NATIONWIDE MONITORING OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN SOUTH AFRICA

Volume II: Provincial data on the presence, levels and sources of per- and polyfluoroalkyl substances (PFAS) in water sources

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WATER RESEARCH COMMISSION

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Report to the
Water Research Commission

by

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This report forms part of a set of three reports, *viz:*
- *Nationwide Monitoring of Per- and Polyfluoroalkyl Substances in Water in South Africa*. Volume I: Development, optimisation and validation of an LC-MS method for detection and quantification of per- and polyfluoroalkyl substances in water (WRC Report No. TT 931/1/23)
- *Nationwide Monitoringo of Per- and Polyfluoroalkyl Substances in Water in South Africa*.Volume II: Provincial data on the presence, levels and sources of per- and polyfluoroalkyl substances (PFAS) in water sources (this report)
- *Nationwide Monitoring of Per- and Polyfluoroalkyl Substances in Water in South Africa*.Volume III: Summary report on distribution, sources and health effects of per- and polyfluoroalkyl substances in water (WRC Report No. TT 931/3/23)

EXECUTIVE SUMMARY

BACKGROUND

Per- and polyfluoroalkyl substances (PFASs) are synthetic chemicals used in textiles, packaging, papers, carpets and building and construction materials. Other usage includes, but not limited to, cosmetic formulation, insecticides, paints, non-stick cookware, firefighting foams, hydraulic fluids, waxes and others. Their widespread usage is because of their unique thermal stability and excellent surfactant capacity. During usage or disposal of products treated with PFASs, these chemicals can be released from products into the environment. Other routes of releases into the environment include, among others, during production, military and firefighting operations, discharge of treated effluent and sludge, as well as leachate from landfills. The presence of polyfluoroalkyl substances (PFASs) in water resources is of concern because of their bioaccumulative, persistent, long-range transport and toxic characteristics. Their presence in the environment, particularly water, therefore, needs to be monitored.

PROJECT AIMS

The overall aims of the project were to:

1. Monitor the concentrations of legacy and emerging PFASs in different water sources in pre-selected cities and towns from all the nine provinces in South Africa;
2. Use an appropriate model to identify the PFASs sources and assess the amounts of pollution by resolving the measured mixture of chemical species into the contributions from the individual source types;
3. Develop a nationwide database on PFASs concentrations in different water sources from different parts of the country, and
4. Apply a test battery of bioassays covering a range of endpoints commonly responsive to drinking water to monitor water quality of source and drinking water.

METHODS

1. Selection of sampling sites and collection of water samples

For the purposes of this study, water samples were collected in selected sites in all 9 provinces of South Africa, and the following water sources were sampled for analysis:

- Wastewater effluent (final treated wastewater effluent from a wastewater treatment plant)
- Surface water (from rivers and dams)
- Groundwater
- Drinking water – final treated water from a drinking water treatment plant and household tap water samples from the suburban areas
- Bottled water
- Rainwater

Two sampling approaches were evaluated in this study: grab and passive sampling.

Grab samples were collected from all the sampling sites in all 9 provinces during the dry and wet season. At each site, water samples were collected in clean high-density polyethylene bottles from the various water sources. After collection, the samples were kept in ice and transported to laboratory and prepared for analysis.

Passive sampling was also conducted using Polar Organic Chemical Integrated Sampler (POCIS). The POCIS was deployed at a wastewater treatment plant in the Gauteng Province for two weeks and POCIS extracted on day 7 and 14. Grab samples were also taken on similar days from the same spot where the POCIS was mounted.

Monitoring the concentrations of legacy and emerging PFASs in different water sources

Prior to monitoring, it was necessary to first develop, optimise, and validate an appropriate analytical method to determine the presence and concentrations of PFASs in various water sources in South Africa. Details of the procedures followed for the development, optimisation and validation of an LC-MS method for the detection and quantification of PFASs in high- and low concentration samples are presented in **Volume I** of this set of three reports. Two LC-MS methods were optimised and validated for use in this nationwide PFASs monitoring programme, one for high and another for low PFASs concentration samples.

