Perfluorooctane acid (PFOA) and Perfluorooctane sulfonate (PFOS) in the Plankenburg (Stellenbosch) and Diep (Milnerton) Rivers, and potential remediation using *Vitis vinifera* leaf litter

By

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DECLARATION

I, Fagbayigbo Bamidele Oladapo, declare that the contents of this thesis represent my own unaided work, and that the thesis 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.

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ABSTRACT

This study represents the first monitoring campaign to assess the seasonal trend of nine perfluorinated compounds (PFCs) in surface water and sediment from the Plankenburg and Diep Rivers in the Western Cape, South Africa. An analytical protocol was developed and validated for qualitative and quantitative routine determination of nine perfluorinated compounds (PFCs), in water and sediment samples using Ultra performance liquid chromatography-mass spectrometry quadrupole time of flight (UPLC-QTOF-MS). This method was applied to determine levels of PFOA and PFOS in environmental samples. Samples were collected along the Diep (Milnerton) and Plankenburg (Stellenbosch) Rivers respectively. Samples were pre-treated, cleaned-up and extracted using solid-phase extraction (SPE) procedures with hydrophilic-lipophilic balance (HLB) C-18 cartridges. Seasonal variation and distribution of PFCs in surface water and sediment was also investigated. Levels of PFCs were monitored in four seasons (summer, autumn, winter and spring) to establish their trend in the environment. The removal of PFOA and PFOS from aqueous solutions using agro-waste biomass of *Vitis vinifera* (grape) leaf litter was also studied. Activated carbons were produced from the biomass and chemical activation achieved with phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) for the modification of the carbons' (AC-H_3PO_4 and AC-KOH respectively). Activated carbons were characterized using Fourier Transform infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Brunauer- Emmett-Teller (BET) in order to understand the removal mechanisms of the contaminants by activated carbons. The effects of solution concentration, pH, adsorbent dosage, contact time, and the temperature were optimized for evaluation of the removal efficiency of the activated carbons. Adsorption isotherm models were used to analyze the equilibrium data obtained and kinetic models were applied to study sorption mechanisms. A fixed bed column study was conducted using: AC-H_3PO_4 adsorbent. Experimental parameters such as initial concentration of the solution, column bed height, flow rate and initial concentrations of the influent were optimized to establish the best adsorption efficiency parameters of the column system. Breakthrough curve and exhaustion time were predicted using Adam-Bohart, Yoon-Nelson, and Thomas models for the fixed bed column under varying experimental conditions.

The method was validated and gave good linearity with correlation coefficients (R^2) ranging between 0.991 and 0.999 for all the investigated compounds. Limits of detection (LOD) ranged between 0.02 ng/l and 0.08 ng/l, while the limit of quantification (LOQ) ranged from 0.065 ng/l and 0.261 ng/l. Recovery studies that were carried out in a replicate assays which gave results ranging from 83 % to 112 % for the nine perfluorinated compounds. PFOA and PFOS were detected in surface water samples of the Diep River at levels ranging from 51.0 to 1929.8 ng/l

for PFOA and levels ranging from 34.7 to 546.1 ng/l for PFOS. Levels of PFOA in Plankenburg River ranging from ND to 1311.25 ng/l and levels of PFOS ranging from 41.0 ng/l to 1126.0 ng/l in all seasons. Levels of PFOA and PFOS in the corresponding sediment samples of both rivers ranged between 0.8 and 214.5 ng/g dry weight (dw) for PFOA and levels varied between ND and 134.0 ng/g dry weight (dw) for PFOS in Diep River. Levels of PFOA varied between 13.3 and 72.81 ng/g dry weight (dw) and PFOS ranged between ND and 128.5 ng/g dry weight (dw) in Plankenburg River, in all the investigated seasons. The concentration of PFCs in sediment samples were higher than levels observed in surface water. Levels of PFOA and PFOS were found to be lower than the threshold limits established for PFOA and PFOS in surface water by EU water regulations, Environment Canada, and USEPA. Results were consistent with levels of PFCs previously reported in surface water and sediments both in South Africa and elsewhere. Water quality parameters such as pH, temperature, salinity, electrical conductivity (EC) and total dissolved solids (TDS) were investigated. There was a significant relationship ($p<0.05$) between water quality parameters and seasons. Partitioning distribution coefficient value log K_{OC} for PFOA and PFOS gave a maximum value of 1.311 and 1.316 cm^3/g, respectively suggesting anthropogenic activities. Surface morphology of the produced adsorbent showed the abundance of microspores (> 60%) with BET total surface area of 295.488 (m^2/g) and 158.67 (m^2/g) for AC-H_3PO_4 and AC-KOH activated carbons, respectively. The results obtained from adsorption isotherm models fitted well into Freundlich isotherm for both AC-KOH and AC-H_3PO_4. Maximum adsorption capacities for AC-H_3PO_4 were 78.90 and 75.13 mg/g for PFOA and PFOS, respectively. Kinetic study revealed that equilibrium was reached before 60 min on both adsorbents for both compounds, and thermodynamic studies indicated that removal process was exothermic and spontaneous. Removal efficiencies were 95% and 90% for PFOA using AC-H_3PO_4 and AC-KOH respectively. Corresponding values for PFOS were 94% and 88%. The better adsorbent (AC-H_3PO_4) and the optimized condition got from the batch experiments were used for a fixed column study. Results from the column models showed that maximum capacities for AC-H_3PO_4 adsorbent were 145.35 and 111.23 mg/g for PFOA and PFOS respectively. This indicated that the breakthrough curve and exhaustion time of the system increased concurrently with the increase in bed height, while flow rate enhanced the efficiency of the column bed. This study demonstrated that activated carbons produced from *V vinifera* leaf litter biomass successfully removed PFOA and PFOS in both batch adsorption and fixed bed column studies.

Keyword: PFCs, PFOA, PFOS, Surface water, Sediment, *Vitis vinifera*, UPLC-QTOF-MS

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DEDICATION

To my Lord Jesus Christ,

the Alpha and Omega, who made manifest of His glory in my weakness.

Removal of PFOA and PFOS from aqueous solutions using activated carbon produced from Vitis vinifera *leaf litter*

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RESEARCH ARTICLE

Removal of PFOA and PFOS from aqueous solutions using activated carbon produced from *Vitis vinifera* leaf litter

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Abstract The removal of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from aqueous solutions using agro-waste biomass of *Vitis vinifera* (grape) leaf litter was studied. Activated carbons were produced from the biomass and chemical activation achieved by using phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) for the modification of the carbons' surface morphology. Activated carbons were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy and Brunauer–Emmett–Teller (BET) in order to understand removal mechanisms of the contaminants by activated carbons. The effect of solution concentration, pH, adsorbent dosage, contact time and temperature was evaluated to optimize the removal efficiency of activated carbons. Adsorption isotherm models were used to analyse the equilibrium data obtained, and kinetic models were applied to study sorption mechanisms. The results fitted well into Freundlich isotherm with both AC-KOH and AC-H_3PO_4 having high K_f values. Maximum adsorption capacities for AC-H_3PO_4 were 78.90 and 75.13 mg/g for PFOA and PFOS, respectively. Equilibrium was reached before 60 min on both adsorbents, and thermodynamic studies indicated that the process was exothermic and spontaneous. Surface morphology showed the abundance of microspores (>60%) with BET total surface area of 295.488 and 158.67 m^2/g for AC-H_3PO_4 and AC-KOH activated carbons, respectively. Removal efficiencies were 95 and 90% for PFOA using AC-H_3PO_4 and AC-KOH, respectively; corresponding values for PFOS were 94 and 88%. Adsorbents' removal capacities depended on the physicochemical characteristics of adsorbents.

Keywords Activated carbons · Adsorption · PFOA · PFOS · *V. vinifera*

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Introduction

In recent time, freshwater resources are faced with major pollution threats due to the intrusion of contaminants such as perfluorinated compounds (PFCs). PFCs are anionic surfactants with the high energy carbon–fluorine (C–F) bond that gives great stability; they also possess high surface activity and resistance to natural biodegradation (Castiglioni et al. 2015). These physicochemical characteristics allow PFCs to be highly persistent in nature, and hence bioaccumulative tendencies in the environment (Giesy and Kannan 2002). Extensive application of perfluoroalkyl substances in various manufacturing processes, such as pulp and paper, surface coating, textiles and pharmaceutical and petrochemical industries, have been identified as sources of these contaminants into the environment (Paul et al. 2008). Large volumes of industrial effluents with residues of various organic contaminants ultimately find their way into natural water bodies (Strynar et al. 2012). Pollution has led to the decline in natural

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ORAL PRESENTATION

- SETAC Africa 7th annual Meeting, Langebaan, South Africa (Oct 9-13, 2015)
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  Partitioning and sorption of PFOA and PFOS in sediment samples obtained from the Diep and Plankenburg Rivers, South Africa

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Seasonal variations and distribution of selected PFCs in surface water and sediment from the Diep and Plankenburg Rivers, Western Cape Province, South Africa

- Fagbayigbo B.O., Opeolu B.O, Fatoki O.S. and Akenga T.A.
  Adsorption of PFOA and PFOS from contaminated water using agro-waste leaf biomass (Vitis vinifera) in a fixed-bed column study.

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GLOSSARY

BAF	Bioaccumulation factor
BCF	Bioconcentration factors
BET	Brunauer, Emmett and Teller
b_T	Constant in Temkin isotherm (J/mol)
Ca	Amount of adsorbed adsorbate on the adsorbent (mg/g)
Ce	Equilibrium concentration of adsorbate in the bulk solution (mg/L)
C_e	Equilibrium concentration of the adsorbate
CNH	Carbon, Nitrogen and Hydrogen
Co	Initial concentration of the adsorbate aqueous solution
c_o	Liquid-phase concentration
C_s	Adsorbate monolayer saturation concentration
c_t	Liquid-phase concentration at given time
diPAP	Polyfluoroalkyl phosphate diester
dw	Dry weight
E	Mean free energy (J/mol)
ECF	Electrochemical fluorination
ESI	Electrospray ionization
ESI-MS/MS	Electrospray-ionization tandem mass spectrometry
FASA	Perfluoroalkane sulfonamide
FASAA	Perfluoroalkane sulfonamido acetic acid
FASE	Perfluoroalkane sulfonamido ethanol
F_{oc}	Fraction of organic carbon
FOSA	Perfluorooctane sulfonamide
FTIR	Fourier transform infrared spectroscopy
FTOHs	Fluorotelomer alcohols
GC	Gas chromatography
h_o	Initial adsorption rate (mg/g/min)
HPLC	High performance liquid chromatography
K_1	Pseudo first - order rate constant/min
K_2	Rate constant of pseudo second - order adsorption (g/mg min)
Kc	Thermodynamic equilibrium constant
k_d	Distribution coefficient
K_{D-R}	Dubinin-Radushkevich (D-R) isotherm constant
K_F	Freundlich isotherm constant
K_L	Langmuir isotherm constant
k_{oc}	Organic carbon partitioning coefficient
K_T	Temkin isotherm constant
LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
M	Mass of the absorbent
monoPAP	Polyfluoroalkyl phosphate monoester
MRM	Multiple reaction monitoring mode
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry

N	Number of variables
N	Normality
n_f	Exponent in Freundlich isotherm
NMR	Nuclear magnetic resonance
n_T	Constant in Temkin isotherm
OC	Organic carbon
OECD	Organisation for Economic Co-operation and Development
PAP	Polyfluoroalkyl phosphate ester
PCB	Polychlorinated biphenyls
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substance
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCA	Perfluoroalkyl carboxylic acid
PFCs	Perfluorinated compounds
PFDA	Perfluorodecanoic acid
PFHpA	Perfluoroheptanoic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPA	Perfluoroalkyl phosphonic acid
PFPeA	Perfluorooentanoic acid
PFSA	Perfluoroalkane sulfonic acid
PFUnDA	Perfluoroundecanoic acid
POSF	Perfluorooctanesulfonyl fluoride
PP	Polyporopylene
PTFE	Polytetrafluoroethylene
q_e	Amount of adsorbate adsorbed at equilibrium per unit weight of the adsorbent (mg/g)
q_m	Maximal substance amount of adsorbate per gram of the adsorbent
q_{max}	Maximum monolayer adsorbate adsorption capacity (mg/g)
q_t	Amount of adsorbate adsorbed at any time (mg/g)
QTOF	Quadrupole time-of-flight
R	Gas constant (J/mole K)
SPE	Solid phase extraction
T	Absolute temperature
T	Time (sec)
TEM	Transmission electron microscope
TOC	Total organic carbon
triPAP	Polyfluoroalkyl phosphate triester
UPLC-QTOF	Ultra performance liquid chromatography quadrupole time of flight
V	Volume
α_E	Constant in Elovich rate equation (g min2/mg)
B	Constant in Elovich rate equation (g min/mg)
ΔG^o	Standard Gibbs free energy (kJ/mol)
ΔH^o	Standard enthalpy change (kJ/mol)
ΔS^o	Standard entropy change (J/K/mol)
E	Polanyi potential = RT ln(1+1/Ce)

CHAPTER ONE

1.0 INTRODCTION

1.1 Background to the study

Perfluorinated compounds (PFCs) are among the group of emerging organic contaminants present in the environment. PFCs are unique organic compounds in which all the hydrogen molecules in the carbon-chain are replaced by fluorine molecules. These include the oligomers and polymers made up of neutral and anionic surface active compounds with high thermal, chemical and biological inertness (Buck et al., 2011, Castiglioni et al., 2015). They belong to members of a chemical group referred to as perfluoroalkylated substances (PFAS) which comprise a vast range of fluorinated compounds. PFAS and their derivatives such as Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) have drawn the most public attention and research interest in recent times due to their environmental relevance and health implications (Domingo et al., 2012). PFCs are highly soluble organics and are moderately soluble in water, with consequent availability in the aquatic environment. PFOA and PFOS have been identified as important chemical additives due to their unique physicochemical characteristics. Literature has reported PFOA and PFOS to be persistent, bio-accumulative compounds in various environmental matrices and biological samples, and are toxic to animals and potentially dangerous to humans even at lower concentration (Jogsten et al., 2012, Giesy & Kannan, 2002b). Perfluorinated compounds have been in use for over half a century as components of a variety of consumer and industrial products, such as surfactants, lubricants, adhesives, refrigerants, paper-coating, fire retardants, propellants and insecticides etc. due to their unique characteristics, such as thermal stability, water-repellent, dirt-repellent, grease-repellent, among others (Key et al., 1997, Giesy & Kannan, 2002a, Carloni, 2009). Various applications of PFC-containing substances in the manufacturing chain have resulted in the widespread distribution of PFCs and their derivatives in environmental matrices. Residues of PFCs in environmental matrices have been detected in various samples across the globe, including Asia, Australia, North America and in the Europe (Loos et al., 2008, Giesy&Kannan, 2002b).

The enormous applications of PFCs containing substances have resulted in their ubiquity in the environment, and other derivatives of fluorinated compounds being detected in environmental matrices (Lin et al., 2014). The occurrence of PFCs in different biological and environmental media varies from a few parts per million (ppm) to a number of parts per trillion (ppt). They have a tendency toward bio-magnification and environmental accumulation. The bio-magnification of PFCs in the food chain has been reported, and it has

been suggested that this is responsible for their occurrence in some organisms and environmental matrices such as domestic and industrial wastewater discharged into municipal drains, urban surface water, streams and receiving waters (Fromme et al., 2007). Elevated levels of PFCs were reported in aquatic environments at a higher concentration in the samples collected from urban areas than in those collected from remote areas, which probably indicates the contribution of urbanization and industrial activities to the incidence of PFC contamination in different environmental matrices (Giesy & Kannan, 2002b).

In animal studies, various health issues have been associated with high dosages of PFCs (DeWitt et al., 2012), indicating possible adverse effects when they are ingested by humans. Studies show that PFCs and their derivative compounds could trigger health problems in exposed organisms such as hepatotoxicity, developmental toxicity, immune toxicity, neurotoxicity, hormonal effects and tumorigenic potential (Wang et al., 2015b, Han et al., 2012). Some studies also revealed that the liver is the bodily organ that is most affected by PFCs in exposed animals. Sub-chronic exposures to relatively high doses of PFCs also appeared to suppress various aspects of adaptive immunity in exposed animals (DeWitt et al., 2014, Dong et al., 2015). Han et al. (2012) reported that the exposure of animal models to PFOA resulted in high residual concentration in tissues. PFOS concentration in Tilapia (*Oreochromis niloticus*) was 1100 ng/g wet weight and up to 3673 µg/l of PFOS was observed in mullet (*Mugilincilis*) bile fish tissue. Concern has consequently been raised by various international organizations responsible for human health and the safety of the environment regarding the pending menace of elevated concentrations of PFCs in the environment.

Measures to reduce the levels of PFCs and their derivatives in the environment are crucial. Some fluorotelomer compounds including PFOA, PFOS and their precursors were included in Annex B of the Stockholm convention on persistent organic pollutants (POPs) as priority contaminants (Wang et al., 2009). As a result, some developed nations have enacted strict regulations prohibiting the use and manufacture of certain PFCs. Statutory threshold limits for drinking water have been published by some fluoro–chemicals-producing nations. United States Environmental Protection Agency (USEPA) has established provisional thresholds limits of 200 ng/l and 400 ng/l for PFOA and PFOS respectively in drinking water (USEPA, 2009). However, legislation against the application of PFCs and its derivatives are still lacking in several countries, including South Africa. Nevertheless, some international regulatory organizations such as USEPA, UNEP, Environmental Canada, etc., have intensified their awareness campaign against the impending environmental and health implications of unchecked levels of PFCs.

Urgent abatement measures are needed to eliminate or reduce the threats posed by perflourinated alkyl substances and their derivatives (PFOA and PFOS) in environmental matrices. Several methods for the removal of various contaminants in water have been reported in the literature (Zareitalabad et al., 2013; Mohammed et al., 2016). Studies have revealed that conventional water treatment methods have not been effective in the removal of PFCs from water and wastewater systems (Xiao et al., 2013). Alternative eco-friendly abatement methods have thus been suggested by several researchers. These methods include adsorption technology, which could be explored for the possible removal of PFCs from water systems so as to eventually reduce the availability of contaminants in the environment. In the literature, biosorption techniques have been widely applied for the treatment of contaminated water bodies, wastewaters, drinking water etc., with the aid of activated carbons (AC) (Wang et al., 2012, Xu et al., 2015 & Ali etbal., 2012). Activated carbons are generated from various precursors, such as synthetic adsorbent and agro-based adsorbent such as agro-waste materials, which gives good and efficient removal potential for the organic contaminant (Deng et al., 2012). However, the use of agro-based materials to generate activated carbons is perhaps the best abatement measure for the removal of organic contaminants in polluted water available presently (Ghaedi et al., 2015).

1.2 Perfluorinated compounds in the global environment

The global distribution of PFCs is attributed to its wide-ranging applications in several domestic and industrial processes (Post et al., 2012). PFOA and PFOS have been detected in environmental components such as air, water, soil, sediments, and in living organisms across the world (Rankin et al., 2016, Wang et al., 2012), and this occurrence was the result of anthropogenic activities rather than natural processes (Lindim et al., 2016). PFOA and PFOA have been detected in biota and environmental samples obtained from as far as the polar region (Llorca et al., 2012) and in the ocean (Wild et al., 2014), as well as every continent in the world (Wild et al., 2014). Elevated levels of PFCs were detected in the urban and industrialized regions of the world, indicating the contribution of anthropogenic activities, while trace concentrations of PFCs were mostly detected in areas far away from human activities (Post et al., 2012, Castiglioni et al., 2015). The global distribution of PFCs in the environment could increase significantly if not adequately checked, especially in regions where environmental awareness and legislation are still lacking. Effective legislation was suggested as a tool to decrease the concentration of PFCs in environment, providing that it is adequately enforced (Shoeib et al., 2016). The availability of PFCs in the environment at elevated levels could lead to serious health implications for both flora and fauna, which ultimately bio-magnify and affect human health.

1.3 Health Effects

PFCs have been identified as potential toxicants in the environment that could trigger health problems in biota, including higher animals and microorganisms upon exposure at elevated levels. Exposure of organisms to PFOA and PFOS at elevated concentrations could lead to serious health consequences such as hepatotoxicity, developmental toxicity, immune toxicity, neurotoxicity, endocrine toxicity, gene toxicity and tumorigenic potential, among others (Han et al., 2012).

Epidemiological studies, however, provided links between PFCs and human health risk, thus, it was reported that PFOA and PFOS have a high affinity for binding B-lipoproteins and liver fatty acid-binding protein in animal tissues (Gallo et al., 2012). Studies also revealed that PFOS may induce DNA breakage and affect DNA repairs, thereby disturbing the homeostasis of metabolism (Hoff et al., 2003). In another study, there is a possibility of PFOS interfering with the metabolism of fatty acid, thereby deregulating lipids and lipoproteins metabolism (Casals-Casas & Desvergne, 2011, EFSA, 2008b). PFOA and PFOS are readily soluble in the body fluid, and this enhances their absorption into organism's body via oral exposure, followed by bio-accumulation in serum, kidney, and liver which precedes the consequent adverse health effect on the organism (Kabir et al., 2015, Sundström et al., 2012).

In addition, exposure of PFCs to developing foetus and infants have been reported globally (So et al., 2006). PFCs are also described as toxic chemicals that could potentially impair developing embryo in an animal study, which could ultimately result in abnormal effect on babies at birth (Fromme et al., 2007, Kim et al., 2011). Studies also reveal that PFOA and PFOS may reach offspring from parents via movement through the placenta (Kim et al., 2011, Midasch et al., 2007) and in breast feeding (Bonefeld-Jorgensen et al., 2011). The correlation between PFOA and PFOS levels in cord serum and reduced birth weight, ponderal index, and head circumference of infants was reported by (Washino et al., 2009, Apelberg et al., 2007). Also, associated effect of high dosage of PFOA and PFOS levels in the male organism could affect the quality of sperm produced (Joensen et al., 2009) and ability to change the adult thyroid hormone levels (Dallaire et al., 2009) of laboratory animals. Due to these reports, potential health effect of PFCs threshold limits has been published by USEPA and some national environmental and health agencies (USEPA, 2009, Giesy & Kannan, 2002b, & Post et al (2012).

1.4 Abatement method

In this study abatement method was developed for the removal of PFOA and PFOS from contaminated water. Previous studies revealed that most conventional water treatment plants were not effective for complete removal of PFOA and PFOS in wastewater systems, and, therefore, end up in the water distribution pipes and ultimately in the environment (Anumol et al., 2016, Ali et al., 2012 & Ahmad et al., 2013). However, the agro-based biomass of *Vitis vinifera* leaf litter was explored in this study for the removal of some selected PFCs in water as a remediation approach using adsorption techniques. Adsorbents produced in this study were further applied in a fixed bed column study to establish its practical applicability in a fix-bed flowing system. Various adsorption isotherms and kinetic models were applied to have an insight into sorption mechanisms. The information obtained from physicochemical characterization of the produced adsorbents were used to investigate the surface reactivities and the adsorbate/adsorbent interactions.

1.5 Statement of research problem

The quality of water resources is steadily declining due to the increase in the release of contaminants into surface water such as municipal drains and in the flowing rivers with consequent release into coastal waters. Such contaminants include perfluorinated compounds (PFCs) such as PFOA and PFOS. The sources of these contaminants include domestic, industrial and agricultural activities among other sources (Kissa, 2001a). PFCs have been used in industrial and consumer applications such as stain and water resistant coatings for fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, and insecticide formulations (Giesy & Kannan, 2002b, Post et al., 2012, Valsecchi et al., 2016).

The distribution and presence of residues of PFCs including PFOA and PFOS have been reported in humans and in different environmental matrices. Residues of PFCs are therefore, widely distributed and have been found in environmental components such as water, sediment, silt and biological samples, across the globe (Wang et al., 2016a, Naile et al., 2010, Ahrens et al., 2010). Evidence has also suggested the presence of the compounds in both domestic and industrial wastewaters. This may, however, be due to urbanization, industrialization, and malfunctioning of wastewater treatment plants. Other possible sources include food via packaging materials or cookware and more direct exposure from the ambient environment.

Serious concerns have been raised over the contributions of PFOA and PFOS in the perturbation of environmental quality, and the threat they pose to both human and environmental health. PFOA and PFOS were recently listed among emerging organic pollutants that may cause detrimental effects on humans. Human exposure to PFOA and PFOS is likely to occur via different routes such as ingestion, dermal and inhalation. PFOS has been shown to bio-accumulate in fish, seafood, fowl, meat, fruits, vegetables, eggs, milk and dairy products (Liu et al., 2015a, Fromme et al., 2007, Ericson et al., 2009). Health effects of PFOA and PFOS and other PFC compounds include damage to immune and hormonal systems, carcinogenicity and mutagenicity. They may also increase the risk of anorexia, blood cancer, high cholesterol level, hyperactivity, and liver damages (Olsen et al., 2003, Hoffman et al., 2010b). Due to this associated health implications, PFOA and PFOS were recently listed among the group of persistent organic pollutants (POPs) of the Stockholm Convention as a result of their chemical and thermal stability (UNEP, 2009).

In South Africa and most developing countries, various applications of PFCs containing compounds are still on-going with consequent portent risks to environmental quality. The accumulation of these compounds in different environmental matrices is not unexpected because of their resistance to degradation, hence the need for this study.

1.6 Justification for the study

The application of PFOA and PFOS in a wide array of industrial and domestic processes has consequently resulted in environmental contamination. Adverse health effects and environmental hazards associated with the presence of PFCs released into the environment from human activities are enormous. There had been increased concern within the scientific and public health community about the worldwide contamination of surface waters and sediments by emerging persistent organic pollutants such as the PFCs (Astrahan et al., 2017 & Post et al., 2012). Elsewhere, studies have been conducted by some researchers, institutions, and government agencies to investigate the levels, distribution and characterization of these chemicals in different environmental matrices (i.e. water, soil, sediments), and remediation (Chen et al., 2012b, Pico et al., 2012 & Eriscon et al., 2009). Such information concerning the networks of rivers, coastal waters, sediments, soils in South Africa, especially Cape Town environment is scarce and lacking.

It is, therefore, imperative, that the status of PFOA and PFOS and other PFCs be determined and characterized in different environmental matrices. This will be a basis for assessing the health implications and facilitate the need for remediation if found at elevated levels. There is a need for routine monitoring and assessment of PFCs in different

environmental matrices in order to promote human and environmental health. The U.S. Environmental Protection Agency, Environment Canada, and some other agencies have issued preliminary human health risk assessments on PFOA, PFOS and related substances (USEPA, 2009, EC, 2012). This study, therefore, seeks to assess and monitor PFCs in different environmental matrices. Abatement methods such as adsorption technology using eco-friendly (leaf litter) biomass to remove PFCs from water and sediments need to be investigated for effective remediation UNEP (2009).

1.7 Research objective

1.7.1 Broad objective

The broad objective of this study is to assess levels of selected perfluorinated compounds including PFOA and PFOS in the Plankenburg and Diep rivers, South Africa, and their possible removal using *V. vinifera* leaf litter.

1.7.2 Specific objectives

1. To develop suitable analytical methods for the identification and quantification of PFCs especially PFOA and PFOS in water and sediment samples.
2. To assess the levels of PFCs including PFOA and PFOS in water and sediment samples of the Plankenburg and Diep rivers.
3. To assess seasonal trends occurrence and distribution of PFOA and PFOS in the Plankenburg and Diep rivers.
4. To determine the physicochemical characteristics of charred and uncharred grape leaf litter using FTIR, BET and SEM.
5. To utilize *V. vinifera* leaf litter to remove PFOA and PFOS from contaminated water samples.

1.8 Significance of the study

Water is becoming increasingly scarce globally. South African water resources are under threat from industrial and agricultural pollution due to the release of organic contaminants into water bodies. This has resulted in water quality deterioration and consequently, less available fresh water. Plankenburg and Diep rivers are among the important freshwater resource in Western Cape that need protection. They serve as habitats for several plant and animal species that need protection (DWAF, 2015).

The determination of the concentrations of PFOS, PFOA and other derivatives of PFCs in these rivers will provide information about their levels in the aquatic systems. Seasonal variations in levels of the selected perflourinated compounds will also be established. *V.vinifera* leaf litter is abundantly available in Western Cape Province, South Africa. Biomass of the leaf litter will also be used for possible removal of PFOA and PFOS from contaminated water.

1.9 Delimitation of the study

In this study, collection of samples was restricted to surface water and sediment samples along the Diep (Milnerton) and Plankenburg (Stellenbosch) rivers. These rivers were chosen to reflect the impact of different anthropogenic activities along both river courses. This research focused on nine perflourinated compounds including PFOA and PFOS. Among the numerous agro-waste biomasses, *V.vinifera* leaf litter was selected for investigation into its biosorption potential.

CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter offers an overview of perfluorinated compounds (PFCs), including PFOA and PFOS in the environment. It provides insight into the sources, availability, fate and distribution within various components of the environment. The route of exposure, toxicology and health implications of PFCs, and the existing legislative framework, are discussed. Analytical protocols for the determination of PFCs in environmental matrices are reviewed. Abatement methods available for the removal of PFCs in water such as adsorption techniques are also discussed.

2.1 Perfluorinated compounds

Perfluorinated compounds (PFCs), including perfluorooctanoic acids (PFOA) and perfluoroctane sulfonate (PFOS), are members of the vast group of emerging anthropogenic pollutants perfluoro alkyl substances (PFAS) present in the environment (Wang et al., 2016b). PFAS are divided into three main groups: perfluorinated carboxylic acids (PFCAs) perfluorinated sulphonic acids (PFSAs) and perflourinated phosphoric acid (PFPAs). PFAS are represented by the general formula F (CF2) n-R; perfluorinated compounds (PFCs) are made of varying lengths of carbon chain ranging between C-4 and C-16, with lipophilic head and hydrophilic end group that endows them with unique physicochemical characteristics. The presence of chemical moiety in this compound results in cationic (+ve), anionic (-ve) and non-ionic (neutral) active-surface charges on individual perfluoroalkyl compounds. For example, neutral end groups are processes CH_2-CH_2-OH (fluorotelomer alcohol) and SO_3 NH_2 (perfluoroalkyl sulphonamide), as obtained in perfluorooctane sulphonamide (PFOSA); anionic end groups are the carboxylates (COO), the sulfonates (SO_3) and the phosphates (OPO_3); while cationic end groups include the quaternary ammonium group attached to the fluorinated hydrophobic part of the compounds (Parsons et al., 2008).

Among the known organic compounds, fluorinated compounds are known to be among the inert substances and the formation of carbon fluorine (C-F) bond is perhaps the strongest bond ever encounter in organic chemistry (Liang et al., 2016). As a result of this exceptional physiochemical stability, fluorinated compounds possess great resistance to thermal and chemical reactivities. Hence it's application across wide range sectors including manufacturing industries, agriculture and domestic products, among others (Castiglioni et al., 2015, Schultz et al., 2004). The hierarchy of PFAS is presented in (Figure 2.1) showing different sub-division of its derivatives (Buck et al., 2011).

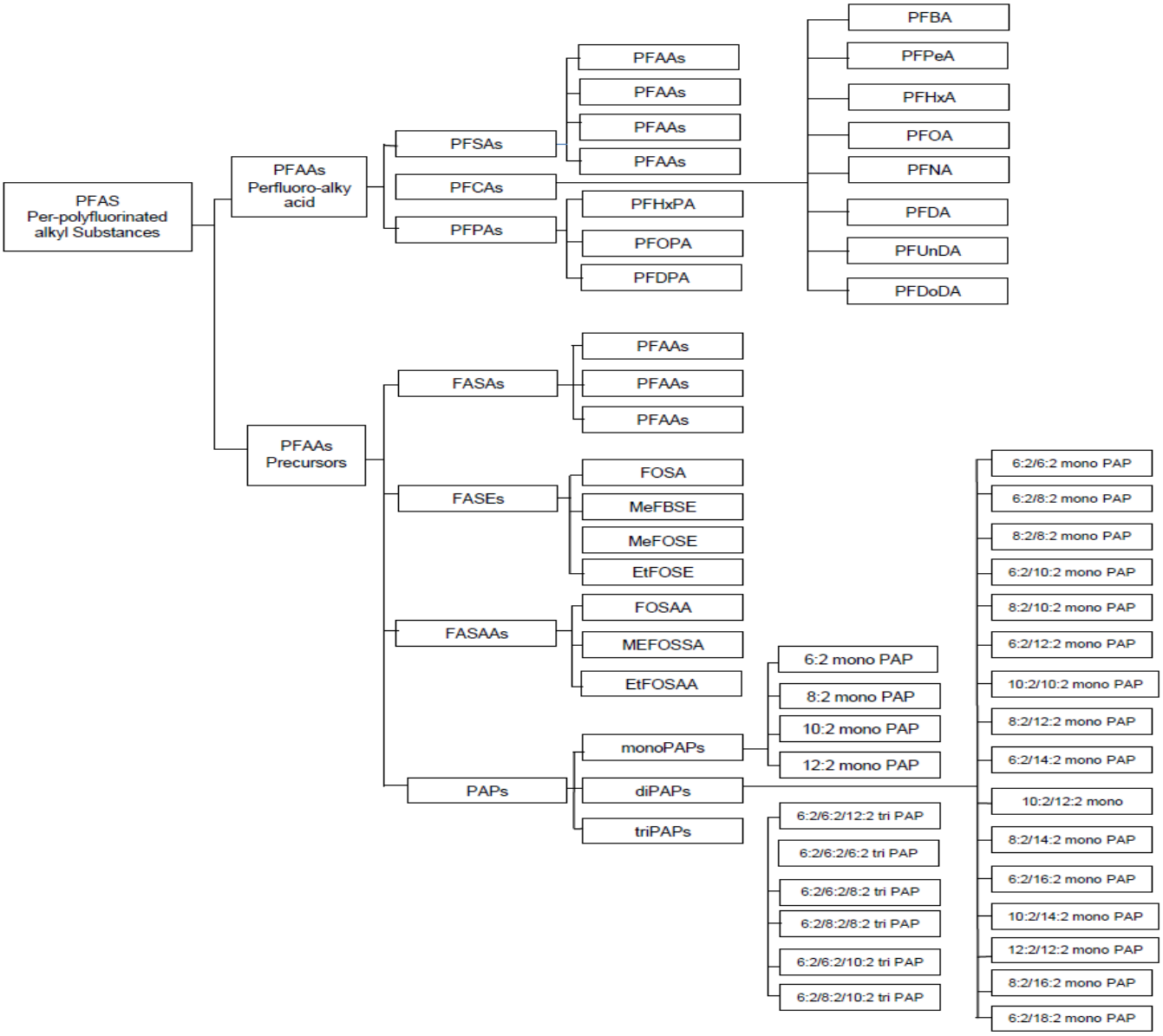


Figure 2.1: Hierarchy tree for PFSA family (Buck et al., 2011)

2.1.1 Perfluorooctanoic acid (PFOA)

PFOA is also a fully fluorinated alkyl compound. The typical structure of PFOA is linear with a carboxylic group at the edge of the chain. PFOA can be produced from breaking down its precursors synthetically. It also appears after degradation of fluorotelomer alcohol in nature. Due to the stability of PFOA in nature, it was found suitable as a constituent in various industrial applications. Similar to the case with PFOS, the availability of PFOA and its derivatives in nature has raised concern due to their detrimental health and environmental implications (Benford et al., 2008).

2.1.2 Perfluorooctane sulfonate (PFOS)

PFOS is a complete fluorinated alkyl compound with eight carbon atoms and sulfonate group at one edge of the chain. PFOS is an end product biochemical degradation of large molecular weight fluorinated alkyl compounds. It is chemically and thermally stable in nature, which explains its bioaccumulation in various environmental and biological components (Post et al., 2012, Carloni, 2009). The presence of surface active properties in PFOS makes it suitable for several applications. According to reports by OECD (2002), PFOS and its precursors were found to be toxic with adverse health implications for exposed organisms. PFOS and its carboxylic compounds (PFOA) have received most attention due to their unique properties (Post et al., 2012). Chemical structure of PFOA and PFOS are presented in Figure 2.2.

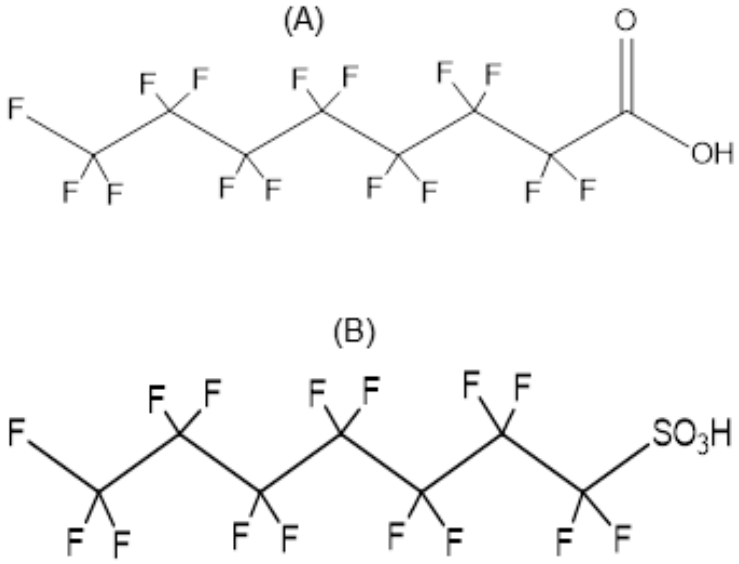


Figure 2.2: Chemical structure of (A) PFOA and (B) PFOS

2.2 PFOA and PFOS Productions Methods

The mass production of PFCs and their derivatives commenced in the late 1940s after World War II, due to their commercial relevance because of a critical need in industry at the time. Demand for PFOA and PFOS as constituents in an array of industrial, agricultural and domestic applications increased, which led to the development of a suitable method of production (Wang et al., 2013). There are two major pathways for the production of PFCs and structurally related compounds.

2.1.1 Electrochemical Fluorination (ECF)

This method was developed by an American scientist and licensed by major manufacturing company 3M to produce PFCs on an industrial scale (3M, 2000). This process is one of the pioneering methods for the production of PFCs on a large and economic scale. Electrochemical fluorination is also known as the fluorination of organic compounds in which anhydrous hydrogen fluoride serves as a precursor. The major products of this reaction are the perfluoroalkyl sulfonyl group ($C_4H_9SO_2F$) and carbonyl fluoride ($C_8H_{17}SO_2F$) (Buck et al., 2011, Wang et al., 2016a). In this process, perfluoroalkylsulfonyl fluoride is the major initiating raw material for the production of fluorinated surfactants. Among the perfluoroalkylsulfonyl fluorides of importance for the process are perfluorobutane sulfonyl (PBSF) to perfluoropentane sulfonyl (PPSF), perfluorohexane sulfonyl fluoride (PHxSF), perfluorooctane sulfonyl fluoride (POSF), and perfluorodecane sulfonyl fluoride (PDSF) (Buck et al., 2011). The production pathway for PFOA and PFOS is illustrated in Figure 2.3.

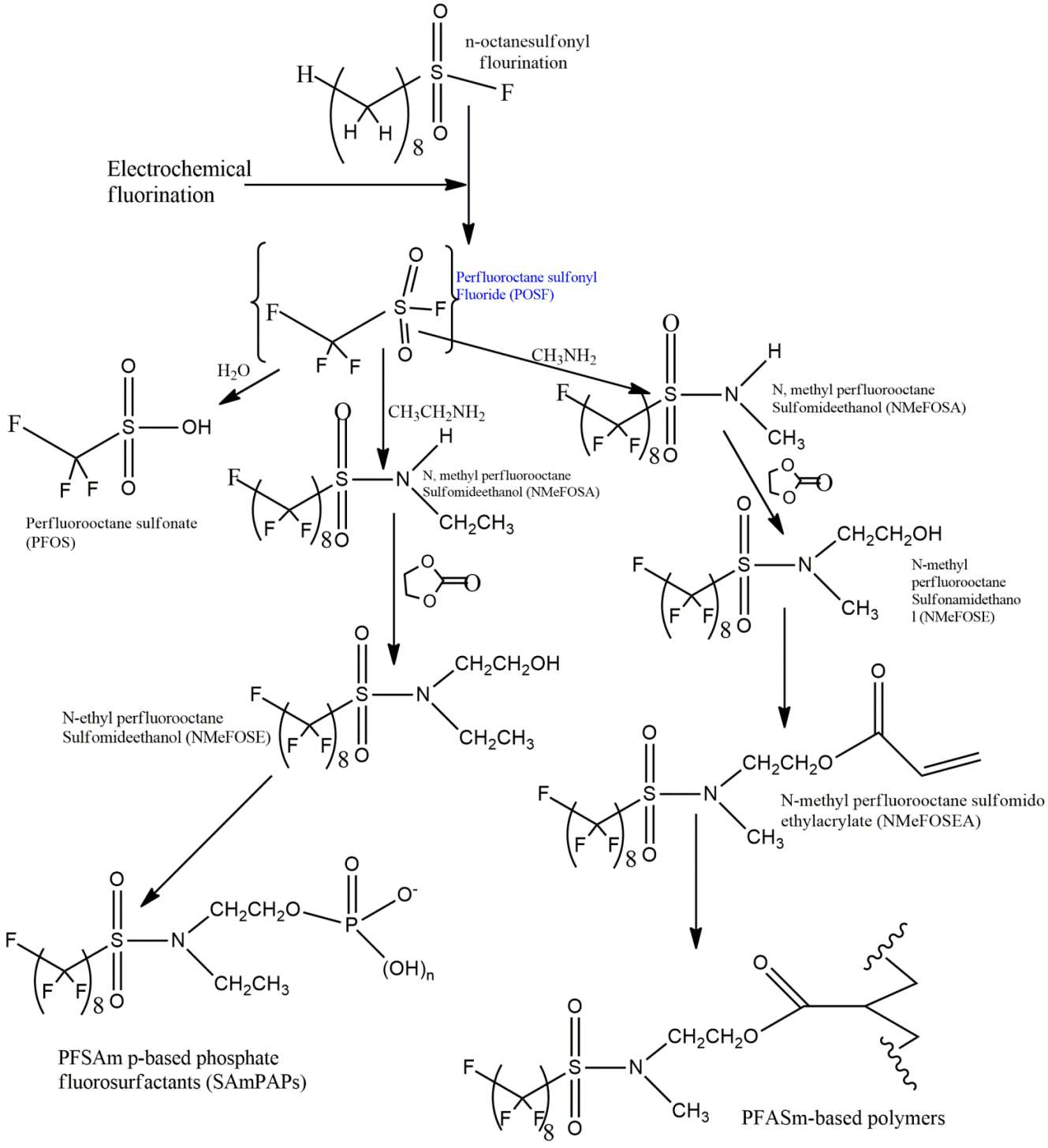


Figure 2.3: Electrochemical fluorination production pathway for PFOA and PFOS (Buck et al., 2011)

2.2.1 Telomerization

Telomerisation is another major production pathway for the syntheses of perfluoroalkyl substances. This production line was initiated by sister company DuPont, USA, for the industrial production of fluorinated compounds (Paul et al., 2008). This reaction process starts with fluoroiodination of tetrafluoroethylene (TFE) to produce pentafluoroiodoethane. This product is then further reacted with varying numbers of C-F carbon chain length for the tetrafluoroethylene (TFE) compound to yield a mixture of corresponding perfluoroalkyl iodide telomers. Homologous fluoroalkyl chains generated during the telomerisation process are linear with even numbers of fluorinated carbons (Paul et al., 2008, Wang et al., 2016b). Simultaneously, oxidation of pentafluoroiodoethane is used to produce corresponding carboxylate, while hydrolysis of perfluoroalkylethyl iodide yields alcohol, which serves as an intermediate for end products like acrylate and methacrylate polymers, ethoxylates, and phosphates (Parsons et al., 2008). Figure 2.4 illustrate telomerization production pathway of PFCs as described by (D'eon & Mabury, 2011).

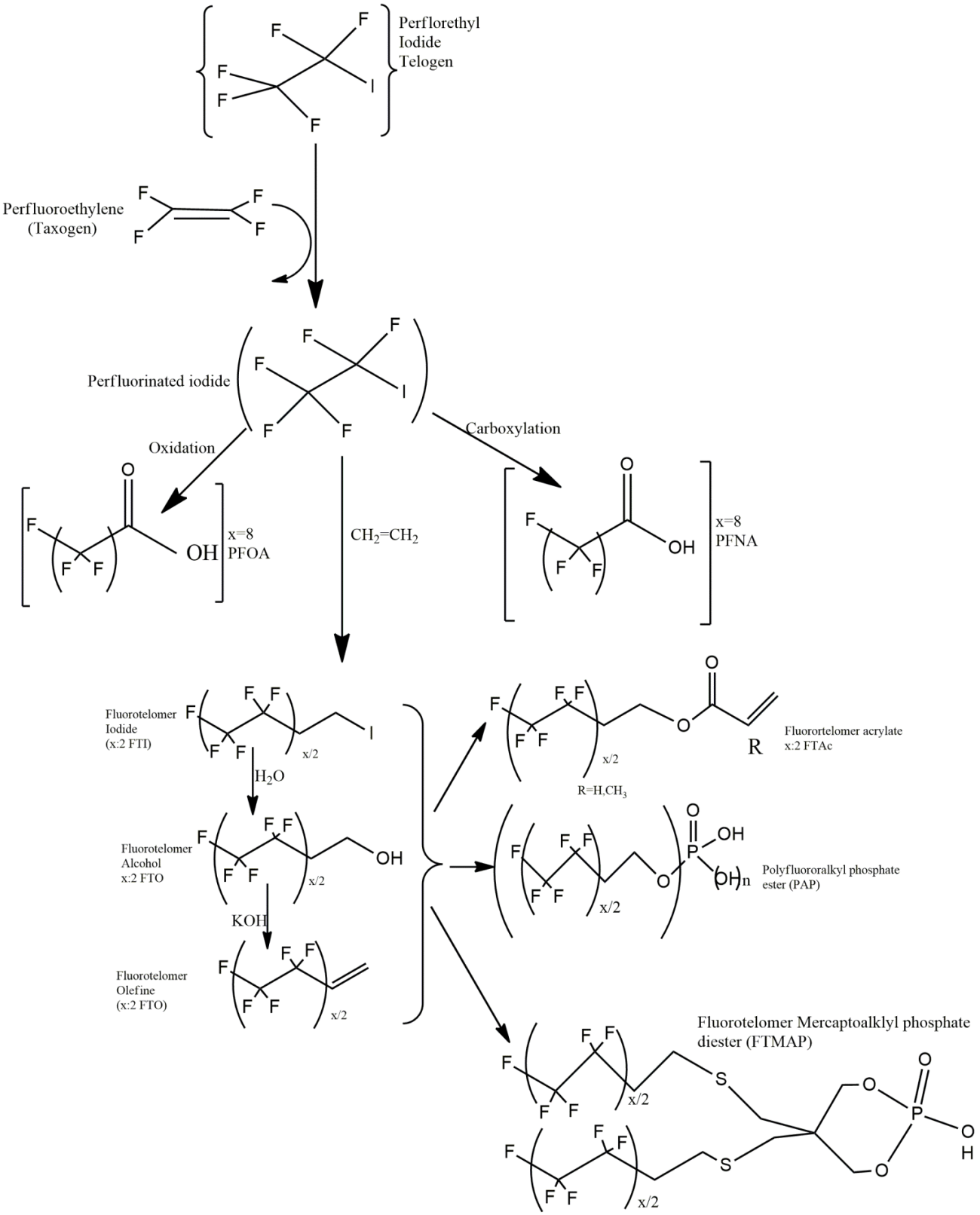


Figure 2.4: Telomerization production pathway of PFCs (D'eon&Mabury, 2011)

The two production pathways are not identical, and the telomerisation process can be contrasted with the electrochemical fluorination (ECF) process in terms of product yield. The end product of the ECF process has a mixture of linear and branched chains of perfluoroalkyl compounds, with both odd and even carbon chain numbers of poly-per fluoroalkyl groups in the system. Meanwhile, the end product of the telomerisation process contain evenly distributed carbon chains (Wang et al., 2016b). At the moment, there is limited information available on the volume of fluorinated alkyl substances produced industrially through both ECF and telomerisation globally (Paul et al., 2008). Currently, most industrial production of PFCs continue to depend on these two processes, whose derivative intermediate substances were perfluorinated sulfonyl and carbonyl fluoride for ECF and telomerisation, respectively (Parsons et al., 2008).

2.3 Physicochemical characteristics of PFCs

The physicochemical characteristics of perfluorinated compounds (PFCs) have been thoroughly explored for their various applications. For instance, the solubility of PFCs in water and in organic solvents is generally low. They possess a hydrophobic chain and lipophobic functional groups which impact on their ability to adsorb onto the surfaces of a variety of materials in different environmental matrices (Wang & Shih, 2011).

The presence of hydrophilic and hydrophobic parts in PFCs leads to the tendency for them to collect at an interface between water and organic solvent or between a liquid and solid surface (Kannan et al., 2002). The distribution of PFCs between octanol and water (K_{ow}), is difficult to determine for these compounds (Kissa, 2001a). Prevedouros et al. (2006) reported that the dissociated acid of perfluorooctane has a negligible vapour pressure, high water solubility and moderate sorption to solids, so accumulation in surface waters is expected. The unique characteristic of PFCs makes them suitable for several applications. A highly polarized C-F bond present is a very strong covalent bond arising from fluorination, and it usually results in strengthening of the adjacent C-C bonds (Kissa, 2001a). Also, substitution of hydrogen for fluorine in perfluorinated surfactants contributes to the persistence of perfluorocarbons relative to hydrocarbon analogs (Liu et al., 2011a). Hence, perfluorinated compounds, especially PFOA and PFOS, are extremely stable and persistent in the environment and are considered almost un-degradable by nature (Post et al., 2012). Physicochemical characteristics of PFOA and PFOS are presented in Table 2.1.

Table 2.1: Physicochemical characteristics of PFOA and PFOS

Physicochemical properties	**PFOA**	**PFOS**
CAS Number	335-67-1	2795-39-3
Physical Description (physical state at room temperature and atmospheric pressure)	White powder/waxy white solid	White Powder
Molecular weight (g/mol)	414	538 (potassium salt)
Water solubility (mg/L at 25 ^{o}C)	9.5 X 10^{3}(purified)	570 (purified) 370 (freshwater), 25 (filtered seawater)
Melting Point (^{o}C)	45 to 50	> 400
Boiling point (^{o}C)	188	Not measurable
Vapor pressure at 20 ^{o}C (mm Hg)	0.017	2.48 X10^{-6}
Air water partition coefficient (Pa.m^{3}/mol)	Not available	< 2 X10^{-6}
Octanol-water partition coefficient (log Kow)	Not measurable	Not measurable
Organic-carbon partition coefficient (log Koc)	2.06	2.57
Henry's law constant (atm m^{3}/mol)	Not measurable	3.05 × 10^{-9}
Half-Life	Atmospheric: 90 days Water: > 92 years (at 25º C) Photolytic: > 349 days Sonolysis: 20 to 63 minutes	Atmospheric: 114 days

Notes: g/mol – grams per mole; mg/l – milligrams per liter; ^{o}C – degree Celsius; mm Hg – millimeters of mercury; Pa m^{3}/mol – pascal-cubic meters per mole; atm m^{3}/mol – atmosphere-cubic meters per mole. (Liang et al., 2016, Benford et al., 2008, USEPA, 2009a)

2.4 Uses of PFCs

The unique characteristics of perfluorinated compounds, notably their high thermal stability and resistance to degradation, have made them suitable for many applications. These include the production of aqueous film-forming foams for fire-fighting activities, hydraulic aviation fuels, chrome plating, and the photography industry. PFCs are also widely used as components of polymers in food packaging, non-stick cookware, surface-active agents in waterproof clothing and stain-resistant carpeting, and as ingredients in some painting materials (Post et al., 2012, Jahnke & Berger, 2009, Prevedouros et al., 2006).

Their unique high surface activity, thermal and acid resistance, hydrophobic and hydrophilic characteristics have been extensively exploited in the electronics, engineering, chemical and medical industries (Lewandowski et al., 2006). The various industrial uses of perfluorinated substances and the derivatives of PFOA and PFOS are presented in Table 2.2.

Table 2.2: Industrial application of perfluorinated compound and derivatives

S/N	Industries	Uses	Reference
1	Aviation, Aerospace and defense	Additives in aviation Hydraulic fluid	Darbra et al. (2011)
2	Automobile	To improve fuel delivery system and to prevent seepage or excess vaporization through the walls	Banks et al. (1994)
3	Biocide	Active ingredient for some plant growth regulators and herbicides, enhance pesticide formulation.	Tsai et al. (2002).
4	Construction products	Coating of architectural materials, fabrics, metal, stones, tiles and additives to paint.	Banks et al. (1994)
5	Fire Fighting	Use as film former and fuel repellant	Wang et al. (2013)
6	Electronics	Insulators, Solder sleeves and flame retardant	Drobny et al. (2008) and Kutz et al. (2011),
7	Household product	Wetting agent or surfactant in product such as floor polishes and cleaning agent, non-stick coating.	Banks et al. (1994),
8	Metal plating	Wetting agent and mist suppressing agent	Darbra et al. (2011)
9	Oil and mining production	Use as surfactant in oil well stimulation	Posner et al. (2013)
10	Food Processing	Fabrication materials	Kutz et al. (2011)
11	Energy	Film to cover solar collectors due to weather variability	Banks et al. (1994)
12	Medical articles	Surgical Patches cardiovascular graft; Raw materials for implant in human body.	Banks et al. (1994), Kutz et al. (2011)
13	Paper and packages	Oil and grease repellant	Kissa et al. (2001b)
14	Textile leather and apparel	Raw materials for highly porous fabrics which serves as oil and water repellant and stain release.	Wang et al. (2015a)

2.5 Sources of PFCs

Perfluorinated compounds (PFCs) are primarily synthetic chemical substances; hence their sources in the environment are largely anthropogenic. These sources include releases from the processes leading to the production of PFCs and derivatives containing these materials (Kim & Kannan, 2007, Becker et al., 2008b, Yamashita et al., 2005, Jin et al., 2007). Loganathan et al. (2007) reported that substantial amounts of PFCs, especially fluoropolymers and perfluorinated alkyl chemicals, are released during PFCs' manufacturing processes. Accidental escape of PFCs into the environment during application to consumer articles may also occur (Prevedouros et al., 2006, Stock et al., 2004). Residual products of the unreacted monomers released during the degradation of fluorotelomer-based compounds may also exacerbate the levels of PFOA and PFOS in the environment (KEMI, 2004 & Lin et al., 2015). Other important pathways for releasing perfluorinated compounds into the environment include the cleaning of PFC surface-treated products, and the use of consumer and industrial products containing PFCs. These are believed to be the principal sources of PFC release into municipal wastewater. However, ineffective removal of PFCs during the wastewater treatment process allows their entry into the aquatic environment and consequently into the aquatic food webs and food chain (Boulanger et al., 2005, Higgins & Luthy, 2006). The release of PFCs into the aquatic systems contaminates not only the water system, but also sediment and soils (Sinclair & Kannan, 2006, Higgins & Luthy, 2006, Hansen et al., 2001). Discarded consumer articles containing perfluorinated substances also contribute to PFCs burden in the environment via leaching from landfills (Boulanger et al., 2005, Stock et al., 2004). Sludge application for soil amendment in agriculture could be a potential source of PFCs in the terrestrial environment (Prevedouros et al., 2006, Higgins & Luthy, 2006); their use in fire-fighting foams also contributes to the occurrence of PFCs in the environment (Prevedouros et al., 2006, Simcik & Dorweiler, 2005). Figure 2.5 is a schematic diagram of sources of PFCs entering the environment. Estimated total global levels of PFAS in the environment between 1950 and 2004 and future estimate of total global levels of PFAS in the environment between 2005 and 2050 are presented in Table 2.3 and Table 2.4 respectively.

