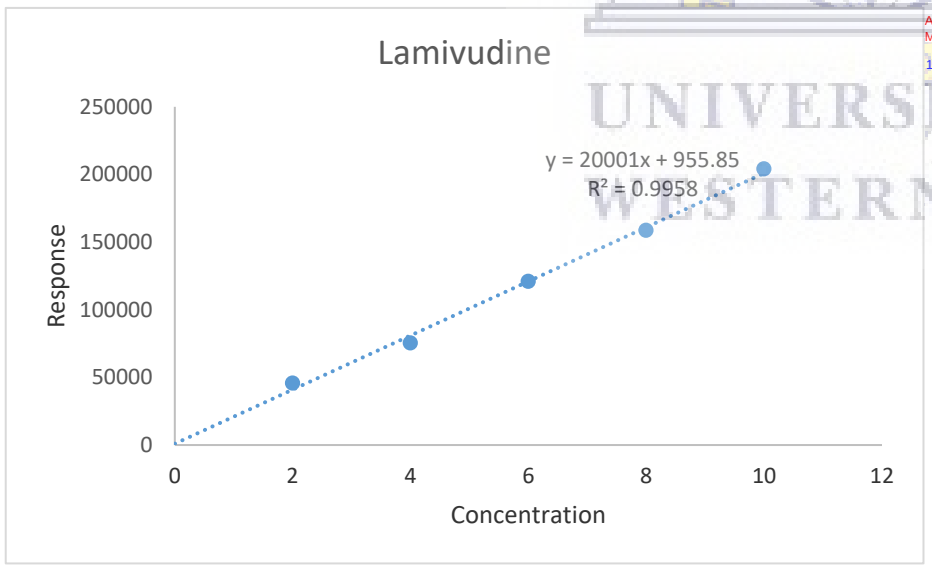


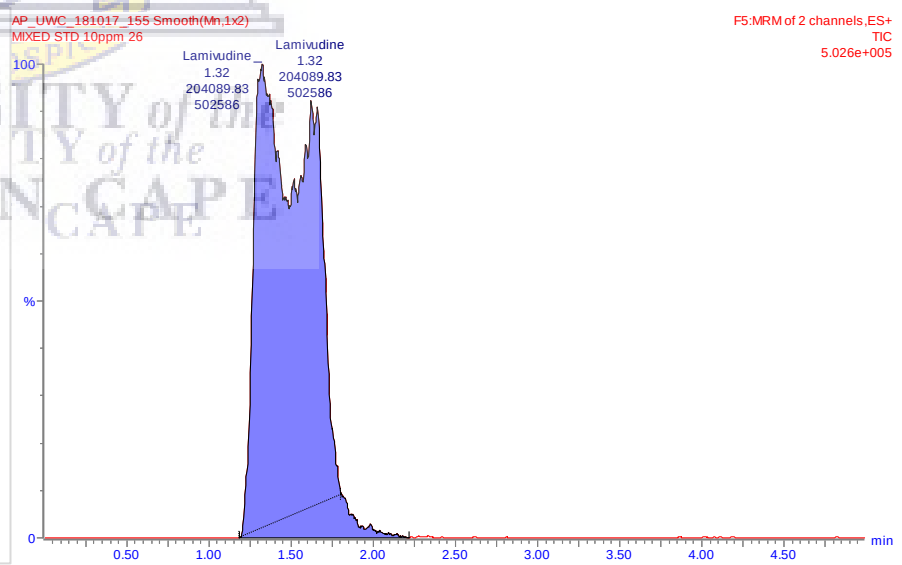


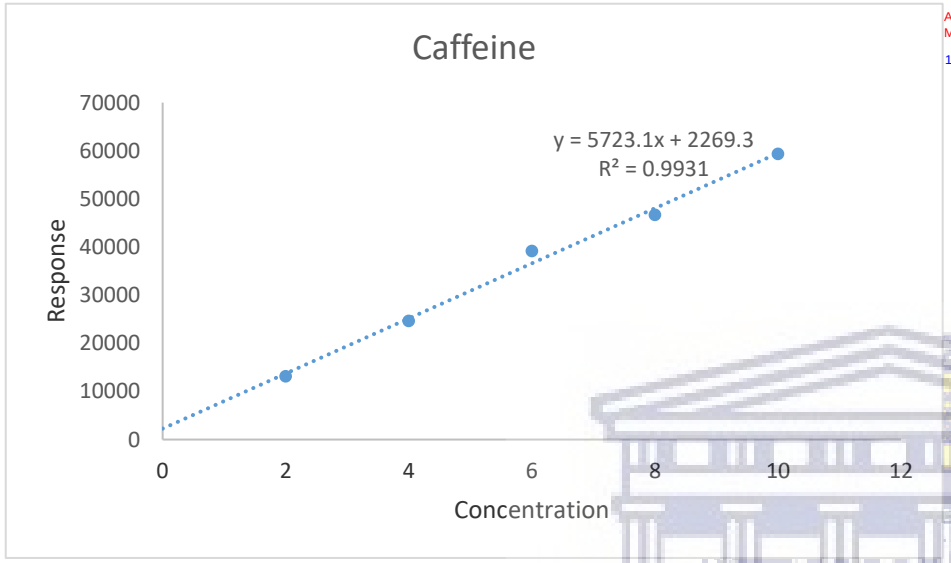


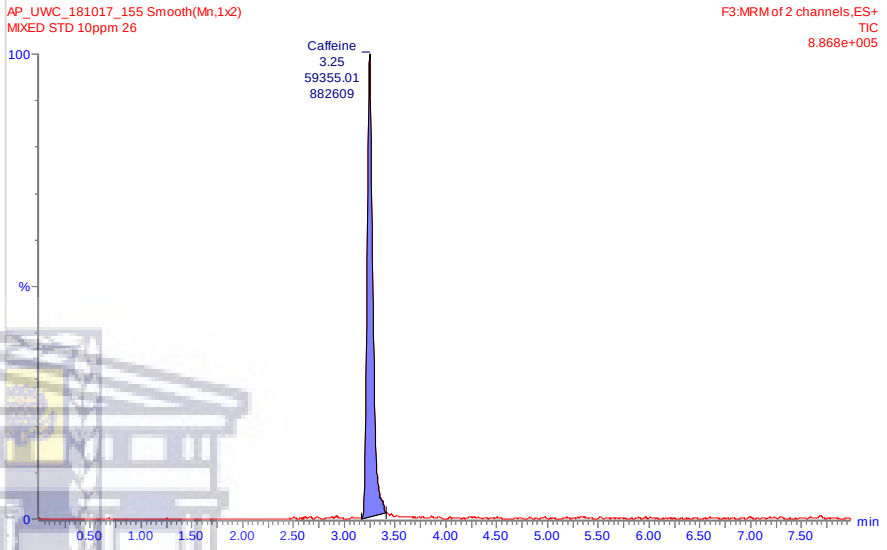


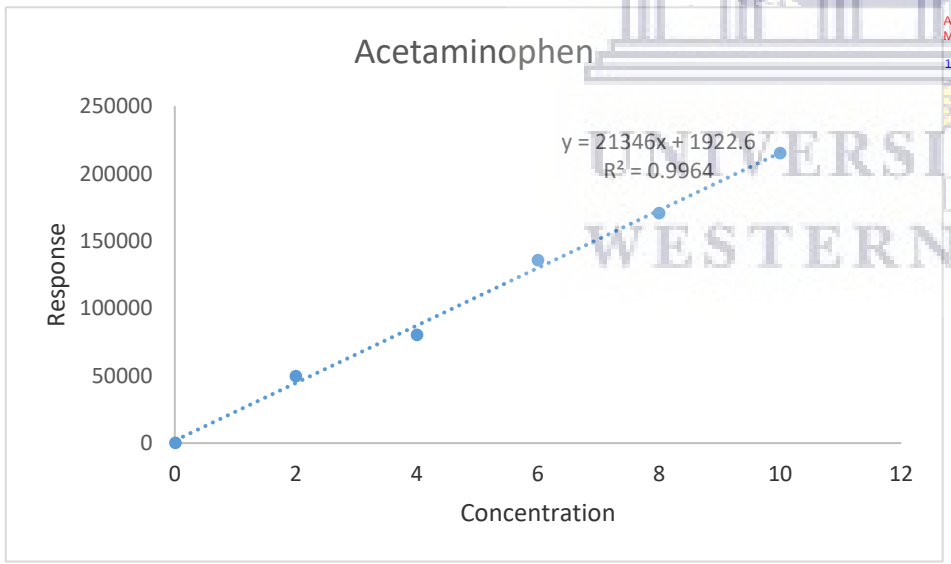


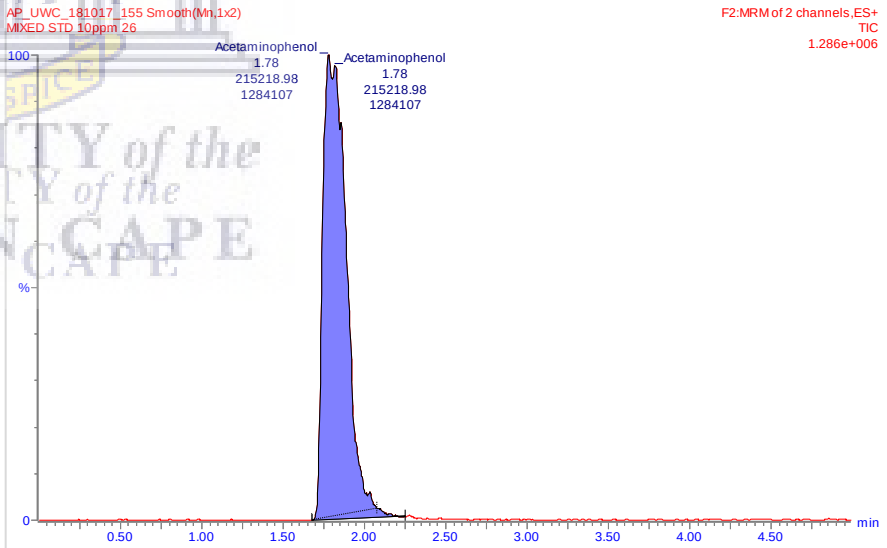












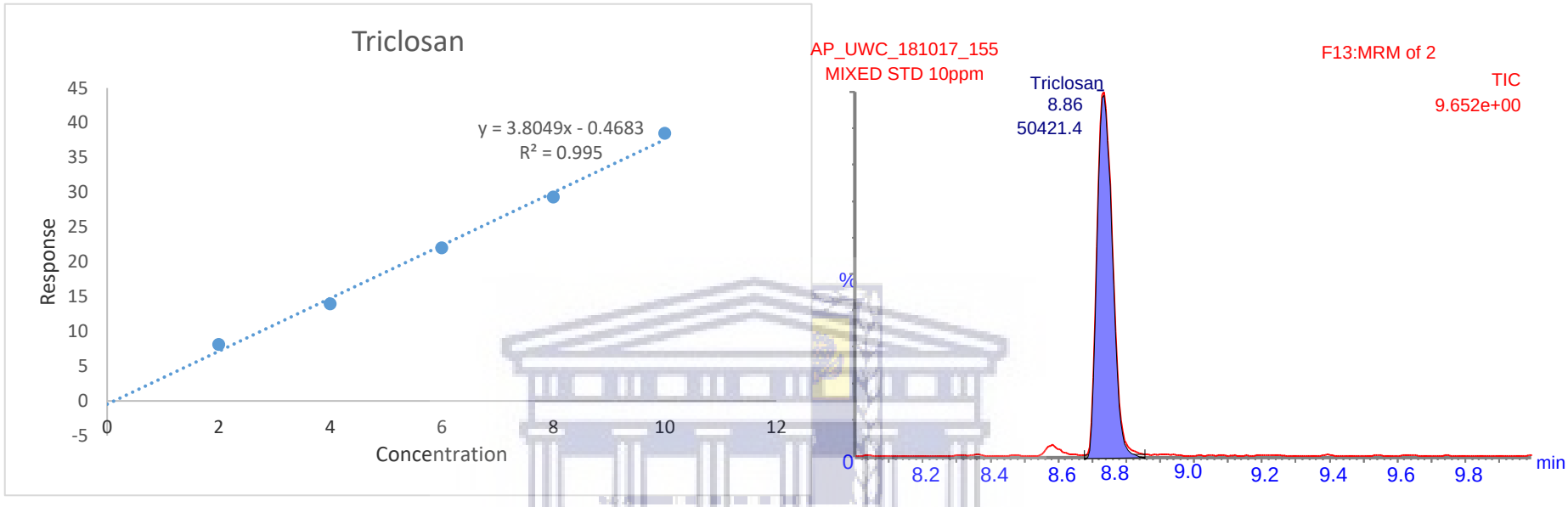


Figure IV. 1: Calibration curves and chromatograms of analysed compounds in samples from False Bay

Table IV. 1: Concentration of target analytes in seawater samples (ng/L) from False Bay.

	1	2	3	4	5	6	7	8
PFUnDA	2.34±0.1	3.09±0.2	4.54±0.1	7.04±0.0	3.31±0.1	3.12±0.1	3.00±0.1	3.18±0.2
PFDA	1.75±0.2	2.45±0.4	1.23±0.1	2.57±0.2	2.34±0.1	3.43±0.1	7.45±0.1	2.43±0.1
PFNA	18.76±0.1	8.03±0.1	11.05±0.2	3.54±0.2	6.41±0.3	4.38±0.2	5.51±0.1	4.38±0.4
PFOA	17.04±0.0	6.50±0.1	3.10±0.0	11.88±0.3	9.40±0.1	4.58±0.5	4.52±0.2	5.90±1.0
PFHpA	12.71±0.2	8.84±0.1	3.25±0.1	12.08±1.9	10.14±0.41	6.91±0.7	6.96±0.2	8.05±0.3
TS	0	0	0	0	0	0	0	0