For the development, optimisation and validation of a method for high PFASs concentration samples, water samples collected from Gauteng province were used for this exercise because of the various industrial activities in the province and hence high levels of known and unknown PFASs may be present in the water samples. For target and non-target PFASs analysis, an LC-MS-8030 triple quadrupole system and a TripleTOF 6600, SCIEX were used, respectively. Targeted provided some specificity and sensitivity for the quantitative analysis; whereas non-targeted analysis leveraged the power of high-resolution modern mass spectrometers to analyse both targeted and undiscovered PFASs. The quantitation of the target compounds was based on internal standard method calibration with concentrations ranging from 1.0-1000 ng/L. An R2=0.99 was achieved in all the calibrations with good precision of the internal standard. The method was then applied to spiked water samples.

Water samples collected from all other provinces were used for the development, optimisation and validation of an LC-MS method for low PFAS concentrations. For the purposes of this project, a target LC-MS/MS (LCMS-8030, Shimadzu) method for PFASs detection and quantification was optimised and validated. Following the identification of emerging PFASs compounds using non-target analysis, more PFASs standards including the sulphonates and alcohol telomers were added to the pool, resulting in the development of four different chromatographic methods comprising **A, B, C** and **D** to ensure good separation of PFASs compounds.

The SPE SupelcoTM Envi18 cartridges purchased from SIGMA Aldrich Ltd were used for all PFASs extraction from all the water samples. Cartridges were first conditioned. Thereafter, the cartridges were then allowed to dry under vacuum for 1 h. The solvent extract was then concentrated under the gentle steam of nitrogen. The reconstituted extract was then transferred to a 2 mL centrifuge tubes and 950 µL of the extract and a 50.0 µL of internal standard added to an autosampler vial. A 10.0 µL of the samples was then injected to the LC-MS/MS.

2. Source apportionment

Multivariate analysis was used to establish inter-relationships between different groups of PFASs, and sample sites and to establish possible sources.

3. Assessing the health effects of PFASs in water using a bioassay method

Samples collected from Northern Cape and Gauteng Provinces were used for this portion of the study. The Yeast bioassay was conducted to determine estrogenic activity in water samples.

RESULTS

Method optimisation and validation

All isomers calibration curves showed linearity, based on correlation coefficients (r) and correlation of determination (r^2) that were greater than 0.99 with good precision of the internal standard. The chromatograms were well separated. The LOD and LOQ values were >0.001 ng/L. The percentage recoveries of the labelled surrogate standards were within the acceptable range.

Distribution of PFASs in water sources in South Africa – grab samples

Analysis using the non-target approach showed that the fluorotelomers were the prominent new compounds. 4:2 Fluorotelomer sulfonic sulfonate, 6:2 Fluorotelomer sulfonate and 8:2 Fluorotelomer Sulfonate were the most dominant fluorotelomers. Their percentage detection ranged from 30-100 and 0-80 for 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) respectively. Other emerging PFASs identified included: perfluorooctane sulphonamide, N-Methyl perfluorooctane sulphonamide, N-Ethyl perfluorooctane sulphonamide; 6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA, 8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA, 6:2 Fluorotelomer carboxylic acid, 8:2 Fluorotelomer carboxylic acid and 10:2 Fluorotelomer carboxylic acid; Perfluorohexyl Iodide and Perfluorooctyl Iodide; 8:2 Fluorotelomer acrylate, 6:2 Fluorotelomer methacrylate and 8:2 Fluorotelomer methacrylate; Perfluoro-2-methoxyacetic acid, Perfluoro-3-methoxypropanoic acid, Perfluoro-4-methoxybutanoic acid, Perfluoro-2-propoxypropanoic acid, Perfluoro(3.5-dioxahexanoic) acid, Perfluoro(3.5.7-trioxaoctanoic) acid and Perfluoro (3.5.7.9-tetraoxadecanoic) acid.