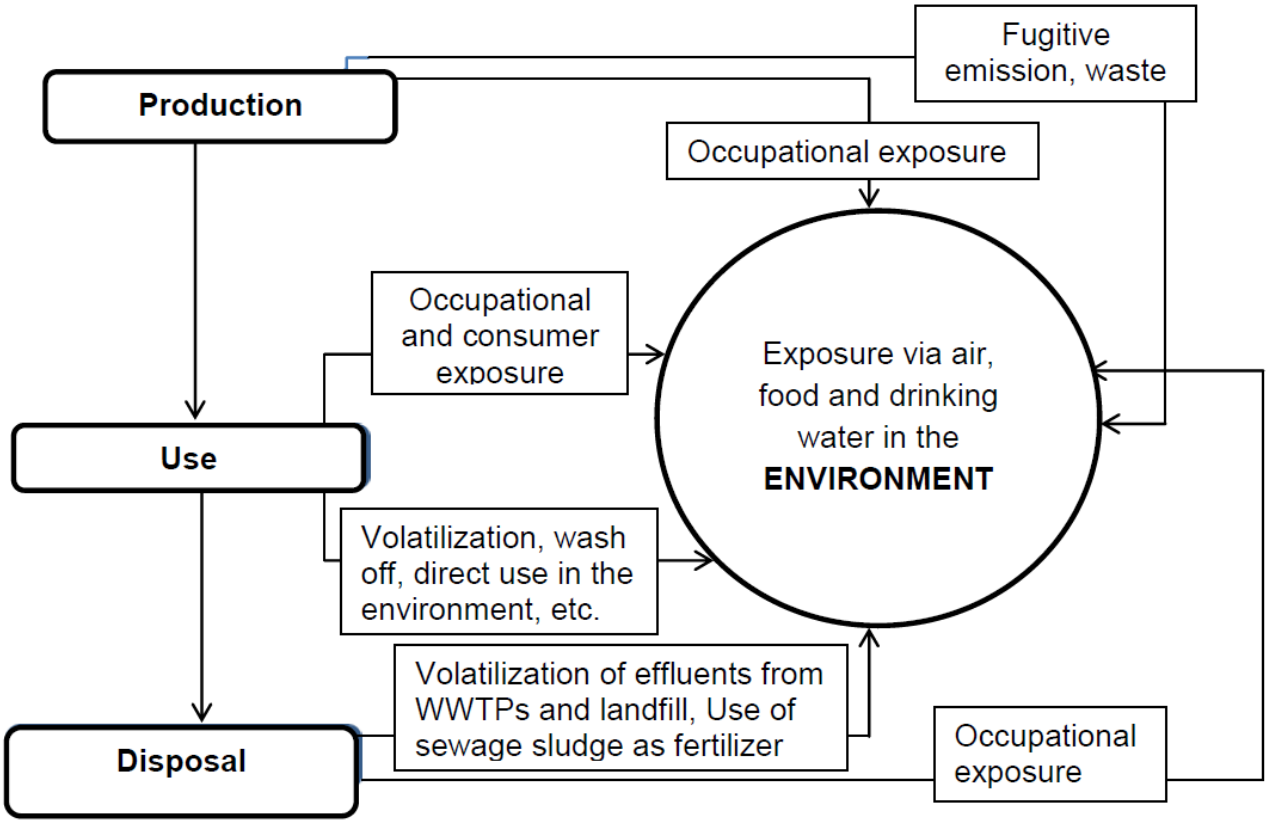


Figure 2.5: Sources of PFCs in the environment (OECD, 2002)

Table 2.3: Estimated total global levels of PFAS in the environment between 1950 and 2004

Environmental Input source	Historical time period (years)	Estimated total global historical PFCA emissions (metric tons)	Estimated total global production (metric tons
Direct PFCA Sources:			
PFCA manufacture			
PFO/APFO	1951-2004	400-700	3600-5700
PFN/APFN	1975-2004	70-20	800-2300
Total manufacture		470-900	4400-8000
Industrial and Consumer Uses			
Fluoropolymer manufacture (APFO)	1951-2004	2000-4000	n/a
Fluoropolymer dispersion processing (APFO)	1951-2004	200-300	n/a
Fluoropolymer manufacture (APFN)	1975-2004	400-1400	n/a
Fluoropolymer processing (APFN)	1975-2004	10-20	n/a
Aqueous fire fighting foams (AFFF)	1965-1974	50-100	n/a
Consumer and industrial products	1960-2000	40-200	n/a
Total direct		3200-6900	
Indirect PFCA Sources:			
POSF-based products			
PFCA residual impurities	1960-2002	20-130	
POSF-based precursor degradation	1960-2002	1-30	
POSF-based AFFF	1970-2002	3-30	
Fluoro-telomer based products			
PFCA residual impurities	1974-2004	0.3-30	
Fluoro-telomer-based precursor degradation	1974-2004	6-130	
Fluorotelomer-based AFFF	1975-2004	< 1	
Total indirect		30-350	
Total source emissions (direct + indirect)	1951-2005	3200-7300	

Ammonium perfluorononoate; APFO = ammonium perfluorooctanoate; ECF = Electrochemical fluorination, a process used to produce fluorinated chemicals; FP = fluoropolymer; FT = fluorotelomer; POSF = perfluorooctanesulfonyl fluoride; PVDF = polyvinylidene fluoride AFFF = aqueous film forming foams (also aqueous fire fighting foams.(Prevedouros et al., 2006, Armitage et al., 2009)

Table 2.4: Estimated total global levels of PFAS in the environment between 2005 and 2050

PFOA emission source	**1950-2004 (min to max) metric tons**	**Percentage of total PFOA emission (average)**	**2005-2050 (min to max) metric tons**	**% of total PFOA emissions (average)**
Direct Sources				
FP manufacturing	2060-4090	72.3%	410-815	86.0%
(APFO)				
APFO manufacturing	370-590	11.8%	20-40	4.2%
FP dispersion	215-340	6.8%	45-75	8.7%
(APFO)				
AFFF-ECF	50-100	1.8%	0	0%
FP manufacturing	3-10	0.1%	<1.2	0.1%
(APFN)				
Consumer &	2-10	0.1%	0	0%
Industrial Products				
APFN manufacturing	1-2	0%	<1	0%
PVDF (APFN)	<1	0%	<1	0%
Total direct sources	2700-5140	92.9%	475-932	99.0%
Indirect sources				
POSF raw material	4-585	5.0%	0	0%
Degradation				
POSF impurities	14-110	1.2%	0	0%
POSF-AFFFs	2-23	0.2%	0	0
FT raw material	3-60	0.6%	1-14	0.8%
Degradation				
FT impurities	<1-17	0.1%	<1-4	0.2%
Total Indirect sources	**23-795**	**7.1%**	**1-18**	**1.0%**
Total Indirect and Direct sources	**2723-5935**	**100%**	**476-950**	**100.0%**

AFFF = aqueous film forming foams (also aqueous fire fighting foams); APFN = ammonium perfluorononoate; APFO = ammonium perfluorooctanoate; ECF = electrochemical fluorination, a process used to produce fluorinated chemicals; FP = fluoropolymer; FT = fluorotelomer; POSF = perfluorooctanesulfonyl fluoride; PVDF = polyvinylidene fluoride. (Armitage et al., 2009).

2.6 Distribution of PFCs in the environment

The distribution of perfluorinated compounds such as PFOA and PFOS into various environmental matrices, such as air, water, plants material, and wastewaters has been reported (Kim & Kannan, 2007, Nakata et al., 2006, Saito et al., 2003, Taniyasu et al., 2003). Figure 2 6 depict the distribution and movement of derivatives of PFCs into various environmental compartments (Hradkova et al., 2010).

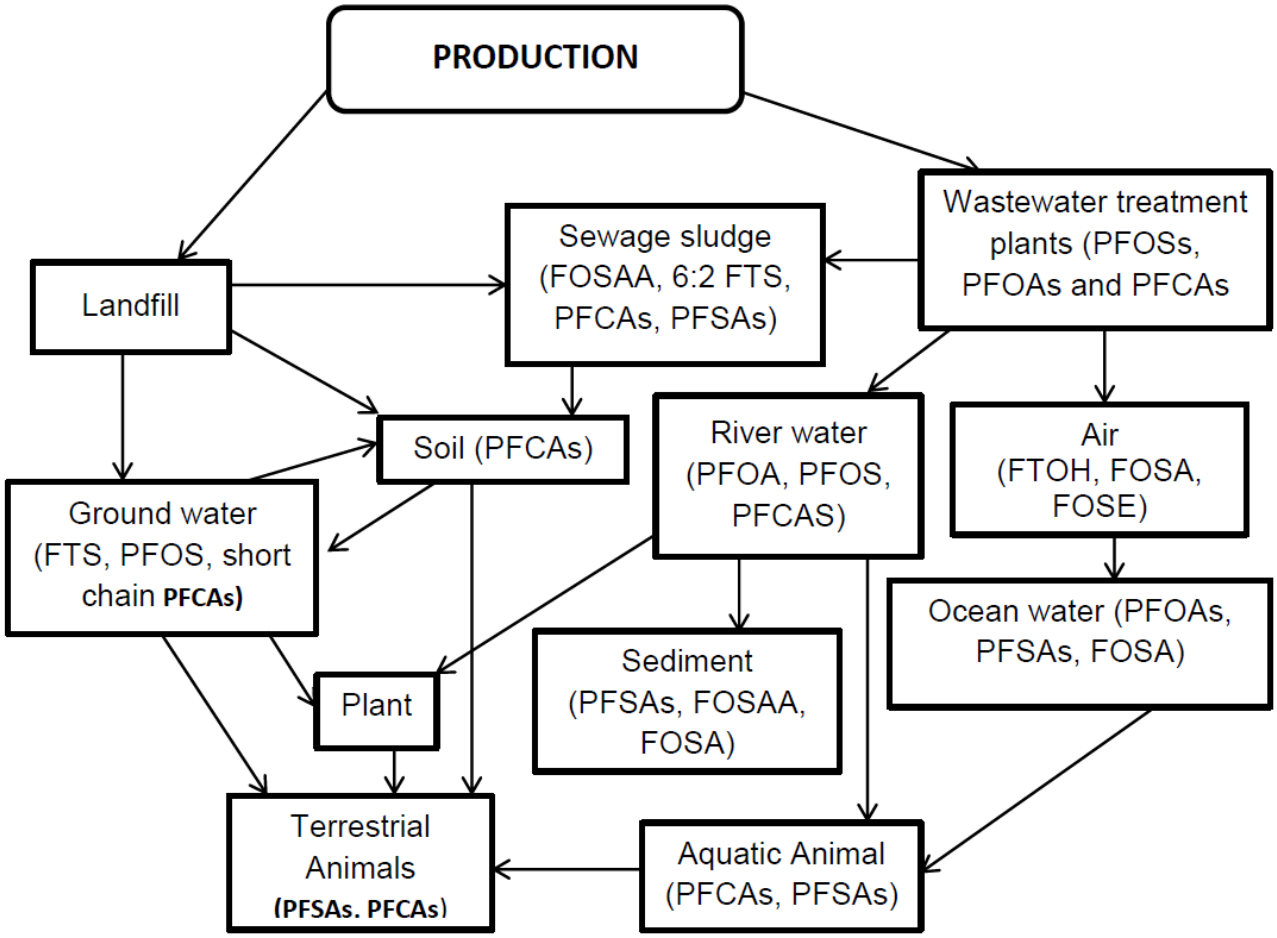


Figure 2 6: Distribution of PFCs in the environmental matrices (adapted from Hradkova et al. (2010)

PFT: Perflouro telomers, FOSAA: Perfluorooctane sulfonamidoacetic acid,
FOSA: Perfluoro-1-octansulfonamide, FOSE: Perfluorooctane sulfonamide ethanol,
FTOH: Fluorinated telomer alcohol, PFSA: Perfluorinated sulfonates amide,
PFCAs: Perfluoroalkylcarboxylic acids

2.6.1 PFCs in Water

The aquatic environment is described as the largest reservoir and sinks for organic and inorganic pollutants. It is highly susceptible to pollution through exposure to environmental contaminants. PFCs find their way into the aquatic environment from several sources (Xiao et al., 2014). Elevated levels of PFOA and PFOS have been reported in various water bodies globally (Rankin et al., 2016, Parsons et al., 2008, Paul et al., 2008). These water bodies include surface water, ground water, wastewater, drinking water, sea water and water in the polar region (Post et al., 2012). The availability of PFCs in water bodies is attributable to their moderate solubility in water, as compared to the low water solubility of most organic contaminants (Prevedouros et al., 2006). Monitoring the PFCs in water bodies can enable calculation of the levels of their presence in the aquatic system. Various reports on the levels of PFOA and PFOS in water bodies have been published (Skutlarek et al., 2006, Naile et al., 2010, So et al., 2007). A study on levels of PFOA and PFOS in environmental and tap water samples in China showed trace concentration (10 ng/l) in tap water in China, while the maximum levels of PFCs in the Yangtze river were 110.6 and 297.5 ng/l, indicating moderately polluted river (Jin et al., 2009). A similar study conducted by Wang et al. (2012) compared the level of PFCs in different surface waters in relation to their proximity to industrialisation. It was revealed that the magnitude of mass flow of PFOA and PFOS decrease with distance away from manufacturing plants, while locations close to industrial plants had a relatively greater concentration of PFCs (Wang et al., 2012)

2.6.2 PFCs in sediment

Sediment has been identified as an important sink and reservoir for a number of environmental pollutants, including PFCs. Studies have shown a correlation between levels of PFCs in the water and the corresponding sediment sample from the same aquatic environment (Chen et al., 2012a). PFCs have been reported in the sediment matrix globally; for example, occurrence of PFOS were reported in sediment samples obtained from Kamogawa River in Japan with levels, ranging between <0.33-11 ng/g dry weight (dw) (Takazawa et al., 2009). In another study in China, Yang et al., (2011) investigated the occurrence of PFCs in surface water and sediment collected from Liao River and Taihu Lake. This study revealed that the levels of PFOS and long chain PFCAs in sediments were much higher than the levels measured in surface water, indicating preferential partition into the sediment compartment.

A similar study was conducted by Pico et al. (2012) to investigate the occurrence of PFCs in water and sediment samples in l'Albufera nature park, Spain. Levels of PFOS in sediments

ranged from 0.10 to 4.80 ng/g dry weight, and levels of PFOA in sediment were from 0.004 to 1.24 ng/g. The sediment–water distribution coefficients (log K_D) in the study ranged between 2.31 and 4.51. This study serves as an environmental benchmark level for PFCs in an unpolluted environment (Pico et al., 2012). In another study by Chen et al., (2011a) PFCs were detected in sediment samples from Bohai Sea off the northern coast of China. Levels of PFOA and PFOS ranged between <0.1 to 2.0 ng/ng^{-1} dry weight and <0.1 to 0.5 ng/ng^{-1} dry weight, respectively. The study established the availability of PFCs in the river system (Chen et al., 2011a). Sediment remains an important compartment of the aquatic system that has the capacity to retain residues of organic pollutants such as PFCs and related organic contaminants.

2.6.3 PFCs in Soil

Levels of PFCs in soil can be measured to determine the load of PFCs in a specific environment. A high concentration of PFCs in the soil has environmental implications that can be used to predict the level of pollution in the vicinity. Although perfluorinated compounds have been reported to adhere poorly to soil surface relative to sediment in the aquatic environment (Chen et al., 2012a), the vast areas of exposed land mean that soil is highly susceptible to pollution associated with organic contaminants. For example, levels of PFCs were detected in soil collected from the vicinity of the fluorine Industry Park in China, with a maximum concentration of 3.14 ng/g. The report suggests that direct emission from manufacturing plants is a major source of PFCs in the soil (Wang et al., 2016a). However, the study also shows that not all cases of organic contamination lead to PFC pollution. For instance, soil contamination was reported in farm land in Germany, where soil conditioner pollutes agricultural soil in various provinces. Levels of PFOA and PFOS were below the detection limit, which implies low PFC adherence to the soil (Yang et al., 2016, Wilhelm et al., 2010). Elevated levels of PFCs in soil could lead to bioaccumulation in plants and living organisms (Jin et al., 2009)

2.6.4 PFCs in the Atmosphere

Atmospheric deposition of organic pollutants has been reported as another threat to the living environment. But determination of PFCs in an atmospheric sample could be quite a challenging exercise due to their physicochemical characteristics. PFCs are moderately soluble in liquid phase (water), a characteristic that tends to encourage PFCs binding into particulate substances present in the atmosphere.

Chaemfa et al. (2010) measured the levels of PFOA and PFOS in the atmosphere of selected areas in Europe using air samplers. They found levels of PFOA ranging between 200-27,000 cm^3 per day, and of PFOS of 1.5-720 cm^3 per day (Chaemfa et al., 2010). Shoeib et al. (2010) conducted a similar survey to monitor atmospheric level of PFCs in the atmosphere over the northeast Atlantic Ocean, and reported PFCs levels ranged between 1.6 and 156 cm^3 per day. The elevated levels of PFCs in most polluted site in the study was associated with air masses that originated over the Atlantic Ocean (Shoeib et al., 2010). However, limited data is available on the level of PFCs in the atmosphere.

2.6.5 PFCs in plants

Studies on levels of PFCs in crops and plant materials are rarely reported in the literature. An investigation was conducted by the Ministry of the Environment in North Rhine-Westphalia in Germany to assess levels of PFCs in various crops grown on farmlands. Crops including maize, grass, rapeseed, black salsify and wheat were studied in areas contaminated by pollution, but levels of PFCs were below the detection limit (Wilhelm et al., 2010).

In a recent study conducted by Bizkarguenaga et al. (2016), PFOA, PFOS, and FOSA were shown to have been absorbed by agricultural crops (lettuce and carrots) that were planted on compost amended soil. The study revealed that PFOA was taken up in the translocation stream and accumulated to a greater degree than PFOS in the lettuce plant. FOSA was degraded to a minimum level below the detection limit. However, in an earlier study, Stahl et al. (2009) reported the bioaccumulation of PFCs in plants for the first time. Significant concentrations of PFCs were transferred from the soil medium into plants (‘carry over’). This study revealed that higher concentrations of PFOA and PFOS in the soil corresponded to the higher concentrations detected in the plant samples.

Biomagnification due to the uptake and storage of PFCs in the vegetative parts of the plants could pose a more serious threat to higher organisms than the transfer of PFCs within the plant’s physiology. Plant uptake, distribution, and storage of PFCs are dependent on the type of plant. The uptake of PFCs from contaminated soil is a potential route of exposure for the food chain, because the substances ultimately end up in higher animals, including humans. This provides an explanation for the presence of PFCs in higher organisms in the food chain.

2.6.6 PFCs in Biota

The presence of PFCs has been reported in various biological samples globally (Armitage et al., 2009). The availability of PFCs in microorganisms and various animal tissues has been attributed to biomagnification via the food chain. Levels of PFCs were reported in various marine and freshwater organisms, especially fishes and sea animals (Berger et al., 2009). Giesy & Kannan, (2002b) conducted a survey to establish the distribution of PFCs in animals in remote locations across the world, covering North America, Europe, the Arctic and the North Pacific oceans. Results were compared to levels of PFCs found in animals from industrial regions of the world. The findings showed that trace levels of PFOS were detected in some of the animals from the remote locations investigated. Other studies established the levels of PFCs in various animals in different environmental matrices (Mhadhbi, et al. 2012, He et al., 2016 & Surma et al 2015b). One study found elevated concentration for PFOS, ranging between 0.47 and 178.55 ng/g, in the liver of fish-eating animals in the vicinity of a fluorotelomer plant in Belgium (Hoffman et al., 2010b).

2.7 Biodegradation of PFC in the environment

PFCs are chemically and biologically stable in the environment. They are resistant to biodegradation, atmospheric photo-oxidation, direct photolysis, and hydrolysis as a result of their strong C-F bon (EFSA, 2008). Studies reveal that some PFCs used in the manufacturing of surface protection products such as 2(N-ethylperfluorooctane sulfonamido) ethanol (N-EtFOSE), can be degraded into PFOS and other PFC metabolites within 25 days in an aerobic wastewater treatment sludge transformer. Empirical data showed that the aerobic incubation of soil with fluorotelomer-based polymer yields residues of 8:2 fluorotelomer alcohol (FTOH) and PFOA, which is attributed to the degradation. However, the half-life of the 8:2 FTOH was estimated to be approximately 28 days (Koch et al., 2007). In another study, anaerobic biodegradation of N-EtFOSE showed no degradation, while that in aerobic medium yielded PFOA in the by-product (Boulanger et al., 2005).

According to Ellis at al. (2004), the atmospheric degradation of fluorotelomer alcohols by hydroxyl radical yields perfluorinated carboxylic acids, while the reaction of hydroxyl radical with 8:2 fluorotelomer alcohol in aqueous systems shows no evidence of the direct photolysis of the fluorotelomer alcohol (Ellis et al., 2004). The major products formed were 8:2 fluorotelomer aldehyde and acid, and PFOA (Gauthier & Mabury, 2005). Thus a possible pathway for degradation of 8:2 fluorotelomer alcohols may result in the production of PFOA, while it has been reported that degradation of 2(N-ethyl perfluorooctane sulfonamido)

ethanol (N-EtFOSE) in an aerobic sludge yields PFOA and PFOS (Wang et al., 2005, Rhodes et al., 2007).

Rhodes et al. (2007) reported that PFC surfactants such as PFOS, PFOA, and nonionic surfactants including partially fluorinated alkyl ethoxylates, perfluorooctane sulfonyl-amidopoly ethoxylate, and perfluorooctane sulfonyl-amidopoly ethoxylate methyl ether, showed no degradation when incubated under aerobic and anaerobic conditions.

Hori et al. (2004) also reported the decomposition of PFOA in an ion exchange membrane to fluoride ions using zerovalent metal in subcritical water. When the membrane and iron powder were heated in subcritical water at 350 ^{o}C for 17 h, 73.2 % of the fluorine content in the initial membrane was successfully transformed to F^- ion indicating effective decomposition. Furthermore, oxidative decomposition of PFOS in water using permanganate has been attempted, at 65 ^{o}C and pH 4.2. As much as 46.8 % of the PFOS was decomposed to yield 5.3 % of F^- and 36.9 % of SO_4^{2-}. It was also noted that the oxidative decomposition of PFOS occurred more readily in acidic conditions (Li et al., 2010).

2.8 Routes of exposure

The presence of PFCs in different organisms is attributable to some identifiable route of exposure such as food consumption. PFCs can be ingested from contaminated foodstuff and polluted water. PFCs have been detected in various foods items, including meat, milk products, fish, vegetables and grains. Residual PFCs can apparently be picked up from contaminated environmental media such as air, soil and water, etc. (Yang et al., 2011). The consumption of contaminated water and food is a major route of exposure to PFOA and PFOS. Sources of PFCs in food include leaching from cookware, food wrapper and microwave popcorn bags made of perfluorinated substances during microwave heating or other contact (Sinclair & Kannan, 2006). Canned food items have been also reported to have considerable levels of PFOA and PFOS (Tittlemier et al., 2007). Several other routes of exposure to PFCs include dermal exposure identified as an unsuspected possible route via contaminated air (Woodruff & Sutton, 2014a, Woodruff & Sutton, 2014b). Occupational exposure to PFCs through inhalation has also been listed as an exposure route (COT, 2006).

In a study conducted by Burris et al. (2001) for 3M Company, it was suggested that inhalation of contaminated dust in the work environment is an important contributor to human exposure. Another study revealed that children may also be at risk to PFCs contamination via toys and materials made from PFCS in the home, classroom and playground (Goosey &

Harrad, 2011). Finally, PFCs have the potential to be available in surface water, wastewater and to accumulate in sediment (Xiao et al., 2013, Eschauzier et al., 2012, Ahrens et al., 2011, Weinberg et al., 2011, Giesy & Kannan, 2002b). Fish and animal foods sourced from contaminated water bodies, could bioaccumulate perfluorinated compounds and consequently induce various environmental and health effects.

2.9 Ecological Implications of PFCs

Bioaccumulation and bio-magnification of PFCs in plant and animal tissues have been identified as transition pathways in the ecological cycle (Gebbink et al., 2016, Xu et al., 2014). PFCs were regularly detected in the serum and tissues of animals via accumulation in the tissues. This is attributed to their consumption of food and drinking of water contaminated with PFCs (Wang et al., 2015b). In order to access the accumulation profile of PFCs in the exposed organisms, individual tissues and organs such as liver, kidney, serum and the whole organism (depending on its size) were analysed. Studies showed that higher concentrations of PFCs (especially PFOA and PFOS) were detected in sediment when compared to the level in water (Ahrens et al., 2015), and higher levels in tissues such as liver and serum relative to other tissues (Gallo et al., 2012).

In a recent study, bioaccumulation of emerging organic compounds including 20 perflouroalkyl substances on soil invertebrate *Eisenia Andrei* (earth worm) was investigated. Bio solid amendment for PFAS increased the concentration from 1.5, 14 fold, and the mean bioaccumulation factor ranged from 2.2 to 198 l/kg (Zheng et al., 2016b). In another study, the bioaccumulation potential of mussels was assessed. Experimental organisms were exposed to varied concentrations of PFCs ranging between 1 $\mu g l^{-1}$ and 10 $\mu g l^{-1}$ for 56 days. The result showed that the bioaccumulation factor (BF) ranged from 15 to 859 l/kg and from 12 to 473 l/kg at 1 $\mu g l^{-1}$ and 10 $\mu g l^{-1}$ for PFOA and PFOS respectively. The study therefore established the bioaccumulation potential of PFCs in aquatic organisms in an aquatic system (Liu et al., 2011a). Bioaccumulation and bio-magnification are responsible for the transfer of PFCs in biota, leading to increased accumulation of organic contaminants among higher organisms in the food chain, including humans (Zeng et al., 2015).

Generally, ecotoxicological studies on PFCs have been based on laboratory organisms being exposed to PFCs at varying concentrations to support their findings. Most reports show that the organism's exposure to PFCs may lead to hepatomegaly and hepatic peroxisome proliferation; liver, testicular (*Leydig* cell), and pancreatic tumors (*acinar* cell), reproductive and developmental deficits; neurotoxicity; and immunotoxicity in exposed organisms etc. (DeWitt et al., 2014).

Zhou et al. (2016) studied the toxicity effect of PFOA on wheat (*Triticum Aestivum L*.). Germination and seedling growth were investigated by conducting a germination trial and a pot trial. The study showed that PFOA had a stimulatory effect on growth and shoot length at <0.2 mg/kg, and an inhibiting of germination rate index of the shoot and root by >800 mg/kg.

In another study conducted by He et al. (2016) on the toxicity of PFOA to earthworms and their enzymatic activities in the soil, PFOA was observed to cause inhibition of all the measurable microbial processes in a dose-dependent manner. There was no mortality in earthworms exposed to 100 mg.kg of PFOA, the weight of the earthworm significantly reduced from 25 mg/kg. Elevated levels of PFCs are potentially toxic to biodiversity in ecological systems.

2.10 Epidemiological Studies of PFCs

Epidemiological studies provide a crucial link between PFCs and human health risk. It has been reported that PFOA and PFOS have a high affinity for binding B-lipoproteins and liver fatty acid-binding protein in animal tissues. Furthermore, PFOS may induce DNA breakage and affect DNA repairs, thereby disturbing the homeostasis of the metabolism (Hoff et al., 2003). It has been reported that there is a possibility of PFOS interfering with the metabolism of fatty acid, thereby deregulating lipids and lipoproteins' metabolism (EFSA, 2008b, Kabir et al., 2015).

Wielsoe et al. (2015) have studied the carcinogenic effect of selected PFCs, including PFHxS, PFOS, PFOA, PFNA, PFDA, PFUnA, and PFDoA. The study established the potential mode of action of these chemicals through the generation of oxidative stress-induced DNA damage and the ability to alter total antioxidant capacity.

Previously, Bonefeld-Jorgensen et al. (2011) conducted a study to investigate the level of PFAS including PFOA and PFOS in the blood serum of breast cancer patients. The result obtained was compared with that of healthy individuals. It was established that exposure to PFOS and PFOA constituted a significantly higher risk factor for cancer. A similar study showed similar trend, suggesting PFOS and PFOA as potential breast cancer risk factors (Bach et al., 2015).

2.11 Health risk assessment of PFCs

Health risk assessment of PFCs is needed in order to assess the health impact of PFC pollution in the environment. PFOA and PFOS have consistently been reported as potential environmental toxicants that may trigger health problems in exposed organisms, which

include humans, animals and other biota. Consumption of fish, animal products and drinking PFC-contaminated water could severely affect human health (Valsecchi et al., 2016). Adverse health and systemic effects of a high dosage of PFCs have been observed in rodents acutely exposed in a study. The liver and serum are the main body tissue types affected during PFC contamination in the study (Austin et al., 2003). The health implications of PFC contamination in exposed animals include hepatotoxicity, developmental toxicity, immune toxicity, neurotoxicity, endocrine toxicity, gene toxicity and tumorigenic potential, among others (Han et al., 2012). Similarly, sub-chronic exposure to doses of PFOS or PFOA could suppress various aspects of adaptive immunity in the organism (DeWitt et al., 2009, Dong et al., 2012). The exposure of tilapia fish (*Oreochromis niloticus*) to concentrations of PFCs was reported to cause a significant increase in the concentration of PFOS (1100 ng/g wet weight) and PFOA (3673 µg/Kg) in the tissue of mullet bile fish (Teng et al., 2009).

Other studies revealed that exposure of developing foetuses and infants to PFOA and PFOS have the tendency to be transferred from parent to offspring via movement through the placenta (Midasch et al., 2007 & Kim et al., 2011). In a similar study, a correlation was found between PFOA and PFOS levels in cord serum and reduced birth weight, ponderal index, and head circumference of infants (Washino et al., 2009, Apelberg et al., 2007). Studies have also revealed that the associations between PFOA and PFOS in an exposed organism could affect sperm quality (Joensen et al., 2009) and changes in adult thyroid hormone levels (Dallaire et al., 2009) of laboratory animals.

Through the risk assessment of PFCs in the ecosystem, PFOA and PFOS have received attention globally, especially the environmental and health threat that they pose to living organisms. This has prompted action by international regulatory organisations, including the U.S. Environmental Protection Agency (USEPA), UNEP, EU, Environment Canada, among others, to draft human health risk assessments of selected PFCs and their precursors. This development has led to the enactment of standard regulatory guidelines in most developed nations (DeWitt et al., 2014). Due to the potential health effect of PFCs, certain limits have been published by regulatory bodies. Table 2.5 shows the acceptable limits of PFOA and PFOS set by regulatory agents for drinking water and some consumer products.

Table 2.5: Recommended tolerable limit of PFOA and PFOS

Recommended tolerable intake levels in water and food by some regulatory bodies	**PFOA**	**PFOS**	**Reference**
US Environmental Protection Agency (Lifetime Health Advisory Limit)	70 ng/l	70 ng/l	USEPA, (2016)
US Environmental Protection Agency (drinking water)	400 ng/l	200 ng/l	USEPA, (2009)
Predicted No Effect Concentration ($PNEC_{UKEA}$)	2500 ng/l	2500 ng/l	Clarke et al. (2010)
Department of Water council ($DWC_{Germany}$)	300 ng/l	300 ng/l	EFSA, (2008a)
Minnesota Department of Health (drinking water)	300 ng/l	300 ng/l	Xiao et al.(2015)
New Jersey Department of Environmental Protection (drinking water)	400 ng/l	200 ng/l	Post et al. (2009)
Drinking Water Commission of German Ministry of Health (drinking water)	1000 ng/l	10000 ng/l	Wilhelm et al. (2010)
European Food Safety Authority (food)	1500 ng/kg	1500 ng/kg	EFSA, (2008a)
UK Committee on Toxicity in Food, Consumer Products and the Environment (food)	3000 ng/kg	3000 ng/kg	Clarke et al. (2010)
German Federal Institute for Risk Assessment (food)	1000 g/kg	1000 ng/kg	Domingo, (2012)

2.12 Regulations and Standard Guidelines for PFCs

Standard regulations and guidelines to check the on-going production and release of PFCs including PFOA and PFOS into the environment have been suggested by independent researchers and various international environmental and health organisations. Among developing nations, including sub-Saharan and Caribbean nations, only a few have responded to the call to restrict the production and application of PFCs, and many countries still lack legislations on PFCs.

The Organisation for Economic Co-operation and Development (OECD) stated that over 600 PFCs were in use across the world in 2007 alone, with two new PFCs being introduced into the chemical family every year. It was estimated that about 750 tons of PFCs were in use in various industrial and domestic applications globally in 2014 (OECD, 2014). According to the screening criteria for persistent organic pollutants (POPs) under the Stockholm Convention, PFOS and its salts together with its precursor, perfluorooctane sulfonyl fluoride (PFOSF), were added to Annex B of the Convention as an organic pollutant with consequently restricted use worldwide (UNEP, 2009). PFOS meets the European Union (EU) criteria for Persistent and Very Persistent Organics. Thus, 183 additional PFOS-related substances with carbon chain lengths of five carbons and higher have been amended to the status of persistent organic pollutant (UNEP, 2009). USEPA's office of water therefore issued a provisional health advisory (PHA) of 0.2 µg/l for PFOS and 0.4 µg/l for PFOA to protect against the potential risks resulting from exposure to this chemical through drinking water (USEPA, 2009). The UK's public health guideline limits for PFOS are 0.3 µg/l and for PFOA are 10 µg/l (UKEA, 2004). Environment Canada (EC) prohibited the importation and manufacture of four fluorotelomer-based compounds from 2004 and in 2006 a proposal was published placing a permanent ban on these four compounds in Canada (EC, 2012). Few states have legislative policies for the use of PFCs and its derivatives, but none from developing countries. There are no known published set limits for perfluorinated compounds in environmental matrices in South Africa.

The build-up of PFCs in the biological component and in different environmental systems has been deemed to have potentially deleterious consequences. There is a need to set limits and guidelines that can be used to reduce levels in the environment and protect human and environmental health. Such guidelines and standards to check the continuous production and release of PFOA and PFOS into the environment have been suggested by various international environmental and health organizations. Regulations and standards for PFOA and PFOS for selected countries are presented in Table 2.6**.**

Table 2.6: Regulations and standard guidelines for PFOA and PFOS in selected countries.

Country	Action	Proposed	Effective date
Canada	Voluntary Environmental performance agreement respecting PFCAs and their precursors in perfluorochemical products sold in Canada.Proposed Risk Management Approach for Perfluorooctanoic acid (PFOA), its salts, and its precursors and long-chain (C9–C20) perfluorocarboxylic acids (PFCAs), their salts and precursors.	Mar 30, 2010, August, 2012	Dec 31, 2015, Pending
U.S	2010/15 PFOA Stewardship Program Significant New Use Rules (SNUR): Perfluoroalkyl sulfonates and long-chain perfluoroalkyl carboxylate chemical substances	January, 2006, August 15, 2012	Dec 31, 2015, Pending
Russia	Ammonium perfluorononanoate (APFO, CAS Nr. 41349-60-4) is regulated in occupational air with a tentative safe exposure level of 0.05 mg/m^3 (Hygiene Norm 2.2.5.2308-07). A number of short- and middle chain PFASs are regulated in occupational air and water, and are generally referred to as low hazardous substances.	Not Indicated	Pending
Norway	Proposed regulations to restrict the production, import, export or sale of consumer products that contain PFOA in consumer products if they exceed certain limit values.	Dec 20, 2011	Pending
Germany	Proposed quality standards and reduction targets applicable to water bodies, wastewater, and soils to be introduced with respect to PFASs.	July, 2007 (first draft); Revised in July, 2009	Pending
European Union	C_{11}–C_{14} PFCAs listed as vPvB-substances on REACH candidate list (Substances of Very High Concern); proposal to list PFOA as well	May, 2009	Dec, 2012; June, 2013

Adapted from: Organisation for Economic Co-operation and Development (OECD) data, (OECD, 2002)

2.13 Water quality parameters

Water resources conservation has been a major priority for various government bodies, international regulatory and non-governmental organizations with the aim of protecting water resources from possible contamination due to the intrusion of various organic pollutants including PFCs (Bagatin et al. 2014). The extent of pollution in aquatic environments can be established from water quality parameters index (WHO, 2014). Hence, water quality parameters are such as pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), and salinity may influence occurrence PFCs in aquatic systems (Weinberg et al., 2011).

2.13.1 Surface water pH

Among water quality parameters, pH is a numerical scale that is used to specify the acidity or alkalinity of an aqueous solution (Roberts & Thomas, 2006). Variety of human activities in the environment such domestic activities, urban development, agriculture, industrial activities; mining and exploration industries, among others have the potential to pollute ecological systems thereby altering the pH of environmental components such as water, soil and sediment etc. (Evans et al., 2005). Therefore, pH is among the water quality parameters that may be used to determine the degree of environmental degradation. The pH of environmental samples may influence the biological and chemical species in an ecosystem and may predict the potential toxicities of chemical species in such environment (Qiao et al., 2016). Deviation in pH from neutral could lead to significant changes in water quality that could consequently stress the living organism available in the ecological system. In South Africa, average pH of surface water range between 6 to 8 (Igbinosa & Okoh, 2009). A considerable large population of freshwater organisms survives at water pH ranges between 6.5-8.0 pH (Odjadjare & Okoh, 2010). Water pH (pKa) is an important parameter necessary to understand the environmental fate and behaviour of PFCs. It's been reported that decreased pH values favoured sorption of PFOA and PFOS onto solid phases (Chen et al., 2009; Fagbayigbo et al., 2017). The compounds will therefore tend to accumulate in sediments in aquatic systems. Conversely, increased solution pH in aquatic environment could lead to a moderate decrease of PFOS and PFOA sorption onto sediment owing to t increased amounts of ligands in the water (Wang & Shil, 2012).

2.13.2 Temperature

Prevailing environmental temperature plays a significant role in the ecological system processes in the aquatic environment. Climatic and weather conditions in an environment are a prime determinant of the observable temperature in the aquatic environment. Other

factors that influence water temperature are prevailing air temperature, surface run-off, turbidity etc. The temperature of the water body can alter water quality parameters such as viscosity, density of the water, among others that may influence the rate of chemical reactions within the aquatic system (Nicholson et al., 2013). Temperature is therefore a major factor necessary for a viable aquatic ecosystem; it is important to establish the optimum temperature that supports living organisms in the aquatic system. Thus, the prevalent temperature could be used to predict the effect of contribution anthropogenic activities into the aquatic system (Olujimi et al., 2012, Dalvie et al., 2015, Palmer et al., 2005). Changes in temperature of aquatic systems can affect the distribution of organisms thereby altering the ecological systems cycles such as predator-prey interactions (Paulse et al., 2009). Also, it can impair developmental stages and genetic selections in some aquatic organisms (Hofmann et al., 2010). At temperature values between 25 and 35 ^{o}C, organisms thrives optimally with abundant productivities in aquatic algae and plants (Dalu et al., 2016). Any significant change in aquatic temperature will consequently lead to the reduction in lifespan or increase in the mortality rate of organisms. Dynamics of temperature regime in aquatic systems influences the distribution and behaviour of available PFAS. PFOA and PFOS are more stable in the environment at temperature and vapour pressure 3.3 x 10^{-4} Pa (20 ^{o}C) (Kato et al., 2013). Increased temperature may enhance the degradation of PFCs, thereby reducing bioavailability in the environment (Hawley and Bledsoe, 2011; Liu et al 2013).

2.13.3 Electrical Conductivity (EC)

Electrical conductivity is an indicator that shows the potential of water to conduct or transmit electrical signals such as heat and sound. It is measured in micro siemens per meter(µS/m) or millimhos per centimeter (mmho/cm)(Loock et al., 2015). EC measures the ionic activities in the solution and the solution capacity which allow easy passage of electric charges. Pure water can be an excellent conductor when substances that could enhance the electrical activities are dissolved into the water. Examples of dissolved substances include; NaCl, KCl, carbonate, among others, which allow for ionic compounds of positively charged ions (cations) and negatively charged ions (anions). EC for ultra-pure water ranges between 5.5 X 10^{-6} S/m and below, EC for drinking water ranges between 0.005 and 0.05 S/m and the average EC for seawater is 5.0 S/m (Boyacioglu, 2006). Fate of PFCs in water systems may be influenced by electrically charged ions present (Ahrens et al., 2010). Increased EC water implies the availability of more charged ions and lower water pH. Consequently, increased electrical conductivity value may be favourable for PFOA and PFOS partitioning into the sediment compartment of an aquatic system (Goshu et al., 2017).

2.13.4 Total Dissolved Solids (TDS)

Total dissolved solids are a general indicator of overall water quality. It is a description of the amount of substances that dissolved in the water. Natural processes such as weathering of rocks, sedimentation, volcanic eruptions, earthquake and degradation processes are responsible for majority of dissolved substances in water bodies (Kurilić et al., 2015). Atmospheric deposition is also a major contributor to total dissolved particles in both fresh and marine waters (Hofmann et al., 2010, Dalu et al., 2016). Therefore, TDS is the summation of mobile charge ions, including mineral salts, dissolved materials, organic and inorganic substances present in the water bodies (Sagar et al., 2015). Increased level of dissolved solids could also be attributed to anthropogenic activities such as industrial exploration processes (e.g mining, quarrying, and petrochemical exploration among others). Some of the noticeable evidence of total dissolved solids in water include odour, taste, rapid corrosion, scaling of pipes, etc. (Boyacioglu, 2006). TDS could be directly related to ionic concentrations in water. Higher values of TDS could result to reduction of free sulphate radicals which could slow down PFOA and PFOS degradation which favours their availability in water system (Sung, 1995). TDS can as well interact with organic contaminants such as PFCs through various binding and adsorption interaction which has considerable influence on their migration and transformation during partitioning (Guam et al., 2013). Hence, low TDS values had no significant impact on availability of PFCs in water (Lee et al., 2012)

2.13.5 Salinity

The salinity of a water body is refers to the total concentration of all dissolved salts in the water. The contributions of dissolved ionic compounds in the water create both positive and negative charge available in the water. Hence, salinity can contribute to the electrical conductivity of the water. Salinity can be measured by both chemical analysis in the laboratory and in-situ by handheld devices. Chemical analyses are often not cost effective, in terms of time and reagents consumption. Salinity measurement is dimensionless. Some of the dissolved salts that contribute to the salinity of water body include; chloride, bromine, calcium, sodium, magnesium, bicarbonate, sulphate, potassium among others (Hofmann et al., 2010). Salinity is an important water quality parameter that influences fate or transportation of PFAS in the aquatic environment. Study conducted by Pan and You (2010), reveals that as salinity increased from 0.18 to 3.31, the distribution coefficient (Kd) between sediment and water linearly increased from 0.76 to 4.70 l/g. The study also suggested that PFOS may be transported over a long distance in estuaries due to changes in water salinity.

2.14 Diep River

The Diep River is one of the major surface water bodies in Cape Town. The river flows through informal settlement, educational and recreational facilities and industrial areas, and empties into the ocean. The river is approximately 60 kilometres in length, from the source pass through the Riebeeck Kasteel mountains north-east of Cape Town. The catchment area of Diep River covers an approximately 1400 km^2 area, which includes a vast area of Malmesbury district and some land in the west of the Paarl district in the Western Cape Province. Major tributaries of Diep River are the Mossel bank River, which drains the Durbanville, Kraaifontein and Agter-Paarl areas while other tributaries include the Klein, Groen and Sout Rivers (Ahmad et al., 2013). The sediment and soil in the river bed consists of alluvium and is predominantly sandy in nature but interspersed with clay and silt layers. The alluvium is about 12 to 18 m deep in the close vicinity of the river, including its banks. The geographical location of Diep River renders it highly susceptible to pollution via several routes of contamination, but mainly the unrestricted application of chemicals through poor agricultural practices for decades (Paulse et al., 2009). Other contributors of contaminants includes the inadequate waste management system, involving littering and dumping, industrial release, and the application of firefighting chemicals to combat wildfires, among other sources. The continuous release of contaminants into the Diep River could lead to significant deterioration of the water quality, making it unfit for usage. According to the Department of Water Affairs and Forestry South Africa (DWAF, 2015), it has been established that Diep River has been subject to deterioration over decades due to bad farming practices, the release of wastewater, industrial effluent, and other land use practices which reduces the quality of surface water (Daso et al., 2013).

2.15 Plankenburg River

Plankenburg River is another surface water body that flows through the beautiful landscape of Stellenbosch wine-land, South Africa. It flows for approximately 10 km before connecting with another river (Krom). Plankenburg River has been on the receiving end of various human activities in the communities that it flows through, including informal settlement, industry and agriculture. Inadequate and unhygienic sanitation characterize the informal settlements, and are synonymous with the downstream of the river. Also, the intrusion of industrial effluent is visible along the course of the Plankenburg before it empties into the Krom River. Agricultural activities are predominantly associated with the upstream reach of the river. The release of pollutants into the water body at any point along the river renders it unsafe for purposes such as domestic use, irrigation, recreational and for drinking. As a result of the activities mentioned above, Plankenburg River is highly susceptible to various

organic contaminants, including perfluorinated compounds. Previous studies have reported on the level of PFCs and other organic contaminants in South African surface water (Okoro et al., 2016, Nekhavhambe et al., 2014), and observed that the contamination was due to identifiable human activities. Thus, levels of PFCs including PFOA and PFOS in the Plankenburg River are not unexpected.

2.16 Method of determination of PFCs

Developing a robust, reliable and sensitive analytical method for the determination the presence of PFCs in environmental samples is quite challenging. This is because of the unique physicochemical characteristics of perfluorinated compounds, such as solubility in water, high stability, and persistence in nature. It is equally important to consider the absence of chromophores in the C-F straight chain of PFCs during the chemical analysis. Historically, determination of organic fluorinated compounds have been possible using oxyhydrogen flame combustion with fluoride ion-selective electrode (Wille et al., 2010a, Codling et al., 2014). Giesy & Kannan, (2002b) conducted an investigation to determine total organic chlorine in the environment using neutron activation and X-ray fluorescence. The major disadvantages of this method included poor sensitivity and an inability to provide structure information.

The application of chromatographic techniques is popular for the determination of micro-organic pollutants in both environmental and biological samples, due to their good sensitivity, reliability and accuracy. Different chromatographic methods have been aligned to enhance sensitivity and accuracy. Several chromatographic methods have been explored for the determination of PFCs in various environmental samples. For example, gas chromatography (GC) coupled with electron captured detector (ECD) has been used for the determination of PFOA in environmental samples (Qiao et al., 2015). Experiments with a UV detector proved unsuitable for the detection of straight chain compounds such as PFCs, because of the absence of chromophore in these compounds (Padrón et al., 2014). The complexity surrounding the determination of PFCs has led to improvement in chromatographic and spectrometric techniques. Liquid chromatography (LC) coupled with mass spectrometric (MS) detector, such as LC-MS/electrospray ionization (ESI) MS and LC-MS/MS have been popularly applied in the detection and analyses of PFOA and PFOS (Loos et al., 2008, Yoo et al., 2011, Tseng et al., 2006, Higgins et al., 2005). These methods were used for the identification and quantification of PFCs, including PFOA and PFOS, providing good sensitivity and peak identification (EFSA, 2008a).

Recently, Surma et al.(2015), reported the use of d-SPE/Micro UHPLC-MS/MS to determine the levels of PFOA and PFOS in the tissue of free-living beaver (*Castor fuber L*.) in Europe. In the study, ten perfluorinated compounds were selected, and PFOA, PFOS, and PFNA were detected in all samples of both male and female beavers at low concentration levels, ranging between 0.55 and 6.61 ng/g for all tissues. This result clearly indicates that SPE/micro coupled with UHPLC-MS/MS is a sensitive method for the analytical determination of PFCs (Surma et al., 2015a).

Ciccotelli et al.(2015) have reported a high-performance liquid chromatography-tandem mass spectrometry method for the determination of PFOA and PFOS in cereal and fish. This method was able to detect analytes at low levels. Validation of this method with the limit of detection (LOD) and limit of quantification (LOQ) varying from 0.50 mg/kg for PFOA and 0.70 mg/kg for PFOS, the recoveries ranged between 95% and 109%. It also showed good linearity (R^2 >0.99), with precision varying between 4.43% and 8.97% of repeatability for PFOA, and 6.30% and 12.33% of repeatability for PFOS.

Previously, Wang and Shih (2011) reported the use of HPLC for the separation of 12 PFCs and investigated analytes were identified using a tandem mass spectrometer fitted with an ESI operated in negative ionization mode. The chromatogram was recorded using a multiple reaction monitoring mode MRM (Wang & Shih, 2011). Approximately 70% of the samples analysed were at a concentration greater than the limit of quantification (LOQ) which ranged from 74.1 pg/l to 2.32 ng/l.

Liu et al. (2010) reported the occurrence of perfluorinated alkyl compounds in human milk from different regions of China. Analytes were separated and quantified using an ultra-performance liquid chromatography system coupled to a triple quadrupole mass spectrometry system, after the solid phase extraction (SPE) clean-up (Liu et al., 2010). The linearity was evaluated using six different concentrations, ranging from 50 ng/l to 5000 ng/l. With a limit of detection (LOD) signal to noise ratio of three, the recovery test was within 83% and 87%. Dauwe et al. (2007) assessed the PFOS level in the blood and liver of small insectivorous songbirds near a flourochemical plant, using a combination of high-pressure liquid chromatography and mass spectrometry. Limit of detection (LOD) of PFOS was determined as three times the signal-to-noise ratio (S/N) 1.5 ng/g w/w. The repeatability and reproducibility tests were done in triplicates and reported values were 80% and 86%, respectively. So et al. (2006) investigated the presence of PFCs such PFOA and PFOS in mussels from South China. An alkaline digestion method coupled with solid phase extraction (SPE) and high-performance liquid chromatography interfaced with high resolution

electrospray in tandem with mass spectrometry was developed for the determination of PFCs. The recovery studies of PFCs reported 92% accuracy, and the method was further assessed to have good linearity.

In a recent study, Martín et al. (2016) used ultra-high performance liquid chromatographic–tandem mass spectrometric analyses (UHPLC–MS/MS) to determine selected perfluorinated compounds in placental tissue samples. Limit of detection and limit of quantification (LOQ) ranged between 0.03 and 2 ng/g, and 0.08 to 6 ng/g, respectively, while the recovery for the spiked samples ranged from 94% and 113%. Generally, the LC-MS technique showed good sensitivity and reliability for the identification and quantitation of PFCs in biological and environmental matrices (Petrovic et al., 2013).

2.17 Solid phase extraction (SPE) and clean-up methods for PFCs

The efficiency and reliability of the solid phase extraction (SPE) method has been compared to other available extraction methods (Moody et al., 2001). SPE has proved to be a reliable method for sample preparation before instrumental analysis. Moreover, sample preparation steps between the collection and the analysis of the sample (such as sample filtration, homogenization, concentration, precipitation, chemical reaction, solvent exchange, solubilization, matrix removal, etc.) could be enhanced with the support of the SPE method (Surma et al., 2015b). Solid phase extraction can be applied without prior sample treatment such as pH adjustment, sample dilution, etc., or SPE can be coupled with other analytical methods to improve the sample quality.

Liu et al. (2011b) applied headspace solid phase micro extraction in-situ supercritical fluid extraction ((HS-SPME)-SFE) coupled with gas chromatography–tandem mass spectrometry (GC-NC-MS/MS), for the determination of perfluorocarboxylic acids in sediment samples. In another study, a solid phase extraction (SPE) method using oasis wax cartridges was used for the extraction of PFCs in water (Ahrens et al., 2009b). In a method developed by Kunacheva et al. (2011) to determine the mass flow of PFCs at central wastewater plants in industrial zones in Thailand, Oasis-HLB SPE tubes were coupled with HPLC–ESI–MS/MS for the analysis to improve the recovery of the short-chain PFCs (C_5-C_7). The method gave good recovery for target analytes. In a comparable study conducted by Zhao et al. (2011) cetyltrimethylammonium bromide (CTAB)-coated silica and sodium dodecyl sulphate (SDS)-coated alumina mixed hemimicelles-based solid phase extraction (SPE) was used for the pre-concentration of PFCs in environmental samples. The study showed that CTAB coated SPE gave better output than SDS coated for PFCs analysis.

2.18 Challenges associated with the analytical determination of PFCs

Challenges associated with the analytical determination of PFCs in environmental and biological samples stem from their unique physicochemical properties. Among the major challenges to analytical determination is the absence of chromosphore in the chemical structure of PFCs, which hinders the application of some analytical techniques such as ultra violet (UV) spectroscopic or liquid chromatography/ UV. Also, the extremely low volatility of PFCs enhances the stability but hinders the possibility of analytical methodologies such as GC-MS, GC/ECD, among others. Hence, PFCs are not easily derivatized to form volatile forms during the analysis. Due to the formation of the strong anions, PFCs have the tendency to adhere to the surfaces of the container, suspended particulates and biomass in the sample, which mars the accuracy of analytes during analysis.

2.19 Abatement methods for PFCs in contaminated water

Development of effective techniques for the removal of perfluorinated compounds from contaminated water is imperative, due to the health and environmental hazards associated with these contaminants. Studies reveal that most of the available conventional water treatment methods are not efficient and often, not feasible for the removal of PFCs (especially PFOA and PFOS) from contaminated water (Bagatin et al., 2014). The application of agro-based waste biomass and other eco-friendly materials has not been fully explored for remediation purposes. Agro-based biomass is a potential candidate for the removal of PFCs from contaminated water, using bioremediation approach involving batch and column adsorption. Bioremediation is the process of degrading contaminants in the environment by using the metabolic potential of microorganisms to degrade a wide variety of organic compounds (Scragg, 2009). The application of biologically based materials or organisms has the potential to remove organic contaminants from environmental matrices (Gupta et al., 2000)

Abatement methods such as biosorption have been explored and reported (Rafatullah et al., 2010). Biosorption techniques could be used to eliminate PFCs from contaminated water and eventually reduce the availability of PFCs in the environment. The removal of organic contaminants in a water system using indigenous agro-based materials has been proposed as a cost-effective and environmentally friendly approach (Ali et al., 2012). Investigation conducted in wastewater treatment plants using activated sludge process for the removal of PFCs were ineffective because of increased concentration of PFCs in the effluents through the degradation of precursors (Zareitalabad et al., 2013). A number of other reports on the

removal of PFOA and PFOS using various sorption techniques have been published (Loganathan et al., 2007, Lein et al., 2008 & Boulanger et al., 2005).

Xu et al. (2015) reported the adsorption of PFOA and PFOS on polyaniline nanotubes (PANTs) from water. Adsorption isotherms for PFOA and PFOS fitted well into Langmuir's isotherm model, maximum adsorption capacities being 1651 mg/g and 1100 mg/g for PFOA and PFOS respectively, on polyaniline emeraldine salt nanotubes (PASNTS). Thermodynamic studies indicated that the adsorption process was endothermic, while electrostatic attraction played an important role in the adsorption mechanism.

Another study conducted by Rattanaoudom et al. (2008) reported the removal of substantial concentrations of PFOA and PFOS from synthetic industrial wastewater using powdered activated carbon (PAC) and hydrotalcite PAC and hydrotalcite achieved greater than 97% removal of both PFOA and PFOS (Rattanaoudom et al., 2012). The sorption behavior of both adsorbents was rapid (5 min to 1 h for equilibrium to be achieved), while the kinetic study showed higher sorption rates for PFOA and PFOS than other adsorbents investigated. However, PAC sorption capacity was found to be limited at higher compound concentration, especially for PFOS.

Deng et al. (2011) investigated the use of polyalumium chloride (PACl) coagulant to remove PFOA and suspended solids (SS) from surface water. The results showed that most PFOA was adsorbed on the PACl particles and removed via the SS in the coagulation process. The addition of powdered activated carbon (PAC) before the coagulation process significantly enhanced the removal efficiency for PFOA. The residual concentration of PFOA was less than 1 µg/l from the initial concentration of 0.5 to 3 mg/l. Yu et al. (2008) reported the removal of PFOS from an aqueous solution using chitosan-based molecularly imprinted polymer (MIP) adsorbents. They reported that the chitosan-based adsorbent had good selectivity for PFOS. The sorption was pH dependent, the amount of adsorbate decreasing with an increase in the pH of the aqueous solution. Chitosan-based MIP adsorbent had an excellent performance in terms of regeneration: it can be used at least five times without loss of adsorption capacity. This indicates its potential for the selective removal of PFOS in wastewater treatment.

Ochoa-Herrra & Sierra-Alvarez (2008) reported the removal of perfluorinated surfactant by sorption into granular activated carbon (GAC), zeolite and sludge (Ochoa-Herrera&Sierra-Alvarez, 2008). The method was used to minimize the release of organic pollutants into the environment. The sorption capacity of the activated carbon for PFOS was observed to be greater than the other adsorbents. Activated carbon displayed a superior sorption capacity

for the surfactant up to 80 mg/L, which indicates that AC adsorption is an efficient treatment technique for the removal of PFOS from aqueous solutions.

Other studies revealed that adsorption with aluminum oxide (Al_2O_3) are also a promising technique for the treatment of highly polluted wastewaters, with a high potential for compound recovery and reuse. Aluminum oxide has been proved to be an effective adsorbant for the removal of PFOA and PFOS at trace levels below those found in wastewater generated by industrial processes (Yu et al., 2008, Ochoa-Herrera & Sierra-Alvarez, 2008, Tanaka et al., 2007, Qiu, 2007).

Hori et al. (2004) reported that the use of persulfate produced a highly oxidative sulfate radical anion (SO4-) which efficiently degrades PFOA to F and CO_2 as major products, when applied to shorter chain perfluorocarboxylic acids (PFCAs). This observation was consistent with another study by Li et al. (2010), who demonstrated that persulfate could be activated using iron and heat to cause the decomposition of PFOA. Kingshott (2008) also assessed different methods to activate persulfate to treat PFOS, and concluded that persulfate activation methods can be used for the treatment of contaminated soils, sediments and groundwater. It was also established that Fenton's reagent, H_2O_2 and heat all activated persulfate, achieving over 97.5% PFOS degradation. Other abatement technologies include ion exchange, nanofiltration (NF) and reverse osmosis (OR) (Ochoa-Herrera & Sierra-Alvarez, 2008, Chen et al., 2011b). These methods are typically more costly than activated carbon and a variety of resin containing different functional groups.

Biosorption techniques offer an environmentally friendly and cost-effective approach to management of organic contaminants such as perfluorinated compounds and its derivatives in the environment.

2.20 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (which is termed an adsorbent), forming a molecular or atomic film called the adsorbate (Moreno-Castilla, 2004). This is different from absorption, where the substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption can be carried out in physical, biological, and chemical systems, and has been widely used in industrial applications, such as activated charcoal, synthetic resins, water purification etc. The nature of the bonding that occurs between the adsorbate and adsorbent depends on the details of the species involved, hence adsorption mechanism can be classified as either

physiosorption or chemisorption processes (Hameed et al., 2008). Adsorption has been found to be superior to other techniques for water purification in terms of cost, simplicity of design and ease of operation (Meshko et al., 2001).

Adsorption has been identified and widely accepted as a better and versatile technique for the treatment of contaminated surface water, wastewaters, drinking water and irrigation water (Xu et al. 2015). Activated carbons generated from different precursors such as natural materials have been explored and reported to produce effective and efficient removal of some identified contaminants (Rattanaoudom et al., 2012). Biosorption is an adsorption technique in which biomass from agricultural materials are used to generate activated carbons for possible removal of organic contaminants from environmental matrices (Xu et al., 2015). Effective results from the application of activated carbons for contaminants' removal were attributed to its well-developed surface morphology such as pore structure, pore volume and surface area of the materials (Sethia and Sayari 2016). Some activated carbons were found to possess relatively large pore volumes that could be exploited for the removal of large organic molecules. Hence, they are suitable for varieties of industrial applications such as solvent recovery, gas separation, catalysis and most importantly, clean-up and purification processes of portable water (Ali et al., 2012). Activated carbons derived from agricultural waste materials that have been previously investigated in some studies include waste from apricot, rubber seed coat, jute fibre, cocoa shell, coconut husk among others (Agarwal et al., 2016, Tekam et al., 2017, Arampatzidou & Deliyanni, 2016, Kobya et al. 2004 & Hameed et al. (2008). Adsorptive capacities of these agro-based activated carbons have been attributed to their surface characteristics.

Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies (USEPA, 2009). In adsorption studies, the quantity adsorbed at equilibrium depends on various factors, including the nature of the surface, pH, temperature, contact time, adsorbent dosage, and concentration of the adsorbate. Adsorption equilibria relationships include the linear, Langmuir, Freundlich, Brunauer, Emmet, and Teller (BET) isotherms. The most commonly used isotherms for the application of activated carbon in water and wastewater treatment are the Langmuir and Freundlich isotherms, describing monolayer and multilayer processes. Various adsorption models were used to illustrate various forms of equilibrium relationships for different adsorbate/adsorbent interactions encountered in adsorption processes in this study.

2.20.1 Vitis vinifera

V. vinifera belongs to a family of woody climber shrubs, potentially as long as 40 metres (Bowers et al., 1996). The plant survives mostly in dry, temperate and semi-arid regions of the world, which includes countries in central Asia and Europe such as Uzbekistan, Ukraine, and Crimea etc. It is also grown in Southern African countries, including South Africa.

In South Africa, over a hundred thousand hectares of land are used for the cultivation of *V. vinifera* grapevines, which are used in wine production on a commercial scale. South Africa is ranked the 7th largest producer of wine globally with the generation of large quantities of leaf litter with practically unknown value. Grape leaves have been used for their biological properties, especially in folk medicine, since ancient times. Özçimen and Ersoy-Meriçboyu have assessed the antioxidative potency of *V. vinifera* leaves as used in the treatment of numerous diseases (Özçimen & Ersoy-Meriçboyu, 2009). The leaves have astringent and haemostatic properties and have been used in the treatment of diarrhea, hemorrhage, varicose veins, hemorrhoids, inflammatory disorder, pain, hepatitis, free-radical related diseases, and externally for centuries in Anatolia to heal wounds and drain furuncles (Lardos & Kreuter, 2000, Gabetta & Bombardelli, 1995, Bowers et al., 1996). Despite these uses, the plant is still underutilized and hence mostly available as waste.