BPA	0	0	0	93.16±2.2	0	0	51.73±0.2	0
DCF	3.70±0.0	2.61±0.1	4.18±0.1	2.75±0.1	2.86±0.3	3.44±0.3	3.41±0.2	3.40±0.3
SMX	2.25±0.1	1.03±0.4	0.66±0.2	0.29±0.0	4.79±0.0	2.38±0.0	0.52±0.0	4.33±0.1
PHE	0.22±0.0	0.32±0.0	0.34±0.2	0.07±0.0	1.48±0.0	0.60±0.0	0.90±0.0	1.45±0.0
CAR	0.95±0.0	0.95±0.2	0.73±0.1	1.19±0.0	1.56±0.1	1.37±0.2	1.54±0.1	1.29±0.0
LA	0.36±0.0	0.31±0.0	0.44±0.2	0.33±0.4	0.35±0.0	0.44±0.1	0.32±0.3	0.31±0.1
CAF	0	0	0	0	0	0	0	0
ACT	1.88±0.1	1.06±0.3	0.96±0.1	0.95±0.1	0.99±0.1	1.48±0.2	1.28±0.0	1.24±0.2
2-N	0	0	0	0	0	0	0	0
NP	0	0	0	0	0	0	0	0

Table IV. 2: Concentration of target analytes in sediment samples from False Bay

	1	2	3	4	5	6	7	8
PFUnDA	80.72±0.6	112.68±0.0	148.46±0.2	66.19±0.7	43.85±1.6	64.74±1.0	69.77±0.2	61.52±2.7
PFDA	59.03±3.1	89.76±1.1	47.54±1.8	51.98±1.2	51.90±1.6	105.51±0.4	61.22±0.4	51.58±0.6
PFNA	107.07±0.1	216.19±0.8	142.68±2.5	72.52±0.9	128.46±0.1	121.01±0.9	239.65±1.5	217.74±2.0