The telomers sulphonates and alcohols were also detected in a number of the water samples including drinking water. 8:2 FTS and 6:2 FTS featured very prominently in a large number of water samples. Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) percentage detection in drinking water treatment plant ranged from 50-83 and 33-100 respectively. However, their detections were less than 60% in bottled and tap drinking water.

Analysis using the target method indicated the presence of PFASs in most of the samples, some at high and some at low levels. Short chain PFASs were more dominant than the long chain in some cases, albeit long chain PFASs such as PFOA and PFOS was one of the most prevalent compounds detected. Among the short chains, PFBS, PFBA, PFPeA, PFHxA, PFHpA and PFHxS were prevalent in numerous water samples. Due to unavailability of the standards of most of these emerging PFASs, they could not be quantified under the target analysis.

Seasonal influence on the concentrations of PFASs in the samples across most of the provinces was noticeable. Higher concentrations were observed in dry season compared to wet season. PFHxA, PFPeA, 8:2 FTS, PFHpA, LPFBS, PFOA, 6:2 FTS, FOET, FHET and PFBA were all detected in the rainwater samples collected in the Gauteng Province.

Octanol/water partition coefficient (K_{ow}) values obtained from the literature were used to assess the tendency of the PFASs detected (KwaZulu-Natal samples) in the present report to move from the aqueous phase into organic. In some drinking water/tap water, PFOA, L-PFHxS, PFHxA, PFHeA, 8:2 FTS, PFNA, PFHpA, PFUdA, 6:2 FTS, FOET, FHET and PFBA were detected in all the samples. These PFASs compounds have K_{OW} values of 2.829-6.82, indicating their tendency to move from the aqueous phase to the organic phase, hence their detection in most of the water samples.

Monitoring of PFASs concentrations in water using passive sampling method

All PFASs targeted were detected except 6:2 FTS, PFDOA, 8:2 FTS, and PFHxDA. 4-2 FTS had the highest concentration of 81.67 ng/L. The same trend was also observed in grab samples, although FOET exhibited the highest concentration of 22.36 ng/L in this case. Generally, on day 7, the PFASs concentrations recorded for POCIS higher than the grab samples except for FOET. On 14 day, the mean PFASs concentrations for POCIS-HLB ranged 0.94-98.86 ng/L. PFNA had the highest concentration of 94.04 ng/L. On the other hand grab sample had mean concentration range of LOD-30.55 ng/L. PFHxA had the highest concentration of 30.55 ng/L. The PFASs concentrations in POCIS were significantly higher than that of grab samples. The difference between the concentrations recorded for the two sampling method was because grab samples provided only snap shot concentrations, while POCIS-HLP provided time weighted average concentrations.

Source apportionment

Multivariate statistical analysis (PCA) was used to establish inter-relationships between different groups of PFASs, and sample sites and to establish possible sources. From the PCA analysis, some PFASs showed similar sources; while others showed different sources. This trend was also observed with the sampling sites. Therefore, based on the land use activities around the sampling sites, the presence of PFASs detected in the water samples may have originated from the current/historical usage of PFASs in various activities.

Assessing the human health effects of PFASs using a bioassay method

Estrogenic activity was detected in 12 of the 14 samples tested, whereas cytotoxicity was determined in 9 of the 14 samples. The water samples Ei ranged from below limit of quantification to a maximum of 718 ng. These are significantly higher than the recommended trigger value for drinking water. Compared to dry season, a higher EDC concentration was observed during wet season, notably in wastewater and drinking water treatment facilities. This suggested that the current treatment techniques are unable to remove EDC chemicals. Of the 18 standard PFASs chemicals subjected to bioassay test, only PFOS exhibited cytotoxicity. Therefore, the observed estrogenic activity and cytotoxicity in the water samples may have been caused by PFOS, which demonstrated estrogenic action in yeast bioassays. However, other contaminants in the water samples such as trace metals may have also contributed to the observed estrogenic action since metals that exert metalloestrogens were detected in the water samples.