Previous studies on *V. vinifera* have confirmed its chemical constituents that include organic acids such as malic, oxalic, fumaric, ascorbic, citric, tartaric and, phenolic acids, tannins, anthocyanins, lipid, enzymes, carotenoids, terpenes and reducing or non-reducing sugars (Gabetta & Bombardelli, 1995). The abundance of *V. vinifera* in Cape Town, South Africa, enables its use as a relatively cheap material for an environmentally friendly solution to remove or reduce PFOA and PFOS and other fluorinated compounds in the water and the environment at large. There is no previous study in the literature that reported the use of *V. vinifera* leaf litter for the removal of PFOA and PFOS. Also, information on the potential of *V. vinifera* leaf biomass as an adsorbent for organic pollutants' removal is non-existent. Hence the uniqueness of this presents study. Adsorption capacities of some previously used agro-based adsorbent are presented in Table 2.7.

Table 2.7: Adsorption capacities of some adsorbents

Adsorbent precursor	Adsorbate	Adsorption capacity	Reference
Potato peel	Bisphenol-A	454.62 mg/g	Arampatzidou & Deliyanni, (2016)
Wallnut wood	Methylene Blue	18.51 mg/g	Arampatzidou & Deliyanni, (2016)
Pea nut hull	Remazol brilliant Blue	149.25 mg/g	Zhong et al. (2012)
Ephedra strobilacea char	Methylene Blue	31.152 mg/g	Agarwal et al. (2016)
Hazenut shell	Cr(VI)	19.27 mg/g	Kobya et al. (2004)
Chitosan Flakes	Heavy metals (Cu^{2+}, Zn^{2+})	21.0 mg/g	BASSI et al. (2000)
Alumina	PFOA	157 mg/g	Wang & Shih, (2011)
Alumina	PFOS	252 mg/g	
Cocoa shell	Reactive Red-2	40.02 mg/g	Tekam et al. (2017)
Coconut husk-based	2, 4, 6-trichlorophenol	716.10 mg/g	Hameed et al. (2008)
Sucrose spherical carbon (SC)	Methylene Blue	704.2 mg/g	Bedin et al. (2016)

2.20.2 Carbonization

Carbonization is a chemo-physical process for the conversion of organic materials. It can occur as a natural process, as in the coalification of organic material, which occurs only under geological influences or artificial synthesis using pyrolysis. For carbonization to take place, plant-based products such as leaves, straw, grass, wood chippings, fir cones etc., are placed in a pressure vessel together with water and a suitable catalyst (Wang & Wang, 2007, Hameed et al., 2008). The reactor is then closed, limiting the supply of air, and heated under pressure. This process generally takes place at temperatures between 180°C and 220°C for 4 h to 12 h or at optimized conditions, after which the mixture is cooled down and the vessel is opened. The resulting biochar can be further incinerated or utilized industrially as brown-coal. Hydrothermal carbonization is based on a simple chemical process; namely the splitting of water from carbohydrates (dehydration). The end product of the carbonization process is the biochar or activated carbon (Guan et al., 2013).

2.20.3 Activated carbon

Activated carbon is defined as a microcrystalline, non-graphitic form of carbon with a porous structure that has been processed to develop its internal porosity (Alhamed, 2002). This material is characterized by a large specific surface area of 500-2500 m^2/g. This is an important physical property of activated carbon which makes it suitable for the adsorption of gasses and dissolved solutes or dispersed substances from liquids. Activated carbon has been used effectively in the past to remove toxic and bio-refractive substances such as insecticides, herbicides, chlorinated hydrocarbons, and phenols, typically present in many water bodies (Khalkhali & Omidvari, 2005). The effectiveness of the adsorption of substances by activated carbon is inversely related to the compound's solubility in water. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies (Khalkhali & Omidvari, 2005, Guan et al., 2013).

2.20.4 Application of activated carbons for removal of contaminants in water

The provision of potable water remains vital for human society. The removal of PFCs (especially PFOA and PFOS) from water and wastewaters is extremely important. Several approaches including ion exchange resin, advanced oxidation, sonochemical, physical and chemical methods of adsorption for the removal of organic contaminants including PFCs in water, and have proved comparatively efficient (Anumol et al., 2016, Gao et al., 2016, Senevirathna et al., 2010). Some of these methods have been reviewed found relatively

expensive and ineffective for complete removal PFCs from water systems (Du et al., 2015, Wilhelm et al., 2010).

Production of activated carbons from agro-based materials has been reported widely. Its benefits include availability, cost effectiveness and ease of biodegradability among others often used as alternatives for synthetic adsorbents (Guan et al., 2013). Agro-waste biomasses have been investigated as potential adsorbents for the removal of contaminants from the water systems, due to their several advantages (Yahya et al., 2015). Activated carbons previously tested in sorption studies include those produced from orange peel, rice husk, saw dust, banana peel and lignite, among others (Amarasinghe, 2016, Lasheen et al., 2012, Arami-Niya et al., 2016, Agarwal et al., 2016).

Application of agro-based biomass as adsorbent has been widely investigated in a fixed-bed column adsorption systems (Foroughi-dahr et al., 2016, Liao et al., 2013). This technique has proved to have potential for the removal of contaminants such as PFCs during water treatment processes (Meng et al., 2013). However, the application of modified activated carbons in a fixed-bed column has been reported as a potential adsorbent for removal of these contaminants (Chen et al. (2012b) studied the application of modified activated carbons from corn stalk in a fixed-bed column study. Efficient removal of contaminants was achieved at optimized column study parameters such as bed height and flow rate. The initial concentration of contaminants was analyzed by fix-bed column models which include Adam-Bohart, Nelson-Yoon and Thomas Models to interpret the data obtained. Previous studies have experimented with the column model using different adsorbents such as bamboo charcoal, Alumina and Jackfruit (*artocarpus heteopyllus*) leaf powder for the removal of environmental contaminants from wastewater and water systems (Uddin et al., 2009, Liao et al., 2013 & Wang et al., 2011)

Tian et al, (2013) conducted a study on the removal of the organic contaminants sulfamethoxazole (SMX) and sulfapyridine (SPY) using carbon nanotubes (CNTs) in a fixed-bed column experiment. They reported that the method is efficient for the removal of the target analytes with maximum adsorption capacities of 67.9 and 91.9 mg/g for SMX and SPY respectively (Tian et al., 2013). Another study reported the adsorption of salicylic acid from aqueous solution using wollastonite-based imprinted adsorbent in a fixed-bed column experiment. The result showed that WMIP significantly affected the selective adsorption of salicylic acid from an aqueous solution, with an excellent eluting performance and regeneration (Meng et al., 2013).

Fadzil et al. (2016) conducted a study to evaluate the sorption capacities of chemically modified rubber leaf powder, CA-modified (citric acid modified) and MG-modified (monosodium glutamate modified) for the removal of lead (II) in a fixed-bed column experiment. The results indicated that the adsorption capacity of 109.95 mg/g MG-modified adsorbent was superior to CA-modified with adsorption capacity of 97.19 mg/g. In another study, adsorbent was produced from dried orange juice residue and was used for the removal of fluoride in a fixed-bed column experiment. The study demonstrated that fluoride ion was successfully removed from a waste plating solution below the acceptable threshold limit for potable water in Japan (Paudyal et al., 2013). Currently, there are few studies that have reported the application of fixed-bed column experiments for the removal of emerging contaminants such as PFCs in water.

CHAPTER THREE

3.0 RESEARCH METHODOLOGY

The chapter describes the study area, experimental set-up and models applied, as well as the quality control and assurance measures taken.

3.1 Description of study area for monitoring programme

The research was carried out in Plankenburg and Diep Rivers located in Cape Town, Western Cape as shown in Figure 3.1. The sampling locations were presented in Table 3.1.

Table 3.1: Description of sampling locations

Sampling Rivers	Sampling Stations	Coordinates	Description of sampling locations
Plankenburg River	PKA	-33.930769 S, 18.851696 E	Upstream
	PKB	-33.925036 S, 18.851910 E	Informal settlement
	PKC	-33.919695 S, 18.852591 E	Industrial effluent
	PKD	-33.906662 S, 18.846319 E	Downstream (connection to another river)
Diep River	DPA	-33.837625 S, 18.519621 E	Sewage
	DPB	-33.879072 S, 18.521131 E	Industrial effluent
	DPC	-33.881853 S, 18.489755 E	Downstream (proximity to ocean)

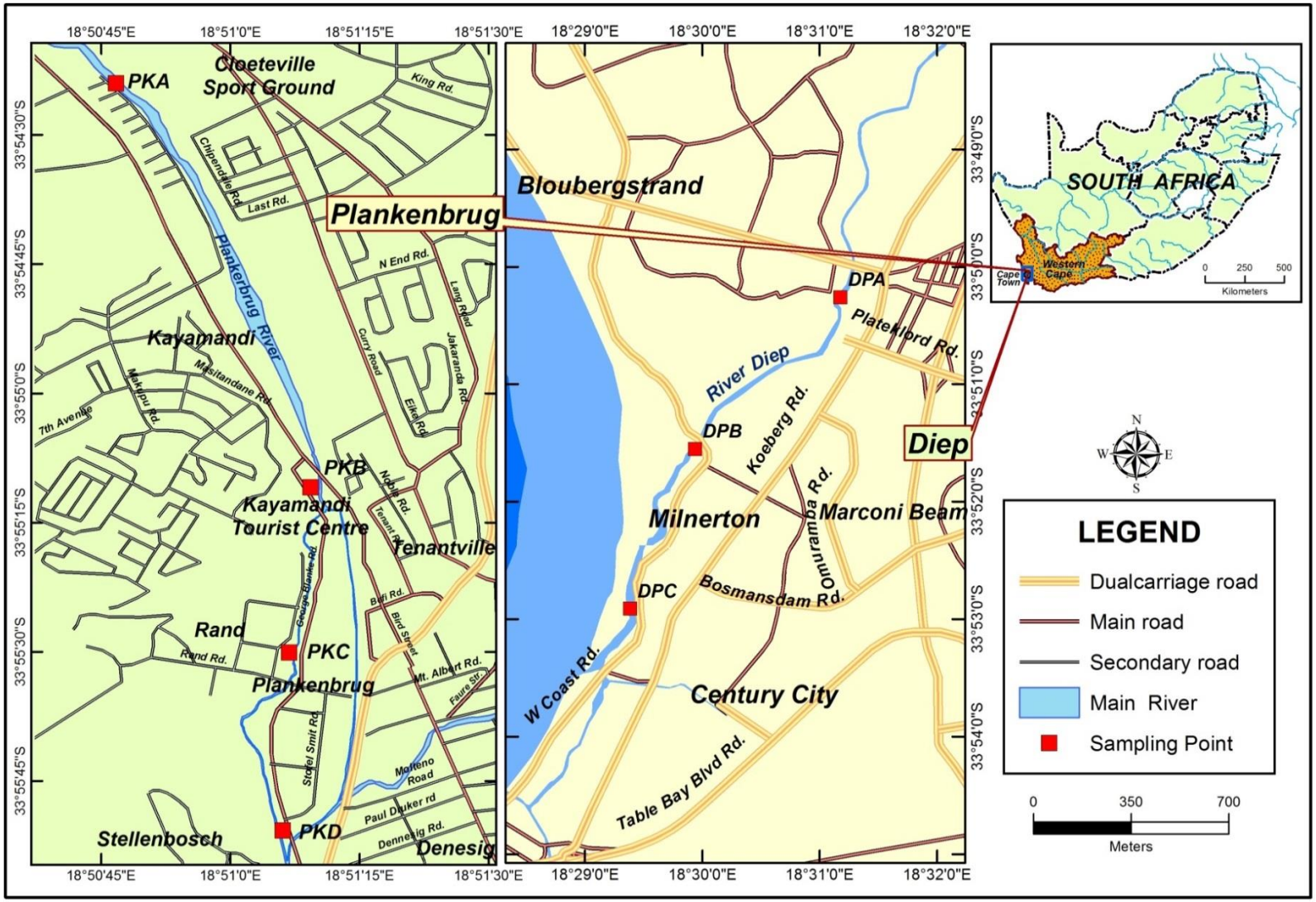


Figure 3.1: Map of the study area showing Plankenburg and Diep Rivers Western Cape Province, South Africa.

3.2 Experimental

3.2.1 Materials

Equipment and materials used include; conical flask, beaker, measuring cylinder, analytical weighing balance, magnetic stirrer, water bath, sieve (0.01 mm aperture), filter paper, funnel, desiccator, wash bottle, mortar and pestle, concentrator tubes, amber glass, vacuum pump, analytical balance, nitrogen evaporative concentrator, pH meter, thermometer, DO meter, column reservoir, screw caps, waders, a standard net (300 x 300 mm frame, 950 µm-mesh), solid phase extraction (SPE-HLB) hydrophilic-lipophilic balance (HLB) cartridge (500 mg, 12 mL) supplied by Sulpeco, Sigma Aldrich (Germany). Milli-Q water was obtained through the synthesis of distilled water by Milli-Q synthesis system integral with LC-Pack polisher from Merck Millipore, USA; sampling trays, a bucket, magnifying glass, forceps, scoring sheets, a picture field guide and a manual.

3.2.2 Chemical Standards and Reagents

All the chemicals and reagents used in this study were analytical grade (>99 %). Heptadecafluorooctanesulfonic acid (PFOS) was purchased from Fluka Analytical (USA), Perflurooctanoic acid (PFOA) and Perflouoroheptanoic acid (PFHpA) (Alfa Aesar, USA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), Tricosafluorododecanoic acid (PFDoDA) (Sigma Aldrich, Germany), Perfloro (2-ethoxyethane) sulfonic acid (PFBS), and Perfluoropentanoic acid (PFPeA) from Alfa Aesar, USA. Mass-labelled internal standards (IS) [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were obtained from Wellington Laboratories (Guelph, ON). Standard Reference Material (SRM) sediment was purchased from (Sigma-Aldrich, Germany). Potassium hydroxide (KOH) was obtained from Merck Millipore, USA, Phosphoric acid (H_3PO_4) (Merck Millipore, USA). Stock solutions of individual compounds were prepared in methanol (LC-MS Ultra Chroma-solv, Sigma Aldrich Germany), Ammonium Acetate (Merck Millipore, USA); Milli-Q water was obtained through the synthesis of distilled water by the Milli-Q synthesis system integral with LC-Pack polisher from Merck Millipore, USA. Membrane syringe filters 0.45 µm polyethersulphone (Sigma-Aldrich, Germany). All the working standard solutions used for calibration and recovery studies were freshly prepared and stored at 4^{o}C before use.

3.2.3 Preparation of standard solutions

Standard stock solutions of the nine individual perfluorinated compounds were prepared at a concentration of 1000 ng/l in 100% methanol and stored at 4^{0}C in the dark before use. A cocktail-mixture of the standard solutions was prepared from individual stock solutions with

methanol. Milli-Q water was spiked with 25 ng/l of the cocktail mixture and applied as matrix match solution.

3.2.4 Preparation of mobile Phase

Mobile phase solution used for ultra-performance liquid chromatography quadruple time of flight mass spectroscopic (UPLC-QTOF-MS) analysis was prepared in Milli-Q water with 2 mM ammonium acetate and methanol, as mobile phase A and B, respectively. The addition of ammonium acetate to the solutions served as buffer ionization enhancement of the perflourinated compounds during analysis. Buffered water and methanol solutions were passed through a 0.22 µm nylon filter to remove particulate impurity before use as a mobile phase in the UPLC-QTOF-MS system.

3.2.5 Solid phase extraction (SPE) procedure for water

Extraction of PFCs in the water sample was carried out using a solid phase extraction (SPE) C18 HLB-cartridge (0.5 g, 12 cm^3), and was conditioned by allowing 10 ml of 100 % methanol followed by 5 ml of Milli-Q water at constant flow rate depending on the gravity. The ^{13}C-labelled internal standards [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were added into Milli Q water before the extraction procedure. Simulated wastewater was filtered using 0.45 µm polyethersulphone membrane syringe filters and allowed to flow through the pre-conditioned SPE cartridge at a constant flow rate under gravity. The resultant effluent was discarded while the cartridge was allowed to drip to dryness. . Recovery of target analytes was achieved by passing 5 ml of 100 % methanol through the SPE cartridges, eluents were collected into a 50 ml polypropylene (PP) tube and the process repeated thrice (Llorca et al., 2009).

3.2.6 Solid phase extraction (SPE) procedure for sediment

Each composite sediment sample was sieved through a 250 µm aperture and 3 g of sample carefully weighed into 15 ml centrifuge tubes using analytical balance. The ^{13}C-labelled internal standards [$^{13}C_4$]-PFOS and [$^{13}C_4$]-PFOA were added into the nalgene tubes before the extraction procedure. About 10 ml of 1% acetic acid was added into a tube, vortexed for 30 min and heated in a sonication bath for 20 min at 55 ^0C. It was then centrifuged at 10000 rpm for 5 min. The resultant eluent was decanted into a clean 50 ml tube. This procedure was repeated with 3.5 ml of 9:1 (v/v) methanol and 1% acetic acid twice, while the final extraction was carried out with 10 ml of 1 % acetic acid into a 50 ml polypropylene (PP) tube, to make 27 ml eluent, this method was adapted from the literature with modifications (So et

al., 2007) and (Hu & Yu, 2010). Recovered extract from water and sediment was concentrated under a high purity N_2 gas stream to dryness, reconstituted back into 1 ml with 100% methanol, and transferred into 2 ml vials for instrumental analysis using UPLC- QTOF-MS.

3.3 Method optimization and validation

Due to the complexity surrounding environmental samples, the liquid chromatography-mass spectrometry (LC-MS) method is highly susceptible to matrix effect. Method validation terms are crucially important. Validation guidelines for this report include: linearity, recovery studies, specificity, precision and accuracy, limit of detection (LOD), and limit of quantification (LOQ). These parameters were checked to verify the sensitivity and efficiency of the method for its application to various environmental samples.

3.3.1 Precision and accuracy

The precision and accuracy of the analytical method were determined by testing the reproducibility and repeatability of the method. Analytical runs were carried out in triplicate for mixed compounds of PFCs in milli-Q water on different days, with similar properties and following the same analytical procedure and clean-up techniques, in order to determine the reproducibility of the results. Their repeatability was confirmed by analysing three collected samples at different times on the same day, following a similar process.

3.3.2 Detection limits and linearity

Linearity, limit of determination (LOD) and limit of quantification (LOQ) were evaluated and statistically calculated. The instrumental response was based on a signal to noise ratio of three and the linear range was determined by replicated injections of a diluted series of cocktails of all the nine perflourinated compounds. Calibration graphs for the investigated compounds and co-efficient of correlation (R^2) were determined. The instrumental response was based on the signal to noise ratio of three and the linear range was also determined by replicated injections of dilution series of cocktail of all the nine perflourinated compounds. Triplicate injections of blank (55:45) % of 2 mM of ammonium acetate in methanol and Milli-Q water gave values 10 times lower than the limit of detection (LOD). The limit of quantification (LOQ) was achieved with an average of three standard deviations within a series of five standards runs for three days for the validation of the experiment.

3.3.3 Matrix effect

The presence of interfering co-existing substances in the samples could hinder the accurate measurement of PFCs in a complex environmental matrix. The magnitude of this effect could suppress or enhance the ionization of the target analyte in the gross sample. The magnitude of this effect could suppress or enhance the ionization of the target analyte in the gross sample. Additions of internal standards were used to overcome the effect of drifting and matrix effect during the determination of PFCs in environmental samples.

3.3.4 Recovery study

Recovery for the determination of all the analytes were achieved using spiked mixtures (concentrations 125, 250 and 500 ng/l) of the nine PFCs in Milli-Q water. Ambient surface water and sediment samples were spiked with concentrations (125, 250 and 500 ng/kg) of PFCs prior to SPE. The spiked and unspiked samples were then processed for extraction of PFCs. The estimation of recoveries from the spiked samples after the extraction was determined relative to the values obtained from the unspiked samples. The effect of matrix interference was evaluated by recovery studies. Recovery studies were conducted with the standards of the nine PFCs (PFOS, PFOA PFNA, PFUnDA, PFDoDA PFDA, PFPA, PFBS and PFHeA) in Milli-Q water in the laboratory at quantifiable concentrations. ^{13}C labelled PFOA and PFOS were added as internal standards to check Instrumental variability of the analysis. Blanks samples were included in each of the sampling trip and subjected to field samples' clean-up procedures.

3.4 Sample collection, preparation and analysis

Sample collection was consistently carried out for a period of 12 months (January to December 2015), spanning summer, autumn, winter and spring. Water samples were collected in 500 ml polypropylene (PP) bottles with teflon-lined caps that were washed and rinsed with distilled water and methanol. Surface water samples were collected in quadruplicates from each of the sampling stations monthly, which added-up to thirty-two (32 samples) including blank samples. Sampling stations on the Plankenburg (4 points) and Diep (3 points) Rivers are presented in Figure 3.1. A total of (336) water samples were collected during the sampling period of 12 month. Water samples were filtered by passing them through 0.45 µm polyethersulphone membrane syringe filters, to remove possible debris and particles before the extraction procedure. Sediment samples were collected at same sampling locations in aluminium foil pre-treated with methanol and stored in the ice chest at 4^0C in the field before been transferred to the laboratory.

Sediment samples at a depth of (0-3 cm) were also collected at the same sampling locations. Sediment samples were collected using a pre-cleaned hand trowel and placed in aluminium foil that had been pre-cleaned with methanol and distilled water. The trowel was cleaned in between sampling points using methanol and Milli-Q water. Triplicate samples were collected from each sampling point. Twenty-one samples from four sampling points along the Plankenburg River (n=12) and three points on the Diep River (n=9). Total of (252) sediment samples were collected during the sampling period of 12 months. The samples were also stored in an ice-chest on the field, later transferred into a refrigerator frozen at −20 ^{o}C in the laboratory before analysis. Prior to analysis, frozen sediment samples were thawed and air dried to dryness, sieved using a 67 mm mesh and stored in polypropylene bags at room temperature (Higgins & Luthy, 2006, Pan & You, 2010).

Recovered extracts from surface water and sediment samples were concentrated under a high purity N_2 gas stream to dryness, reconstituted back into 1 ml with 100% methanol, and transferred into 2 ml vials for instrumental analysis using UPLC-QTOF-MS. A summary of the experimental procedure is illustrated in Figure 3.2.

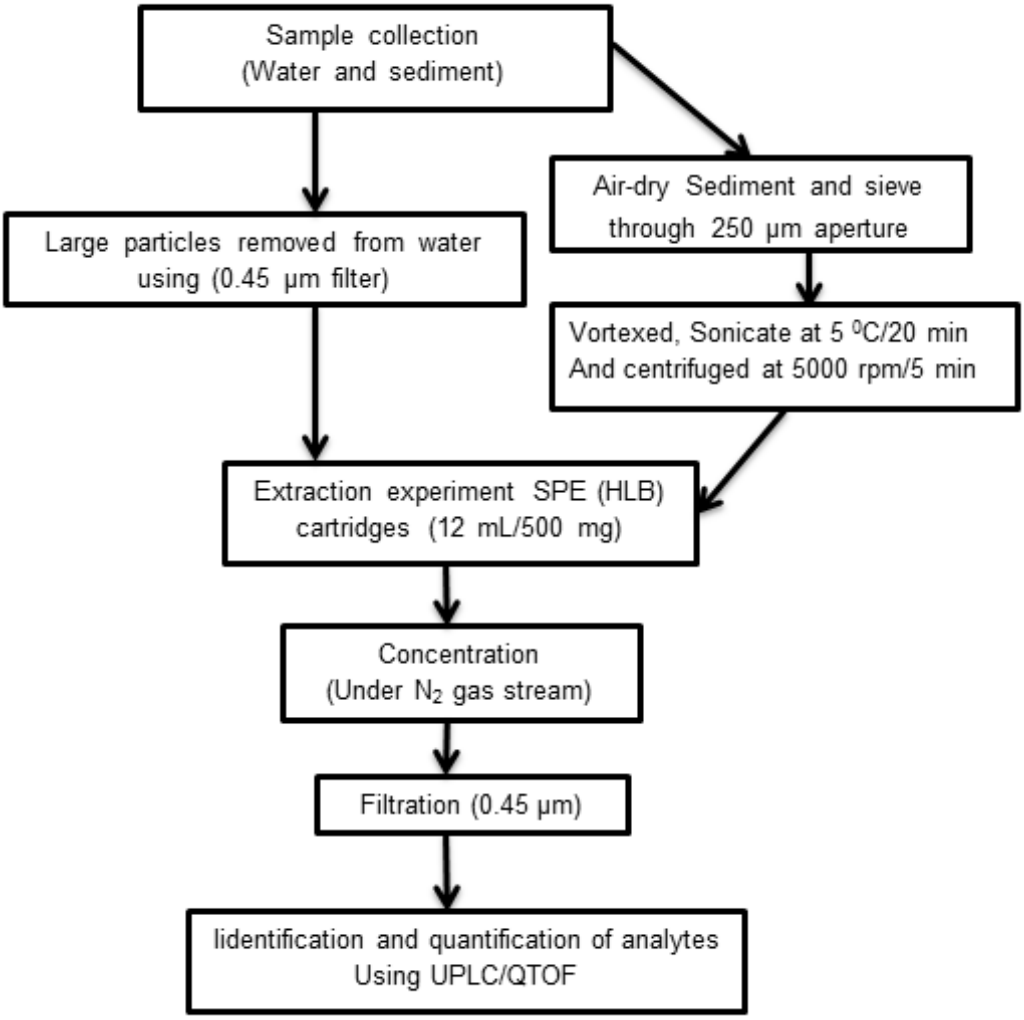


Figure 3.2: Schematic diagram showing the experimental protocol for water and sediment analysis

3.4.1 UPLC-QTOF-MS separations

Sample identification and quantitation of perfluorinated compounds were performed in ultra-performance liquid chromatography quadrupole time of flight (UPLC-QTOF-MS) technology by Acquity UPLC system (Waters Corporation, Milford, MA, USA). Samples were injected at a flow rate of 0.3 µl/min into the guard column (5mm long, internal diameter) before passing into the reverse phase C-18 column (4.6 µm particle size, 150 mm length, 5.0 internal diameters) supplied by Sigmal Aldrich, Germany. The target analytes were ionized and separated with 2 mm of ammonium acetate in Milli-Q water as mobile phase A, while 2 mM of Ammonium acetate in methanol as mobile phase B. The binary gradient was set at 55% of B for 4 min and increased to 9 % at 4 min. The condition returned to original concentration in the 9th minute of the run and the column was allowed to equilibrate for 2 min of 55% of mobile phase B. The total run time for the analysis was 11 min, with a good and quick separation time for the nine perfluorinated compounds. The mass spectrometer was coupled with (QTOF) quadrupole time of flight and operated in negative ion mode electrospray ionization (ESI). The full scan ranges between m/z (100-1000) molecular weight and the quantification of compounds of interest were achieved by extraction of the mass chromatogram from full scan recording of the cone voltage and mass to charge value obtained.

The standard reference solution was pumped simultaneously during the analysis into the Liquid Chromatography Mass spectroscopy system at a constant flow rate of 3 µL/min. Mass to charge ratio (m/z) of the reference solution was within the range of 119.0363 to 998.0164 of 2.5 mm (Hexakis1H, 1H, 3H-tetrafluoropropoxy) phosphine 97.0 % purity and 100 % Acetonitrile (99.9% HPLC grade). This enabled the accurate measurement of the masses of ions within the range of standard reference to be detected, while the resulting chromatogram and spectra were recorded for qualitative identification and quantification of the analytes. This instrument was supported by Masslynx 4.1, SCN803 software. The optimization parameters used in the mass spectrometer parameters for time of flight (TOF) are listed in Table 3.2.

Table 3.2: UPLC-QTOF-MS instrumental parameters

TOF Parameters	**values**		
Mass Spectrometer	Operated in (negative mode) ESI		
Drying Gas Temperature	250 ^{0}C		
Cone gas	0 l/h		
Nebulizer gas	600 l/h		
Capillary Voltage	3200V		
Cone voltage	30V		
Q-TOF Premium acquisition rate	0.15 s inter scan delay		
Drying gas	Argon Gas		
Collision gas Pressure	5.3x1^{-5} Tor		
Binary gradient	Time (min)	% A	% B
		45	55
	4	10	90
	8	10	90
	9	45	55
	11	45	55
Instrument supported by	Masslynx 4.1 SCN803 software		

3.5 Quality assurance and quality control (QA/QC) procedure

- Instrument contamination was avoided by strict adherent to laboratory ethics, and methanol was used to rinse all laboratory wares before use.
- The effect of co-eluting compounds was overcome by the standard addition method.
- Analysis of each of the investigated compounds was done in triplicates and variations noted, ensuring the precision of the method.
- Blank and standard reference material (SRM) determination were carried out alongside the run standards to establish the contribution of analytical signals, which include the effect of mobile phase solvent, instrumental response, and possible human error.
- Standard mixture of nine PFCs- PFPeA, PFBS, PFHpA, PFOA PFOS, PFNA, PFDA, PFUnDA, PFDoDA were analysed. ^{13}C labelled PFOA and PFOS were added as internal standards to check Instrumental variability of the analysis.
- Method and instrumental responses were estimated; the limit of detection (LOD) and the limit of quantification (LOQ) of the instrument were achieved through the blank determination to estimate the signal to noise ratio of 3:1and 10:1 respective for LOD and LOQ.

- Calculations

The concentrations of the PFCs present in surface water and sediment samples obtained in this study were estimated using:

$$\text{Conc. of analyte in water (ng/l)} = \frac{\text{conc.of analytes (ng/l) X total volume of extract (ml)}}{\text{volume of sample (g)}} \quad (1)$$

$$\text{Conc. of analyte in sediment (ng/g)} = \frac{\text{conc.of analytes (ng/l) X total volume of extract (ml)}}{\text{mass of sample (g)}} \quad (2)$$

3.6 Determination of physicochemical parameters of surface water

Physicochemical parameters of the surface water sample were measured in-situ using hand held multi-parameter instrument (groline hydroponic waterproof pH/EC/TDS/Temperature portable meter - HI9814, Hanna instrument, USA) to determine the quality of the surface water. The water quality parameters measured were pH, temperature, electrical conductivity, turbidity, total dissolved solids (TDS).

3.7 Determination of physicochemical parameters of sediment

3.7.1 Fraction of organic carbon

Accurately weighed 1g sediment samples were transferred into pre-cleaned conical flask in the laboratory. Ten ml of 1N $K_2Cr_2O_7$ was added to a conical flask containing 1g sediment and swirled to mix. Twenty ml of concentrated sulphuric acid was added to the mixture and allowed to cool for 30 min. The mixture was diluted with 200 ml of Milli-Q water. Four (4) drops of ferroin indicator were added, and then 0.4 N ferrous sulphates were used to titrate until the end point was reached (yellow-blue-green colour). Two blanks (without sediments) were prepared in the same way as the soil sediments. Each sediment sample was titrated in triplicates. This method was based on the Walkley-Black chromic acid wet oxidation method for the determination of organic carbon.

3.7.1 Organic matter

Approximately 3 g of sediment samples were weighed using pre-cleaned crucibles. The crucibles containing sediments were transferred into the oven, heated at 300 ^{0}C for 36 h and allowed to cool to room temperature before being re-weighed. Values obtained were used to estimate for total organic matter of individual sediment obtained.

$$\text{Total organic matter (\%)} = \frac{x-y}{x} \text{ X } 100 \quad (3)$$

x = Initial weight of crucible and sediment before ignition (g)

y = final weight of the crucible and sediment after ignition (g)

3.7.2 Particle size

The sediments were homogenized and air dried. Approximately 50 g samples from each sampling locations were accurately weighed using analytical balance (Perkin Elmer, USA). The sediments were sieved using 3 different mesh sizes (10, 125 and 250 µm) to obtain different particles sizes of the sediment.

3.8 Partitioning experiment

Sediment samples were homogenized, air dried and sieved. 5.0 g sediment samples from each sampling location were weighed accurately using an analytical balance and transferred into 500 ml amber bottles filled with 250 ml laboratory simulated wastewater spiked with 250 ng/l PFCs. The samples were agitated using an orbital shaker at 120 rpm on a water bath at a constant temperature of 25 ^{0}C. The experimental set-up was agitated for 24 h for equilibrium to be attained and then allowed to settle before decantation. Levels of PFCs adsorbed onto the sediment and available in aqueous solution were determined using liquid chromatography mass spectrometry. The concentrations obtained were used to evaluate for partitioning coefficient and distribution of PFCs, in both solid and aqueous phases. Partitioning equilibrium parameters such as partitioning distribution (K_D) and partitioning coefficient (K_{OC}) were evaluated and were used to deduce their environmental distribution. These parameters were expressed in equations 4 to 6 respectively.

$$K_D = C_S / C_W \qquad (4)$$

where C_S (ng/g) is the concentration of the contaminants in the sediment and C_W is the concentration in the surface water.

$$K_{OC} = K_D \times 100 / f_{oc} \qquad (5)$$

f_{OC} represent the fraction of organic carbon, and the value can be calculated from total organic carbon expressed in equation 5.

$$f_{oc} = TOC(\%) / 100 \qquad (6)$$

From equation 6, T_{OC} represent the total organic carbon

3.9 Kinetics study for the distribution of PFOA and PFOS in water and sediment

In order to have insight into the sorption mechanisms of PFOA and PFOS in the sediment samples, a sorption study was carried out in 50 ml polypropylene nalgene tubes purchased from Kimix (South Africa), pre-cleaned using 100% methanol to eliminate possible impurities. A 1g homogenized sediment sample was accurately weighed into the 50 ml PP nalgene tubes containing 25 ml simulated wastewater containing 250 ng/l of mixed PFCs. Tubes were agitated in the shaker at 120 rpm and kept at 25^0C over a water bath for a period of 1000 min for equilibrium to be attained. The experiment was intercepted at designated intervals ranging between 25 and 1000 min, when 0.5 ml of supernatants was drawn with a micropipette to ascertain the levels of PFCs in the agitated solution using UPLC-QTOF-MS. The procedure was repeated twice with different prepared samples to confirm the repeatability of the results. Kinetic models such as Pseudo first order kinetics, Pseudo second order kinetics, Elovich rate equation and Webber-Morris Intra-particle diffusivity models were used to analyse the data obtained.

3.10 Adsorption study

3.10.1 Preparation of activated carbon

The agro-waste leaf litter biomass of *V. vinifera* was collected from a wine farmland in Stellenbosch, South Africa, and was used as the raw material for the preparation of the adsorbent. Collected leaves were washed under a running tap and rinsed with distilled water for the removal of soil particles. They were then air dried for 48 h and transferred into an oven at 80 ^{0}C for 12 h to reduce the moisture content to the barest minimum. The dried leaf biomass was pulverized and sieved through 500 µm aperture mesh to obtain fine and uniform particles, then transferred into the desiccator before the carbonization and activation processes.

3.10.2 Carbonization process

The carbonization of the leaf litter biomass was carried out in a pyrolysis chamber in the absence of air. The biomass was subjected to thermal treatment by loading the pulverized leaf litter into the steel tubular container inside the tube furnace at 25 ^{0}C/min to attain pre-determined temperatures of 450, 600, 750 and 900^0C. A steady flow of nitrogen gas was maintained at 150 ml/min flow rate in the pyrolysis chamber for 120 min to eliminate moisture.

3.10.3 Chemical activation

The charcoal (20 g) was exposed to 100 ml each of 3M H_3PO_4 and KOH to produce AC-H_3PO_4 and AC-KOH respectively. The mixture was left to stand for 24 h to enhance the surface activity of the activated carbons. After chemical activation, the activated carbons were thoroughly washed with distilled water until the pH of the effluent was neutral. It was then dried in the oven at 70 ^{0}C for 12 h to remove all moisture and subsequently used for adsorption experiments.

3.11 Characterization of adsorbents

The elemental composition of untreated leaf biomass, AC-KOH and AC-H_3PO_4 activated carbons were determined using Energy Dispersive Spectroscopy (EDS). The activated carbons and untreated biomass were further characterized by Fourier Transmittance Infra-red spectrometry (FTIR), Brunauer-Emmett-Teller (BET) surface area measurement, and Scanning electron microscopic (SEM) analysis.

3.11.1 Fourier transmittance infra-red spectrometry (FTIR)

Infrared spectra of the activated carbons (AC-KOH, AC-H_3PO_4) and untreated biomass were obtained. Spectra pellet discs were prepared using the pressure disc technique at ratio 1:25 of adsorbent to potassium bromide (KBr), using a Perkin Elmer FTIR spectrometer (Spectrum 1000, USA) in ambient conditions. The recorded spectra were within 4000- 400 cm^{-1} for an average of 5 scans with resolution of 4 cm^{-1} at constant velocity for the rotating mirror.

3.11.2 Scanning electron microscopic analysis (SEM)

The surface morphologies of the untreated biomass and the activated carbons (AC-KOH and AC-H_3PO_4) were determined before and after the adsorption process using SEM (NOVA Nano SEM 230, USA). Samples were coated with a thin layer of gold using a gold sputtering device (JOEL, JFC-1600) to enhance the visibility of the surface morphology. The electric tension in the detector used was set at 25 kV at 5 mm.

3.11.3 Brunauer–emmett–teller (BET)

Surface properties such as the pore area, pore volume and pore size distribution of the activated carbons were determined by nitrogen adsorption and desorption isotherms, using an Automatic Adsorption Instrument (Quanta chrome Corp. Nova-1000 g gas sorption, USA). Prior to the measurement, samples were degassed at 170 ^{0}C for 13 h. Nitrogen

adsorption and desorption data were recorded at a liquid nitrogen temperature of 77 K. The surface area of the activated carbon was calculated using the BET equation. The pore distribution, micropore and mesopore volumes were determined by the BJH method, while the external surface areas of the activated carbons were determined by the t-plot method.

3.12 Batch studies

Batch experiments were conducted in triplicates using AC-KOH and AC-H_3PO_4 activated carbons as adsorbents. Laboratory-simulated wastewater containing a mixture PFOA and PFOS ranging between 0.125 and 1 mg/l was measured into 50 ml nalgene tubes, containing 30 ml Milli-Q water and 0.05 g of the adsorbent. Experiments were carried out at 150 rpm in an orbital shaker at 25 ^{0}C for 24 h. Adsorption isotherms' studies were conducted with adsorbent dosage of 0.02 g and 0.05 g at pH values 4 and 9. The mixture was filtered through 0.45 µm filter after 24 h and the filtrate analysed using UPLC-QTOF-MS to determine the levels of PFOA and PFOS. The percentage removal and amount adsorbed at equilibrium, q_e, (mg/g) using the activated carbons were calculated by equations 7 and 8, respectively.

$$\mathrm{y} = 100(C_o - C_e/C_o) \qquad (7)$$

$$\mathrm{q_e} = (\mathrm{C_o} - \mathrm{C_e})\mathrm{v/w} \qquad (8)$$

In the equation above, C_o and C_e are initial concentration and equilibrium concentration (mg/L) respectively, y is the percentage removed; v is the volume of solution (ml) and w (gram) represents the weight of activated carbon.

3.12.1 Adsorption Isotherm models

Adsorption isotherm models were applied to analyse the data obtained from adsorption experiments, in terms of amount of adsorbate that was adsorbed on the adsorbent relative to conditions such as concentrations, temperature, pH, adsorbent dosage, among others. Adsorption models were used in this study to determine the adsorption parameters which include the maximum adsorption capacity of the produced activated carbons (AC-KOH and AC-H_3PO_4). The following isotherm models could be applied in analysing the equilibrium data obtained for the removal of PFCs, especially PFOA and PFOS.

3.12.1.1 Langmuir isotherm

The Langmuir isotherm model was founded on the hypothesis of a monolayer adsorption, where adsorbate is expected to occupy only the hypothetical surface layer of the site where

adsorption is taking place (Langmuir, 1918). The Langmuir isotherm represents the equilibrium distribution of adsorbate ions between the aqueous phase and the adsorbent. The Langmuir model also assumes that equal energies during adsorption onto sites in the solid surface were distributed without further adsorption of the adsorbate on the surface of the adsorbent (Moreno-Castilla, 2004). Based on this hypothesis, the Langmuir equation is represented by equation 9 and linearized in equation 10.

$$q_e = q_m K_L C_e / 1 + K_L C_e \qquad (9)$$

$$1/q_e = 1/q_m + 1/q_m K_L C_e \qquad (10)$$

C_o and C_e represent the initial and equilibrium concentrations of adsorbate at equilibrium (mg/L), q_e represents the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g), q_m represent the maximum monolayer coverage capacity (mg/g), while K_L is the Langmuir isotherm constant (L/mg). Values of q_m and K_L were deduced from the slope and intercept by plotting $1/q_e$ against $1/C_e$. An Important dimensionless feature of the langmuir isotherm parameters, which is also called separation factor R_L, was estimated from the equation. The value of R_L obtained was evaluated from equation 11 and used to predict the nature of the adsorption process. Adsorption is considered unfavourable if R_L>1, while R_L=1 indicates linearity, and R_L < 0 means that adsorption is favourable.

$$R_L = 1/(1 + (1 + K_L C_o) \qquad (11)$$

3.12.1.2 Freundlich isotherm

The Freundlich isotherm model is the adsorption model used to describe multilayer adsorption and reverse adsorption (which is not an ideal form of adsorption such as that represented in monolayer). It also provides a perfect description of the non-uniform distribution of the heat of adsorption and adsorbent affinity over a heterogeneous surface (Hameed et al., 2008). The Freundlich isotherm is applicable to both monolayer and multilayer. Based on this assumption, the empirical equation for Freundlich's isotherm model is presented as:

$$q_e = K_f C_e^{1/n} \qquad (12)$$

K_f represents the Freundlich isotherm constant (mg/g), n the adsorption intensity, C_e the equilibrium concentration of adsorbate at equilibrium (mg/l), and q_e the amount of adsorbate that is adsorbed per gram of adsorbent at equilibrium (mg/g). A summary of Freundlich's equation is linearized and expressed in equation 13.

$$\log q_e = \log k_f - 1/n \log C_e \qquad (13)$$

Values for K_f and 1/n were estimated from the intercept and slope of the plot of log q_e against log C_e. K_f is the indicator of adsorption capacity onto the heterogeneous surface. The value of 1/n indicates the strength of the adsorption process, which depends on the adsorption intensity, and could be used to give an estimate of the adsorption capacity of the adsorbent (Wang&Shih, 2011). If the value of 1/n is <1 the adsorption process is favourable, while a value of 1/*n* >1 indicates that the adsorption process shows an agreement between both liquid and solid phases in the system. *n*=1 shows that partitioning between liquid and solid phase is independent of adsorbate concentration (Cheng et al., 2015). Also, the value of k and n as represented in equation 12 depends on changes in the temperature of the aqueous medium, which may lead to considerable changes in the quantity of the adsorbed analytes (Hameed et al., 2008). The lower the values obtained for the heterogeneity parameter (1/n), the greater the expected heterogeneity. The expression is linear if 1/n is equal to 1. The expression of (1 < n < 10) indicates a favourable sorption process (Hameed et al., 2008, Dada et al., 2012).

3.12.1.3 Temkin isotherm

Temkin isotherm model was used to describe adsorption parameters that would express adsorbent-adsorbate interactions, with less emphasis on extremely low and large concentrations of the analytes. Temkin equation represented in (equation 9) and the linearized form illustrated in equation 11) were used by plotting q_e against In C_e, this was use to determine the adsorption constant, K_T from the slope and intercept to derive and b_T respectively (Hameed et al. 2008).

$$q_e = RT/b_T \ \ln(K_T C_e) \qquad (14)$$

$$B = RT/b_T \qquad (15)$$

$$q_e = B \ln K_T + B \ln C_e \qquad (16)$$

K_T (L/g) represent temkin isotherm equilibrium binding constant, b_T (KJ/mol) is the Temkin isotherm constant, R stands for universal gas constant (8.314 J/mol/K), T (K) is the temperature (ideal gas constant 298 K), and B, represents the constant related to heat of sorption (J/mol) in equations 14-16 (Hameed et al. 2008).

3.12.1.4 Dubnin-Radushkevich (DBR) isotherm

The Dubnin-Radushkevich (DBR) isotherm is an adsorption model that describes the high degree of rectangularity in an adsorption model. It was initially conceived for the adsorption of subcritical vapour onto micropore in a pore filling process. The DBR isotherm is applicable to the analysis of equilibrium data in an adsorption process with Gaussian energy distribution onto a heterogeneous surface. This model is most applicable for adsorption systems with high solute activities, and it is sometimes applied to moderately ranged concentrations of data sets. It is important to note that the Dubinin-Radushkevich isotherm is a temperature-dependent model, which makes it suitable to analyse adsorption data at different temperatures. Equation 17 represents the Dubinin-Radushkevich isotherm model, and the values for q_{DRB} and K_{ad}, were derived from the linearized equation 18 and 19, by plotting Inq_e against $\boldsymbol{\mathcal{E}}^2$.

$$q_e = (q_{DRB})exp(K_{ad}\mathcal{E}^2) \qquad (17)$$

$$\ln q_e = \ln q_{DRB} - (K_{ad}\mathcal{E}^2) \qquad (18)$$

$$\mathcal{E} = RT \ln q_e \,[1 + 1/C_e] \qquad (19)$$

q_e represents the amount of adsorbate adsorbed at equilibrium (mg/g), q_{DRB} is the theoretical isotherm saturation capacity (mg/g), K_{ad} (mol^2/kJ^2) represents the Dubinin-Radushkevich isotherm constant and $\boldsymbol{\mathcal{E}}$ stands for the derived Dubinin-Radushkevich isotherm constant. This model is mostly applicable to distinguish between adsorption mechanisms, which is due to chemisorption and physiosorption processes with respect to the mean of free energy (Dada et al., 2012).

3.13 Kinetic studies

Kinetic studies were carried out to investigate the adsorption rate and the interaction of the adsorbents. Activated carbons (0.05 g) were accurately weighed into 50 ml nalgene tubes containing a 30 ml solution of simulated wastewater (a mixture of 0.5 mg/l of PFOA and PFOS). The mixture was agitated in an orbital shaker at a constant temperature of 298.15 ^{o}K. Supernatants were collected at a predetermined time intervals ranging from 5 to 120 min. The concentrations of the analytes in the supernatants were determined, and the quantities of PFOA and PFOS adsorbed q_t (mg/g) by adsorbents after adsorption was calculated from equation 20.

$$\mathrm{q_t} = (C_o - C_t)v/m \qquad (20)$$

In the above equation, C_o and C_t (mg/g) were the liquid-phase concentrations at initial and at time intervals, *m* is the mass of adsorbent (g) and v is the volume (l) of the solution. Control samples were run simultaneously with the experimental samples to account for possible deviations that might occur during the adsorption process (Igwe & Abia, 2007) .

3.13.1 Kinetic models

Kinetic models are analytical tools used to describe the kinetic rate of the adsorption process. Some of these models were applied to understand the adsorption mechanisms involved in the removal of PFCs in an aqueous solution using produced activated carbons AC-KOH andAC-H_3PO_4. The kinetic models are described as below.

3.13.1.1 Psuedo first-order kinetics

Psuedo first-order kinetics was first presented in 1898 by Lagergren to describe the kinetic process involved in the liquid-solid phase adsorption of malonic and oxalic acids onto charcoal. This experiment was believed to be the first study on kinetic models based on adsorption rate and capacity. In other to distinguish the kinetic equations, Langergren's first order rate equation was called 'pseudo first-order kinetics'. This model is among the most used in studies to describe adsorption of pollutants from contaminated solutions onto the surface of adsorbents, and has been reported by researchers (Cheng et al., 2015, Dada et al., 2012). The algorithm of the pseudo first-order kinetics model, as expressed in equation 21, was used to analyse the experimental data obtained (Cheng et al., 2015):

$$\mathrm{In}(q_e - q_t) = \mathrm{In}\, q_e - k_1\, t \qquad (21)$$

k_1 (min^{-1}) in equation 21 is the equilibrium coefficient of pseudo first order kinetic uptake per minute. Adsorption parameters, q_e and q_t, represent concentrations uptake at equilibrium and concentration adsorbed at time (t) respectively. Values for k_1 and correlation coefficient (R^2) were obtained from the slope of In (qe-qt) versus t (min).

3.13.1.2 Psuedo second-order Kinetics

The psuedo second-order kinetic model describe the adsorption processes of chemical bonding between divalent ion and polar functional groups in solid phase (Ho & McKay, 1999). The rate of adsorption is dependent on the amount of divalent ions on the surface of the adsorbent at the time (t) mins and adsorbed at until the equilibrium is reached. The pseudo second-order kinetic model was also appplied to explain the uptake of PFOA and PFOS by plotting t/qt against contact time t (min) as presented in equation 22.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}(t) \qquad (22)$$

k_2 (min^{-1}) is the equilibrium coefficient of pseudo second-order kinetic uptake per minute. Psuedo second-order rate equation is formerly known as Ho's second-order rate equation, and it is based on adsorption capacity from the concentration of the solution. This model has been successfully applied in a number of studies to understand the mechanism of contaminants in aqueous solutions (Agarwal et al., 2016).

3.13.1.3 Elovich rate equation

The Elovich rate equation was first proposed by Roginsky and Zeldovich in 1971 (Cope, 1972). It was used to describe the kinetics of various biological processes, where a charge concentration is transport across activation energy barriers. The Elovich kinetic model was also applied to determine the adsorption and desorption processes involved in the adsorption process. It was used to deduce the feasibility of applying produced activated carbons in a real life scenario. The Elovich kinetic model is expressed in equation 23 as:

$$q_t = 1/\beta \,.\ln \alpha_E/\beta + 1/\beta \ln t \qquad (23)$$

α, E, β, and qt in equation 23 represent the initial adsorption rate, desorption rate and amount adsorbed at time (t), respectively. The Elovich equation has been widely applied to chemisorption (Igwe & Abia, 2007).

3.13.1.4 Webber-Morris Intra-particle diffusivity

The Webber-Morris intra-particle diffusion kinetic model describes the rates of solute diffusion. It was developed using the linear driving force concept (Igwe&Abia, 2007). Some of the factors that influence sorption processes include: diffusion of adsorbate from the solution to the films surrounding the particles; from films to the particles' surface (external diffusion); and from the particles to the internal sites (pore diffusion). The Webber-Morris model also describes the uptake mechanism of adsorbate such as physiosorption, ion-exchange, complexation, etc. (Gupta et al., 2014). The Webber-Morris intra-particle diffusivity equation is expressed in equation 24.

$$q_t = l + k_p t^{1/2} \qquad (24)$$

In equation 24, k_p represents the intra-particle diffusivity constants, t is time (min), and I, is the boundary layer diffusion effects. Quantity adsorbed (q_t) was plotted against time $t^{1/2}$. The rate coefficient constant (k_p) and boundary layer diffusion effects (I) were obtained from the

slope and intercept of the plot respectively (Opeolu et al., 2010, Cheng et al., 2015, Gupta et al., 2014).

3.14 Thermodynamic studies

Thermodynamics studies were conducted to determine Gibbs's free energy (ΔG^0,KJ/mol), enthalpy change (ΔH^0, KJ/mol) and entropy change (ΔS^0,KJ/mol). Results from these studies were used to provide information about the effect of temperature change on the adsorption process. Change in free energy, ΔG^0 is expressed by the Van't Hoof equation as:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (25)$$

$$\Delta G^0 = -RT\ln(K_c) \qquad (26)$$

$$K_c = C_s/C_e \qquad (27)$$

where K_c is a dimensionless constant in equations 26 and 27, C_e represents concentration at equilibrium, R is the universal gas constant (0.008314 kJ/K) and temperature (Kelvin) is the temperature. Gibbs's free energy (ΔG^0) from equation 25 was substituted in equation 26 to obtain a linear equation, and this was expressed as:

$$\ln K_c = -1/RT\,\Delta H^0 + 1/R\,\Delta S \qquad (28)$$

From equation 28, $\ln K_c$ was plotted against 1/T; the values of ΔH^o and ΔS^o were obtained from the slope and intercept, respectively; and ΔG^0 was calculated using equation 28 (Agarwal et al., 2016).

3.15 Fixed-bed column studies

In order to investigate practical application of the produced activated carbons in a flowing system, better adsorbent (AC-H_3PO_4) from batch adsorption studies was used. Fixed-bed column study adsorption was conducted in the laboratory to remove contaminants (PFOA and PFOS) present in simulated wastewater at varying influent concentrations of 0.5, 1.0, 1.5 and 2.0 mg/l. Column studies were performed in 20 cm length transparent glass column (perplex column) with 1.2 cm internal diameter. Glass wool of 1 cm height and a 0.2 cm transparent sieve was used as a support both to avoid possible contamination and to ensure uniform distribution of solution in the column set up. The column was packed with produced activated carbons (AC H_3PO_4) of 250 mm particle size at varying mass 0.5 g, 1.0 g, 1.5 g, and 2.0 g, to attain the following bed-height 1.3, 2.6, 3.9 and 5.2 cm respectively. The flow

rate of the system was set at 10, 20, 40 and 55 rpm which represent 0.58, 0.64, 0.68 and 0.73 ml/min. The experiment was conducted at the prevailing room temperature 293 K, and pH was adjusted to 4.0 to enhance adsorption. Column adsorption capacity (q_{ed}) was calculated from the equation 29. This experimental set-up was adapted from previous studies (Baral et al., 2009, Chen et al., 2012b, Lim & Aris, 2014). Adsorption capacity of adsorbent in a column study was calculated using equation 29.

$$q_{ed} = \frac{C_{inf}V_{inf} - \sum C_{eff}V_{eff}}{m} \qquad (29)$$

where q_{ed} (mg/g) represents adsorption capacity, C_{inf} is the initial influent concentration; V_{inf} is the initial volume of influent, C_{eff} effluent concentration, V_{eff} is the final effluent volume, and m represents the mass of activated carbons. Experimental set-up is presented in Figure 3.3.

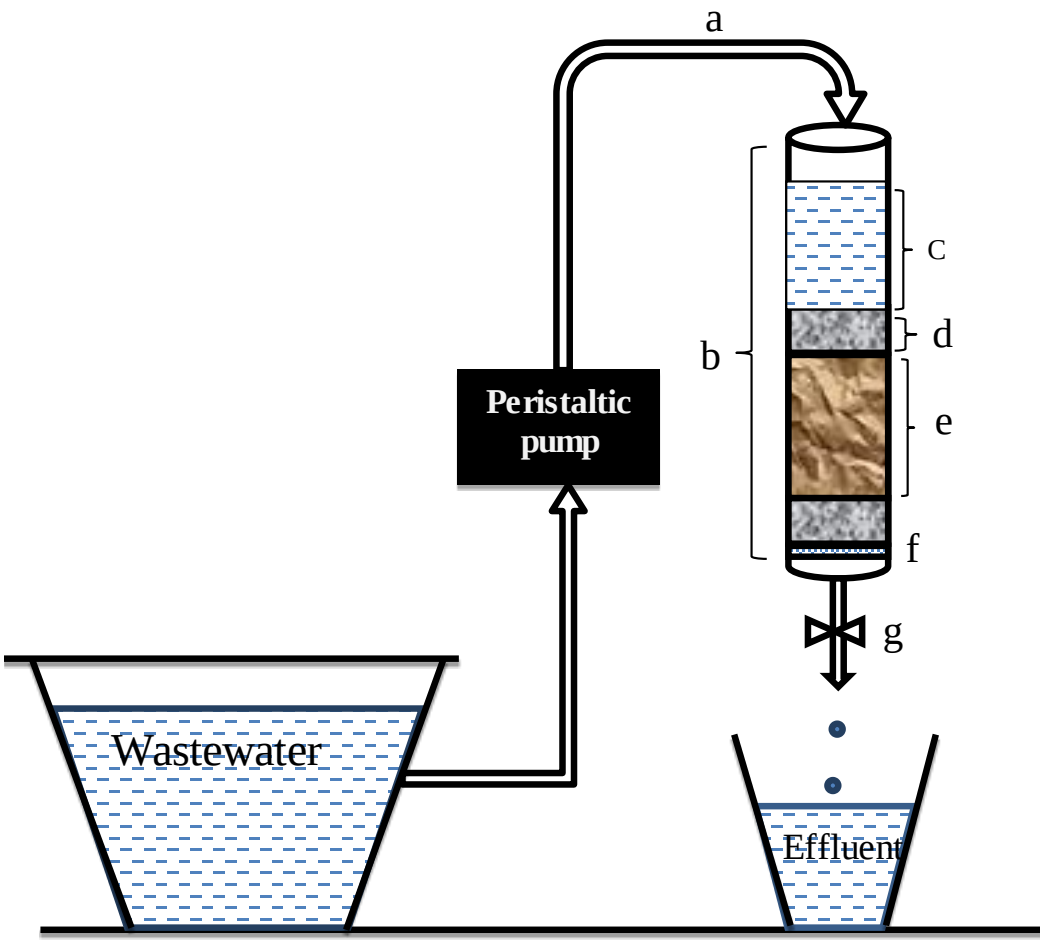


Figure 3.3: Schematic diagram of fixed bed column experimental set-up: (a) tubing; (b) column; (c) influent; (d) glass wool (e) bed height; (f) sieve; (g) tap

3.15.1 Evaluation of the performance of the fix-bed column

A breakthrough curve was derived from the equilibrium data from the column study and was used to evaluate the performance of the fixed-bed column. The breakthrough curve appearance and shape is a vital tool in determining the operation and the response to change of the adsorption column set up (Uddin et al., 2009, Ahmad et al., 2012). The breakthrough point is attained when the concentration of effluent reaches 0.1% of the initial concentration of the influent. When the concentration of the effluent reaches 95% of the concentration in the influent, that point is known as the exhaustion point. The breakthrough curve was achieved by plotting Ct/Co against t (min) or volume (l), while the possible influence of other parameters such flow rate, bed height, pH, etc., were taken into consideration (Foroughi-dahr et al., 2016). From the breakthrough curve, other information such as effluent volume (V_{eff}), Qt_{total}, could be estimated using equations. The total volume of effluent Veff (ml) that flows through the fixed bed column was calculated via equation 30:

$$V_{eff} = Qt_{total} \qquad (30)$$

where Q represents the volumetric flow rate (mL/min) and t_{Total} is the total flow time (min) of the influent (Uddin et al., 2009). The overall concentration of PFCs adsorbed onto the activated carbon in the fixed bed column q_{total} (mg/g) was calculated from equation 31:

$$q_{total} = \frac{QBh}{V} \qquad (31)$$

V represents the total volume of influent, Q is the flow rate and Bh is the bed height.