PFOA	100.53±1.4	117.09±2.5	73.63±0.1	65.66±1.3	92.84±1.8	77.27±0.1	77.67±1.0	64.98±1.8
PFHpA	88.98±0.1	117.02±0.4	72.72±1.8	99.59±0.1	195.79±4.1	86.19±0.8	81.03±1.0	94.13±1.8
TS	0	0	0	0	0	0	0	0
BPA	0	0	0	1046.94±0.4	0	0	1673.13±0.0	0
DCF	138.07±0.2	155.93±0.8	115.05±2.3	101.45±3.1	160.76±0.7	171.89±4.2	92.08±0.2	93.50±3.9
SMX	41.64±0.1	21.59±0.7	12.17±0.5	17.28±0.2	41.15±0.1	26.77±0.3	16.58±0.2	34.33±0.0
PHE	56.55±0.5	15.15±0.2	30.29±0.6	8.89±0.2	18.55±0.3	14.49±0.2	33.97±0.3	25.48±0.2
CAR	41.01±0.1	61.20±0.2	36.10±0.3	33.27±0.7	36.01±0.4	37.41±0.1	33.24±4.0	34.82±1.4
LA	23.23±0.3	37.13±0.8	22.42±0.3	16.02±0.6	15.12±0.7	22.36±1.7	19.03±0.6	20.61±0.8
CAF	0	0	0	0	0	0	0	0
ACT	41.43±1.7	67.92±0.1	44.01±3.3	34.28±5.7	42.13+1.1	48.75±0.1	40.09+0.4	45.07±0.4
2-N	0	0	0	0	0	0	0	0
NP	0	0	0	0	5.18±0.0	17.01±0.0	441.93±5.0	582.58±0.0

Table IV. 3: Concentration of PPCPs, PFCs and industrial chemicals in marine organisms from sites 1 to 8 from False Bay