CONCLUSIONS

Based on the findings, the following conclusions can be made:

- Non-target and target methods for identification and quantification of PFASs in various water sources were successfully developed, validated and used for monitoring the distribution and sources of PFASs in water in South Africa.
- The concentrations of PFASs observed in the present study are, in some cases, higher than the values reported by other researchers in water samples. The PFASs detected in the bottled drinking water in the present study are higher than the IBWA operational limits of 5 ng/L for a single PFASs and 10 ng/L for more than one PFASs. Compared to the health advisory levels at 70 ng/L by the USEPA to protect its sensitive populations from a lifetime of exposure to PFOA and PFOS from drinking water, the concentrations of PFOS and PFOA in drinking water in the present study are generally much lower.
- PFASs compounds were detected in both grab and passive samples. However, the PFASs concentrations in the POCIS passive sampler were higher than the grab samples collected on the same days. The observed difference suggested the cumulative time-weighted concentrations of PFASs with passive samplers compared to one-off grab sampling method.
- The PFASs detected in the bottled drinking water in the present study are higher than the IBWA operational limits of 5 ng/L for a single PFASs and 10 ng/L for more than one PFASs. Compared to the health advisory levels at 70 ng/L by the USEPA to protect its sensitive populations from a lifetime of exposure to PFOA and PFOS from drinking water, the concentrations of PFOS and PFOA in drinking water in the present study are generally much lower except in few drinking water samples.
- Some PFASs showed similar sources; while others showed different sources. This trend was also observed with the sampling sites. It is, therefore, possible that all the land use activities around the sampling sites may have contributed to the observed PFASs in the water samples.
- Estrogenic activity was detected in 12 of the 14 samples tested, whereas cytotoxicity was determined in 9 of the 14 samples. Of the 18 standard PFASs chemicals subjected to bioassay test, only PFOS exhibited cytotoxicity. However, other contaminants in the water samples such as trace metals may have also contributed to the observed estrogenic action since metals that exert metalloestrogens were detected in the water samples.

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ACRONYMS & ABBREVIATIONS

AFFF	Aqueous Film Forming Foam
ASTM	Association of Standardized Test Method
ATSDR	Agency for Toxic Substances and Disease Registry
BFRs	Brominated Flame Retardants
CCD	Charge-Coupled Devices
DCM	Dichloromethane
DEA	Department of Environmental Affairs
DWS	Department of Water & Sanitation
EDC	Endocrine disrupting compound
EFSA	European Food Safety Authority
EtOH	Ethanol
FIA	Flow Injection Analysis
FTCA	Fluorotelomer Carboxylic Acids
FTOH	Fluorotelomer Alcohol
GC-MS	Gas Chromatography-Mass Spectrometer
HDPB	High Density Polyethylene Bottles
HPLC	High Pressure Liquid Chromatography
LC-MS	Liquid Chromatography-mass spectrometry
L-FABP	Liver Fatty Acid-Binding Protein
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
MeOH	Methanol
MRLs	Minimum Risk Levels
MRM	Multiple Reaction Monitoring
MTBE	Methyl Tert-Butyl Ether
NTMP	National Toxicant Monitoring Programme
PCA	Principal Component Analysis
PCBs	Polychlorinated Biphenyls
PCF	Propyl Chloroformate
PES	Polyethersulfone
PFAAs	Per- fluoroalkyl acids
PFASs	Per- polyfluorinate Alkyl substances
PFCAs	Per- fluoroalkyl Carboxylic Acids
PFHxS	Per- fluohexane Sulfonic Acid
PFNA	Per- fluorononanoic Acid
PFOSE	Per- fluorooctane Sulfonamidoethanol
POPs	Persistent Organic Pollutants
POSF	Per- fluorooctanesulfonyl Fluoride