The maximum adsorption capacity of the fixed bed column at equilibrium q_{eq} (mg/g) was calculated from equation 32:

$$q_{eq} = \frac{q_{total}}{x} \qquad (32)$$

where q_{eq} is the maximum adsorption capacity at equilibrium and x is the mass of the adsorbent. Total amount of PFOA and PFOS, column M_{total} was calculated from equation 33 (Oguz & Ersoy, 2010).

$$M_{total} = \frac{C_{inf} Qt_{total}}{V} \qquad (33)$$

M_{total} represents the total concentration of PFOA and PFOS that flows through the column bed throughout the period of the experiment. Concentration removal at equilibrium was calculated from equation 34 (Rocha et al., 2015).

$$C_{eq} = \frac{M_{total} - q_{total}}{V_{eff}} \text{ X Volume (l)} \qquad (34)$$

Percentage removal for PFOA and PFOS in the fixed-bed column was then calculated from equation 35.

$$\text{Percencage \% total removal} = \frac{q_{total}}{M_{total}} X100 \qquad (35)$$

3.15.2 Fixed-bed column models

The rationale behind the design of a fixed-bed column is its ability to successfully predict the concentration of effluent and its relation to time elapsed using appropriate models. Moreover, adsorbent qualities such as the maximum adsorption capacity of the adsorbent is a crucial factor that was taken into account in the design of the fixed-bed column system (Uddin et al., 2009). Some of the fixed-bed column models used to analyse the equilibrium data are described below.

3.15.2.1 Thomas model

The Thomas model is an important model mostly used to describe fixed-bed column experiments. It is an inverse expression of the Bohart and Adams model (Poulopoulos & Inglezakis, 2006, Nwabanne & Igbokwe, 2012). The Thomas model is generally applicable for performance evaluation of the adsorption process in a fixed fixed-bed column study. In this study it was used to determine the maximum adsorption capacity of the adsorbents (AC-H_3PO_4). The Thomas model is expressed in equation 36:

$$\frac{C_{inf}}{C_{eff}} = \frac{1}{1+\exp\left(\frac{K_{th}}{Q}(q_e M - C_{inf} V_{eff})\right)} \qquad (36)$$

The linearized form is expressed in equation 37 and values for K_{th} and q_e were determined from a graph plotting In (Co/Ct)-1 against t.

$$\ln\left(\frac{C_{inf}}{C_{eff}}\right) - 1 = \frac{K_{th} q_e M}{Q} - \frac{K_{th} C_{inf} t}{Q} \qquad (37)$$

In the equation, K_{th} is the Thomas rate constant (mL/min mg), q_e the column maximum adsorption capacity (mg/g), V_{eff} is the effluent volume (ml), M (g) represents the mass (g) of

adsorbent t is the total flow rate time and Q represents the total flow rate (mL/min). The Thomas kinetic model has been used elsewhere to analyse fixed-bed sorption kinetics (Sivakumar & Palanisamy, 2009).

3.15.2.2 Yoon Nelson model

The Yoon Nelson column model was also used in this study. The model was designed by Yoon and Nelson in 1984, to study the breakthrough behaviour of gaseous adsorbate on activated carbon. The model is based on the assumption that the adsorption rate decreases with respect to the concentrations of adsorbate. The Yoon-Nelson equation is presented in equation 38:

$$\ln\left(\frac{C_t}{C_{inf}-C_t}\right) = K_{yn}t - \tau K_{yn} \qquad (38)$$

In the equation, K_{yn} represent the Yoon-Nelson rate constant (min^{-1}) (Paudyal et al., 2013)

3.15.2.3 Adams-Bohart model

The Adams-Bohart model is another significant fixed-bed column model that describes the performance of bed height in a column experiment. This model hypothesized that the rate of adsorption is proportional to the adsorption capacity of the adsorbent and the concentration of the adsorbate. The adsorption process is mainly controlled by the available adsorptive site presence in the surface of the adsorbent. The Adams-Bohart model is most suitable to describe the initial stage of the adsorption at the early stage of the breakthrough curve (Trgo et al., 2011). The model is expressed in equation 39.

$$\ln\left(\frac{C_t}{C_{inf}}\right) = K_{ab}C_{inf}t - K_{ab}N_o\frac{BH}{FC} \qquad (39)$$

where, K_{ab} represent Adams-Bohart constant, F is the flow rate N_o is the saturation limit of the adsorbent (mg/l), and BH represent bed height.

3.15.2.4 Bed Depth and Service Time (BDST) model

The BDST model was developed in 1973 from a previous model proposed by Bohart and Adams in 1920 (Sandhu, et al. 2015). This model is designed to analyse the breakthrough curve in a fixed-bed column experiment for the removal of contaminants (Patel & Vashi, 2012). Equation 40 expresses the relationship between service time and bed-height.

$$t = \frac{BHq_{ed}}{C_{inf}V} - \frac{1}{K_bC_{inf}}\ln\left(\frac{C_{inf}}{C_t} - 1\right) \qquad (40)$$

where *t* represents the service time to reach breakthrough point, and C_{inf} represents the initial concentration of the contaminated water (mg/l), V is the linear flow rate of the water into the fixed bed (ml/min), H is the bed height, K_b stands for the adsorption rate constant (l/mg/min^{-1}) and C_t represents the concentration of the effluent at time t (mg/l) (Tian et al., 2013).

3.16 Desorption study

Desorption studies were conducted to examine the regeneration capacities of the developed activated carbons and also to establish their reusability potentials. Three solvents (acetonitrile, methanol, and hydrochloric acid solution) of different ratios with distilled water were optimized for desorption of PFOS and PFOA from the surface of activated carbons after the adsorption process.

3.17 Statistical analysis

The data obtained were subjected to statistical analysis via two-way ANOVA for repeated measures, Spearman and Pearson correlation using SPSS 24 analytical software. This was done to establish the effect of levels of different sampling stations and seasonal variation on target compounds, also to establish significant different at different among the sampling locations at different seasons. Data were also analysed by box and whisker plot to establish the minimum, median and maximum levels of PFOA and PFOS at different sampling stations. Wiebull modulus analysis and percentile rank using Excel Microsoft office tool was also used to determine environmental hazard assessment from the investigated rivers.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter discusses the method developed for the analysis for analysis of PFCs, physico-chemical properties of surface water and sediment samples, monitoring, partitioning and distribution of PFCs in the selected sampling stations. The abatement method for the removal of PFOA and PFOS in the contaminated water using adsorption techniques and its application in a fixed-bed column study for the removal of PFOA and PFOS in contaminated water was also discussed.

4.1 Method optimization and validation

Analytical protocols for the determination of PFCs in environmental matrices (surface water and sediment) as recommended by USEPA (2009) and ICH guideline standard procedures for the method validation (Jain et al., 2013) were used.

4.1.1 Mobile phase optimization

Mixed solvents consisting of milli-Q water (solvent A) and methanol (solvent B) buffered to pH 6 was used as mobile phases. Mobile phase buffering was achieved by the addition of ammonium acetate 2 mM in both solvents. The pH of Milli-Q water and methanol were optimized at a slightly acidic solution of pH 6, in order to enhance the ionization of PFCs during elution into the mass spectrometer. These steps are similar to those of a previous study reported byBerger & Haukas (2005).

4.1.2 Identification of retention time and ion fragmentation in the chromatogram

Separation of analytes was achieved using a C18-HPLC column (Sulpeco, Sigmal- Aldrich, Germany). Compounds were identified on the basis of their retention time, the ratio of the precursor ions and product ion. They were quantified on the basis of peak areas in the chromatogram of the individual analytes and this took into account the signal-to-noise ratio of a 3:1 minimum (Wille et al., 2010b). The chromatogram of the individual compounds is presented in Figure 4.1. While, the mass spectral for the nine target compounds are presented in Figure 4.2

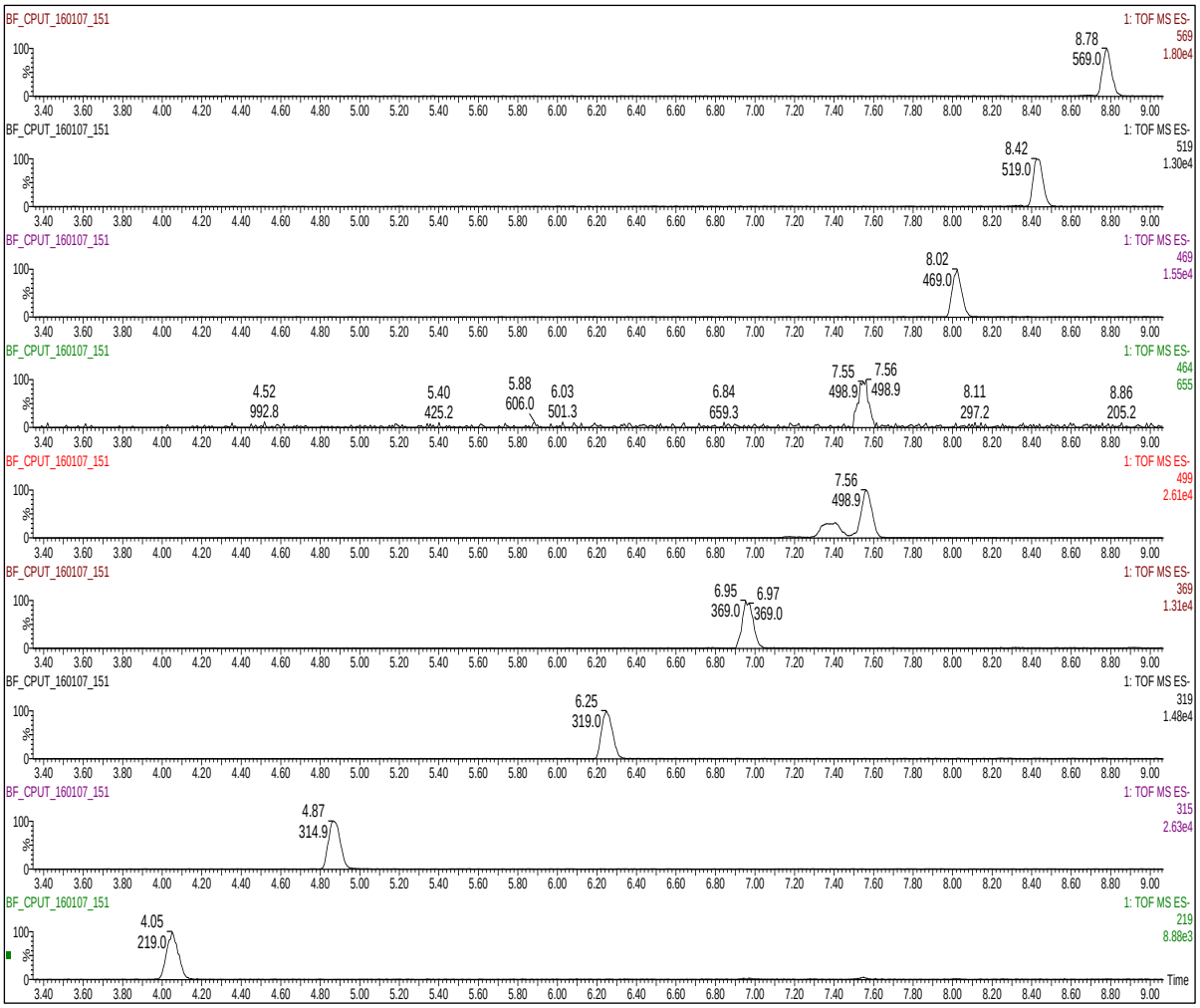


Figure 4.1: Chromatogram showing the peaks of the nine individual PFCs

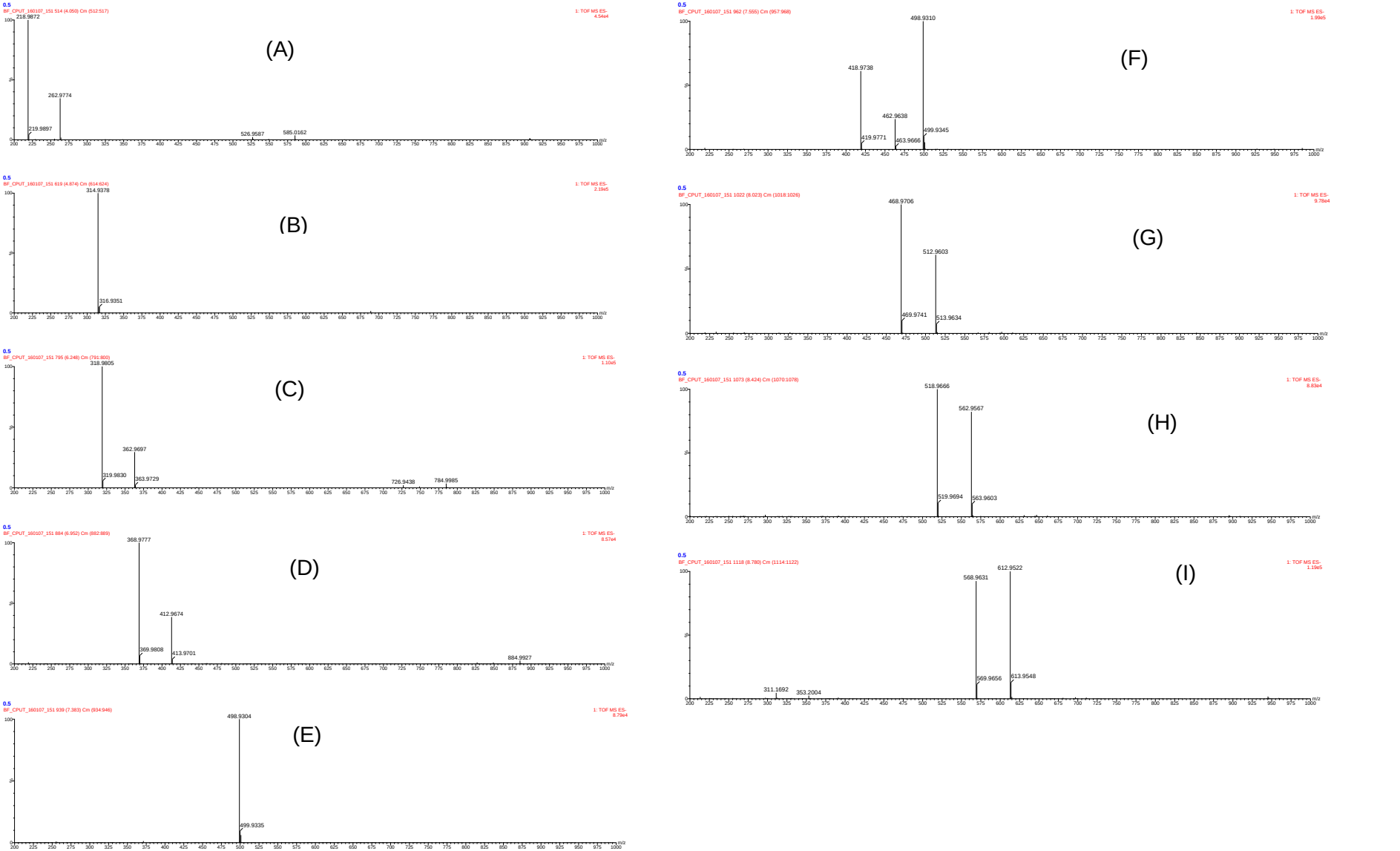


Figure 4.2: Mass spectral for the nine target compounds; (A)-PFBS, (B)-PFPeA, (C)-PFHpA, (D)-PFOA, (E)-PFOS, (F)-PFNA, (G)-PFDA, (H)-PFUnDA, and (I)-PFDoDA

The ionization of PFCs was achieved with QTOF/MS operated in dual electrospray ionization (ESI) interphase. The identification of target compounds was achieved using their abundance ion ratio and mass transition within the specified tolerance limits. The chromatograms of ithe mixture of the nine analytes are shown in Figure 4.3.

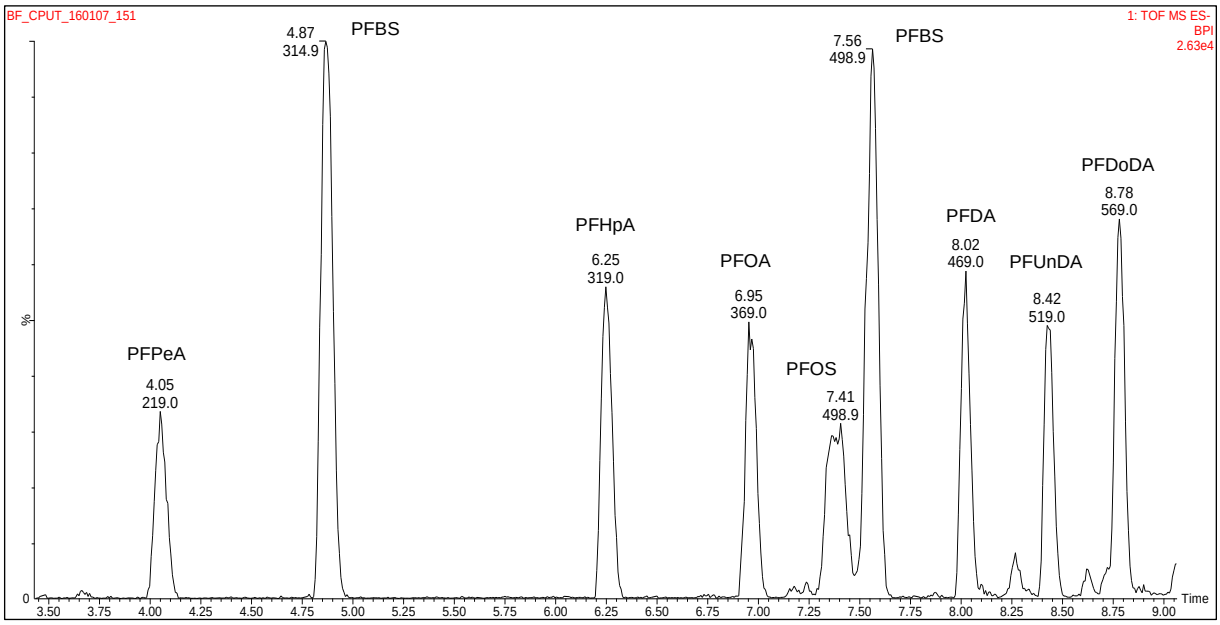


Figure 4.3: Chromatogram of the cocktail of the nine PFCs

The parent ions [M^-] for the investigated compounds were observed in negative mode polarity. The precursor ions for PFOA and PFOS were m/z 499 and 364 respectively. The estimation of signal to noise ratios for the peaks which were more than 10 times above the blank for all the target compounds was achieved in the multiple reaction modes (MRM), Transition of PFOS m/z 498.93 ($C_8F_{17}SO_3^-$ to m/z 498.9 score of 88.77 %) and the PFOA transition of the precursor ion 412.96 ($C_7F_{15}COO$-) to 369.0 is consistent to that reported by Moody et al. (2001), for PFOS, m/z 499 to 99 and PFOA 413 m/z to 369 m/z. Table 4.1 presents the retention time and other properties of the nine PFCs.

Table 4.1: Precursors ion (m/z), MS/Mass transition (m/z) and species of nine PFCs

PFCs	RT	Molecular formula	Molecular weight	Specie	$(M-H^-)$ion (m/z)	Product ion (m/z)	Quantitation Mass transition (m/z)	Score (%)
PFPeA	4.05	C_4F_9COOH	264.05	$(M-H)^-$	262.97	$-(H)^-$	219.00	76.88
PFBS	4.87	$C_4F_9SO_3^-$	316.1	$(M+SO_3)^-$	298.84	$+(SO_3)^-$	314.9	94.7
PFHpA	6.25	$C_6F_{13}COOH$	364.06	$(M-H)^-$	362.96	$-(H)^-$	319.00	82.76
PFOA	6.95	$C_7F_{17}COOH$	414.07	$(M-H)^-$	412.96	$-(H)^-$	369.0	93.93
PFOS	7.41, 7.55	$C_8F_{17}SO3^-$	500.13	$(M+SO_3)^-$	498.93	$+(SO_3)^-$	498.9	88.77
PFNA	7.56	$C_8F_{17}COOH$	464.08	$(M-H)^-$	462.96	$-(H)^-$	419.00	91.69
PFDA	8.02	$C_9F_{19}COOH$	514.09	$(M-H)^-$	512.96	$-(H)^-$	469.00	90.89
PFUnDA	8.42	$C_{10}F_{21}COOH$	564.09	$(M-H)^-$	562.95	$-(H)^-$	519.0	90.87
PFDoDA	8.78	$C_{11}F_{23}COOH$	614.1	$(M-H)^-$	612.97	$-(H)^-$	569.0	92.25

4.2 Method validation and optimization

Due to the complexity surrounding environmental samples, the liquid chromatographic-mass spectrometric (LC-MS) method is highly susceptible to matrix effect. The method was validated using ICH guidelines (Jain & Basniwal, 2013). The validation guidelines for this report include linearity, recovery studies, specificity, precision, and accuracy, limit of detection (LOD) and limit of quantification (LOQ). These parameters were checked to verify the sensitivity and efficiency of the method for detection and quantification.

4.2.1 Linearity and instrumental and method response

Calibration of the instrument showed good linearity for all the investigated compounds. Six calibration points were selected to obtain a line of best fit. The linear response ranged between 31.25 ng/l and 500 ng/l for all the target compounds as presented in Table 4.2.

Table 4.2: Calibration, linearity and Instrumental and method response

PFCs	Range (ng/l)	R/Time (min)	Calibration equation	LOD (ng/l)	LOQ (ng/l)	R^2
PFBS	31.25 -500	5.01	y=6284.4x-39.70	0.01	0.03	0.999
PFPeA	31.25 -500	4.17	y=481.7x-18.93	0.05	0.15	0.994
PFHpA	31.25 -500	6.37	y=744.09x-17.61	0.05	0.17	0.999
PFOA	31.25 -500	7.07	y=932.95x-15.29	0.04	0.10	0.998
PFOS	31.25 -500	7.47, 7.68	y=1175.6x+1.30	0.06	0.19	0.999
PFNA	31.25 -500	7.66	y=730.02x+9.99	0.01	0.04	0.991
PFDA	31.25 -500	8.15	y=1212.1x+9.94	0.02	0.06	0.997
PFUnDA	31.25 -500	8.56	y=1314.6x-4.39	0.02	0.07	0.997
PFDoDA	31.25 -500	8.95	y=1735.7x-8.74	0.02	0.07	0.998

The regression line of best fit which compares the relationship between the concentrations and peak area of the analyte was used for quantitation of the target analyte (external calibration). Linearity was achieved over the concentration range with a correlation coefficient (R^2) greater than (>0.99) for all the compounds investigated which demonstrates a good consistency and suitability for quantitative analysis (Table 4.2). Calibration plots for the nine PFCs are presented in the (Figure 4.4). The LOD ranged between 0.01 and 0.06 ng/l and LOQ ranged between 0.02 and 0.19 ng/l. These values were consistent with those obtained by (Lin et al., 2016) who used LC-ESI-MS/MS methods for trace analysis of PFSAs in the range of 0.06–1000 ng/l. Wang et al. (2016a) reported similar results with LOD ranging between 0.01 and 0.08 ng/l, and a LOQ value range of 0.06 to 0.22 ng/l for perfluoroalkyl substances in water.

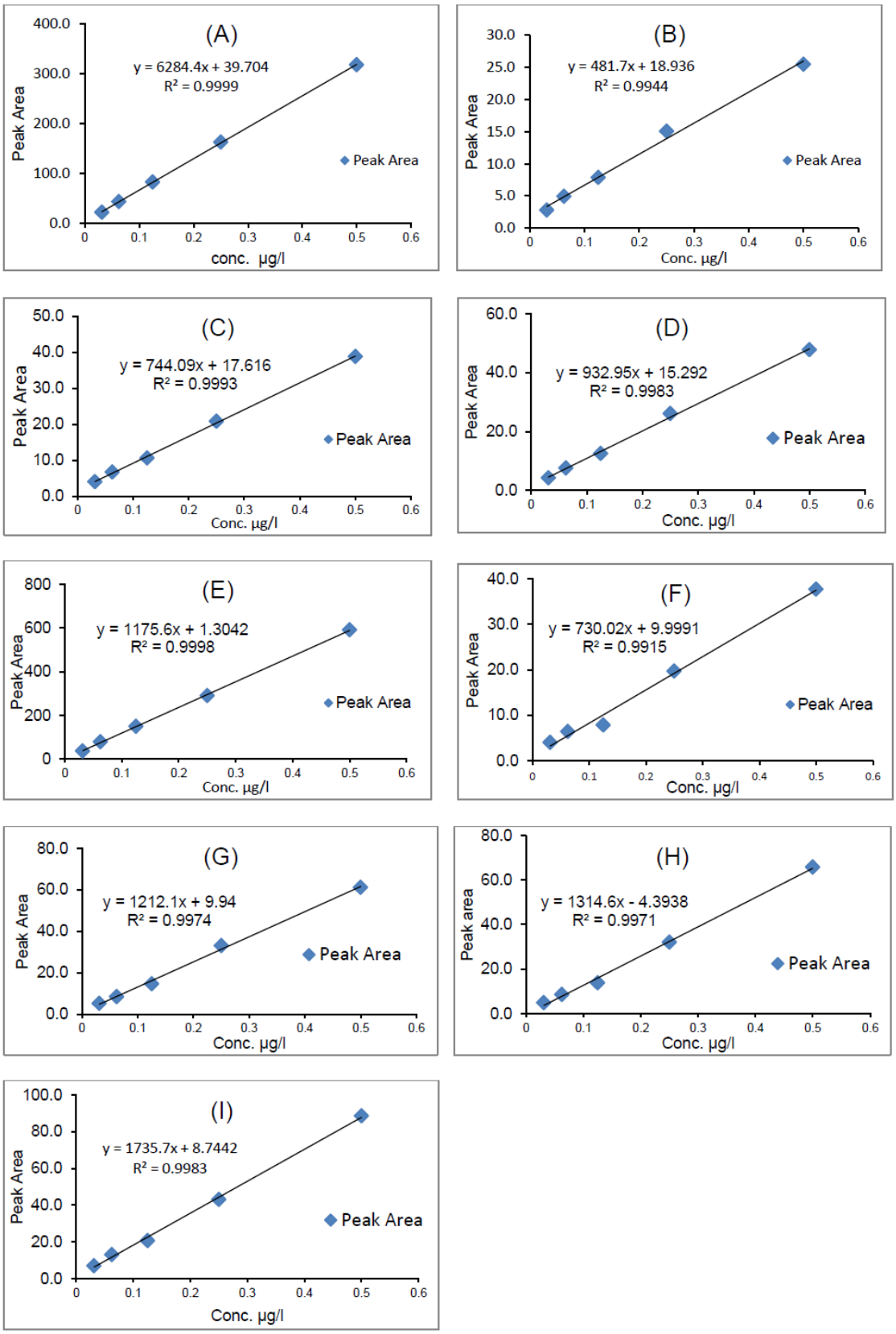


Figure 4.4: Calibration plots of nine PFCs; PFBS (A), PFPeA (B), PFHpA (C), PFOA (D), PFOS (E), PFNA (F), PFDA (G), PFUnDA (H), PFDoDA

4.2.2 Precision and accuracy

In order to validate the data obtained using this method, assessment of the accuracy of the instrument was performed by the injection of blank samples after every 10 injections. Uncontaminated blank injections established that the levels of target analytes were below LOQ. The degree of precision was represented as relative standard deviation (RSD). Milli-Q water was spiked with target analytes concentrations measured to test for the reproducibility and repeatability of the method. Table 4.3 present the optimisation of repeatability, reproducibility and mean relative standard deviation for the nine PFCs.

Table 4.3: Repeatability, reproducibility and mean (±SD) for the nine PFCs (ng/l)

PFCs	Repeatability			Mean +SD	Reproducibility			Mean ±SD
	x-time	y-time	z-time		x-day	y-day	z-day	
PFBS	13.09	12.71	12.43	12.74±0.33	12.65	12.43	12.19	12.42±0.23
PFBA	11.43	10.96	10.59	10.99±0.42	10.63	10.59	10.25	10.49±0.21
PFHpA	55.11	53.28	51.90	53.43±1.61	52.71	51.90	50.30	51.64±1.23
PFOA	16.35	16.03	15.49	15.96±0.43	15.69	15.49	15.03	15.40±0.39
PFOS	8.95	8.53	8.80	8.76±0.21	8.67	8.80	8.47	8.65±0.17
PFNA	13.49	13.08	12.99	13.19±0.27	13.10	12.99	12.50	12.86±0.32
PFDA	18.65	18.56	17.89	18.37±0.42	17.90	17.89	17.43	17.74±0.27
PFUnDA	23.04	22.53	22.20	22.59±0.42	22.21	22.00	22.20	22.14±0.12
PFDoDA	12.16	11.83	11.61	11.87±0.28	11.59	11.61	11.42	11.54±0.10

The repeatability test confirmed that the intraday precision was consistent for all compounds and there was no significant difference ($p>0.05$) in the results obtained during different period times of the day. The results obtained on different days showed a similar trend, hence the method is reproducible.

4.2.3 Recovery procedures for PFCs

The recoveries of the tested compounds from Milli-Q water, surface water and sediment samples using HLB cartridges for clean-up. The recoveries for milli-Q water were 78.5±16.5 % (PFBS), 93.1±7.2 % (PFPeA), 94.4±8.5 % (PFhpA), 93.1±11.4 % (PFOA), 90.6±13.3 % (PFOS), 92.0±6.0 % (PFNA), 87.3±8.8 % (PFDA), 90.0±12.1 % (PFUnDA) and 126.5±14.6 % for PFDoDA for 500 ng/l). Meanwhile, percentage recoveries from surface water at 500 ng/l ranged between 67.84±5.24 and 80.56 ±2.83 spiked of PFCs. Percentage recoveries for sediment at same concentration spiked were lowered ranged between 56.21±4.0 and 69.86±8.63. Percentage recoveries obtained from spiked Milli-Q water gave good recoveries. Low percentage recoveries from ambient surface water and sediment samples could be associated with interferences from environmental matrices. Sediment samples gave the least recoveries due to the complexities of impurities in the sample matrices. Percentage recoveries from spiked Milli-Q water, surface water, and sediment samples for the investigated compounds are presented in Table 4.4. Results from optimized recovery studies were presented in the Appendices A, B and C.

Table 4.4: Mean values (±SD; n=3) for the recovery of target compounds in spiked Milli-Q water, surface water and sediment samples

Target Analytes	Percentage Recoveries (125 ng/l)		Percentage Recoveries (125 ng/kg)	Percentage Recoveries (250 ng/l)		Percentage Recoveries (250 ng/kg)	Percentage Recoveries (250 ng/l)		Percentage Recoveries (250 ng/kg)
	Milli Q water	**Surface water**	**Sediment**	**Milli Q water**	**Surface water**	**Sediment**	**Milli Q water**	**Surface water**	**Sediment**
PFBS	54.4±10.0	42.58±1.6	41.06±7.1	74.50±2.9	71.04±1.7	57.20±2.8	78.50±16.5	78.66±3.2	56.21±4.0
PFPeA	61.6±6.9	51.2±2.9	48.26±6.6	78.13±1.2	71.46±1.2	59.06±2.0	93.12±7.2	75.68±2.5	62.26±2.6
PFHpA	46.4±12.5	50.13±1.2	45.28±3.8	72.60±4.2	68.26±1.4	60.40±1.6	94.40±8.5	68.0±7.6	64.66±7.3
PFOA	57.0±7.4	53.33±1.2	47.44±1.8	76.60±2.4	68.66±2.4	59.33±2.8	93.13±11.4	72.45±7.5	62.60±4.0
PFOS	56.8±2.1	60.75±1.9	54.82±4.4	77.70±2.2	75.33±1.6	62.00±1.44	90.60±13.3	68.32±13.5	60.00±3.7
PFNA	52.2±12.7	57.84±0.7	54.98±3.5	78.53±6.0	154.0±13.8	59.86±0.83	92.01±6.0	70.19±5.5	69.86±8.6
PFDA	61.8±3.2	52.02±2.1	48.90±4.7	75.31±1.2	70.38±2.2	61.21±2.13	87.30±8.8	80.56±2.8	62.53±4.3
PFUnDA	56.2±11.49	61.12±1.2	58.82±1.8	74.13±2.2	69.06±2.2	60.13±1.89	90.00±12.1	67.84±5.2	62.46±3.8
PFDoDA	66.4±7.2	66.69±3.6	61.2±3.9	73.20±2.6	69.46±0.6	61.20±3.17	126.52±14.6	72.42±5.7	60.20±3.2

In a previous study, HLB combined with Sep-Pack tubes was used for SPE extraction of polyfluorinated alkyl substances (PFAS) in ambient surface water gave good recoveries (89.2-98.0 %) for the investigated compounds (Hu & Yu, 2010). It was explained that the non-polar interaction between the C-F bond in the target compounds and the polar characteristics of the synthetic polystyrene bed in the SPE-HLB cartridges favoured the longer retention of PFCs in the SPE, while allowing the passage of interfering matrices (So et al., 2007). It was observed that longer chain PFCs showed a higher percentage recovery than shorter chain PFCs similar to a previous study (Weinberg et al., 2011). Results of this study showed that the extraction procedure is reliable and effective, and significantly trapped target compounds of PFCs onto SPE and allowed the passage of co-eluting solutes in the sample matrix. The Chromatogram for the procedural blank and working standards for the nine target compounds are shown in Figure 4.5

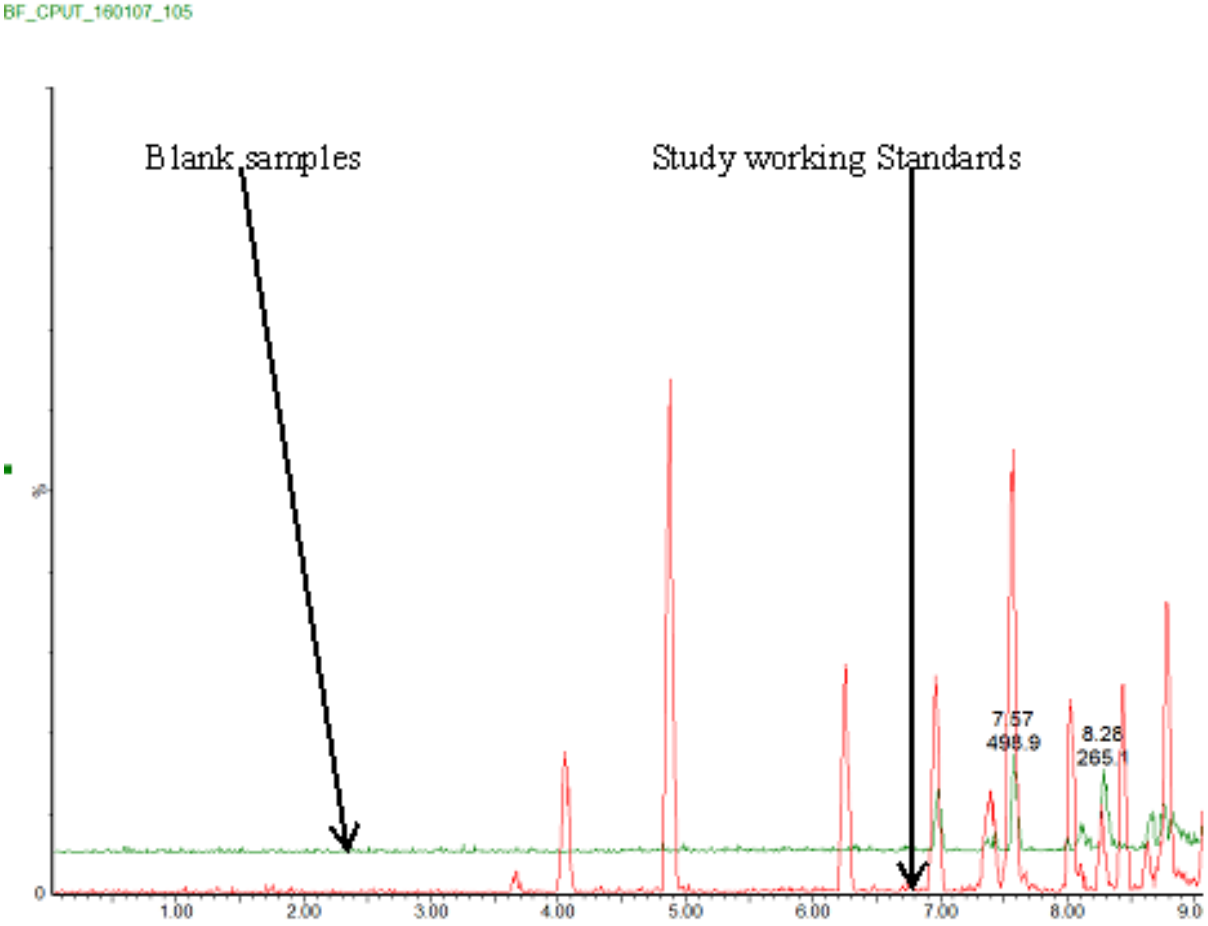


Figure 4.5: Chromatogram for the procedural blank and working standards for the nine target compounds

4.3 Physico-chemical properties of surface water samples of the Plankenburg and Diep Rivers

4.3.1 Surface water pH

The pH data obtained in the different sampling locations of both rivers are presented in Table 4.5.

Table 4 5: Seasonal variation of pH values (mean ± Standard Error) of surface water samples

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	6.50±0.20	6.89±0.17	6.70±0.40	6.60±0.30
PKB	6.70±0.20	6.7±0.10	6.80±0.06	6.58±0.52
PKC	6.90±0.35	7.10±0.10	7.08±0.28	7.09±0.10
PKD	7.04±0.20	7.24±0.01	7.11±0.09	7.07±0.07
DPA	7.66±0.65	7.32±0.20	7.19±0.10	7.20±0.10
DPB	7.60±0.57	7.35±0.21	7.46±0.10	8.03±0.40
DPC	7.73±1.00	8.19±0.09	7.6±0.26	8.40±0.20

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), and PKD: Downstream; Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

The average pH values measured ranged between 6.5 and 7.7 (summer), 6.7 and 8.19 (autumn), 6.7 and 7.6 (winter) and 6.6 and 8.4 (spring). All the pH values recorded in all seasons were within the World Health Organization's (WHO) standard guideline limits for surface water that ranges between pH 6.5 and 8.5 (WHO, 2014).

Sampling point DPC gave the maximum pH (8.4±0.2) during spring while the minimum pH was recorded at point PKA (6.5±0.2) during the summer. Statistical analysis shows that there is a significant relationship between pH values obtained during the spring and autumn periods (see Appendix D). Generally, pH values obtained in this study were consistent with similar investigations elsewhere in Southern Africa (Qiao et al., 2016, Olujimi et al., 2012, Igbinosa & Okoh, 2009).

4.3.2 Temperature

Prevailing surface water temperature plays a significant role in ecological system processes in an aquatic environment. Any significant change in temperature in an aquatic environment may lead to alteration of the ecosystem. The observed temperature values at all the sampling locations are presented in Table 4.6.

Table 4.6: Seasonal variation of temperature (^{0}C) of surface water samples (mean ± Standard Error)

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	19.65±0.07	16.8±20.26	12.76±2.51	17.45±1.48
PKB	20.10±0.40	16.60±1.50	13±20.87	18.40±1.97
PKC	19.85±0.20	16.65±1.76	13.16±30.19	18.30±1.55
PKD	20.15±0.90	16.40±1.55	13.06±3.80	18.29±1.25
DPA	22.60±1.69	17.85±3.70	15.16±1.70	20.55±3.18
DPB	24.60±0.8	21.25±2.80	17.36±2.70	22.45±0.21
DPC	21.50±0.00	17.30±3.50	14.90±2.10	21.00±2.96

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream; Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

Temperatures values ranged between 19.65 and 24.60 ^{0}C (summer), 16.61 and 21.25 ^{0}C (autumn), 12.76 and 17.85 ^{0}C (winter), and 17.45 and 22.45 ^{0}C in spring. The maximum temperature was recorded at point DPB (24.6 ^{o}C) during the summer, while the minimum temperature (12.7 ^{o}C) was measured in winter at PKA. There is a significant positive relationship ($P \leq 0.05$) in temperature values obtained from Plankenburg and Diep Rivers at different seasons; The values were not significantly different from each other. Temperature values observed in this study in all seasons were consistent with those of previous studies on Southern African surface water (Olujimi et al., 2012, Dalu et al., 2016). This suggests that there is no risk to organisms at any of the sampling points due to the effects of temperature. Thus, the prevailing temperature recorded does not appear to alter the homeostatic balance of the ecological system (Kodama-Namba et al., 2013).

4.3.3 Electrical Conductivity (EC)

Electrical conductivity (EC) measured at all the sampling stations ranged between 5.6 and 72.1 (*m*S/cm). The EC values of the surface water at different sampling stations in this study are presented in Table 4.7.

Table 4.7: Seasonal variation of electrical conductivity (*m*S/cm) of surface water samples (mean ± Standard Error)

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	6.15±0.01	5.74±0.01	6.39±0.07	8.30±0.06
PKB	6.45±0.03	5.755±0.02	6.42±0.09	8.30±0.12
PKC	5.58±0.05	5.89±0.07	7.01±0.05	8.40±0.13
PKD	6.11±0.01	6.05±0.04	7.21±0.07	8.50±0.15
DPA	12.58±0.09	8.745±0.01	14.35±0.19	17.70±0.23
DPB	9.90±0.43	13.755±0.00	12.34±0.23	17.00±0.14
DPC	72.95±0.28	72.15±0.74	51.28±0.91	56.10±1.72

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), and PKD: Downstream; Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

A higher value of EC was recorded at point DPC along Diep River, and this is associated with the close proximity of the sampling location to the ocean. Other sampling points along Diep River also recorded high EC values, which were associated with the location of the sampling points close to industrial facilities (DPB) and a residential area (DPA). The values of EC recorded from Plankenburg River ranges between 5.7 and 8.5 similar to department of water affairs and forestry (DWAF) recommended limits (5.5-7.5 *m*S/cm) for water (DWAF, 2015). But EC values measured in Diep River were higher than those measured from Plankenburg River. The EC values of the indicated that the investigated surface water pose no threat to agricultural and recreational purposes. Our observation is consistent with that of similar studies in South Africa with EC values ranged between 5.0 and 8.0 *mS/cm* with an average of 6.8 (Dalu et al., 2016).

4.3.4 Total Dissolved Solid (TDS)

TDS was measured in the surface water samples collected over four seasons. Maximum level of TDS value was recorded at point DPC (491.00±0.43 mg/l), while minimum value was observed at PKC (417.00±0.40 mg/l). The influence of the marine water intrusion at DPC contributed to the high content dissolved salts at the station. Statistically, there is a significant relationship between TDS values from the same rivers. TDS values were evidently higher in Diep River than in Plankenburg River. This suggests that anthropogenic activities such as petro-chemical facility, waste disposal and the influx of sea water into the river at the lagoon were among the factors that might contribute to increase in the TDS values in the river systems. There was no statistical correlation in TDS values among all sampling points in both rivers. However, seasonal measurements showed strong positive significant correlation (Pearson Correlation Coefficient ≥ 0.999) in values obtained for the four seasons ($p \leq 0.01$). Result obtained for TDS are presented in Table 4.8.

Table 4.8: Seasonal variation of total dissolved solids (mg/l) of surface water samples (mean ± Standard Error)

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	439.00±0.30	407.5±0.13	455.00±0.40	592.0±0.40
PKB	455.00±0.20	418.00±0.14	455.00±0.06	598.00±0.08
PKC	418.00±0.08	417.00±0.40	489.00±0.30	586.50±0.07
PKD	433.50±0.10	427.00±0.30	489.00±0.30	608.00±0.10
DPA	742.00±2.7	620.50±0.11	992.00±0.11	1260.00±0.15
DPB	702.00±3.0	974.00±0.008	877.00±0.17	1205.0±0.90
DPC	2511.5±2.30	4915±0.43	2892.10±1.6	3900.00±1.2

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream; Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

4.3.5 Salinity

Salinity values were measured at all sampling points. Like TDS, the highest values for salinity were obtained from sampling point DPC and values ranged between 3.95±2.28 and 7.46±0.66

(dS/m), followed by samples from points DPB and DPA. The high salinity values measured at DPC were due to sea water intrusion into the freshwater system. Also, industrial activities and most probably domestic waste are responsible for the high salinity values from DPB and DPA, respectively. Salinity values in Plankenburg River were lower than those obtained from Diep River. Higher salinity values were recorded during the autumn and spring, relative to winter and summer months. This observation is consistent with salinity values reported in a similar study reported elsewhere (Girjatowicz & Świątek 2016). Salinity values in the surface water samples that ranged between 0.45 and 0.96 (dS/m). The values obtained during the study are represented in Table 4.9.

Table 4.9: Seasonal variation of salinity (dS/m) of surface water samples ((mean ± Standard Error)

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	0.55±0.07	0.56±0.02	0.57±0.03	0.62±0.05
PKB	0.57±0.03	0.56±0.02	0.57±0.04	0.63±0.08
PKC	0.53±0.05	0.57±0.07	0.62±0.03	0.63±0.08
PKD	0.55±0.08	0.58±0.04	0.64±0.02	0.65±0.11
DPA	1.02±0.43	0.86±0.02	1.32±0.09	1.38±0.17
DPB	0.93±0.53	1.39±0.02	1.15±0.18	1.33±0.09
DPC	4.34±4.74	7.46±0.66	3.95±2.28	4.57±1.50

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream; Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

4.4 Aggregate grain size characterisation of sediments in the river systems

The physicochemical characteristics of the sediment samples were investigated. These included particle aggregate, fraction of organic carbon, and total organic matter of sediments. Percentage sand content was the most dominant particle in all the sediment samples investigated, followed by silt particles and then clay particles with the lowest percentage. This is consistent with previous geological studies revealing the dominance of sandy soil in the Cape Town area (Daso et al., 2013). The percentage ratios of clay and silt particles measured at each of the sampling locations were used to propose a possible sorption mechanism for the studied contaminants in

the environment. The percentage of clay was relatively high at sampling points PKC, PKD, DPA and DPB, thereby providing a suitable environment for the decomposition activity of organic contaminants.

Table 4.10: Physicochemical characteristics of sediment samples

Sampling Location	Av. mass of sand (g)	Av. mass of silt (g)	Av. mass of clay (g)	(%) sand	(%) Silt	(%) Clay	f_{oc}	Organic Matter
PKA	39.76	0.54	0.05	79.52	1.09	0.10	0.86	2.69
PKB	30.79	0.65	0.40	61.58	1.31	0.80	0.90	3.89
PKC	12.34	0.79	2.20	24.68	1.58	4.41	2.30	13.42
PKD	14.65	4.53	1.01	29.29	9.06	2.03	0.53	15.23
DPA	31.34	2.99	1.47	62.68	5.99	2.95	2.04	15.23
DPB	33.50	1.50	0.85	67.00	3.01	1.70	1.17	11.86
DPC	25.79	3.30	0.46	51.59	6.61	0.93	0.67	2.02

Table 4.10 shows the physicochemical characteristics of the sediment samples and values obtained indicated there is significant relationship ($p<0.05$) between organic matter (%), clay particle size (%) and fraction of organic carbon (%) in the investigated sediment samples. It was deduced that the higher clay content in the sediment samples collected from sampling locations PKC, PKD, DPA and DPB, might be responsible for the high organic matter and organic carbon. The fraction of organic carbon and extent of clay content in the sediments also indicated the degree of negatively-charged sites available on the sediments. According to Baldock (2014), organic carbon fraction and clay content of sediments indicate the degree of negatively-charged sites available on the sediments. High organic matter content in the sediment samples suggests a high rate of biological activity in the river, Samples collected at points DPA, DPB, PKC and PKD were found to have relatively high organic matter content, and samples PKA, PKB and DPC were found to have low organic matter content. The high values of total organic matter measured were due to the close proximity of sampling locations to human activities such as improper waste disposal systems, decomposition of organic and inorganic wastes from urban, agricultural activities, effluent from industrial activities and sewage.

4.5 Method application to real sample (surface water and sediment)

This method was applied to determine selected perfluorinated compounds (PFCs) in surface water and sediment samples. Identification of PFOA and PFOS in surface water samples showing the peaks and the corresponding chromatograms are presented in Figure 4.6.

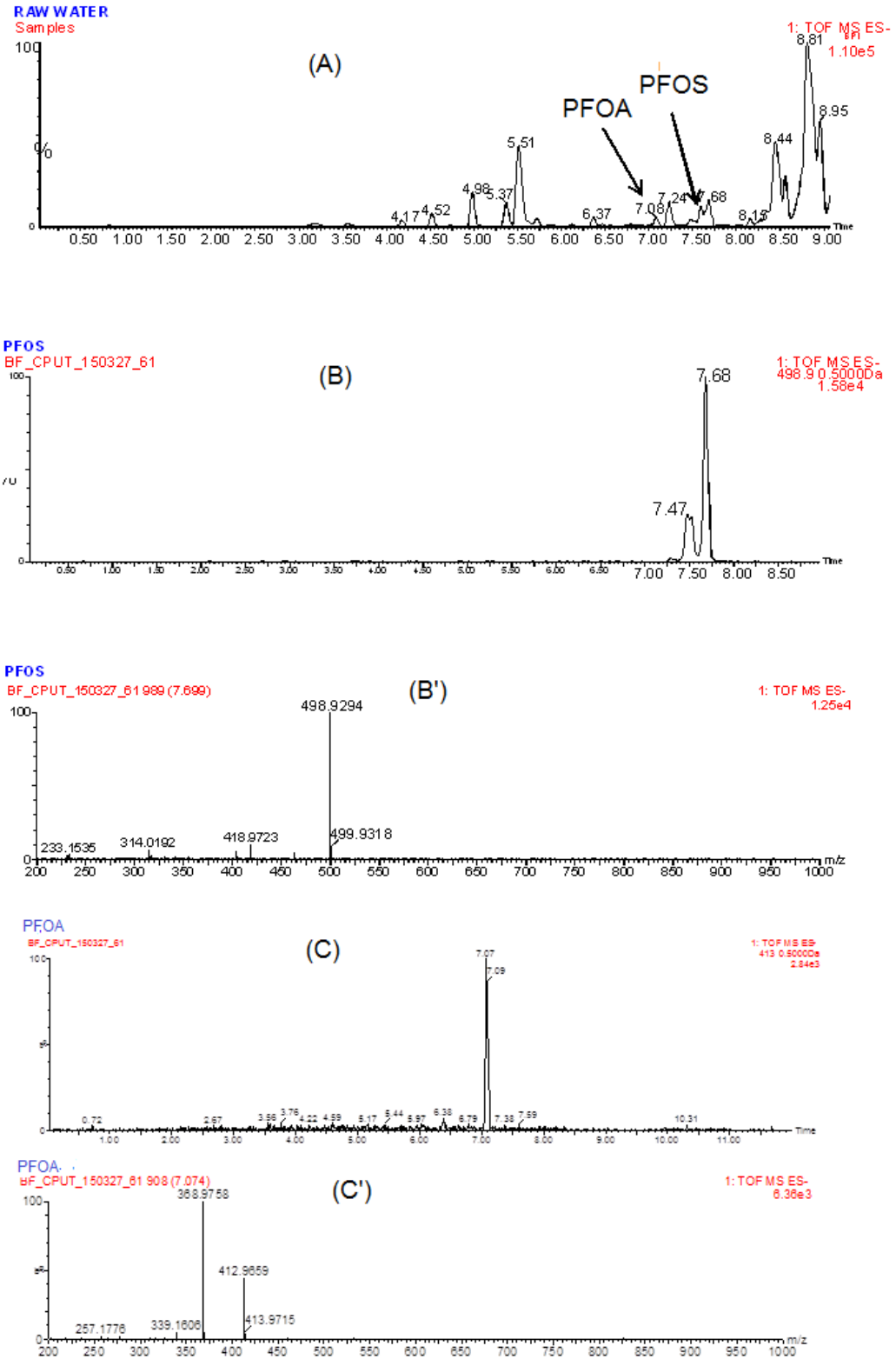


Figure 4.6: Chromatograms showing (A) PFOA and PFOS in raw water sample, (B) PFOS, (B') mass spectrometry (MS) PFOS, (C) PFOA, (C') mass spectrometry (MS) PFOA

4.6 Profiling of PFCs in the river system

The profile evaluation of the investigated PFCs in the river systems indicated that long chain perfluoroalkyl compounds were more dominant, when compared to short chain PFCs. PFNA (>20 %) was the most dominant followed by PFOA (18 %), and then PFHpA (12 %). Similar to water samples, PFNA (28 %) had the highest percentage in corresponding sediment samples, followed by PFOS (25 %), and then PFOA (17 %). Generally, the concentration of longer chain PFCs were higher in contrast to shorter chain PFCs in both surface water and sediment. Figure 4.7 depict the profiling of nine PFCs in both surface water and sediment in the river system

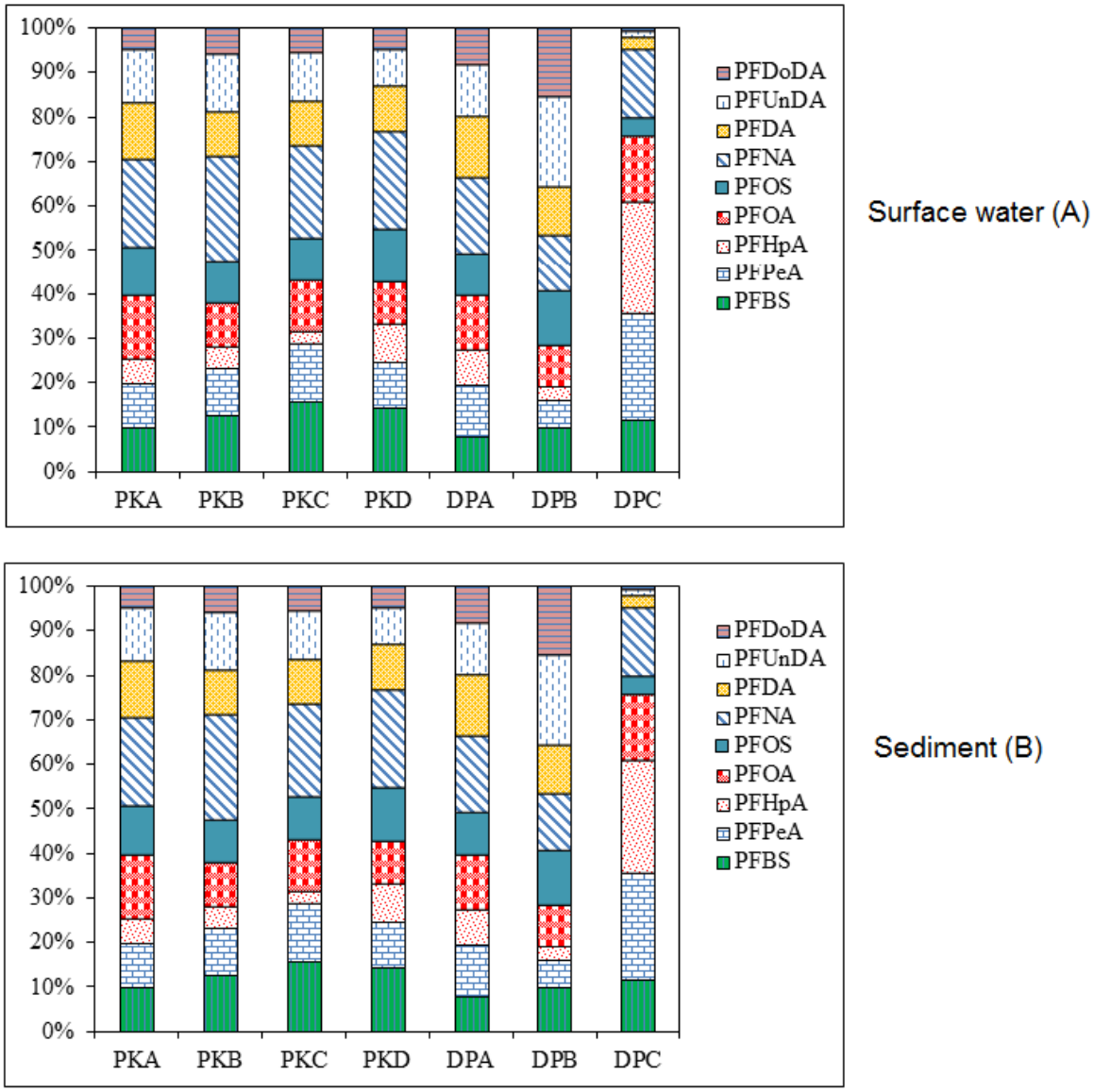


Figure 4.7: Profiling of PFCs in surface water (A) and sediments (B) samples

Perfluoro carboxylic acid (PFCA) was generally estimated to contribute above 70 % of the detected PFCs in both Rivers, while perfluoro sulfonic acid (PFSA) account for less than 30 %. Predominantly, long chained perfluoroalkyl compounds were mostly detected at elevated levels in the sediment. Total concentrations of the PFCA measured at sampling point (PKB, DPA and DPB) were 1780 ng/l (PFOA), 1784 ng/l (PFNA) and 2300 ng/l (PFNA). This observation is consistent with the report by Li et al. (2015), where above 83 % of PFCs were made up of PFCA; with PFOA released into the environment via fluoropolymer manufacturing industry contributed significantly. High concentrations of PFCs at these sampling locations were suspected to be the outcome of anthropogenic activities in the vicinities of both rivers. These include waste from informal settlement (PKB), agricultural farmlands (PKA) and wastewater intrusion from a winery facility and informal settlement (PKC). Sampling station PKC along Plankenburg River was found to be the most polluted. On the other hand, DPA was found to be most contaminated, followed by DPB and the least polluted point was DPC on the Diep River. Elevated levels of PFCs measured in DPA suggest domestic waste pollution of the river from residences close to the sampling point. High levels of PFCs at point DPB might also be due to emissions from a petrochemical facility which is about 2 km away from the sampling points. Low concentration of PFCs at point DPC may be due to its proximity to the ocean and dilution downstream. Concentrations of PFCs in sediment collected from Diep River were more than 100 folds compared to levels detected in corresponding surface water samples. Same accumulation trend (100 folds) was observed in sediments collected of Plankenburg River.

The sources of PFCs in both rivers are essentially very likely to be from domestic and industrial discharges from the immediate surroundings. They include waste release, derived from various chemical products such as electronic waste, fire fighting chemicals, pharmaceutical products, petrochemicals etc. Occurrence of PFCs in the river systems may also be influenced by sampling location and the, physico-chemical quality of the river water. For instance, influx of sea water increases dilution of the river water consequently, reducing the concentration of PFCs available at some of the sampling locations. Values of water quality parameters such as salinity, conductivity and TDS obtained at point DPC (closest sampling station to the ocean) attest to the observation. Levels of PFCs at sampling point DPC for both surface water and sediment samples differ from those of other sampling stations. Levels of PFCs measured in sediment samples were significantly ($p<0.05$) higher than levels surface water samples. This is an indication that larger portion of the PFCs exist in the sediment compartment of the river system.