	Limpet								Mussel				
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**2**	**4**	**6**	**7**	**8**
PFUnDA	89.22±1.1	89.29±0.8	118.20±1.2	92.63±2.2	260.75±0.1	64.06±2.3	46.30±1.7	64.44±0.0	77.27±0.1	125.78±0.5	115.70±1.2	50.60±1.1	95.37±0.9
PFDA	50.96±1.9	46.20±5.2	90.15±1.5	101.94±0.1	45.62±0.4	63.53±0.7	53.69±1.9	54.60±0.0	63.32±0.5	102.64±2.2	80.50±0.3	51.12±1.4	56.32±0.5
PFNA	655.94±5.2	2384.49±9.0	2444.87±8.0	1211.60±6.5	402.57±3.6	1285.58±8.6	1838.34±2.0	187.38±0.1	1452.07±8.2	895.63±2.6	1156.57±6.0	409.78±2.5	661.79±9.3
PFOA	170.05±0.0	305.20±0.7	308.23±0.5	304.76±4.9	103.06±2.1	184.96±0.1	284.32±0.6	64.96±0.0	178.44±5.4	192.20±3.5	134.59±0.1	86.85±1.1	78.61±3.2
PFHpA	148.19±1.9	150.01±3.5	269.48±0.5	499.33±0.1	169.66±0.6	199.79±1.4	259.44±0.5	115.77±2.3	145.31±6.4	275.61±5.3	89.32±2.3	87.48±3.9	123.84±3.5
TS	0	0	0	0	0	0	0	0	0	0	0	0	0
BPA	0	0	4236.20±0.0	1576.34±4.0	0	0	0	0	3238.8±0.5	3642.11±0.8	0	0	0
DCF	484.31±1.4	279.56±0.9	233.81±1.9	780.26±2.3	596.s16±0.9	364.46±5.1	590.06±3.5	754.81±1.1	69.54±0.0	232.33±2.1	148.34±0.1	67.67±0.1	150.96±1.3
SMX	35.85±0.3	92.13±0.0	126.59±4.8	69.29±1.0	272.09±0.1	108.28±3.1	36.12±0.0	87.95±0.0	66.71±6.7	150.88±3.2	78.82±0.0	70.09±3.1	64.44±0.8
PHE	34.84±0.4	62.15±0.7	124.78±0.0	62.36±3.9	40.09±0.0	28.06±0.0	53.55±0.0	65.56±0.0	32.32±0.0	42.09±0.6	29.04±0.5	46.96±0.0	48.56±0.0
CAR	30.50±0.4	31.86±0.1	81.76±0.5	58.93±0.0	33.06±0.2	30.75±2.4	31.32±2.2	22.32±0.5	26.06±0.3	66.00±2.8	29.18±0.3	36.18±0.5	33.06±3.0
LA	15.81±1.5	42.32±0.0	47.98±0.0	40.73±0.0	16.93±0.3	21.36±0.4	21.84±0.4	14.97±0.0	17.00±0.6	40.13±1.2	14.41±0.9	16.13±0.5	14.17±0.1
CAF	0	0	0	0	0	0	0	0	0	0	0	0	0
ACT	42.99±0.1	63.94±2.5	111.77±4.6	34.50±4.8	38.94±1.7	44.00±8.9	43.96±5.2	17.53±4.7	46.67±6.2	85.51±4.5	54.74±2.5	61.94±2.6	52.83±0.0
2-N	0	0	0	0	0	0	0	0	0	0	0	0	0
NP	668.74±1.0	853.14±0.0	2099.50±2.8	1029.80±0.4	517.10±3.5	788.39±0.5	825.34±1.8	788.64±0.1	1163.33±5.5	942.06±0.2	936.86±0.2	339.20±0.0	697.79±0.3

	Sea snail	Sea urchin	Starfish

	1	2	5	6	7	8	2	6	7	8	2	6
PFUnDA	137.79±0.8	100.30±0.4	93.29±2.1	80.01±0.7	46.98±8.3	35.59±0.7	90.30±0.3	41.25±0.1	82.30±0.8	78.34±0.0	39.23±0.7	36.48±0.6
PFDA	39.80±2.0	109.12±0.0	56.49±4.4	50.55±2.9	59.01±1.4	55.18±0.9	51.68±0.9	68.22±1.5	57.40±1.3	57.81±0.5	46.22±0.7	51.11±1.5
PFNA	1866.06±2.9	2350.42±2.6	2119.60±5.3	1962.15±1.4	714.48±0.7	455.43±3.7	859.03±3.5	1094.65±5.5	1096.18±5.2	534.84±0.0	501.61±0.5	716.15±1.9
PFOA	136.15±1.1	274.47±2.7	179.24±2.1	89.07±1.1	93.54±0.2	114.17±0.9	87.09±0.5	90.64±0.4	108.11±2.2	115.14±0.8	109.70±0.5	131.21±0.4
PFHpA	157.65±43	270.89±2,6	128.69±0.4	142.84±3.0	158.43±2.9	75.68±1.0	85.19±0.6	90.95±0.9	105.05±2.2	116.84±0.0	108.56±0.3	130.44±0.3
TS	0	0	0	0	0	0	0	0	0	0	0	0
BPA	0	0	2096.96±8.0	1332.07±0.0	0	0	0	0	0	0	0	0
DCF	260.15±7.6	568.95±3.6	190.82±1.1	243.00±0.7	225.73±3.2	156.23±1.8	113.78±0.7	185.27±2.8	103.60±1.2	193.41±2.2	155.44±1.3	209.88±0.4
SMX	72.64±8.7	178.36±1.8	138.03±0.2	89.21±0.9	57.47±0.2	155.92±0.8	70.01±0.2	67.90±0.6	61.63±8.2	65.19±0.3	68.62±0.4	66.95±4.5
PHE	21.51±0.5	131.22±0.0	47.75±1.1	55.77±0.0	65.41±0.0	34.71±0.0	0	35.68±0.0	55.96±0.0	91.63±0.0	0	55.97±0.0
CAR	41.30±0.1	69.25±0.0	28.12±1.7	29.07±1.8	35.30±0.3	37.16±0.3	38.24±0.3	37.26±0.4	26.44±0.7	36.27±0.3	24.49±0.7	34.39±0.3
LA	23.43±0.0	14.02±1.0	24.91±4.2	21.48±2.3	24.07±0.1	25.23±2.4	27.40±0.6	20.92±1.5	23.75±0.3	25.64±3.6	16.64±4.2	18.54±0.5
CAF	0	0	0	0	0	0	0	0	0	0	0	0
ACT	43.85±0.0	131.08±0.2	116.28±0.8	114.05±0.8	120.75±0.7	118.55±0.8	127.50±0.8	125.24±0.8	129.69±0.8	122.97±0.8	131.99±0.8	134.19±0.8
2-N	0	0	0	0	0	0	0	0	0	0	0	0
NP	1278.29±0.2	2140.44±2.9	2235.35±0.3	2191.51±0.1	824.95±2.1	41.57±0.0	1285.60±9.5	1067.61±2.6	1163.16±5.6	789.42±1.8	937.02±0.1	339.10±0.1

Table IV. 4: Concentration of target analytes in different seaweed species False Bay.

