PERFLUOROOCTANE SULFONATE AND PERFLUOROOCTANOATE CONTAMINATION OF RIPARIAN WETLANDS OF THE EERSTE, DIEP AND SALT RIVERS

By

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DECLARATION

I, **John-Baptist Nzukizi Mudumbi**, declare that the contents of this dissertation represent my own work, and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology and the National Research Foundation of South Africa.

In addition, all intellectual concepts, theories, and methodologies used in this thesis and under review in various journals were derived solely by the candidate and first author of the submitted manuscripts under review. Where appropriate, the intellectual property of others was acknowledged by using appropriate references. The contribution of co-authors, for conference papers and manuscripts under review, was in a research assistance (Mr. A. Rand, GIS assistant) and supervisory capacity (Dr. S.K.O. Ntwampe, Dr. F.M. Muganza and Prof. J. Okonkwo) to meet the requirements of the degree.

Signed **Date**

ABSTRACT

Perfluorinated compounds (PFCs), in particular perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been found in aquatic environments throughout the world. Recent studies have reported that owing to their bioaccumulative nature, PFCs may also be present in various water sources, resulting in human and wild-life exposure. Although, these PFCs usually occur at low concentration levels, their presence in the environment has nevertheless been a concern in both developed and developing countries, since water remains an important natural resource for most living species. Water and sediment from rivers are one of the matrices in which PFC contamination is studied, since rivers receive water from various sources. However, limited studies have been conducted in South Africa on PFC contamination of river water and sediments. Although PFCs are sometimes unintentionally released into the environment, the concentration and type of PFCs that contaminate water sources vary among countries and depend on the types of industry releasing them into the environment, suggesting that PFC contamination patterns can be expected to differ from country to country, with PFOA and PFOS being the predominant perfluorinated contaminants. The aim of this study was therefore to determine the concentration of PFOS and PFOA in riparian wetlands of the Western Cape, focusing on the Eerste, Diep and Salt rivers, which are the primary rivers in the largest catchment areas of the Western Cape, South Africa.

Thus, the target analytes of the study, PFOS and PFOA, were identified and quantified using a high-performance liquid chromatography coupled with tandem mass spectrometry (MS, Model: Nexera LC/MS-8030; Shimadzu-Japan). The MS/MS operational conditions and ion mode were; MS Interface: electrospray ionisation, heat block temperature: 400℃, nebulising gas flow: 3 L/min, dry gas flow: 15 L/min, with MRM transition being 413.10 > 368.90 for PFOA (acquisition time: 2.184 to 6.184 min) and 499.00 > 80.05 for PFOS (acquisition time: 2.503 to 6.503). Acetonitrile (100%) and 2mM ammonium acetate were used for the mobile phase at a flow rate of 0.3 L/min. The process followed (for solid samples) was: 1) sample drying, 2) milling, 3) screening, 4) digestion, 5) sonication, 6) filtration, 7) Solid phase extraction (SPE), 8) analyte elution and 9) analysis; while for water samples the process was: 1) filtration, 2) SPE, 3) analyte elution and 4) analysis.

Sediment granulometry, including characterisation, sediment core water characteristics (i.e. pH, conductivity, salinity, total dissolved solid, nitrates, phosphates, dissolved oxygen, ammonium) and total organic carbon, were also quantified. Accordingly, throughout 2011, river water, suspended solids, sediment and plant samples were collected from the three rivers, for analysis. As plants have been shown to accumulate organic compounds from contaminated sediments, there is a potential for long-lasting ecological

impact and degradation as a result of contaminant accumulation in riparian areas of wetlands, particularly the accumulation of non-biodegradable contaminants such as PFOA and PFOS. Although, PFOS was found to be below the level of detection for all plants assessed during this study, riparian wetland plants including reeds, that is, *Xanthium strumarium, Phragmites australis, Schoenoplectus corymbosus, Ruppia maritime; Populus x canescens, Polygonum salicifolium, Cyperus congestus; Persicaria amphibian, Ficus carica, Artemisia schmidtiana, Eichhornia crassipes*, were studied to determine their susceptibility to PFOA accumulation from PFOA-contaminated riparian sediments with a known PFOA concentration. Furthermore, the prevalence of PFOA and PFOS in river water samples and suspended solids in river water was assessed.

PFOS and PFOA were observed in all the river sediment samples and were found in concentrations of up to 19 ng/g and 187 ng/g for the Salt River; 121 ng/g and 772 ng/g for the Diep River, and 75 ng/g and 193 ng/g for the Eerste River for both PFOS and PFOA, respectively. As the sediment analysed showed a high sorption capacity for both PFOS and PFOA in comparison to plants, the prevalence of both PFOS and PFOA in sediment samples from rivers which irrigation water is sourced for agricultural purposes, can result in agricultural produce contamination. The bioconcentration factor (BCF) indicated that the plants' affinity to PFOA accumulation was *E. crassipes, > P. salicifolium, > C. congestus, > P. x canescens, > P. amphibian, > F. carica, > A. schmidtiana, > X. strumarium, > P. australis, > R. maritime, > S. corymbosus*. The concentration of PFOA in the plants and/or reeds was in the range 11.7 ng/g to 38 ng/g, with a BCF range of 0.05 to 0.37. The highest BCF was observed in sediment for which its core water had a high; 1) salinity, 2) total organic carbon and 3) a pH that was near neutral. As the plants used in this study showed that they have a higher sorption capacity for PFOA, the resultant effect is that riparian plants such as *E. crassipes, X. strumarium,* and *P. salicifolium,* which are typified by a fibrous rooting system, which grow in and closer to the water edge, can exacerbate the accumulation of PFOA in riparian wetlands. Furthermore, PFOA and PFOS were detected in all the river water samples and were found in concentrations of up to 314 ng/L and 182 ng/L for the Diep River; 390 ng/L and 47 ng/L for the Salt River; and 146 ng/L and 23 ng/L for the Eerste River, respectively. In suspended solids, concentrations of PFOS and PFOA were, respectively, 28 ng/g and 26 ng/g for the Diep River; 16 ng/g and < LOD for the Eerste River, and 14 ng/g and 5 ng/g for the Salt River.

Some of the PFOA and PFOS concentrations found, were higher than those previously reported in similar studies in various countries, which suggests that there is a cause for concern, in the Western Cape, South Africa, in relation to the presence of perfluorinated compounds in the three major rivers in the region.

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BIOGRAPHICAL SKETCH

John Baptist Nzukizi Mudumbi was born in Bukavu, Democratic Republic of Congo (DRC), on 13 April 1974. He attended Kakumbo Primary School and matriculated at Nyamokola High School in 1996. During the same year, he enrolled at ISP Bukavu (l'Institut Supérieur Pédagogique de Bukavu) where he obtained a BEd degree in Applied Pedagogy in Geography and Natural Sciences in 1999. He has taught both at primary and high school levels in Bukavu, DRC. In 2006, he enrolled at Cape Peninsula University of Technology, Cape Town, South Africa and obtained a National Diploma in Environmental Management in 2008. In 2009 he completed a BTech degree in Environmental Management at the same University. He is currently employed as a Junior Lecturer at the Cape Peninsula University of Technology in the Department of Occupational and Health studies.

LIST OF OUTPUTS

The following outputs are contributions made by the candidate to scientific knowledge and development during his master's candidacy (2010-2012):

Manuscripts submitted for publication still under review:

Mudumbi, J.B.N., Ntwampe, S.K.O., Muganza, M., Okonkwo, J.O. and Rand, A.M. 2012. Concentrations of perfluorinated compounds in sediment of Western Cape rivers, South Africa. (Submitted to *Soil and Sediment Contamination: An International Journal,* August 2012).

Mudumbi, J.B.N., Ntwampe, S.K.O., Muganza, M. and Okonkwo, J.O. 2012. Susceptibility of riparian wetland plants to perfluorooctanoic acid (PFOA) accumulation. (Submitted to *International Journal of Phytoremediation,* August 2012).

Mudumbi, J.B.N., Ntwampe, S.K.O. Muganza, M.F. and Okonkwo, J.O. 2012. Perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS) in South African river water. (*Submitted to Environmental Monitoring and Assessment, September 2012*).

Local conference list: oral presentations

Evidence of historical perfluorinated compound contamination in sediment of the Eerste, Diep and Salt Rivers*,* South Africa. Joint International Conference on Science and Technology for Development in Africa, 26 – 28 June 2012, Cape Town (South Africa).

Perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS) in South African river water (*3rd Southern African Regional Biennial YWP Conference, 16-18 July 2013: Music Conservatorium, University of Stellenbosch, South Africa*).

Submitted abstracts

Riparian River/Wetland Plants and Reed Grasses as biosorbents for perfluorooctanoic acid (PFOA). (*Submitted for a poster presentation on Research day at Cape Peninsula University of Technology).*

DEDICATION

This dissertation is dedicated to my family and Vero Nyembo for their resolute support, love and prayers.

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GLOSSARY

Abbreviation/Units	Description
AFFFs	Aqueous Fire Fighting Foams
ASTM	American Society for Testing and Materials methods
BAFs	Bioaccumulation factors
BCF	Bioconcentration factor
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
DDT	Dichlorodiphenyltrichloroethane
DO	Dissolved oxygen
DWAF	Department of Water Affairs and Forestry
d.w.	Dry weight
ECF	Electro-chemical fluorination
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
ESI	Electrospray ionisation
EU	European Union
FAO	Food and Agriculture Organisation
GIS	Geographic Information System
GPS	Global Positioning System
HCB	Hexachlorobenzene
HFCs	Hydrofluorocarbons
HPA	Health Protection Agency
IOMC	Inter-Organization Programme for the Sound Management of Chemicals
IPCC	Intergovernmental Panel on Climate Change
IPCS	International Programme on Chemical Safety
ISO	International Standard Organisation
LC/MS/MS	Liquid chromatography tandem mass spectrometry
LOD	Limit of detection
LOI	Loss-on-ignition
MCES	Metropolitan Council of Environmental Services
mg/kg b.w.	Milligram per kilogram body weight
MWWTPs	Municipal wastewater treatment plants

N_2O	Nitrous oxide
ND	Not detected
NF_3	Nitrogen trifluoride
ng/g w.w.	Nanogram per gram wet weight
ng/g	Nanogram per gram
ng/kg d.w.	Nanogram per kilogram dry weight
ng/L	Nanogram per litre
ng/mL	Nanogram per millilitre
OCPs	Organochlorine pesticides
OECD	Organisation for Economic Co-operation and Development
OPPT	Office of Pollution Prevention and Toxic
OSPAR	Protection of the Marine Environment of the North-East Atlantic
PAHs	Polycyclic aromatic hydrocarbons
PBT	Persistent, bioaccumulative and toxic
PCBs	Polychlorinated biphenyls
PFCs	Perfluorinated chemicals/perfluorinated compounds
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
POPs	Persistent organic pollutants
POTW	Publicly Owned Treatment Works
PP	Polypropylene
PTS	Persistent toxic substances
RSD	Relative standard deviation
SC POPs	Stockholm Convention on Persistent Organic Pollutants
SPE	Solid phase extraction
SPM	Suspended particulate matter
S.S.	Suspended solids
t/a	tons per annum
TOC	Total organic carbon
UN	United Nations
UNDESA	United Nations Department of Economic and Social Affairs
UNEP	United Nations Environment Programme
US	United States

USA	Unites States of America
USCS	Unified Soil Classification System
US-EPA	United States Environmental Protection Agency
WHO ROE	World Health Organisation Regional Office for Europe
WHO	World Health Organization
WWF	World Wildlife Fund
WWTP	Wastewater treatment plant

Terms/Acronyms	**Definition**
• **Bioaccumulation**:	The retention of a non-biodegradable compound and those that decay gradually
• **Biodegradable**:	Capable of decomposing rapidly under natural conditions.
• **Hydrolysis**:	A process whereby a molecule is cleaved by reacting with water. In this process one part of the molecule bonds to hydroxide ion (OH^-) and the other to the hydrogen ion (H^+)
• **Hydrophilic:**	Character of a molecule or substi^{t}uent in a molecule to interact with polar solvents, in particular with water, or with other polar groups.
• **Hydrophobic:**	Character of a molecule to be insoluble in water; the extent of insolubility; not readily absorbing water; resisting or repelling water, wetting, or hydration by water.
• **Oleophobic:**	character of a molecule to repel oil.
• **Photolysis**:	a process whereby a molecule is split by photon from light energy.
• **Sediment:**	Soil, sand, and minerals washed from land into water, usually after rain, and they pile up in reservoirs, river beds and harbours.
• **Riparian wetlands**:	wetlands for which their hydrology is highly influenced by their proximity to river or tributary stream of any size. These include areas which the overbank flow of a river or tributary exerts considerable influence on their hydrology. Classes of riparian wetlands are based on their landscape position within the Hydro-geomorphological River or tributary network. These

classes include estuarine, riverine, headwater, flat/depressional wetlands, etc.

- **Wetlands**: are defined as terrestrial and aquatic systems which have the water table at, near, or above the land surface. Rivers, marshes, swamps, bogs, wet meadows, sloughs, potholes, and tide flats are all examples of wetlands.
- **Riparian area/zone:** is an area or zone between land and a river or tributary, i.e., located by the banks of a river or other body of water. These zones can be periodically soaked because of both surface and subsurface water flows and their soils are usually alluvial (water deposited) making them historical/geochemical repositories of river or tributary pollution.

PREFACE (THESIS ORGANISATION)

The overall aim of the study was to determine the prevalence of perfluorinated chemicals (i.e. PFOA and PFOS) in the Western Cape Province environmental matrices, and thus establish a platform for PFCs being documented in this province in particular and in South Africa, in general. The Harvard referencing style is used throughout the thesis. The materials and methods used in this study are also explained. This thesis is subdivided in to the following chapters:

- Chapter 1 serves as an overall introduction, providing background information on worldwide freshwater demand and its usage. Furthermore, the chapter presents the overall research problem and questions, the overall objectives for the study and the significance of the study, and also delineates the research that was conducted.
- Chapter 2 presents the literature reviewed. This chapter offers a general overview of persistent organic pollutants and their prevalence in various environmental matrices, as well as their environmental and health effects. It then highlights the new emerging persistent organic pollutants; in this case perfluorinated chemicals (PFCs).
- Chapter 3 provides an overall overview of the study area, focusing on three Western Cape Province rivers (i.e. the Diep, Eerste and Salt rivers).
- Chapter 4 presents the materials and methods used in this study.
- Chapter 5 is the results chapter. In this chapter, an investigation of PFOA and PFOS prevalence in river water and sediments is discussed, as well as their presence in suspended solids and selected riparian plants. Each result section is accompanied by a discussion and a summary outlining the conclusions of this chapter.
- Chapter 6 is the overall discussion and conclusion. In this chapter all the research questions in Chapter 1 are answered. This chapter also makes recommendations for future research.
- Chapter 7 contains the references.

CHAPTER ONE

INTRODUCTION

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INTRODUCTION

1.1 Background

Worldwide water demand and usage has increased dramatically due to an increasing population and industrial activity (Vigneswaran and Sundaravadivel, 2004). This has resulted in water shortages with associated consumption restrictions being imposed by municipalities in regions were water resources are in decline (City of Cape Town, 2004). Environmental issues such as climate change and global warming have exacerbated the situation, making the depletion of water resources one of the major problems. Furthermore, an increase in industrial activity has increased the wastewater generated, which is released into water sources such as rivers, lakes and aquifers. One of the major concerns in this regard is the pollution of these water sources with persistent organic pollutants (POPs). Quante *et al.* (2011) have indicated that, at present, there are more than 18 million organic compounds which are known and used in various industrial applications; subsequently, although a small portion of these substances end up in wastewater and drinking water sources, some exhibit properties which lead to environmental degradation and others have been shown to be detrimental to human and animal health. Although South Africa is rich in natural resources, water, a strategic resource, is in short supply. According to the literature reviewed, the average annual rainfall for South Africa as a whole is ± 497 mm, compared to the world average of ± 860 mm. Consequently, South Africa has one of the lowest conversions of rainfall runoff (DWAF, 1993). For Southern Africa, the region where South Africa is geographicaly situated, it is predicted that a decrease in rainfall in the range of 15 to 25% will occur by 2050 (Schulze and Perks, 1999), thus making the preservation of water sources a priority.

According to the Stockholm Convention (2001), POPs are chemical organic compounds which are resistant to environmental degradation (biological, chemical, and photolytic), thus become prevalent in the environment for long periods, bioaccumulating through the food chain, and having the potential to cause adverse effects in humans and animals. Similarly, Albaigés (2005) reported that POPs are to a varying degree long-lasting in the marine environment, thus have the ability to bioaccumulate in fatty tissues and can potentially cause detrimental effects along the foodchain. Furthermore, their persistent nature is as a result of either a long half-life of the pollutant or its continuous release into the environment. Currently, perfluorinated organic chemicals or compounds (PFCs), which are fully fluorinated, are one of the prominent POPs being studied worldwide. Quante *et al.* (2011) have indicated that new POPs are often polar, less volatile and belong to different compound classes and their origin is a result of a number of applications; consequently, this makes their treatment and monitoring in environmental matrices important.

PFCs are human-made and do not occur naturally in the environment. They have been produced in relatively large quantities since the 1950s (Giesy and Kannan, 2001; Paul *et al.*, 2009; Naile *et al.*, 2010). They are characterised by chains of carbon atoms where hydrogen atoms are replaced with fluorine atoms (Kissa, 2001). Perfluorooctanoate (PFOA, $C_7F_{15}COO$-) and perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3$-) are representatives of perfluorinated chemicals and, owing to their strong carbon-fluorine bonds; they are reported to bioaccumulate in aquatic systems and the environment. Möller *et al.* (2009) reported that these two compounds are persistent, bioaccumulative substances and have been detected in various environmental matrices such as freshwater (McLachlan *et al.*, 2007), marine waters (Ahrens *et al.*, 2009a, 2009b, Yamashita *et al.*, 2004), air (Jahnke *et al.*, 2007), soil (Higgins and Luthy, 2006) and various organisms (Giesy and Kannan, 2001).

The chemical properties of these compounds have made them useful for the manufacturing sector. Möller *et al.* (2009) reported that PFCs consist of both a hydrophilic and a hydrophobic head with oleophobic carbon chains, which make them moderately water soluble. Because of their special chemical and physical properties, i.e., water, oil and soil repellence, they are used in a wide range of applications and consumer products such as paper, leather, textile coatings, and fire-fighting foam. This includes the production of various products in the polymer industry (Kissa, 2001).

However, according to Möller *et al*. (2009), PFCs meet the criteria of PBT (persistent, bioaccumulative and toxic) compounds. PFOS was recently listed as a POP (persistent organic pollutant) by the COP-4 Stockholm Convention (UNEP 2009). Furthermore, Fromme *et al*. (2008) and Lau *et al*. (2007) stated that toxic effects (e.g. gastrointestinal and thyroid hormone defects) of PFCs have been verified and the lead compounds PFOA and PFOS, are suspected to be carcinogenic. It is for these reasons that one of the manufacturers (3M Company) ceased the manufacture of perfluorinated products (3M Company, 2000). In South Africa, the occurrence of these organic chemicals in aquatic systems, for example. in rivers, drinking water, etc., have yet to be reported and documented. However, Hanssen *et al.* (2010) reported the presence of PFOS and PFOA in maternal serum and cord blood for a South African study, indicating possible ingestion. Furthermore, it was reported in the study that the highest concentrations of PFOS and PFOA were found in urbanites as well as in rural dwellers. Thus, these results would indicated that this is a serious environmental concern as far as rivers are concerned, as they constitute the only substantial source of freshwater in the country for drinking and agricultural use. To date, most of environmental studies of PFOA/PFOS have been conducted in developed countries.

1.2 Research problem

According to the Health Protection Agency (HPA, 2009a), the main routes of exposure to PFOS and PFOA is via inhalation of contaminated air or by ingestion of contaminated water or food. However, both the Committee on Toxicity of Chemicals in Food Consumer Products and the Environment (2005) and HPA (2009b) have reported that both compounds, that is PFOS and PFOA, are essentially non-volatile and the general public would not be expected to be exposed via inhalation. Today, wetlands are of environmental importance; they range from being cradles of biological diversity, providing water and primary productivity upon which countless species of plants and animals depend for survival. Therefore, owing to their non-biodegradable characteristics, if present in these wetlands, human, animals and plants in these areas will be susceptible to PFC exposure. The prevalence of these compounds has been reported in other countries, but in South Africa in general, and the Western Cape in particular, they remain unreported and undocumented in the aquatic environment which includes rivers for which their water is used for agricultural purposes.

The present research is the first study in South Africa reporting on PFOA and PFOS presence in river water, sediment and plants in the riparian wetlands of the Salt, Eerste and Diep rivers.

1.3 Research questions

The concentration of perfluorinated compounds (PFCs) was determined to be high in river water in areas with an active manufacturing sector (Kissa, 2001; Möller *et al.*, 2009). Since the Western Cape is one of the provinces in which the manufacturing sector is active, this study consequently answers the following questions:

- What are the levels of perfluorinated compounds, PFOS and PFOA, in the riparian wetlands of the Eerste, Diep and Salt Rivers?
- Is there a correlation between the identified river catchment usage, with the prevalence of PFOS/PFOA in the samples?

- Will there be a variation in the concentration of the identified perfluorinated contaminants in the water, sediment, suspended solid and plant samples?
- Which of the three rivers will have the highest concentration of PFOS/PFOA and why is this the case? That is, what is the relationship of PFOA/PFOS accumulation in relation to total organic carbon in the sediment?
- What type of sediment is prevalent in the three rivers under investigation?
- Is there a correlation and/or similarities between the concentration of both PFOS and PFOA in comparison to other studies in other countries?

1.4 Aims and objectives

The main aim of this study was to determine the concentration of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in riparian wetlands of the Western Cape. The focus was on the Eerste, Diep and Salt rivers.

The following were the objectives of the study:

- To analyse and quantify perfluorooctane sulfonate and perfluorooctanoate in the water, sediments, suspended solids and plant samples from the riparian wetlands of the Eerste, Diep and Salt rivers.
- To determine the physical characteristics of the sediment prevalent in the three rivers and the physico-chemical characteristics of the sediment core water and other environmental parameters linked to PFOS and PFOA accumulation in the rivers.
- To correlate PFOS/PFOA distribution in the three rivers to catchment usage, that is, for domestic, industrial and/or agricultural activity.

1.5 Significance of the study

The present research reports on the presence of PFOA and PFOS in the riparian wetlands of South African rivers. The results obtained constituted a contribution to a POP monitoring database for South Africa.

1.6 Delineation of the study

The proposed study focused only on the analysis and quantification of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in water, sediments and plants from three rivers (the Eerste River, the Diep River and the Salt River). The source of these PFCs was not assessed in this study nor was their effect on plants and animals.

CHAPTER TWO

LITERATURE REVIEW

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of global water availability

Water is an essential resource for a variety of species including humans. Although it is one of the most critical resources, it is under threat around the world. According to the US Department of Interior (2006) and Jackson (2008), total water availability on earth's surface is distributed as follows: 3% is fresh water and 97% is salt water. Of the 3% fresh water, 1% is attributed to lakes, rivers and streams as depicted in Figure 2.1(a) and (b).

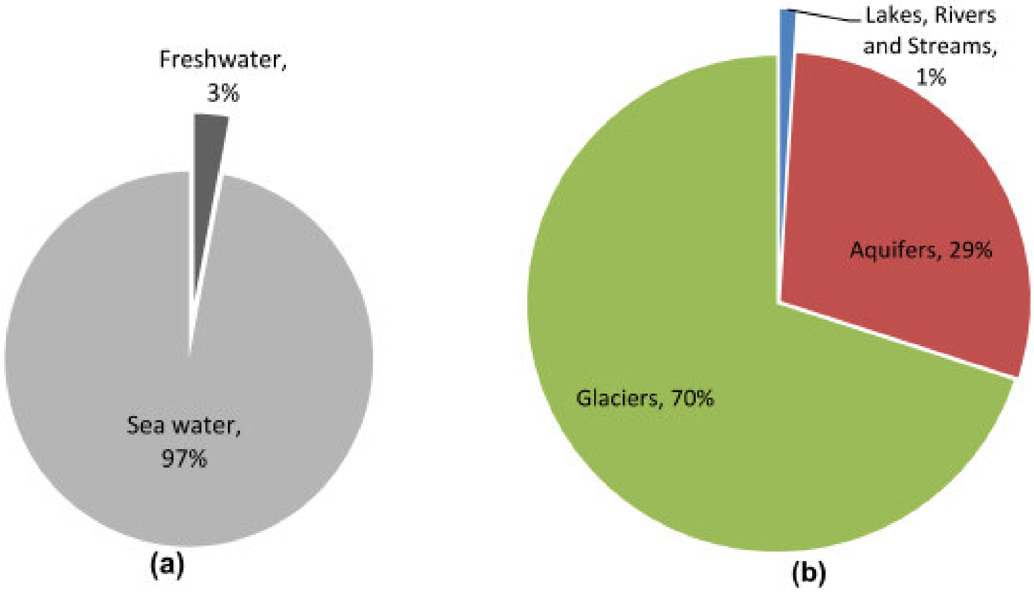


Figure 2.1: (a) Global water availability; **(b)** Global freshwater allocation

By 2030, water usage is expected to increase by 40%, and 17% more water will be required for food production to meet the needs of the growing population. Moreover, by 2025, it is estimated that 1.8 billion people will be living in regions with water scarcity, and two out of three people in the world could be living under conditions of water stress (UNDESA, 2009). Furthermore, with industrial activity, different organic chemicals have been generated and released in water streams such as rivers, lakes and municipal drainage systems. Today, some of these compounds are regarded as persistent organic pollutants (POPs). One of the emerging POPs are perfluorinated chemicals (PFCs). South Africa is located in a predominantly semi-arid part of the world. The climate varies from desert and semi-desert in the west to sub-humid along the eastern coastal area, with an average rainfall for the country of about 450 mm per year, which is well below the world average of about 860 mm per year (Schulze *et al*., 1993; Poonyth *et al*., 2002). As a result, South Africa's water resources are, in global terms, scarce and limited (DWAF, 2002). Furthermore, South Africa is mainly dependent on surface water (dams and rivers) resources for most of the urban, industrial and irrigation water supplies in the country (Basson, 2011).

2.2 Persistent organic pollutants

According to the Geneva Inter-Organisation Programme for the Sound Management of Chemicals (IOMC, 2002), in partnership with the United Nations (UN), the United Nations Environmental Programme (UNEP), the Food and Agriculture Organization (FAO) and the World Health Organization (WHO), POPs may be described as chemicals that are stable and persist in the environment, bioaccumulate in organisms and the food chain, are toxic to humans as well as animals and have chronic effects such as the disruption of reproductive, immune and endocrine systems, as well as being carcinogenic. They are transported in the environment over long distances to places far from the points of release by various means, including waterways. These chemicals can enter the environment in several ways, including spillages, release from waste dumps, industrial and agricultural waste, urban/agricultural runoff and the burning of various materials, thus being distributed in various environmental matrices, including water, air, soils, sediments and living organisms (Wania *et al*., 1993; Corsolini *et al*., 2005; Si, 2008). Given the fact that POPs have bioaccumulation potential and can travel long distances by water, atmospheric exchange and agricultural runoffs, POPs can be detected even in pristine areas such as the Antarctica and the Arctic regions, regions with minimum direct anthropogenic disturbance (Wania, 2003; Taniguchi *et al*., 2009).

In 1997, in order to limit POPs transportation and environmental contamination, the international community decided to work towards the establishment of a convention that would serve as an international, legally binding instrument, to reduce and/or eliminate the release of POPs, as identified in the UNEP Governing Council Decision 19/13C (IOMC, 2002).

Under the Stockholm Convention of POPs (COP-4) for global action, in 1995 the UNEP listed twelve POPs which are also known as the "*dirty dozen*". The Governing Council took a decision 18/32 to begin investigating POPs, and their persistence in the environment (Ritter *et al*., 2007 and Si, 2008). The compounds consist of four POPs including dioxins, furans, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) (SC POP, 2008d), and eight pesticides, also known as organochlorine pesticides, which are aldrin, chlordane, dichloro-diphenyl-trichloroethane (DDT), dieldrin, endrins, heptachlor, mirex and toxaphene (UNEP, 2003).

2.2.1 Environmental and health effects of persistent organic pollutants

Although environmental pollution and degradation has always been present in society, the technological and chemical revolutions of the 19th and 20th centuries have increased the levels of toxic materials and associated environmental degradation to an unprecedented level in human history (Graham and Miller, 2001; Adeola, 2004). In addition, scientific and technological breakthroughs in the synthesis and production of chemical compounds have contributed to remarkable societal prosperity on one hand and, on the other, to new arrays of unexpected and detrimental environmental effects as a result of these chemicals (Adeola, 2004). According to Fu *et al.* (2003), several POPs targeted by the Stockholm Convention are of concern given that they contaminate the environment and are toxic. Some of them are persistent, having a long half-life, and toxic, i.e. carcinogenic, and are still in widespread production and use, in both industrialised and less industrialised countries. Currently, these compounds have been reported in regions where they are not produced or synthesised (WHO ROE, 2003).