Results showed that the between the perfluoroalkyl carboxylic compounds (PFPeA, PFHpA, PFOA, PFNA, PFDA PFUnDA and PFDoDA) occurrence in water and sediments did not differ statistically ($p<0.01$) at most of the sampling locations, similarly, ANOVA analysis using

multivariate showed that sampling locations have no significant effect on levels of PFCs ($P>0.05$, $F=3.72$). The perfluoroalkyl sulfonates (PFAS compounds- PFOS and PFBS) also occurred similarly in both water and sediment samples analysed. There are however significant differences in the occurrence of the carboxylic compounds and the sulphonates ($p<0.05$). The result was similar to other studies reported elsewhere; Chen et al.(2012a) reported that levels for PFCs in the aquatic environment ranging between 5.3 and 615 ng/l in the water, also, levels of perfluoroalkyl carboxylic compounds were found at higher concentrations relative to perfluoroalkyl sulfonate compounds. Trace concentrations of PFCs detected in the surface water in this study is consistent with Yang et al. (2011) who reported 12.15 and 4.8 ng/l in surface water. In a comparative study, Shao et al. (2016) reported the total concentrations of PFOA and PFOS ranged from 66.2 to 185 ng/l and 44.8 to 209 ng/l in surface water from Shuangtaizi estuary respectively.

4.7 Levels of PFCs in surface water and sediment samples

The levels of PFCs in the surface water samples at most sampling locations were at trace levels (ng/l) and are presented in (Appendices B and C) for Plankenburg and Diep rivers respectively. The measured levels of PFCs in the both surface water and sediment samples collected from the sampling stations are presented in Table 4.11 and 4.12 respectively.

Table 4.11: Mean concentrations ± SE (ng/l) of nine PFCs in surface water from sampling locations (January-December, 2015); n=12

Sample Stations	PFBS	PFPeA	PFHpA	PFOA	PFOS	PFNA	PFDA	PFUnDA	PFDoDA	Field Blank	ΣPFCs
PKA	193.50±38.06	270.50±88.54	237.00±105.76	262.75±147.32	180.25±63.54	335.5±168.27	198.25±83.54	290.75±208.91	170.50±94.70	<LOD	2139.01
PKB	132.00±37.61	300.25±61.74	195.50±102.83	333.00±148.54	195.50±33.91	314.25±129.13	222.75±62.16	325.75±171.73	117.25±48.94	<LOD	2136.25
PKC	165.50±42.90	288.25±89.30	354.25±150.32	262.50±126.86	281.50±148.62	391.5±194.41	180.50±72.94	366.50±187.60	231.25±167.41	<LOD	2521.75
PKD	92.30±39.54	266.75±112.43	247.00±128.37	319.25±136.62	126.75±39.27	286.25±216.33	177.50±92.17	227.25±150.53	199.50±151.57	<LOD	1942.50
DPA	119.75±46.84	430.25±211.31	418.00±238.91	417.00±219.90	284.50±89.13	479.25±312.01	226.00±149.72	225.25±162.46	176.75±124.11	<LOD	2776.75
DPB	138.00±28.56	208.75±51.45	300.50±146.40	293.75±118.91	240.75±91.70	314.75±141.34	234.25±88.01	323.75±143.43	160.00±27.25	<LOD	2214.50
DPC	167.50±36.50	268.25±111.23	202.50±127.62	186.75±91.64	135.00±34.54	232.25±81.05	79.25±30.25	69.25±36.48	58.50±17.48	<LOD	1399.25
Total Conc.	1008.57	2033.01	1954.75	2075	1444.25	2353.75	1318.5	1828.5	1113.75		

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream
Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)
Limit of detection=LOD, n=12.

Table 4.12: Mean concentrations ± SE (ng/g) of nine PFCs in sediment from sampling locations (January-December, 2015); n=12

Sampling Stations	PFBS	PFPeA	PFHpA	PFOA	PFOS	PFNA	PFDA	PFUnDA	PFDoDA	Field Blank	ΣPFCs
PKA	26.75±15.75	25.75±11.89	15.00±4.80	39.50±6.4	30.75±14.55	59.50±19.57	33.25±12.26	34.25±11.40	16.00±6.34	<LOD	280.75
PKB	35.25±28.92	30.75±19.43	13.50±2.78	27.75±8.0	27.5017.20	67.25±34.66	27.75±16.81	38.75±22.45	17.00±12.67	<LOD	285.50
PKC	36.50±28.81	30.25±26.96	8.00±0.94	29.25±16.3	24.00±14.12	53.00±29.92	21.50±20.87	25.50±19.55	14.75±5.39	<LOD	242.75
PKD	29.00±22.77	20.25±8.15	16.25±9.18	18.00±5.0	21.00±7.81	43.50±21.12	19.75±7.62	15.50±4.72	9.50±6.65	<LOD	192.75
DPA	31.25±20.73	49.50±39.14	34.25±18.34	51.50±29.2	39.75±16.59	73.25±35.00	51.75±37.11	48.50±25.57	36.75±18.32	<LOD	416.50
DPB	29.00±21.82	17.75±13.87	10.00±1.42	26.75±17.8	35.00±29.83	38.25±19.63	32.75±24.29	61.75±50.70	48.75±35.33	<LOD	300.02
DPC	34.00±23.04	73.00±70.01	78.75±63.78	44.50±16.9	13.50±7.4	47.75±20.5	8.00±4.6	3.75±3.0	2.50±1.0	<LOD	305.75
Total Conc.	221.75	247.25	175.75	237.25	191.5	382.5	194.75	228.01	145.25		

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream
Diep River: DPA Sewage effluent, DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)
Limit of detection=LOD, n=12.

The concentration of the PFCs in the surface water samples ranged between <LOD and 2533.3 ng/l, with mean concentrations of 444.0 ng/l at all sampling stations. PFNA is the most detected PFCs in surface water samples, with the highest concentration of 2533.3 ng/l for PFNA at sampling station DPA followed by PFPeA (403.5 ng/l), PFOA (390.4 ng/l) and PFHpA (387.3±644.8). Levels of PFCs in sediment samples ranged between <LOD and 329.0 ng/g with mean concentrations of 57.2 ng/g at all sampling stations. As with levels in the surface water samples, PFNA (64.4ng/g) was the most detected compound in the sediment samples, followed by PFUnDA (57.2 ng/g), PFDA (51.2 ng/g) and then PFOA (46.3 ng/g). Statistical analysis (two-way ANOVA, multivariate test) revealed significant relationship ($p<0.05$) between PFCA values detected in surface water and the sediment samples. However, the levels of PFCs in the sediment samples were significantly higher ($p<0.05$) than levels detected in corresponding surface water samples at most sampling points.

4.7.1 Levels of PFOA and PFOS in surface water

The measured levels of PFOA and PFOS in surface water samples of the Plankenburg and Diep Rivers are presented in Table 4.13.

Table 4.13: Levels (ng/l) of PFOA and PFOS in surface water samples of the Plankenburg and Diep River

	PFOA					PFOS				
Sampling Locations	Min	Max	Median	Mean±SD	Total	Min	Max	Median	Mean±SD	Total
PKA	<LOD	1352.70	100.00	250.76±423.65	2256.87	<LOD	742.19	128.50	193.41±246.93	1740.77
PKB	<LOD	1357.33	129.00	252.59±418.02	2273.37	<LOD	521.68	103.00	161.82±184.83	1456.42
PKC	6.67	1126.25	107.40	206.34±350.51	1857.06	<LOD	283.66	112.00	113.05±82.92	1017.49
PKD	<LOD	1311.25	125.37	238.39±411.56	2145.59	25.85	224.09	69.25	83.51±63.76	751.63
DPA	51.00	1929.80	230.00	390.45±583.54	3514.06	34.73	546.10	134.50	230.92±191.16	2078.32
DPB	<LOD	1176.20	189.00	304.62±355.71	2741.60	37.93	700.81	227.50	288.24±193.80	2594.21
DPC	<LOD	686.70	152.00	218.28±234.73	1964.60	<LOD	475.15	98.63	154.39±143.39	1389.57

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream,
Diep River: DPA (Sewage effluent), DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

The maximum concentrations of PFOA and PFOS in Plankenburg River were 1357.33 ng/l and 742.19 ng/l respectively, while the corresponding values in the Diep River were 1929.80 ng/l and 700.81 ng/l respectively. Levels of PFOA and PFOS in water samples at the different the sampling stations are represented in box and whisker plots in Figure 4.8.

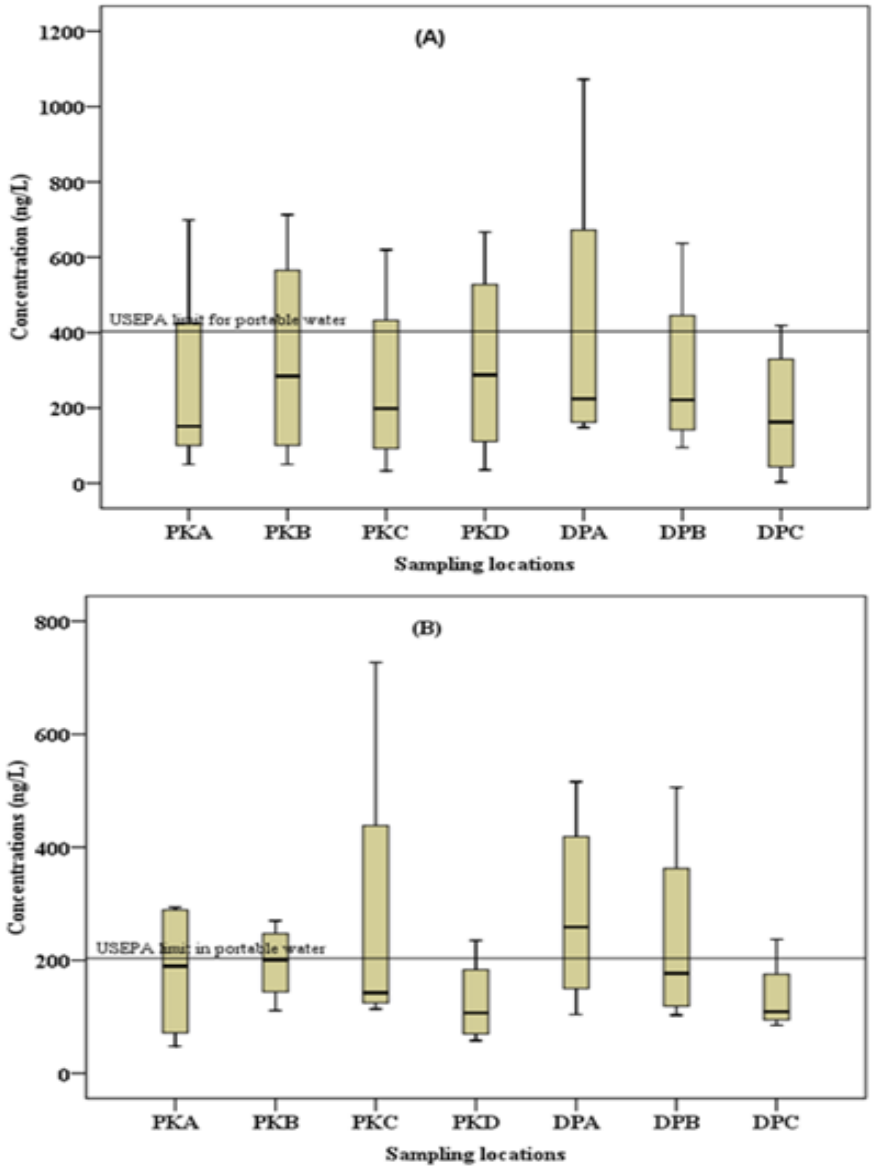


Figure 4.8: Box and whisker plot showing levels (ng/l) of PFOA (A) and PFOS (B) in surface water samples

The levels of PFOA and PFOS were generally low at most sampling points, and below USEPA threshold limits 400 ng/l and 200 ng/l for PFOA and PFOS respectively. Higher concentration of PFOA was recorded at sampling station DPA, relative to other sampling locations. Also, high concentrations of PFOS were observed at points PKC, DPA and DPB. The high PFOS levels could be attributed to domestic and industrial activities in the vicinity of sampling locations. There were significant differences ($p<0.05$) in concentrations of PFCs obtained from most sampling locations along Plankenburg and Diep Rivers. In a comparative study reported by Pan et al. (2014), the levels of PFOA and PFOS in the surface water were 18.03 ng/l and 0.72 ng/l respectively. Consistent levels of PFOA and PFOS which ranged between 0.4 - 123 ng/l; and 4.2 - 2600 ng/l, respectively, were also reported by Lein et al. (2008). Liu et al. (2015b) and Wang et al. (2016a), reported PFOA level of 0.37 mg/l and 0.97 mg/l in water collected from locations close to perfluoroalkyi facilities in Japan and China respectively. The reported levels values by Becker et al. (2008a), were more than 100 fold higher (250 ng/l) than those observed in this study, while lower levels were reported in coastal waters studied by Naile et al. (2013). Comparison of levels of PFOA and PFOS with those from similar studies is presented in Table 4.14.

Table 4.14: Comparative levels of PFOA and PFOS in surface water samples

Study locations		PFOA (ng/l)	PFOS (ng/l)	Reference
Pearl river, China		0.07-55	0.09-3.1	So et al. (2004)
Yodo river, Japan		0.4-123	4.2-2600	Liu et al. (2015)
Yangtze River, China		18.03	0.72	Pan et al. (2014)
Pearl River, Delta South China		0.24-16	0.02-12	So et al. (2004)
Estuarine and coastal areas of Korea		4.11- 450	2.95-68.6	Naile et al. (2010)
Eerste River, South Africa		147	23	Mudumbi et al. (2014)
Salt River, South Africa		390	47	Mudumbi et al. (2014)
Plankenburg River, Stellenbosch	PKA	(ND-1352.7)100	(ND-742.19)128	This study
	PKB	(ND-1357.3)129	(ND-521.63)153	This study
	PKC	(6.67-1126.25)123	(41-1126.25)155	This study
	PKD	(ND-1311.25)125	(32-425.85)73	This study
Diep River, Milnerton Cape Town	DPA	(51-1929.8)279	(34.73-546.1)354	This study
	DPB	(ND-1176.2)189	(37.93-530.81)227.5	This study
	DPC	(ND-686.7)152	(ND-475.15)98.1	This study

ND= Not detected

The low concentrations of most of the detected PFCs could be attributed to the influence of dilution and dispersion of the contaminants within different compartments of the aquatic systems. Increased concentrations of PFOA and PFOS in the aquatic environment above the threshold limit may trigger alteration in the ecosystem (Koschorreck et al., 2015).

4.7.2 Levels of PFOA and PFOS in sediment

The measured levels of PFOA and PFOS in the sediment samples collected from the different sampling points are presented in Table 4.15. The maximum concentrations of PFOA and PFOS in Plankenburg River were 115.5 ng/g and 153.0 ng/g respectively. The corresponding values in the Diep River were 214.50 ng/g and 246.25 ng/g.

Table 4.15: Levels of PFOA and PFOS (ng/g) in sediment samples of the Plankenburg and Diep River

	PFOA					**PFOS**				
Sampling locations	Min	Max	Median	Mean±std	Total	Min	Max	Median	Mean±std	Total
PKA	13.33	72.81	31.88	38.34±20.42	345.13	<LOD	128.5	15.53	28.35±39.28	255.22
PKB	<LOD	70.50	17.65	26.80±20.01	241.25	<LOD	153.00	3.03	25.14±49.05	226.34
PKC	<LOD	115.50	16.80	25.43±36.76	228.91	<LOD	112.00	11.63	21.27±35.84	191.47
PKD	<LOD	35.24	13.22	17.95±14.05	161.61	<LOD	69.25	17.82	21.83±25.62	196.54
DPA	0.80	214.50	31.51	46.39±66.06	417.51	<LOD	134.5	31.19	37.24±41.21	335.16
DPB	<LOD	98.00	14.82	26.35±33.16	237.18	<LOD	246.25	1.89	35.20±80.23	316.87
DPC	8.87	152.00	31.71	40.08±43.24	360.77	<LOD	49.69	2.55	11.79±17.06	106.17

Plankenburg River: PKA (Upstream), PKB (Informal Settlement), PKC (Industrial effluent), PKD: Downstream
Diep River: DPA (Sewage effluent), DPB (Effluent from Petrochemical facilities), DPC (Downstream proximity to ocean)

The box and whisker plot (Figure 4.9) showed that the detection of PFOA and PFOS in the sediments at most of the sampling points were at levels which ranged from less than detection limit (<LOD) to 128.5 ng/g (dw) in Plankenburg river and from <LOD to 246.25 ng/g (dw) in the Diep River.

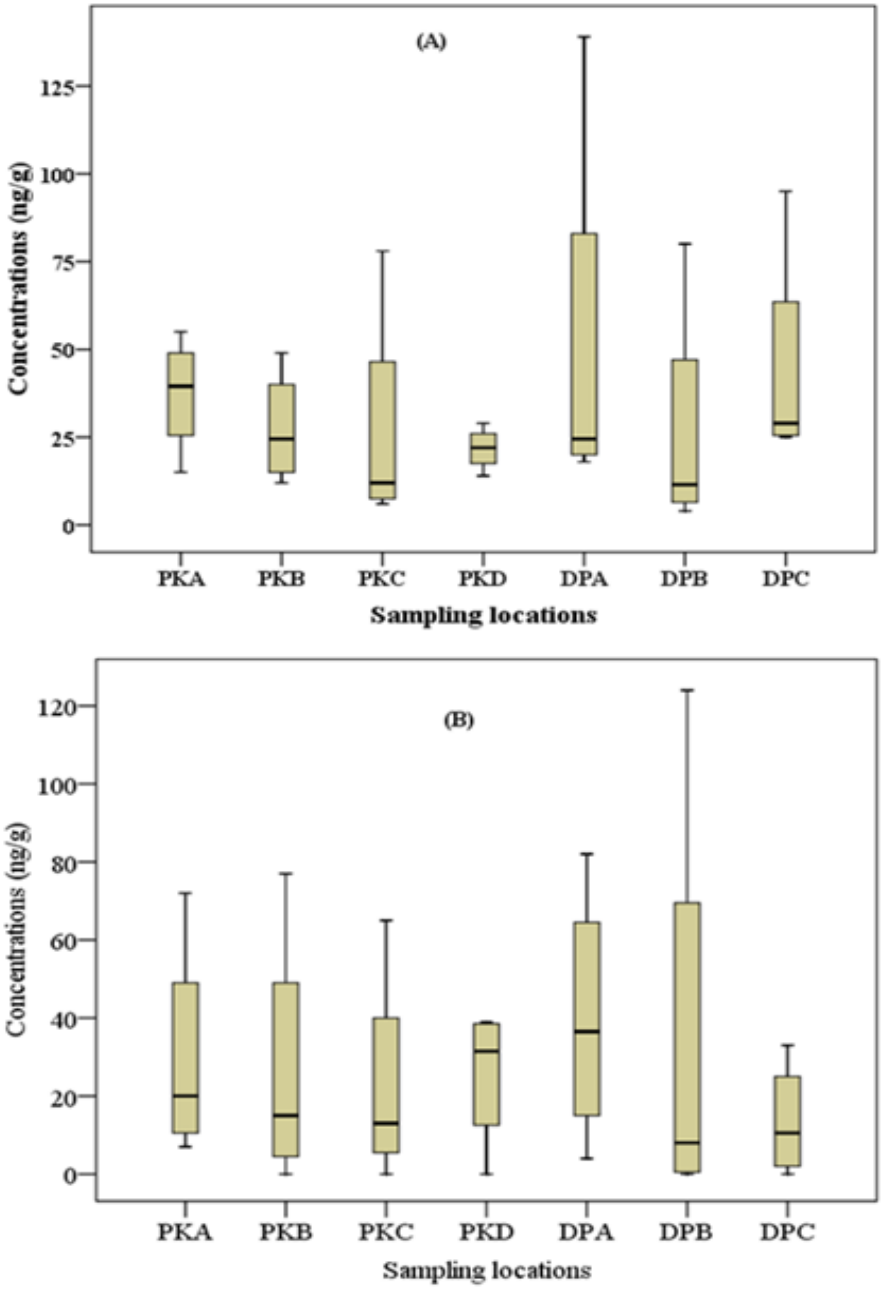


Figure 4.9: Plots of levels (ng/g) of PFOA (A) and (B) PFOS (B) in sediment samples of the Plankenburg and Diep Rivers

The mean concentrations of PFOS in Plankenburg and Diep Rivers during study was generally low, with concentrations that ranged between <LOD and 114 ng g (dw), while that for PFOA was 40 ng/g (dw), and ranged <LOD – 152 ng/g. There were some relationships (positive and negative) in the occurrence of PFOA and PFOS in the sampling points ($p<0.01$) with Pearson's Correlation Coefficients of 0.585 and -0.493 for water and sediments respectively in both Rivers. ANOVA multivariate revealed that there were significant differences ($p<0.05$) in the levels of PFOA and PFOS in the seven stations. Combined effects of locations and PFCs' levels had an F-value of 17.481 and p-value of 0.006 (Appendix L). This suggests that activities surrounding sampling locations significantly influenced the levels of PFCs.

In a study reported by Mudumbi et al. (2014) comparable concentrations, were detected in sediment samples collected from Salt and Eerste Rivers on the Cape flats in Cape Town . They reported 16 ng/g (PFOA) and below detection limit (PFOS) for Salt River and 5 ng/g (PFOA) and 14 ng/g (PFOS) for Eerste River. Lu et al.(2015) reported a total concentrations ranging between 0.25 and 1.1 ng/g for PFOA, and <LOD and 3.1 ng/g for PFOS in in sediment samples of Zhuijiang and Huangpu Rivers, Japan. In another study, the background concentrations of PFOA and PFOS ranged between <LOD and 0.1 ng/g; and 0.25 and 1.50 ng/g, respectively (Perra et al., 2013), much lower than levels observed in this study. The levels observed by Perra et al. (2013) were higher than those reported by Klosterhaus et al. (2012) in four rivers of San Francisco Bay, California, USA, with concentrations between <LOD and 1.30 ng/g (dw); and in Taihu Lake in China, with concentration of < 2 ng/g (dw) (Yang et al., 2011). Other workers also showed higher levels of PFOA and PFOS than levels reported by Bao et al. (2009) which ranged between 0.20 and 0.64 ng/g for PFOA and below <LOD and 0.46 ng/g for PFOS. Levels of PFOS in Daliao River system of northwest China was 536.7 ng/g (dw), which is 10-fold higher those measured Plakenburg and Diep Rivers sediments.

Levels of PFOA and PFOS obtained from this study were subjected to probabilistic hazard assessment to predict the possibility of exceeding regulatory values in both surface water and sediment. Mean concentrations of quadruplicate samples collected over twelve months from seven sampling points (4 on the Plankenburg River and 3 from the Diep River) were ranked using Weibull probabilistic approach and percentile ranking previously reported (Berninge and Brooks, 2010; Corrales et al., 2013 & Connors et al., 2014). Percentile for environmental distribution and percentage exceedence of PFOA and PFOS in surface water (ng/l) and sediment (ng/g) from the Plankenburg and Diep Rivers are presented in Table 4.16.

Table 4.16: Equation for regression lines and values corresponding to percentile for environmental concentration distribution of PFOA and PFOS in surface water (ng/l) and sediment (ng/g) in the Plankenburg and Diep Rivers.

							Centile Values			Percentage Exceedence		
Compounds	Matrix	River	n	R^2	a	b	25%	50%	75%	PNEC(UKEA)	DWC (Germany)	USEPA Limits
PFOA	Surface water	Plankenburg	48	0.9581	0.7278	-3.9692	756.98	897.1	1045.78	8%(4/48)	56%(27/48)	54%(26/48)
		Diep	36	0.8984	0.6919	-3.9693	1194.4	1309.33	1455.82	0%(0/36)	52%(19/36)	50%(18/36)
	Sediment	Plankenburg	48	0.9561	1.0479	-3.4532	55.039	71.038	86.3			
		Diep	36	0.9695	0.9305	-3.2649	88.29	119.717	145.33			
PFOS	Surface water	Plankenburg	48	0.9	0.7662	-4.001	909.5	1036.74	1207.7	12.5%(6/48)	58%(28/48)	56%(27/48)
		Diep	36	0.9042	1.0375	-5.621	446.43	526.99	595.03	0%(0/36)	55%(20/36)	50%(18/36)
	Sediment	Plankenburg	48	0.817	0.7002	-2.0485	10.31	51.88	84.36			
		Diep	36	0.7631	0.5986	-1.7602	24.34	100.01	155.52			

Percentage Exceedence is based on the Predicted No Effect Values ($PNEC_{UKEA}$) 2500 ng/l, USEPA limits 400 ng/l (PFOA) and 200 ng/l (PFOS) and $DWC_{Germany}$ 300 ng/l for both (PFOA and PFOS).

NB: surface water centile unit =ng/l; sediment = ng/g.

At 75th centiles, distribution of PFOA in the Plankenburg and Diep Rivers water samples were 1045.78 and 1455.82 ng/l respectively. The corresponding values for PFOS were 1207.7 ng/l and 595.03 ng/l. For sediment samples, distribution of PFOA was 86.30 ng/g (Plankenburg) and 145.33 ng/g (Diep), The values for PFOS were 84.36 ng/g and 155.52 ng/g for the Plankenburg and Diep Rivers respectively. Percentile values showed higher concentrations of PFOA in the Diep River than in the Plankenburg River water samples. This indicated higher load of PFOA in the Diep River than those observed in Plankenburg.In contrast, PFOS had higher value in the Plankenburg River than the Diep suggesting that pollution load and sources differed for both rivers.

Probabilistic hazard assessment was employed to examine the likelihood of exceedence of predicted no effect concentrations (PNEC) by UK Environmental Agency (EA) 2500 ng/l for PFOA; Department of Water Council (DWC, Germany) - 300 ng/l for each of PFOA and PFOS for potable water; United States Environmental Protection Agency (USEPA) threshold limits for water - 400 and 200 ng/l for PFOA and PFOS respectively. Distribution pattern in the investigated rivers were similar, Percentage exceedence values for PNEC (UKEA) were below 17% in both rivers. For PFOA, USEPA and DWC threshold limits were exceeded, with distributions of 54 and 56% for Plankenburg River, 50 and Diep River (52%). Percentages exceedent for PFOS in Plankenburg River were 56 and 58% for USEPA and DWC respectively, and percentage exceedence of 50% and 55% for Diep River. Measured environmental concentration distributions of PFOA and PFOS in environmental matrices (surface water and sediment) from the Plankenburg and Diep rivers are presented in Figure 4.10. This study revealed that the Plankenburg River had a higher percentage exceedent value for PFOA, and the Diep River had greater burden of PFOS in both its surface water and sediment.

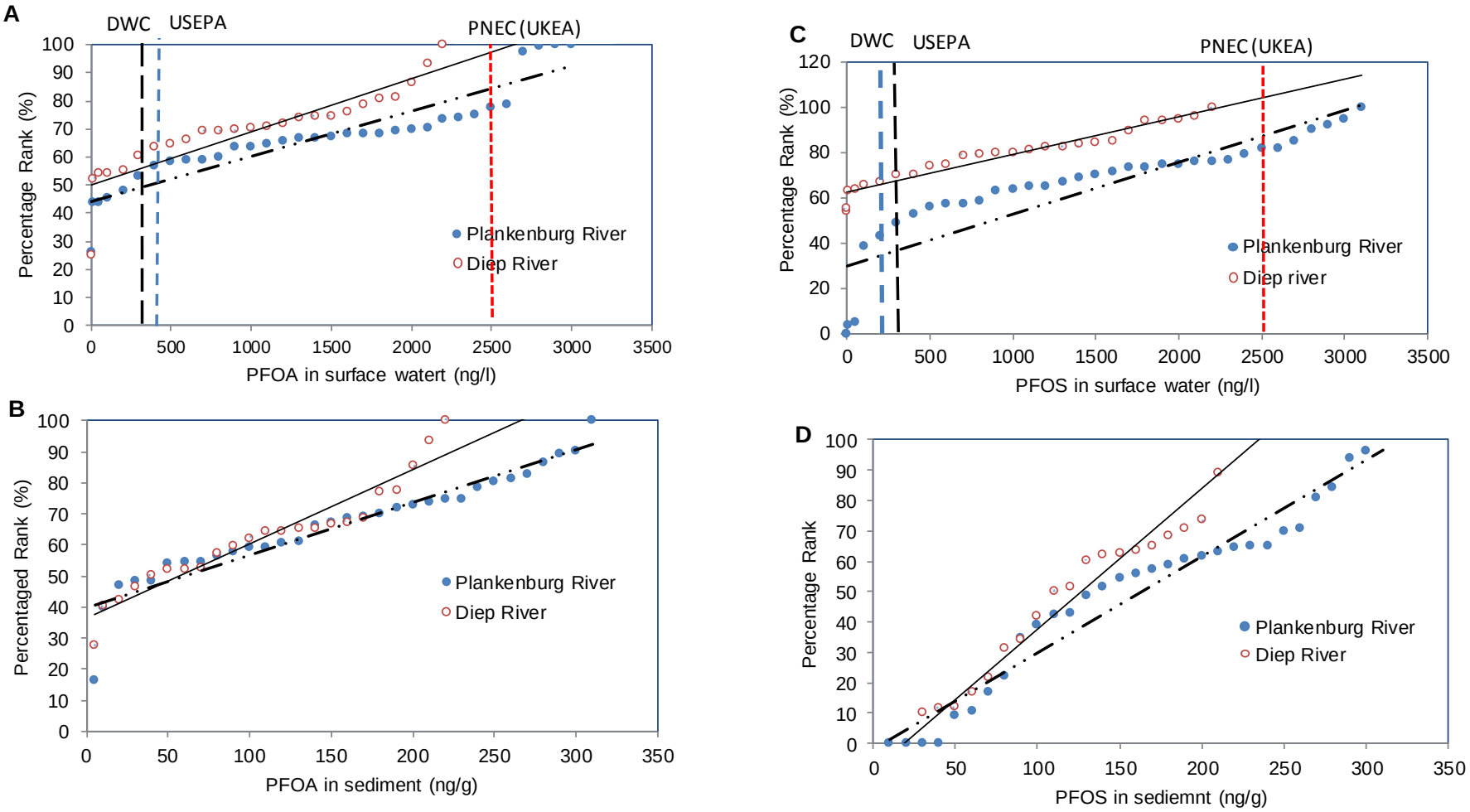


Figure 4. 10: Probabilistic hazard assessment approach.

Environmental concentration distributions of PFOA in surface water (A), PFOA in sediment (B), PFOS in surface water (C) and PFOS in sediment (D) in Plankenburg and Diep Rivers. Vertical lines correspond to Predicted No Effect Concentrations ($PNEC_{UKEA}$) 2500 ng/l; USEPA limits of 400 ng/l (PFOA) and 200ng/l (PFOS), Department of Water council ($DWC_{(Germany)}$) is 300 ng/l for both PFOA and PFOS in water samples

The comparisons of the observed levels of PFOA and PFOS in this study and those reported elsewhere are presented in Table 4.17.

Table 4.17: Comparison of levels of PFOA and PFOS in sediments with other studies

Study location		PFOA (ng/g)	PFOS (ng/g)	Reference
Orge River (Near Paris), France		<0.07	4.3	Labadie & Chevreuil (2011)
Sydney Harbour		N.D-0.16	0.80-6.2	Thompson et al. (2011)
Taihu Lake, China		<0.02-0.52	0.06-0.31	Yang et al. (2011)
Lake Constane Alphine Lake, Austria		<0.13-0.82	N.D-<0.94	Clara et al. (2009)
Roter Main River, Bayreuth, Germany		<.0.02-.175	0.05-0.537	Becker et al. (2008a)
Haungpin River Shanghai, China		0.20-0.64	N.D-0.46	Bao et al. (2009)
L'albufera National Park, Valencia, Spain		0.03-10.9	0.10-4.80	Pico et al. (2012)
Plankenburg River, Stellenbosch, South Africa	PKA	(13.3-72.81)31.88	(ND-128.5)15.53	This study
	PKB	(10-70.5)17.65	(ND-153)3.03	This study
	PKC	(ND-115.5)16.80	(ND-112)11.63	This study
	PKD	(ND-35.24)13.22	(ND-69.25)17.82	This study
Diep River, Milnerton Cape Town, South Africa	DPA	(0.8-214.5)31.51	(ND-134.5)31.19	This study
	DPB	(ND-98)9.7	(ND-246.25)1.89	This study
	DPC	(8.86-152)31.71	(ND-49.690)2.55	This study

ND= Not detected

4.8 Seasonal variation of PFCs in surface water samples

Seasonal variations in the levels of nine PFCs in water samples were investigated in the study period. The detected concentrations of ∑9PFCs in surface water samples at all sampling locations during different seasons, ranged between 223 ng/l and 943 ng/l (summer), <LOD and 137 ng/l (autumn), <LOD and 167 ng/l (winter) and 9 ng/l and 600 ng/l (spring). Results were presented in the Appendix I. PFCs occurrence was in the order: summer > spring > autumn > winter. Of all the PFCs, PFNA was the most prevalent with higher concentrations at most of the sampling stations across the seasons; while shorter chains PFCs were less prevalent. However, the observed concentrations of ∑9PFCs at the different sampling stations across the seasons were not significantly different ($p>0.05$; (Sig; 0.08) from each other. Two-way ANOVA using multivariate test showed that seasons had significant effects ($p<0.05$) on concentrations of PFCs measured at different sampling stations. Figure 4.11 represents the seasonal variations of PFCs in water samples at individual sampling stations.

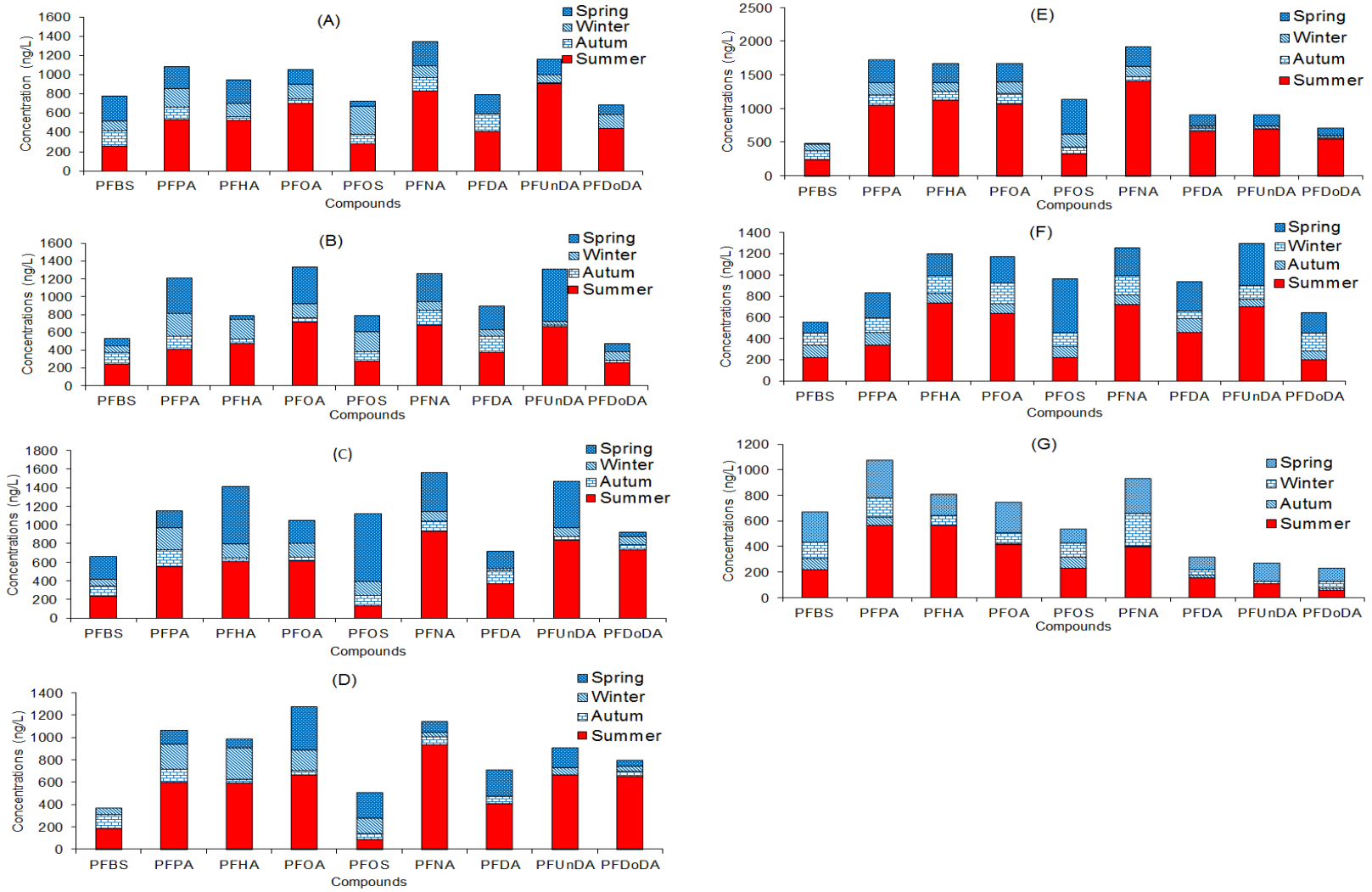


Figure 4.11: Seasonal variation of PFCs in surface water samples from different sampling locations; PKA (A) PKB (B) PKC (C) PKD (D) DPA (E), DPB (F) and DPC (G).

4.9 Seasonal variation of PFCs in sediment samples

Generally, highest concentrations of PFCs were detected measured in sediment samples in summer and the least (<LOD) in autumn. The concentrations of the ∑9PFCs in sediment samples collected from all the sampling stations ranged between <LOD ng/g and 150 ng/g (summer), <LOD ng/g and 37 ng/g (winter), <LOD ng/g and 46 ng/g (autumn) and <LOD ng/g and 80 ng/g (spring), results were presented in the Appendix J. The highest PFCs concentration (278.5 ng/g) was obtained in sediment sample at sampling point DPA during summer, while the least level (<LOD) was measured in sediment samples during autumn in sampling station DPC. The distribution of the PFCs in both rivers was not significantly different except at DPC where higher levels of some compounds were recorded in summer months (Figure 4.15). But the levels detected in all sampling stations were significantly different over the four seasons. There were significant correlations ($p<0.01$) between levels of the PFCs at sampling points PKA, PKB and PKC. Using two-way ANOVA, data suggests that significant differences occurred in levels of both PFOA and PFOS in sediment samples collected in the four seasons. This implies that seasons played some role in PFCs occurrence. In contrast, there was no significant difference in levels of both compounds within sampling locations over the four seasons. This suggests that increases in sediment concentration were not significant within the sampled locations.

Fluctuations in the levels of PFCs in different seasons maybe attributed in part to dilution of the river systems through rain. On the other hand, the high concentration of PFCs measured during summer is an indication accumulation of the compounds released from anthropogenic activities coupled with less water volume and flow. The levels of PFCs recorded in summer are a clear indication that prevailing climatic and weather conditions might influence occurrence of PFCs in the aquatic environment. Levels of PFCs reported in this study are consistent with previous studies conducted elsewhere (Perra et al., 2013, Lu et al., 2015, Gebbink et al., 2016, Ahrens et al., 2015). Figure 4.12 presents the seasonal variation of PFCs in sediment samples over four seasons at different sampling stations.

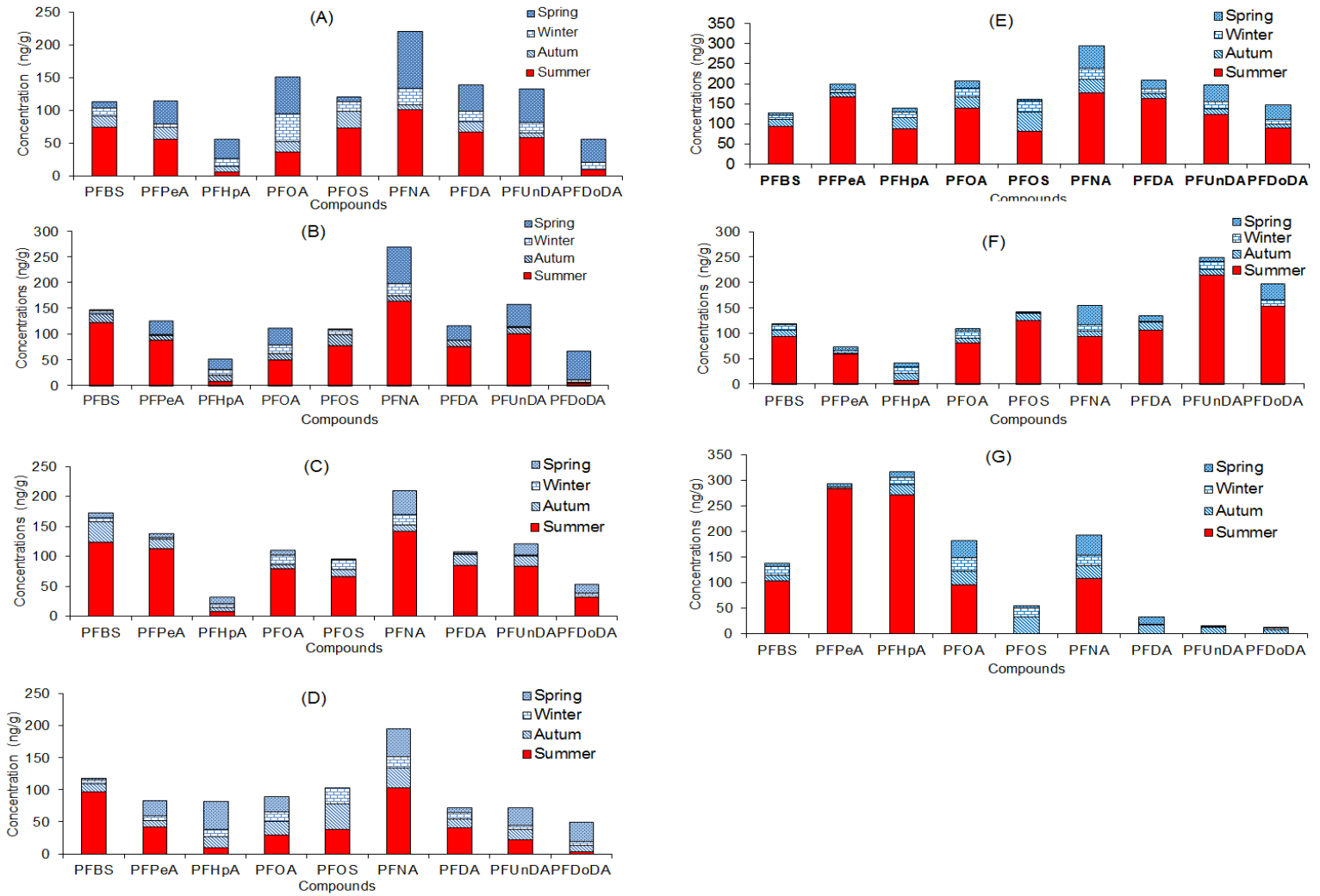


Figure 4.12: Seasonal variation of PFCs in sediment samples from different sampling locations; PKA (A) PKB (B) PKC (C) PKD (D) DPA (E), DPB (F) and DPC (G).

4.10 Seasonal variability of PFOA and PFOS in surface water and sediment

The distribution and seasonal variability of PFOA and PFOS, was investigated to determine the trend in levels in the environmental matrices (water and sediment) with respect to climatic conditions.

4.10.1 Seasonal levels of perfluorooctanoic acid (PFOA)

Sampling covered the four seasons in South Africa to establish influence of the seasonal variations on PFOA occurrence in surface water and sediment samples.

PFOA is one of the most discussed PFCs, drawing the attention of leading environmental scientists and international regulatory bodies globally (Giesy & Kannan, 2002b, Helm et al., 2011). Studies have revealed that the presence of PFOA in environmental components could have serious and hazardous effects on exposed organisms (Wang et al., 2015b, Dalvie et al., 2015). In this study, PFOA levels ranged between 6.66 and 2144.3 ng/l. The seasonal concentrations of PFOA in surface water samples are presented in Table 4.18.

Table 4.18: Mean levels (ng/l ± SE) of PFOA in surface water samples

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	1398.7±923.97	100±70.71	457.13±129.63	301.04±106.44
PKB	1427.8±909.92	100±70.71	453.93±42.30	291.60±10.34
PKC	1241.75±714.70	66.66±37.71	457.39±53.77	91.25±31.51
PKD	1334.75±910.57	70±49.49	563.49±78.53	177.35±88.68
DPA	2144.3±1212.9	296.66±115.49	528.14±116.71	544.95±10.09
DPB	1274.2±762.40	190±134.35	767.81±168.88	509.59±186.66
DPC	838.7±378.09	6.66±4.71	737.78±207.99	381.45±185.02

ND=Not detected

Summer had the maximum concentration of PFOA in surface water (2144.3 ng/l). Values of PFOA in the Diep and Plankenburg Rivers were significantly higher than published permissible threshold limit (400 ng/l) for PFOA in water (USEPA, 2009). Levels of PFOA reported in this study are consistent with values obtained elsewhere in surface water which ranged between <LOQ and detection and 2730 ng/l (Liu et al., 2015a). However, levels of PFOA in sediment samples were 10 fold higher than levels measured in the corresponding surface water samples. Maximum concentration in the sediment samples stands at is 279.37 ng/g at DPA during the summer period. Overall concentrations of PFOA at all seasons were presented in Table 4.19.

Table 4.19: Mean levels (ng/g ± SE) of PFOA in sediment samples

Sampling points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	72.16±14.02	30±2.35	131.12±25.35	111.84±6.70
PKB	98.23±30.24	24.43±3.13	54.80±5.68	63.77±22.90
PKC	156.81±52.45	6.66±4.71	47.36±15.30	18.07±12.78
PKD	58.74±8.30	12.2±5.51	42.93±17.34	47.73±15.05
DPA	279.37±105.80	33.88±6.65	67.07±17.70	37.18±25.16
DPB	161.45±24.43	21.11±8.61	44.91±13.30	9.70±6.85
DPC	191.96±79.22	25.56±5.53	77.91±10.12	65.32±1.34

ND=Not detected

4.10.2 Seasonal levels of perfluoroctane sulfonate (PFOS)

Levels of PFOS in surface water samples were generally low, but were higher than published threshold limit published by USEPA (200 ng/l). Maximum concentration of PFOS in surface water with concentrations levels of 1135.24 ng/l was obtained at point DPB. Seasonal variations of PFOS in surface water from different sampling locations are presented in Table 4.20**.**

Table 4.20: Mean levels (ng/l ± SE) of PFOS in surface water samples

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	568.2±220.05	190.21±134.49	884.59±393.88	97.77±50.78
PKB	540.8±166.02	223.45±157.43	673.66±258.73	18.51±11.15
PKC	270.14±32.62	228.68±58.84	452.64±122.94	66.02±46.68
PKD	165.7±19.23	117.05±20.54	397.83±96.08	71.05±13.68
DPA	644.63±265.61	209.43±34.10	1090.92±177.83	133.33±45.15
DPB	439.1±37.75	307.68±163.91	1135.24±279.39	712.19±192.07
DPC	475.15±335.98	171.63±18.12	613.96±46.26	128.83±0.82

ND=Not detected

Levels PFOS reported by Mudumbi et al. (2014) were 182 ng/l for Diep River; 47 ng/l for Salt River and 23 ng/l for Eerste River. Maximum concentration of PFOS (248.14 ng/g) in sediment sample was measured at sampling station DPB as shown in Table 4.21. However, levels in sediment samples were 4 fold higher than values in the corresponding surface water samples consistent with similar study by (Chen et al., 2011a). Anthropogenic activities seem to contribute to burden in environmental samples. Industrial production processes, domestic activities from informal settlements, atmospheric deposition, un-intended release from agricultural activities, fire-fighting operations and possible biodegradation of larger fluorotelomer compounds are possible sources of PFOS into water bodies. Levels of PFOS in sediment samples are presented in Table 4.21.

Table 4.21: Mean levels (ng/g ± SE) of PFOS in sediment samples

Sampling Points	Summer (Dec-Feb)	Autumn (March-May)	Winter (June-August)	Spring (Sept-Nov)
PKA	144.03±79.88	52.45±0.01	44.22±18.65	14.51±2.09
PKB	155.33±106.53	42.23±6.52	27.09±13.10	1.68±1.19
PKC	131.3±65.54	11.63±8.22	46.95±16.80	1.59±1.12
PKD	76.42±43.89	43.80±0.758	76.31±29.97	ND
DPA	165.69±73.05	79.82±4.96	79.69±28.09	9.96±7.045
DPB	248.14±172.78	63.2±1.69	5.03±1.64	0.50±0.35
DPC	ND	44.81±7.36	52.89±27.78	8.47±3.23

ND=Not detected

4.11 Distribution and Partitioning study

The distribution and partitioning of PFOA and PFOS between the environmental compartments are among the important parameters used to determine the environmental fate and behaviour of contaminants in the aquatic environment (Pan & You, 2010, Zhao et al., 2015). PFOA and PFOS have attracted most attention among PFCs, because they are responsible for a significant proportion of reported environmental contamination (Brooke et al., 2004, Lindstrom et al., 2011, Chen et al., 2015). Assessment of the information on the distribution of PFCs in the environment will help reveal their availability and possible threat to aquatic biota. Partitioning and distribution play a crucial role in understanding the fate and mobility of pollutants in the environment (Yang et al., 2011). In this study, some factors that may influence sorption of PFCs in the aquatic environment were optimized under the laboratory conditions using sediment samples. They include influence of pH, Ca^{2+} and carbon chain length.

4.11.1 Influence of pH on sorption of PFOA onto sediment

The influence of pH is one of the determinants of partitioning and sorption of pollutants in the environmental compartments. Slight changes in pH in an aquatic system can significantly influence the sorption of contaminants such as PFCs in the aquatic system. It was observed that pH 4 favoured the sorption of PFOA in the aqueous medium; due to the presence of abundant hydrogen ions (H^+). The interaction between the charged molecules of PFOA and the solution charged molecules could also contribute to availability of hydrogen ion in the solution. pH 4 gave the maximum adsorption capacities when compared to higher pH values of pH 6 and 9. This agrees with previous studies on the partitioning behaviour of organic compounds in an aqueous media (Higgins & Luthy, 2006). Also, the effect of pH could influence sorption of organic compounds in aquatic systems, due to reactivity of hydrogen bond which exists as hydroxyl (OH^-) and hydrogen (H^+) present in the aqueous solution. This observation is also consistent with others that demonstrated that sorption is favoured at lower pH 4.0 and 7.5 than values >8 (Brooke et al., 2004; Wang & Shih, 2011). Previous investigations of the partitioning behaviour of other PFCs onto surfaces demonstrated the trend that sediment–water distribution depends on solution pH (Higgins & Luthy, 2006). Figure 4.13 illustrates the sorption of PFOA at varied pH values on sediments samples collected from the Plankenburg River.

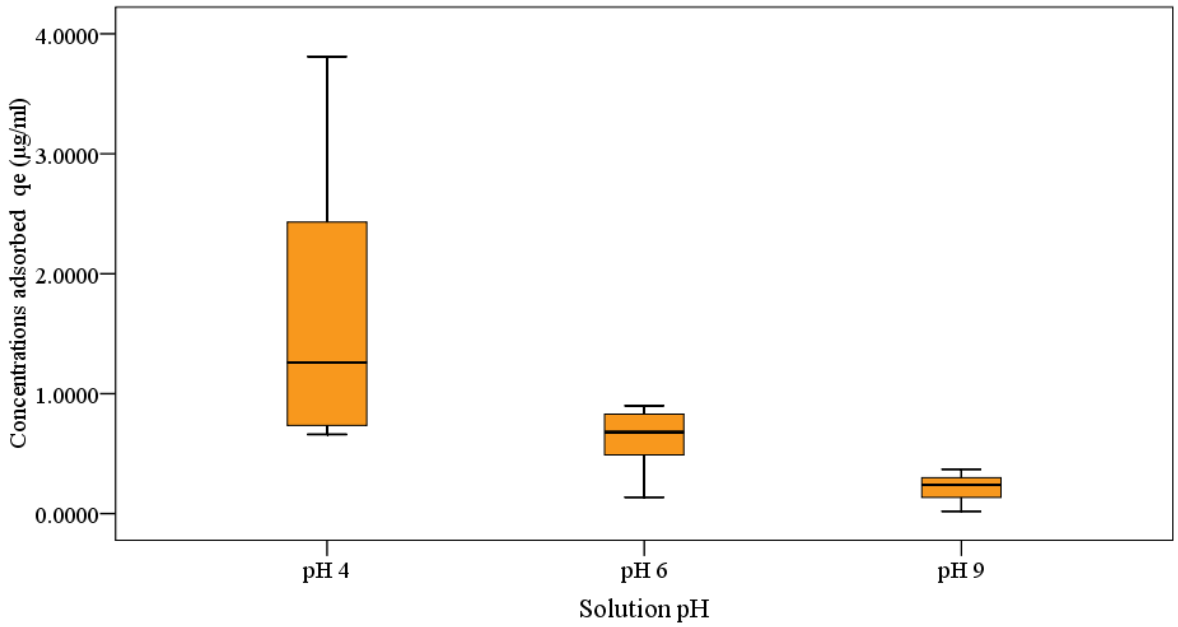


Figure 4.13: Effect of pH on sorption of PFOA onto sediment samples from Plankenburg River

4.11.2 Influence of Ca^{2+} on sorption of PFOA

The presence of cations is a determinant of the survival of the organisms' presence in the aquatic environment. The influence of Ca^{2+} was investigated for the adsorption of PFOA unto onto selected sediment samples. pH 4 was maintained in the system, concentration of Ca^{2+} ranged from 0.005 M to 0.5 M and concentration of adsorbate (PFOA) ranged between 0.5 - 2.5 mg/l. An increase in the concentrations of Ca^{2+} in the solution enhanced the sorption of PFOA onto sediment samples. It was also observed that sorption rates of PFOA at higher Ca^{2+} concentrations of 0.5 M is higher than Ca^{2+} concentration at 0.005 M which differ markedly. The electrostatic interaction and solubility properties of PFOA are increased as the Ca^{2+} in the aqueous solution increases, thereby creating a charged environment that enhances the sorption of PFOA onto the sediment samples. Other workers had reported that the presence of divalent cations such as Ca^{2+} and Mg^{2+} in aqueous solutions enhanced the adsorption of PFCs onto negatively charged sediment particles (Higgins & Luthy, 2006, Senevirathna et al., 2010). Adsorption of PFOA at increasing Ca^{2+} concentration is represented in Figure 4.14.

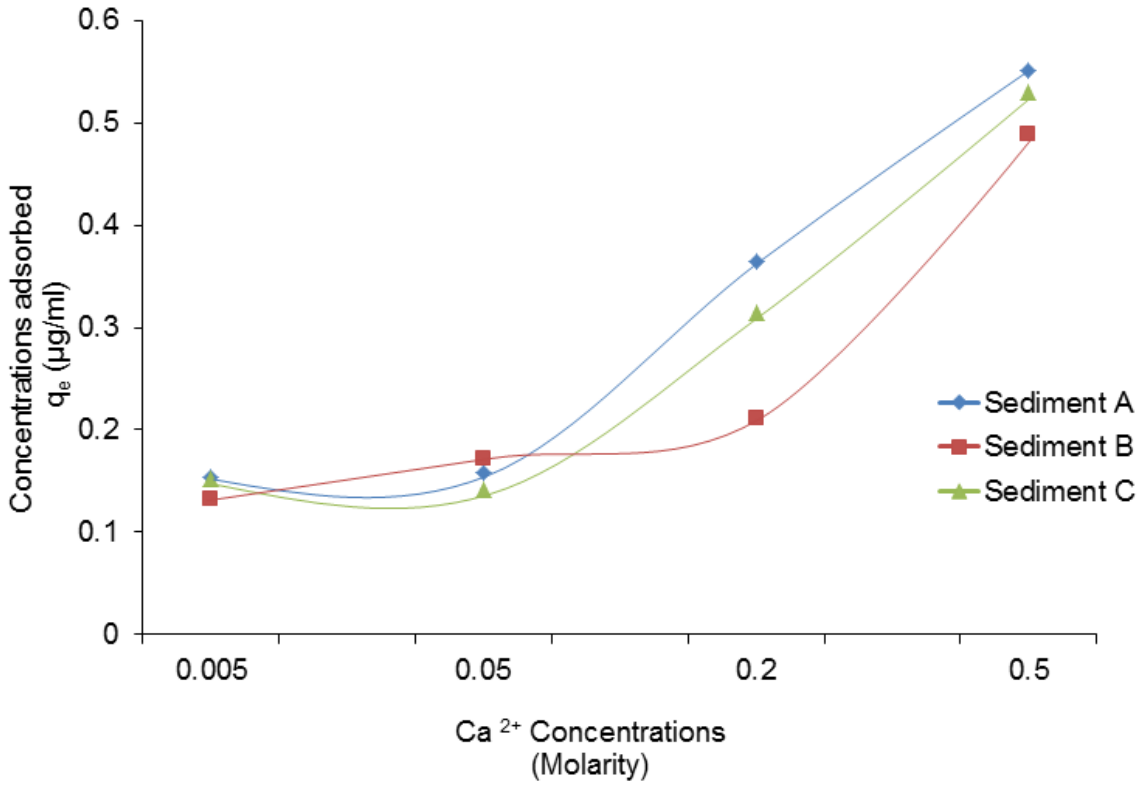


Figure 4.14: Effect of Ca^{2+} concentration on sorption of PFOA onto sediment samples

4.11.3 Influence of carbon chain length on log K_D values

The influence of carbon chain length was also investigated; the calculated log K_D values for long chain perfluorinated compounds were consistently higher than those for shorter chain length. The values log K_D obtained for PFHpA, PFOA, PFNA and PFUnDA increased with carbon length. The observation was same for results obtained from different sediment samples. The observation was consistent with other studies that reported that the length of carbon-fluorine influenced the partitioning of heavy molecular weight organic contaminants in aqueous media (Elmonznino, 2016, Zhang et al., 2013, Krippner et al., 2014). Figure 4.15 illustrates the influence of carbon chain length on log K_D (L/g) values of PFCs.