	1b	1c	2a	2b	2c	3c	4a	4b	4e
PFUnDA	80.90±0.4	40.85±2.3	45.96±4.4	322.54±2.0	45.96±4.4	62.61±0.0	43.19±0.4	78.06±0.0	54.66±1.5
PFDA	13.86±0.5	53.72±6.5	72.76±0.5	97.12±0.7	49.70±0.2	69.29±0.0	54.62±0.5	53.12±3.0	51.61±1.0
PFNA	351.29±8.7	185.76±0.9	597.84±4.7	1094.39±5.4	1233.04±4.4	852.24±2.6	2009.24±2.4	1071.58±9.8	502.15±1.3
PFOA	131.19±0.5	61.07±0.4	122.08±1.4	214.78±0.0	105.63±0.6	115.49±5.3	2309.23±2.2	271.91±0.7	105.67±0.6
PFHpA	221.18±0.2	98.22±1.4	154.71±2.2	2040.03±2.9	77.65±0.6	91.55±0.4	166.57±6.2	332.24±2.3	107.49±0.4
TS	0	0	0	0	0	0	0	0	0
BPA	1275.09±0.2	0	2274.54±9.8	0	0	0	0	1709.02±0.0	2359.72±0.2
DCF	115.24±2.8	101.50±1.8	153.94±0.7	309.11±1.5	154.78±0.2	210.43±1.6	205.31±2.2	262.61±2.9	105.57±4.4
SMX	29.03±0.5	13.22±0.0	21.93±0.4	25.53±0.0	67.51±0.1	30.90±0.2	175.76±1.7	22.66±0.1	23.76±0.1
PHE	21.68±0.0	15.77±0.2	165.10±0.0	111.36±0.0	64.43±0.5	39.30±5.1	163.66±2.0	37.91±0.0	10.29±0.0
CAR	33.40±1.1	32.18±1.4	54.15±1.6	46.34±0.3	35.26±1.8	35.28±1.8	34.24±0.0	37.00±1.7	34.64±0.0
LA	14.13±0.2	6.30±0.0	31.97±0.7	14.34±1.7	9.90±0.5	11.06±0.4	17.94±0.1	20.77±2.5	14.14±2.0
CAF	0	0	0	0	0	0	0	0	0
ACT	30.78±2.3	23.82±0.9	47.75±0.1	36.16±4.6	147.61±0.8	25.06±2.3	94.28±0.0	42.95±0.2	39.92±4.6
2-N	0	0	0	0	0	0	0	0	0

NP	641.78±8.7	1163.21±6.7	1358.82±0.0	1184.17±0.1	697.49±0.4	729.05±0.9	1241.01±0.1	1059.73±0.0	523.25±0.1

	5b	**5d**	**6b**	**7a**	**7b**	**8b**	**8c**	**8e**
PFUnDA	67.81±0.2	66.75±1.3	116.37±0.3	51.40±0.1	50.93±0.6	81.30±0.1	90.40±0.1	88.65±2.4
PFDA	56.51±4.4	53.03±1.0	50.54±2.9	55.18±0.9	51.36±1.1	51.97±1.4	56.33±0.5	60.67±3.3
PFNA	1175.55±3.3	357.98±0.4	1873.41±1.1	1157.39±5.3	1222.78±2.7	1883.85±0.8	358.01±0.6	716.28±2.2
PFOA	115.47±5.4	137.27±1.4	74.89±0.1	90.39±0.4	122.10±1.4	187.19±2.2	61.08±0.4	187.14±2.2
PFHpA	89.22±2.0	136.01±1.2	74.88±0.7	90.00±0.5	87.11±1.4	187.20±2.7	61.00±0.5	320.02±0.23
TS	0	0	0	0	0	0	0	0
BPA	0	1444.92±0.4	0	0	0	0	0	0
DCF	282.58±1.0	205.94±1.3	109.76±1.5	204.99±0.1	264.06±1.0	108.11±0.8	211.59±0.1	284.58±1.8
SMX	66.97±4.5	30.64±0.0	68.59±0.4	69.43±0.1	61.64±8.2	121.02±0.0	70.01±0.2	33.10±0.2
PHE	58.78±0.0	64.09±0.0	34.70±0.0	111.42±0.0	64.09±0.0	91.69±0.0	74.66±5.9	70.46±0.0
CAR	54.16±1.6	34.25±0.4	25.99±2.4	58.65±1.6	32.85±2.4	37.03±1.7	35.09±0.2	38.80±0.4
LA	12.78±0.5	19.28±0.7	14.22±0.5	11.34±0.5	15.66±0.5	8.46±0.5	17.10±0.5	19.00±0.7
CAF	0	0	0	0	0	0	0	0
ACT	143.18±0.8	44.74±1.7	140.89±0.7	145.43±0.8	138.68±0.8	149.93±0.8	136.44±0.8	40.62±9.5
2-N	0	0	0	0	0	0	0	0

NP	788.36±0.1	728.13±0.3	920.31±0.6	41.57±0.0	437.38±1.4	875.66±5.2	697.82±0.1	556.64±3.8

a= *Ulva* sp; b= *Gelidium pristoides;* c= *Bifurcaria brassicac formis;* d= *Caulerpa filiformis;* e= *Aeodes Orbito*