Owing to the rapid development of industrial and increasing agricultural activity, including municipal development, the use of organic chemicals has increased, causing environmental pollution and degradation problems. These developmental activities have adversely affected air and water quality (Fu *et al.,* 2003). In addition, Adeola (2004) mentions that the case of POPs is mostly paradoxical; while millions of lives have been saved through their application, for example in controlling malaria; several millions have also suffered serious adverse health effects from acute and chronic exposure and toxicity. However, the International Programme on Chemical Safety (IPCS, 1995) has indicated that as is the case with many environmental pollutants, it is difficult to establish causality of illness or disease that is directly attributable to exposure to a specific POP or a group of POPs. The challenge in this regard is further underscored by the fact that POPs rarely occur as individual compounds and individual field studies are frequently insufficient to provide compelling evidence of cause and effect (IPCS, 1995).

Moreover, Hileman (1993) and the IPCS (1995) have indicated that, experimentally, POPs have been associated with significant environmental impact in a wide range of species and at virtually all trophic levels. Nevertheless, Babcock (1977) and the IPCS (1995) have mentioned that, while acute effects of POP intoxication have been well documented, adverse effects associated with chronic low-level exposure in the environment over an extended period, are of particular concern. In this regard, Allen *et al.* (1979) and the IPCS (1995) reported that, for some POPs, there is experimental evidence to show that such low-level cumulative exposure may be associated with chronic non-lethal effects, including potential immunotoxicity, dermal effects, impairment of reproductive systems and carcinogenicity. For instance, Tryphonas *et al*. (1991), Hileman (1993) and IPCS (1995) indicated that POPs immunotoxicity is associated with exposure to different POPs. Investigators have demonstrated immune dysfunction as a plausible cause for increased mortality among marine mammals and have also demonstrated that consumption of diets contaminated with POPs in seals, may lead to vitamin and thyroid deficiencies and thus concomitant susceptibility to microbial infections and reproductive disorders (IPCS, 1995).

Furthermore, Wren (1991) and the IPCS (1995) have reported a direct cause and effect relationship in mink and ferrets between PCB exposure and immune dysfunction, reproductive failure, increased mortality, organ deformations and adult mortality. Hansen *et al.,* (1985), demonstrated a correlation between environmental concentrations of PCBs and dioxins with reduced viability of larvae in fish species. Meanwhile, egg shell abnormalities in birds, resulting in the extinction of certain bird species has been indicated by the World Wildlife Fund (WWF, 1999) as a result of POP exposure. For instance, in Lake Apoka (USA), stunted penis, hormone disruption and reproductive failure was reported among alligators by Adeola (2004), Abelsohn *et al*. (2002), Jones and deVoogt (1999), WWF (1999) and Swan *et al.* (1997). Additionally, during a study of beluga whales by Adeola (2004), the effects of POP exposure observed included the development of cancerous cells, twisted spines and skeletal deformation and death.

As far as human exposure is concerned, the IPCS (1995) has indicated that it is difficult to establish cause and effect relationships in human exposure to POPs and related incident of diseases. Moreover, typical routes of exposure include workplace (in agriculture and manufacturing industries), dietary exposure and direct contact with contaminants in the air, buildings, water, lawns, parks and soil (Lallas, 2002 ; Adeola, 2004). Furthermore, the IPCS (1995) indicates that workers' exposure to POPs during waste management is a significant source of occupational risk in many countries. According to the IPCS (1995), there is scientific evidence that some POPs have the potential to cause significant adverse effects in humans at local, regional and a global level through their long-range transportation. In the study, it was mentioned that, occupational and accidental high-level exposure to POPs, is a major concern, which results in acute and chronic worker exposure; and the risk was determined to be high, particularly in developing countries where the use of POPs in tropical agriculture has resulted in a large number of deaths and injuries.

A typical example of exposure to POPs and the risks that are involved, is from the Philippines where Endosulfan, an organochlorine insecticide, became the number one cause of pesticide-related acute poisoning among subsistence rice farmers and mango sprayers (Adeola, 2004). In addition, laboratory studies have provided supporting evidence that selected organochlorine chemicals may have carcinogenic effects and act as strong tumour promoters.

2.2.2 Persistent organic pollutants: suggested sources of contamination

For agrochemical POPs their source is clear - the deliberate application to crops and soils (Jones and deVoogt, 1999). In addition, according to Lohmann *et al.* (2007) and Harrad (2010), organochlorine pesticides, and other industrial chemicals, were intentionally produced for various uses, for example as flame retardants, as ingredients in consumer products, including electronic goods; which generally result in their unintentional release in to the environment, some in the form of e-waste (Wong *et al.*, 2007). In addition, the use of fire-fighting foams, vehicles and the burning of wood, have been mentioned as potential contributors to POP release in to the environment in developing countries (Harrad, 2010). Organic pollutants can enter the coastal environment by a number of processes and once introduced to this environment, they are subject to biogeochemical cycling, sinking, and other environmental processes (Dachs and Méjanelle, 2010).

Additionally, Boucher *et al.* (2009); Ashwood *et al.* (2009); and Fernie *et al.* (2008, 2009) have indicated that the low rate of escape of POPs into water reservoirs (i.e. streams), or stock of materials and products, is a source of concern because it could result in exposure that could cause subtle toxicological effects in humans and biota. Kemmlein *et al.* (2003) and Webster *et al.* (2009) have reported that, an increasing number of materials containing POPs, are used in building materials, in goods and in various consumer products. For the POPs contained in consumer products, their low vapour pressure can thus result in a slow but significant release into the environment (Harrad, 2010). The release can come from direct volatilisation as well as microscale abrasion of plastics (Kemmlein *et al.*, 2003; Webster *et al.*, 2009). Following release, the fate of the POP compound in the environment is largely based on its physico-chemical properties and the characteristics of the environment (Zhang *et al.*, 2009).

The process of environmental transport and incorporation into food supplies will be accelerated if the compound is in the biosolids applied to agricultural lands, in wastewater effluents discharged to surface waters and in landfills adjacent to agricultural lands, and if industrial facilities that use the compound are located near sources of food (Kelley *et al.*, 2007). They can also be transferred from mother to infant via breast milk, and umbilical cord serum (Suzuki *et al*., 2005).

2.3 Persistent organic pollutants in environmental matrices

2.3.1 Persistent organic pollutants in Water

In a report by the UNEP (2002) on persistent toxic substances (PTS) in sub-Saharan Africa, it was indicated that sub-Saharan African fresh waters (rivers, lakes, groundwater, estuaries and rainwater) are contaminated by a broad spectrum of 14 measured PTS. From the data, the following range of concentrations (ng/L) in rivers was found: Endosulfan (≤ 4843), Atrazine (0.38 to 44000), PCBs (≤ 0.3), Dieldrin (≤ 921), DDT (≤ 350), HCB (≤ 9.4), Heptachlor (≤ 5.3), Chlordane (0.02) and HCH (≤ 0.1). Nonylphenols were reported for a river in South Africa at 4 ng/L while PAHs were detected in Madagascar at 300 ng/L (UNEP, 2002). Mirex, PAHs and Endrin were not detected in rivers in South Africa or Nigeria (UNEP, 2002).

Furthermore, the same report indicated that the reported range of concentrations (ng/L) for the PTS detected in lakes (Malawi, Nakuru, etc.) was as follows: Endosulfan (≤ 18.5), Atrazine (0.004 to 97705), PCBs (≤ 2.0), Dieldrin (0.01 to 11.4), DDT (0.06 to 8.1), Heptachlor (≤ 100), Chlordane (0.9 to 30.9) and HCH (≤ 0.1). PAHs were reported for only a lake in Madagascar at a concentration of 300 ng/L. In South Africa, PCBs were detectable in rivers as early as 1974 (2 ng/L). Moreover, more recent data about the levels of PCBs in lakes, rivers, dams and streams (≤ 2000 ng/L) have been reported from Nigeria, South Africa, Zimbabwe, Kenya and Cote d'Ivoire (UNEP, 2002).

2.3.2 Persistent organic Pollutants in Aquatic sediments

Si (2008) indicates that POPs such as PCBs, OCPs and PAHs are frequently found in various environmental matrices including the marine environment owing to their particular affinity for suspended organic matter which sinks readily to the river bottom. In addition, it has been mentioned by Harrad (2010) that, because of their hydrophobic nature, upon reaching an aquatic environment, POPs are very quickly sequestered by organic-rich particles and accumulate in sediments where they are ultimately buried. This provides historical evidence of contamination as the layers of sediment increasingly accumulate on top of each other.

Additionally, sediments tend to integrate contaminants over long periods of time and are often the best matrix for assessing spatial and temporal concentrations of hydrophobic organic contaminants (Harrad, 2010). Sediments are thought to act as the ultimate sink for

POPs and sediment samples have been extensively analysed to understand levels of pollution, especially along coastal areas and other aquatic environments affected by pollution (Galindo-Reyes *et al.*, 1999; Harrad, 2010). However, Si (2008) indicated that sediments may not be the ultimate sink, for these contaminants may return to the water compartment again once the physico-chemical characteristics of the water change or if sediments are resuspended by water currents. Nevertheless, as a result of their lipophilic properties, most POPs accumulate rapidly in sediment than in other environmental media (De Boer *et al.,* 2001; Si, 2008).

2.3.3 Persistent Organic Pollutants in Soil

According to Harrad (2010), soils, particularly those with a high concentration of organic carbon content like peat, are natural sinks for POPs. As such, these contaminants enter the soil through wet and dry atmospheric deposition, accidental spillages, sewage sludge application, and direct pesticide application. As a result of this, during the rainy season, some of the contaminated soil is washed away (i.e. runoff process) into streams and rivers.

2.4 New emerging persistent organic pollutants

According to Quante *et al*. (2011), there are more than 18 million known organic compounds; and although only a few portions of these substances display properties that render them hazardous to the environment, the number of organic contaminants is high and, in principle, their use is unrestricted. The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR, 2005; Quante *et al*., 2011) indicated that nearly 2000 of these compounds are estimated to be prevalent in the environment. Consequently, in May 2009, the SC POPs listed an additional nine POPs which are currently of concern; these are: hexachlorocyclohexane; hexachlorocyclohexane; hexabromodiphenyl ether and peptabromodiphenyl ether; tetrabromodiphenyl ether and pentabromodiphenyl ether; chlorodecone; hexabromobiphenyl; lindane; pentachlorobenzene; and PFOS/PFOA salts. Furthermore, only twelve pollutants are considered to be traditional POPs that are treated and regulated by the UN POP Convention (UNEP, 2006). According to Quante *et al.* (2011), while traditional POPs are mostly non-polar, lipophilic compounds and belong to a few compound classes or polycyclic aromatic hydrocarbons (PAHs), new emerging pollutants exhibit properties which are different from traditional pollutants. Additionally, the study reported that these new compounds are often polar and less volatile, belong to many different compound classes and originate from a great number of different applications as indicated in Table 2.1.

Table 2.1: List of emerging pollutants (Quante *et al.,* 2011 ; Ahrens, 2009)

Class/Application	**Compound name**
Mixed compounds	2,5-Dichloroaniline; 3-Chloronitrobenzene; 4-Chloronitrobenzene; 2-Chloronitrobenzene; 2,5-Dichloronitrobenzene; 3,4-Dichloronitrobenzene; Xanthenone; Methylbenzothiazol; Benzotriazol; Bis-(4-chlorophenyl) sulfone; Bisphenol A; Bis(ethylhexyl) phthalate; Bis(ethylhexyl) phthalate; Dichloro-bis(propyl)ethers (sum of 2 isomers), and Bis(ethylhexyl) phthalate
Surfactants	Nonylphenols (sum of isomers); Nonylphenolmonoethoxylates (sum of isomers); Nonylphenol-diethoxylates (sum of isomers); Octylphenol; Octylphenolmonoethoxylate; and Octylphenol-diethoxylate
Pesticides	Monobutyltin; Dibutyltin; Tributyltin; Triphenyltin; Monooctyltin; Dioctyltin; Tricyclohexyltin; Atrazine; Deethylatrazine; Irgarol; Pentachlorophenol; Simazine; Terbuthylazine; Diuron; Mecoprop; Isoproturon; Bentazon; 2,4-D; Bentazon; MCPA; Endosulfan I; Alachlor; Trifluralin; and Chlorpyrifos-ethyl
***Perfluorinated compounds(PFC)**	***Perfluorooctanoate (PFOA)** and **Perfluorooctane sulfonate (PFOS)** Perfluroalkyl sulfonates (PFSAs); Perfluroalkyl sulfinates (PFSiAs); x:2 Fluorotelomer sulfonates (x:2 FTS); Perfluoroalkyl carboxylates (PFCAs); Perfluoroalkyl phosphonates (PFPAs) ; Fluorotelomer carboxylates (x:2 FTCA); Fluorotelomer unsaturated carboxylates (x:2 FTUCA); x:2 Fluorotelomer olefins (x:2 FTolefin); x:2 Fluorotelomer alkohols (x:2 FTOH); x:2 Fluorotelomer acrylates (x:2 FTA); x:2 Fluorotelomer aldehydes (x:2 FTAL); Perfluoroalkyl sulfonamides (FASAs); Perfluoroalkyl sulfonamidoethanols (FASEs); Perfluoroalkyl sulfonamidoacetic acids (FASAAs)
Phosphate Esters	Trisbutoxyethyl phosphate (TBEP); Tri-*n*-butyl phosphate (TBP); Tris (1-chloro-2-propyl) phosphate (TCPP); and Tris(1,3-dichloro-2-propyl) phosphate (TDCP)
Pharmaceutical/Personal care product	Clofibrinic acid; Carbamazepin; Oxazepam; Diclofenac; Primidon; HHCB (musk fragrance); and AHTN

A sole focus of this research

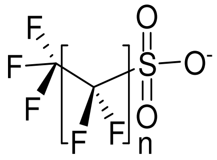
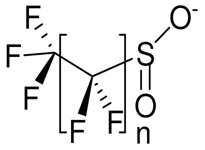
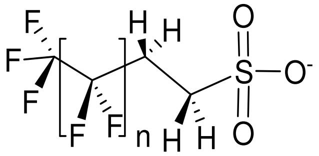
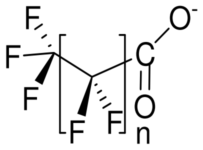
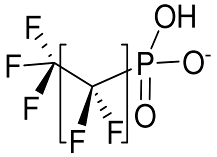
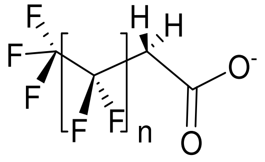
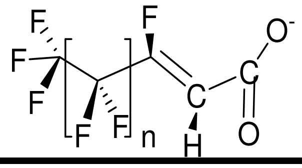
2.4.1 Perfluorinated chemicals (PFCs)

Persistent organic pollutants (POPs) have been a concern for decades and recently perfluorinated chemicals (PFCs) have appeared on the list of POPs (Yong, 2007). Perfluorinated compounds are manmade chemicals (Kissa, 2001) that do not occur naturally in the environment. Their production started in the 1950s (Renner, 2001) and historically, research on POPs has focused principally on chlorinated compounds, although other halogenated compounds, including fluorinated compounds, have also been found to be persistent and bioaccumulative in the environment. Scientists assumed that because many of these compounds are incorporated into polymers, they would not travel readily into the environment and accumulate in living organisms (Renner, 2001).

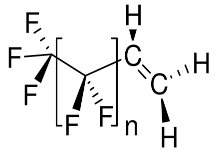
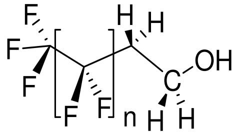
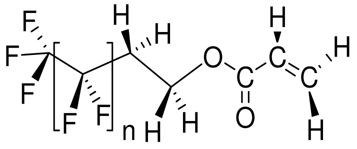
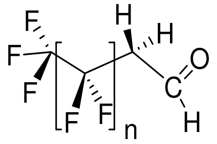
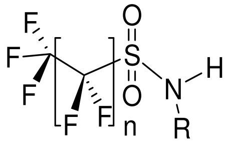
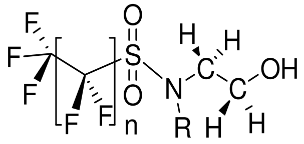
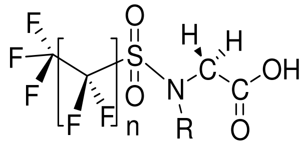
The occurrence of these compounds (i.e. PFCs) in human serum was reported for the first time in 1968 (Taves, 1968). According to Giesy and Kannan (2001), as well as Olsen *et al.* (1999), improvements in analytical techniques during the 1990s, resulted in the characterisation of several PFCs in environmental samples, animals and humans (Giesy and Kannan 2001; Olsen *et al.*, 1999). Thus, these results had the consequence that, in the year 2000, the 3M Company voluntarily phased out the production of perfluorooctanesulphonyl fluoride (POSF), which is a major precursor to the synthesis of several PFCs (Ahrens, 2009).

PFCs are found in fast-food packaging, paper plates, stain-resistant carpets, carpet cleaning solutions, windshield washing fluid and fire-fighting foam, as well as in some adhesives, cosmetics, pharmaceuticals, electronics, cleaning products, polishes and waxes, insecticides and paints. For example, PFOA is also used in the manufacture of non-stick cookware (e.g. Teflon) and waterproof fabrics (e.g. Gore-tex, etc) (3M Company, 2000; Kissa, 2001). Since then, these chemicals have been detected in freshwater (McLachlan *et al.*, 2007) and marine waters (Ahrens, Barber *et al.*, 2009a; Ahrens, Yeung *et al.*, 2009b; Yamashita *et al.* 2004), air (Jahnke *et al.*, 2007), soil (Higgins and Luthy, 2006) and organisms (Giesy and Kannan, 2001). According to Ahrens (2009), D'eon *et al.,* (2006), Ellis *et al.* (2004) and Martin *et al.* (2006) there are several hundred types of PFCs, which can be divided into ionic and neutral PFCs. Table 2.2 gives a list of relevant groups of the ionic and neutral PFCs prevalent in the environment, with their respective chemical structures.

Table 2.2: Groups of ionic and neutral PFCs (Ahrens, 2009)

Compound groups	Acronym	chemical structure	Typical PFCs
Ionic PFCs			
Perfluroalkyl sulfonates	PFSAs		n = 3-9
Perfluroalkyl sulfinates	PFSiAs		n = 5,7,9
x:2 Fluorotelomer sulfonates	x:2 FTS		n = 5,7,9
Perfluroalkyl carboxylates	PFCAs		n = 1-17
Perfluroalkyl phosphonates	PFPAs		n = 5,7,9
Fluorotelomer carboxylates	x:2 FTCA		n = 5,7,9
Fluorotelomer unsaturated carboxylates	x:2 FTUCA		n = 4,6,8

Cont: Table 2.2

Compound groups	**Acronym**	**chemical structure**	**Typical PFCs**
Neutral PFCs			
x:2 Fluorotelomer olefins	x:2 FTolefins		n = 5,7,9,11
x:2 Fluorotelomer alcohols	x:2 FTOH		n = 3,5,7,9,11
x:2 Fluorotelomer acrylates	x:2 FTA		n = 5,7,9
x:2 Fluorotelomer aldehydes	x:2 FTAL		n = 7
Perfluoroalkyl sulfonamides	FASAs		n = 7, R = H n = 7, R = CH_3 n = 7, R = C_2H_5 n = 3, R = CH_3
Perfluoroalkyl sulfonamidoethanols	FASEs		n = 7, R = CH_3 n = 7, R = C_2H_5 n = 3, R = CH_3
Perfluoroalkyl sulfonamidoacetic acids	FASAAs		n = 7, R = CH_3 n = 7, R = CH_3 n = 7, R = C_2H_5

2.4.2 Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS)

PFCs comprise a wide range of different substances, and consist of a hydrophilic functional group and a hydrophobic fluorinated chain which can vary in chain length. The hydrophobic part is fully or partially fluorinated and can be linear or branched. PFOA and PFOS are the typical chemicals of these two groups, which have eight carbons “C8” (Yong, 2007; Ahrens, 2009). The chemical structure of these compounds is shown in Figure 2.2.

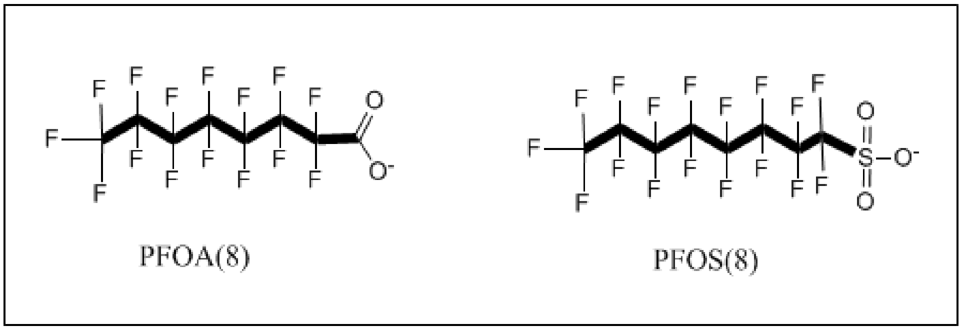


Figure 2.2: Structure of PFOA and PFOS (Ahrens, 2009)

The most studied PFCs are perfluorooctanoate (PFOA) and (PFOS) (Stahl *et al.*, 2009; Lechner and Knapp, 2011; Ahrens, 2009). Figure 2.3 depicts the emission of PFOA/PFOS in Europe, while Figure 2.4 portrays a global distribution of PFOS and PFOA in the northern and southern hemisphere.

Although there are multiple studies that report on PFOA and PFOS distribution in the countries of the northern hemisphere, there is limited information on the distribution of both PFOA and PFOS in the southern hemisphere (see Figure 2.4), particularly in African countries.

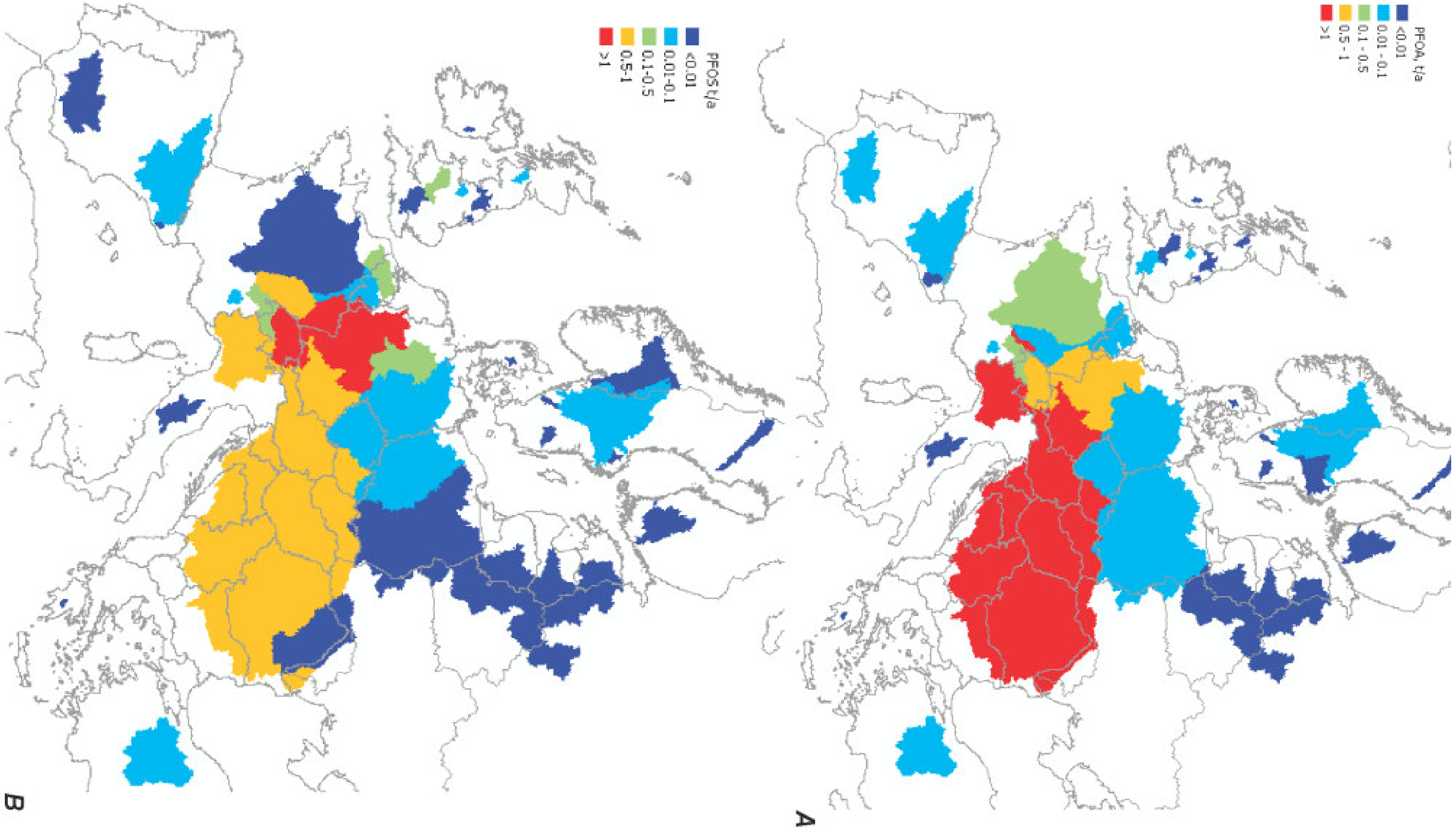


Figure 2.3: Map of (A) PFOA and (B) PFOS emissions (t/a) for monitored catchments in Europe (Pistocchi and Loos, 2009) (**t/a** = tons per annum)

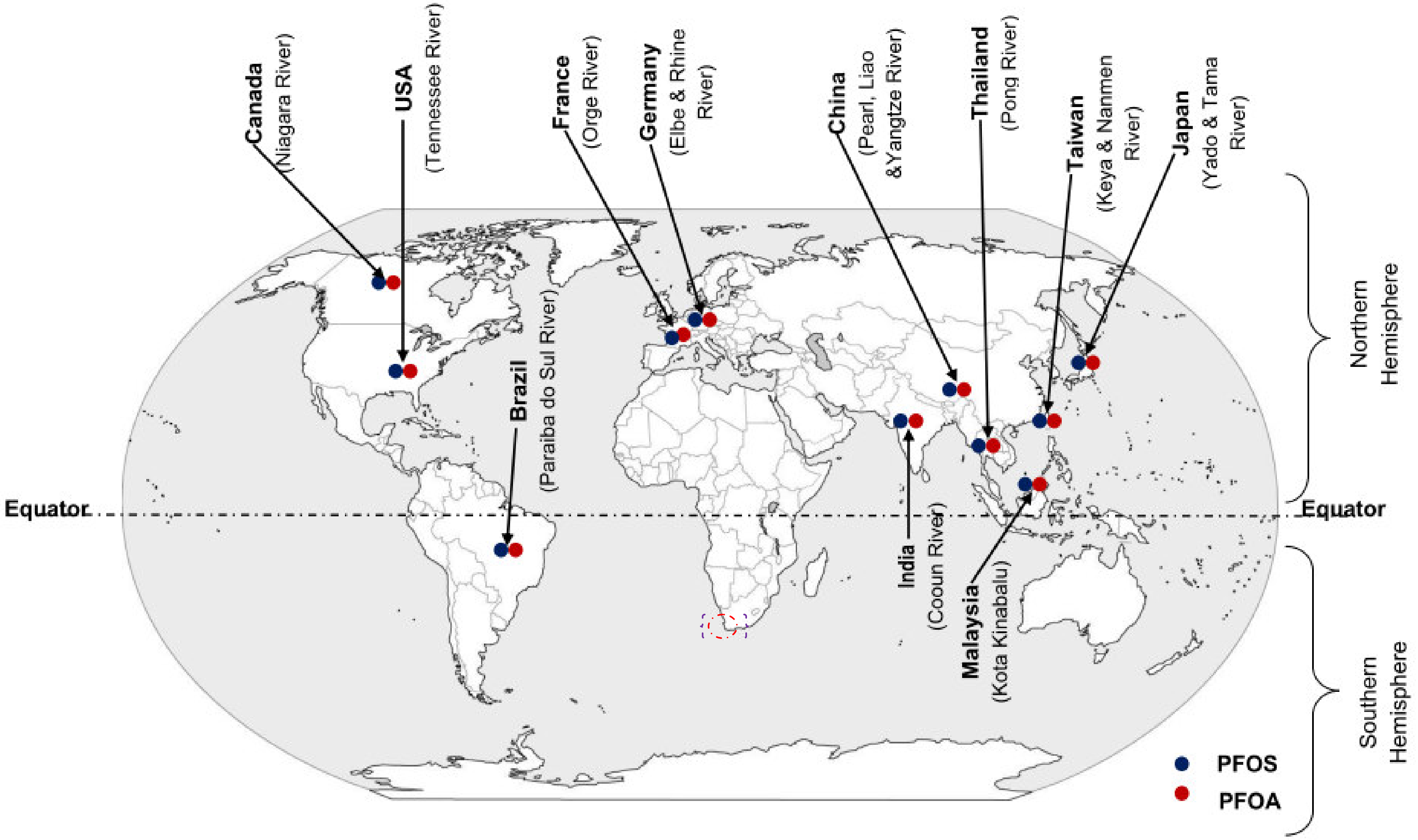


Figure 2.4: Global detection of PFOS and PFOA in river water and sediment

2.5 Production and application of perfluorinated chemicals

2.5.1 Production of perfluorinated chemicals

PFCs are manufactured basically by means of two synthesis routes, which are exemplified in Figure 2.5 (Ahrens, 2009; Yong, 2007). The first is electrochemical fluorination (ECF), which was invented in the early 1940s by Joseph Simons of the 3M Company (Simons, 1950; Ahrens, 2009). The ECF is a free-radical process and yields a product mixture of linear and up to 30% branched isomers with even and odd numbers of carbon atoms in the chain (Giesy and Kannan, 2002). In the ECF process, a mixture of hydrocarbons (different carbon chain lengths including branched isomers) with a functional group is subjected to fluorination, which produces a mixture of perfluorinated products with the same homologue and isomer pattern (Herzke *et al.*, 2009). This process is shown in Figure 2.5a. The second process, telomerisation, was developed by Dupont and has been used since the 1950s. According to Lange *et al.* (2006), products based on telomerisation are manufactured by a number of companies, including DuPont, Asahi Glass, Atofina, Clariant, and Daikin. The process is depicted in Figure 2.5b

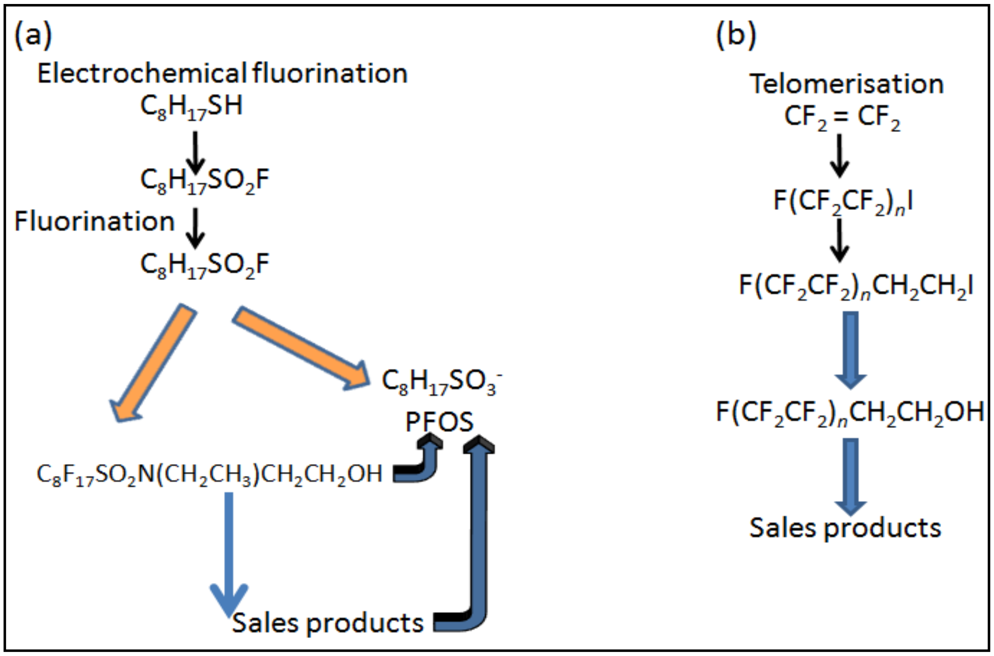


Figure 2.5: Manufacturing processes of PFCs *(a)* electrochemical fluorination and *(b)* telomerisation (Yong, 2007; Ahrens, 2009).