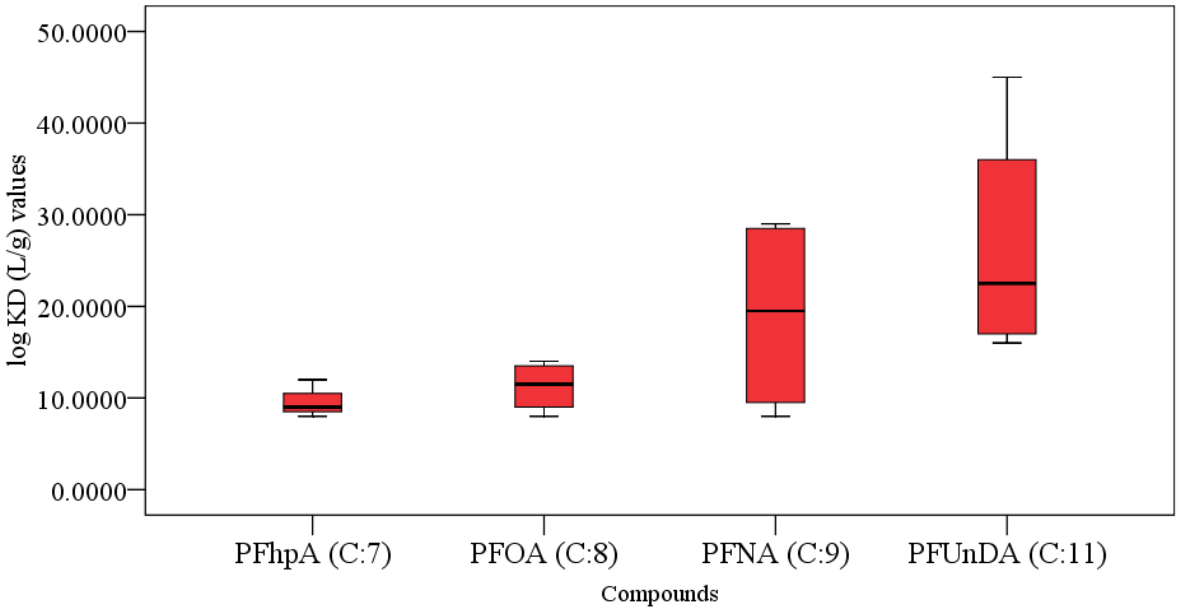


Figure 4.15: Influence of the length of carbon chain on log K_D values of PFCs after sorption

4.12 Distribution and Partitioning of PFOA and PFOS in water and sediment

Distribution and partitioning between different compartments is one of the parameters used to evaluate environmental fate and behaviour of contaminants, in the aquatic environment (Ahrens et al., 2010, Labadie & Chevreuil, 2011). Information on the distribution and partitioning pattern of PFCs in the environment may therefore be indicative of their availability status, and the possible threat they pose to aquatic life. The Partitioning distribution (log K_D) and partitioning coefficients (log K_{oc}) of PFOA and PFOS in the Plankenburg and Diep Rivers are presented in Table 4.22.

Table 4.22: Distribution coefficient (log K_D) and partitioning coefficients (log K_{oc}) of PFOA and PFOS in the Plankenburg and Diep Rivers

Samples locations	PFOA		PFOS	
	log K_{OC} (cm^3/g)	log K_D (cm^3/g)	log K_{OC} (cm^3/g)	log K_D (cm^3/g)
PKA	1.28±0.39	0.69±0.39	1.16±0.53	0.82±0.34
PKB	1.15±0.26	0.83±0.25	1.06±0.44	0.92±0.37
PKC	0.94±0.18	0.89±0.14	0.79±0.45	1.05±0.55
PKD	1.15±0.28	0.95±0.35	1.27±0.75	0.82±0.67
DPA	0.74±0.06	0.97±0.13	0.89±0.38	0.81±0.36
DPB	0.68±0.37	1.20±0.38	1.17±0.44	1.61±1.37
DPC	1.61±0.79	0.74±0.17	1.20±0.42	0.85±0.31

The partitioning coefficients (log K_{OC}) for PFOA and PFOS were determined relative to organic carbon fraction (f_{OC}) in the sediment, because it provides a realistic representation of the partitioning of the pollutants in the aqueous solution (Lodge & Cook, 2016). Low values of log K_{OC} imply that PFCs predominantly exist in the dissolved phase and can be rapidly dispersed and diluted within the aqueous solution. High log K_{OC} values would imply higher concentrations of the PFCs in sediments, with strong association with particulate materials and sediment and consequently, less mobile. In this study, partitioning distribution (log K_D) of PFOA ranged between 0.69 and 1.20 cm^3/g and between 0.81 and 1.61 cm^3/g for PFOS. The minimum value for log K_D was obtained in sediment from sampling point PKA and the maximum observed at DPB. Log K_{oc} values for PFOA varied between 0.68 and 1.61 cm^3/g while values for PFOS ranged from 0.79 cm^3/g to 1.20 cm^3/g. The minimum value of log K_{OC} was obtained in sediment samples from sampling point PKC for PFOS and point DPB for PFOA. The maximum log K_{OC} was observed at PKD for PFOS and from PKA for PFOA. The partitioning behaviour of PFCs has the potential to influence their bioavailability, chemical and microbial transformation in the aquatic environment (Higgins et al., 2007, Ahrens et al., 2010).

The environmental distribution of PFOA and PFOS in the aquatic environment is based on the partitioning coefficient, partitioning distribution and sorption mechanism. The sediment compartment had the higher levels of PFOA and PFOS than concentrations in the aqueous

phase. This implies that sorption was higher on the sediment surface. The background levels of PFOA and PFOS in sediment samples from the investigated rivers were slightly lower than the levels reported in similar studies in China and North America (Liu et al., 2015a, Rankin et al., 2016). The partitioning coefficients (log K_{oc}) obtained for PFOA and PFOS in this study were generally lower than values obtained by Ahrens et al. (2015), where log K_{oc} for PFOS and PFOA was 4.7 and 4.5 cm^3/g, respectively. Values of log K_{oc} for most of the sediment samples suggest extensive adsorption of PFOA and PFOS. Certain water quality parameters (e.g. water pH and the presence of ionic substances) have been reported to influence the sorption of PFOA and PFOS in aquatic environments (Pan et al., 2009). The carbon chain length is another factor that could also contribute to sorption of PFOA and PFOS in aquatic systems. The longer chain length of compounds made them relatively stable in nature due to their molecular weight (Zhang et al., 2013), when compared to shorter chain fluorinated compounds. Therefore, mobility of PFOA and PFOS in the aquatic system could lead to bioaccumulation in the environmental components, which means they could easily be picked up by living organisms, with consequent environmental and health implications. Distribution, degradation, reactivity, and mobility contribute significantly to the fate of PFOA and PFOS in the environment. Table 4.23 presents log K_D and log K_{OC} values obtained in this study as compared to those from other studies.

Table 4.23: Comparison of Partitioning distribution (K_D) and partitioning coefficient (K_{OC}) with other studies

Sample Locations		PFOA			PFOS		
		log K_D (cm^3/g)	log K_{OC} (cm^3/g)	Reference	log K_D (cm^3/g)	log K_{OC} (cm^3/g)	Reference
Tokyo Bay, Japan		1.20	4.7	Ahrens et al. (2010)	0.96	4.5	Ahrens et al. (2010)
Lake Michigan sediment, USA		NA	2.06	Higgins & Luthy (2006)	7.42	2.8	Johnson et al. (2007)
Liao river , China		2.30	NA	Yang et al. (2011)		2.57	Higgins & Luthy (2006)
Yangtse River, China		0.77	1.5	Li et al. (2011)		3.7	Labadie & Chevreuil (2011)
Pearl River, South China		2.58-4.75		Zhao et al. (2014)		3-6.26	Zhao et al. (2014)
Youngsan and Nakdong water shed, Japan		0.35±0.3	2.0±0.5	Hong et al. (2013)	0.83 ±0.3	2.5± 0.5	Hong et al. (2013)
Selected surface waters, The Netherlands		1.83±0.40	2.63±0.34	Kwadijk et al. (2010)	2.35±0.35	3.16±0.7	Kwadijk et al. (2010)
Dalian coast china				Chen et al. (2011a)	1.44±0.11	3.47±0.07	Chen et al., (2011a)
Yangtze River china					3.2± 0.5	4.3±0.5	Pan & You (2010)
Plankenburg River, South Africa	PKA	2.15	2.09	This study	2.01	1.95	This study
	PKB	2.16	2.12	This Study	1.56	1.51	This study
	PKC	2.04	2.40	This study	2.25	2.61	This study
	PKD	1.90	1.62	This study	2.30	2.02	This study
Diep River, South Africa	DPA	2.00	2.30	This study	2.29	2.60	This study
	DPB	2.00	2.05	This study	1.38	1.43	This study
	DPC	1.98	1.81	This study	1.05	0.87	This study

4.13 Sorption mechanism of PFOA and PFOS onto the sediment

The sorption mechanisms of PFOA and PFOS onto sediment samples were also studied. Kinetic models were used to analyse the equilibrium data. Sorption equilibrium was attained before 400 min of contact time for both compounds. This result is consistent with values obtained in previous investigations (Johnson et al., 2007, Barton et al., 2007, Zhou & Keller, 2010). The effects of contact time on PFOA and PFOS sorption onto sediment samples of the Plankenburg and Diep Rivers are presented in Figure 4.16. However, Higgins & Luthy (2006) reported that equilibrium was only attained for sorption onto sediments after 10 days contact time. A plot of q_t (mg/g) versus t (min) showed that sorption increased at increasing contact time.

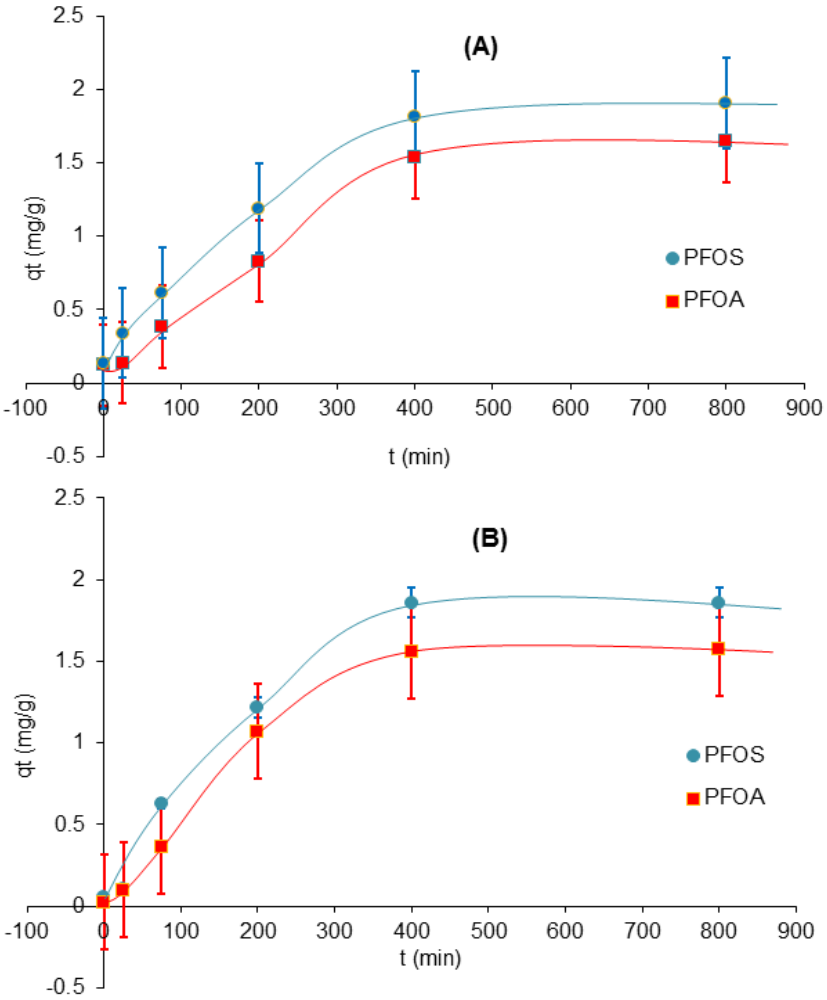


Figure 4.16: Sorption kinetics for PFOA and PFOS onto sediment samples from Plankenburg (A) and Diep (B) Rivers

Data obtained were subjected pseudo first-order kinetics, pseudo second-order kinetics, Elovich rate equation and Webber-Morris intra-particle diffusion rate models. Kinetic parameters for the sorption of PFOA and PFOS are presented in Tables 4.24 and 4.25 respectively. Sorption data for all sediment samples fitted well into the Elovich rate equation model for PFOA with R^2 values >0.9. Most of the data obtained from the samples for the sorption of PFOA onto the sediment fitted well into both pseudo second-order kinetics and the Elovich rate equation, with the correlation coefficient (R^2) values above >0.9 for most of the sediment sample. Other sample parameters showed that the maximum value for pseudo second-order was 42.9 mg/g/min, which implies that the initial sorption rate was high for PFOA. The maximum amounts of PFOA adsorbed at equilibrium per unit weight $q_{e,}$ were 4.9 mg/g and 2.3 mg/g for sediments obtained from PKD and DPA respectively.

Table 4.24: Kinetics models for PFOA in sediment samples

Kinetic Models	Parameters	PKA	PKB	PKC	PKD	DPA	DPB	DPC
Pseudo 1st order Kinetics	K_1 (min^{-1})X10^{-5}	0.60	0.50	0.40	0.40	0.40	0.40	0.30
	q_e (mg/g)	4.08	4.44	4.31	4.22	4.42	4.39	4.49
	R^2	0.6	0.63	0.56	0.57	0.49	0.54	0.5
Pseudo 2nd order kinetics	K_2 (g/mgmin^{-1})	1.19	0.79	0.18	0.53	0.47	2.19	0.37
	q_e (mg/g)	0.01	0.02	0.13	0.04	0.02	0.01	0.05
	h	0.02	5.05	$3.4x10^{-3}$	1.06	$6.4x10^{-4}$	4.62	1.09
	R^2	0.84	0.84	0.9	0.9	0.85	0.97	0.82
Elovich equation rate	β (g/mg^{-1})	3.13	2.92	3.63	3.85	3.37	3.05	4.1
	α_E (mg/g min^{-1})	5.17	1.02	6.76	6.85	5.86	1.5	0.44
	R^2	0.98	0.94	0.98	0.98	0.97	0.9	0.93
Intra-particle Diffusion	K_p	0.09	0.09	0.07	0.07	0.07	0.09	0.06
	I	1.53	1.71	1.44	1.25	1.32	1.51	1.22
	R^2	0.86	0.87	0.81	0.83	0.76	0.78	0.73

Table 4.25: Kinetics Models for PFOA in sediment samples

Kinetic Models	Parameters	PKA	PKB	PKC	PKD	DPA	DPB	DPC
Pseudo 1st order Kinetics	K_1 (min^{-1})X10^{-5}	0.20	0.40	0.40	0.40	0.40	0.50	0.50
	q_e (mg/g)	4.09	4.44	4.31	4.22	4.42	4.39	4.49
	R^2	0.3	0.65	0.55	0.81	0.57	0.94	0.78
Pseudo 2nd order kinetics	K_2 (g/mgmin^{-1})	0.27	0.29	0.33	0.21	0.49	0.48	0.7
	q_e (mg/g)	0.64	0.07	0.11	0.09	0.05	0.03	0.02
	h	0.11	$1.7x10^{-3}$	$4.4x10^{-3}$	$2.3x10^{-3}$	$1.3x10^{-3}$	0.69	$1.6x10^{-4}$
	R^2	0.99	0.87	0.98	0.84	0.93	0.79	0.85
Elovich equation rate	β (g/mg^{-1})	8.19	3.29	3.82	4.45	3.25	3.92	2.98
	α_E (mg/g min^{-1})	19.39	6.04	6.99	8.83	19.41	30.46	5.54
	R^2	0.83	0.98	0.98	0.94	0.98	0.8	0.97
Intra-particle Diffusion	K_p	0.02	0.08	0.07	0.06	0.08	0.08	0.1
	I	1.12	1.59	1.33	1.44	1.48	1.82	1.88
	R^2	0.54	0.89	0.83	0.96	0.82	0.97	0.94

The results were similar for PFOS, except for the PKA and DPB samples that had R^2 values of 0.83 and 0.80, respectively. Sorption kinetics for sediments from PKA and PKC fitted well into pseudo second-order kinetics with R^2 values of 0.97 and 0.94 respectively, while sediments obtained from points PKD, DPA, and DPC fitted better into the Elovich rate equation for the sorption of PFOS with R^2 values >0.90. For PFOS, values obtained for the pseudo second-order rate K_2 constant and the Elovich equation constant α_E were 1.7 g/mg/min and 1.2 g/mg/min for sediment samples PKD and DPA, respectively. The results from the Elovich rate equation and pseudo second-order kinetics models suggest that chemisorption mechanism is the controlling step in the sorption process. The kinetics mechanism implies that a fast initial transfer onto the surface layer occurred as indicated by values obtained for *h* and α_E. The results indicated slow diffusional transport of organic matter into the internal pores of the sediment. In sum, the aqueous solution and solid interface were easily accessible to the adsorbates (PFOA and PFOS), such that equilibrium was rapidly reached.

4.14 Production of activated carbons, optimization and characterization

Activated carbons were prepared at optimized conditions in the pyrolysis chamber at varying oven temperatures and duration. Carbonization at 900 ^{0}C generated the smallest amount of charcoal. The maximum quantity of charcoal was produced at 450 ^{0}C, but this was of poor quality. In the literature, carbonization at 600 ^{0}C and above is reported to yield relatively reduced quantities of char, due to the increasing aromatization process of the biochar (Xue et al., 2015). The quantity of char obtained from the carbonization process was in the order 900 ^{0}C <750 ^{0}C <600 ^{0}C < 450 ^{0}C. The initial dry weight of leaf biomass (25 g) was reduced to 12.9, 8.51, 6.94 and 6.19 g at temperatures of 450, 600, 750 and 900 ^{0}C, respectively. This result was similar to that of Komkiene & Baltrenaite (2016), who reported that carbonization at 700±5 ^{0}C for 45 min produced a well-developed pore structure on the surface of the activated carbons. Optimal quality and yield of charcoal was achieved after 2 h charring at 750 ^{o}C. Table 4.26 presents the char yield of activated carbons at optimized parameters.

Table 4.26: Activated carbon yield and characteristics at different temperatures and duration

		Initial wt. (grams)	**Final wt. (grams)**	**% char**	**Char Quality**
Temperature (^{0}C)	450	25.0	12.9	51.63	Brown
	600	25.0	8.51	34.04	Dark brown
	750	25.0	6.94	27.71	Shinning black
	900	25.0	6.19	24.76	Shinning black
Time (min) @ 750 ^{o}C	**Time**	**Initial wt.**	**Final wt.**	**% char**	**Char Quality**
	60	25.0	9.48	37.92	Brown
	90	25.0	7.54	30.16	Dark brown
	120	25.0	6.97	27.88	Shinning black
	150	25.0	6.59	26.36	Shinning black

Chemical activation of the charcoal was optimized using 0.5 M, 1.0 M and 3.0 M of KOH and H_3PO_4. Poor pore structures were developed at the minimum concentration (0.5 M), with brownish products of the activated carbons. However, at 3.0 M chemical impregnation, remarkable shining black charcoal was produced. This suggested well-developed pore structures with the abundance of micropore and mesopores on the surface of the activated carbon. This observation is consistent with the previous study by (Izquierdo et al., 2003), who reported that chemical impregnation at high concentrations (between 2 and 5 M) enhanced the development of pore structures on the surface of adsorbents. 3 M KOH and H_3PO_4 chemical activation yielded desirable quantity and quality adsorbents. AC-H_3PO_4 had the maximum carbon content with 62.13 %, when compared to AC-KOH (57.29 %), inactivated charcoal (54.06 %) and untreated *V. vinifera* leaf litter biomass (38.35 %) as presented in (Table 4.27).

Chemical activation with phosphoric acid (H_3PO_4) decreased the pH of the solution with a possible tendency to enhance the adsorption process. In the literature, H_3PO_4 has been reported to be a highly efficient chemical activation agent for lignocellulose materials at room temperature (Hameed et al., 2008). This is due to its potential to activate the cleavage of bonds between cellulose and lignin. Studies also reveal that phosphoric acid could enhance the formation of phosphate linkage between the fragments of biopolymers pyrolytic (Ghasemian & Palizban, 2016). Additionally, chemical activation with potassium hydroxide (KOH) increased the pH of the solution, and hence the acidic group on the surface of the activated carbons enhanced the electrostatic interactions (Bedin et al., 2016). Raw grape leaf litter biomass and untreated char were generally neutral. Table 4.27 presents the chemical compositions of untreated biomass and activated carbons.

Table 4.27: Elemental composition of untreated biomass, inactivated char and chemically modified activated carbons

Element	Untreated Biomass (%)	Inactivated Char (%)	AC-KOH (%)	AC-H_3PO_4 (%)
Carbon	38.35	54.06	57.29	62.13
Oxygen	60.51	43.41	40.27	36.45
Calcium	0.86	1.98	1.47	0.65
Silicon	0.03	0.23	0.41	0.44
Magnesium	0.02	0.07	0.37	0.07
Aluminium	0.03	0.01	0.04	0.00
Sulphur	0.19	0.16	0.07	0.23
Potassium	38.35	0.04	0.07	0.02
Total	100.00	100.00	100.00	100.00

The results of BET surface area and pore structure analysis provided the estimation of specific characteristics of the activated carbons. BET total surface areas for AC-H_3PO_4, AC-KOH and the untreated leaf biomass of *V. vinifera* are presented in Figure 4.17.

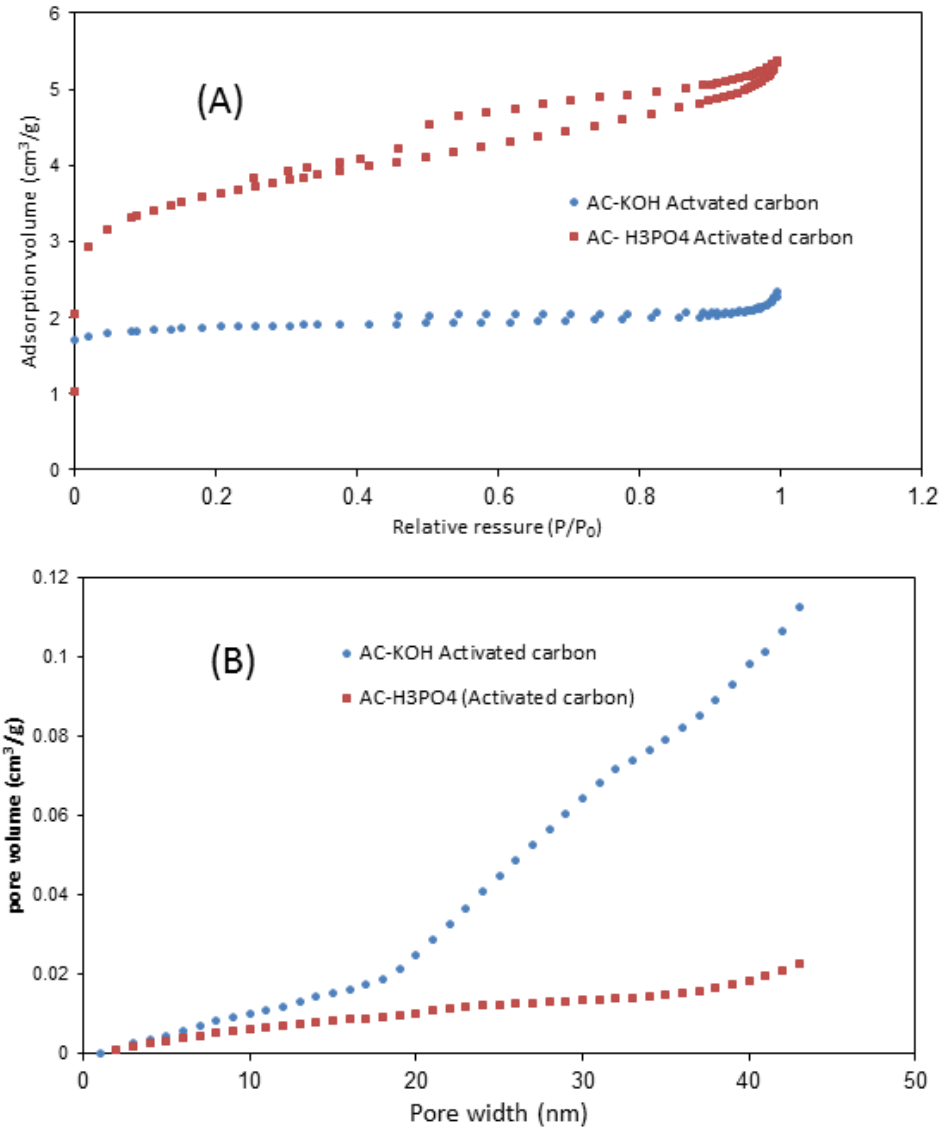


Figure 4.17: BET for Nitrogen adsorption volume to relative pressure P/P0

(A) AC-H_3PO_4 and AC-KOH (B) cummulative pore volume for AC-H_3PO_4 and AC-KOH

The quantity of analytes adsorbed increased dramatically in the initial stages with relatively low pressure, and continued to increase slowly before the 1.0 (P/P_0) value was attained, indicating that adsorption was favourable at low pressure (Xin-hui et al., 2012). The continuous increase in adsorption capacity of the adsorbents beyond 0.1 (P/P_0) mark of relative pressure clearly indicated that adsorption was Type II isotherm, according to the IUPAC classification; this represents a deviation from Langmuir isotherm. A cumulative pore volume distribution chart is presented in Figure 4.17. It suggests that available pores on the activated carbons were mostly microporous. The average pore widths were 19.90 nm and 38.19 nm for AC-KOH and AC-H_3PO_4 respectively. Also, the percentage abundance of microspore volumes available on pore surfaces of AC-H_3PO_4 and AC-KOH were 63.7 % and 62.4 %, respectively. Summary of BET surface characteristics of untreated biomass of *V. vinifera*, AC-H_3PO_4, and AC-KOH are presented in Table 4.28. This is consistent with Sethia & Sayari. (2016) who prepared activated adsorbents from sucrose spherical carbons impregnated with KOH, and reported that adsorbents possess well-developed surface characteristics, with a BET total surface area of 1534 cm^2/g and 82.6 % micro-pores.

Table 4.28: Summary of BET surface characteristics of untreated biomass and activated carbons

Parameters	**Untreated Biomass**	**AC-H_3PO_4**	**AC-KOH**
BET Total Surface Area (m^2/g)	15.182	295.48	158.67
External surface area (m^2/g)	16.604	174.18	124.49
Average Pore Diameter (nm)	193.525	38.19	19.90
Pore Volume (cm^3/g)	-	0.1127	0.0789
Micropore Volume cm^3/g	*	0.0719	0.0493
MicroPore Volume (%)	-	63.7	62.4
Mesopore Volume (cm^3/g)	-	0.0408	0.0296
Mesopore Volume (%)	-	36.2	37.6

* The micropore area is not reported because either the micro-pore volume is negative or the calculated external surface is larger than total surface area.

FTIR spectra of untreated biomass *V. vinifera,* AC-KOH and AC-H_3PO_4 are presented in (Figure 4.18) showing spectra bands of functional groups available on the surface activated carbons. The FTIR spectra at the region of 3448.1, 3840.04 and 3649.98 cm^{-1} were assigned to OH^- free alcohol and interlayered water present in the untreated precursor, and disappeared after carbonization and activation process. This observation was similar to study elsewhere by Xu et al. (2015). A sharp absorption spectrum at 2921.24 cm^{-1} band was assigned to as C-H in unmodified activated carbons. This band slightly shifted to 2922.09 and 2921.68 cm^{-1} bands after chemical treatment, which were assigned to the presence of chelate compounds band of CH_2 symmetric stretching (Bedin et al., 2016). Spectrum band 1654.10 cm^{-1} representing alkenyl C=C stretching slightly, shifted towards 1616.60 and 1604.31cm^{-1} after chemical activation with H_3PO_4 and KOH respectively. This indicated the presence of double bond C=O, C=C, N=N, and COO- asymmetric stretching. Also, 1384.15 cm^{-1} bands significantly shifted to 1317.07 and 1317.45 $cm,^{-1}$ indicating the presence of CH_3 band (Socrates, 2004). The presence of 781.95, 781.94, 873.90 and 1107.07 cm^{-1} bands were observed on FTIR spectra for AC-H_3PO_4, AC-KOH activated carbons and untreated precursor, clearly suggested the presence of C=CH_2 (Ahmad et al., 2013). Overall results obtained from the physicochemical characterization of the produced activated carbons (AC-H_3PO_4 and AC-KOH) shows that they could be explored for possible removal of contaminants.

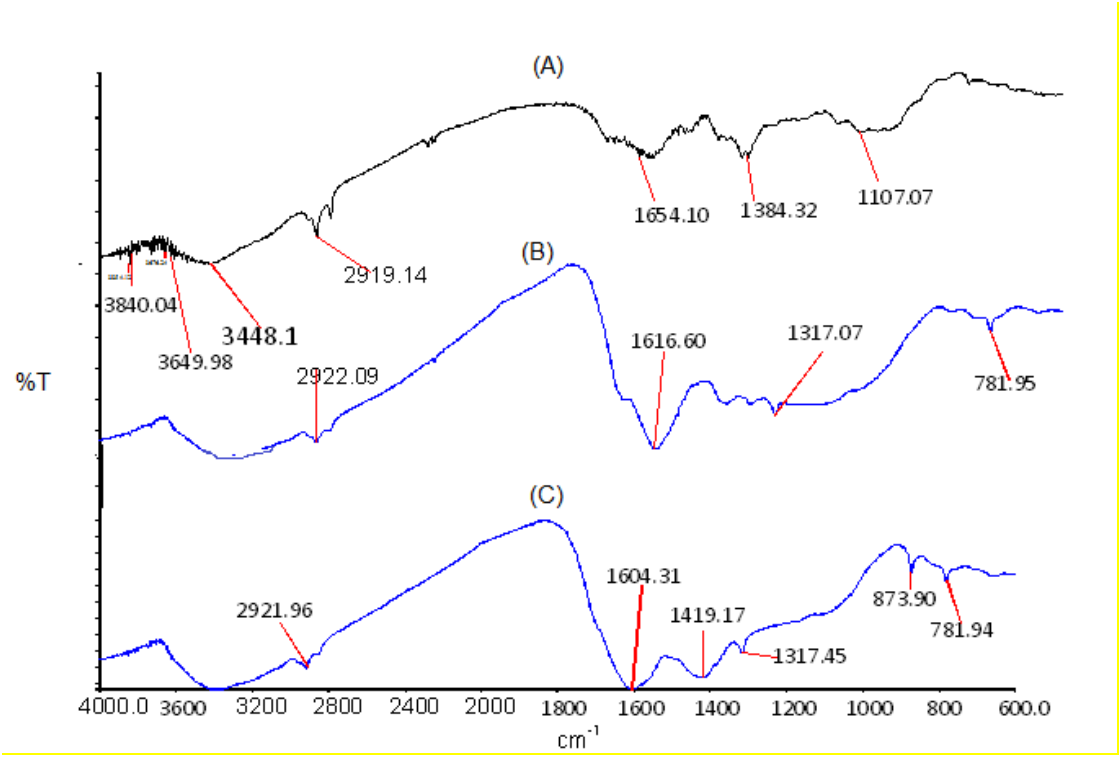


Figure 4.18: FTIR spectrum for (A) un-treated biomass (B) AC-KOH; (C) AC-H_3PO_4

Micrograph images of the adsorbents were viewed at 10 µm magnification to provide a visible surface morphology of the activated carbons (Figure 4.19). SEM images showed well-developed pore structures, increased pore volume and relative abundance of micropores and mesopores were observed on both AC-KOH and AC-H_3PO_4. These properties were attributed to the presence of polyphosphate structures on the surface of the biomass, as reported elsewhere (Prahas et al., 2008). The surface texture of untreated biomass was poorly developed and there were no visible blurry changes in the surface morphology.

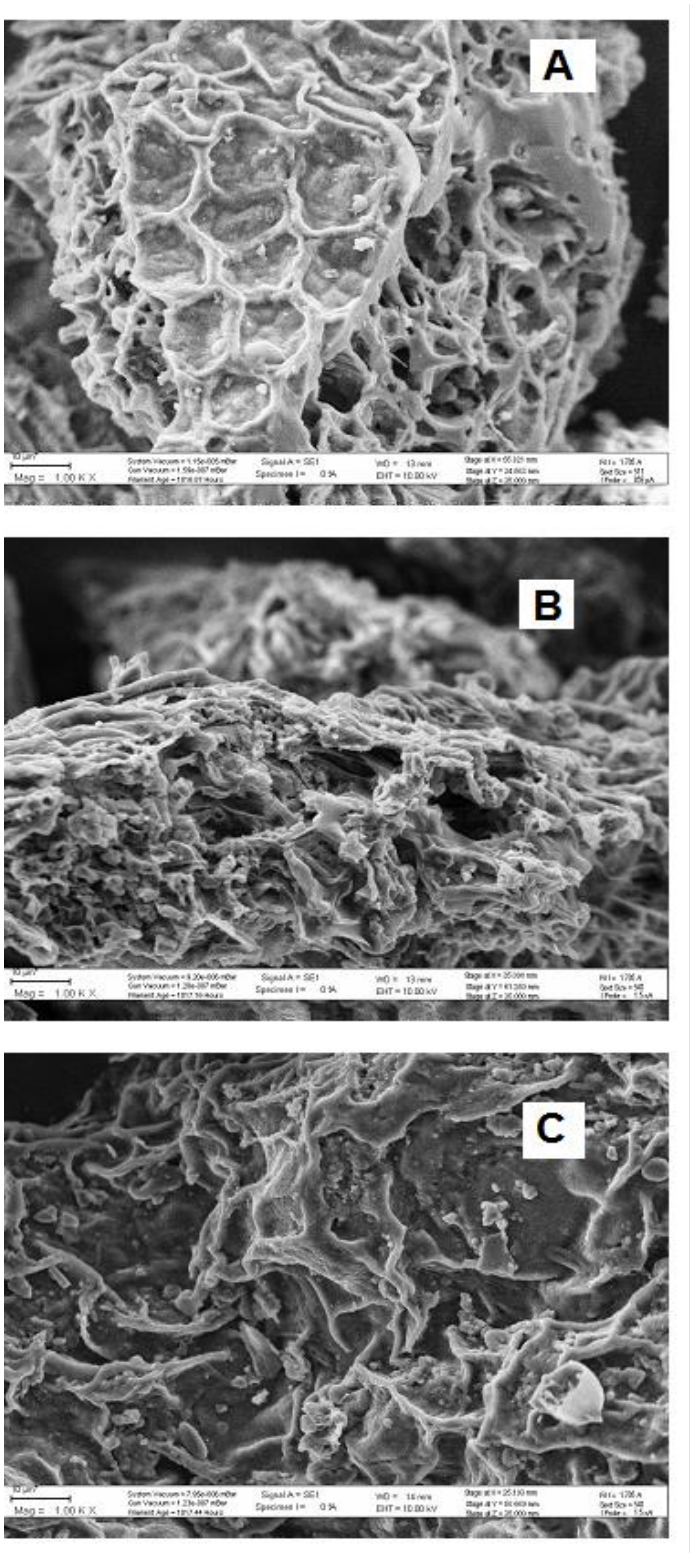


Figure 4.19: SEM image for modified and unmodified activated carbons

(A) AC-H_3PO_4; (B) AC-KOH; (C)Un-treated biomass

4.15 Optimization for the removal of PFOA and PFOS from aqueous solutions

4.15.1 Effect of pH

The pH plays a critical role in the removal of organic contaminants from aqueous solutions to the surface of activated carbons. Factors that influence pH include electrostatic interaction, H^+ and OH^- bonding, and the interaction of electron donor and acceptor between the adsorbent and aqueous solution (Bedin et al., 2016). The adsorption of organic contaminants such as PFOA and PFOS onto the surface of adsorbents is due to strong reactivity dependency on H^+, and OH^- present in the aqueous solution. pH is, therefore, important for the sorption of PFOA and PFOS onto mineral surfaces such as activated carbons. In this study, activated carbons were studied under acidic and basic conditions. Figure 4.20 shows that adsorption was favourable in acidic medium (pH 4) in contrast to studies in the alkaline medium (pH 9).

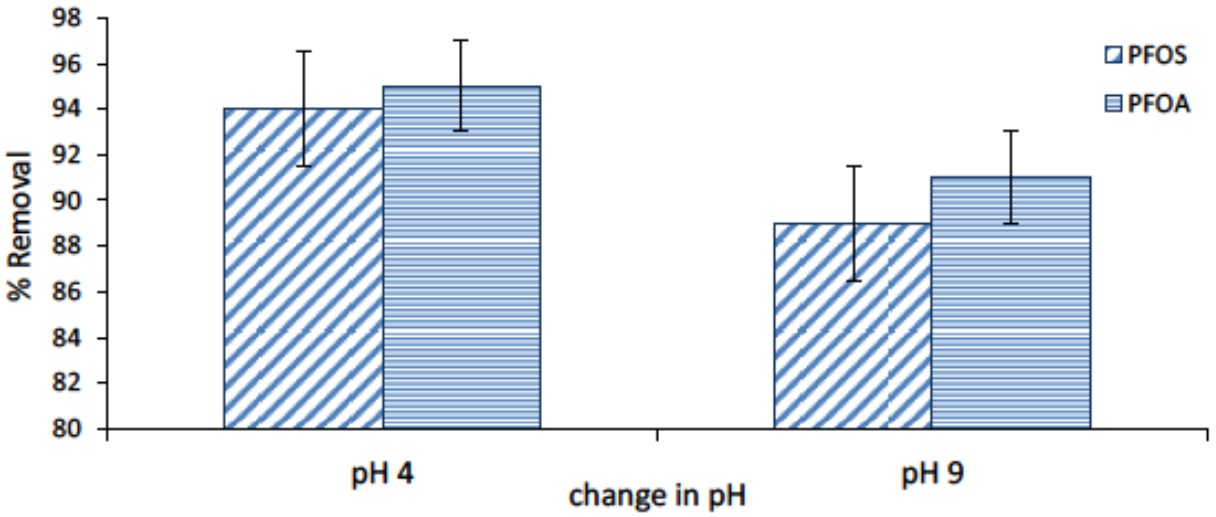


Figure 4.20: Percentage removal of PFOA and PFOS using AC-H_3PO_4 at pH 4 and pH 9, 0.05 g adsorbent dosage, 120 rpm, temperature 298 K at 160 min

This observation is consistent with results previously reported by Wang & Shih. (2011), who noted that sorption of PFOS in aqueous solution was elevated at pH 3. Levels of analytes adsorbed in acid media were significantly higher than sorption in the alkaline media. It is also interesting to note that, at lower pH, the electrostatic attraction between adsorbate and adsorbent is enhanced (Johnson et al., 2007). It was also deduced that the abundance of OH^- ions in the alkaline media could hinder the diffusion of organic molecules onto the active sites on the surface of activated carbons, thus reducing the chances of adsorption (Kobya, 2004). A similar trend was reported by Moreno-Castilla (2004), who observed that the rate of adsorption at pH 2 was

favourable when compared to adsorption at pH 9. It was demonstrated that adsorption of PFOS onto carbonaceous surfaces was driven by non-electrostatic attraction (Johnson et al., 2007), but that electrostatic interaction played a significant role in the adsorption mechanism when pH values in the aqueous solution were low. This is due to the repulsiveness of negatively charged components present, which reduced the surface electrostatic force in the solution (Ghasemian & Palizban, 2016). The adsorptive removal of PFOA and PFOS could further be attributed to parameters such as the surface morphology of the adsorbents.

4.15.2 Effect adsorbent dosage

Adsorbent dosage plays an important role in the determination of the sorption capacity of activated carbon at a given initial concentration of contaminants in aqueous solutions. The effects of adsorption dosage were investigated to determine the removal efficiency of AC-H_3PO_4 at 0.02 g and 0.05 g dosages of activated carbons. The percentage removal for PFOA and PFOS in aqueous solution was higher for both compounds at 0.05 g adsorbent dosage, as shown in Figure 4.21.

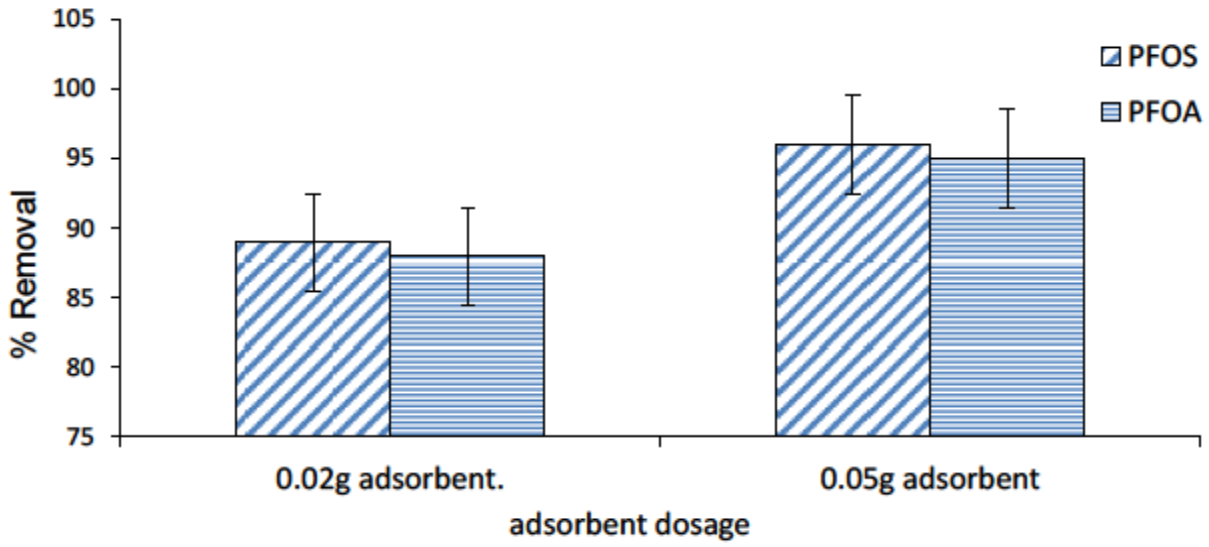


Figure 4.21: Percentage removal of PFOA and PFOS using 0.02 g and 0.05 g using AC-H_3PO_4

Removal efficiency at the higher adsorbent dose (0.05 g) showed remarkable percentage removal (>90 %) for both PFOA and PFOS. In contrast, an adsorbate dosage of 0.02 g yielded a lower percentage removal (<90 %) for both compounds. A similar trend was reported in the study carried out by Xu et al. (2015) who indicated that adsorption was more effective at higher doses of adsorbents. Concentration of the analytes at different dosage levels also contributed immensely to adsorption. Saturation was easily achieved for 0.02 g compared to a 0.05 g adsorbent dose. Generally, removal of PFOA and PFOS was most effective at the higher adsorbent dosage and at constant solution concentration.

4.15.3 Effect of concentration

Concentrations of PFOA and PFOS in the aqueous solutions used for optimization studies ranged between 0.125 mg/l and 1.0 mg/l. This range represents environmentally relevant levels of PFOA and PFOS. Higher concentrations represent an unusual pollution scenario that could nevertheless occur. Concentrations of PFCs within this range (0.1 and 2.0 mg/l) have been reported by Johnson et al. (Johnson et al., 2007). Percentage removal using 0.02 g and 0.05 g adsorbent dosages for both PFOA and PFOS was highest at 0.125 mg/l. At increasing concentrations of PFOA and PFOS, removal efficiency decreased, especially with the 0.02 g adsorbent dosage suggesting that adsorbate load could influence adsorption process. This is presented in Table 4.29

Table 4.29: Percentage removal of PFOA and PFOS at varied concentration using AC-H_3PO_4

Concentration (mg/l)	**Adsorbent dosage (0.02g)**		**Adsorbent dosage (0.05g)**	
	PFOS (% Removal)	PFOA (% Removal)	PFOS (% Removal)	PFOA (% Removal)
0.125	93.27	92.5	98.27	99.00
0.25	90.17	88.54	93.08	91.27
0.50	87.48	87.57	89.97	89.85
0.75	87.69	87.01	98.21	98.23
1.00	85.78	85.29	96.32	95.95

Other conditions used were pH 4, contact time of 24 h and shaking speed of 120 rpm

These findings suggest that higher concentration of PFOA and PFOS in aqueous solution could enhance the formation of semi-micelles and micelles in solution, and this could possibly accumulate on the surface of the adsorbents, thereby enhancing adsorption of the analytes (Wang & Shih, 2011).

4.16 Adsorption equilibrium isotherms

Adsorption isotherms are important models that describe equilibrium and adsorption behaviour of analytes onto the surface of solid phase adsorbents at optimized temperature and pH. The adsorption equilibrium isotherms are presented in Figure 4.22.

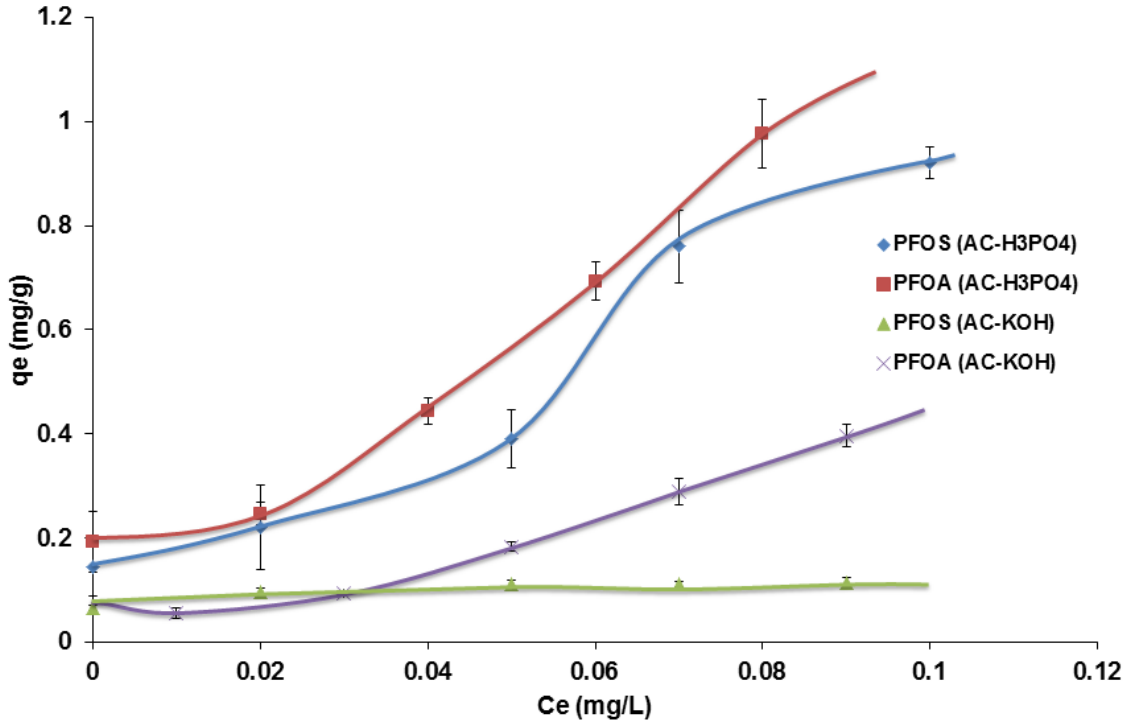
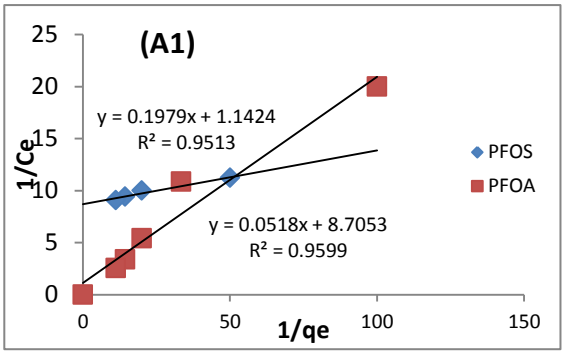


Figure 4.22: Effect of concentration on PFOA and PFOS removal using AC-KOH and AC-H_3PO_4 (pH 4, contact time for 24 h and shaking speed of 120 rpm)

The amount of adsorbates and the removal efficiency of adsorbents can be deduced from the adsorption isotherm models. Experimental equilibrium data obtained from this study were subjected to four adsorption equilibrium isotherms (Langmuir, Freundlich, Temkin and Dubinin-Radushevich isotherm models), expressed previously in equations (7) to (19). The Langmuir model was applied to describe the sorption of adsorbate onto the monolayer surface of the adsorbent. This model assumes that there are uniform energies of adsorption on the surface of the adsorbent, with no transmigration of adsorbate onto other layers on the adsorbent (Xu et al., 2015, Ali et al., 2012). Due to the understanding of this assumption, langmuir model was applied. Maximum adsorption capacity for monolayer coverage q_m of Langmuir isotherm for both adsorbents (AC-KOH and AC-H_3PO_4) were 57.9 mg/g and 78.6 mg/g respectively for the removal of PFOA from aqueous solutions. Corresponding values for PFOS were 51.8 mg/g and 75 mg/g for AC-KOH and AC-H_3PO_4 respectively. Separation factor R_L for both adsorbents were 0.69 and 0.98 for AC-KOH and AC-H_3PO_4 respectively indicating that adsorption was favourable with both adsorbents. The adsorption data fitted well into Langmuir isotherm model with correlation coefficients (R^2) ranging between 0.92 and 0.99 for PFOA and PFOS respectively (Figure 4.23).



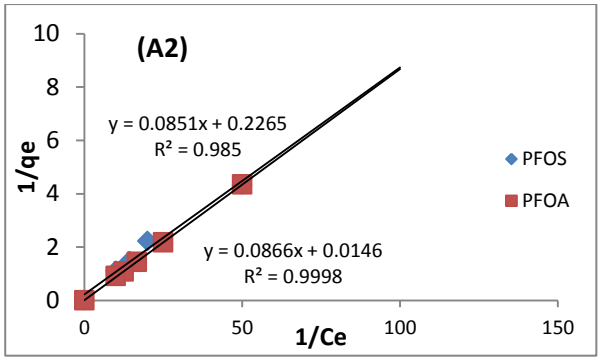
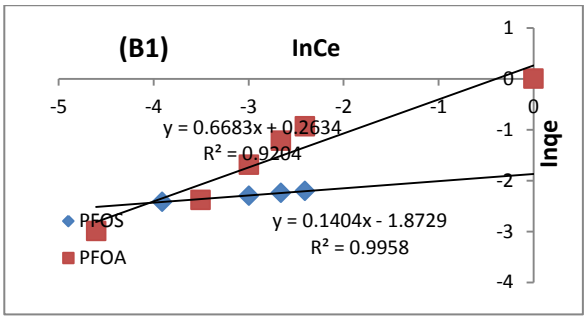


Figure 4.22 A: Langmuir isotherm models for AC-KOH (A1), AC-H_3PO_4 (A2)



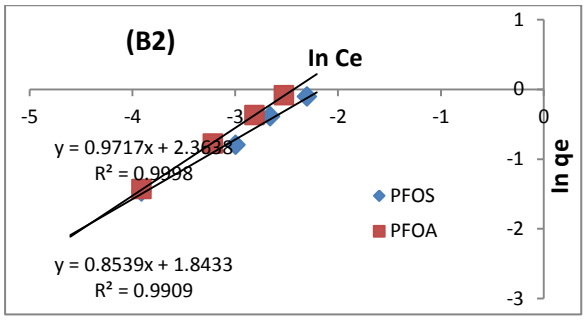
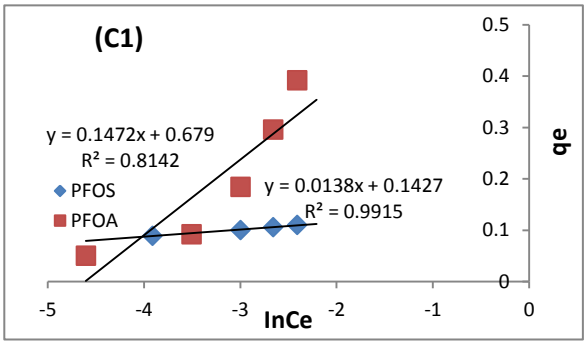


Figure 4.22 B: Freundlich isotherm models for AC-KOH (B1), AC-H_3PO_4 (B2)



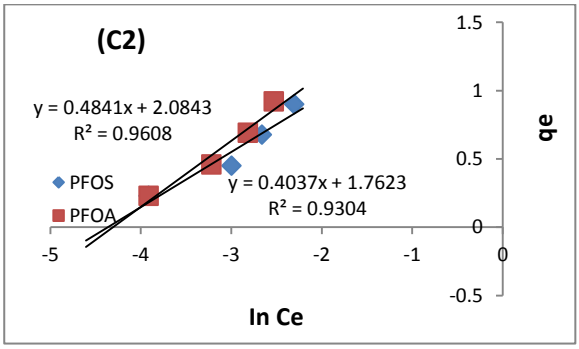
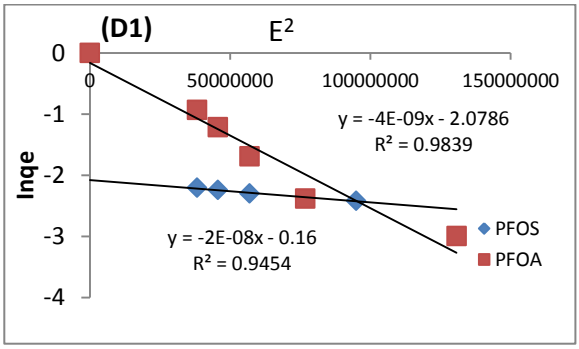


Figure 4.22 C: Temkin isotherm models for AC-KOH (C1), AC-H_3PO_4 (C2)



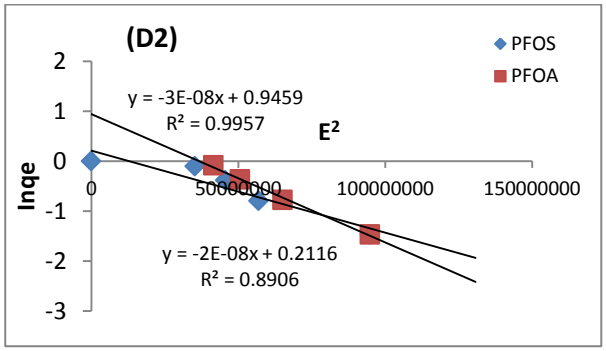


Figure 4.22 D: Dubinin – Radushkevich (DRB) isotherm models for AC-KOH (D1), AC-H_3PO_4 (D2)

Figure 4.23: Adsorption isotherm plots for PFOA and PFOS

The Freundlich adsorption isotherm was applied to describe the multi-layered adsorption of PFOA and PFOS onto the activated carbons. Freundlich's isotherm model showed that adsorption onto activated carbons is multi-layered on the adsorbents' surfaces, with correlation coefficient (R^2) >0.99, presented in Table 4.30. Values of 1/n were 0.6683 and 0.9717 for AC-KOH and AC-H_3PO_4 respectively for PFOA. Corresponding values for PFOS were 0.1404 and 0.8539 respectively. The n-values were > 1 and < 10 indicated that the adsorption of PFOA and PFOS onto AC-KOH and AC-H_3PO_4 was favourable. Hence, adsorption process was best described by Freundlich isotherm model

Temkin isotherm model was used to describe adsorption parameters that would express adsorbent-adsorbate interactions, with less emphasis on extremely low and large concentrations of the analytes. This model assumes that, adsorption process is dependent on the change in temperature and all other molecules present in the solution, which may hinder linearity (Ghasemian & Palizban, 2016). Plots of the model are presented in figures 4.23A-D. From Temkin isotherm plots, values for K_T and b_T were obtained. In AC-H_3PO_4, K_T (l/g) values were 176.23 and 208.43 l/g for PFOA and PFOS respectively. The values using AC-KOH were 14.27 and 67.90 l/g for PFOA and PFOS respectively. Similarly, temkin isotherm constant (b_T) values for AC-H_3PO_4 were 40.37 (PFOS) and 48.41(PFOA) kJ/mol and AC-KOH values were 1.380 (kJ/mol) and 14.72 (kJ/mol) for PFOA and PFOS respectively. Correlation coefficient (R^2) indicated that adsorption data also fitted well into Temkin isotherm model.

The Dubinin-Radushkevich isotherm model was used to describe the adsorption mechanism. This model relates to Gaussian energy distribution on heterogeneous surfaces (Dada et al., 2012). It is most applicable to adsorption systems with high solute activities, and it can sometimes be applied to moderately ranged concentrations of data sets. It is important to note that the Dubinin-Radushkevich isotherm is a temperature-dependent model, which makes it appropriate to analyse adsorption data at different temperatures. This model is mostly applicable to distinguish between adsorption mechanisms, which is due to chemisorption and physiosorption processes with respect to the mean value of the free energy. From adsorption data obtained, the values of q_{DRB} for AC-H_3PO_4 were 21.6 and 94.5 mg/g for PFOA and PFOS respectively, while the values of q_{DRB} obtained for AC-KOH were -2.078 and -0.16 mg/g, respectively. The AC-H_3PO_4 adsorbent showed the best result for the removal of PFOA and PFOS from aqueous solution, at 236.38 mg/g and 184.33 mg/g adsorption capacity, respectively. The adsorption efficiency of the produced activated carbons was deduced from correlation coefficient (R^2) values obtained in the study. Maximum R^2 values were 0.99 (PFOA) and 0.99 (PFOS) for both AC-H_3PO_4 and AC-KOH. This result is consistent with the Freundlich isotherm

model, which assumes that adsorption behaviour relates to strong heterogeneous and multilayer surfaces. There was also evidence of adsorption onto the monolayer coverage on the surface of adsorbents, as revealed in values obtained from the Langmiur isotherm model. Adsorption isotherm models plot are presented in Table 4.30.

Table 4.30: Adsorption isotherm parameters for removal of PFOA and PFOS using AC-KOH and AC-H_3PO_4

Isotherms Model	**Parameters**	**AC-KOH**		**AC-H_3PO_4**	
		PFOS	**PFOA**	**PFOS**	**PFOA**
Langmuir	R^2	0.95	0.95	0.98	0.99
	q_m (mg/g)	51.80	57.90	75.13	78.90
	K_L (L/mg)	0.17	0.01	0.22	0.01
	R_L	0.51	0.69	0.83	0.98
Freundlich	R^2	0.99	0.92	0.99	0.99
	K_f	87.29	26.34	184.33	236.38
	1/n	0.14	0.66	0.85	0.97
	n	7.12	1.49	1.17	1.02
Temkin	R^2	0.99	0.81	0.93	0.96
	K_T (L/mg)	14.27	67.91	176.23	208.43
	b_T (kJ/mol)	1.38	14.72	40.37	48.41
Dubinin – Radushkevich	R^2	0.98	0.94	0.89	0.99
	q_{DRB}	-2.07	-0.16	0.21	0.94
	K_{ad}	-4.0×10^{9}	-2.0×10^{8}	-2.0×10^{8}	-3.0×10^{8}

In addition, the surface textures of the adsorbents AC-KOH and AC-H_3PO_4 were altered after adsorption, due to the accumulation of analytes after the adsorption process as by revealed on micrograph images (Figure 4.24). Remarkable blurry images of activated carbons after adsorption were due to changes in the external and internal surface areas, and the degree of porosity of the activated carbons. Organic compounds with large molecular weights such as PFOA and PFOS could penetrate into the developed inner pores of the adsorbents. It was also assumed that adsorbed analytes could replace the existing molecules on the surface of the modified activated carbons during the adsorption process (Zhang et al., 2014).