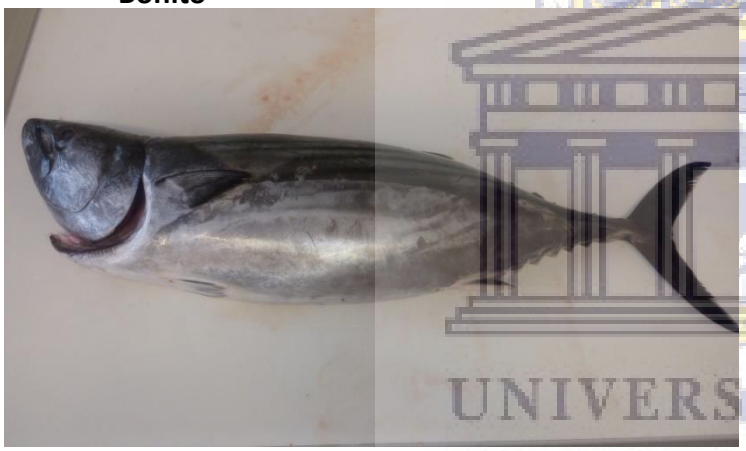
Pictures of species sampled in this study

Fish species

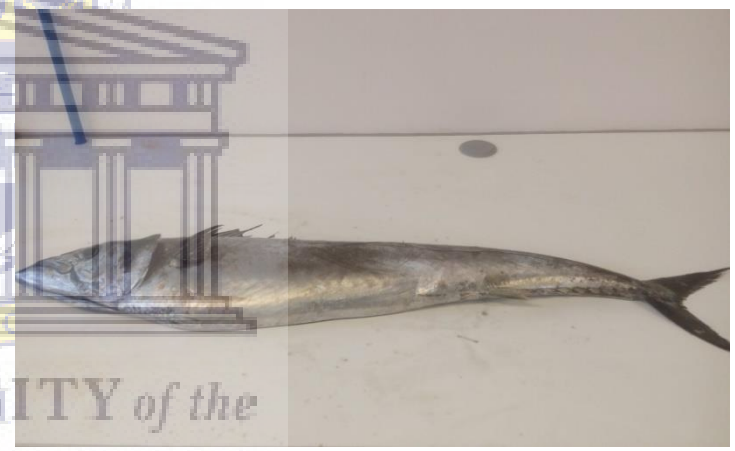
Panga

Hottentot

Bonito



Snoek



Marine invertebrates

Mussels

Limpets

Sea urchin

Sea snail

Starfish

Seaweeds

***Ulva* sp**

Gelidium pristoides

Bifurcaria brassicac formis

Caulerpa filiformis

Aeodes orbitosa

Codium fragile

RECREATIONAL FISHING PERMIT

ANNUAL (0919S) ☐ MONTHLY (0919M) ☐

DEPARTMENT OF AGRICULTURE, FORESTRY AND FISHERIES

PRIVATE BAG X2, ROGGEBAAI 8012 ☎ (021) 402 3911 FAX (021) 402 3362

www.daff.gov.za

This permit is issued to the permit holder whose name appears below, subject to the conditions hereunder and the restrictions in respect of areas, species, minimum sizes, bag limits and fees payable as determined in terms of the Marine Living Resources Act, 1998 (Act No. 18 of 1998), and / or the regulations and notices promulgated thereunder as amended from time to time.
Please Note: This permit is NOT applicable for Freshwater Recreational Fishing.

PERSONAL DETAILS (All fields must be fully completed)

IDENTITY NO.		OR PASSPORT NO.	A08942308
DATE OF BIRTH	08 MARCH 1988	TITLE	MRS
INITIALS	C.Y.		
SURNAME	OJEMATE		
POPULATION GROUP	BLACK ✓ WHITE	COLOURED	ASIAN
GENDER	MALE	FEMALE ✓	
EMPLOYED	YES	NO ✓	

RESIDENTIAL ADDRESS (All fields must be fully completed)

BUILDING NAME	HECTOR PETERSON RESIDENCE	BUILDING NO.	B102
STREET NAME	UNIVERSITY OF THE WESTERN	STREET NUMBER	
SUBURB	CAPE BELLVILLE		
CITY	CAPE TOWN	POSTAL CODE	
AREA CODE	TELEPHONE NO.	PERMIT NO.	MAM 16 082910
CELLPHONE NUMBER	0634941449		

LANGUAGE PREFERENCE (please tick): AFRIKAANS | ENGLISH ✓ | NDEBELE | N. SOTHO | S. SOTHO | SWATI | TSONGA | TSWANA | VENDA | XHOSA | ISIZULU

TYPE OF PERMIT REQUIRED

1	Angling	2	Spearfishing	3	Cast/throw net	4	Marine Aquarium Fish
5	Scuba Diving in MPA's	6	West Coast Rock Lobster ONLY ANNUAL PERMIT AVAILABLE	7	East Coast Rock Lobster ONLY ANNUAL PERMIT AVAILABLE	8	Mud Crab
9 ✓	Molluscs, including Octopus and Squid; Worms and other Invertebrates and Aquatic Plants. (No recreational fishing of Abalone is permitted)						
10	Additional fee per vessel for recreational fishing from such vessel (Only one person on such vessel requires this type of permit.).						
11	Drag net (50 prawns only in KZN) ONLY ANNUAL PERMIT AVAILABLE	12	Hoop net (Glassies and squid only in KZN) ONLY ANNUAL PERMIT AVAILABLE	13	Mussel (30 mussels only in KZN) ONLY ANNUAL PERMIT AVAILABLE	14	Oyster (25 oysters only in KZN) ONLY ANNUAL PERMIT AVAILABLE

NOTE:

1. In KwaZulu-Natal the following activities no longer require a separate permit from KZN Nature Conservation Service : use of a drag net or hoop net, fishing for Sand Prawn, Mussel, Oyster, Octopus or Mole Crab. When these activities are conducted in KwaZulu-Natal, this national permit issued by the South African Post Office is valid and options 11, 12, 13 and/or 14 above apply; whichever is indicated upon purchase of the permit.
2. No more than 10kg Aquatic Plants and 10 Aquarium Fish shall be collected per day.