The basic units of the electrochemical fluorination process, perfluorooctanecarbonyl fluoride (POCF) and perfluorooctanesulfonyl fluoride (POSF) can be converted in to several polymeric products (Kissa, 2001). However, there is limited information on the production volume of PFCs for polymeric products. The 3M Company, the major producer of POSF, increased production volume from around 300 tons of POSF in 1970 to over 3,600 tons in 2000 (Ahrens, 2009). In addition, the estimated global historical production of perfluorocarboxylates (PFCAs), which is one of the ECF process derivatives, is between 4,400 and 8,000 tons (2006 data), while the total global (both direct and indirect) emissions to the environment were between 3,200 and 7,300 tons (Prevedouros *et al.*, 2006). Among the various forms of PFCAs, PFOA is the compound that is most detected in the water environment and in biota. Other derivatives, such as the polyfluorinated and fluorinated alcohols (FTOHs) obtained when the telomerisation manufacturing process is used, were estimated to be 5,000 tons (2000 to 2002 data) (Betts, 2003) which increased to between 11,000 and 14,000 tons per year after 2002 (Dinglasan-Panlilio and Mabury, 2006).

The Organization for Economic Cooperation and Development (OECD, 2002) and Paul *et al.* (2009), on the other hand, reported that up until 2002, approximately 4,500 tons of PFOS-related chemicals were produced worldwide annually, with a total historical production of 100,000 tons; moreover, new production sites are being commissioned in Asian countries (Herzke *et al.*, 2009). In addition, Pistocchi and Loos (2009), Prevedouros *et al.* (2006) and McLachlan *et al.* (2007) indicate that PFOA is mainly used as a polymerisation aid in the production of fluoropolymers (such as polytetrafluorethylene/PTFE), and therefore, it originates mainly from direct industrial emissions; PFOS, on the other hand, has widely dispersed emission sources. Emissions of PFOS in the environment may be “direct” (released during manufacture, application and use of perfluoroalkylsulfonates [PFAS]) or “indirect” (released as chemical impurities formed during manufacture of perfluorooctane sulfonyl fluoride [POSF]), or by breakdown in the environment from POSF derivatives, which are precursors of PFOS.

2.5.2 Application of perfluorinated chemicals

Owing to their unique physico-chemical properties and their combination of oleophobic and hydrophilic characteristics, PFCs have been widely used in many consumer products for over 50 years. Figure 2.6 shows some of the properties described above (Kissa 2001). Furthermore, their surfactant properties make them suitable for aqueous fire-fighting foams (AFFFs), while their lipid-and-water-repellent properties serve as stain repellents on carpets, textiles, leather, home furnishing, paper products, non-stick cookware and many kinds of cleaning products (Ahrens, 2009). Moreover, PFCs are applied in metal plating, photographic, lubricants, varnishes, gasoline and hydraulic fluids (Paul *et al*., 2009). Specific applications of PFOS include surface treatment, in the semiconductor, paper and pulp industries, while PFOA is used as an emulsifier and a surfactant in mining and oil well drilling (EFSA, 2008), as well as in insecticide formulations, (OECD, 2002); in floor polishes and food containers (Kissa, 2001). In 2000, the 3M Company reported that POSF-based products were used for coatings on packaging products (USA: 41%, EU: 33%), impregnation of textiles, leather and carpets (USA: 37%, EU: 49%), ingredients in the production of industrial surfactants, additives and coating mixtures (USA: 10%, EU: 15%), and AFFFs (USA: 3%, EU: 3%) (Schultz *et al.,* 2003).

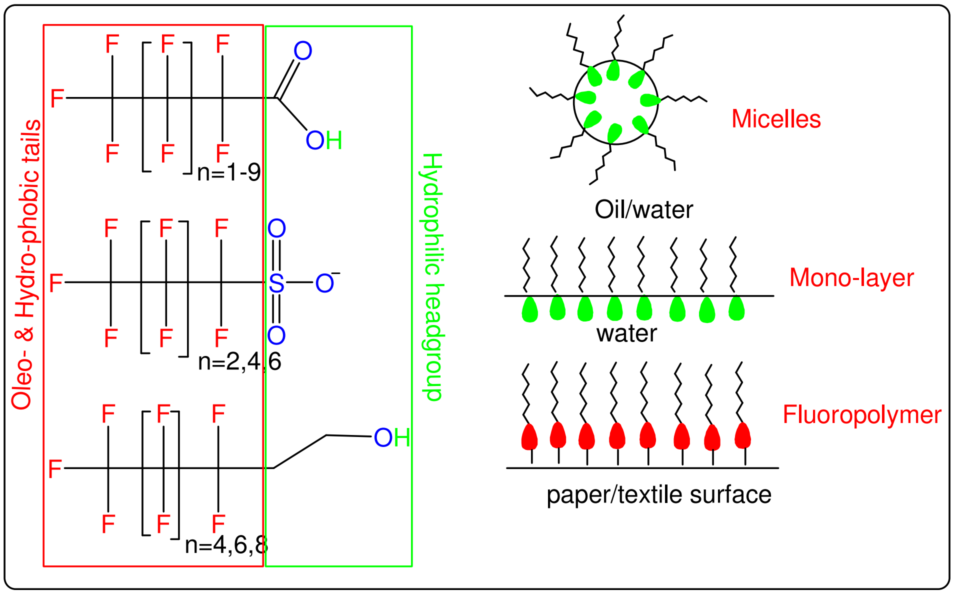


Figure 2.6: Perfluorinated chemicals physico-chemical properties (Ahrens, 2009)

These properties make PFCs desirable for use in commercial products, but their stability also causes some PFCs to be persistent and thus bioaccumulate in the environment (Kissa, 2001). Furthermore, fluorinated chains, combined with the low polarisability of fluorine, make fluorocarbons not only more highly hydrophobic than the corresponding hydrocarbons, but also lipophobic (Hoang and Mecozzi, 2004).

2.6 Bioaccumulation, persistence and toxicity of perfluorinated compounds

2.6.1 Bioaccumulation potential of PFOA and PFOS in wildlife

The determination of partition coefficient for a contaminant in water (K_{ow}) is a useful means of estimating the bioaccumulation potential of the contaminant. Nevertheless, the

OECD (2002) and the EPA (2002a) state that the partition coefficient for most of PFCs is unknown because PFCs are surfactants and a third layer is formed during measurement (Yong, 2007). To calculate the bioaccumulation potential of a compound in the environment, an estimation of its bioaccumulation factor (BAFs) should also be determined. Bioaccumulation factors (BAFs), or bioconcentration factors (BCFs), are calculated as a ratio of the average concentration in an organism in relation to the concentration in environmental matrices. BAFs represent the accumulation potentials of known organic compounds from a defined environment to organisms. Accordingly, in a study conducted by the OECD (2002), BAFs of PFOS were found to be high in Bluegill sunfish (*Lepomis macrochirus*) and in Carp (*Cyprinus Carpio*). In a similar study by the EPA (2002), the BAFs of PFOA were found to be about twice as much in Fathead minnow (*Pimephales promelas*), when compared to BAFs for PFOS. Furthermore, the first survey of PFOS in Japan showed high BAFs of PFOS in fish in the Tokyo Bay, in which PFOS concentration was as high as 3 to 558 ng/g w.w. (Taniyasu *et al.*, 2003). In addition, the EFSA (2008) reports that PFOA has been shown to bioaccumulate in fish but in most cases less than PFOS.

Generally, PFOA concentrations in fish and fishery products were determined to be lower than those of PFOS (EFSA, 2008). Furthermore, Martin *et al.* (2003) reported that the accumulation of PFOA was mainly in the liver and blood. The PFOA concentration detected in edible tissue samples of several fish, crustacean and other species from various European waters were: 1.1 to 3.2 ng/g wet weights (w.w.) (van Leeuwen *et al.*, 2006). Additionally, several studies conducted in Asia (China, Japan and Taiwan) determined elevated PFOA levels in different aquatic species of dietary interest. Gulkowska *et al*. (2006) and So *et al*. (2006a) detected PFOA in 61 samples of several species, including a large fraction of molluscs, (<0.204 to 1.67 ng/g w.w.). Higher concentrations, in the range of 6.0 to 22.9 ng/g w.w., were also determined by others (Nakata *et al.*, 2006; Tseng *et al.*, 2006). Different studies by Hoff *et al.* (2005) and Houde *et al.* (2006b) reported that the presence of PFCs in wildlife had stagnatal patterns. For an example, PFOA and PFOS have been reported in liver samples from cormorants, raccoon dogs, eagles and large-bill crows (Senthilkumar *et al.,* 2007). Other studies in which PFOA/PFOS were found in wildlife are shown in Table 2.3.

Table 2.3: Concentrations of PFOA and PFOS in wildlife (ng/g wet weight)

Species	PFOA [ng/g w.w.]	PFOS [ng/g w.w.]	Countries	References
Cormorants (M/F)	1.2 – 7.3	154	Japan	Senthilkumar *et al.* (2007).
Raccoon dog (M/F)	3.5 – 6.1	33		
Eagle (M/F)	1.1–3.0	61		
Large-bill crow (M/F)	>0.07–0.60	13		
Birds	n.d.	2570	USA	Brooke *et al.* (2004)
Polar bear	n.d.	1700-4000	Canada	Martin *et al.* (2004).
Arctic fox		6.1–1400		
Bald eagle	n.d.	1–2570	USA	Giesy and Kannan (2001)
Birds (liver)	n.d.	11–882	USA	Sinclair *et al.* (2006)
Birds (egg)	95–201	185–314	Korea	Yoo *et al.* (2008)
Albatross livers	<0.6–2.45	<5	Southern Ocean	Tao *et al.* (2006)
Elephant seals	n.d.	<0.08–3.52		
Polar skuas (egg)	n.d.	2.1–3.1		
Polar skuas (blood)	n.d.	<0.24–1.4		
Turtles	2.5–180	1–38	Alaska, Norway, and Antarctica	Kannan *et al.* (2001)
Fish	n.d.	0.07–1.02	Canada	Martin *et al.* (2004)
Wood mice	n.d.	180 000	Belgium	Hoff *et al.* (2004)
Crab	<9.5	<0.3	Japan	Nakata *et al.* (2006)
Filefish	<3.0	0.84	Japan	Nakata *et al.* (2006)
Dolphin	3.1	143	Italy	Kannan *et al.* (2002)
Dolphin	1.12–0.29	90.5–42.4	Brazil	Quinete *et al.* (2009)
Fish fillet	<0.417	985	USA	Oliaei *et al.* (2006)
Red panda	0.33–8.20	0.80–73.80	China	Dai *et al.* (2006)
Giant panda	0.32–1.56	0.76–19.00	China	Dai *et al.* (2006)

n.d.: not detected

2.6.2 Environmental persistence of PFOA and PFOS

Perfluorooctane sulfonate (PFOS) is extremely persistent. It does not hydrolyse, photolysis or biodegrade in various environmental conditions tested (OECD, 2002). According to the UNEP (2006), a study on the hydrolysis of PFOS in water was performed following US-EPA OPPTS protocol 835.2210. A study was conducted at pH varying from 1.5 to 11.0 and a temperature up to 50℃ to facilitate hydrolysis, but there were no indications of any degradation. The half-life of PFOS was also determined to be greater than 41 years (UNEP, 2006). A similar study on the photolysis of PFOS in water following US-EPA OPPTS protocol 835.5270 was conducted, with limited evidence of direct or indirect photolysis being observed under the evaluated conditions. The indirect photolytic half-life of PFOS at 25℃ was calculated to be more than 3.7 years. Biodegradation of PFOS was evaluated under a variety of conditions, including aerobic biodegradation using activated sewage sludge, for contaminated sediment and soil. This included anaerobic biodegradation studies using sewage sludge. However, none of these studies demonstrated any signs of PFOS biodegradation (UNEP, 2006). Similarly, PFOA can remain in the human body for long periods after exposure. A study by Olsen *et al.,* (2007) of retirees from a PFC manufacturing facility, showed the average half-life of PFOA in blood was determined to be 3.8 years.

2.6.3 Perfluorinated chemical detection in environmental matrices

2.6.3.1 Perfluorinated chemicals in river water

In a study conducted on the Elbe River (Germany) sampling from several sites along the river tested positive for 17 PFCs. PFOA was found to be the predominant contaminant with concentrations ranging from 2.8 to 9.6 ng/L, while the detection of PFOS varied between 0.5 to 2.9 ng/L (Ahrens *et al.,* 2009). In addition, a study carried out on the Cooum River (India) showed greater PFOS concentrations, 3.91 ng/L, in water samples, with PFOA being found in 55% of the water samples at a maximum concentration of 23.1 ng/L (Yeung *et al.*, 2009).

Similarly, in a study on the Yodo River (Japan) reported that most of the samples had PFOS concentrations in the range of 1 to 100 ng/L, while PFOA concentrations were within the range of 10 to 100 ng/L. It was found that PFOA was higher in most samples (Lien *et al.*, 2008). Additionally, Möller *et al.* (2009) reported that 27 PFCs were quantified in the Rhine River with the composition being dominated by base compounds, PFOS and PFOA. A Chinese study has examined the concentrations of 14 perfluorinated compounds (including PFOS and PFOA) in water samples taken from the Pearl and Yangtze Rivers (So *et al.*, 2007) for which PFOS levels were found to be 0.9 to 99 ng/L and less than 0.01 to 14 ng/L, respectively, while PFOA concentrations were 0.85 to 13 ng/L and 2.0 to 260 ng/L, respectively.

Moreover, Lin *et al.* (2010) conducted a study on both the Nanmen and Keya rivers (Taiwan). These are rivers which receive water from two municipal wastewater treatment plants (MWWTPs) in the region. Lin *et al.* therefore, sampled river water of the Keya River at locations upstream and downstream of the Nanmen-Keya confluence. It was found that the downstream locations contained a high level of PFOS (61.9 ± 61.2 ng/L) and PFOA (34.9 ± 4.1 ng/L) compared with locations upstream. In a recent study conducted in China by Yang *et al.* (2011) on the Liao River and Taihu Lake, PFOS was only detected in two samples (i.e. water samples) from the Liao River in low concentration but in high concentration in the Taihu Lake which indicated possible mobility. Additionally, concentrations of PFOA and PFOS were detected at greater levels in all river water samples that were collected by Senthilkumar *et al.* (2007) in a study on river water and sediment from Japan.

In a study on the Orge River (France) by Labadie and Chevreuil (2011) PFOS and PFOA were detected in water samples with concentrations ranging from 24.0 to 12.8 ng/L, respectively. Perfluorinated chemicals have been also detected in many other water bodies such as tap water (Harada *et al.,* 2003), rainwater (Loewen *et al.,* 2005), coastal water (So *et al.,* 2004) and seawater (Yamashita *et al.,* 2005). This indicated that river water is a major source of PFC mobility in aquatic systems.

2.6.3.2 Perfluorinated chemicals in river sediment

Previous studies have focused on the analysis of PFCs in biota and aqueous systems; little attention has been paid to their distribution in solid matrices –such as river sediments, mainly because of the occurrence of these chemicals is low and their analysis is difficult (Si, 2008). However, sediments are considered to be one of the major adsorbent for contaminants in the aquatic environment (de Boer *et al.*, 2001). Additionally, Yang *et al.* (2011) have indicated that sediment is an important component of a water system and plays an important role in the environmental transport and fate of persistent organic pollutants. Moreover, Covaci *et al.* (2005) show that well-laminated sediments can provide information on past environmental contamination and thus make it possible to assess the impact of environmental pollution on localised ecosystems. Furthermore, Si (2008) mentions that organic pollutants such as polychlorinated biphenyls (PCFs), organochlorine pesticides (OCPs) and PFCs are frequently found in the marine environment; as they have a particular affinity for suspended organic matter which settles easily.

Sediment has been suggested as a reservoir for non-ionic hydrophobic organic pollutants, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). However, Martin *et al.* (2003) have mentioned that most PFCs exhibit hydrophobic and hydrophilic properties. Consequently, their partition behaviour between water and sediment may differ from that of the non-ionic hydrophobic chemicals; an assertion corroborated by, Yang *et al.* (2011). However, other physico-chemical characteristics of either the carrier (river water) and/or absorbent (sediment) might have a significant effect on the partitioning (Ahrens *et al*., (2009). On the other hand, in a study conducted on the Diliao River system (China), Bao *et al.* (2009) indicated that PFOS concentration of 0.29 ng/g d.w. was determined in the first layer, i.e., was around 1.7-fold higher than the average at 10 cm depth, while PFOA concentration of 0.17 ng/g d.w. was about 1.2-fold higher in the first layer than at a depth of 10 cm.

Furthermore, Li *et al.* (2010) reported a PFOA concentration of 2000 ng/kg in sediments downstream the Nanmen River (Shanghai, China) and a PFOS concentration of 89 700 ± 10500 ng/kg, respectively, while a study on the Zhujiang River (Shanghai, China) found that PFOS was the dominant PFC contaminant detected at all sampling sites evaluated. Moreover, in other samples PFOA contributed 100% of all the target analytes; that is, levels of PFOS were determined as being below the limit of detection (LOD) while those of PFOA ranged between 0.09 and 0.29 ng/g d.w. with a median of 0.21 ng/g d.w. A similar study conducted by Senthilkumar *et al.* (2007) has reported a PFOA concentration of 2.3 ng/g d.w. in samples from the Katsura River (Japan). In a study conducted in Shanghai (China) to determine the quantitative characterisation of short and long-chain perfluorinated acids in solid matrices, the results indicated PFOA concentration in the sediment collected was always higher than PFOS and their concentrations were in a range of 2.4 to 118 ng/g d.w. (Li *et al.,* 2010).

2.7 Possible sources of PFOA and PFOS contamination

2.7.1 PFOA and PFOS in municipal wastewater discharge

Studies conducted on wastewater from WWTPs have indicated the presence of PFCs in the discharged effluent. Oliaei *et al.* (2006) mention that the Metropolitan Council of Environmental Services (MCES) main metro wastewater treatment plant (metro WWTP), located in St. Paul, Minnesota, is one of the largest wastewater treatment plants in the USA, and treats an average of 8 025 507m^3 of wastewater per day from approximately 62 communities and 800 industries. Consequently, a study on wastewater discharge from this plant indicated that, of the compounds detected in the influent samples, PFOS and PFOA were found at the highest concentrations; 53 and 46 ng/L respectively for both compounds, which is relatively low.

In another study by Schultz *et al.* (2006), effluents from 10 US WWTP were analysed in order to understand the behaviour of PFCs during wastewater treatment. It was found that PFCs in all the wastewater effluent exhibited a “fingerprint” of several PFCs, including PFOA/PFOS. In a study in Japan, PFOS and PFOA occurrence was detected in all wastewater samples collected with a much higher concentration of PFOS (48.1 to 560.9 ng/L) at one WWTP as compared to 5.3 to 29.8 ng/L at another, for the same compound. PFOA concentration was detected in the range of 31.8 to 1057.1 ng/L (Yu *et al*., 2009), indicating that there is a wide variation in PFC concentration in wastewater of different WWTP.

In general terms, the occurrence of PFCs has been reported in wastewater effluent in various cities around the world (Boulanger, *et al*., 2005; Schultz, *et al*., 2006a; Sinclair and Kannan, 2006), for example in European countries (Alzaga and Bayona, 2004); in Asia, that is, Japan (Nozoe, *et al*., 2006), as well as in the sludge samples from sewage treatment plants (Schröder, 2003; Higgins *et al*., 2005; Houde *et al*., 2006a). For instance, Oliaei *et al.* (2006) indicated that MCES WWTP discharges into the Mississippi River (USA) and, in a study conducted on the river, revealed that samples contained PFCs, of which PFOA/PFOS were found at the highest concentrations for both the effluent and the sludge samples, an indication that WWTPs might be one of the major sources of PFC contamination in river water, as most WWTPs discharge their wastewater into rivers. Some of the WWTP discharge is disinfected and passed through an activated carbon bed, however, there is ample evidence suggesting minimal removal of PFCs using current treatment technology. Studies done in other countries have documented high PFC concentrations directly downstream of the effluent discharge from industrial wastewater treatment facilities (Oliaei *et al.* 2006).

A study by Saito *et al.* (2004) on PFOA and PFOS concentrations in surface water in Japan found PFOA in samples collected at the mouth of the Ai River, the location of the Aigawa Ryuiki industrial wastewater disposal site, at a level of 67 000 ng/L (ppt). The 67 000 ng/L level in the mouth of the Ai River is consistent with the PFOA levels determined by 3M at times when monitoring their Cottage Grove wastewater treatment plant discharge. In 2001, 3M published the results of a “Multi-City Study” which analysed PFOS/PFOA in a variety of media, including effluent from publicly owned treatment works (POTW) and POTW sludge (3M Multi-City Study, n.d.). This study looked at POTWs in four cities known to have PFC manufacturing facilities (Decatur, Alabama) or industrial use or supply chain use of PFCs (Mobile, Alabama; Columbus, Georgia; and Pensacola, Florida) and two cities of similar geographic location that did not have an industrial source of PFCs contributing to a POTW (Cleveland, Tennessee and Port Lucie, Florida). Accordingly, the highest concentrations of the PFCs analysed were observed in samples from the POTW effluent and sludge in Decatur (Alabama). Decatur is one of the two 3M manufacturing facilities in the US that produces PFCs. POTW effluent from Decatur contained PFOS of up to 5 290 ng/L and PFOA of up to 2 420 ng/L (3M Company, 2001; Oliaei *et al*., 2006).

In another study by Berger *et al.* (2004), in which PFC contamination was quantified in sediment, sewage sludge, water and biota from participating Nordic countries, PFCs in wastewater effluents were found to be at levels in the range of 20 ng/L. The study found high variability in the concentration of PFAS in sewage sludge, with results ranging from 0.15 ng/L in a sample from a Finnish POTW to 3.8 ng/L in a sample from a Swedish POTW. This study found PFOS and PFOA to be the dominating PFCs in sewage sludge.

2.7.2 PFOA and PFOS from landfills: Contamination of ground-water

Landfills play an imperative role in controlling waste. However, they also cause environmental pollution owing to released leachate. Landfills have, historically, been the most common method of organised waste disposal and remain the preferred method of waste disposal in many regions of the world. Thus, they may contain waste resulting from several decades of disposal and decomposition with subsequent release of organic compounds that can have adverse environmental, wildlife and human health consequences (Eggen *et al*., 2010). PFCs have also been also reported in landfills. In a study conducted by Bossi *et al.* (2008), PFCs in percolate from landfill sites were below the detection limit. From this study it was concluded that landfill sites do not contribute to PFC pollution of the environment. However, Weinberg *et al.* (2011) determined that landfills have volatile and semi-volatile PFCs in all gas-phase samples collected. The PFCs detected include perfluorobutyric acid (PFBA, 59%), followed by perfluorohexanoic acid (-PFHxA-, 16%), PFOS (11%) and PFOA (9%). Additionally, the concentrations of PFOA and PFOS in the water phase from other landfills were in the respective ranges of 590 to 757 ng/L and 455 to 2920 ng/L, and showed a shift in the higher concentration of PFOS than PFOA (Eggen *et al*., 2010).

In addition, PFOA/PFOS have been reported in groundwater. Schultz *et al.* (2004) indicated concentrations of PFOS and PFOA (up to 2300 and 6570 μg/L, respectively) in groundwater collected from military bases where aqueous film-forming foams (AFFF) are used for fire-training activities. According to Cheng *et al.* (2008), the Minnesota Pollution Control Agency detected (2006) PFOS and PFOA in groundwater deriving from disposal sites in the Minneapolis (St. Paul) area. Furthermore, a study on leachate from Pine Bend landfill (USA) by the 3M Company (2001) detected concentrations of 52.7 ng/L and 47.5 ng/L for both PFOS and PFOA respectively. These concentrations were higher than in a similar study conducted by Berger *et al.* (2004) in the European Nordic environment, that is, 0.3 ng/L (PFOA) and 0.66 ng/L (PFOS). The 3M Company study demonstrated that PFCs have entered groundwater reservoirs, with PFOS and PFOA ranging from <0.0043 to 0.114 and $<$ 0.008 to 1.6 ng/mL respectively (3M, 2001).

2.7.3 Perfluorinated chemicals adsorption on different soils and sediments

Soils and sediments contain a variety of organic materials (e.g. organic acids), and have the ability to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together, and sorb and desorb both naturally occurring and anthropogenically introduced organic compounds (EPA, 2002). These characteristics have enabled researchers to determine what is called the total organic carbon (TOC) in environmental matrices such as water, soil and sediment. TOC is the measure of how much organic carbon if found in a given sample (e.g. water, sediment, soil, etc.) and is often used as an indicator of its presence in soil or sediment (EPA, 2002).