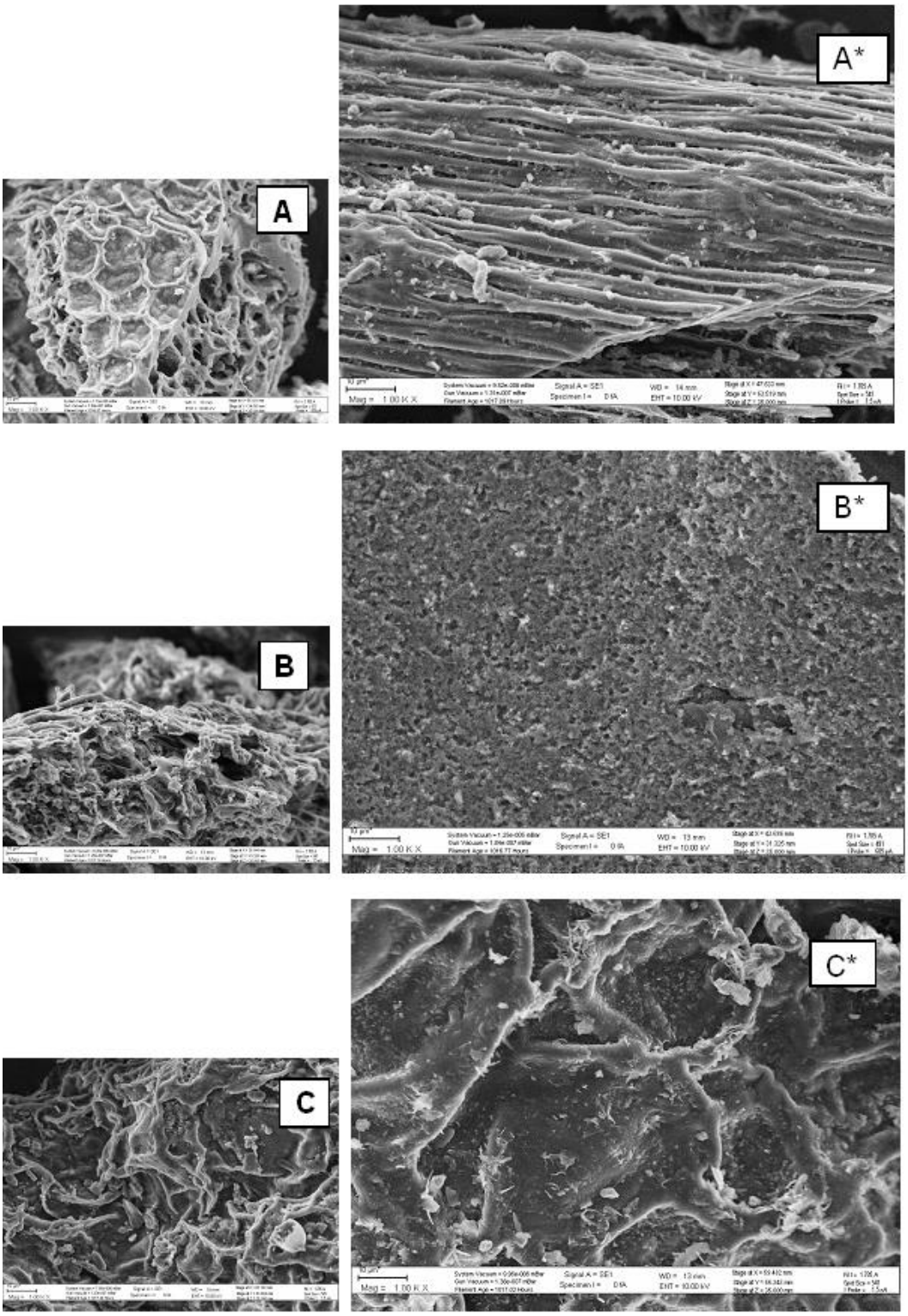


Figure 4.24: SEM image for modified and unmodified activated carbons after adsorption

(A) AC-H_3PO_4 (B) AC-KOH (C)Un-treated biomass before sorption. Asteriked plates are respective adsorbents after sorption

4.17 Kinetic studies

Kinetic studies were conducted in order to understand the sorption mechanism of PFOA and PFOS onto the modified activated carbons, and to interpret the adsorption data obtained. The sorption mechanisms of PFOA and PFOS onto AC-KOH and AC-H_3PO_4 adsorbents were analyzed using four kinetic models (pseudo first-order kinetics, pseudo second-order kinetics, Elovich rate equation and Webber-Morris intra-particle diffusion rate) and have been previously expressed in equations 20-24. There was an initial rapid adsorption rate from 30 min up to 60 min for both PFCs using the two activated carbons (Figure 4.25). A similar study by Yu et al. (2009) using commercial activated carbons reported that equilibrium was attained at an average of 48 h, for the removal of some selected PFCs from aqueous solutions.

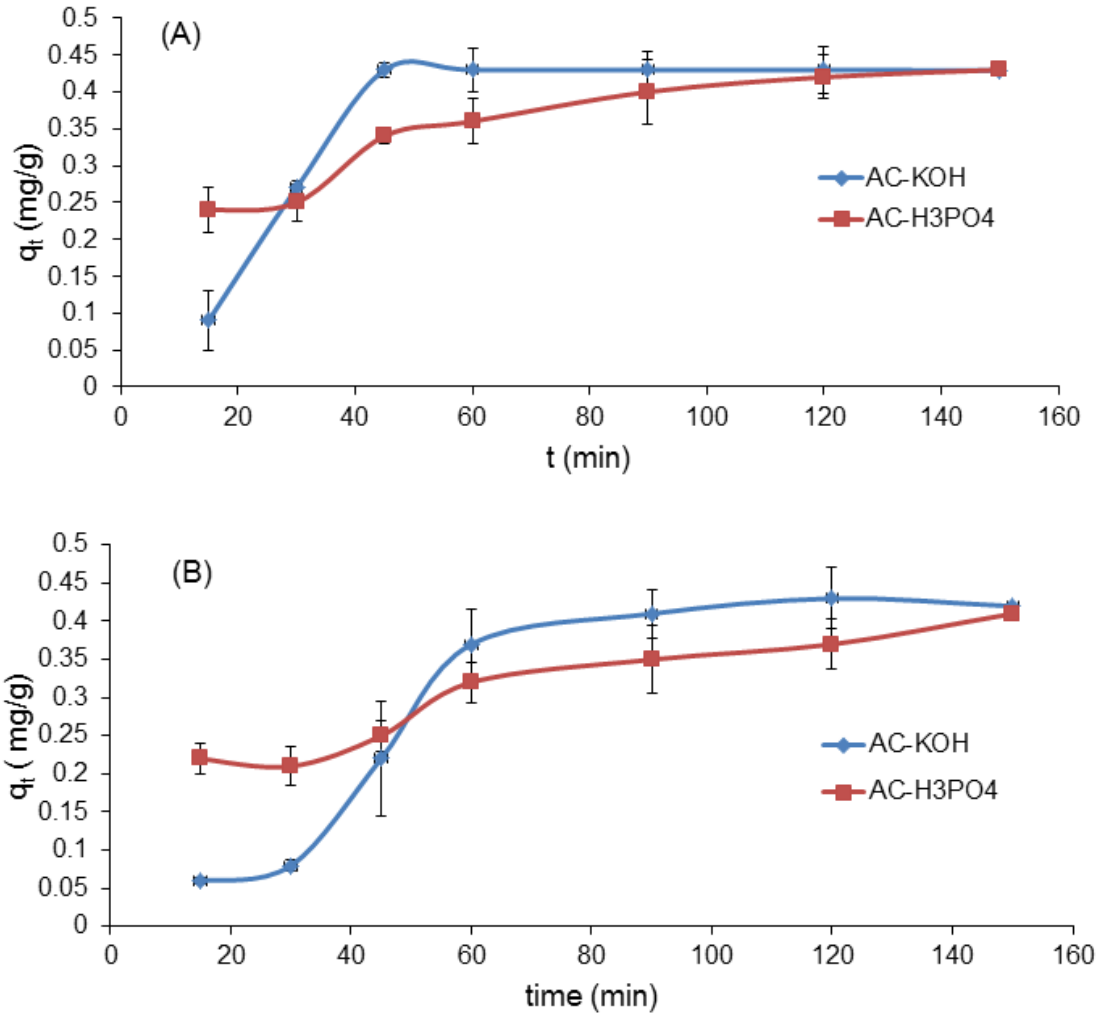
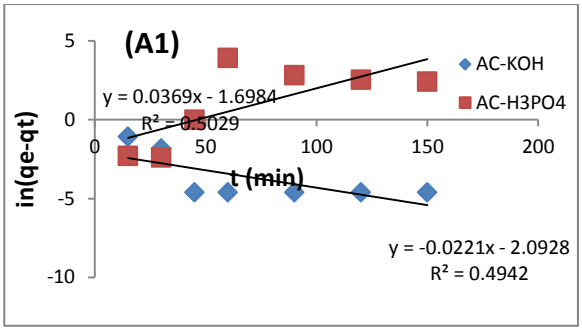


Figure 4.25: Adsorption kinetics equilibrium using AC-KOH and AC-H_3PO4 for the removal of PFOA (A) and PFOS (B).

Pseudo first order kinetics, K_1 values obtained for AC-KOH was 0.211 min^{-1} and 0.084 min^{-1} for PFOA and PFOS respectively. And, K_1 values for AC-H_3PO_4 were 0.532 and 0.036 and 0.029 min^{-1} for PFOA and PFOS respectively. Correlation coefficients (R^2) for the model using AC-KOH were 0.49 and 0.44 for PFOA and PFOS respectively. Corresponding R^2 values using AC-KOH were 0.50 and 0.90 for PFOA and PFOS respectively. Adsorption capacities, q_e using AC-H_3PO_4 were 1.69 and 0.55 mg/g for PFOA and PFOS respectively. The values obtained with AC-KOH_4 were 2.09 and 2.46 mg/g for PFOA and PFOS respectively. Results suggested that pseudo first order kinetics model did not apply to the adsorption data obtained due to poor linearity. Pseudo second-order kinetic model was used to explain the uptake of PFOA and PFOS by plotting t/q_t against contact time t (min) as presented in Figure 4.26.



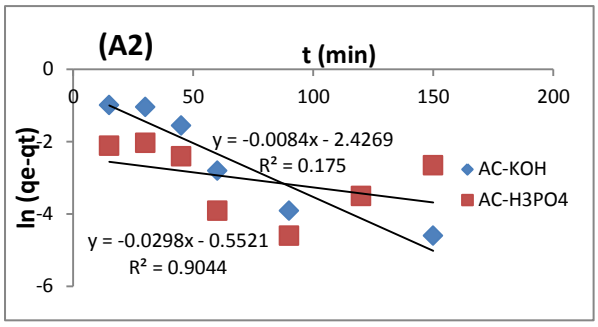
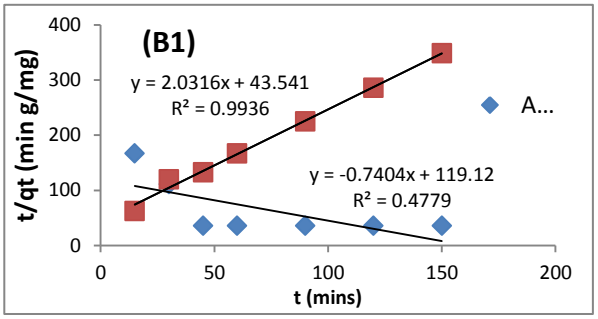


Figure 4.25 A: Pseudo first order kinetic models for adsorption of PFOA (A1) PFOS (A2) on AC-KOH and AC-H_3PO_4



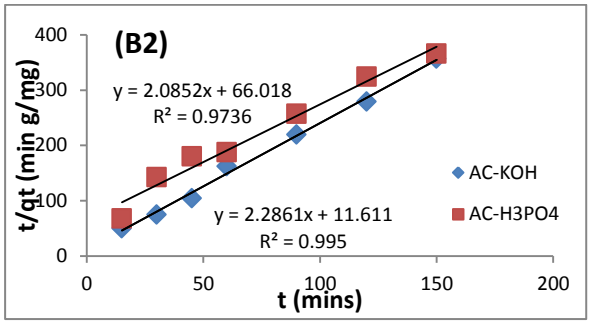
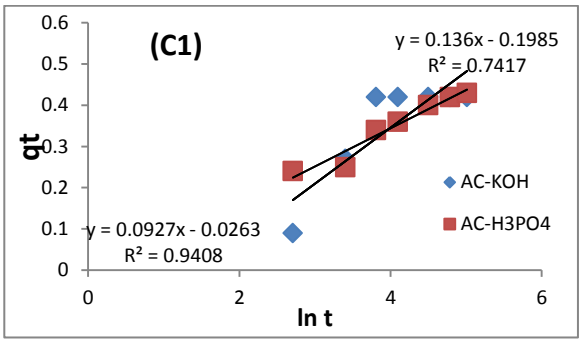


Figure 4.25 B: Pseudo second order kinetic models for adsorption of PFOA (B1) PFOS (B2) on AC-KOH and AC-H_3PO_4



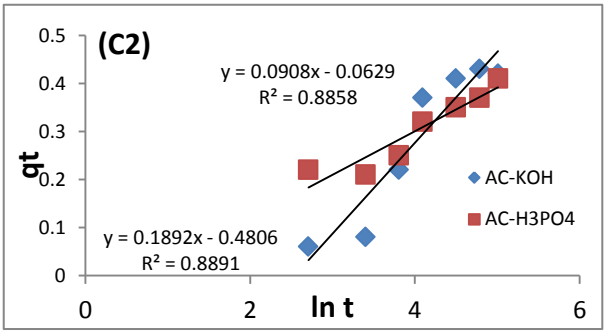
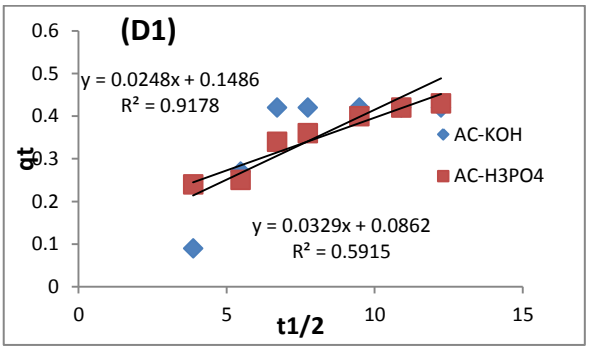


Figure 4.25 C: Elovich rate equation models for adsorption of PFOA (C1) PFOS (C2) on AC-KOH and AC-H_3PO_4



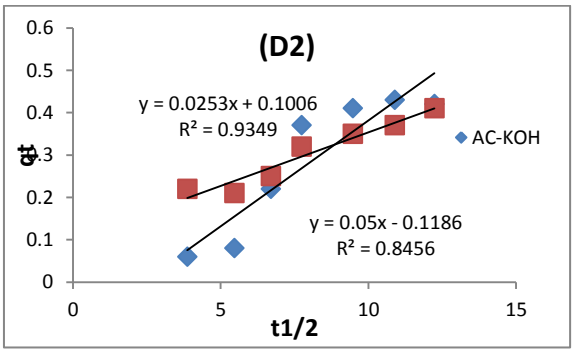


Figure 4.25 D: Intra-particle diffusion models for adsorption of PFOA (D1) PFOS (D2) on AC-KOH and AC-H_3PO_4

Figure 4.26: Kinetic models for adsorption of PFOA and PFOS on AC-KOH and AC-H_3PO_4

Correlation coefficients (R^2) for Pseudo-second order kinetics were 0.995 (PFOS) and 0.47 (PFOA) using AC-KOH and 0.97 (PFOS) and 0.99 (PFOA) with AC-H_3PO_4. These values suggest chemisorption as a major PFCs removal mechanism using AC-H_3PO_4. The maximum adsorption capacity of the activated carbon was 119.12 mg/g for the removal of PFOA using AC-KOH indicating that pseudo second-order model favoured the removal of PFOA from aqueous solutions. Other parameters responsible for the adsorption kinetics could include surface characteristics such as the degree of porosity of the adsorbents (Figure 4.25B).

Elovich's kinetic model was also applied to determine the adsorption and desorption mechanisms involved in the adsorption process. Value obtained from this model could use to deduce the feasibility of the application of produced activated carbons to real life scenarios. The values in the sorption of PFOA onto AC-H_3PO_4 for α were 0.18 mg/g min^{-1}, for β, 0.48 mg/g, with a correlation coefficient (R^2) of 0.88. Corresponding values for PFOS using AC-H_3PO_4 were α, was 0.0927 mg/gmin^{-1}, for β was 0.026 g/mg, and 0.94 for R^2. The results from the application of this model suggested that a higher rate of adsorption (α) than desorption (β) supported the fast uptake of PFOA and PFOS in the initial stage. The adsorption rate decreased over time, in line with chemisorption being the controlling mechanism. Hence, elovich's kinetic model also described the kinetic process strongly.

The adsorption mechanism was summarized in stages using the Webber-Morris intra-particle diffusivity equation plot. The plot showed multi-linearity, indicating that there were two or more stages in the process. Graphical presentations are presented in Figure 4.27. Equilibrium was attained before 60 min. The adsorption mechanism for the removal of PFOA involved two stages- an initial stage with a steady increase in adsorption up to 40 min, and a second stage of intra-particle diffusion that proceeded slowly due to the low concentration of analytes available in the aqueous solution.

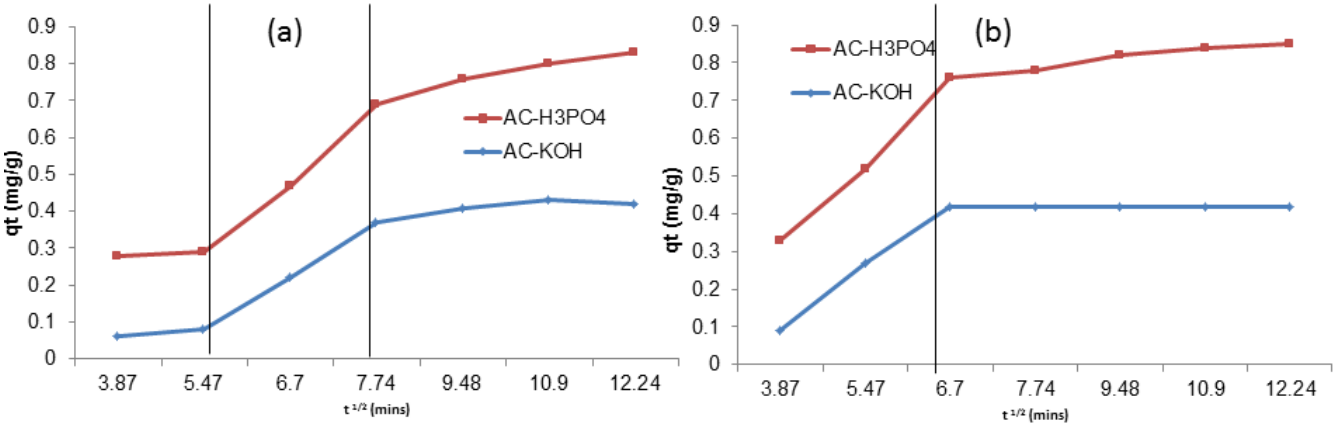


Figure 4 27: Adsorption kinetics of intra particle diffusion for AC-KOH and AC-H_3PO_4 for PFOA (a) and PFOS (b)

Table 4.31 presents the adsorption kinetics parameters for AC-KOH and AC-H_3PO_4. The adsorption kinetics models revealed that the equilibrium data interpretation fitted well into more than one model. The correlation coefficient (R^2) values obtained were greater than >0.9 for AC-H_3PO_4, as illustrated by the Elovich rate equation, the intra-particle diffusivity equation and the pseudo second-order kinetic models. The pseudo second-order kinetics and Elovich rate equation models yielded the highest correlation coefficient values with R^2 values of 0.9408 and 0.9736 for PFOA and PFOS respectively. This study thus establishes that data fitted well into both pseudo second-order kinetics and Elovich rate equation models described the sorption process best; chemisorption mechanism was therefore partly responsible for adsorption (Bäuerlein et al., 2012).

Table 4.31: Adsorption kinetics models' parameters using AC-KOH and AC-H_3PO_4 for PFOA and PFOS removal

Models	Parameters	AC-KOH		AC-H_3PO_4	
		PFOS	PFOA	PFOS	PFOA
Pseudo first order kinetics	q_e	2.46	2.09	0.55	1.69
	$K_1(min^{-1})X10^{-2}$	0.84	2.11	2.98	3.69
	R^2	0.44	0.49	0.90	0.50
Pseudo second order kinetics	q_e (mg/g)	11.61	119.12	66.01	43.04
	K_2 (g(mgmin^{-1})	2.28	0.74	2.08	2.03
	R^2	0.99	0.47	0.97	0.99
Elovich rate equation	α (mg(gmin)$^{-1}$)	0.09	0.19	0.09	0.18
	β (g mg^{-1})	0.02	0.13	0.06	0.48
	R^2	0.94	0.74	0.88	0.88
Intraparticle diffusion	K_D	0.11	0.08	0.10	0.14
	i	0.05	0.03	0.02	0.02
	R^2	0.84	0.59	0.93	0.91

4.18 Thermodynamic Studies

Temperature is an important factor influencing adsorption rates and capacities. Experiments to determine the influence of temperature on the adsorption of PFOA and PFOS were conducted at a temperature range of 293 K to 308 K. Other conditions were pH 4, adsorbent dosage of 0.05 g, contact time of 120 min and shaking speed of 120 rpm. From thermodynamics studies, it was observed that changes in temperature affected the quantity of adsorbates on the surface of the adsorbents. At increased temperatures, the mobility of the adsorbates increased in the solution, thereby enhancing the adsorption process. When the temperature was reduced, the mobility of the adsorbates was reduced. This observation suggests that the adsorption process was exothermic because adsorbate molecules adhered more to the surfaces of activated carbons. Table 4.32 presents the equilibrium parameters for the adsorption of PFOA onto activated carbon AC-H_3PO_4 and AC-KOH.

Table 4.32: Equilibrium parameters for the adsorption of PFOA onto activated carbon AC-H_3PO_4 and AC-KOH at different temperatures

	Adsorbent	**Temp. (K)**	**Constants**			
			q_m(mg/g)	**K_L**	**R_L**	**R^2**
Langmuir	AC-H_3PO_4	298.00	78.90	0.01	0.98	0.99
		303.00	67.00	0.19		0.99
		308.00	61.70	-0.02		0.98
	AC-KOH	298.00	57.90	0.01	0.69	0.95
		303.00	43.00	1.79		0.95
		308.00	41.00	1.37		0.99
Freudliuch	Adsorbent	**Temp. (K)**	**Constants**			
			K_f	**1/n**	**n**	**R^2**
	AC-H_3PO_4	298.00	236.38	0.97	1.02	0.99
		303.00	97.83	0.46	2.18	0.98
		308.00	94.71	0.38	2.63	0.97
	AC-KOH	298.00	26.34	0.66	1.49	0.92
		303.00	84.18	0.96	1.03	0.96
		308.00	76.63	0.96	1.03	0.99

Thermodynamics studies were conducted to determine Gibbs free energy (ΔG^0, KJ/mol), enthalpy change (ΔH^0, KJ/mol) and entropy change (ΔS^0, KJ/mol). Results from the study were used to provide information about the effect of temperature changes on the adsorption process. Change in free energy, ΔG^0 was expressed previously as Van't Hoof equations 25 to 28. The summary of thermodynamic parameters is presented in Table 4.33.

Table 4.33: Thermodynamic parameters for the adsorption of PFOA onto activated carbon AC-H_3PO_4 and AC-KOH

Adsorbent	Temp. (K)	Percentage Recovery	q_m(mg/g)	ΔG^0,kJ/mol	ΔH^0, kJ/mol	ΔS^0,kJ/mol
AC-H_3PO_4	298	94±1.4	78.90	-11.03	-82.48	24.46 x 10^3
	303	91±0.70	67.00	-10.86		
	308	88±00	61.70	-10.80		
AC-KOH	298	92± 1.4	57.90	-13.31	-21.66	5.81 x 10^3
	303	87±7.07	43.00	-12.67		
	308	78±4.24	41.00	-12.13		

All the values obtained for ΔG^o were negative. This indicates that removal was spontaneous during the adsorption processes. It was also observed that the ΔG^o value increased with a rise in temperature suggesting that sorption of PFOA onto the activated carbons was most favourable at the lower temperature as presented in Table 4.32. In addition, AC-H_3PO_4 achieved maximum adsorption q_m (78.90 mg/g) with K_L value of 0.0146 at the minimum temperature of 298.15 K. AC-KOH achieved q_m (57.90 mg/g) with K_L values of 0.0142 at the minimum temperature. The ΔH^o value of -21.66 kJ/mol obtained for AC-KOH was attributed to both physiosorption and chemisorption. The large positive value obtained for (ΔS^o) entropy is a clear indication of increasing mobility in the system, due to the availability of unused energy during the adsorption process (Ali et al., 2012).

4.19 Desorption Studies

Desorption studies were conducted to examine the regeneration capacity of the developed activated carbon and also to establish their reusability potentials. Three solvents (acetonitrile, methanol, and hydrochloric acid solution) of different ratios with distilled water were optimized for desorption of PFOA and PFOS from the surface of activated carbons after the adsorption process. Desorption was 99 % for PFOA and PFOS using 100% methanol, 96 % and 85% using 100 % acetonitrile 0.1M HCl respectively. Regenerated activated carbons (AC-H_3PO_4 and AC-KOH) were reused successfully for uptake of PFOA and PFOS from aqueous solutions. During desorption experiments, >90 % recovery of adsorbates was achieved for both activated carbons. Adsorption capacities of the produced activated carbons in this study relative to those reported elsewhere are presented in Table 4.34.

Table 4.34: Adsorption capacities of some published agro-based and synthetic activated carbons used for the removal of PFOA and PFOS

Precursor	Adsorbate	Adsorption capacity	Reference
Powdered Activated Carbon	PFOA	2.92 mmol/g	Yu et al. (2009)
	PFOS	1.04 mmol/g	Yu et al. (2009)
Hydrotalcite	PFOA	27.04 mmol/g	Rattanaoudom et al. (2012)
	PFOS	52.12 mmol/g	Rattanaoudom et al. (2012)
PAC	PFOA	1.35 mmol/g	Rattanaoudom et al. (2012)
	PFOS	1.19 mmol/g	Rattanaoudom et al. (2012)
Cocoa shell	PFOA	212.02 mg/g	Ahmad et al. (2012)
Alumina	PFOA	157 mg/g	Wang & Shih, (2011)
	PFOS	252 mg/g	Wang & Shih, (2011)
DOW L493	PFOS	7.93 µg/g	Senevirathna et al. (2010)
Amb XAD4	PFOS	1.95 µg/g	Senevirathna et al. (2010)
Dow V493		9.29 µg/g	Senevirathna et al. (2010)
Amb IRA 400	PFOS	0.90 µg/g	Senevirathna et al. (2010)
Dow Marathon A	PFOS	2.01 µg/g	Senevirathna et al. (2010)
Filtrasorb 400	PFOS	0.18 µg/g	Senevirathna et al. (2010)
AC-H_3PO4	PFOA	75.13 mg/g	This study
ACH_3PO4	PFOS	78.90 mg/g	This study
AC-KOH	PFOS	26.3 mg/g	This study
AC-KOH	PFOA	87.27 mg/g	This study

Although commercially available synthetic activated carbons have been reported to have higher adsorption capacities than agro-based activated carbons (Senevirathna et al., 2010), environmental and health risks associated with most of the available synthetic activated carbons have not been fully investigated and they are often expensive. Agro-based activated carbons sourced from *V vinifera* leaf litter are alternative adsorbents for the removal of contaminants from water and wastewater systems.

4.20 Application of modified activated carbon AC-H_3PO_4 in a fixed bed column study

Continuous fixed-bed column experiments were carried out using modified activated carbons with phosphoric acid, sourced from agro-based biomass of *V vinifera* leaf litter as an adsorbent (AC-H_3PO_4) for the removal of PFOA and PFOS in contaminated water. It's been reported AC-H_3PO_4 had better removal capacities for PFOA and PFOS in water, with maximum adsorption capacities for AC-H_3PO_4 being 75.13 and 78.90 mg/g for PFOA and PFOS in batch experiments (Fagbayigbo et al., 2017). Hence, the choice of AC-H_3PO_4 for fixed bed column studies. The optimized column parameters included bed height, flow rate and change in the initial influent concentration. Column performance was evaluated using the breakthrough curves for adsorption of PFOA and PFOS onto the packed column bed, and equilibrium data were analysed using the Adams-Bohart, Yoon Nelson and Thomas models.

4.21 Optimization studies for column experiments

4.21.1 Effect of change in Bed height

The breakthrough curve showing different bed-height is presented in Figure 4.28. At different bed heights; 1.3, 2.6, 3.9 and 5.2 cm, significant changes were observed in both exhaustion time and effluent volume (V_{eff}). At increased bed height, exhaustion time and the volume of effluent increased, which could be attributed to the increase in contact time of the influent in the column (Baral et al., 2009). The steepness of the breakthrough curve decreased with an increase in the bed height (from 1.3 to 5.2 cm), which led to the broadening of the mass transfer zone (Ahmad & Hameed, 2010). The effect of bed height in this study influenced the uptake of PFOS by the activated carbon in the fix-bed column experiment.

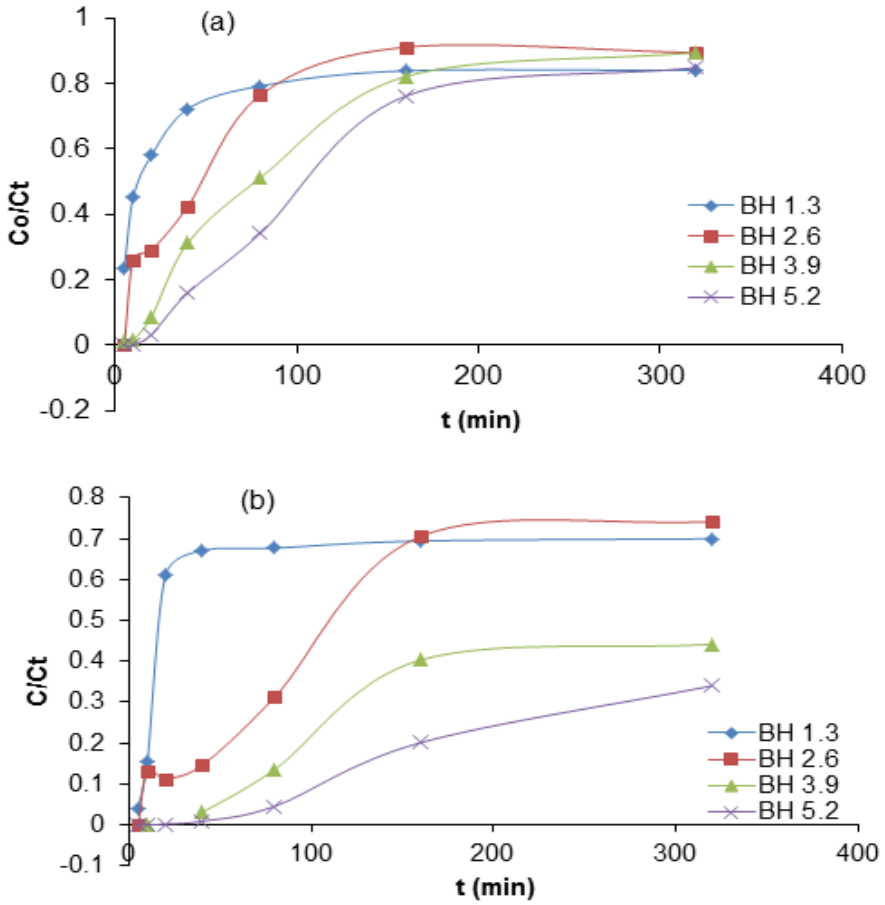


Figure 4.28: Effect of bed-height on PFOA (a) and PFOS (b) adsorption unto AC-H_3PO_4 at pH 4, Initial conc. of 1.0 mg/l and flow rate of 0.64 ml/min

It was also observed that the adsorption capacity of AC-H_3PO_4 in the packed column increased with increasing bed height, with corresponding increases in percentage removal PFOA and PFOS. The increased percentage removal of PFCs with an increasing bed height, may be attributed to increase in surface area of adsorbent, providing abundant sorption sites (Ahmad & Hameed, 2010, Chen et al., 2012b, Baral et al., 2009). It was observed from the result that bed heights of 3.9 cm and 5.2 cm showed steady increase in sorption of PFOS as depicted on the breakthrough curve (Figure 4.28), maximum percentage recovery was obtained with bed height 3.9 cm (91 %) and 5.2 cm (92 %) for PFOS.

4.21.2 Effect of influent flow rate

Flow rate is another crucial parameter that influences the performance of a fixed bed column system. Figure 4.29 shows the breakthrough curve at various flow rates (0.58, 0.64, 0.68 and 0.73) ml/min of influent into the fixed bed column system.

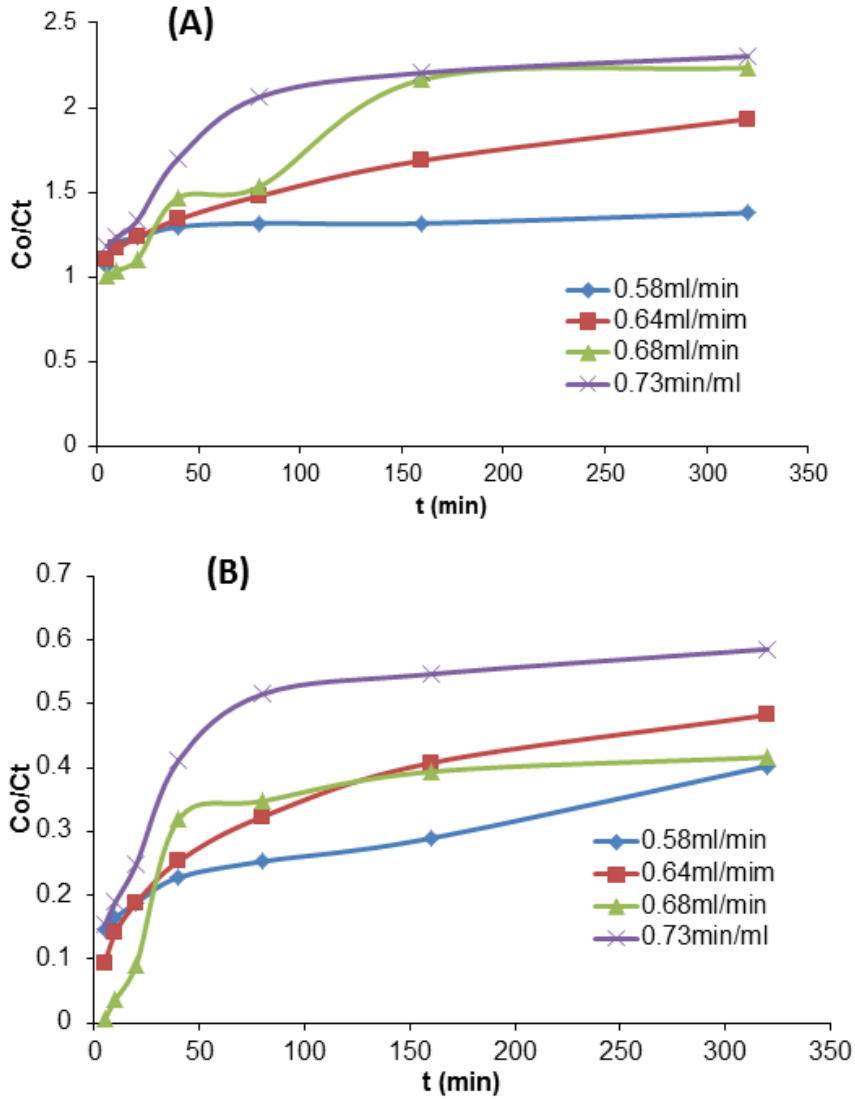


Figure 4.29: Effect of bed-height, PFOA (a), PFOS (b) adsorption unto AC-H_3PO_4 at pH 4, Initial conc. of 1.0 mg/l and Bed height of 3.9 cm

From the illustration in Figure 4.28 the breakthrough curve is most rapid at maximum flow rate. An increased flow rate of influent from minimum to maximum flow (0.58 to 0.73 ml/min) led to increase in effluent volume from 205 ml to 225 ml; an increase from 85% to 95% of the influent volume passing through the fixed bed column. This observation implies that at higher flow rates the external film mass resistance on the surface of the adsorbent has minimum resistance to the flow of influent, and tends to decrease the contact time with the contaminants. The saturation time of the adsorbent therefore decreased at high flow rates resulting in reduced removal efficiency of the adsorbent (Mohammed et al., 2016). It was observed that the breakthrough curve becomes steeper and slope move to the right side with increase in the flow rate. This implies that the time of interaction between the molecules of PFOA and PFOS and the active

sites on the surface of the adsorbent was inadequate. Bonding capacity was hindered due to insufficient contact time in the fixed bed column (Liao et al., 2013). Hence, the flow rate in the column system influenced the uptake of PFOA and PFOS in the influent. An increase in the flow rate could hinder the optimum adsorption capacity of the adsorbent and reduce the percentage removal of the contaminants (Li et al., 2011).

4.21.3 Breakthrough curves of AC-H_3PO_4 and effects of initial adsorbates concentration

The initial concentration of PFOA and PFOS in the contaminated water influenced the breakthrough curve (Figure 4.30).

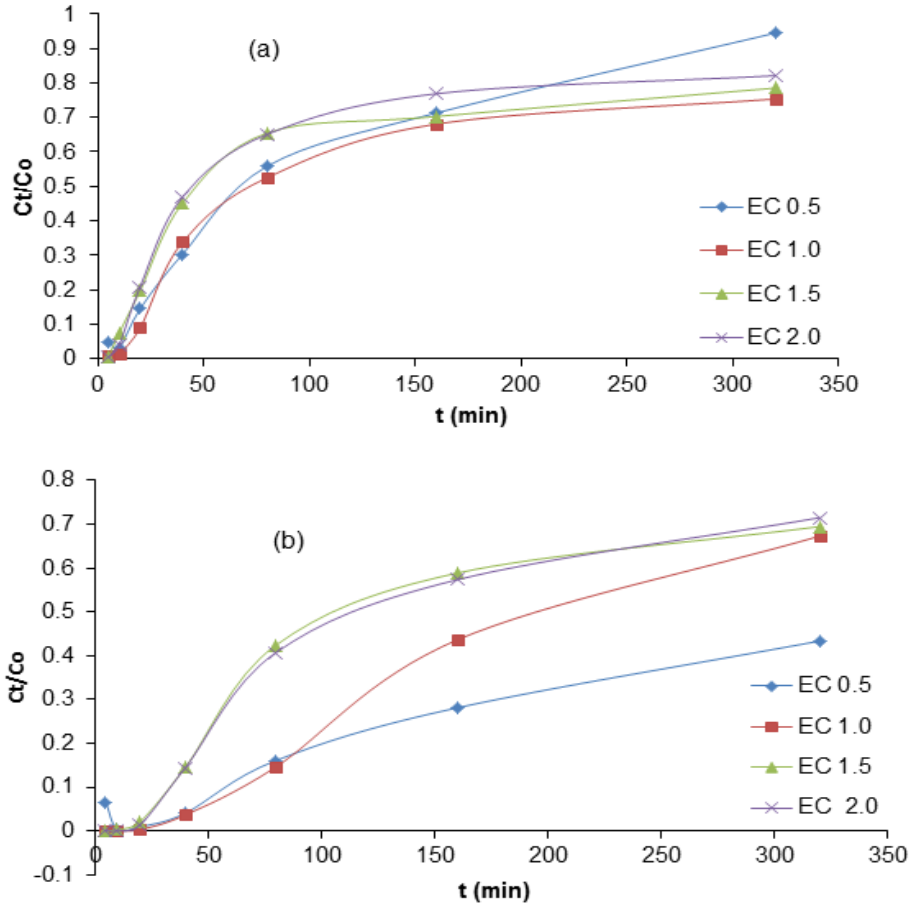


Figure 4.30: breakthrough curves of AC-H_3PO_4 and influence of PFOA (a), PFOS (b) concentration on sorption at pH 4, flow rate of 0.64 ml/min. of 1.0 mg/l and Bed height of 3.9 cm.

Sorption of PFOA and PFOS onto the surface of the adsorbents reached saturation point faster with higher concentration of contaminants. Highest removal of PFOA and PFOS was reached at the maximum concentration 0.5 mg/l. At lower concentrations of influent, high percentage removal for of PFOA and PFOS at 92.05 % and 86.65 % respectively was recorded (Table 4.35). This observation implies that a higher concentration of influent could enhance the mass transfer of contaminants, reaching the saturation point of the adsorbent in a short time, leading to a decrease in exhaustion time (Baral et al., 2009). Based on this observation, steeper breakthrough curves indicated that the mass transfer zone in the column system is short, and the sorption process in the fixed bed column is mostly controlled by the intra-particle diffusion kinetic model (Kumar & Chakraborty, 2009). Other workers have revealed that the adsorption capacities of adsorbents in a fixed-bed column increased with increasing concentrations of contaminants. An abundance of contaminants in aqueous solutions enhanced the rapid transfer of analyte from the solution onto the sorbent, thereby increasing the diffusion coefficient (Chen et al., 2012b, Uddin et al., 2009). Table 4.35 presents the results of PFOA and PFOS adsorption in a fixed bed study.

Table 4.35: Optimization for of the removal PFOA and PFOS in a fixed bed column study

	C_o Initial conc. (mg/l)	FR (ml/min)	BH Bed Height (cm)	V_{eff} (ml)	C_{eq} (mg/l)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg/g)	Total Percentage Removal
PFOA Removal	1.0	0.64	1.3	204.8	0.10	0.59	0.50	101.86	85.78
	1.0	0.64	2.6	204.8	0.06	0.59	0.53	107.82	90.81
	1.0	0.64	3.9	204.8	0.05	0.59	0.54	109.70	92.40
	1.0	0.64	5.2	204.8	0.09	0.59	0.51	102.98	86.74
	1.0	0.58	3.9	185.6	0.01	0.46	0.46	30.74	98.27
	1.0	0.64	3.9	204.8	0.09	0.70	0.62	41.82	88.99
	1.0	0.68	3.9	217.6	0.17	0.87	0.71	47.94	82.18
	1.0	0.73	3.9	33.6	0.27	0.87	0.61	40.81	70.31
	0.5	0.64	3.9	204.8	0.04	0.50	0.46	30.73	92.05
	1.0	0.64	3.9	204.8	0.12	0.97	0.87	58.46	89.85
	1.5	0.64	3.9	204.8	0.36	1.40	1.10	73.69	78.53
	2.0	0.64	3.9	204.8	0.40	1.27	0.94	62.85	73.74
PFOS Removal	1.0	0.64	1.3	204.8	0.09	0.53	0.45	91.26	85.40
	1.0	0.64	2.6	204.8	0.06	0.53	0.48	48.36	90.51
	1.0	(0.64	3.9	204.8	0.05	0.53	0.48	19.18	91.28
	1.0	0.64	5.2	204.8	0.05	0.53	0.49	11.08	92.04
	1.0	0.58	3.9	185.6	0.34	0.56	0.30	20.29	54.21
	1.0	0.64	3.9	204.8	0.34	0.67	0.40	26.68	58.91
	1.0	0.68	3.9	217.6	0.57	0.96	0.46	30.88	47.82
	1.0	0.73	3.9	33.6	0.60	1.01	0.45	30.08	44.35
	0.5	0.64	3.9	204.8	0.10	0.65	0.56	37.83	86.65
	1.0	0.64	3.9	204.8	0.22	1.05	0.86	57.94	82.18
	1.5	0.64	3.9	204.8	0.40	1.26	0.94	62.67	74.06
	2.0	0.64	3.9	204.8	0.68	1.43	0.87	58.48	60.96

Other parameters calculated at various initial concentrations, flow rate and bed height at (solution pH 4, V=250 ml, t_{Total}=320 min)

4.22 Fixed bed column adsorption kinetics models

In order to understand the adsorption mechanisms and kinetic processes in the fixed bed column, models were used to describe the dynamics of the column system and to predict the fate of the contaminants through the breakthrough curve and other column parameters. Equilibrium data obtained were analysed using three kinetic models; Adams-Bohart, Yoon-Nelson, and Thomas Models.

4.22.1 Thomas Model

The Thomas model was applied to describe the kinetic mechanism in fixed bed adsorption column (Sivakumar & Palanisamy, 2009). The Thomas model kinetic coefficient constant (K_T), adsorption capacities (q_o) of the adsorbent and correlation coefficient (R^2) values, were derived from the plot of In (Co/Ce)-1 against t (min). The maximum adsorption capacity q_e for PFOA and PFOS were 111.23 and 145.35 mg/g, respectively. PFOA had the highest adsorption capacity at the maximum concentration 2.0 mg/l while; PFOS was most adsorbed at the lowest concentration (0.5 mg/l). Adsorption capacity decreased with increasing bed height for the removal of both PFOA and PFOS, while it increased with increasing flow rate and initial concentration. This observation is consistent with a study by Nwabanne & Igbokwe, (2012). Values obtained for correlation coefficient, R^2 were higher than those of other models. At increasing bed height and increasing initial influent concentration, R^2 values (>0.90) suggests that equilibrium data obtained from breakthrough curves fitted well into the model, an observation similar to previous studies elsewhere (Mangaleshwaran et al., 2015, Nwabanne & Igbokwe, 2012). A summary of the results are presented in Table 4.35.

4.22.2 Yoon-Nelson model

The Yoon-Nelson model provides information for understanding the initial kinetic mechanism of adsorbate in a fixed bed column study. Several studies reported the application of the Yoon-Nelson model to describe the kinetic mechanism in a fixed bed column experiment (Mohammed et al., 2016, Lim & Aris, 2014, Tian et al., 2013, Chen et al., 2012b). In this study, values for the Yoon-Nelson kinetic constant (K_{YN}), the time required for 50% breakthrough to be attained ($\boldsymbol{\tau}$), and the correlation coefficient (R^2) were obtained from the plot of $InC_e/(C_o-C_e)$ against *t* (min) in a straight line graph. Results (Table 4.35), showed that the range of values obtained in this study for the Yoon-Nelson constant (K_{YN}) were consistent with similar studies reported by Biswas and Mishra (2016). However, the low correlation coefficient (R^2) values obtained imply that the experimental data does not fit the Yoon Nelson model. A similar result was obtained in a study by

Lim and Aris (2014), where 50% sorption onto the column bed was achieved after 24 h. However, another study reported R^2 values higher than 0.88, indicating the validity of the Yoon Nelson kinetic model in that context (Zheng et al., 2016a). In this study, R^2 values were below 0.88 in all the experiments, indicating that the Yoon Nelson model could not predict sorption in a fixed bed column system.

4.22.3 Adams Bohart Model

The Adams-Bobart kinetic model was also applied to analyze equilibrium data obtained in this study. The model describes the early part of the breakthrough curve. Adams-Bohart constant K_{AB} (l/mg/min), the saturation point of the adsorbent represented by N_O (min/mg) and the correlation coefficient (R^2) are estimated from the linear plot of In (Ct/Co) against t (min). Values of K_{AB}, N_O and R^2 are presented in Table 4.36. The results showed that the correlation coefficient (R^2) values increased with increasing bed height (BH) for PFOA and PFOS, while values decreased with increasing flow rate. The saturation point increased when the initial concentration of the contaminants was increased and decreased with increasing bed height. (K_{AB}) values suggest the dominance of external mass transfer at the early stage of the adsorption process (Ahmad & Hameed, 2010, Mohammed et al., 2016). Adam-Bohart model provides a comprehensive approach to evaluating the performance of a fixed bed column (Chen et al., 2012b).

Table 4.36: Thomas and Nelson-Yoon and Adams-Bohart models' parameters in fixed bed adsorption studies

		PFOA				PFOS			
Bed Height (cm)									
Models	Parameters	1.3 cm	2.6 cm	3.9 cm	5.2 cm	1.3 cm	2.6 cm	3.9 cm	5.2 cm
Thomas	K_{th} x10^{-3}	1.65	3.04	3.59	3.45	01.99	3.37	3.06	3.21
Model	q_e (mg/g)	40.58	26.45	27.22	27.95	71.29	71.49	46.85	34.01
	R^2	0.67	0.782	0.823	0.90	0.32	0.86	0.90	0.90
Yoon	K_{yn} x10^{-3}	4.3	6.0	16.0	12.00	7.40	16.80	10.40	8.00
Nelson	τ (min)	74.72	97.06	178.58	196.19	115.66	191.86	175.44	147.90
	R^2	0.57	0.71	0.60	0.71	0.28	0.51	0.69	0.86
Adams	K_{ab} x10^{-3}	3.45	2.89	15.45	11.03	7.35	18.55	9.81	6.13
Bohart	N_o min/mg)	108.80	73.12	31.52	27.07	96.13	43.62	33.12	68.86
	R^2	0.1651	0.20	0.49	0.59	0.24	0.37	0.52	0.715
Flow Rate (ml/min)									
Models	Parameters	0.58 ml/min	0.64 ml/min	0.68 ml/min	0.73 ml/min	0.58 ml/min	0.64 ml/min	0.68 ml/min	0.73 ml/min
Thomas	K_{th} x10^{-3}	2.68	2.55	2.78	2.57	0.92	1.56	1.61	2.29
Model	q_e (mg/g)	53.01	35.64	95.91	53.68	61.17	24.05	75.99	92.44
	R^2	0.979	0.87	0.428	0.540	0.96	0.88	0.62	0.719
Yoon	K_{yn} x10^{-3}	9.20	5.80	6.80	8.20	5.70	8.40	10.10	7.1
Nelson	τ (min)	190.80	102.96	101.76	160.30	660.19	457.57	271.86	385.29
	R^2	0.87	0.81	0.32	0.37	0.86	0.66	0.41	0.55
Adams	K_{ab} x10^{-3}	8.85	3.13	4.17	6.22	3.70	5.06	7.72	3.30
Bohart	N_o min/mg)	31.30	54.74	52.84	51.46	70.01	58.82	65.38	80
	R^2	0.73	0.71	0.27	0.321	0.86	0.66	0.37	0.55
Initial concentration (mg/l)									
Models	Parameters	0.5 mg/l	1.0 mg/l	1.5 mg/l	2.0 mg/l	0.5 mg/l	1.0 mg/l	1.5 mg/l	2.0 mg/l
Thomas	K_{th} x10^{-3}	2.93	5.87	6.46	6.99	3.00	5.11	6.00	3.81
Model	q_e (mg/g)	48.13	22.67	69.16	111.23	145.35	88.59	30.52	72.15
	R^2	0.76	0.89	0.39	0.69	0.95	0.98	0.96	0.86
Yoon	K_{yn} x10^{-3}	12.10	15.90	14.30	12.10	9.50	23.70	19.30	16.91
Nelson	τ (min)	175.66	183.70	159.00	207.85	185.98	235.36	224.09	241.68
	R^2	0.62	0.57	0.47	0.3678	0.78	0.75	0.56	0.47
Adams	K_{ab} x10^{-3}	13.91	9.74	6.82	6.157	7.38	15.49	10.39	8.30
Bohart	N_o min/mg)	27.48	51.75	60.78	72.78	42.33	58.36	69.14	82.73
	R^2	0.58	0.47	0.34	0.30	0.65	0.68	0.50	0.42

4.23 Desorption studies for column study

Desorption study was conducted to evaluate the recovery of PFOA and PFOS and assess the regeneration capacity of the spent activated carbons. While the reusability of the adsorbent in batch adsorption studies was established in our previous report (Fagbayigbo et al., 2017), here, the desorption of target analytes after a fixed bed column experiment was investigated. In this study, desorption of adsorbed PFOA and PFOS was achieved using 90% methanol, with >90 % recoveries unlike the values for 50 % methanol and deionized water (Table 4.37). The adsorption capacity of the AC-H_3PO_4 remained unchanged after three repeated cycles. This study thus confirms the reusability potential of AC-H_3PO_4, similarly to a study by Xiao et al. (2013) who reported 83% analytes recovery when 100% methanol was used as a desorption solvent for the regeneration of the adsorbent.

Table 4.37: Desorption experiment at different cycle with deionized water, 50% methanol and 90% methanol

Desorbing Agent	PFOA			PFOS		
	Percentage Recovered			Percentage recovered		
	First cycle	Second cycle	Third cycle	First cycle	Second cycle	Third cycle
Deionized water	42.3	46.1	41.2	44.9	41.5	46.5
50% methanol	72.3	69.0	71.8	75.4	71.1	68.6
90% methanol	92.2	89.1	93.6	94.9	93.8	96.2

Maximum capacities for ACH_3PO_4 in a fixed bed column studies were 145.35 for PFOA and 111.23 mg/g for PFOS. The results were compared with other studies using different adsorbents, as presented in Table 4.38.

Table 4 38: Comparison of adsorption capacity in the fixed bed column study in this study with previous studies

Biomass used in the Fixed bed column	Adsorbate	Maximum adsorption capacity (q_o) (mg/g)	Reference
Corncobs	Phenol	67.6	Rocha et al. (2015)
Amberlite XAD-4	Perflourinated surfactant	400.0	Wang et al. (2011)
XAD Resin XAD-2		309.2	Wang et al. (2011)
XAD-Hp		183.1	Wang et al. (2011)
Phoenix tree leaf powder	Methylene Blue	149.0	Han et al. (2009)
Lignocellulosic waste	Drimarine Black	20.76	Noreen et al. (2013)
Bamboo Charcoal	CL-B dye		
	Tetracycline	46.5	Liao et al. (2013)
	Chloraphenicol	36.4	
Jackfruit (*artocarpus heteopyllus*) leaf powder	Methylene Blue	267	Uddin et al.(2009)
Waste of Soya oil industry	Methylene Orange	16.6	Mittal et al. (2007)
Bottom ash of Thermal Power plant	Methylene Orange	3.6	Mittal et al. (2007)
AC-H_3PO_4 *V.vinifera* leaf biomass	PFOA	111.2	This study
	PFOS	145.3	This study

CHAPTER FIVE

5.0 CONCLUSION

The assessment of nine perfluorinated compounds (PFCs), including PFOA and PFOS, in surface water and sediment samples of the Plankenburg and Diep Rivers, Cape Town was carried out. Possible pollution abatement of the compounds in water using *V. vinifera* leaf litter as adsorbent in both batch and fixed bed column studies was also investigated.

Prior to environmental monitoring, an analytical protocol for the routine determination of the analytes in environmental samples was developed using UPLC-QTOF-MS. Excellent clean up and extraction procedures were achieved using hydrophobic and lipophilic balance (HLB) solid phase extraction cartridges. The method was validated and used to determine the levels of PFCs in surface water and sediment samples. The method detected all the perfluorinated compounds of interest in less than 9 min of analytical run time. The fragmentation pattern of the compound obtained in mass spectroscopy enabled clear identification and confirmation of the target analytes. The method offers good sensitivity and selectivity for the determination of PFCs in surface water and sediment. Reproducibility and repeatability tests confirmed the robustness of the method for routine application for PFCs measurement in environmental samples.

Seasonal variations of PFCs were established in the river system and maximum levels were detected in summer months. However, low concentration of PFCs were found in surface water samples obtained from the vicinities of farming communities and recreational areas upstream of both rivers. Also high concentrations were measured in sampling points close to informal settlements and industrial areas. Elevated levels of PFCs were largely attributed to industrial activities and the poor waste management systems associated with informal settlements. Corresponding levels of PFCs in sediment samples from the same sampling points were higher than those obtained from surface water. Perfluoroalkyl carboxylic acid compounds such as PFOA, PFNA and PFBA were the most frequently detected compounds among the PFCs investigated, in both surface water and sediment samples. The priority compounds PFOA and PFOS were detected alongside other the compounds at elevated levels in both rivers. The study revealed that long chain PFCs were more prevalent in sediment samples than shorter chain fluorinated compounds, presumably due to their higher molecular weight. The higher concentrations of PFCs measured in the sediment compartment suggests that sediment is a potential sink for PFCs in river systems.

The partitioning and distribution of the nine PFCs in the river systems were evaluated using partitioning coefficient, log K_{OC} and distribution coefficient, log K_D values. Partitioning coefficient values suggested that PFCs are most available in the sediment compartment of both rivers. Sediment samples obtained from Diep River had higher log K_{OC} values than those from the Plankenburg River. Furthermore, the physicochemical characteristics of the sediments and quality of the aquatic environment, such as the presence of cations, pH values, and length of the perfluoalkyl carbon chain greatly influenced the sorption of PFCs onto the sediment compartment.

An attempt was made to remediate PFCs contaminated water samples using grape leaf litter. This study pioneers the use of grape leaf litter to produce activated carbons modified in both acidic (H_3PO_4) and basic (KOH) media. These adsorbents were found to be effective for the removal of PFOA and PFOS in aqueous solutions using adsorption techniques. The activated carbons are potential cheaper alternatives to commercially available adsorbents. Adsorption kinetic models revealed that chemisorption and physiosorption were the controlling mechanisms for removal of PFOA and PFOS from aqueous solutions. Thermodynamics studies showed that the adsorption process was endothermic and spontaneous. The well-developed surface morphology, abundance of microspores and large surface areas of the activated carbons contributed to removal efficiencies. *V. vinifera* leaf biomass was shown to be an eco-friendly, more accessible alternative adsorbent that may be explored for the removal of other environmental contaminants in water.

Furthermore, the adsorbent with the highest adsorption capacity in the batch adsorption study, AC-H_3PO_4, was used in fixed-bed column studies. The result revealed that the uptake of PFOA and PFOS in the column system was influenced by column study parameters such as bed height of the adsorbent, flow rate of the influent into the system, and initial PFCs concentration in the influent. Percentage removal of PFOA and PFOS in the fixed bed column study increased with increasing bed height, decreased with increasing flow rate and initial concentration. Optimum removal was achieved at the minimum concentration of PFOA and PFOS.