PP	Polypropylene
PPARs	Activate Peroxisome Proliferator-Activated Receptors
R^2	Correlation Coefficients
ROS	Reactive Oxygen Species
RQS	Resource quality services
RSD	Relative Standard Deviation
SPE	Solid Phase Extraction
St	Saint
STP	Sewage Treatment Plants
TCM	Trichloromethane
TDIs	Tolerable Daily Intakes
TFE	Tetrafluoroethylene
TIC	Total Ion Chromatogram
ToF-HRMS	Time of flight - High Resolution Mass Spectrometry
TUT	Tshwane University of Technology
USEPA	United States Environmental Protection Agency
WAX	Weak Anion Exchange
WTPs	Water Treatment Plants
WVDEP	West Virginia Department of Environmental Protection
WWTPs	Wastewater Treatment Plants

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CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

The presence of PFASs in source waters is, in most cases, not removed by conventional water treatment processes due to the design and treatment processes to remove these contaminants effectively during water purification or treatment. Water users and consumers, may be exposed unintentionally to PFASs with their concomitant toxic effects in such instances. It is for these reasons that monitoring of PFASs in South African source waters are particularly important. This exercise would contribute towards critically reviewing the current drinking water guidelines in order to address the challenges that PFASs may pose in South African source waters. Data generated on PFASs will contribute towards the National Toxicant Monitoring Programme (NTMP). Targeted and non-targeted were used to monitor PFASs in this exercise. Targeted provides an unparalleled level of specificity and sensitivity for the quantitative analysis. However, for new and emerging compounds, this approach is not effective in detecting emerging compounds. Nontarget analysis leverages the power of high-resolution modern mass spectrometers to analyse both target and undiscovered chemicals.

1.2 PROJECT AIMS

The objectives of the overall project were to:

1. Monitor the concentrations of legacy and emerging PFASs in different water sources in pre-selected cities and towns from all the nine provinces in South Africa;
2. Use appropriate model to identify the PFASs sources and assess the amounts of pollution by resolving the measured mixture of chemical species into the contributions from the individual source types;
3. Develop a nationwide database on PFASs concentrations in different water sources from different parts of the country and
4. Apply a test battery of bioassays covering a range of endpoints commonly responsive to drinking water to monitor water quality of source and drinking water.

However, in order to achieve the aforementioned aims, it was necessary to:

- develop appropriate and testable analytical method to determine the presence and concentrations of PFSAs in various water sources and 2) optimize and validate the method before sample collection, treatment and analysis. This aspect is covered in **Volume I** of this report.

- **Volume II** (this report) addresses Aims 1 to 4, and the data is presented per province.

- **Volume III – is a summary report covering Aims 1 to 4.**

1.3 SCOPE AND LIMITATIONS

1.3.1 Scope

The overall project was to identify and quantify PFASs in source water in all the provinces in South Africa in order to present an overview of the presence and levels of PFASs in water systems in the country. Target and non-target approaches were used, chromatographic method developed, optimized and validated through the analysis of calibration standards and selection of multiple reaction monitoring (MRM). Polar Organic Chemical Integrated Sampler (POCIS) and HDPE were used for passive and grab sampling respectively. Water samples were collected from wastewater treatment plants, drinking water treatment plants, surface water (river water), groundwater (borehole), commercial bottled water, tap water and rainwater. Samples collected were stored in cold room and, thereafter, filtered (when deemed necessary), centrifuged and extracted using the USEPA solid phase extraction (SPE) 537.1 methods.