The focus of this study is not, however, to determine the TOC in water and sediment, but rather to try and understand whether there is a link between TOC and PFC adhesion (i.e. PFOA/PFOS) on sediment. Thus, in soils and sediments there are three forms of carbon that may be present: elemental carbon, inorganic carbon and organic carbon (naturally occurring). Furthermore, according to the EPA (2002b), organic matter in sediment is critical to the partitioning and bioavailability of sediment-associated contaminants. To explain this, Talley *et al.*, (2002) mentioned that, although a greater number of POPs are being found particularly on coal-derived particles, POPs on sediment fractions are more mobile and available.

Furthermore, naturally occurring organic carbons are derived from decomposed plants and animals. In soils and sediments, a wide variety of organic carbon forms are present and range from freshly deposited litter (e.g. leaves, twigs, branches) to highly decomposed forms such as humus (EPA, 2002b). In addition to the naturally occurring organic carbon is the carbon that derives as a result of contamination through anthropogenic activities; and the spills or releases of contaminants into the environment increase the TOC content of the soil or sediment.

A study by Higgins and Luthy (2006) suggests a correlation between the PFC content of the sediment and TOC. However, in a similar study by Becker *et al.* (2008), no correlation was reported. Nevertheless, Johnson *et al.* (2007) mention that it is likely that PFOA and PFOS adsorption is also partially controlled by electrostatics; this means that inorganic materials will effluence the fate of and transport to these PFCs in an aquatic system, as well as other factors, for example the pH values of water and sediment, and temperature (Becker *et al.*, 2008). Furthermore, Ahrens *et al.* (2009) investigated the behaviour of PFCs in solid matrices and revealed that partitioning varied, depending on conditions such as TOC, pH-value and metal ion presence. In addition, Bentivegna *et al.* (2004) indicated that sediments with a high percentage of small grains, such as silt and clay, have high surface-to-volume ratios and can adsorb more contaminants than sediments composed of large grains, such as sand.

Furthermore, Calvet (1989) indicated that PFCs with a low partition coefficient predominantly exist in the dissolved phase and can be rapidly dispersed and diluted in an aquatic system. On the other hand, Pan *et al.* (2009) mentions that PFCs with a high partition coefficient associated with particulate matter become less mobile and this behaviour leads to their bioaccumulation in sediment. Furthermore, Calvet (1989) reported that the more lipophilic a compound is, the higher the tendency for this compound to accumulate in biota; and PFCs have this characteristic. Moreover, Liber *et al.* (1996) and Bentivegna *et al.* (2004) reveal that organic carbon can directly adsorb contaminants from solutions applied to sediment, while Peltier *et al.* (2003) mentions that sources of organic carbon can also contain contaminants accumulated by plants that have been exposed to the contaminant during their lifetime.

2.7.4 PFOA and PFOS mobility from soils/sediment to plants

A study by Stahl *et al.* (2009), which was conducted to assess the adsorption and mobility of PFOS and PFOA from contaminated soil to plants, showed that PFOA was found to be more readily absorbed by various agricultural crops, that is, maize, oats and perennial ryegrass, than PFOS.

Furthermore, PFCs have been reported to be carried over from soil/sediment to plants. In a study on the soil-to-plant carryover of PFCs, the results show that concentrations of PFOA and PFOS in plants, that is, spring wheat, oats, potatoes, maize and rye grass, varied depending on the concentrations applied to the soil (Stahl *et al.*, 2009). In the same study, PFOA concentrations were found to be higher than PFOS concentrations. In addition, it was observed that the uptake and storage was much more intensive in the leaf portion of the plant than in the storage organs including tubers (Stahl *et al.*, 2009). Most importantly, the study revealed that the concentrations of both PFOA and PFOS increased directly in line with increasing concentration of the substances applied to the soil. In a similar study, this time investigated using carrots, potatoes and cucumbers, an increase in concentrations of PFOA and PFOS in soil resulted in their increase in the plants; for all of the three plants, the transfer rates of both compounds (i.e. PFOA/PFOS) was 10 times higher (Lechner and Knapp, 2011). The transfer from soil to plants provides a possible explanation for the presence of PFCs in foodstuffs, including agricultural produce, and in human serum, or breastmilk (Stahl *et al.*, 2009).

2.7.5 Perfluorinated chemicals as greenhouse gases

The EPA (2011a) recently mentioned that PFCs are extremely potent and persistent greenhouse gases that are the inadvertent by-products of production. According to the Intergovernmental Panel on Climate Change (IPCC) in the *Revised 1996 Guidelines*, greenhouse gases are both natural and anthropogenic substances that have been recognised by the international scientific community as having the potential to bring about climate change. Annexure A of the Kyoto Protocol of 1997 lists six greenhouse gases: carbon dioxide (CO_2), methane (CH4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorinated chemicals (PFCs) and sulphur hexafluoride (SF_6). In 2006, the IPCC listed more greenhouse gases in the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. These include the nitrogen trifluoride (NF_3), trifluoromethyl sulphur pentafluoride (SF_5CF_3), halogenated ethers and other halocarbons (IPCC, 2006).

2.8 Risks associated with PFOA and PFOS: Contamination effects

2.8.1 Exposure to perfluorinated chemicals

From the literature reviewed, the major sources of PFC exposure in humans are not very well understood. Dietary intake is thought to be a major source of PFCs in humans; for instance, Moore (2010) states that the exposure pathways for PFOA outside manufacturing facilities are not completely understood. Some scientists speculate that PFOA and related chemicals can be ingested, inhaled or possibly adsorbed through dermal contact. However, Prevedouros *et al.* (2006) report that exposure can result from eating animals exposed to

PFCs through water, soil and dust that is contaminated by PFCs, as well as the degradation of consumer products containing PFCs. In addition, it is estimated that 2 to 12 tons of PFCs per year are transported to the Arctic through oceanic and atmospheric currents, which contributes to human and animal exposure.

Furthermore, as PFCs bioaccumulate in the bodies of animals, humans are, thus, exposed to PFCs through the consumption of animal products. A recent study in Spain found PFCs in a wide variety of food sources, with fish and dairy products representing the most significant source of exposure (Tittlemier *et al.*, 2007). On the other hand, Ericson *et al.* (2008) reported in another study from Canada that beef was found to be the most significant dietary source of PFOS.

2.8.2 Perfluorinated chemicals in humans

As a result of their widespread use and persistence of PFCs, nearly everyone in the general population now has detectable levels of PFCs in their blood (Kubwabo *et al.*, 2004; Calafat *et al.*, 2007). According to Hansen *et al.* (2001), PFCs are often detected in human blood, serum and plasma, as well as in tissues (Maestri *et al.*, 2006). Yong (2007) mentions that PFCs in human serum seemed directly correlated with contaminations in surface water or drinking water, which were strongly suspected to be caused by local industrial emissions. For instance, people in the USA (Olsen *et al.*, 2003; Calafat *et al.*, 2006) and Korea were estimated to have the highest concentration of PFOS in their blood (>30 ng/mL), while people of India had the lowest concentration, that is, 3 ng/mL (Kannan *et al.,* 2004). In addition, contamination of PFOA was identified in the human serum of residents in Osaka and Kyoto (Japan), and very high concentrations of PFOS were detected in the blood of people living in coastal cities in China (Harada *et al.*, 2004).

2.8.3 Perfluorinated chemical related health effects

In common with other chemicals that have the potential to cause health effects just because they are bioaccumulative, persistent and toxic, PFOA and PFOS have the potential to cause health problems.

2.8.3.1 Perfluorinated chemicals are carcinogenic

A mortality study on workers at a perfluorooctanesulphonyl fluoride-based flurochemical production facility in Decatur (Alabama, USA) by Alexander *et al.* (2003) revealed workers in the facility had increased rates of bladder cancer, although the findings were limited by the small sampling size. The highly exposed workers had serum PFOS concentrations between 1 and 2 µg/mL. The potential carcinogenicity of PFOS was examined in a two-year dietary bioassay in rats, where a significant increase in the incidence of hepatocellular (liver) adenomas in both males and females at the highest PFOS dose occurred. This study also found that female rats had a significant increase in combined hepatocellular adenomas and carcinomas. In addition, the study found that there was a significant increase in follicular cell adenomas and combined thyroid follicular cell adenomas and carcinomas in the male rats at high PFOS doses (OECD, 2002).

A risk of prostate cancer was associated with the period of employment (length of exposure) for employees exposed to PFOA, although PFC concentrations were not measured in this study (Gilliland and Mandel, 1993). However, on the basis of few human studies and the indecisive relevance of the tumours from the rat studies, the EPA in its January 2005 report summary stated that PFOA may be best described as “suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential” (EPA, 2005). Nevertheless, in February 2006, the EPA Science Advisory Board advised the EPA that PFOA is a “likely carcinogen” based on its assessment of available studies (Oliaei *et al.*, 2006).

2.8.3.2 Perfluorinated chemicals can cause infertility

It has also been found that women with higher serum levels of PFOA and PFOS have an increased risk of infertility. Women who required a period of greater than 12 months to achieve pregnancy had median PFOS concentrations of 38.3 ± 13.0 ng/mL, while women who achieved pregnancy in less than one month had median concentrations of 35.5 ± 12.8 ng/mL (Fei *et al.,* 2009). A similar trend was seen for PFOA concentrations of 6.3 ± 2.7 ng/mL and 5.6 ± 2.6 ng/mL, respectively (Fei *et al.*, 2009). Women in the higher PFC category were also more likely to have irregular menstrual cycles. In men, it was determined that high levels of PFCs contribute to poor semen quality. Young men with high combined levels of PFOS and PFOA were found to have less than half the number of normal sperm than men with low levels of PFOA and PFOS (Joensen *et al.,* 2009).

2.8.3.3 Perfluorinated chemicals have a depressive effect on the immune system

Rats that were exposed to PFOA were found to have reduced production of lymphocytes (immune system cells) by both the spleen and the thymus (Yang *et al.*, 2001) and the suppression of the humoral immune response (immunity that is mediated by antibodies secreted by B cells) in both *in vivo* and *ex vivo* systems (Yang *et al.,* 2002).

Moreover, PFOA exposure was also determined to enhance the immune response to environmental allergens, which increases the severity of allergies (Fairley *et al.*, 2007).

2.9 Summary

A variety of species, including humans, depend on water for survival. However, around the world, this indispensable resource is under threat. It is expected that by 2020 water demand by humans for drinking and food production will increase by 40% and 17%, respectively. With industrial activities, different organic chemicals are generated and released in water streams such as river, lakes and municipal drainage systems, and this has exacerbated water shortages, as complex treatment methods are required for the removal of POPs.

These POPs include the "*dirty dozen*" used in the agricultural sector as pesticides and insecticides, some of which have been generated by industrial activities. Consequently, these compounds end up in the environment, thus contaminating vital resources. Today, POPs have been detected in various environmental matrices, including water, aquatic sediment, soils, and agricultural produce, as well as in humans, which is evidence of POP distribution along the food chain.

One of the new emerging POPs are PFCs. Owing to their unique properties and a combination of oleophobic and hydrophilic characteristics, PFCs have been used in many consumer products for over 50 years. According to the literature reviewed, the most investigated PFCs are PFOA and PFOS (the sole focus of this research). Just like the "*dirty dozen*", PFCs (PFOA and PFOS) have the potential to bioaccumulate in environmental matrices, making them persistent. Consequently, they have been detected in human serum, drinking water, river water and sediment, soils and plants, fish livers, and wildlife. PFCs are reportedly carcinogenic and infertility pathogenic and have a depressive effect on the immune system. However, limited research has focused on PFOA and PFOS contamination in the southern hemisphere, particularly in South Africa, where river water is used for various anthropogenic activities, and which include consumption.

CHAPTER THREE

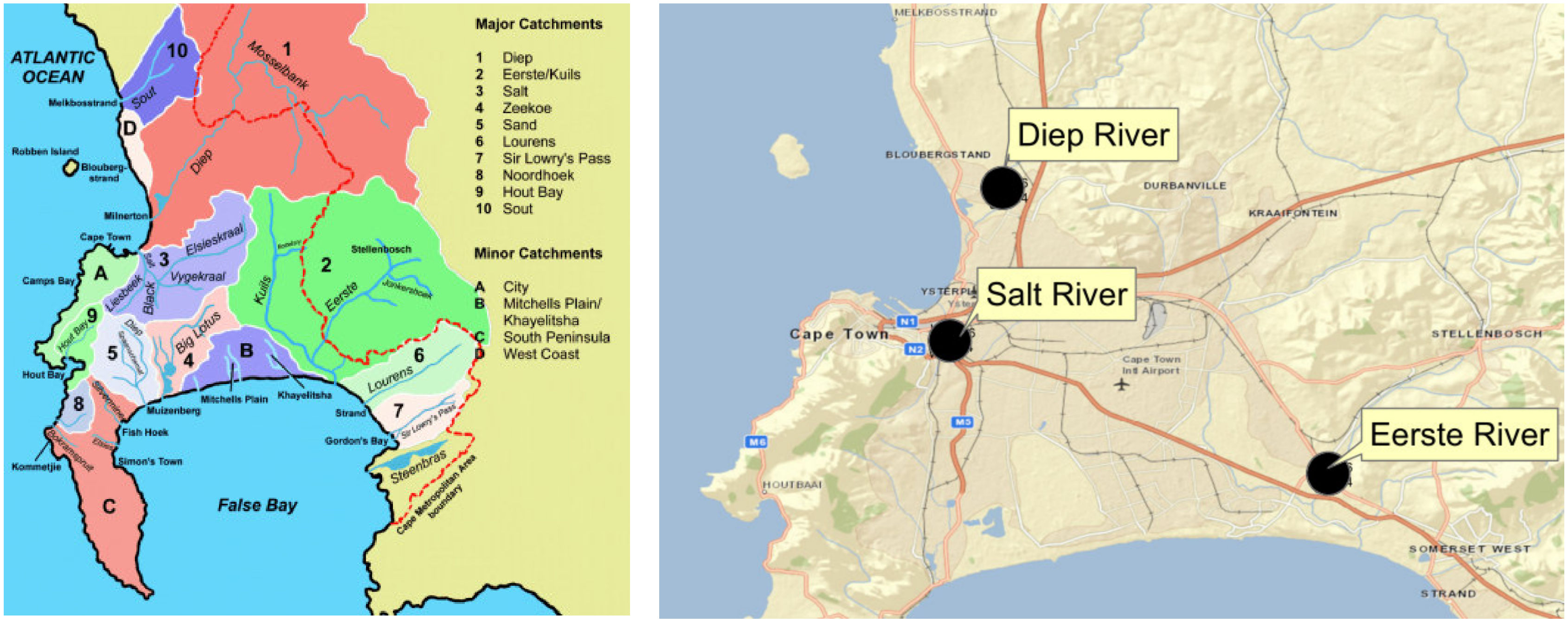
STUDY AREA

CHAPTER THREE

STUDY AREA

3.1 Overview: rivers selected for observation

The three rivers, that is, the Diep, Eerste and Salt rivers, were selected for the following reasons: 1) they are part of the three biggest catchments areas in the Western Cape and have a large surface water network (Ogutu, 2007); 2) they have a similar mean annual runoff range of 1305 to 2085 $e10^6$ m^3 (Midgley *et al.*, 1990), while each of the rivers have several tributaries (as illustrated in Figs 3.2, 3.3, 3.4); and 3) they have similar soil/sediment characteristics, that is, a sandy texture which facilitates the subsurface accumulation of organic matter, and thus contaminant accumulation.



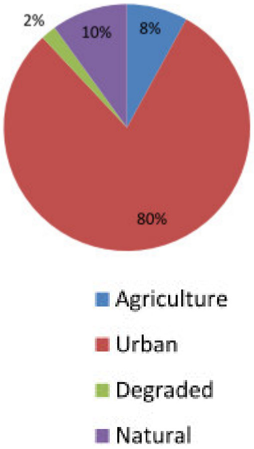
A **B**

Figure 3.1: A) Size classification of the catchment areas in the Western Cape, South Africa (Ogutu, 2007) B) Overview of sampling sites

3.1.1 Salt River

The Salt River is one of two major rivers in the central management area of the City of Cape Town, and it consists of the Elsieskraal, Black and Liesbeek tributaries, which drain the Tygerberg Hills, the north-western portion of the Cape Flats and the east-facing slopes of Table Mountain, respectively. Many of these tributaries have been canalised (DWAF, 2005). The Black tributary rises in the present-day Arderne Gardens and flows along Water Street in Lynfrae, Rondebosch and Keurboon Park. The river is periodically polluted by effluent from the industrial and residential areas in and around Cape Town. Pollutants have included hexane and associated compounds, oils and paraffin from industrial sources and the algaecides and herbicides used in vegetation control along the river. Most of the organic matter that enters the Salt River come from the Black River, which carries water darkly stained by organic material leaching from the fynbos vegetation through which it flows, including particulate material that is growing in the rich effluent emanating from the Athlone WWTP (DWAF, 2005; Brown and Magoba, 2009). Figure 3.1 depicts the Salt River and its tributaries.

[a]% Land-use classification in the catchment



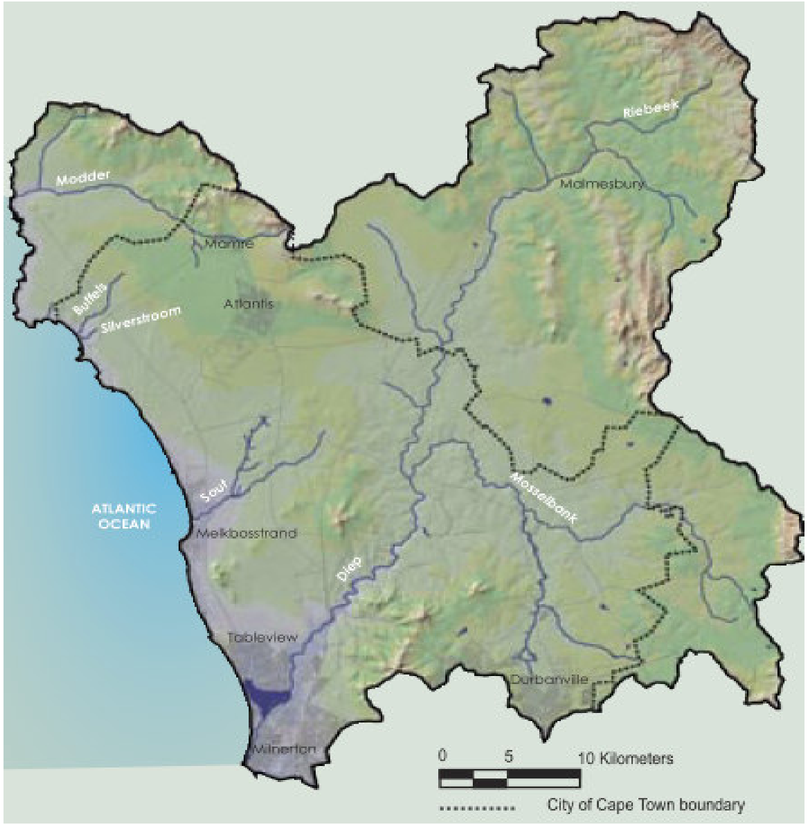
[b]Mean annual runoff
1305 to 2085 (10^6 m^3)

[c]Soil/sediment classification
Structured
Sandy texture
Subsurface accumulation of organic matter

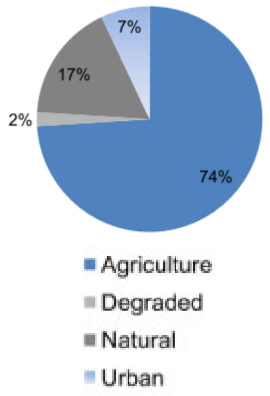
Figure 3.2: Salt River catchment with its tributaries and land-cover usage [a](DWAF, 2005;[b]Midley *et al.,* 1990; [c]Breedlove and Fraser, 2000).

3.1.2 Diep river

The Diep River is located in the South Western Cape region, north of Cape Town. The river rises from the Riebeek-Kasteel Mountains, north-east of Malmesbury, before discharging into Table Bay (i.e. Atlantic Ocean) north of Cape Town. The river is approximately 65 km long with a catchment area of 1495 km^2. Agriculture, mainly temporary commercial dry land agriculture, permanent commercial irrigated agriculture and commercial forestry, accounts for about 74% of the catchment land-cover area of the river. About 2% of the catchment area is comprised of degraded shrub land and bush land, while 17% is natural, consisting of shrub land, bush land, grassland, and water bodies and wetlands (Rietvlei) (DWAF, 2001). Various tributaries join the Diep River on its way to the sea (Figure 3.3). They include the Klein River, the Riebeek River, the Groen River, the Swart River, the Platklip River, the Sout River and the Mosselbank River (Brown and Magoba, 2009). Additionally, the catchment is made up of Malmesbury group (shale), Cape granite, Klipheuwel group (conglomerates) and sandy sediments. According to the DWAF (2003), about 95% of population in the area has waterborne sewage systems with the remainder being served by septic tanks and soak-away areas.



[a]% Land-use classification in the catchment



[b]Mean Annual Runoff
1305 to 2085 (10^6 m^3)

[c]Soil/Sediment Classification
Structured
Sandy texture
Subsurface accumulation of organic matter

Figure 3.3: Diep river catchment with its tributaries and land-cover usage [a.](DWAF, 2005);[b.]Midley *et al.*, (1990); [c.]Breedlove and Fraser (2000).

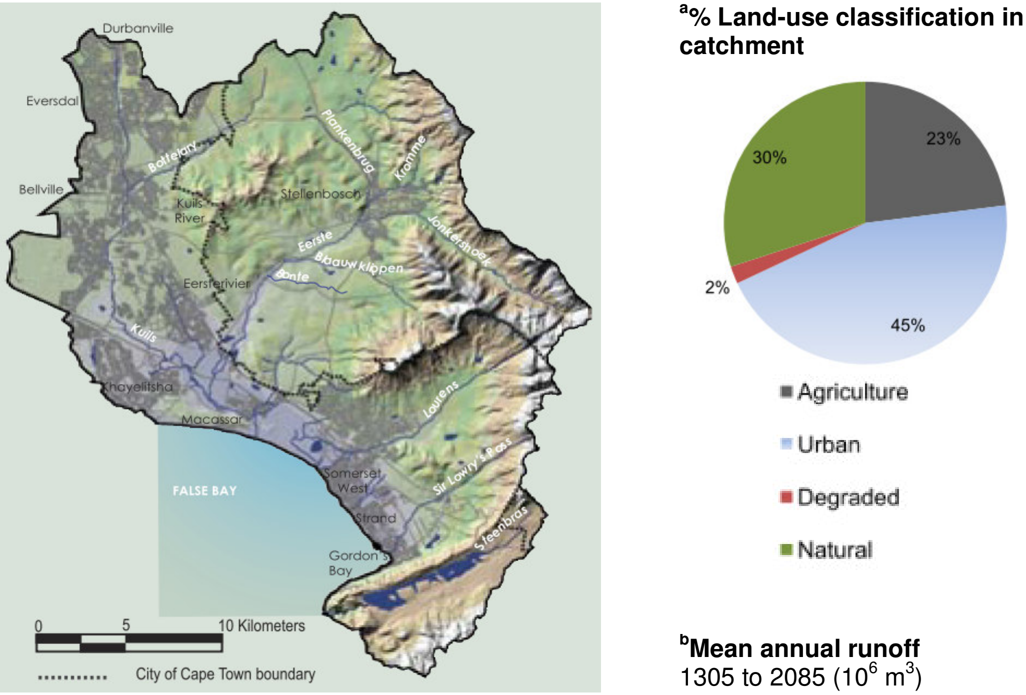
Wastewater from three WWTPs is discharged into the Diep River at Milnerton, Kraaifontein and Malmesbury. In addition, the Vissershok landfill site, which receives hazardous waste, has a soak-away area near the river. There are also a number of general waste sites in the catchment area. Furthermore, agricultural runoff from the dairy industry has also been identified as a cause of nutrient enrichment and a reduction in water quality in the Diep River (DWAF, 2003). The Diep River flows through the Riebeek-Kasteel Mountains, where development is unlikely and runoff is high, and consequently greater impacts can be expected in the lower catchment area owing to increasing human activity (DWAF, 2001). The catchment area comprises the Swartland and Sandveld regions in the western lowland area of the Western Cape. The Swartland is named after the *renosterbos* (vegetation which is seasonally black in colour) that was abundant in the area, while the Sandveld is named after its sandy soils. The flat topography of the catchment area makes it attractive for agricultural and urban development (DWAF, 2003). In addition, treated wastewater from urban areas and agricultural runoff (e.g. dairy industry) causes nutrient enrichment and reduces the water quality in the Diep River.

3.1.3 Eerste river

The Eerste River is generally a rocky narrow river whose headwaters rise in the Jonkershoek Mountains and the Forest Reserve (see Fig. 3.4) (Somers and Nel, 2003; Ngwenya, 2006).

From its sources, the river flows in a north-westerly direction towards Stellenbosch and through the Cape Flats to where it discharges into False Bay at Macassar Beach (DWAF, 1993). The Eerste River is approximately 40 km long with a catchment of 420 km^2 (DWAF, 1993). In addition, the river comprises a mountain stream zone (Jonkershoek), 7 km long from its headwaters; the upper zone, which starts 5 km from the lower end of the Jonkershoek valley to its confluence with the Plankenburg River in Stellenbosch; and the lower zone which stretches from Stellenbosch to the estuary at False Bay (DWAF, 1993; Ngwenya, 2006). In its lower zone, the Eerste River is joined by the Veldwagters, Blouklip, and Kuils rivers. Figure 3.4 provides a map of the Eester River.

Petersen (2005) states that the Eerste River is a typical urban river that has been physically and biologically modified as a result of urban activity. Two WWTPs, namely the Maccassar and Stellenbosch wastewater treatment plants, are discharged into the Eerste River (Brown and Magoba, 2009), which contributes to the pollution of the river. In addition, along its course, the river traverses an array of used land which is indicated as having had a progressively negative impact on the quality of its water (DWAF, 1993; Hendricks, 2003; Joseph, 2003). Furthermore, it has been reported by the DWAF (2004) that the water quality deteriorates downstream, starting at the Eerste River's confluence with the Plankenburg River. It is at this downstream point that the river receives treated municipal effluent (8.4 million m^3/annum) from the Stellenbosch WWTP (DWAF, 1993; 2004).



[b]Mean annual runoff
1305 to 2085 (10^6 m^3)

[c]Soil/sediment classification
Structured
Sandy texture
Subsurface accumulation of organic matter

Figure 3.4: Eerste River catchment with its tributaries and land-cover usage [a.](DWAF, 2005;[b.]Midley *et al.,* 1990; [c.]Breedlove and Fraser, 2000).

3.2 POP studies in the Eerste, Diep and Salt rivers

There have been very few POP studies specifically conducted in the identified rivers. Although, several studies have focused on metal and pesticide contamination (Ayeni *et al*., 2010; Jackson, 2008; Odendaal *et al*., 2011; Maharaj, 2005; Feng, 2005) (i.e. soil and water) in the Western Cape province, limited information has been forthcoming about emerging persistent organic pollutants such as PFOS and PFOS.

CHAPTER FOUR

MATERIALS AND METHODS

CHAPTER FOUR

MATERIALS AND METHODS

4.1. Introduction

Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been detected in river water (Lein *et al.*, 2008; Ahrens *et al.*, 2009; Yeung *et al.*, 2009; Möller *et al.*, 2009; Lin *et al.*, 2010; Labadie and Chevreuil, 2011), in river sediment (De Boer *et al.*, 2001; Yang *et al.*, 2011; Covaci *et al.*, 2005 ; Bao *et al.*, 2009 ; Li *et al*, 2010), in fish liver (EFSA, 2008 ; Martin *et al.*, 2003 ; Van Leeuwen *et al.*, 2006 ; Nakata *et al.*, 2006), in wildlife (Hoff *et al.*, 2005 ; Houde *et al.*, 2006b ; Senthilkumar *et al.*, 2007), and in soils and plants (Stahl *et al.*, 2009; Lechner and Knapp, 2011). The analysis of PFCs (PFOA/PFOS) is difficult because of insufficient chemical standards and inadequate sample preparation methods, but also because most of the published sample preparation methods do not provide clear cleanup procedures (Si, 2008). Moreover, low efficiency is experienced when extracting PFCs from solids (Yong, 2007).

In this study, the method used to analyse PFOA/PFOS was based on the current ISO 25101 (2009) methodology using solid phase extraction (SPE), followed by liquid chromatography combined with electrospray tandem mass spectrometry (LC-MS/MS). These techniques, which have been used before by Hansen *et al.* (2001), Higgins *et al.* (2005), Powley *et al.* (2005), Schultz *et al.* (2006), Yong (2007), Si (2008), were applied in this study to investigate PFOA/PFOS prevalence in the Eerste, Salt and Diep rivers, which pass through three major catchments areas and have a large surface water network in the Western Cape province of South Africa. For analysis quality, PFC-free water was transported to sampling sites and processed with environmental samples.