GENERAL PERMIT CONDITIONS

1. This permit is valid for a period of one month from the date of issue in the case of a monthly and in the case of an annual permit, one year from the date of issue, except for, East Coast Rock Lobster and West Coast Rock Lobster permits, which are only valid from the date of issue until the day preceding the respective closed seasons. The aforementioned two permits also expire when the catch return has been completed in full (40 entries), in which case a new permit may then be obtained by folowing the application procedure.
2. No permit is valid during such closed seasons as stipulated from time to time in the regulations and notices promulgated under the Marine Living Resources Act, 1998.
3. Daily catches as stipulated in the regulations shall not be exceeded, including by means of taking out more than one permit at the same time.
4. Fish caught or collected in terms of this permit may not be sold, bartered, donated or traded.
5. This permit is not transferable.
6. This permit is valid only if the signature and identity number (or passport number - foreign visitor only) of the permit holder have been inscribed thereon in indelible ink and if the official receipt, as issued by the, South African Post Office, is attached to this permit.
7. This permit and the identity document (or passport - foreign visitor only) of the permit holder must be available for inspection purposes at the time and location where the activity in respect of which the permit has been issued, is exercised.
8. The catch return on the reverse hereof must be completed punctually and in full in indelible ink before and immediately after each rock lobster fishing effort. Only one catch return entry per line is permitted.
9. Failure to comply with any permit condition renders the permit holder liable to a fine and/or prosecution, and/or withdrawal of this permit.

DISCLAIMER

1. This permit is not refundable if lost, stolen or damaged and when irregularities are discovered after the permit has been issued.
2. No duplicates or reprints of this permit will be issued by the South African Post Office or the Department of Agriculture, Forestry and Fisheries.
3. This permit is only applicable for use in the ocean and river mouths as stipulated in the Marine Living Resources Act (Act No. 18 of 1998) and cannot be used for fishing in freshwater systems which may

DECLARATION BY PERMIT HOLDER

I hereby confirm that I have acquainted myself with the conditions of this permit, the provisions of the Marine Living Resource Act, 1998, and the regulations and notices promulgated thereunder and that I understand them.

Place of Issue KOEBERG

Signature of Permit Holder

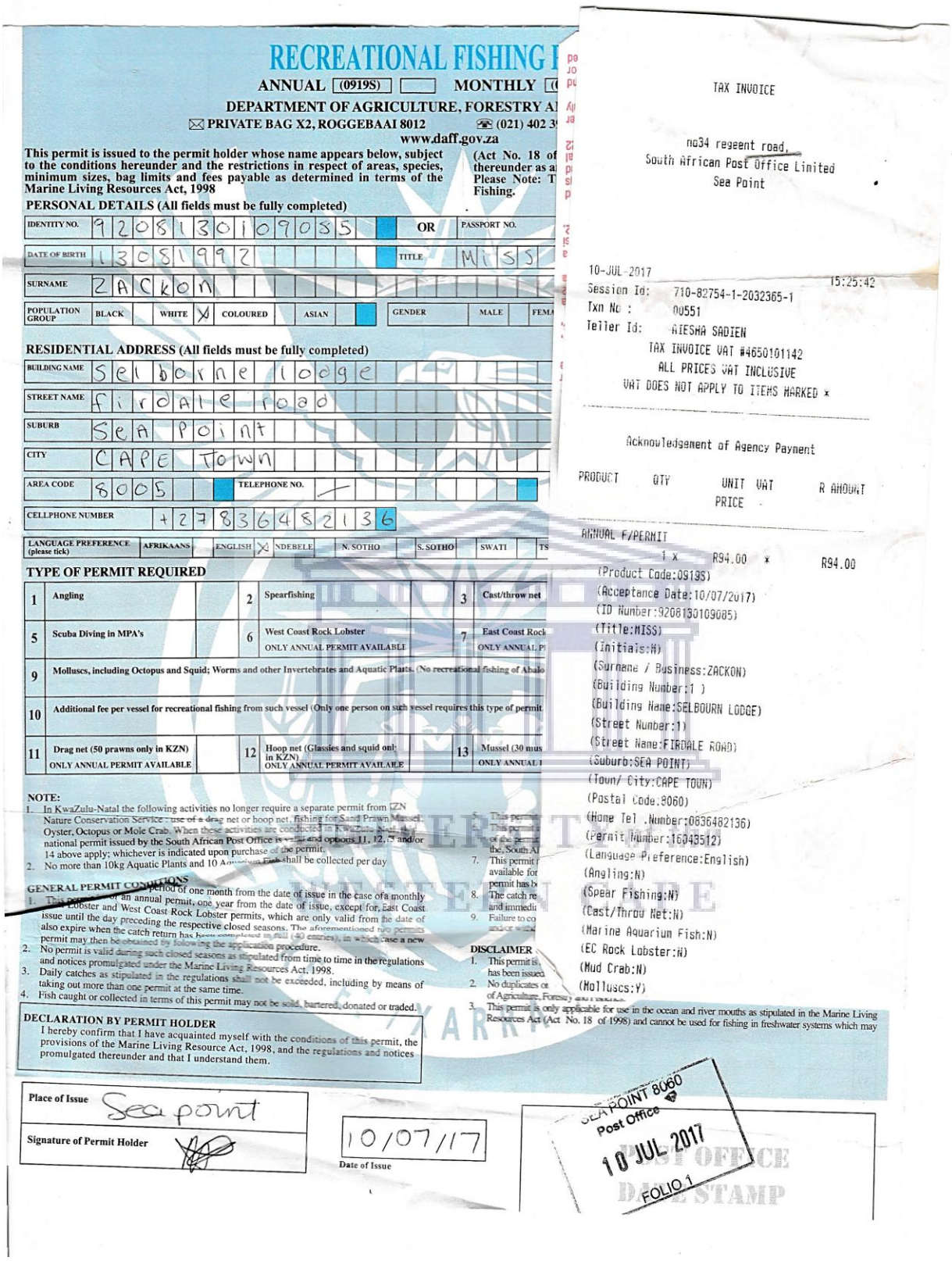
Date of Issue 23/08/18

TXN 01331

POST OFFICE

Rev. CC

KOEBERG 2018-08-23 COUNTER 3



RECREATIONAL FISHING

ANNUAL (0919S) ☐ MONTHLY (

DEPARTMENT OF AGRICULTURE, FORESTRY A

✉ PRIVATE BAG X2, ROGGEBAAI 8012 ☎ (021) 402 3

www.daff.gov.za

This permit is issued to the permit holder whose name appears below, subject to the conditions hereunder and the restrictions in respect of areas, species, minimum sizes, bag limits and fees payable as determined in terms of the Marine Living Resources Act, 1998 (Act No. 18 of thereunder as a Please Note: T Fishing.