1.3.2 Limitations

Seasonal (wet and dry seasons) samples were collected from all the following provinces, Eastern Cape, Free State, Gauteng, KwaZulu-Natal, Limpopo, Mpumalanga, North West and Northern Cape except western Cape where only one wet season sample was collected. Thie was because it was decided to assign the Western Cape Province monitoring programme to the late Dr Rehana Malga-Enus research group at Stellenbosch University. Sample collection from pristine areas was not possible because of inaccessibility of the identified areas.

1.4 REPORT LAYOUT

This report (Volume II) addresses all the aims of the project, however, it contains the database of the information obtained through the nationwide monitoring conducted as dictated by Aim 3. The database report is presented as follows:

- Chapter 1 – Introduction
- Chapter 2 – A framework for nationwide monitoring of PFASs
- Chapters 3 to 11 – Provincial data on the presence, levels and sources of PFASs in different water sources
- Chapter 12 – Assessment of toxicity of the water sources and implications for human health
- Chapter 13 – Conclusions and recommendations.

CHAPTER 2: FRAMEWORK FOR NATIONWIDE MONITORING OF PFASS

2.1 INTRODUCTION

The overall project was focused on nationwide monitoring of PFASs in different water systems from all the provinces in South Africa in order to present an overview of the presence, levels, sources, as well as human health risks of PFASs. In line with the aims of the study, a framework for nationwide PFASs monitoring was developed as means for environmental protection and public health. The elements of the monitoring framework adopted in this study, from selection of PFASs of interest to reporting of results is covered in the sections below. This report addresses Aim 3 of the project, which focuses on the development and presentation of a database on PFAS levels in the different provinces.

2.2 PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs) OF INTEREST

The overall aim of this project was develop an understanding of the presence and levels of PFASs within the water environment, potential health risks, and guiding regulatory actions to mitigate exposure and contamination. Selecting target analytes for monitoring is a critical step in analytical chemistry, particularly in environmental monitoring. In this instance, the availability of standards is one of the practical considerations taken into account in this study, as standards are essential for calibration, method validation, and quality control. For the purposes of this study, several PFASs standards were purchased in methanol from Wellington Laboratories (Ontario, Canada). Tables 2.1 and 2.2 show the list of standards, comprising legacy and emerging PFASs, as well as labelled PFASs internal standards that were purchased for the purposes of this study. Calibration curves were prepared by diluting a stock solution of 2000 ng/mL of PFASs mixture in methanol. A 10-point calibration curve was constructed with ranges from 0.1-1000 ng/L for all PFASs analytes. LOD and LOQ were calculated from formula 3σ and 10σ of the response/slope of calibration curve, respectively. Further details on method development and validation are presented in Volume I of this report.

Table 2.1: PFAS standards for LC-MS method development for high concentrations

Name of compound	Acronym
MPFHxA_$^{13}C_2$	MPFHxA_$^{13}C_2$
MPFNA_$^{13}C_5$	MPFNA_$^{13}C_5$
MPFDA_$^{13}C_2$	MPFDA_$^{13}C_2$
Sodium perfluoro-1-hexanesulfonate	L-PFHxS
Perfluoro-n-dodecanoic acid	PFDoA
Perfluoro-n-heptanoic acid	PFHpA
Perfluoro-n-hexanoic acid	PFHxA
Perfluoro-n-hexadecanoic acid	PFHxDA
Perfluoro-n-nonanoic acid	PFNA
Perfluoro-n-octadecanoic acid	PFODA
Perfluoro-n-pentanoic acid	PFPeA
Perfluoro-n-tetradecanoic acid	PFTeDA
Perfluoro-n-tridecanoic acid	PFTrDA
Perfluoro-n-undecanoic acid	PFUdA
Potassium perfluoro-1-butanesulfonate	L-PFBS
Sodium perfluoro-1-decanesulfonate	L-PFDS
Sodium perfluoro-1-heptanesulfonate	L-PFHpS
Sodium perfluoro-1-nonanesulfonate	L-PFNS
Sodium perfluoro-1-octanesulfonate	L-PFOS