4.2. Water; sediment and riparian wetland plant sampling

Perfluorinated chemicals have been detected, reported and documented worldwide using environmental matrices. In South Africa, this has not been the case. Accordingly, river water, sediment, plant and suspended solid samples were considered in this study as matrices potentially subjected to PFC contamination in South African rivers.

4.2.1 Sampling sites: maps and co-ordinates

Water, sediment and plant samples were collected along the riparian areas of the three rivers. To maintain consistency during sampling, a global positioning system (GPS) was used throughout the sampling process to note the coordinates of places where the samples were taken. Additionally, water, sediment and plant samples were collected in polypropylene (PP) bottles and were stored at –20℃ prior to analysis. Sediment samples were collected using a stainless Multi-Stage Sludge and Sediment Sampler (AMS, USA), to a depth of 40 cm, and transferred into PP sampling vials and air dried and stored at room temperature until used. This method has been used before by Naile *et al.* (2010) and Bao *et al.* (2010). Figure 4.1 depicts the AMS Multi-Stage Sludge and Sediment Sampling Kit. To avoid or, alternatively, minimise any possibility of sample contamination, the containers used for the storage of the both the water and the sediments samples were thoroughly rinsed with analytical grade methanol and deionised water prior to use. It should be noted that Teflon bottles and Teflon-lined caps, including glass bottles, were avoided throughout the experiment to avoid sample contamination, as is suggested by Harada *et al.* (2003).

Figure 4.1: AMS Multi-Stage Sludge and Sediment Sampler

Table 4.1: Sampling points, sampling point coordinates and dates

Site	Sample ID	Coordinates		Dates (2011)
		Latitude	*Longitude*	
EERSTE RIVER	W.1	S34°01’50.8”	E18°44’51.4”	10/3
	W.2	S34°01’50.9”	E18°44’51.8”	
	W.3	S34°01’50.6”	E18°44’51.7”	
	W.4	S34°01’49.2”	E18°44’52.0”	
	W.5	S34°01’48.8”	E18°44’52.3”	
	W.6	S34°01'50.9"	E18°44'51.9"	10/10
	W.7	S34°01'51.1"	E18°44'52.1"	
	W.8	S34°01'50.5	E18°44'51.5"	
	W.9	S34°01'49.9"	E18°44'51.8"	
	W.10	S34°01'49.7"	E18°44'51.8"	
	W.11	S34°01'50.9"	E18°44'51.9"	19/11
	W.12	S34°01'51.1"	E18°44'52.1"	
	W.13	S34°01'50.5"	E18°44'51.5"	
	W.14	S34°01'49.9"	E18°44'51.8"	
	W.15	S34°01'49.7"	E18°44'51.8"	
	W.16	S34°01'49.4"	E18°44'51.6"	
	S.1	S34°01'50.9"	E18°44'51.9"	10/10
	S.2	S34°01'51.1"	E18°44'52.1"	
	S.3	S34°01'50.5"	E18°44'51.5"	
	S.4	S34°01'49.9"	E18°44'51.8"	
	S.5	S34°01'50.9"	E18°44'51.9"	19/11
	S.6	S34°01'51.1"	E18°44'52.1"	
DIEP RIVER	W.1	S33°49'49.7	E18°31'13.8"	21/4
	W.2	S33°49'49.7"	E18°31'14.0"	
	W.3	S33°49'50.0"	E18°31'14.0"	
	W.4	S33°49'54.5"	E18°31'15.8"	
	W.5	S33°49'54.2"	E18°31'15.2"	
	W.6	S33°49'48.3"	E18°31'13.0"	28/6
	W.7	S33°49'50.1"	E18°31'13.7"	
	W.8	S33°49'47.4"	E18°31'13.2"	10/10
	W.9	S33°49'51.9"	E18°31'14.4"	
	W.10	S33°49'52.6"	E18°31'14.7"	
	W.11	S33°49'53.3"	E18°31'14.9"	
	W.12	S33°49'54.0"	E18°31'14.9"	
	W.13	S33°49'54.9"	E18°31'15.0"	
	W.14	S33°49'55.4"	E18°31'14.7"	
	W.15	S33°49'47.4"	E18°31'13.2"	19/11
	W.16	S33°49'51.9"	E18°31'14.4"	
	W.17	S33°49'51.9"	E18°31'14.6"	
	W.18	S33°49'53.7"	E18°31'14.9"	
	W.19	S33°49'55.0"	E18°31'16.3"	
	W.20	S33°49'56.5"	E18°31'16.9"	
	S.1	S33°49'47.4"	E18°31'13.2"	10/10
	S.2	S33°49'51.9"	E18°31'14.4"	
	S.3	S33°49'52.6"	E18°31'14.7"	
	S.4	S33°49'53.3"	E18°31'14.9"	
	S.5	S33°49'47.4"	E18°31'13.2"	19/11
	S.6	S33°49'51.9"	E18°31'14.4"	
SALT RIVER	W.1	S33°55'32.9"	E18°29'10.8"	19/3
	W.2	S33°56'08.7"	E18°28'54.3"	
	W.3	S33°56'08.7"	E18°28'54"	
	W.4	S33°56'08.7"	E18°28'53.8"	
	W.5	S33°56'08.7"	E18°28'54.4"	
	W.6	S33°56'14.4"	E18°28'89.2"	16/9
	W.7	S33°56'14.1"	E18°28'88.9"	
	W.8	S33°56'01.2"	E18°28'48.4"	11/10
	W.9	S33°55'59.9"	E18°28'48.3"	
	W.10	S33°55'57.8"	E18°28'47.2"	
	W.11	S33°55'56.4"	E18°28'47.1"	
	W.12	S33°55'56.1"	E18°28'47.2"	
	W.13	S33°55'54.9"	E18°28'46.0"	
	W.14	S33°55'54.4"	E18°28'46.6"	
	W.15	S33°56'01.2"	E18°28'48.4"	19/11
	W.16	S33°56'59.9"	E18°28'48.3"	
	W.17	S33°55'57.8"	E18°28'47.2"	
	W.18	S33°55'56.4"	E18°28'47.1"	
	W.19	S33°55'54.9"	E18°28'46.0"	
	W.20	S33°49'56.5"	E18°31'16.9"	
	S.1	S33°56'14.4"	E18°28'89.2"	16/9
	S.2	S33°56'14.1"	E18°28'88.9"	
	S.3	S33°56'08.4"	E18°28'53.2"	
	S.4	S33°56'04.6"	E18°28'49.7"	
	S.5	S33°56'01.2"	E18°28'48.4"	19/11
	S.6	S33°56'59.9"	E18°28'48.3	

W: water; S: sediment

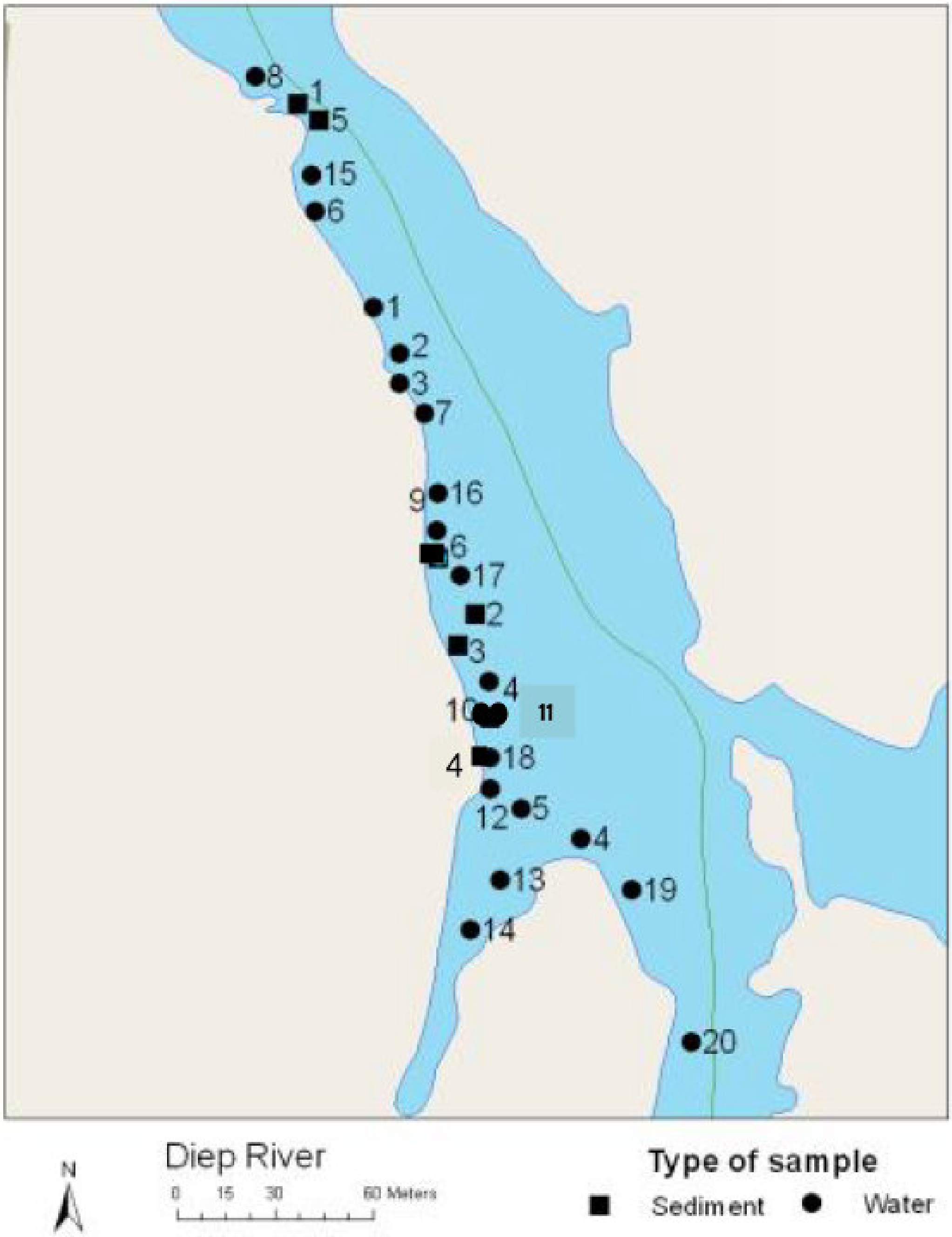


Figure 4.2A: Diep River: geographical representation of sampling coordinates with respect to individual rivers and/or riparian areas where river water and sediment were sampled

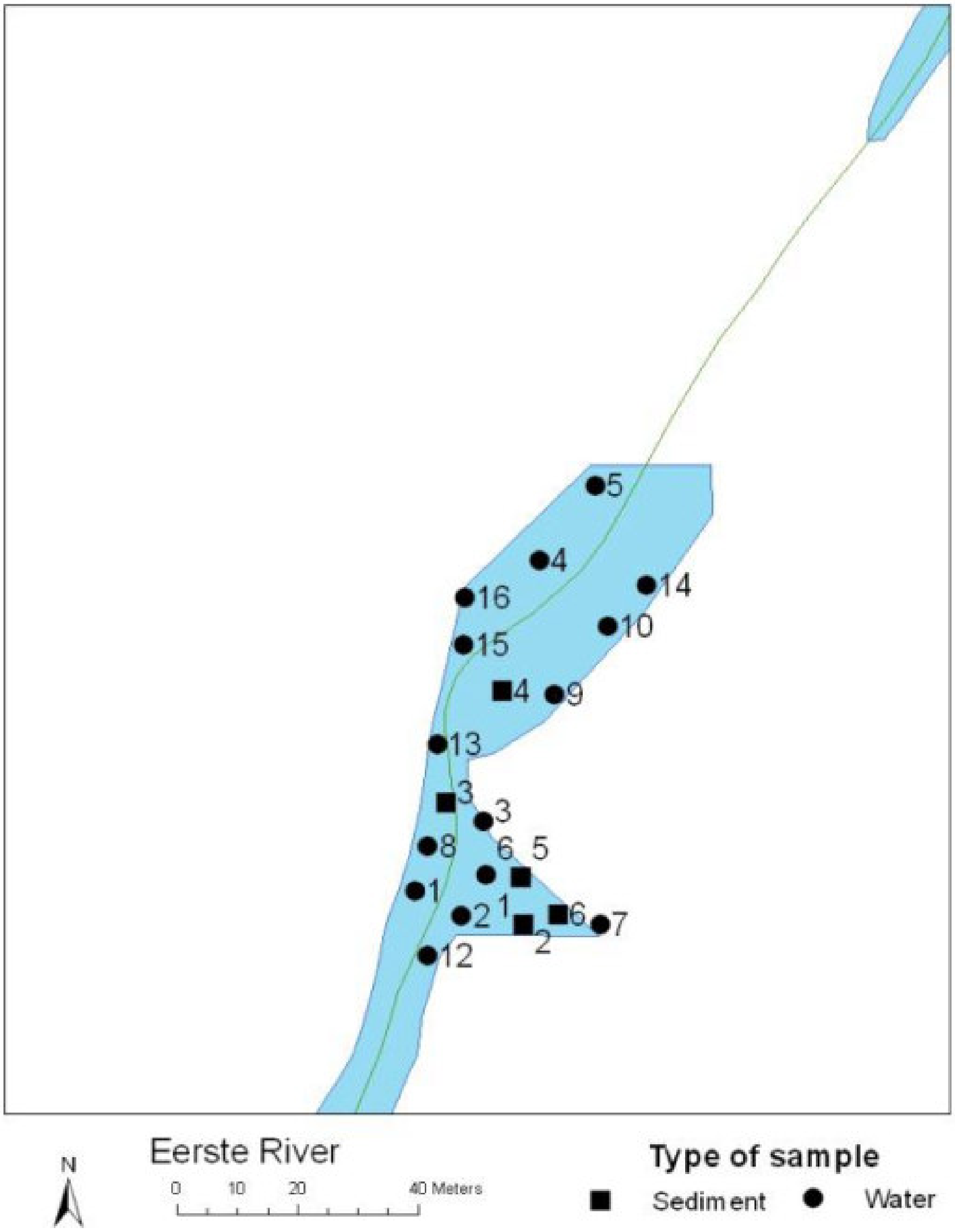


Figure 4.2B: Eerste River: geographical representation of sampling coordinates with respect to individual rivers and/or riparian areas where river water and sediment were sampled

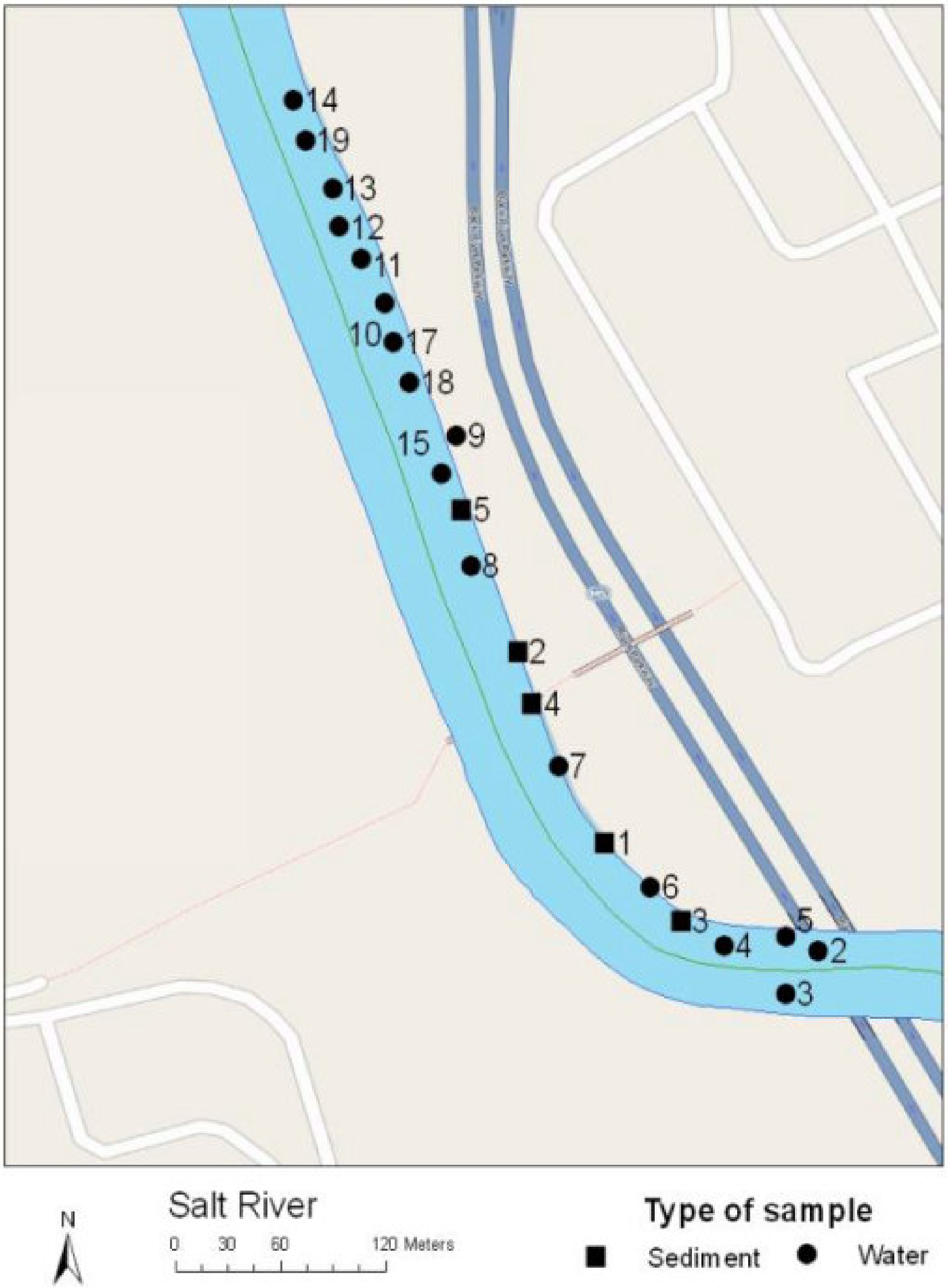


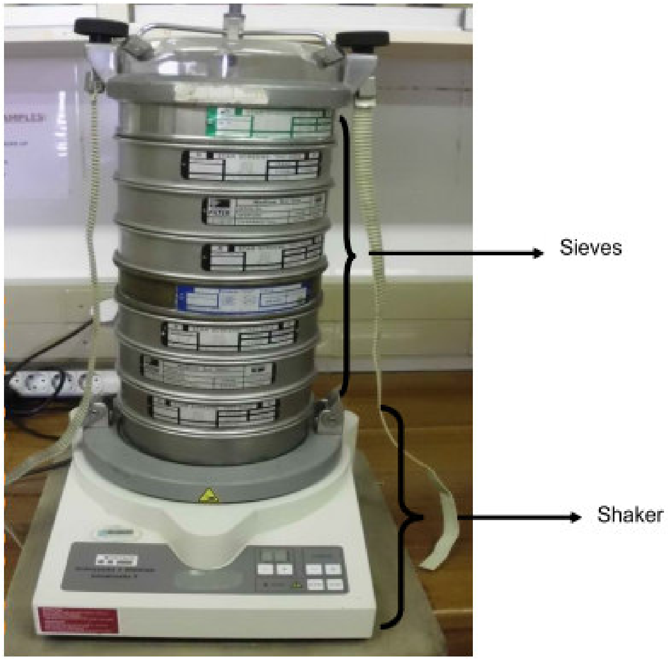
Figure 4.2C: Salt River: geographical representation of sampling coordinates with respect to individual rivers and/or riparian areas where river water and sediment were sampled

4.2.2 Quantification of physicochemical characteristics of the sediment core water

The characteristics of the sediment core water were quantified using an YSI multi-function probe (YSI, USA) to quantify the following parameters: pH; conductivity, dissolved oxygen, nitrates and ammonium-N. Furthermore, the concentration of phosphates in the water was quantified using Merck cell test kits (Darmstadt, Germany) and a Spectroquant NOVA 60. The Merck phosphate test cell kit (0.05 to 9 mg/L PO_4-P), which determines orthophosphates and total phosphorus was used, and involved the digestion of orthophosphate ions in sulphuric acid, which react with molybdate ions to form molybdophosphoric acid, which was reduced to phosphomolybdenum by ascorbic acid. This allowed photometric determination of phosphates using a Spectroquant.

4.2.3 Sediment characterisation and Total organic carbon determination

Sediment characterisation was done using the American Society for Testing and Materials methods (ASTM, 1992) coupled with the Unified Soil Classification System (USCS) chart. Thus, sediment grain sizes were determined by oven drying the sediments for 24 hours, milling, and then sieving them using different-sized meshes and a shaker to classify whether the sediment was gravel, sand, silt or clay (ASTM method DIN-4188), as previously done by Bentivegna *et al.* (2004). The different-sized sieves used were 2000 µm, 1180 µm, 500 µm, 425 µm, 300 µm, 250 µm, 212 µm, 150 µm, and 106 µm, as depicted on Figure 4.2. Some sediment from each sampling point was used for the determination of total organic carbon (TOC).



*Sieve size (µm)	Sieve number	Grain size (mm)
4750	4	4.5
2000	10	2.0
1180	16	1.12
500	35	0.500
425	40	0.400
300	50	0.280
250	60	0.250
212	70	0.200
150	100	0.140
106	140	0.100

Figure 4.3A: Different-sized sieving screens and shaker used.

US standard sieve sizes

To classify the sediment types of the three rivers, the USCS (Figure 4.3a, b) was used with US standard sieve sizes, as shown in Figure 4.2.

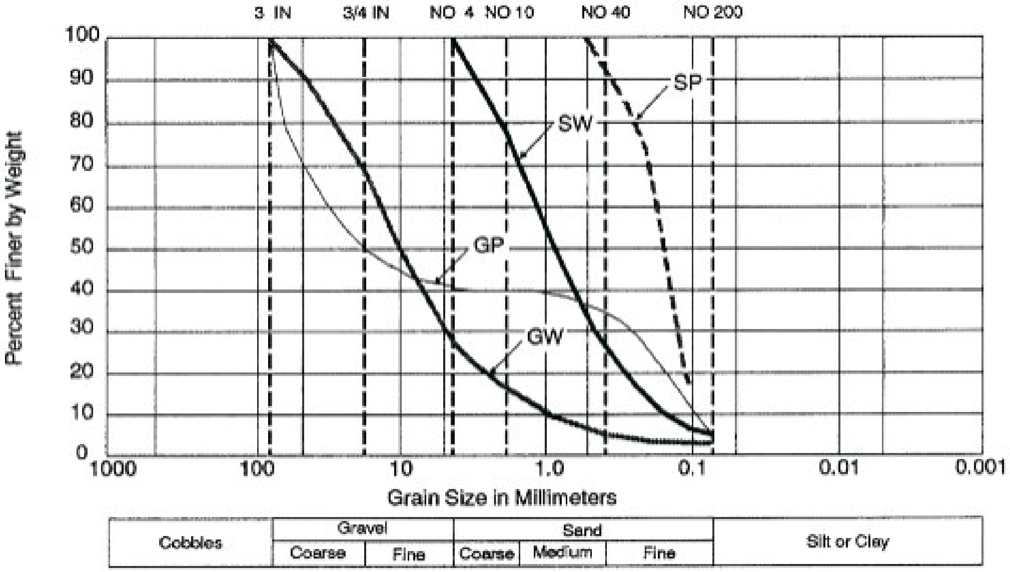


Figure 4.3B: A graphical representation of the Unified Soil Classification System (n.d.)

Table 4.2: Unified Soil Classification System (United States Army Corps of Engineers, n/d)

MAJOR DIVISIONS			**GROUP SYMBOLS**	**DESCRIPTION**
COARSE GRAINED SOILS **(More than half retained on no. 200 sieve)**	Gravels More than half coarse fraction retained on no. 4 sieve (4 500 µm)	Clean gravels (Little or no Fines,)	GW	Well graded gravels, gravel – sand mixtures, little or no fines
			GP	Poorly graded gravels, gravel – sand mixtures, little or no fines
		Gravel with Fines (Appreciable Fines)	GM	Silt gravels, gravel – sand – silt mixtures
			GC	Clayey gravels, gravel – sand – clay mixtures
	Sands More than half coarse fraction passes on No. 4 Sieve (4 500 µm)	Clean sands (Little or no Fines)	SW	Well-graded sands, gravelly sands, little or no fines
			SP	Poorly graded sands, gravelly sands, little or no fines
		Sands with Fines (Appreciable Fines)	SM	Silty sands, sand – silt mixtures
			SC	Clay sand, sand – clay mixtures
FINE GRAINED SOILS **(More than half passes no. 200 sieve)**	Silts and clay Liquid limit < 50%		ML	Inorganic silts and very fine sands, silty or clayey fine sands, clayey silts
			CL	Inorganic clays of low to medium plasticity, lean clays
			OL	Organic silts & organic silty clays of low plasticity
	Silts and clays Liquid limit > 50%		MH	Inorganic silts, fine sand or silty soils, elastic silts
			CH	Inorganic clays of high plasticity, fat clays
			OH	Organic clays of medium to high plasticity, organic silts
Highly organic soils			PT	Peat and other highly organic soils

Fines: <0.075mm (no. 200 sieve size)

Collected samples, prior to TOC analysis and/or estimation, were frozen at -20 °C to reduce the degradation of organic compounds by either volatilisation or microbial degradation. The TOC was estimated using the loss-on-ignition (LOI) method, which involves the thermal destruction of organic matter in the sediment, at a temperature of 950 °C (Heiri *et al*., 2001; Santisteban *et al*., 2004), after which the difference in gravimetric weight prior to and after thermal treatment was used to determine the percentage of TOC (Eq. 4.1).

$$\text{TOC}(\%) = \frac{\text{Organic Carbon (g)}}{\text{W (g)}} \text{ X } 100 \qquad \textbf{4.1}$$

Where:
W (g) is the dry sediment analysis weight (g),
Organic carbon is the difference in weight prior and after thermal treatment.

The samples were corrected for moisture/water content by drying overnight at 60 °C in a drying oven. All samples were combusted in ceramic boats and a Nabertherm furnace (Germany), without the use of any accelerants. Previously, the percentage coefficient of variation among various samples using the LOI method was determined to be 3 to 6% (Schumacher, 2002), which was deemed to be statistically insignificant for the purposes of this study. Furthermore, experimental factors, such as variations in sample size, exposure time and positioning of samples in the furnace, were determined to contribute insignificantly to the consistency of the results at a temperature of 950 °C (Heiri *et al*., 2001).

Some of the sediment cores, that is, samples which were not used for TOC determination and sediment classification, were used to extract water such that the core water physicochemical characteristics could be quantified.

4.2.4 Sampling of riparian wetland plant samples

Plant samples used in this study were collected from three Western Cape rivers, the Diep, Eerste and Salt rivers, using a pair of stainless steel scissors to harvest the vegetative parts (leaves) of each of the plants/reeds. Samples were then transferred into methanol pre-rinsed polypropylene (PP) bottles, while noting the location of each sampling site. The coordinates of the sampling locations were the following: Eerste River – Lat: S34°01' (49.9 to 51.1"), Long: E18°44' (51.8 to 52.1); Diep River – Lat: S33°49' (47.4" to 53.3"), Long: E18°31'

(13.2" to 14.9"); Salt River (Lat: S33°56' (04.6" to 59.9"), Long: E18°28' (48.3" to 89.2"). The plant species randomly selected were: Diep River – *X. strumarium*, *P. australis*, *S. corymbosus*, and *R. maritime;* Eerste river – *P. x canescens, P.salicifolium,* and *C. congestus;* Salt River – *P. amphibian, F. carica, A. schmidtiana* and *E. crassipes.* Vegetative compartments, mostly leaves, of several riparian plant species were sampled, oven dried at 60 °C and ground to a fine powder using a methanol-washed mortar and pestle. Thereafter, a similar method that was used for sediment treatment was used, that is, chemical pre-treatment in % acetic acid followed by two cycles of sonication before filtration and SPE extraction (see section 4.4.2). The plants were randomly selected; however, sampling took place at the same location where the water samples and sediment samples were obtained (see Table 4.1 for GPS coordinates, i.e. within a 100 m stretch of the riparian area where the river water and sediment samples were taken).

The site-specific riparian plant/sediment bioconcentration factor (BCF = $PFC_{plant}/PFC_{sediment}$) was determined as a parameter to assess the transfer of either PFOS and/or PFOA from the sediment to the plants. In order to avoid contamination, plant samples were stored in polypropylene bottles before processing and without a prewash.

4.2.5 Identification of riparian wetland plants

An identification handbook, *Aquatic and Wetland Plants of Southern Africa* (Cook, 2004), was used to identify plant samples, after which the assistance of a botanist was sought to verify the identification of individual plants.