PERSONAL DETAILS (All fields must be fully completed)

IDENTITY NO.	9208130109085	OR	PASSPORT NO.
DATE OF BIRTH	13081992	TITLE	MISS
SURNAME	ZACKON		
POPULATION GROUP	BLACK ☐ WHITE ☒ COLOURED ☐ ASIAN ☐	GENDER	MALE ☐ FEMA

RESIDENTIAL ADDRESS (All fields must be fully completed)

BUILDING NAME	Selborne lodge
STREET NAME	firdale road
SUBURB	Sea Point
CITY	CAPE Town
AREA CODE	8005
TELEPHONE NO.	/
CELLPHONE NUMBER	+27836482136

LANGUAGE PREFERENCE (please tick): AFRIKAANS ☐ ENGLISH ☒ NDEBELE ☐ N. SOTHO ☐ S. SOTHO ☐ SWATI ☐ TS

TYPE OF PERMIT REQUIRED

1	Angling	☐	2	Spearfishing	☐	3	Cast/throw net
5	Scuba Diving in MPA's	☐	6	West Coast Rock Lobster ONLY ANNUAL PERMIT AVAILABLE	☐	7	East Coast Rock ONLY ANNUAL PI
9	Molluscs, including Octopus and Squid; Worms and other Invertebrates and Aquatic Plants. (No recreational fishing of Abalo						
10	Additional fee per vessel for recreational fishing from such vessel (Only one person on such vessel requires this type of permit						
11	Drag net (50 prawns only in KZN) ONLY ANNUAL PERMIT AVAILABLE	☐	12	Hoop net (Glassies and squid onl in KZN) ONLY ANNUAL PERMIT AVAILABLE	☐	13	Mussel (30 mus ONLY ANNUAL I

NOTE:

1. In KwaZulu-Natal the following activities no longer require a separate permit from [ZN Nature Conservation Service - use of a drag net or hoop net, fishing for Sand Prawn, Mussel, Oyster, Octopus or Mole Crab. When these activities are conducted in KwaZulu-Natal, the national permit issued by the South African Post Office is valid and options 11, 12, 13 and/or 14 above apply; whichever is indicated upon purchase of the permit.
2. No more than 10kg Aquatic Plants and 10 A[illegible] Fish shall be collected per day

GENERAL PERMIT CONDITIONS

1. This [illegible] period of one month from the date of issue in the case of a monthly permit or an annual permit, one year from the date of issue, except for, East Coast Rock Lobster and West Coast Rock Lobster permits, which are only valid from the date of issue until the day preceding the respective closed seasons. The aforementioned two permits also expire when the catch return has been completed in full (40 entries), in which case a new permit may then be obtained by following the application procedure.
2. No permit is valid during such closed seasons as stipulated from time to time in the regulations and notices promulgated under the Marine Living Resources Act, 1998.
3. Daily catches as stipulated in the regulations shall not be exceeded, including by means of taking out more than one permit at the same time.
4. Fish caught or collected in terms of this permit may not be sold, bartered, donated or traded.
5. This permit [illegible]
6. This permit [illegible] of the permit [illegible] the, South Af
7. This permit [illegible] available for permit has b
8. The catch re[illegible] and immedi
9. Failure to co[illegible] under [illegible]

DISCLAIMER

1. This permit is [illegible] has been issued
2. No duplicates or [illegible] of Agriculture, Forestry [illegible]
3. This permit is only applicable for use in the ocean and river mouths as stipulated in the Marine Living Resources Act (Act No. 18 of 1998) and cannot be used for fishing in freshwater systems which may

DECLARATION BY PERMIT HOLDER

I hereby confirm that I have acquainted myself with the conditions of this permit, the provisions of the Marine Living Resource Act, 1998, and the regulations and notices promulgated thereunder and that I understand them.

Place of Issue	Sea point
Signature of Permit Holder	
Date of Issue	10/07/17

SEA POINT 8060 Post Office 10 JUL 2017 FOLIO 1 POST OFFICE DATE STAMP

TAX INVOICE

no34 regeent road,
South African Post Office Limited
Sea Point

10-JUL-2017 15:25:42
Session Id: 710-82754-1-2032365-1
Txn No : 00551
Teller Id: AIESHA SADIEN

TAX INVOICE VAT #4650101142
ALL PRICES VAT INCLUSIVE
VAT DOES NOT APPLY TO ITEMS MARKED *

Acknowledgement of Agency Payment

PRODUCT	QTY	UNIT PRICE	VAT	R AMOUNT
ANNUAL F/PERMIT	1 x	R94.00	*	R94.00

(Product Code:09135)
(Acceptance Date:10/07/2017)
(ID Number:9208130109085)
(Title:MISS)
(Initials:M)
(Surname / Business:ZACKON)
(Building Number:1)
(Building Name:SELBOURN LODGE)
(Street Number:1)
(Street Name:FIRDALE ROAD)
(Suburb:SEA POINT)
(Town/ City:CAPE TOWN)
(Postal Code:8060)
(Home Tel .Number:0836482136)
(Permit Number:16043512)
(Language Preference:English)
(Angling:N)
(Spear Fishing:N)
(Cast/Throw Net:N)
(Marine Aquarium Fish:N)
(EC Rock Lobster:N)
(Mud Crab:N)
(Molluscs:Y)