Performance of the fixed bed column system was evaluated with three kinetic models. The Thomas model best described fixed-bed column process. However, the combination of the results obtained from the other models also provided insights into adsorption mechanisms for PFOA and PFOS in the column system. The study demonstrated that activated carbons produced from *V vinifera* leaf biomass successfully removed PFOA and PFOS in both batch and fixed bed column studies.

5.1 Recommendation

The results obtained from this study have established the baseline information on the levels of nine PFCs, including PFOA and PFOS, in surface water and sediment in the Diep (Milnerton) and Plankenburg (Stellenbosch) Rivers, South Africa. Due to the environmental and health concerns associated with elevated level of PFCs in the environment, the following recommendations are made:

- Evaluation and assessment of risk associated with exposure to elevated levels of PFCs in the aquatic environment should be carried out.
- Further studies need to be conducted to establish the levels and bioaccumulation of PFCs in biological samples, including benthic organisms, higher animals, humans and other susceptible species.
- PFCs including PFOA and PFOS should be reduced in industrial applications; manufacturing processes should find alternative safe chemicals to PFCs in their manufacturing chain, especially in South Africa.
- Strict legislation should be enacted by South African law and policy makers against PFCs, especially PFOA and PFOS, and related chemical production and application.
- International trade involving the importation of PFCs (especially PFOA and PFOS) and related chemicals should be banned in South Africa
- Correct information on the safe handling of PFC-related products should be provided on product label and safety data sheets to avoid the risks associated with PFCs.

In order to improve on batch and column studies for the removal of PFOA and PFOS in contaminated water, further research should be conducted in the following areas:

- Possible removal of other detected PFCs and organic contaminants in the water systems.
- Improve the surface characteristics of produced activated carbons from *V. vinifera* leaf biomass for enhanced efficiency.
- Investigation of the influence of other ions on the removal of PFCs in water.

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APPENDICES

APPENDIX A: Recoveries of nine PFCs from Milli-Q water at different concentrations (ng/l)

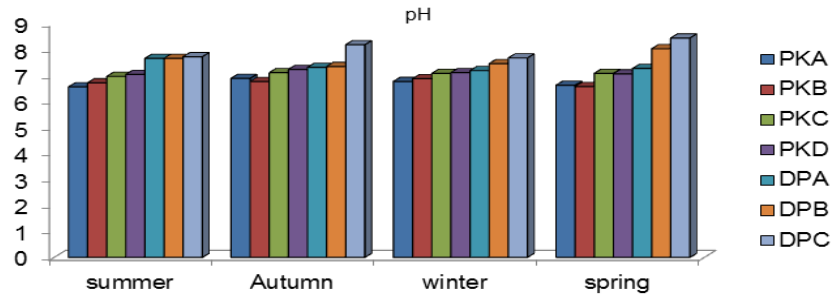
		125 ng/l				250 ng/l				500 ng/l			
Mili Q water	Compounds	A	B	C	Mean±SD	A	B	C	Mean±SD	A	B	C	Mean±SD
	PFBS	53.6	44.8	64.8	54.4±10.0	71.2	75.6	76.8	74.53±2.9	76.4	91.3	89.2	78.5±16.5
	PFPeA	69.6	58.4	56.8	61.6±6.9	78.4	76.8	79.2	78.13±1.2	94.1	89.7	90.7	93.1±7.2
	PFHpA	60.8	37.6	40.8	46.4±12.5	73.6	68	76.4	72.66±4.2	95.12	93.9	94.62	94.4±8.5
	PFOA	65.6	52	53.6	57.06±7.4	74.4	76.4	79.2	76.66±2.4	92.1	96.54	95.54	93.1±11.4
	PFOS	58.4	57.6	54.4	56.8±2.1	77.6	80	75.6	77.73±2.2	94	86.1	89.5	90.6±13.3
	PFNA	66.4	48.8	41.6	52.26±12.7	84	79.6	72	78.53±6.0	93.3	91.9	93.2	92.0±6.0
	PFDA	62.4	64.8	58.4	61.86±3.2	76.4	74	75.6	75.33±1.2	90.1	91.7	94.5	87.3±8.8
	PFUnDA	64.8	43.2	60.8	56.26±11.4	72	74	76.4	74.13±2.2	92.7	89.76	92.46	90.0±12.1
	PFDoDA	73.6	59.2	66.4	66.4±7.2	75.6	70.4	73.6	73.2±2.6	98	134.8	106.3	126.5±14.6

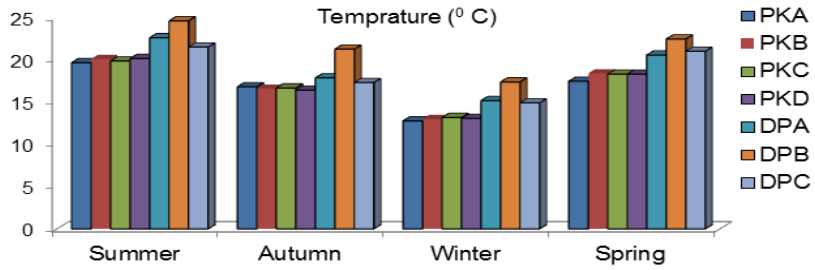
APPENDIX B: Recoveries of nine PFCs from surface water at different concentrations (ng/l)

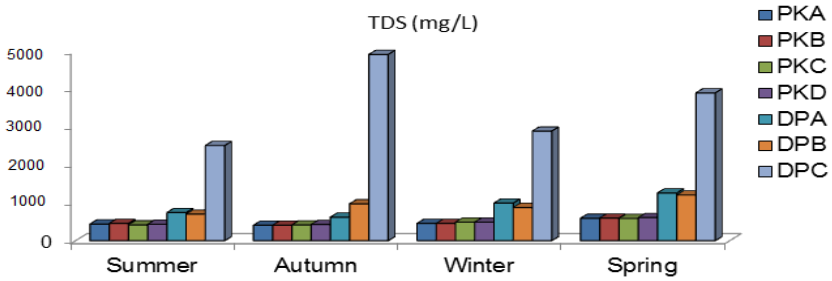
Surface water	Compounds	125 ng/l				250 ng/l				500 ng/l			
		A	B	C	Mean±SD	A	B	C	Mean ±SD	A	B	C	Mean±SD
	PFBS	42.96	44	40.8	42.58±1.6	69.12	71.6	72.4	71.04±1.7	75.6	82	78.4	78.66±3.2
	PFPeA	51.76	53.84	48	51.2±2.9	70.4	72.8	71.2	71.46±1.2	73.2	78.24	75.6	75.68±2.5
	PFHpA	50.4	48.8	51.2	50.13±1.2	69.6	66.8	68.4	68.26±1.4	76.8	63.4	63.82	68.00±7.6
	PFOA	54.4	52	53.6	53.33±1.2	66.4	68.4	71.2	68.66±2.4	75.2	78.2	63.96	72.45±7.5
	PFOS	61.304	58.56	62.4	60.75±1.9	73.6	76.8	75.6	75.33±1.6	58.8	62.4	83.78	68.32±13.5
	PFNA	58.64	57.288	57.6	57.84±0.7	74.44	75.6	312	154.01±1.3	76.42	65.8	68.36	70.19±5.5
	PFDA	54.4	51.28	50.4	52.02±2.1	68.4	70	72.76	70.38±2.2	78.2	83.7	79.78	80.56±2.8
	PFUnDA	60.08	62.48	60.8	61.12±1.2	67.2	71.6	68.4	69.06±2.2	63.6	73.7	66.22	67.84±5.2
	PFDoDA	70.4	66.48	63.2	66.69±3.6	70	69.6	68.8	69.46±0.6	65.8	75.2	76.28	72.42±5.7

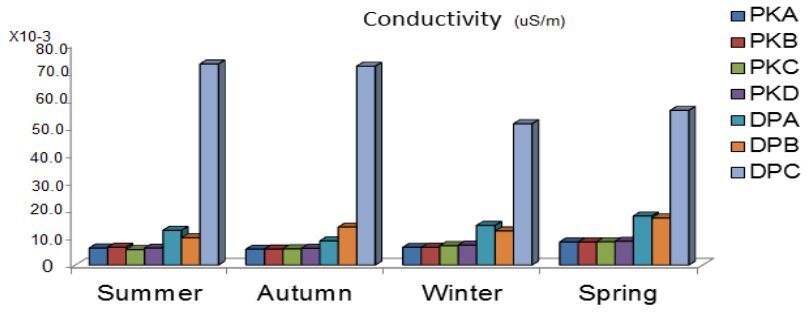
APPENDIX C: Recoveries of nine PFCs from sediment at different concentrations (ng/kg)

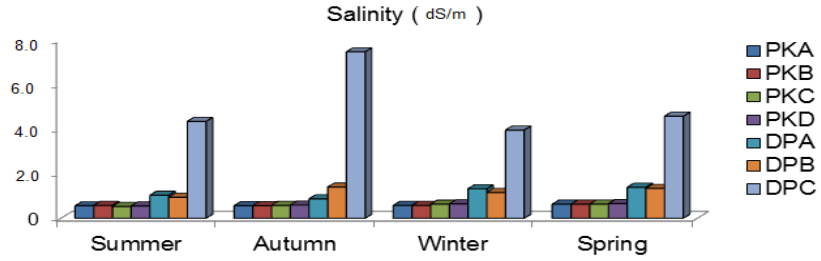
		125 ng/kg				250 ng/kg				500 ng/kg			
Sediment	Compounds	A	B	C	Mean±SD	A	B	C	Mean±SD	A	B	C	Mean±SD
	PFBS	45.6	44.8	32.8	41.06±7.1	59.2	54	58.4	57.21±2.8	51.6	57.8	59.24	56.21±4.0
	PFPeA	53.6	50.4	40.8	48.26±6.6	61.2	56.8	59.2	59.06±2.2	59.2	63.64	63.96	62.26±2.6
	PFHpA	44.8	49.36	41.68	45.28±3.8	60.4	58.8	62	60.41±1.6	56.8	71.4	65.8	64.66±7.3
	PFOA	48.96	48	45.36	47.44±1.8	59.6	56.4	62	59.33±2.8	63.4	58.2	66.2	62.6±4.0
	PFOS	57.84	56.96	49.68	54.82±4.4	61.6	60.8	63.6	62.92±1.4	63.8	56.4	59.8	60±3.7
	PFNA	58.4	55.2	51.36	54.98±3.5	60.8	59.6	59.2	59.86±0.8	64.2	79.8	65.6	69.86±8.6
	PFDA	54.4	46.48	45.84	48.90±4.7	63.64	60.4	59.6	61.21±2.1	66.2	63.6	57.8	62.53±4.3
	PFUnDA	56.8	59.2	60.48	58.82±1.8	60.8	58	61.6	60.13±1.8	63.6	65.6	58.2	62.46±3.8
	PFDoDA	64.96	61.6	57.04	61.20±3.9	63.6	62.4	57.6	61.20±3.1	59.8	57.2	63.6	60.2±3.2



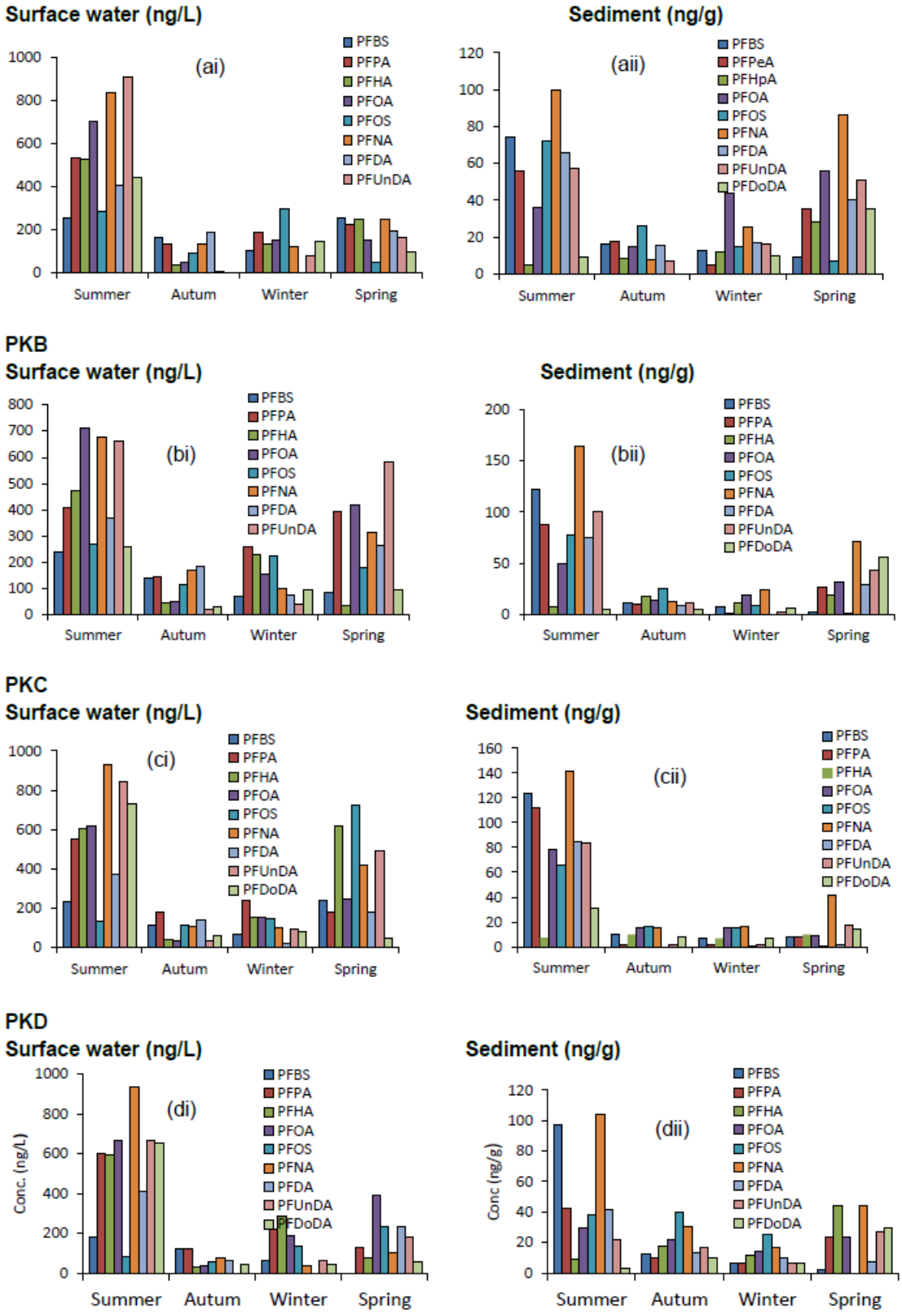




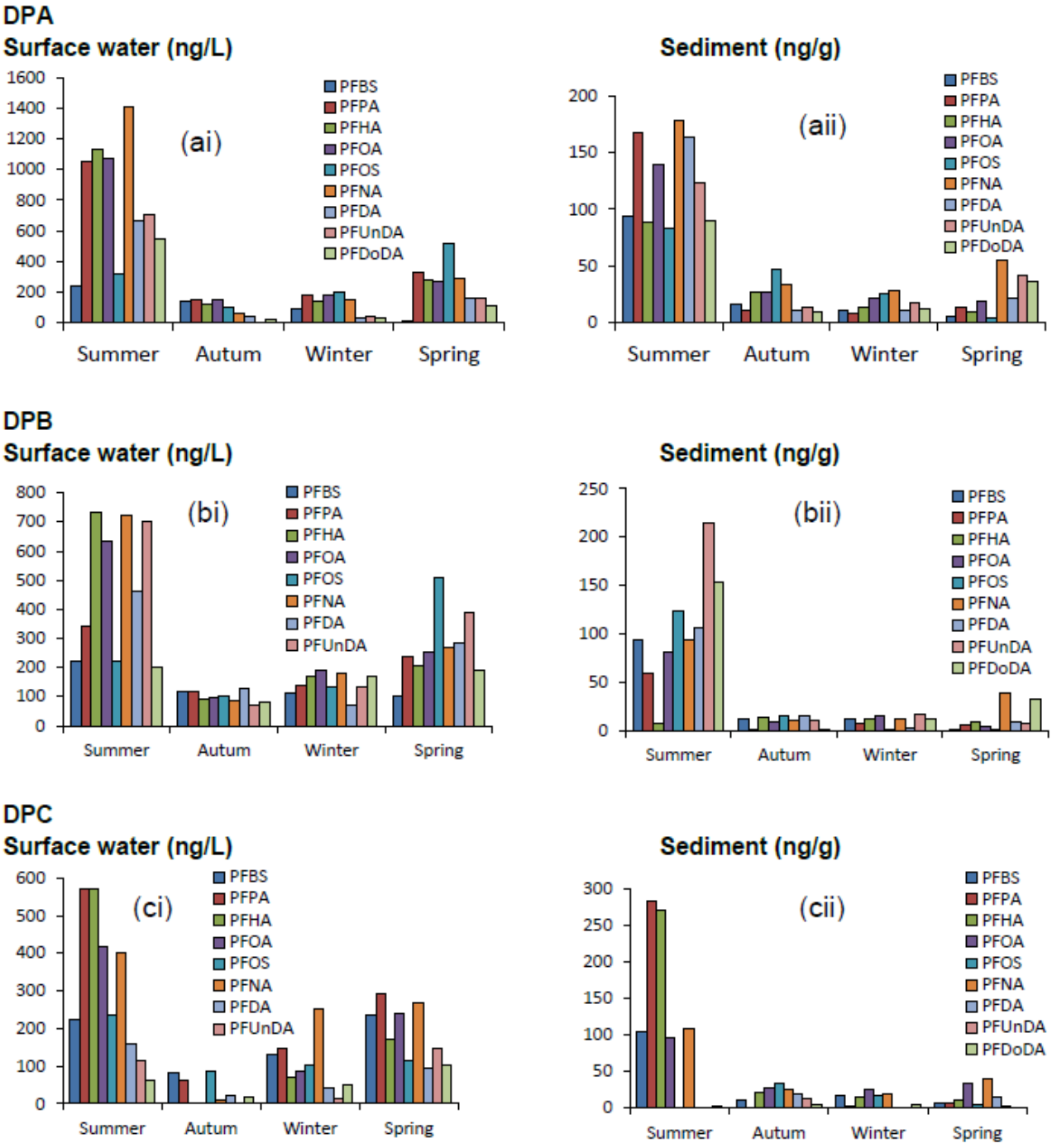




APPENDIX D: Physicochemical parameters of the surface water



APPENDIX E: Levels of nine PFCs in surface water and sediment from Plankenburg River



APPENDIX F: Levels of nine PFCs in surface water and sediment from Diep River

APPENDIX G: Mean concentrations ng/l± SD (n=4) of PFCs in surface water

		Summer			Autumn			Winter			Spring		
Sampling Stations	Compounds	DEC	JAN	FEB	MARCH	APRIL	MAY	JUNE	JULY	August	September	October	November
PKA	PFBS	171.25±79.2	365.27±64	148.50±58	108.88±102	226.66±131	100.01±41	191.49±103	111.27±124	LOD	462.00±102	170.39±120	49.19±117
	PFPeA	353.43±57	948.08±177	111.51±91	90.00±152	LOD40	270.00±76	363.74±40	144.22±12	64.01±80	205.64±85	151.64±41	249.29±95
	PFHpA	351.68±93	1055.05±87	LOD	25.55±64	6.67±89	70.01±92	254.00±122	60.57±98	92.50±49	370.43±129	165.39±57	125.76±121
	PFOA	466.23±51	1352.70±84	46.00±17	33.33±106	LOD	100.02±120	289.62±106	135.51±51	32.00±75	75.25±103	100.34±75	225.78±66
	PFOS	189.4±55	439.71±51	128.53±166	63.40±52	LOD	190.21±103	142.40±34	742.19±79	LOD	12.97±66	32.59±55	84.80±40
	PFNA	555.33±146	1500.01±209	166.02±151	90.04±189	40.00±100	230.11±78	285.72±42	87.56±77	LOD	180.94±47	167.27±126	320.86±64
	PFDA	272.70±80	702.12±73	116.03±102	125.22±257	65.67±133	310.95±42	LOD	LOD	LOD	105.48±123	131.55±124	289.16±103
	PFUnDA	606.83±133	1712.52±128	108.71±70	3.33±102	LOD	10.01±120	84.32±117	17.775±49	147.00±65	63.04±15	110.15±80	267.47±82
	PFDoDA	293.99±82	881.97±130	LOD	LOD	LOD	LOD99	116.29±65	319.75±37	LOD	72.42±77	65.21±12.4	123.22±91
PKB	PFBS	157.93±78.0	229.31±138	244.50±213	92.22±149	166.67±124	110.73±101	73.46±123	135.67±53	LOD	111.33±67	56.77±58	58.97±60
	PFPeA	271.93±155	640.30±134	175.50±225	96.67±58	LOD	290.08±46	336.93±128	146.85±87	289.73±49	585.33±94	261.78±86	200.04±62
	PFHpA	316.35±54	949.05±236	LOD	30.01±125	LOD	90.41±78	137.17±82	145.71±38	403.01±112	12.06±100	23.91±105	59.68±87
	PFOA	475.94±56	1357.33±163	70.51±188	33.33±239	LOD	100.01±34	200.10±53	124.83±97	129.32±83	153.12±40	279.32±55	684.86±124
	PFOS	180.26±152	387.18±171	153.00±234	74.48±245	0.40±96	223.05±70	48.98±85	521.68±67	103.01±67	17.14±49	118.08±45	337.10±47
	PFNA	451.43±51	1078.43±74	276.81±56	113.33±116	40.00±125	300.00±130	194.28±61	95.83±73	LOD92	379.20±81	209.61±92	249.65±96
	PFDA	245.80±91	586.48±112	151.23±157	122.22±214	46.67±48	320.03±52	LOD	LOD	226.00±92	288.38±40	177.24±43	243.36±126
	PFUnDA	440.65±90	1119.96±190	202.00±227	13.33±176	40.01±61	LOD±131	63.21±61	5.95±92	49.50±92	215.39±80	389.67±99	953.62±131
	PFDoDA	170.91±93	512.73±59	LOD251	17.77±140	53.33±54	LOD	80.6±134	189.05±55	10.50±48	89.27±78	63.23±38	100.44±41
PKC	PFBS	157.36±75	225.60±134	246.50±225	77.77±250	173.33±130	60.01±129	128.83±44	81.22±42	LOD130	481.5±116	160.50±52	LOD78
	PFPeA	369.10±89	884.30±498	223.75±230	121.11±257	213.33±121	150.00±58	352.93±68	181.08±107	186.01±61	172.97±60	119.44±54	185.36±72
	PFHpA	405.48±75	1201.95±356	14.52±215	26.66±160	40.03±54	40.00±72	184.85±113	167.32±65	112.50±34	LOD	410.03±132	1230.65±130
	PFOA	413.91±91	1126.25±233	115.50±239	22.22±213	6.67±124	60.54±44	211.99±57	107.40±65	138.09±45	367.91±36	163.75±69	123.34±69
	PFOS	90.04±103	158.14±124	112.03±185	76.22±128	72.73±65	155.95±114	127.98±73	283.66±89	41.73±44	166.02±129	485.09±79	1289.42±88

	PFNA	620.71±146	1626.15±228	236.51±72	74.44±242	53.33±107	170.00±37	233.3±57	77.34±88	LOD0	108.17±88	280.86±134	734.41±87
	PFDA	250.44±120	586.32±177	165.03±155	94.44±58	73.33±43	210.06±65	LOD	LOD	74.00±80	144.22±47	121.40±118	220.00±49
	PFUnDA	561.1±157	1519.32±492	164.11±237	24.44±129	73.33±99	LOD	287.95±124	LOD	3.52±126	89.44±51	328.48±100	896.64±104
	PFDoDA	488.94±110	1414.32±235	52.50±73	40.00±63	120.96±42	LOD	160.81±113	90.85±96	1.00±52	22.91±81	32.48±113	74.55±126
PKD	PFBS	122.03±105	171.52±168	194.58±175	83.33±128	180.00±127	70.88±71	65.91±94	119.37±86	LOD	LOD	LOD	LOD
	PFPeA	398.60±139	1110.12±119	85.77±113	80.93±171	40.09±71	200.01±96	206.55±107	246.78±41	210.94±94	158.04±56	86.26±130	100.60±115
	PFHpA	395.43±66	1186.20±124	LOD	20.50±246	LOD	60.92±42	70.49±108	196.94±103	600.02±82	13.26±124	51.21±99	140.37±83
	PFOA	444.97±59	1311.25±118	23.5±151	23.33±230	LOD	70.96±61	125.37±131	162.12±98	276.00±40	25.96±100	259.17±69	751.38±68
	PFOS	55.23±92	96.45±260	69.25±91	39.07±170	44.78±68	73.05±95	141.24±54	224.09±68	32.52±34	45.20±124	157.07±58	425.85±41
	PFNA	622.95±97	1722.92±125	146.86±205	51.11±247	33.33±35	120.76±122	85.58±94	12.17±115	10.5±49	77.80±63	66.31±109	121.13±125
	PFDA	274.33±67	740.57±143	82.50±125	43.33±109	70.14±49	60.00±119	LOD	LOD	LOD	158.48±95	156.40±90	310.72±52
	PFUnDA	443.54±139	1287.12±117	43.50±234	LOD	LOD	LOD	56.55±103	LOD	139.09±53	176.87±120	119.65±78	182.17±100
	PFDoDA	436.56±70	1302.79±161	7.84±222	28.89±176	86.67±35	LOD	58.49±97	75.23±133	LOD	73.34±56	38.57±63	42.19±65
DPA	PFBS	157.42±65	288.27±79	184.01±83	93.33±158	160.09±112	120.46±133	80.48±80	113.01±37	64.49±76	LOD94	8.20±62	24.62±63
	PFPeA	702.46±81	1773.40±188	334.00±170	167.88±241	163.66±70	340.03±93	333.05±119	423.40±128	252.15±134	300.03±109	222.29±48	366.84±43
	PFHpA	751.92±132	2093.27±125	162.50±119	84.44±202	93.33±120	160.98±124	155.26±84	362.67±46	172.64±103	222.95±102	188.66±125	343.04±166
	PFOA	714.76±107	1929.80±770	214.59±147	98.88±226	66.67±51	230.2±46	195.03±42	282.11±53	159.04±46	279.61±104	181.65±88	265.33±107
	PFOS	214.87±114	510.13±174	134.58±90	69.81±252	128.83±122	80.86±66	546.1±77	190.82±80	245.64±51	34.73±10.8	44.47±77	98.60±95
	PFNA	937.28±144	2533.35±91	278.51±158	11.11±216	33.33±122	LOD	235.95±128	210.52±95	148.82±43	295.52±101	127.97±84	88.21±103
	PFDA	444.46±84	1069.40±171	264.02±77	25.55±132	76.67±116	LOD	LOD	LOD	LOD	132.41±97	44.13±48	LOD
	PFUnDA	468.26±62	1225.83±75	179.06±134	LOD	LOD	LOD	356.38±103	LOD	118.79±82	77.20±127	25.73±129	LOD
	PFDoDA	363.36±79	945.1±234	145±161	17.78±230	53.33±114	LOD	239.98±115	23.79±44	87.89±66	25.47±112	11.16±43	8.02±51
DPB	PFBS	149.20±135	259.69±143	188.21±84	76.67±85	160.94±95	70.23±37	37.29±115	138.88±68	58.73±59	103.54±116	67.67±109	99.32±85
	PFPeA	227.77±119	575.64±149	107.50±97	112.22±50	86.67±55	250.00±115	218.08±82	520.24±77	246.17±93	139.36±41	159.83±117	340.27±51
	PFHpA	489.45±83	1468.35±84	LOD	62.22±131	6.67±117	180.63±89	142.73±44	319.04±77	153.95±75	76.36±56	137.57±41	336.39±38
	PFOA	424.73±75	1176.22±223	98.92±186	63.33±63	LOD	190.40±91	130.78±35	448.03±44	192.97±120	122.80±97	169.83±111	386.78±183

	PFOS	146.36±130	192.85±62	246.25±185	102.51±198	37.93±121	269.75±64	206.93±101	700.81±78	302.58±34	491.91±118	237.33±102	220.28±148
	PFNA	482.92±74	1298.77±260	150.95±160	115.56±137	46.67±123	300.22±52	176.84±134	470.55±121	215.77±38	138.53±122	146.22±110	300.33±100
	PFDA	307.85±52	719.05±204	204.50±66	151.11±221	63.33±71	390.65±107	LOD	LOD	LOD	365.30±126	188.34±93	199.72±110
	PFUnDA	467.60±165	1073.80±145	329.00±180	46.67±176	LOD	140.00±118	422.65±99	31.53±126	151.39±110	482.93±55	193.52±43	97.63±78
	PFDoDA	135.22±87	187.92±212	217.75±259	54.44±136	13.33±84	150.30±92	210.30±85	825.12±39	345.14±67	256.411±88	126.46±71	122.96±111
DPC	PFBS	149.24±149	242.22±157	205.5±227	55.56±74	126.67±84	40.90±109	44.76±129	181.88±93	75.57±116	364.66±116	156.33±108	104.34±35
	PFPeA	380.65±164	583.95±103	558.87±229	42.22±110	86.67±113	40.23±125	304.19±34	532.86±36	279.07±37	61.93±76	162.50±77	425.57±35
	PFHpA	380.89±154	613.17±69	529.50±239	LOD	LOD	LOD	163.32±67	497.72±123	220.37±95	52.16±46	113.09±120	287.11±70
	PFOA	279.56±134	686.70±182	152.65±215	2.22±18	6.67±11.8	LOD	206.45±43	470.83±42	225.76±83	59.90±92	127.15±56	321.55±182
	PFOS	158.38±138	475.15±120	LOD	57.21±138	98.63±124	73.02±44	182.09±120	257.87±107	146.63±67	65.06±11.3	42.94±69	63.84±42
	PFNA	266.31±121	627.95±204	171.00±124	6.67±238	20.03±69	LOD	169.95±125	341.48±102	170.47±76	178.49±117	179.92±86	361.28±133
	PFDA	105.08±54	315.25±110	LOD	15.56±113	46.67±108	LOD	LOD	LOD	LOD	LOD	64.16±19	192.48±104
	PFUnDA	76.11±97	228.35±114	LOD	LOD	LOD	LOD	242.49±97	LOD	80.87±87	26.40±13	98.70±68	269.72±92
	PFDoDA	41.22±140	118.17±190	5.50±19	13.33±50	40.52±127	LOD	193.78±41	52.23±57	82.03±81	2.43±121	69.90±91	207.29±81

APPENDIX H: Mean concentrations ng/l± SD (n=4) of PFCs in sediment

		Summer			Autumn			Winter			Spring		
	Compounds	DEC	JAN	FEB	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPT	OCT	NOV
PKA	PFBS	49.5±27	148.5±85	LOD	10.89±7	14.33±8	18.33±9	7.15±4.0	30.74±15	LOD	2.74±1.2	6.03±2.5	15.36±11
	PFPeA	37.16±10	111.5±35	LOD	11.98±7	17.06±12	18.90±5.6	LOD	14.40±12	LOD	28.36±12	23.59±8	42.42±12
	PFHpA	3.50±1.0	LOD	10.52±5	5.92±5	8.86±7	8.98±6.2	22.58±8.7	3.08±1.0	11.33±4	29.31±16	18.86±11	27.27±8
	PFOA	24.05±10	46.93±28	26.16±13	10.01±5	13.33±10	16.66±8	31.88±16	72.81±5	26.43±5	60.66±6	37.28±10	51.18±14
	PFOS	48.01±18	128.50±17	15.53±10	17.48±12	26.24±12	26.21±10	35.71±14	LOD	8.51±8	5.77±6	4.83±1.0	8.73±11
	PFNA	66.70±36	166.05±68	34.12±15	5.18±4	LOD	15.56±15	38.44±13	21.04±16	17.24±8	114.14±15	57.48±15	58.30±8
	PFDA	44.03±11	116.11±71	16.15±6	10.37±13	7.81±4.4	23.33±6	LOD	LOD	50.49±128	28.68±15	26.78±18	51.67±25
	PFUnDA	38.41±31	108.08±16	7.25±1.5	4.82±1.2	LOD	14.46±8	12.47±12	32.55±14	3.815±4	50.68±14	34.02±6	51.37±6
	PFDoDA	6.26±1.3	LOD	18.80±16	LOD	LOD	LOD	20.06±8	1.05±0.9	9.51±7	36.89±7	23.42±6	33.31±13
PKB	PFBS	81.50±39	244.55±46	LOD	11.03±6	22.11±15	11.58±8	10.20±7	11.12±7	LOD	2.37±1.6	1.38±05	1.79±1.2
	PFPeA	58.51±13.6	175.52±64	LOD	7.03±11	4.43±1.4	16.60±11	2.49±1.3	1.12±12	LOD	23.49±4	17.72±9.1	29.67±13
	PFHpA	4.72±1.3	LOD	14.17±12	8.41±10	10.93±16	15.23±11.7	19.66±7	1.02±1.4	14.11±14	31.16±8	12.84±7	7.36±6.1
	PFOA	32.74±11	70.50±10	27.75±10	8.14±16	14.43±4	10.02±7	17.65±13	12.91±4	24.23±4	48.08±15	21.25±4	15.69±11
	PFOS	51.77±12	153.11±74	2.33±1.1	14.07±12	16.51±11	25.73±7.1	24.06±10	LOD	3.03±13	1.68±1.1	0.56±1.5	LOD
	PFNA	109.75±57	276.62±128	53.25±13	7.04±4	12.23±8	8.90±11	16.44±13	LOD	55.14±18	121.99±58	47.178±14	19.52±6
	PFDA	50.33±13	151.03±47	LOD	8.51±12	8.87±8	16.67±10.2	LOD	LOD	LOD	39.36±14	18.99±14	17.62±14
	PFUnDA	67.33±11	202.93±113	LOD	7.77±10	8.90±3.1	14.43±10	6.91±7	LOD	LOD	66.77±29	28.62±14	19.10±6
	PFDoDA	3.07±2.6	LOD	9.29±1.5	0.74±1.1	LOD	2.23±0.9	7.47±11	LOD	9.4±10	101.32±14	37.03±4	9.793±5.1
PKC	PFBS	82.16±6	246.5±119	LOD	11.45±1.9	20.90±1.5	13.47±14	6.62±4	13.47±16	LOD	1.93±1.6	5.15±4.2	13.47±15
	PFPeA	74.33±81	223.08±111	LOD	5.74±7	13.33±10	3.95±11	0.491±0.5	3.95±4	LOD	11.44±7	5.11±7	3.90±1.2
	PFHpA	4.83±3.3	14.52±10.4	LOD	2.10±1.10	5.57±3.7	0.75±1.1	19.47±12	0.75±1.6	LOD	18.96±14	6.57±5.1	0.75±1.15
	PFOA	52.27±18	115.51±64	41.31±13	2.22±1.9	6.67±1.6	LOD	30.55±18	LOD	16.80±6	18.07±14	6.02±5	LOD
	PFOS	43.76±12	112.02±16	19.32±13	3.87±4.2	11.63±4	LOD	33.45±14	LOD2	13.55±11	1.59±1.4	0.53±0.7	LOD

	PFNA	94.15±48	236.82±175	46.47±13	3.71±2.4	11.13±11	LOD	29.85±7	LOD	19.35±5	82.32±15	27.4±15	LOD
	PFDA	56.29±10	165.09±29	3.87±12	6.28±6	18.87±17	LOD	LOD	LOD	2.50±1.9	4.31±1.8	1.43±0.65	LOD
	PFUnDA	55.65±45	164.02±126	2.85±1.7	5.55±1.5	16.67±1.3	LOD	3.55±2.6	LOD	1.75±0.13	5.84±2.6	11.94±10	LOD
	PFDoDA	20.52±12	52.54±37	9.07±9	LOD	LOD	LOD	17.13±13	LOD	4.65±4	28.50±15	9.50±4	LOD
PKD	PFBS	64.83±19	194.5±115	LOD	7.74±1.4	14.33±16.0	8.92±7.0	16.02±15	3.22±1.1	LOD	3.92±1.7	1.40±0.5	0.27±0.7
	PFPeA	28.56±13	85.70±16	LOD	6.67±5	14.43±14	5.57±2	14.39±6	4.77±2.7	LOD	24.67±11.9	15.84±11	22.86±14
	PFHpA	6.16±1.3	LOD	18.51±11	1.84±1.5	3.33±11	2.20±9	33.24±8	0.51±10	LOD	58.91±26	29.26±16	28.88±4
	PFOA	19.58±12	23.54±4	35.24±11	4.06±14	2.21±1.5	10.09±4	33.6±13	LOD	9.33±13	34.51±11	15.91±10	13.22±14
	PFOS	25.47±13	69.25±28	7.17±5	14.60±12	22.44±12	21.36±8	58.4813	LOD	17.82±14	LOD	LOD	LOD
	PFNA	69.27±37	146.21±66	61.8±16	7.77±4	7.76±3.9	15.56±5	46.27±21	LOD	3.71±1.1	67.74±10	29.58±11	20.99±12
	PFDA	27.51±10	82.52±27	LOD	14.07±8	15.56±5	26.67±13	LOD	LOD	30.52±12	4.47±7	5.1±2.5	10.84±6.5
	PFUnDA	14.50±6.7	43.50±25	LOD	6.63±9	5.56±13	14.31±9	19.41±11	LOD	LOD	52.54±15	17.718	0.59±15
	PFDoDA	2.33±1.2	7.02±10	LOD	LOD	LOD	LOD	20.27±5.4	LOD	LOD	55.10±35	19.43±5	3.21±16
DPA	PFBS	62.63±19	184.02±34	3.92±4.6	11.44±7	16.33±10	18.93±9	16.02±13	14.48±6	2.22±1.3	11.66±5.7	3.88±9	LOD
	PFPeA	111.33±76	334.81±92	LOD	4.07±8	5.57±7	6.65±6.0	14.39±9	9.37±15	1.35±0.9	19.70±10	9.11±8	7.65±6
	PFHpA	58.93±10	162.50±7	14.3±8	9.48±13	6.67±3.9	21.82±16	33.24±15	0.99±1.0	7.57±5.1	18.65±12	6.21±4.2	LOD
	PFOA	93.12±62	214.50±105	64.875±10	11.29±9	12.23±5	21.65±10	33.60±16	1.95±1.1	31.51±12	36.38±24	12.39±1.3	0.80±0.15
	PFOS	55.23±23	134.51±65	31.19±11	26.60±16	43.42±27	36.41±10	58.48±40	5.60±4.3	15.60±6	9.96±3.4	3.32±1.5	LOD
	PFNA	118.52±107	278.52±114	77.075±26	9.82±5	7.81±5	21.68±10	LOD	1.01±1.13	37.06±11	109.52±75	36.77±14	0.81±0.14
	PFDA	109.30±66	264.07±110	63.925±21	17.78±12	30.93±17	23.35±12	LOD	LOD	35.23±14	42.25±21	15.08±14	2.76±1.3
	PFUnDA	82.61±49	179.75±114	68.80±25	4.24±13	4.43±5	8.38±8	19.41±14.2	3.30±1.8	30.99±16	81.96±36	27.56±14	0.72±0.5
	PFDoDA	59.81±27	145.08±95	34.45±13	LOD	LOD	LOD	20.27±14	1.05±1.0	14.75±7.8	72.34±29	24.11±14	LOD16
DPB	PFBS	62.66±12	188.02±44	LOD	11.22±12	17.67±16	16.03±14	7.49±9	26.33±18	LOD	1.83±1.4	0.61±15	LOD
	PFPeA	39.75±12	107.51±13	11.76±14	1.66±0.13	3.33±5	1.65±1.13	0.21±1.7	8.96±13.7	10.81±6	4.62±6.2	4.01±2.6	7.43±4.11
	PFHpA	5.13±13	LOD	15.40±4	5.38±4.5	7.83±5	8.35±6	19.40±5	3.09±10	14.52±14	16.79±4	5.59±7.3	LOD
	PFOA	53.81±26	98.02±22	63.45±11	7.03±13	4.46±14	16.65±9	1.745±1.3	14.82±1.6	28.35±11	9.70±11	3.23±1.8	LOD

	PFOS	82.71±47	246.25±115	1.89±0.7	21.06±14	32.88±18	30.41±7	LOD	1.75±0.15	3.28±1.6	0.50±1.1	0.16±1.12	LOD
	PFNA	62.73±30	150.09±74	38.27±10	9.45±15	6.67±10	21.78±9	LOD	11 3.755±1.15	31.83±10	76.71±12	25.60±9.5	0.11±0.13
	PFDA	70.61±13	204.50±105	7.34±6.0	15.01±13	13.33±12	31.72±16	LOD	2.75±1.4	3.80±1.7	19.27±9	6.42±6	LOD
	PFUnDA	142.76 ±8	329.08±112	99.32±7	7.58±41	1.10±1.2	21.65±15	LOD	5.75±15	44.3±24	10.26±6	4.71±1.0	3.89±1.3
	PFDoDA	102.16±11	217.75±89	88.73±10	LOD	LOD	LOD	0.85±0.8	4.75±1.10	28.50±10.6	63.93±4.1	21.31±15	LOD
DPC	PFBS	69.21±11	205.53±144	2.10±1.1	5.88±3.1	11.03±10	6.65±4.9	16.28±11	32.15±12	1.45±1.4	10.38±7	4.51±2.8	3.15±5
	PFPeA	188.96±76	558.02±211	8.98±6.1	LOD	LOD	LOD	LOD	6.25±7	3.85±5.0	8.719±4.6	4.52±4.6	4.84±3.8
	PFHpA	180.46±6	529.58±64	11.73±10	5.50±4.9	7.76±8	8.75±2	33.28±12	4.27±2.4	6.155±10	11.43±9	6.69±8	8.63±7
	PFOA	63.98±28	152.00±111	39.96±13	8.52±6	8.86±8	16.70±5	36.56±6	24.97±15	16.38±11	33.63±5	21.77±5	31.74±15
	PFOS	LOD	LOD	LOD	14.93±11	27.61±11	17.25±15	49.69±11	0.65±0.15	2.55±1.9	6.52±2.15	2.82±0.8	1.94±0.6
	PFNA	72.08±16	171.93±74	45.26±12	7.77±5.6	3.30±1.91	20.06±13	31.55±12	1.94±1.5	24.93±12	48.81±17	26.13±12	29.58±11
	PFDA	LOD	LOD	LOD	14.07±10	5.56±1.6	36.65±15	LOD	LOD	1.49±1.1	11.50±4	9.95±9	18.38±15
	PFUnDA	LOD	LOD	LOD	8.76±2.3	1.19±10	25.05±14	2.54±1.3	LOD	0.60±0.9	LOD	1.31±1.0	3.94±1.6
	PFDoDA	1.83±1.3	5.53±6	LOD	LOD	LOD	LOD	10.15±7.0	LOD	0.83±1.1	0.45±0.8	0.35±0.4	0.59±1.6

APPENDIX I: Seasonal variation of PFCs in surface water samples (Mean ± Standard Error)

Sampling Stations	Compounds	Summer	Autumn	Winter	Spring
PKA	PFBS	228.34±119.1	145.18±70.7	100.92±96.1	227.19±212.1
	PFPeA	471.24±430.9	120±137.4	190.65±155.1	202.19±48.9
	PFHpA	468.91±537.2	34.07±32.5	135.69±103.6	220.52±131.3
	PFOA	621.64±667.0	44.44±50.9	152.37±129.6	133.79±80.6
	PFOS	252.53±164.9	84.53±96.8	294.86±393.8	43.45±37.1
	PFNA	740.44±685.9	120.00±98.4	124.42±146.3	223.02±85.0
	PFDA	363.61±303.4	166.96±127.4	LOD	175.40±99.3
	PFUnDA	809.11±821.1	4.44±5.0	83.03±64.6	146.87±107.0
	PFDoDA	391.98±449.0	LOD	145.34±161.8	86.95±31.6
PKB	PFBS	210.57±46.2	122.96±38.8	69.71±67.9	75.69±30.8
	PFPeA	362.57±245.3	128.88±147.6	257.59±98.8	349.04±206.9
	PFHpA	421.8±483.2	40.01±45.8	228.62±151.0	31.88±24.7
	PFOA	634.59±657.9	44.44±50.9	151.31±42.3	372.46±277.8
	PFOS	240.35±128.4	99.31±113.3	224.55±258.7	157.44±163.5
	PFNA	601.91±421.7	151.11±134.0	96.70±97.1	279.49±88.6
	PFDA	327.73±228.9	162.96±141.1	75.33±130.4	236.32±55.89
	PFUnDA	587.54±476.2	17.77±20.3	39.55±29.8	519.56±385.8
	PFDoDA	227.88±261.0	23.70±27.1	93.38±89.9	84.31±19.0
PKC	PFBS	209.82±46.6	103.70±60.9	70.01±65.1	214±245.1
	PFPeA	492.13±347.3	161.48±47.1	240.00±97.8	159.25±35.0
	PFHpA	540.64±605.1	35.55±7.6	154.89±37.7	546.67±626.2
	PFOA	551.88±519.3	29.62±27.4	152.46±53.7	218.36±131.1
	PFOS	120.06±34.7	101.63±47.0	150.88±122.9	646.67±578.6
	PFNA	827.62±717.7	99.25±62.1	103.54±118.8	374.48±323.4
	PFDA	333.92±222.7	125.92±73.5	24.66±42.7	161.88±51.6
	PFUnDA	748.14±696.7	32.59±37.3	97.16±165.2	437.97±414.2
	PFDoDA	651.92±695.3	53.33±61.1	84.22±80.1	43.31±27.4
PKD	PFBS	162.67±37.0	111.11±60.0	61.76±59.7	LOD
	PFPeA	531.46±524.9	106.6±83.2	221.11±22.2	114.95±38.09
	PFHpA	527.20±603.9	26.66±30.5	289.14±276.5	68.28±65.25
	PFOA	593.22±656.5	31.11±35.6	187.83±78.5	345.49±370.3
	PFOS	73.64±20.9	52.02±18.3	132.61±96.01	209.35±195.6
	PFNA	830.63±808.7	68.14±45.7	36.08±42.8	88.41±28.9
	PFDA	365.81±338.4	57.77±13.4	LOD	208.53±88.5
	PFUnDA	591.38±634.8	LOD	65.18±69.9	159.58±34.6
	PFDoDA	582.08±659.9	38.51±44.1	44.57±39.4	51.35±19.1
DPA	PFBS	209.90±69.1	124.44±33.5	85.99±24.7	10.94±12.5
	PFPeA	936.62±747.7	223.85±100.6	336.02±85.6	296.39±72.3
	PFHpA	1002.56±989.4	112.59±41.2	230.19±115.0	251.55±81.0

	PFOA	953.02±882.1	131.85±86.5	212.06±63.2	242.20±52.9
	PFOS	286.50±197.7	93.08±31.4	327.52±191.2	59.26±34.4
	PFNA	1249.71±1159.4	14.81±16.9	198.43±44.8	170.55110.0
	PFDA	592.62±422.6	34.07±39.0	LOD	58.84±67.4
	PFUnDA	624.35±540.5	LOD	158.39±181.4	34.31±39.3
	PFDoDA	484.48±413.5	23.70±27.16	117.19±111.0	14.88±9.3
DPB	PFBS	198.93±56.0	102.22±50.1	78.29±53.5	90.14±19.6
	PFPeA	303.60±243.1	149.62±87.8	328.14±166.9	213.16±110.5
	PFHpA	652.61±747.6	82.96±88.5	205.23±98.7	183.45±135.9
	PFOA	566.31±552.8	84.44±96.7	257.24±168.1	226.48±140.8
	PFOS	195.15±49.9	136.74±119.6	403.44±261.9	316.53±152.1
	PFNA	643.90±591.0	154.07±130.9	287.72±159.5	195.05±91.2
	PFDA	410.46±272.1	201.48±169.0	LOD	251.12±99.0
	PFUnDA	623.47±396.1	62.22±71.2	201.86±200.3	258.03±200.5
	PFDoDA	180.31±41.7	72.59±70.1	460.18±323.1	168.62±76.0
DPC	PFBS	198.98±46.8	74.07±46.2	100.72±71.9	208.44±137.7
	PFPeA	507.53±110.6	56.29±26.3	372.02±139.8	216.67±187.7
	PFHpA	507.85±117.6	LOD	293.79±178.8	150.79±121.9
	PFOA	372.75±279.2	2.96±3.3	301.01±147.3	169.53±135.8
	PFOS	211.17±241.9	76.28±20.9	195.53±56.8	57.25±12.4
	PFNA	355.08±241.0	8.88±10.1	227.30±98.8	239.89±105.1
	PFDA	140.11±160.5	20.74±23.7	LOD	85.54±98.0
	PFUnDA	101.48±116.2	LOD	107.77±123.4	131.61±124.9
	PFDoDA	54.96±57.5	17.7720.3	109.33±74.6	93.21±104.4

APPENDIX J: Seasonal variation of PFCs in sediment samples (Mean ± Standard Error)

Sampling Station	Compounds	Summer	Autumn	Winter	Spring
PKA	PFBS	66±75.6	14.51±3.7	12.63±16.0	8.05±6.5
	PFPeA	49.55±56.7	15.98±3.5	4.80±8.3	31.46±9.7
	PFHpA	4.67±5.3	7.89±1.7	12.33±9.7	25.15±5.5
	PFOA	32.07±12.1	13.33±3.3	43.70±25.3	49.71±11.7
	PFOS	64.01±58.1	23.31±5.0	14.74±18.6	6.45±2.0
	PFNA	88.94±68.6	6.91±7.9	25.57±11.3	76.64±32.4
	PFDA	58.71±51.5	13.83±8.3	16.83±29.1	35.71±13.8
	PFUnDA	51.22±51.5	6.42±7.3	16.28±14.7	45.36±9.8
	PFDoDA	8.35±9.5	LOD	10.20±9.5	31.23±6.9
PKB	PFBS	108.67±124.4	14.66±6.3	7.10±6.1	1.85±0.4
	PFPeA	78.05±89.3	9.37±6.4	1.20±1.2	23.63±5.9
	PFHpA	6.3±7.2	11.21±3.5	11.60±9.5	17.12±12.4
	PFOA	43.65±23.3	10.85±3.2	18.26±5.6	28.34±17.3
	PFOS	69.03±76.8	18.77±6.1	9.03±13.1	0.74±0.8
	PFNA	146.33±115.7	9.39±2.6	23.86±28.3	62.89±53.0
	PFDA	67.11±76.8	11.34±4.6	LOD	25.33±12.1
	PFUnDA	89.77±102.8	10.37±3.5	2.30±3.9	38.17±25.2
	PFDoDA	4.08±4.6	0.99±1.1	5.62±4.9	49.38±47.0
PKC	PFBS	109.55±125.5	15.27±4.9	6.69±6.7	6.87±5.9
	PFPeA	99.11±113.5	7.66±4.9	1.46±2.1	6.82±4.0
	PFHpA	6.44±7.3	2.81±2.4	6.74±11.0	8.76±9.3
	PFOA	69.69±40.0	2.96±3.3	15.78±15.3	8.03±9.2
	PFOS	58.35±48.0	5.17±5.9	15.65±16.8	0.70±0.8
	PFNA	125.54±98.5	4.94±5.6	16.39±15.1	36.58±41.9
	PFDA	75.06±82.1	8.38±9.6	0.83±1.4	1.91±2.1
	PFUnDA	74.13±82.2	7.40±8.4	1.76±1.7	15.92±18.2
	PFDoDA	27.36±22.5	LOD	7.26±8.8	12.66±14.5
PKD	PFBS	86.44±99.0	10.32±3.5	6.41±8.4	1.86±1.8
	PFPeA	38.08±43.6	8.88±4.8	6.38±7.3	21.13±4.6
	PFHpA	8.22±9.4	2.45±0.7	11.25±19.0	39.02±17.2
	PFOA	26.10±8.1	5.42±4.0	14.31±17.3	21.21±11.5
	PFOS	33.96±31.8	19.46±4.2	25.43±29.9	LOD
	PFNA	92.35±46.6	10.37±4.5	16.65±25.7	39.44±24.8
	PFDA	36.66±42.0	18.77±6.8	10.16±17.6	6.81±3.5
	PFUnDA	19.33±22.1	8.84±4.7	6.47±11.2	23.61±26.4
	PFDoDA	3.11±3.5	LOD	6.75±11.7	25.91±26.5
DPA	PFBS	83.51±91.8	15.25±3.4	10.90±7.5	5.18±5.9
	PFPeA	148.44±170.0	5.42±1.2	8.37±6.5	12.15±6.5
	PFHpA	78.57±76.0	12.65±8.0	13.93±17.0	8.29±9.4

	PFOA	124.16±79.4	15.05±5.7	22.35±17.7	16.52±18.1
	PFOS	73.64±54.0	35.47±8.4	26.56±28.0	4.42±5.0
	PFNA	158.03±106.3	13.10±7.4	28.11±23.9	49.03±55.3
	PFDA	145.74±104.8	23.71±6.1	11.74±20.3	20.01±20.2
	PFUnDA	110.13±60.0	5.65±2.3	17.90±13.9	36.75±41.3
	PFDoDA	79.75±57.9	LOD	12.02±9.8	32.15±36.8
DPB	PFBS	83.55±95.7	14.96±3.3	11.27±13.5	0.81±0.9
	PFPeA	53.00±49.2	2.21±0.9	6.66±5.6	5.35±1.8
	PFHpA	6.84±7.8	7.17±1.5	12.33±8.3	7.46±8.5
	PFOA	71.75±23.2	9.38±6.4	14.97±13.3	4.31±4.9
	PFOS	110.28±124.4	28.08±6.1	1.67±1.6	0.22±0.2
	PFNA	83.64±58.7	12.60±7.9	11.86±17.3	34.14±39.0
	PFDA	94.13±100.6	20.01±10.1	2.18±1.9	8.569.8
	PFUnDA	190.35±122.0	10.11±10.5	16.68±24.0	6.29±3.4
	PFDoDA	136.21±70.9	LOD	11.35±14.9	28.41±32.5
DPC	PFBS	92.26±103.6	7.84±2.7	16.63±15.3	6.01±3.8
	PFPeA	251.95±279.9	LOD	3.36±3.1	6.02±2.3
	PFHpA	240.53±264.1	7.34±1.6	14.57±16.2	8.92±2.3
	PFOA	85.317±58.9	11.36±4.6	25.97±10.1	29.03±6.3
	PFOS	LOD	19.91±6.7	17.63±27.7	3.76±2.4
	PFNA	96.11±66.2	10.37±8.6	19.46±15.5	34.84±12.2
	PFDA	LOD	18.76±16.0	0.47±0.8	13.27±4.4
	PFUnDA	LOD	11.60±12.2	1.05±1.3	1.75±2.0
	PFDoDA	2.44±2.8	LOD	3.65±5.6	0.47±0.1

APPENDIX K: Statistical Analysis ANOVA (Multivariate Tests)

Multivariate Tests[b]

Effect		Value	F	Hypothesis df	Error df	Sig.
Samples stations	Pillai's Trace	.935	85.713[a]	1.000	6.000	.000
	Wilks' Lambda	.065	85.713[a]	1.000	6.000	.000
	Hotelling's Trace	14.285	85.713[a]	1.000	6.000	.000
	Roy's Largest Root	14.285	85.713[a]	1.000	6.000	.000
Compounds	Pillai's Trace	.792	22.853[a]	1.000	6.000	.003
	Wilks' Lambda	.208	22.853[a]	1.000	6.000	.003
	Hotelling's Trace	3.809	22.853[a]	1.000	6.000	.003
	Roy's Largest Root	3.809	22.853[a]	1.000	6.000	.003
Samples Stations * Compound	Pillai's Trace	.744	17.481[a]	1.000	6.000	.006
	Wilks' Lambda	.256	17.481[a]	1.000	6.000	.006
	Hotelling's Trace	2.914	17.481[a]	1.000	6.000	.006
	Roy's Largest Root	2.914	17.481[a]	1.000	6.000	.006

a. Exact statistic

b. Design: Intercept

Within Subjects Design: Samples + Compound + Samples * Compound

APPENDIX L: Statistical Analysis ANOVA (Tests of Within-Subjects Effects)

Tests of Within-Subjects Effects

Measure:MEASURE_1

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Samples stations	Sphericity Assumed	257280.571	1	257280.571	85.713	.000
	Greenhouse-Geisser	257280.571	1.000	257280.571	85.713	.000
	Huynh-Feldt	257280.571	1.000	257280.571	85.713	.000
	Lower-bound	257280.571	1.000	257280.571	85.713	.000
Error(Samples)	Sphericity Assumed	18009.929	6	3001.655		
	Greenhouse-Geisser	18009.929	6.000	3001.655		
	Huynh-Feldt	18009.929	6.000	3001.655		
	Lower-bound	18009.929	6.000	3001.655		
Compounds	Sphericity Assumed	16320.571	1	16320.571	22.853	.003
	Greenhouse-Geisser	16320.571	1.000	16320.571	22.853	.003
	Huynh-Feldt	16320.571	1.000	16320.571	22.853	.003
	Lower-bound	16320.571	1.000	16320.571	22.853	.003
Error(Compound)	Sphericity Assumed	4284.929	6	714.155		
	Greenhouse-Geisser	4284.929	6.000	714.155		
	Huynh-Feldt	4284.929	6.000	714.155		
	Lower-bound	4284.929	6.000	714.155		
Samples stations * Compounds	Sphericity Assumed	12686.286	1	12686.286	17.481	.006
	Greenhouse-Geisser	12686.286	1.000	12686.286	17.481	.006
	Huynh-Feldt	12686.286	1.000	12686.286	17.481	.006
	Lower-bound	12686.286	1.000	12686.286	17.481	.006
Error(Samples stations*Compound)	Sphericity Assumed	4354.214	6	725.702		
	Greenhouse-Geisser	4354.214	6.000	725.702		
	Huynh-Feldt	4354.214	6.000	725.702		
	Lower-bound	4354.214	6.000	725.702		

APPENDIX M: Statistical Analysis ANOVA (Tests of Within-Subjects Effects)

Tests of Within-Subjects Contrasts

Measure:MEASURE_1

Source	Samples	Compound	Type III Sum of Squares	df	Mean Square	F	Sig.
Samples stations	Linear		257280.571	1	257280.571	85.713	.000
Error(Samples)	Linear		18009.929	6	3001.655		
Compound		Linear	16320.571	1	16320.571	22.853	.003
Error(Compounds)		Linear	4284.929	6	714.155		
Samples Stations * Compounds	Linear	Linear	12686.286	1	12686.286	17.481	.006
Error(Samples*Compounds)	Linear	Linear	4354.214	6	725.702		

APPENDIX N: Pictures of Sampling Stations along Plankenburg River PKA, PKB. PKC and PKD

A (PKA): Down stream
B (PKB): Industrial location
C (PKC): Informal settlement
D (PKD): Agricultural farm land

APPENDIX O: Pictures of sampling stations along Diep River DPA, DPB and DPC

A (DPA): Up stream
B (DPB): Industrial location
C (DPC): Close Proximity to the sea