4.3. Sample preparation: Solid phase extraction

4.3.1 Water samples

All river water samples were collected and stored in polypropylene bottles. Prior to collection, the bottles were rinsed with analytical grade methanol and Milli-Q water. After collection, samples were kept on ice and brought back to the laboratory immediately where they were kept in the fridge at -20 °C until they were analysed. Before the analysis, the water was thawed at ambient temperature (23 °C). The salinity and pH of the water was measured using a 230 mm Brineometer (Zeal, England) and a Metrohm pH-meter, respectively. Additionally, to remove the suspended particulate matter (SPM) from the river water, the samples were centrifuged in methanol rinsed 15 ml polypropylene Greiner Bio-one test tubes at 3000 rpm (Megafuge 1.0) for 4 minutes. Prior to use the tubes were rinsed with methanol

(Sigma-Aldrich). Thereafter, the water samples were filtered through polypropylene membrane filters (0.22 µm, Cameo syringe filters, Sigma Aldrich) attached to methanol rinsed 10 ml polypropylene syringes (Becton Dickinson syringes, Sigma Aldrich) prior to solid phase extraction (SPE). The water samples were used without pH adjustment or dilution.

4.3.2 Sediment, suspended solids and plant extracts

Thereafter, 2 g of dry samples (sediment and plant leaves) and 1 g of suspended solids were transferred to a clean 15 mL polypropylene centrifuge tube to which 10 mL of 1% acetic acid solution was added. Each tube was sonicated using a high powered piston probe sonicator (Sonics, vibra-cell sonicator, 20 KHz ± 50 Hz) for 1 minute at ambient temperature. The probe was rinsed with methanol between sample treatments to reduce cross contamination. After sonication the polypropylene tubes were centrifuged at 3 000 rpm for 4 minutes and the recovered acetic acid-based extracts were decanted into an empty 50 mL polypropylene tube. An aliquant of 3 mL of the 90:10 (v/v) methanol and 1% acetic acid mixture was then added to the original tube to resuspend the pellet formed and the contents were again sonicated for 1 minutes, before being centrifuged and decanted into the second polypropylene tube with the extracts from the first centrifugation cycle. This process was repeated using a 10 mL acetic acid (1% acetic acid) solution.

All extracts recovered were combined and then filtered (0.22 µm, Cameo syringe filters, Sigma Aldrich) before passing through the SPE. Although some of the water samples contained little suspended solids, others contained significant amounts, which were separated using a methanol-treated Munktell filter paper (dia.: 70 mm, 65 g/m^2) before being oven dried until a constant weight was achieved. The suspended solids were then recovered and treated in the same way as the sediment samples before SPE and LC/MS/MS analysis. Plant sample pre-treatment was performed using the method previously used by Quinete *et al.* (2009) and adapted by Chen *et al.* (2012) with minor changes. The vegetative parts of the eleven plant samples were randomly collected from the three rivers (i.e. Eerste, Diep and Salt rivers) and transferred into pre-rinsed polypropylene bottles. After collection, the plants were oven dried for 24 hours at about 100 ℃. Thereafter, samples were milled into powder form. Subsequently, 2 g from each of the dry samples were transferred to a clean 15 mL polypropylene centrifuge tube, to which 5 ml Milli-Q water had been added, and then homogenised using a high powered piston probe sonicator for 1 minute at ambient temperature. The probe was rinsed with analytical grade methanol between sample treatments to reduce cross contamination. Subsequent to sonication, 1 ml of mixture was transferred into a second clean 15 ml polypropylene centrifuge tube and 11 ml of 0.01N

NaOH/MeOH was added. The extract mixture and 0.01N NaOH/MeOH were then sonicated for 1 minute at ambient temperature. Thereafter, the polypropylene tubes were centrifuged at 3 000 rpm for 4 minutes and the supernatants were decanted into a clean 15 ml tube. Prior the extraction, the supernatants were filtered using polypropylene 0.22 µm Cameo syringe filters (Sigma Aldrich), and a volume of 15 ml was recorded for each sample before passing through the SPE.

Figure 4.4: Solid-phase extraction (SPE) vacuum manifold with mounted Supelco-Select HLB SPE cartridges

Solid-phase extraction (SPE) was carried out using Supelco-Select HLB SPE cartridges (500 mg solid phase, 12ml tubes), a method similar to that proposed by So *et al.* (2004), ISO 25101 (2009) and OSPAR (2010). Cartridges were preconditioned by eluting 5 mL of methanol followed by 5 mL of Milli-Q water at a rate flow of one to two drops per second. The solid phase was kept wet for optimal extraction. A volume of 40 and 25 mL of water and sediment/plants extracts, respectively, were loaded onto the cartridge, at a flow rate of one to two drop(s) a second. The cartridge was then washed with 5 mL of 40% (v/v) methanol in Milli-Q water, as reported by Naile *et al.* (2010), in order to rinse contaminants off the solid-phase. Thereafter they were allowed to run dry. The samples and extracts used during loading had a salinity of $<1\%$ and a pH >7 for effective extraction of PFOS and PFOA, as previously determined by Gonzalez-Barreiro *et al.* (2006). For the SPE extraction, a large volume sampler (24 port Visiprep sampler, Supelco) was used. Figure 4.5 depicts the Supelco VisiPrep SPE vacuum manifold used during the sample preparation stage. The filtrate recovered was then discarded.

PFOA and PFOS were eluted from the HLB SPE cartridges using 10 mL of analytical grade methanol and further concentrated to a volume of ~1 mL using nitrogen gas before LC/MS/MS analysis.

4.4 LC/MS/MS quantification

4.4.1 Analytical conditions and parameters for PFOA and PFOS quantification

The liquid chromatography (LC) system (Nexera UHPLC with LCMS-8030, Shimadzu, Japan) used was coupled with a tandem mass spectrometer (LC-MS/MS) to determine PFOA and PFOS concentration in each of the extracts. A volume of 10 µl from the recovered extracts was injected into LC/MS/MS for a total run time of 6.5 minutes. The mobile phase constituents were 100% Acetonitrile (ACN) and 2 mM CH_3COONH_4 at a flow rate of 0.3 L/min. The gradient was t = 0.01, 2% ACN; t = 4 min, 98% ACN; t = 6 min, 98%; and was reduced to 2% ACN. The separation column (Shimpack FC-ODS, 150 x 2mm, 3.0µm; Shimadzu, Japan) was maintained at 40 ℃. Quantitative analysis was performed in the multiple reaction monitoring mode and the collusion gas was used at energies of 10 v (PFOA) / 45 v (PFOS). The mass spectra were then taken employing electrospray ionisation (ESI) in a negative mode. Optimised conditions and parameters for the LC/MS/MS system used are shown in Table 4.3 without the use of a guard column.

Table 4.3: Operational conditions and parameters used during PFOA and PFOS analysis.

<table>
<tr><td>1. SPE cartridge elution conditions and injection volume and final extracts volume:</td><td>SPE elution conditions: 10 ml methanol
N_2 gas blow down to around 1 ml
LC injection volume:10 µl</td></tr>
<tr><td>2. LC/MS/MS model used and supplier:</td><td>Model: Nexera UHPLC with LCMS-8030
Supplier: Shimadzu (Asia Pacific) Pte Ltd</td></tr>
<tr><td>3. MS/MS operational conditions and Ion mode:</td><td>MS interface: ESI
Heat block temp: 400 °C
DL Temp: 250 °C
Nebulising gas flow: 3 L/min
Dry gas flow: 15 L/min

MRM settings:
<table>
<tr><th>Compound</th><th>MRM Transition</th><th>+/-</th><th>Q1 Pre-bias (V)</th><th>CE (V)</th><th>Q3 Pre-bias (V)</th><th>Acquisition time (min)</th></tr>
<tr><td>PFOA</td><td>413.10>368.90</td><td>-</td><td>14</td><td>10</td><td>25</td><td>2.184–6.184</td></tr>
<tr><td>PFOS</td><td>499.00>80.05</td><td>-</td><td>17</td><td>50</td><td>30</td><td>2.503–6.503</td></tr>
</table>

Ion mode: Electrospray ionisation(ESI)</td></tr>
<tr><td>4. Guard column used, characteristics and supplier:</td><td>No guard column used.</td></tr>
<tr><td>5. Separation column used, characteristics, supplier, temperature(i.e. operational parameters):</td><td>Column: Shim-pack FC-ODS 150 x 2 mm, 3.0µm (P/No:228-40512-05)
Column Temperature used: 40 ^{0}C
Supplier: Shimadzu (Asia Pacific) Pte Ltd</td></tr>
</table>

Table 4.3: ***cont:***

6. Mobile phase constituents, concentration, flow rate, and gradient operational parameters:	Mobile phase: 100% Acetonitrile and 2 mM CH_3COONH_4 Flow Rate: 0.3 L/min Gradient: $T_{0.01}$ = 2% Acetonitrile $T_{4.00}$ = 98% Acetonitrile $T_{6.00}$ = 98% Acetonitrile $T_{6.01}$ = 2% Acetonitrile $T_{9.00}$ = 2% Acetonitrile
7. Calibration standards used, concentration, range, and supplier:	Analytical standards of PFOA and PFOS were purchased from Sigma-Aldrich. Stock solution of PFOA and PFOS were prepared in 100% Methanol and store at –20 ^{0}C. Different concentration 0.5 ng/L, 1 ng/L, 5 ng/L, 10ng/L, 50 ng/L PFOA and PFOS were prepared by appropriate dilution of the stock solutions.
8. Overview and general comments of LC/MS/MS conditions and parameters used: Shimadzu LCMS-8030 is a robust, sensitive and reliable instrument for the study of pharmaceuticals in water samples. Five concentrations were used for doing calibration in this experiment, PFOA and PFOS gave linear results with excellent sensitivity with R^2 values of 0.99 or greater.	

4.4.2 LC/MS/MS calibration curves for PFOA and PFOS

For calibration standards, curves in the range of 0, 0.5, 1, 5, 10, and 50 ng/L were used with a correlation coefficient (R^2) of 0.99 being achieved for each run (see Fig. 4.5A and B).

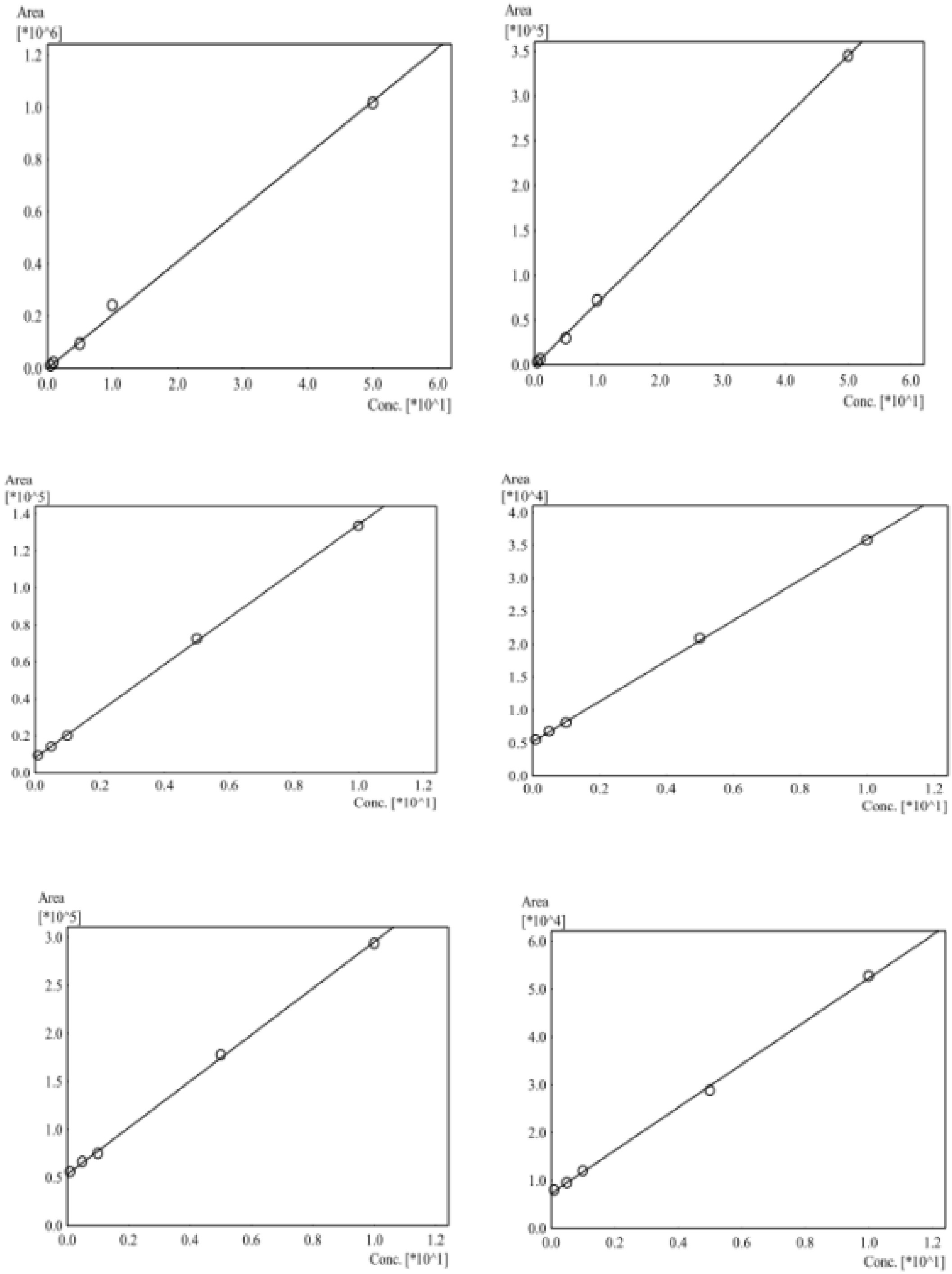


Figure 4.5A: Calibration curves for the determination of PFOA and PFOS

4.4.3 LC/MS/MS chromatographs for PFOS and PFOA

PFOA and PFOS were identified by their retention time, including the specific MRM settings used (413.10>368.90, PFOA; 499.00>80.05, PFOS). The mean of two injected samples was used for every sample.

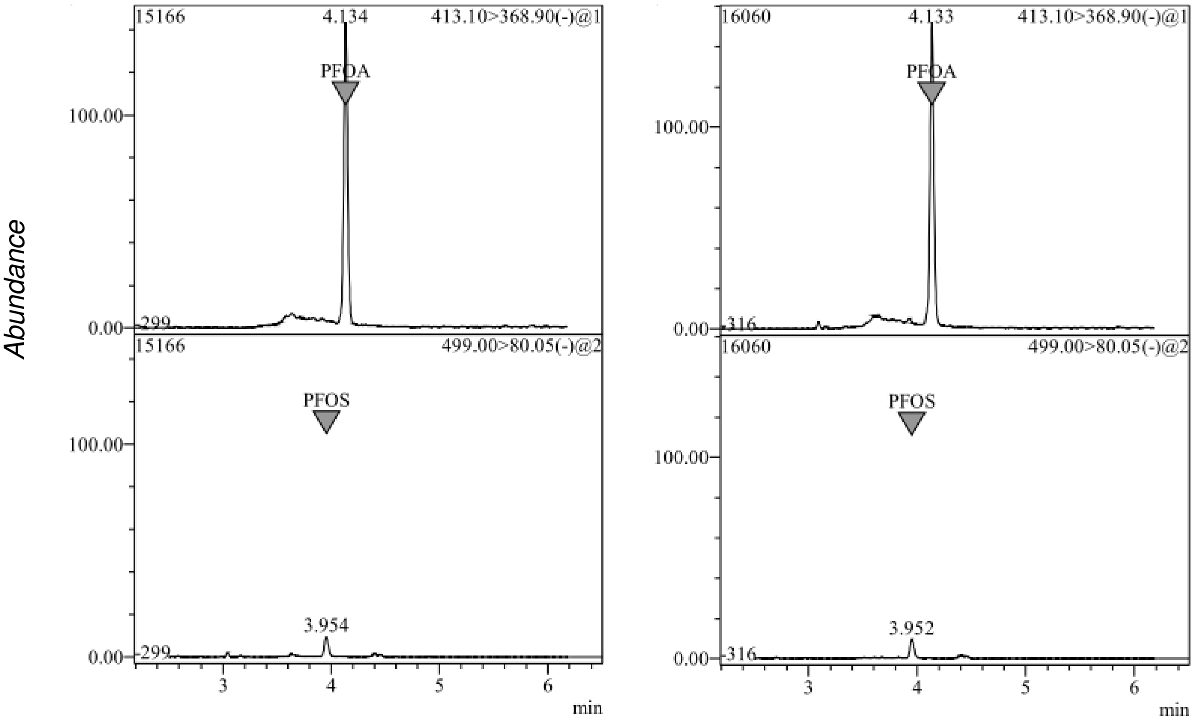


Figure 4.5B: LC/MS/MS chromatograms of PFOA and PFOS.

4.4.4 Validation and Statistical analysis and field quality samples

The percentage relative standard deviation (%RSD) was monitored for the following parameters: retention time, area and height of peak from which concentration was calculated. For %RSD < 0.01, the standard deviation was considered negligible. Additionally, the limit of detection (LOD), described as the lowest concentration that the instrument can differentiate from blanks, at an S/N ratio ≥ 3, was 0.03 ng/g for PFOS and 0.5 ng/g for PFOA for eluents used in the analysis. The mean of two injected samples was used for every sample processed.

Furthermore, field matrices were prepared when collecting each batch of samples by preparing and exposing deionised water in 2-litre polypropylene bottles to the environment, and transportation and storage facilities such that contamination can be detected during analysis.

CHAPTER FIVE

RESULTS

CHAPTER FIVE

RESULTS

5.1 Concentrations of perfluorinated compounds in sediment of Western Cape Rivers

5.1.1 Introduction

Since sediment has been suggested as a reservoir for non-ionic hydrophobic organic pollutants, such as PCBs and OCPs, the hydrophobic-hydrophilic properties of compounds such as PFCs suggest that their partition behaviour between water and sediment may differ from those of non-ionic hydrophobic compounds (Martin *et al.,* 2003; Yang *et al*., 2011), thus reducing their adsorption capacity to particulate matter. This suggests that their prevalence in the aqueous phase should be high in order for the contaminants to be detectable in the sediment.

In South Africa, the occurrence of these organic chemicals, i.e. PFOA and PFOS, in aquatic systems, e.g. rivers, wetlands, riparian areas, drinking including irrigation water sources, have yet to be reported and documented. Although, Hanssen *et al.* (2010) reported the presence of PFOS and PFOA in South African maternal serum and cord blood, i.e. humans, their source is largely unknown while there is no environmental study which reports their prevalence and/or concentration in the South African aquatic environment including agricultural produce.

Therefore, by adequately quantifying PFOA and PFOS in river sediment studied, suggested historical contamination of riparian wetlands in South Africa.

5.1.2 Objectives

Since very few studies have been conducted on the identified rivers, that is, Salt, Diep and Eerste rivers, for the presence of emerging persistent organic pollutants such as PFCs, the objectives of this results section were as follows:

- To determine the concentration of PFOA/PFOS in sediment samples.
- To determine what type of sediment facilitates adhesion in PFOA and PFOS.

- To determine the physical characteristics of the sediment type prevalent in the three rivers and the physico-chemical data of the sediment core water.

5.1.3 Results and Discussion

5.1.3.1 PFOA/PFOS in river sediment

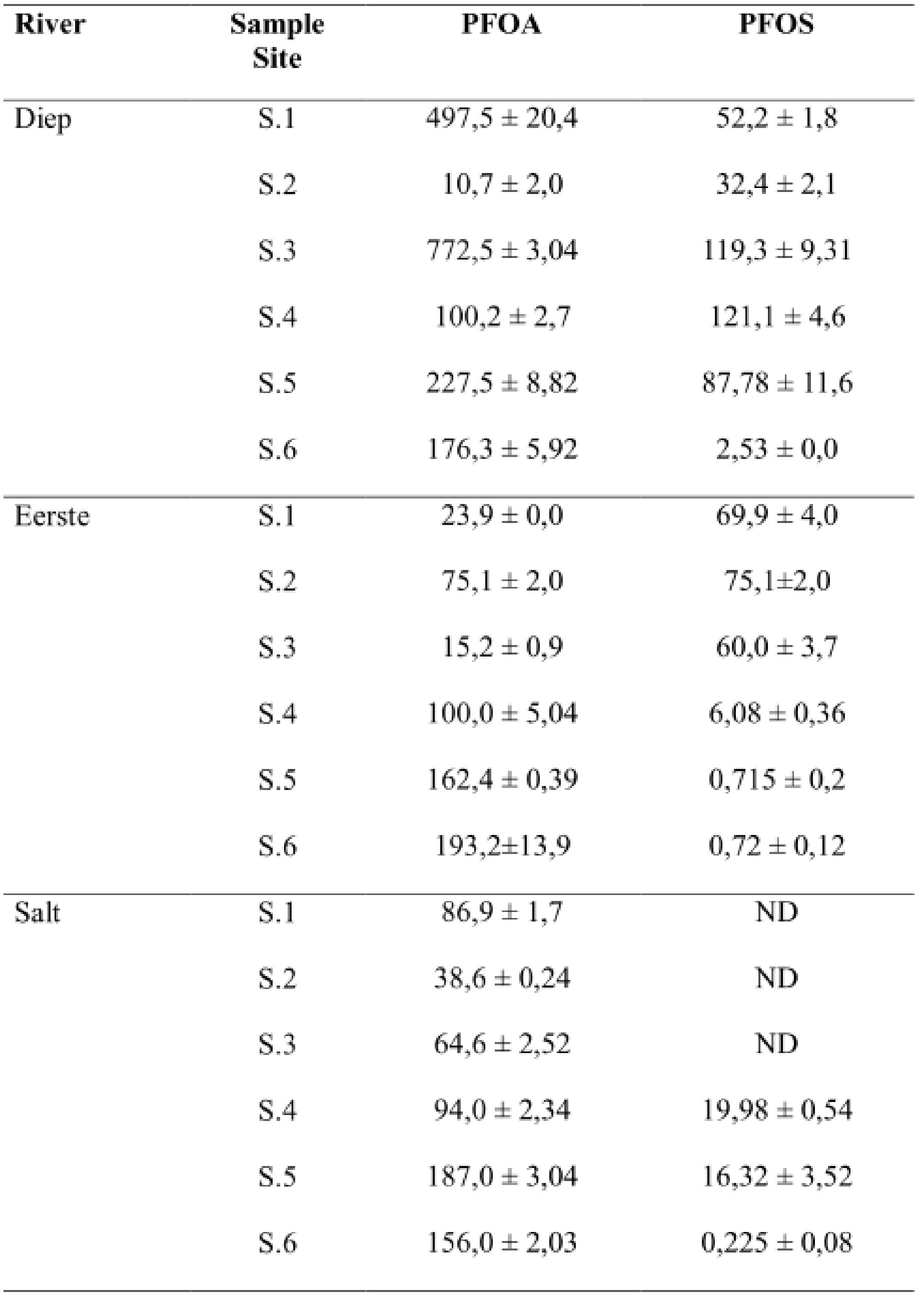
Concentrations of PFOS and PFOA were observed in all the river sediment samples, with PFOA concentration being highest and thus PFOA was the dominant contaminant. The results in Table 5.1, indicate the prevalence of PFOA and PFOS as directly determined from the sediment extracts after SPE treatment, that is, extraction and recovery from the solid phase using methanol. The concentrations of PFOA and PFOS obtained after quantification were then correlated with the mass of sediment (2 g) used during the extraction.

These results show that PFOS concentration in the Salt River ranged from below the detection limit to 19.98 ng/g, while PFOA concentration was 38.6 to 187 ng/g. For the Diep River the concentrations ranged between 2.53 and 121.1 ng/g and 10.7 and 772.5 ng/g for PFOS and PFOA, respectively; while for the Eerste River they ranged from 0.72 to 75.1 ng/g and 15.2 to 193.2 ng/g, respectively. Overall, the Diep River had the highest concentration of PFOA and PFOS during the period under evaluation in comparison with the Eerste and Salt rivers. As the three rivers receive discharge from WWTPs, the prevalence of PFOA suggested that WWTP effluent might be a contributing factor, as has been previously suggested by Yu *et al.* (2009) and Oliaei *et al.* (2006). The concentrations of both PFOA and PFOS are far higher than those previously reported in similar studies in various countries, where the concentration of PFOA and PFOS respectively were found to be 0.06 ± 0.02 and 0.20 ± 0.2 ng/g (USA; Becker, 2008; Houde *et al.*, 2006); 2.3 and 0.29 ng/g (Japan; Senthilkumar *et al.*, 2007); 1.70 to 73.5 and 0.06 to 0.64 ng/g (China; Shi *et al.*, 2012); 49 ± 3.0 and 28 ± 0.65 ng/g (Germany, Ahrens *et al.*, 2011); < 0.3 ± 7.5 and 0.02 to 85 ng/g (Canada; Stock *et al.*, 2007; Becker, 2008); < 0.005 and 0.023 ng/g (Indonesia; Harino *et al.*, 2012); 0.35 to 2.82 and 0.56 to 6.70 ng/g (Brazil; Quinete *et al.*, 2009); and 0.004 to 1.24 and 0.10 to 4.80 ng/g (Spain; Pico *et al.*, 2012).

The highest concentration of PFC contamination observed in the Diep River can be attributed to the size of the catchment, which is the largest catchment area by far under evaluation compared with the Eerste/Kuils and the Salt catchments. Although, the Diep River might receive larger run-off surface water owing to the size of its catchment area, this area is populated mainly by shrub and agricultural land; although it was expected that both the Salt and the Eerste rivers would have the highest PFOA and PFOS contamination as a result of the urban and industrial-based anthropogenic activities in both catchment areas.

Furthermore, as the Diep River catchment area has the largest percentage of land used for agricultural purposes, there is a significant risk of PFC-related contamination in the area. Indeed, other studies have suggested that PFOA and PFOS can accumulate in legumes and vegetative parts of agricultural produce when river water is used for irrigation (Stahl *et al*., 2009). Additionally, as there are five WWTPs discharging into the river (i.e. Potsdam, Malmesbury, Kraaifontein, Klapmuts, and Kalbaskraal) and several landfills, including general waste disposal sites, it may be hypothesised that some of the leachate from these sites contributes to PFC contamination in the river.

Table 5.1: Concentration of PFOA/PFOS in sediment (ng/g dry wt.)



River	Sample Site	PFOA	PFOS
Diep	S.1	497,5 ± 20,4	52,2 ± 1,8
	S.2	10,7 ± 2,0	32,4 ± 2,1
	S.3	772,5 ± 3,04	119,3 ± 9,31
	S.4	100,2 ± 2,7	121,1 ± 4,6
	S.5	227,5 ± 8,82	87,78 ± 11,6
	S.6	176,3 ± 5,92	2,53 ± 0,0
Eerste	S.1	23,9 ± 0,0	69,9 ± 4,0
	S.2	75,1 ± 2,0	75,1±2,0
	S.3	15,2 ± 0,9	60,0 ± 3,7
	S.4	100,0 ± 5,04	6,08 ± 0,36
	S.5	162,4 ± 0,39	0,715 ± 0,2
	S.6	193,2±13,9	0,72 ± 0,12
Salt	S.1	86,9 ± 1,7	ND
	S.2	38,6 ± 0,24	ND
	S.3	64,6 ± 2,52	ND
	S.4	94,0 ± 2,34	19,98 ± 0,54
	S.5	187,0 ± 3,04	16,32 ± 3,52
	S.6	156,0 ± 2,03	0,225 ± 0,08

ND: concentration was below the detection limit. Samples were collected in duplicate for PFOA and PFOS quantification. Injections duplicated for each sample.

5.1.3.2 Sediment characterisation and characteristics of sediment core water

Sediment characteristics have been previously determined to influence the sorption capacity of PFOS and PFOA in different types of sediment (Higgins and Luthy, 2006; Ahrens *et al.*, 2011; Chen *et al.*, 2012). It has been established that sandy sediments with a low organic content have the lowest sorption capacity for various organic pollutants, with a higher sorption capacity being observed for sediments with a higher organic content. This is particularly of interest when the sorption of PFOA was considered for different types of sediment. In several studies (Pan *et al*, 2011; Li *et al.,* 2010; Becker *et al.*, 2008), for sediment with a high organic content, PFOA was identified as a contaminant that is sorbed more easily when compared to PFOS. However, limited information was obtained from the sediments about the role of core water characteristics, including organic content, which can be attributed to the promotion of microbial activity and the attachment of microorganisms to sediment particulate matter, thus influencing the sorption of PFCs such as PFOA.

The association between the physico-chemical characteristics of the core water and the sediment samples (Table 5.2) in relation to PFOA/PFOS sorption was studied. As such, it was observed that all three rivers had high salinity content, that is, greater than the 5.10^{-6} mg/L permissible for rivers, lakes and ponds (Tanji *et al.*, 2007), and the observed range was 1.39 ± 0.7 mg/L for the Diep River, 223 ± 13 mg/L for the Eerste River, and 418 ± 58 mg/L for the Salt River. Furthermore, both the Eerste and the Diep rivers had low nitrate concentration ranging between 2.2 ± 0.4 ng/L and 3.4 ± 0.5 ng/L, respectively; while the Salt River had the highest, that is, 15.4 ± 6.1 ng/L, which was greater than the 10 ng/L permissible for freshwater as stated by the EPA (2011b).

Additionally, the ammonium concentration was high for all three rivers as it exceeded the EPA allowable limit of 0.004 ± 0.001 mg/L, that is, 3.16 ± 0.67 mg/L in the Diep River; 2.11 ± 0.43 mg/L in the Salt River; and 1.19 ± 0.11 mg/L in the Eerste River. Previous studies have indicated that nutrients (e.g. ammonium, phosphorus, nitrates, etc.) support microbial growth (Benner *et al.*, 1995; Anne *et al.*, 2006; Pascoal and Cassio, 2004), although other factors such as pH, temperature and osmotic pressure may also play an important role in the sustainability of microbial growth and attachment on different types of sediment. Phosphate, is an inorganic trace metal from which phosphorus can be obtain, and is widely used in the agriculture sector as a fertiliser. Its concentration was low for both the Diep and Eerste rivers, 1.095 ± 0.115 mg/L and 1.015 ± 0.025 mg/L, respectively; but its concentration was greater than the 2 mg/L permissible according to the IFC environmental health and safety guidelines (2007) and was 3.56 ± 0.11 mg/L for the Salt River.

These results indicate that the three rivers under evaluation had high nutritional components which support microbial growth. The TOC, on the other hand, was high in sediment grain size, that is, > 0.5 mm for the Salt River, followed by the Diep River with sediment size of < 0.1 mm, and ranged from 25.1 to 20.88% (w/w), respectively. However, for sediment grain size of < 0.5 to > 0.1 mm for the Eerste River, TOC was observed to be high (8.85%). This study has also observed that the high %TOC for the Salt River (25.1%) was as a result of the high plant material content of this river. The eutrophication described by Brown and Magoba (2009) was evidenced in this study by the large amounts of plant material observed in-situ. This phenomenon is associated with low dissolved oxygen and high nitrate and phosphate levels, as observed for the Salt River. Therefore it is justifiable to conclude that plant decomposition was low for both the Eerste and Diep rivers as a lower presence of nitrates including phosphates was observed in comparison to the concentrations observed in the Salt River. For the Diep River, it can be surmised that, the low presence of nitrates and dissolved oxygen (DO) concentration was due to aerobic-type microbial contamination, while the water of the Salt and Eerste rivers can be associated with photosynthetic-type microorganism blooms, as a high level of DO and a low ammonium concentration was observed. In certain instances, low DO and a high pH in the aquatic environment, encourage the release of phosphates in the aqua's phase which assists in the growth of algae, thus contributing to a high TOC in grain sizes which are < 0.1mm. In a study by Oliaei *et al.* (2006) on the Mississippi river, PFCs were investigated in floating algae, and the PFC prevalent was PFOS, which suggested either entrapment or sorption by the algal blooms. This study indicates that the bioconcentration of PFOS was from water to algae. Furthermore, Ding *et al.* (2012) indicate that the accumulation of PFCs in algae increases with increasing fluorinated carbon chain length.

Table 5.2: Characteristics of the core water recovered and the sediment samples

Core water								
Sampling site	pH	Conductivity µS/cm	Salinity (mg/L)	TDS (mg/L)	NO^-_3 (mg/L)	PO_4^{3-} (mg/L)	DO (mg/L)	NH^+_4-N (mg/L)
Diep river	8.08 ± 0.33	$^{\#}2.72 \pm 0.14(e10^3)$	$^{\%}1.39 \pm 0.07(e10^3)$	$^{*}1.93 \pm 0.1(e10^3)$	3.42 ± 0.54	1.1±0.12	7.36±0.68	3.16 ± 0.67
Eerste river	7.91 ± 0.3	464.5 ± 26.5	223 ± 13	330 ± 19	2.16 ± 0.44	1.02±0.03	7.81±0.56	1.19 ± 0.11
Salt river	7.43 ± 0.18	857.5 ± 114.5	418 ± 58	609 ± 82	15.43 ± 6.06	3.58 ± 0.11	7.44 ± 0.86	2.11 ± 0.43
Control (Rain water)	7.17 ± 0.31	65.05 ± 27.45	35.65 ± 11.85	46.1 ± 19.6	0.3 ± 0.045	0.06 ± 0.01	8.23 ± 0.12	0.36 ± 0.23

Sediment Granulometry				
Sampling site PFOA/PFOS range	%TOC (w/w) > 0.5mm	%TOC (w/w) < 0.5 mm to >0.1 mm	%TOC (w/w) < 0.1mm	Classification/Observation
Diep river	12.5	2.38	20.88 ± 4.2	**Observation:** coarse grained sediment with more than half the sample mass being retained on sieve sizes with aperture sizes greater than that of no. 200 sieve (75µm), with more than half the fraction passing no. 4 sieve (4500µm). With very little fines.
Eerste river	15.51	8.85 ± 0.9	20	
Salt river	25.1	6.3 ± 2.3	8.3	
				Class: Poorly graded and/or gravelly sediment with most of the sediment being retained by sieve no's 10 to 400 (2000 to 106 µm grain size).

*# - mS/cm; % - g/L; * - g/L*

All sediments from the Diep, Eerste and Salt rivers were observed to be poorly graded and gravelly with coarse grains, with more than half of the screened samples being retained by a 75 µm sieve, while most the grains passed the 4500 µm sieve. Furthermore, minimal fines were obtained for all samples screened, with >50% being retained on screen sizes between 2000 to 106 µm.

5.1.3.3 Overriding factors associated with the sorption of PFOA and PFOS onto poorly graded-coarse sediments of the Diep, Eerste and Salt Rivers

Previous studies (Ahrens *et al.*, 2011; You *et al.*, 2010; Chen *et al.*, 2012; Higgins and Luthy, 2006) have indicated PFOA and PFOS sorption onto sediment being associated with physicochemical characteristics such as salinity, %TOC, salinity and pH. In this study, it was observed that PFOA sorption onto the sediment was high at a higher pH (> 8), high %TOC in smaller grain sizes (< 0.1mm), and high salinity, instead of low salinity including pH (< 8) as observed for the Diep River. The prevalence of PFOS concentration, however, was lower under similar conditions, a similar phenomenon previously reported by You *et al.* (2010). For the Eerste River, PFOS concentration in the sediment samples was lower at a lower pH (> 7.95), %TOC (>16% and 20% w/w) for sediments grains < 0.1 mm and > 0.5 mm, respectively, with low nitrate, phosphates and ammonium concentrations under a high salinity. For the Salt River, although high salinity was measured as 418 mg/L with a high %TOC in grain sediment of size > 0.5 mm, and a high phosphate content, PFOS were below the detection limit in samples S1, S2 and S3 with PFOA and PFOS concentrations being high in sample S5, as ionic organic chemicals, such as PFOA and PFOS, salinity and pH largely increase their extent of sorption on to solid matrices (You *et al.*, 2010).

In most cases in which the quantification of PFOS and PFOA was conducted, PFOA concentration in the aqueous phase was high, indicating poor binding mechanism to coarse sediments, with a low %TOC. Additionally, for muddy sediments, consisting of clay and silt granules including a larger size of fines and with high organic carbon, a higher sorption capacity of organic chemicals such as PFOA and PFOS is expected. Previously, it was ascertained that the partition variations for PFCs in sediment-free water studies are minimal when the partitioning coefficients were normalised against the organic carbon. This suggests that the binding and/or sorption mechanisms of PFC in sediments is strongly related to the organic carbon content of the sediment, with minimal influence of other parameters such as salinity, pH, and conductivity.

Although a larger percentage of studies associated with the determination of PFOS and PFOA partitioning and/or distribution in river studies neglects to account for detailed characterisation of the sediment as a function of either organic content for different fractions in the studied sediment, it is imperative to assess and account for plant- and microbial-based organic content in sediments in association with the sorption of PFOA and PFOS. From this study, it was logical to hypothesise that for larger sized sediment fractions (> 0.5mm), having a high %TOC associated with abiotic decay in plant-based materials, minimal PFC adsorption will occur in comparison to sediment fraction sizes < 0.1 mm, and having a high %TOC associated with microbial-based attachment onto the sediment. It is for these reasons that it was logical to surmise that sediment with a high microbial content, in which the microorganisms are attached to the sediment, will contribute largely to the sorption of PFOA in comparison to PFOS in sandy sediments, which generally have a poor sorption capacity for PFCs, particularly for PFOS. In addition, others (Ahrens *et al.*, 2011) have concluded that PFOS associated adsorption is meagre and losses from the sediment are based largely on river outflows losses, that is, washout from the sediment.

5.1.4 Summary

The Western Cape is one of the industrialised regions of South Africa. Previous studies in this region have focused mainly on heavy metal contamination in sediments. Accordingly, nothing has been reported previously on PFC concentration in the province. The present study determined the concentrations of both PFOA and PFOS in sediments from the Diep, Eerste and Salt rivers. PFOA and PFOS were observed in all samples collected, with PFOA being the predominant contaminant. The results also indicated the relationship between PFOA and PFOS sorption on sediments with both sediment and core water physico-chemical characteristics. In certain instances, the concentrations were higher than those previously reported in other countries around the world.

5.2 Susceptibility of Riparian Wetland Plants to Perfluorooctanoic Acid (PFOA) Accumulation

5.2.1 Introduction

PFOA is the predominant bioaccumulative organic chemical in plants (Lechner and Knapp, 2011). Although several treatment strategies have been implemented to bio-remediate contaminated matrices, a new remediation approach involves the use of artificial wetlands in which aquatic and/or riparian wetland plants are used in order to remove PFCs from either contaminated water or sediment (Chen *et al.*, 2012), suggesting that some of the common wetland plants have an affinity to PFCs including PFOA; hence they are susceptible to bioaccumulate PFOA in the natural environment. Several studies have reported that wetland plants accumulate organic pollutants such as atrazine, chlorotoluron, herbicides, chloroacetanilide, nitro-glycerine (Cherian and Oliveira, 2005; Pilon-Smits and Freeman, 2006; Reinhold *et al.*, 2010). Marchand *et al.* (2010) concluded that the accumulation of pollutants depends on the type of wetland, riparian area, sediment core water characteristics and the rooting system of individual plants. Furthermore, the carryover of PFOA from contaminated soil to plants varies, depending on the concentration of the contaminant in the sediment (Stahl *et al.*, 2009); including the total area of transfer as a function of the rooting system of each plant (Schachtschneider *et al.*, 2010). For this study, PFOS in all riparian wetland plants was found to be below the detection limit.

5.2.2 Objectives

Therefore, the main objectives of this section were as follows:

- To determine the susceptibility of common riparian wetland plants and reeds in the natural environmental to effects of PFOA accumulation by quantifying PFOA concentrations in each plant from the known PFOA concentration in riparian wetland sediment. This was done because most studies use controlled laboratory studies, which do not represent natural environmental conditions. This is important, particularly for studies that focus on the bioaccumulation of PFOA.
- To determine the carryover of PFOA from sediment into plant samples, that is, the bioconcentration factor.

5.2.3 Results and Discussion

5.2.3.1 PFOA concentration in different riparian wetland plant/reed species

It has been previously indicated that the uptake of pollutants from soil to plants depends on the type of plants used in the sorption of organic pollutants (Marchand *et al.*, 2010). Furthermore, the sorption of a particular contaminant is highly dependent on its chemical structure and concentration (EPA, 1990). Some plant species showed greater pollutant accumulation potential than others (Schachtschneider *et al.*, 2010). In this study, the susceptibility of eleven common riparian wetland plants and reeds to PFOA accumulation was investigated. Consequently, PFOA was observed in all the species studied from all of the three rivers observed. Overall, plant accumulation of PFOA was higher in the *E.*

crassipes (38.3 ± 1.2 ng/g) species from the Salt River, followed by the *X. strumarium* species (20.0 ± 0.17 ng/g), from the Diep River, and then the *P. salicifolium* species from the Eerste River (17.5 ± 4.56 ng/g). When compared with similar studies (Yoo *et al*., 2011; Stahl *et al*., 2009), the results obtained were higher in terms of PFOA accumulation in the plants. This is because of the average (n = 6) PFOA concentration found in the sediment, that is, 104.6 ± 1.98 ng/g for the Salt River, 297.5 ± 7.15 ng/g; for the Diep River and 95.0 ± 3.71 ng/g for the Eerste River. This was also observed by Stahl *et al.* (2009), whose study indicated that the higher the concentration of PFOA in the sediment, the higher the pollutant accumulation in the plants, particularly the vegetative parts of the plants. The lowest concentration of PFOA was found in the following plant species; *S. corymbosus* (13.8 ± 0.6 ng/g), *C. congestus* (13.7 ± 0.52), *P. amphibian (*13.4 ± 0.22), *P. x canescens* (13.3 ± 1.44 ng/g), *F. carica* (12.5 ± 0.19) and *A. schmidtiana* (11.7 ± 0.6 ng/g). This represented a significantly higher PFOA concentration in the sediment compared with that found in the plants.

5.2.3.2 Sorption capacity as a function of bioconcentration factor (BCF), root system and sediment characteristics

The bioconcentration factor (BCF), which is the ratio of the concentrations of the contaminant in the plant to those in the sediment, can be represented as either a fraction or a percentage. Furthermore, as the rooting system can have an influence on the uptake rate and persistence of a contaminant in the vegetative parts of the plants under evaluation, it was also imperative to analyse the rooting system for each of the plants. Table 5.3 summarises the %BCF and PFOA concentration in the riparian plants studied, including the rooting systems of each plants. The %BCF for the different plant species was 6.7% (*X. strumarium*), 5.2% (*P. australis*), 4.8% (*R. maritime*) and 4.6% (*S. corymbosus*) for the Diep River. For the Eerste River, the percentages were 18.4% (*P. salicifolium*), 14.4% (*C. congestus*) and 14.0% (*P. x canescens*); while for Salt River they were 36.6% (*E. crassipes*), 12.8% (*P. amphibian*), 11.9% (*F. carica*) and 11.1% (*A. schmidtiana*). The results obtained in this study concur with the results previously obtained by Marchand *et al.* (2010), Yoo *et al.* (2011) and Stahl *et al.* (2009), which indicated that PFOA was readily absorbed by various plants. Since plant roots are an important part for the direct uptake of organic compounds from different sediments with varying pollutant concentrations in the riparian areas (Bell, 1992; E.A., 2006), plant species with fibrous roots seemed likely to have a higher %BCF for PFOA in comparison to those with a taproot system. This is because PFOA accumulates largely on the top soil, which results in fibrous roots having a larger transfer area available for PFOA uptake.

The sediment from all the three rivers was classified as poorly graded and/or gravelly, with most of the sediment being retained by sieve no's 10 to 400 (2000 to 106 µm grain size). Therefore, the retainment of PFOA would have been minimal. In this study, core water quality parameters, such as pH, salinity (mg/L), and %TOC, were also analysed. Some of the Salt River's plants, particularly *E. crassipes,* were observed to have the highest %BCF, indicating that the plant had the highest accumulated PFOA concentration of 38.3 ± 1.2 ng/g in comparison with all the other species evaluated. The top soil in the sediment of the Salt River had the highest %TOC associated with plant decay, which was observed in-situ. This can have a bio-augmentation effect in the sediment, which can facilitate the uptake rate of organic contaminants into the plants – hence their accumulation.

From the results, it was also clear that the frequent submersion of some of the plants may result in a higher sorption capacity for PFOA. Furthermore, although the Diep River had a higher PFOA in the sediment, it was likely that the salinity and a higher pH resulted in reduced sorption of PFOA in the plants. Generally, there is limited knowledge about the effect of soil ecological parameters such as bio-augmentation, including eutrophication, on organic chemical sorption and accumulation in riparian wetland plants. Since it was expected that a high %BCF would be observed in species obtained from the Diep River, which had the highest average PFOA concentration in the sediment (297.5 ± 7.15 ng/g), the observed results suggested that other parameters might have played a significant role, even for *S. corymbosus* species, which has a fibrous root system compared to that of *E. crassipes*, which had the highest PFOA accumulation, a phenomenon attributed to the plant's growth site preference of individual plants. In this case, plants such as *E. Crassipes,* which prefer to grow in constantly submerged areas, might have had a high PFOA accumulation, which suggests that PFOA contaminated water is more likely to cause increased sorption of PFOA than polluted sediment.

Table 5.3: Summary of studied riparian wetland plants, with their PFOA concentration, root system, and percent bioconcentration factor

River	**Sediment characteristics**			**Plant species**	**Root system**	**PFOA**	**%BCF**
PFOA conc./n = 6/ Sediment/core water (ng/g d.w.)	**pH**	**Salinity (mg/L)**	**%TOC**			**(ng/g)**	
Diep (297.5 ± 7.15)	8.08 ± 0.33	1.39±0.07(e10^3)	12.5	*X. strumarium*	Fibrous root	20.0 ± 0.17	6.7
				P. australis	Tap root with small thick lateral roots	15.6 ± 0.57	5.2
				S. corymbosus	Fibrous root	13.8 ± 0.60	4.6
				R. maritime	Fibrous root (delicate, unable to penetrate deeply)	14.2 ± 0.24	4.8
Eerste (95.0 ± 3.71)	7.91 ± 0.30	223±13	15.51	*P. x canescens*	Tap root	13.3 ± 1.44	14.0
				P. salicifolium	Tap root	17.5 ± 4.56	18.4
				C. congestus	Shallow tuft of fibrous roots	13.7 ± 0.52	14.4
Salt (104.6 ± 1.98)	7.43 ± 0.31	418±58	25.1	*P. amphibian*	Fibrous root	13.4 ± 0.22	12.8
				F. carica	Fibrous roots (shallow)	12.5 ± 0.19	11.9
				A. schmidtiana	Extensively fibrous roots	11.7 ± 0.60	11.1
				E. crassipes	Fibrous root	38.3 ± 1.20	36.6

Highly saline environments can decrease the absorption of long-chain organic compounds with a complex structure, as plants' rooting systems absorb them as solutes via osmosis. Thus, having a saline environment would have resulted in a negative osmosis potential (Dogar *et al.*, 2012), with plant species having a higher affinity to other solutes with a simpler chemical structure than PFOA. Other species considered to be alien species in the South African environment, for example *P. salicifolium*, tend to have had a higher affinity for PFOA; however, their presence in the environment should be carefully monitored as the rooting system of these species is regarded as water-hungry, which can further increase the sorption of organic pollutants from the sediment core water. Additionally, the limited sorption of PFOA by plants with a taproot system, such as *P. Australis* and *P. x canescens,* indicated their limited biosorption capacity for PFOA. These plants generally grow further away from the water ridge, with less submersion frequency.

Although wetland riparian plants can be used as biological remediation agents for chemically contaminated sediments in constructed wetlands (Hellström, 2004), the contamination of water sources and riparian wetlands in an environment in which these plants are prevalent would suggest that an escalation of the ecological impact that the contaminants would have might be magnified, thus further endangering wetland ecosystems and the food chain associated with the contaminated wetlands. From an environmental perspective, the results observed in this study indicated that the accumulation of PFOA by the wetland plants under observation was largely higher than any other wetland plants in previous studies (Yoo *et al.*, 2011; Stahl *et al.*, 2009). Since other studies use laboratory studies, which negate environmental factors including seasonal variations (Mudumbi *et al.*, 2012), this study presents an assessment of PFOA accumulation in riparian wetlands which, in turn, will contribute to the effective management of wetlands in which PFOA is a major pollutant.

5.2.4 Summary

There is limited information about the susceptibility of riparian wetland plants, including reeds, to PFOA accumulation. In this study, PFOA was observed in all of the eleven plant species randomly collected from riparian areas, with *E. crassipes* having the highest bioconcentration factor of the eleven. Although the study was conducted in riparian areas with a high PFOA concentration, the resultant higher PFOA contamination in sediment was not directly proportional to a high PFOA absorption and/or accumulation in the plant. Wetlands are the main sources of water and they support ecological systems in riparian areas, thus the susceptibility of some of the wetland plants to pollutant accumulation will have a negative effect on the food chain in the riparian areas. Additionally, for riparian areas with sediment core water with fewer saline properties, plants and reeds with a fibrous root system had a greater susceptibility to PFOA accumulation in comparison to those growing in saline areas. These results can, therefore, contribute to the establishment of a database for monitoring the accumulation of PFCs, in particular PFOA, in riparian vegetation.

5.3 Perfluorooctanoate (PFOA) and Perfluorooctane sulfonate (PFOS) in South African river water

5.3.1 Introduction

In certain cases, the concentration of PFOS and PFOA in river water can be up to several hundred parts per billion with the concentration of PFOS being in most cases being higher in the water that that of PFOA, owing to its low adsorption capacity to solid matrices found in nature (Lin *et al*., 2009), in comparison with other matrices such as sediments and plants. This section reports on the prevalence and concentrations of PFOS and PFOA in the water, and in suspended solids, of the three major rivers of the Western Cape (South Africa), which flow thorough the largest catchment areas (Diep, Salt and Eerste/Kuils) in the province.

The findings suggested widespread PFOA and PFOS contamination of Western Cape rivers. It should be noted that some of the river water is used for irrigating agricultural produce.

5.3.2 Objectives

The main objectives of this part of the research was:

- To determine the prevalence and concentrations of PFOS and PFOA in South African river water and in suspended solids.
- To determine the distribution of PFOS/PFOA in river water and suspended solids.
- To determine the seasonal variation of PFOA and PFOS concentrations in the river water.

5.3.3 Results and Discussion

5.3.3.1 PFOA/PFOS in river water and suspended solids

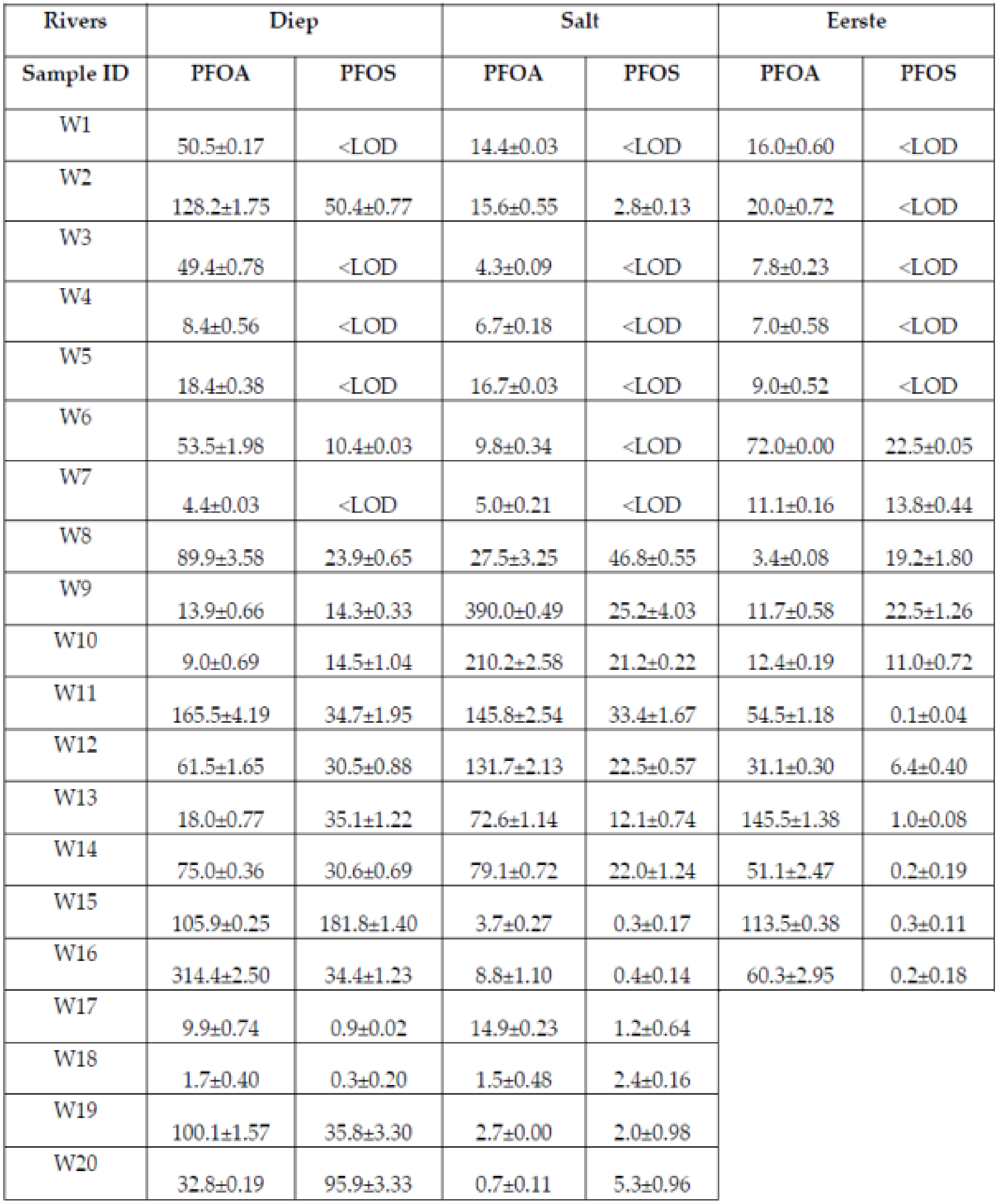
Most studies on PFOA and PFOS partitioning on, and/or distribution, in an aquatic environment have focused largely on river water and sediment. Little evidence has been found of these compounds partitioning onto suspended solids. In South Africa, these contaminants have remained unreported and undocumented, both in river water and suspended solids.

From all the river water samples collected (n = 56), twenty for both the Salt and Diep Rivers, and sixteen for the Eerste River, concentrations of PFOS and PFOA were observed in all the three rivers, with PFOA being the most prevalent PFC. However, for some individual samples, PFOS was not detected, simply because concentrations were below the limit of detection (LOD) which was, for both PFOA and PFOS, 0.03 and 0.5 ng/L, respectively. The results are summarised in Table 5.4.

In the river water from the three rivers, concentrations of PFOA and PFOS ranged from 1.7 ± 0.40 to 314.4 ± 2.50 ng/L and < LOD to 181.8 ± 1.40 ng/L for the Diep River; 0.7 ± 0.11 to 390.0 ± 0.49 ng/L and < LOD to 46.8 ± 0.55 ng/L for the Salt River; and 3.4 ± 0.08 to 145.5 ± 1.38 ng/L and < LOD to 22.5 ± 1.26 ng/L for the Eerste River. Overall, of the three rivers investigated, the Diep River had the highest concentration of PFOA and PFOS during the period under evaluation. However, the sampling point (i.e. W9) with the greatest concentration of PFOA was observed in the Salt River, with a maximum of 390.0 ng/L, while the greatest concentration of PFOS, that is, 181.8 ng/L, was observed in the Diep River at sampling point W15. Additionally, PFOA was observed in all samples from all 56 sampling locations on the three rivers under evaluation, while PFOS was found to be below the LOD in four Diep River samples, six Salt River samples, and five Eerste River samples. In a similar study, Pan *et al.* (2011) found PFOA to be the most prominent PFC in river water in the Tianjin River in China.

In suspended solids, both PFOA/PFOS were detected, with PFOA being the most significant contaminant (Table 5.5). The greater PFOA and PFOS concentration in water from the Diep River sampling point, W15 (Table 5.4), was also observed in suspended solids for this sample, that is, between 28.3 and 26.28 ng/g for PFOA and PFOS, respectively. In this case both contaminants were similar. For the Eerste River, PFOS remained undetected in suspended solids as was the case for the water, that is, for samples W3 and W4. From these results there is evidence of a relationship between PFC concentration in water and in suspended solids of the same water.

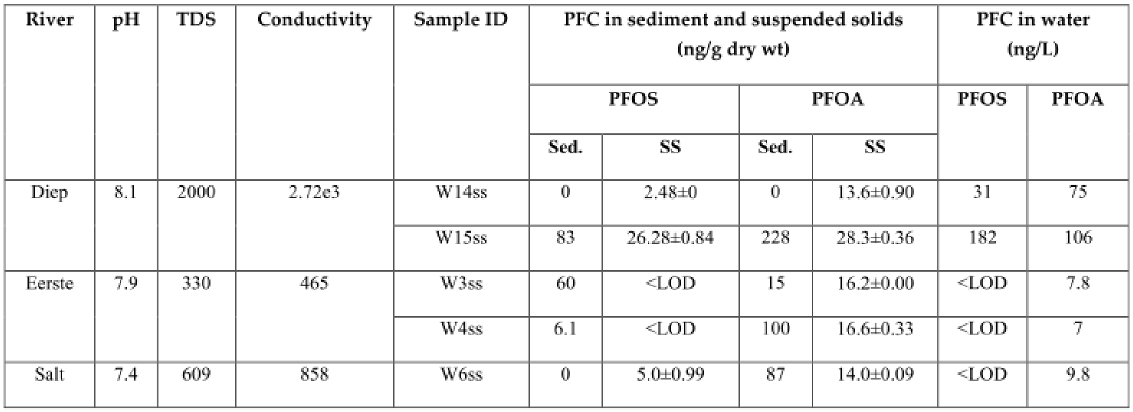
Table 5.4: Concentration of PFOA/PFOS in river water (ng/L)



Rivers	Diep		Salt		Eerste	
Sample ID	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
W1	50.5±0.17	<LOD	14.4±0.03	<LOD	16.0±0.60	<LOD
W2	128.2±1.75	50.4±0.77	15.6±0.55	2.8±0.13	20.0±0.72	<LOD
W3	49.4±0.78	<LOD	4.3±0.09	<LOD	7.8±0.23	<LOD
W4	8.4±0.56	<LOD	6.7±0.18	<LOD	7.0±0.58	<LOD
W5	18.4±0.38	<LOD	16.7±0.03	<LOD	9.0±0.52	<LOD
W6	53.5±1.98	10.4±0.03	9.8±0.34	<LOD	72.0±0.00	22.5±0.05
W7	4.4±0.03	<LOD	5.0±0.21	<LOD	11.1±0.16	13.8±0.44
W8	89.9±3.58	23.9±0.65	27.5±3.25	46.8±0.55	3.4±0.08	19.2±1.80
W9	13.9±0.66	14.3±0.33	390.0±0.49	25.2±4.03	11.7±0.58	22.5±1.26
W10	9.0±0.69	14.5±1.04	210.2±2.58	21.2±0.22	12.4±0.19	11.0±0.72
W11	165.5±4.19	34.7±1.95	145.8±2.54	33.4±1.67	54.5±1.18	0.1±0.04
W12	61.5±1.65	30.5±0.88	131.7±2.13	22.5±0.57	31.1±0.30	6.4±0.40
W13	18.0±0.77	35.1±1.22	72.6±1.14	12.1±0.74	145.5±1.38	1.0±0.08
W14	75.0±0.36	30.6±0.69	79.1±0.72	22.0±1.24	51.1±2.47	0.2±0.19
W15	105.9±0.25	181.8±1.40	3.7±0.27	0.3±0.17	113.5±0.38	0.3±0.11
W16	314.4±2.50	34.4±1.23	8.8±1.10	0.4±0.14	60.3±2.95	0.2±0.18
W17	9.9±0.74	0.9±0.02	14.9±0.23	1.2±0.64		
W18	1.7±0.40	0.3±0.20	1.5±0.48	2.4±0.16		
W19	100.1±1.57	35.8±3.30	2.7±0.00	2.0±0.98		
W20	32.8±0.19	95.9±3.33	0.7±0.11	5.3±0.96		

For samples with a negligible PFOS concentration in the water, the PFOS concentration in suspended solids was also negligible. In addition, with higher PFOS concentration in river water samples, the concentration of PFOS in suspended solids was far less than that in the water. However, for PFOA, when a higher PFOA concentration in the suspended solids was observed, an even lower PFOA concentration was found in the river water. This suggests that PFOA adheres to mobile sediment particles, thus making its mobility in river systems greater than PFOS. In general terms, the concentration of both PFCs (i.e. PFOA and PFOS) was greater in river sediment than in the water and suspended solids, an indication of the persistent deposition and adhesion of these PFCs onto solid matrices in river systems. Furthermore, this also is an indication of historical contamination of the Diep, Salt and Eerste rivers by PFOA and PFOS.

Table 5.5: Concentration of PFOS and PFOA in sediment and suspended solids (ng/g d.w.)



River	pH	TDS	Conductivity	Sample ID	PFC in sediment and suspended solids (ng/g dry wt)				PFC in water (ng/L)	
					PFOS		PFOA		PFOS	PFOA
					Sed.	SS	Sed.	SS		
Diep	8.1	2000	2.72e3	W14ss	0	2.48±0	0	13.6±0.90	31	75
				W15ss	83	26.28±0.84	228	28.3±0.36	182	106
Eerste	7.9	330	465	W3ss	60	<LOD	15	16.2±0.00	<LOD	7.8
				W4ss	6.1	<LOD	100	16.6±0.33	<LOD	7
Salt	7.4	609	858	W6ss	0	5.0±0.99	87	14.0±0.09	<LOD	9.8

5.3.3.2 Seasonal variation of PFOA and PFOS concentration

In most of the river water samples, PFC (i.e. PFOA/PFOS) concentration showed significant variation for the different seasons. Figure 5.1(A, B and C) shows the 2011 average rainfall (Zandvlei Trust, 2011) in the Western Cape province of South Africa where the rivers under observation are located. Thus, PFOS concentrations decreased perceptibly during the dry season and were even below the detection limits for individual samples, while increasing during the wet season for all the three rivers. PFOA, on the other hand, remained detectable in all samples; although concentrations were higher during rainy periods and decreased as dry periods approached. Yu *et al.* (2009) indicate that rainfall significantly affects PFC concentrations and distribution in surface water, which includes river water.

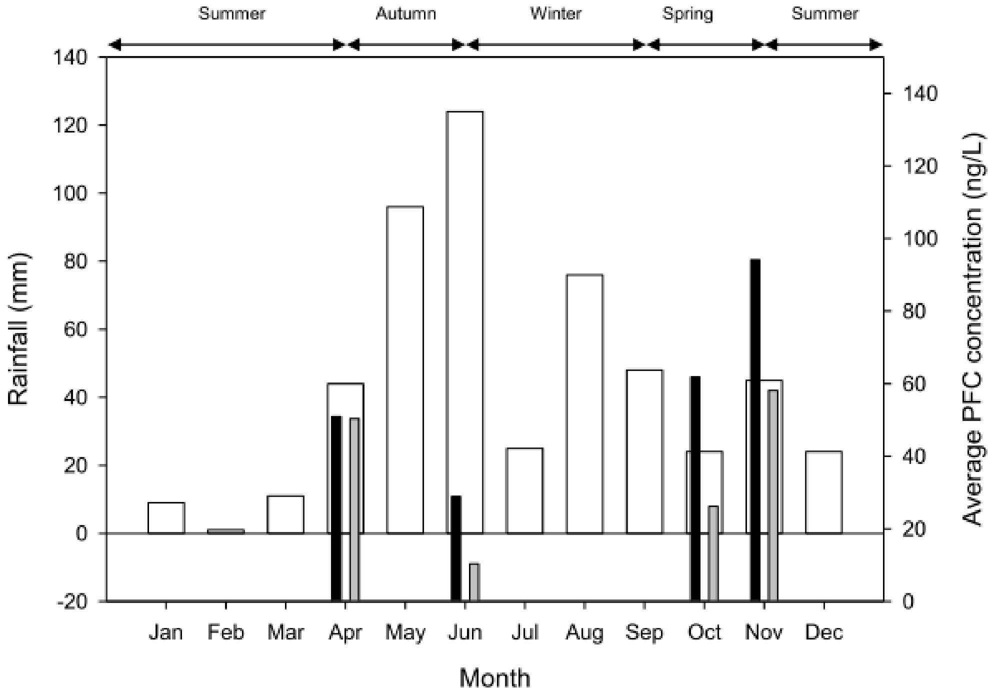


Figure 5.1A: Diep River (Black-PFOA; Grey-PFOS)

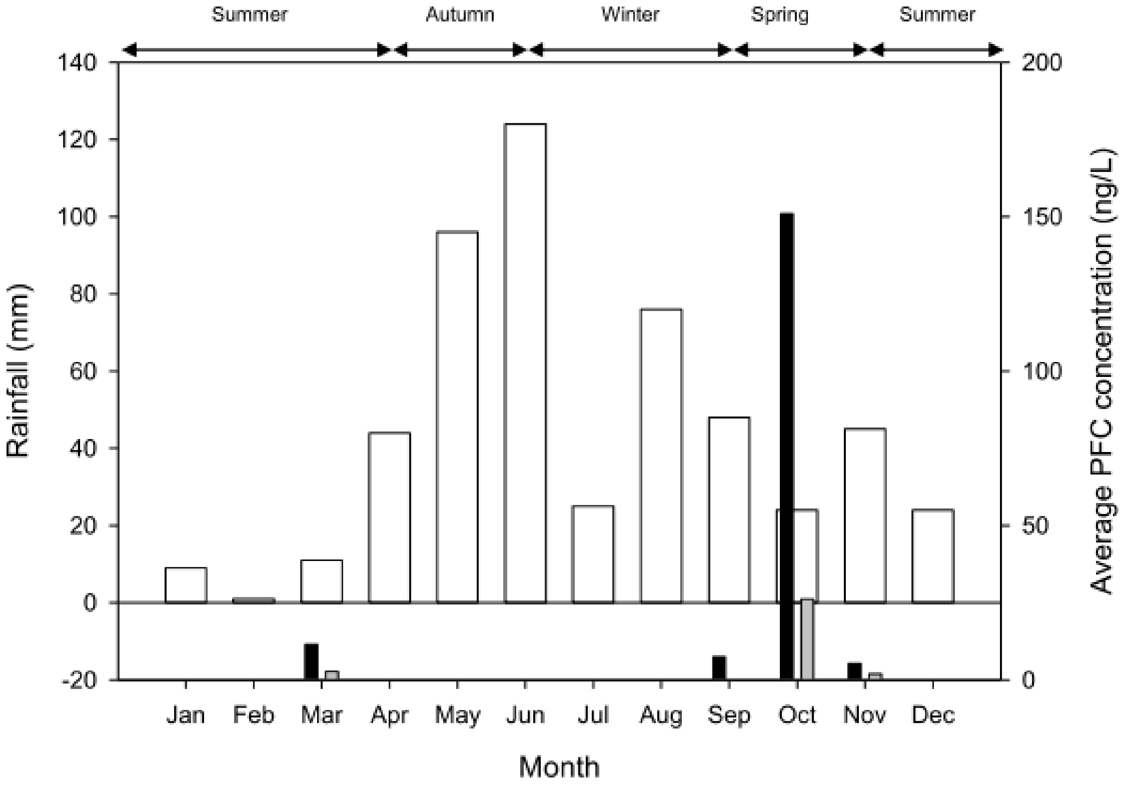


Figure 5.1B: Salt river (Black-PFOA; Grey-PFOS)

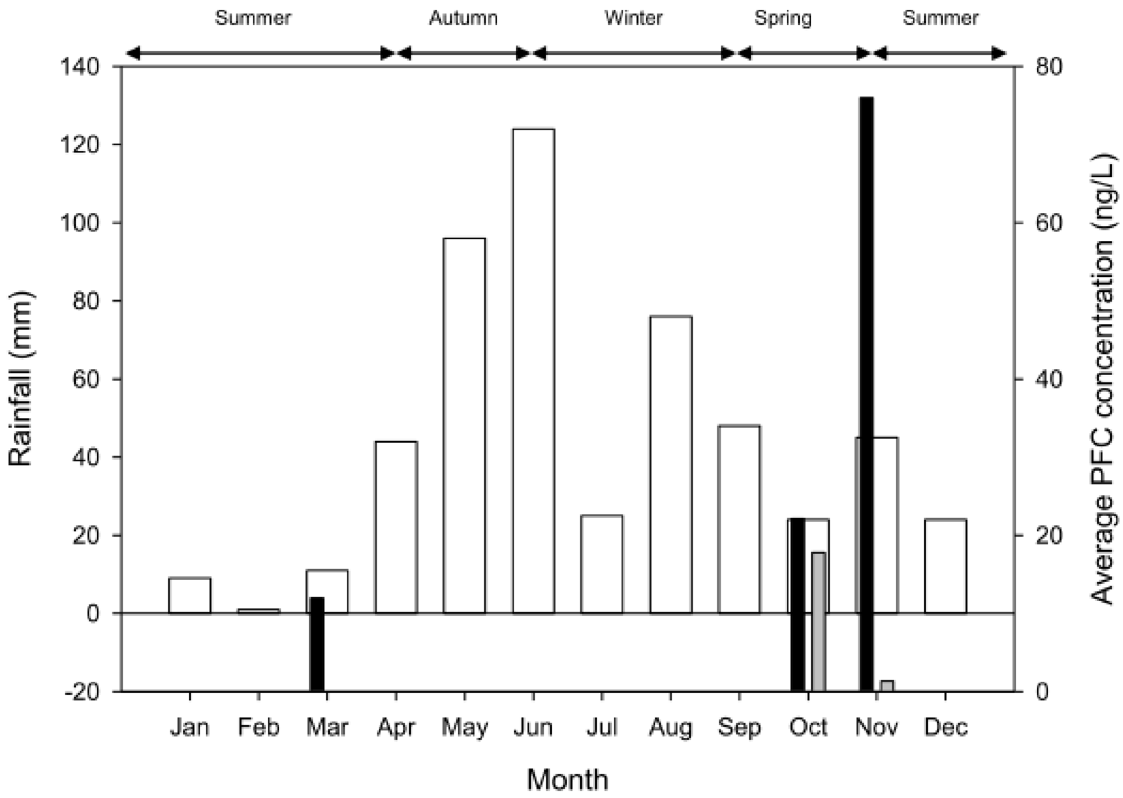


Figure 5.1C: Eerste river (Black-PFOA; Grey-PFOS)

Figure 5.1 (A) (B) and (C): Average monthly rainfall and PFC concentration in samples (n = 2 min/n = 7 max) collected during 2011. Wet season (April–November); Dry season (December–March). Columns: White-Rainfall/Black-PFOA/Grey-PFOS

The results show that samples collected between March and April 2011 (Table 4.1 and 5.4) had, in general, lower PFOA concentrations, while PFOS remained, in most cases, below the limit of detection for all the rivers under study. Previously, Loewen *et al.* (2005) observed low concentration of PFOS in precipitation, while a higher PFOA concentration in rainwater was reported by Scott *et al.* (2006) in the USA and Canada. Additionally, Yu *et al.* (2009) mention that runoff water could potentially be a source for PFCs during wet periods, since rainfall might result in the pickup of PFC contaminants (e.g. oil, fire-fighting foam, etc) from various sources. Both PFOA and PFOS concentrations from this study were higher than those previously reported in similar studies in selected countries during various seasons of the year. In Sweden and Finland, concentration of PFOA and PFOS were found to be, respectively, 17 ng/L and 11 ng/L (Kallenborn *et al.*, 2004); 2.8 to 9.6 ng/L and 0.5 to 2.9 ng/L (Germany, Ahrens and Felizeter, 2009); 0.97 to 21 ng/L and 0.89 to 5.73 ng/L (Japan, Saito *et al.*, 2004); 0.55 to 2.3 ng/L and < LOD to 0.52 ng/L (China, Wang *et al.*, 2011), 49.5 ng/L and 14.2 ng/L (Spain, Pico *et al.*, 2012).

In a previous study, it was observed that grain sediment sizes from the three rivers (i.e. Diep, Eerste and Salt) were between > 0.5 mm and < 0.1 mm; thus they were susceptible to being suspended in water. For the Diep River, PFOA and PFOS concentrations in suspended solids were higher, 28 and 26 ng/g, respectively, as compared to a study by Ahrens *et al.* (2011) where the results showed the lowest tested suspended solid concentrations were 6 and 15 ng/g, respectively, with PFC concentration in the water being 25 and 31 ng/L. Additionally, these high concentrations in suspended solids for the Diep River can be explained by the observed high concentration (i.e. 228 ng/g) in this river's sediment. Other factors, such as the physico-chemical characteristics of the water can play a vital role. In this study, PFC concentrations increased in suspended solids with the following parameters, pH, > TDS and > conductivity, playing a significant role. PFC concentration in suspended solids decreased under low pH, TDS and conductivity (see Table 5.5).

A PFOA concentration was found to be lower in water (106 ng/L) than in sediment (228 ng/g) for the Diep River during the wet season, and higher in suspended solids (16.6 ng/g) than in water (7 ng/L) for the Eerste River during the dry season. Additionally, it was observed that during high rainfall (45 mm), PFOA/PFOS concentrations are evenly distributed (28.3 and 26.28 ng/g) in suspended solids, especially when PFCs are higher in the river water, thus suggesting that the sorption of PFOA is faster onto environmental matrices/sediment in comparison with PFOS.

Since PFOA was found to be higher than PFOS in suspended solids, this implies that PFOA was higher in the top soil/sediment than PFOS, thus resulting in the mobility of the suspended solids being due to river water flow movement. It was therefore hypothesised that PFOS is used less than PFOA in products in the region. More studies are required to support this hypothesis. Moreover, an increase in the %TOC in fraction sediment of grain size > 0.5 mm to < 0.1 mm led to increased PFOA in suspended solids. This is surmised by the fact that the study area, particularly for the Salt River, has a high plant microbial content, in which the microorganisms are attached to the sediment. This has, in turn, contributed largely to the sorption of PFOA onto suspended solids compared to PFOS sorption which was supported by biofilm attachment to the sediment. Similarly, as the Diep River catchment area has the largest percentage of land used for agricultural purposes, there is a significant risk of PFC-related contamination in the area, as other studies have suggested that PFOA and PFOS can accumulate in legumes and the vegetative parts of agricultural produce (Stahl *et al.*, 2009). Furthermore, owing to the presence of several municipal landfills and general waste disposal sites, and the fact that three WWTPs discharge into the Diep River, it could be hypothesised that the water from these sites contributes to PFC contamination of the Diep River.

5.3.4 Summary

South Africa is a water-scarce country with an average annual rainfall of ± 497 mm, compared with a standard world average of ± 860mm. As rivers are possible sources of freshwater in the country, river water contamination in the Western Cape, South Africa, could result in the wide distribution of contaminants in the ecosystem. Research in this area is important as the Western Cape Province has a large agricultural sector, and available information on PFC contamination in river water and suspended solids from the Diep, Eerste and Salt rivers is limited. In this study, PFOA and PFOS were observed in all river water as well as the samples of suspended solids that were collected, with PFOA being the predominant contaminant of both river water and suspended solids. Results also indicate the relationship between PFOA sorption onto suspended solids and water physico-chemical characteristics. In addition, this study observed higher PFC concentrations in river water during the wet season than during the dry season. In certain instances, the concentrations were higher than those previously reported in other countries. In this study, PFCs were determined up to a concentration of 314 ng/L (PFOA, Diep River); 390 ng/L (PFOA, Salt River) and 145 ng/L (PFOA, Eerste River), with the highest PFOS being 181 ng/L (Diep River); 46.8 ng/L (Salt River) and 22.5 ng/L (Eerste River).

CHAPTER SIX

OVERALL

DISCUSSION AND CONCLUSIONS

CHAPTER SIX

OVERALL DISCUSSION AND CONCLUSIONS

6.1 Overall discussion

In this study, the Diep, Eerste and Salt river riparian wetlands were found to be contaminated with perfluorinated compounds, that is, PFOS and PFOA. In certain cases, the concentration levels of both contaminants were higher than those previously reported in similar studies in other countries. These compounds were investigated in river water, suspended solids and sediments from the three rivers, as well as in plants randomly selected from the same area under study. In river water, PFOA and PFOS were found in concentrations of, respectively, up to 314 and 182 ng/L for the Diep River; 390 and 47 ng/L for the Salt River; 146 and 23 ng/L for the Eerste River. In suspended solids, concentrations of PFOS and PFOA were, respectively, 28 and 26 ng/g for the Diep River; 16 and < LOD for the Eerste River; and 14 and 5 ng/g for the Salt River. In sediments, PFOS and PFOA were observed in all the river sediment samples and were found in concentrations up to 19 ng/g and 187 ng/g for the Salt River; 121 ng/g and 772 ng/g for the Diep River; and 75 ng/g and 193 ng/g for the Eerste River for both PFOS and PFOA, respectively. In plants, on the other hand, only PFOA was observed, and the concentration level was found to be in the range of 11.7 to 38 ng/g with a BCF range of 0.05 to 0.37.

Furthermore, a significant correlation was found between the identified river coverage areas and the prevalence of PFOS/PFOA in the respective samples. For example, the three catchments areas, that is, the Diep, Eerste and Salt rivers, as previously mentioned display similarities with regards to their annual rainfall runoffs. This aspect can play a significant role in PFC levels in riparian areas. Thus, it was observed that the three rivers had high PFC concentration levels as rainfall increased. Furthermore, the prevalence of both PFOS/PFOA varied with the catchment size and type of activities in the area. For instance, the Diep River catchment is bigger in size with various anthropogenic activities, such as agriculture and WWTPs. Therefore, the high levels of PFCs, as observed from the results section, indicate a link between sediment, sediment core water characteristics and PFC retainment. Additionally, for the Eerste River catchment area, the levels of contamination observed were hypothetically attributed to the use of PFC-containing products associated with the agricultural activities in the areas of Stellenbosch and Wellington, as well as the residential areas in the same region. However, it was expected that these contaminants would be higher in the Salt River catchment because it is closer to city of Cape Town and flows mainly through an urban area. However, this was not the case. Other factors, such as the physicochemical characteristics of the samples (e.g. the pH, TDS, conductivity, salinity, TOC and DO), the microbial activity and the attachment of microorganisms to sediments contributed significantly to the levels of contaminant concentration in the rivers under study.

Overall, the sediment samples were the only ones in which both PFOS/PFOA were detected. For both the Diep and the Eerste rivers, for instance, both PFOS and PFOA were constantly detected, with PFOA being the predominant contaminant in the sediment of all the three rivers. This is an indication of historical contamination. Moreover, PFOS concentration was undetected, that is, < LOD, in three sediment samples from the Salt River. The results for this category of samples are summarised in Table 5.1.

In water samples, concentrations of PFOS and PFOA were lower compared to those in sediment samples; moreover, PFOA was found to be the predominant contaminant, with a higher concentration in the Diep River. However, for the individual samples, sample W9 from the Salt River had the highest PFOA concentration, while sample W15 from the Diep River had the highest PFOS concentration. Moreover, PFOS was found to be <LOD in some samples from the three rivers; these samples were collected mostly during the dry season, that is, a period of low rainfall. This suggests that rainfall contributes to PFC concentration in riparian wetlands.

PFOA and PFOS concentrations were found to be lower in suspended solids than in sediments and water samples. However, in certain cases, PFOA concentrations were higher in suspended solids than in water. For instance, PFOA concentration was investigated in water samples W3 and W4 from the Eerste River as well as in the suspended solids in the same water samples; subsequently, PFOA was found to be higher in the suspended solids than in the water.

The absorption of PFOA from the environment by certain riparian plants was also investigated. It was accordingly discovered that riparian wetland plants are more or less susceptible to PFOA accumulation, depending on the root system of the plant. In this study, eleven plants were randomly selected from the three catchment areas under investigation. PFOA accumulation was found to be higher in *E. Crassipes*, a plant species from the Salt River, and the second highest BCF was observed in the *X. Strumarium* species from the Diep River. Although most of these plants have a similar root system (i.e. fibrous root), it was expected that the accumulation of PFOA will be consistent, particularly the BCF; however, this was not observed. The influence of other factors, such as the pH and salinity, on PFOA accumulation in these riparian plant species was investigated. For example, under both higher pH (i.e. 8.08) and salinity, low PFOA accumulation in plants from the Diep River catchment was observed. However, as pH and salinity decreased for both the Salt and the Eerste rivers, so did the PFOA accumulation in the plants. Furthermore, in this study, a relationship was observed between PFOA/PFOS accumulation and TOC in the sediment. For instance, PFOA sorption onto sediment was higher in sediment with a grain size of < 0.1 mm for the Diep River under a higher %TOC, while for the Eerste River, PFOS sorption onto sediment was lower in sediment with a grain size of < 0.1 mm and > 0.5 mm under low %TOC. For the Salt River, at high %TOC, PFOS was <LOD in grain sediment of size > 0.5 mm for individual samples (i.e. S1, S2 and S3); however, in S5 both PFOS and PFOA were higher as a result of not only high TOC, but also the high salinity and pH. Moreover, the type of sediments prevalent in the three rivers investigated was characterised by poorly graded gravelly coarse grains with minimal fines.

In addition, PFOS and PFOA concentrations observed in the Diep, Eerste and Salt rivers were, in most cases, higher than those previously reported in similar studies in other countries. Table 6.1 summarises the comparison of PFOS and PFOA concentrations from this study and those from other countries.

Furthermore, the overall distribution of PFOA was higher than that of PFOS in all the samples (i.e. sediment, water and suspended solids, as well as plant samples). However, for individual samples, one case was found where PFOA was similarly distributed in suspended solids (i.e. SS15) from the Diep River. Nevertheless, PFOS remained below the LOD in all eleven plant species that were randomly selected from the catchment areas.

Table 6.1: Comparison of PFOA and PFOS concentrations in water and sediment samples from South Africa and other countries

Sample category: Example	**PFOA**	**PFOS**	**Country**	**References**
Water	17 ng/L	11 ng/L	Sweden	Kallenborn *et al.* 2004
	2.8 to 9.6 ng/L	0.5 to 2.9 ng/	Germany	Ahrens *et al.* 2009
	0.97 to 21 ng/L	0.89 to 5.73 ng/L	Japan	Saito *et al.* 2004
	0.55 to 2.3 ng/L	< LOD to 0.52 ng/L	China	Wang *et al.* 2011
	49.5 ng/L	14.2 ng/L	Spain	Pico *et al.* 2012
	0.92 to 59.2 ng/L*	**0.60 to 15.2ng/L***	**South Africa**	**This study**
Sediment	0.06 ± 0.02 ng/g	0.20 ± 0.2 ng/g	USA	Becker, 2008; Houde *et al.* 2006
	2.3 ng/g	0.29 ng/g	Japan	Senthilkumar *et al.* 2007
	1.70 to 73.5 ng/g	0.06 to 0.64 ng/g	China	Shi *et al.* 2012
	49 ± 3.0 ng/g	28 ± 0.65 ng/g	Germany	Ahrens *et al.* 2011
	< 0.3 ± 7.5 ng/g	0.02 to 85 ng/g	Canada	Stock *et al.* 2007; Becker, 2008
	< 0.005 ng/g	0.023 ng/g	Indonesia	Harino *et al.* 2012
	0.35 to 2.82 ng/g	0.56 to 6.70 ng/g	Brazil	Quinete *et al.* 2009
	0.004 to 1.24 ng/g	0.10 to 4.80 ng/g	Spain	Pico *et al.* 2012
	4.2 to 165.6 ng/g*	**2.4 to 39.9 ng/g***	**South Africa**	**This study**
Plants	103.6 ± 15.8 ng/g	4.1 ± 0.46 ng/g	Germany	Lechner and Knapp, 2011
	32 ng/g	12 ng/g	Germany	Stahl *et al.* 2009
	11.7 to 38 ng/g*	**< LOD***	**South Africa**	**This study**

**** Averaged range***

6.2 Overall: Conclusion

Water is a necessity for all living organisms. Most of the water that humans consume comes from two sources, surface water (rainfall and its runoff into rivers or dams) and groundwater (underground water stores or aquifers). Today, people worldwide are facing water shortages, and this has had a negative effect on their wellbeing, in one way or other. In South African terms, the situation is alarming. The country's water resources are, in terms of geographical location, extremely scarce. Rainfall across the country remains unevenly distributed, with some provinces receiving more rain than they need.

In South Africa, surface water resources (i.e. rivers and dams) are the main sources of freshwater and water is used by three main consumers, that is, the urban population, agriculture and industry. Consequently, these are in competition for the limited water sources, and increasing scarcity has led to enormous deficits in the equitable allocation of water to these competing sectors. It have been predicted that by 2050, farmers in South Africa will have to increase their use of water if they are to meet South Africa's demand for food. However, the reality is that South Africa has limited water; and this fact will place constraints on all future developments that South Africa as a country might want to accomplish.

According to the literature reviewed, poor monitoring of chemical products used in agricultural and industrial sectors has resulted in certain POPs being distributed in the environment. Subsequently, these contaminants have run off into surface water resources, such as rivers, and are consequently polluting the water.

As with everywhere else in the world, the quality of water in the South Africa remains threatened by the uncontrolled application of products containing POPs by both the agricultural and industrial sectors, applications which are done during the production of goods. Unfortunately, during the discharge of industrial wastewater, as well as rainfall and irrigation runoff on agricultural land, these POPs find their way into surface water resources. Their prevalence in the aquatic environment has been investigated in several studies that have been reported and documented worldwide, including South Africa. However, new emerging POPs, such as PFCs (i.e. PFOA and PFOS) have yet to be reported and documented in South Africa in general, and in the Western Cape Province in particular. Therefore, this study truly represents the first research on PFOA and PFOS contamination that has been reported in the South African environment.

6.3 Recommendations

This research study reported on perfluorooctane sulfonate and perfluorooctanoate contamination of the riparian wetlands of the Eerste, Diep and Salt rivers. However, the following aspects still need to be addressed:

- New analytical methods for PFC detection in plant tissues should be developed in order to improve the detection of PFOS.
- Potential PFC sources in South Africa should be evaluated.
- The PFCs present in other regions of South Africa should be profiled.
- The concentration of other perfluorinated compounds in the South African environment should be profiled.

CHAPTER SEVEN

REFERENCES

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