Name of compound	Acronym
Perfluoro-n-butanoic acid	PFBA
Perfluoro-n-decanoic acid	PFDA
Perfluoro-n-octanoic acid	PFOA
Sodiumperfluoro-1-dodecanesulfonate	L-PFDoS
Sodium perfluoro-1-pentanesulfonate	L-PFPeS
Labelled PFAS internal standards	
perfluoro-n-[1,2-$^{13}C_2$] octanoic acid	M2PFOA
perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	MPFDA
perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid	MPFHxA
Surrogate standards	
perfluoro-n-[1,2,3,4, 5-$^{13}C_5$] nonanoic acid	MPFNA

Table 2.2: PFAS standards for LC-MS method development for low concentrations

Name of compound	Acronym
Sodium 1H,1H,2H,2H-perfluorohexane sulfonate(4:2)	4:2 FTS
Sodium 1H,1H,2H,2H-perfluorodecane sulfonate(8:2)	8:2 FTS
Sodium 1H,1H,2H,2H-perfluorooctane sulfonate(6:2)	6:2 FTS
2-Perfluorohexyl ethanoic acid (6:2)	FHEA
2-Perfluorooctyl ethanol (8:2)	FOET
2-Perfluorohexyl ethanol (6:2)	FHET
Sodium perfluoro-1-hexanesulfonate	L-PFHxS
Perfluoro-n-dodecanoic acid	PFDoA
Perfluoro-n-heptanoic acid	PFHpA
Perfluoro-n-hexanoic acid	PFHxA
Perfluoro-n-hexadecanoic acid	PFHxDA
Perfluoro-n-nonanoic acid	PFNA
Perfluoro-n-octadecanoic acid	PFODA
Perfluoro-n-pentanoic acid	PFPeA
Perfluoro-n-undecanoic acid	PFUdA
Potassium perfluoro-1-butanesulfonate	L-PFBS
Sodium perfluoro-1-decanesulfonate	L-PFDS
Sodium perfluoro-1-heptanesulfonate	L-PFHpS
Sodium perfluoro-1-octanesulfonate	L-PFOS
Perfluoro-n-butanoic acid	PFBA
Perfluoro-n-octanoic acid	PFOA
Isotopically labelled internal standards	
perfluoro-n-[1,2-$^{13}C_2$] octanoic acid	M2PFOA
MPFHxA_$^{13}C_2$	MPFHxA_$^{13}C_2$
MPFDA_$^{13}C_2$	MPFDA_$^{13}C_2$
Surrogate standards	
perfluoro-n-[1,2,3,4, 5-$^{13}C_5$] nonanoic acid	MPFNA
perfluoro-n-[1,2-$^{13}C_2$]undecanoic Acid	MPFUdA
sodium perfluoro-1-hexane[18O2]sulfonate	MPFHxS

Apart from availability of standards, the selection of specific PFAS compounds for monitoring should be based on factors like their presence in the study area, known or suspected sources of contamination, and their relevance to health concerns. In this instance, the use of non-target analytical methods can be valuable in the discovery of new or unknown PFASs. As such both targeted analysis of PFASs using an LC-MS-8030 triple quadrupole system and the non-targeted analysis using PFASs using TripleTOF 6600, SCIEX were employed in this study to cover a wide range of PFASs.

2.3 SAMPLING STRATEGY

Development of a strategic sampling plan that considers the geographical distribution of monitoring sites, including surface water, groundwater, drinking water sources, wastewater discharges, rainwater and bottled water. An attempt was also made to include routine monitoring sites and locations with known or suspected PFAS contamination sources. The samples were collected over the dry (June-August) and wet (October-April) seasons of South Africa and under various hydrological conditions to account for temporal variations.

2.3.1 Sampling sites and sample collection

For the purposes of this study, water samples were collected in selected cities across all 9 provinces of South Africa (Figure 2.1).

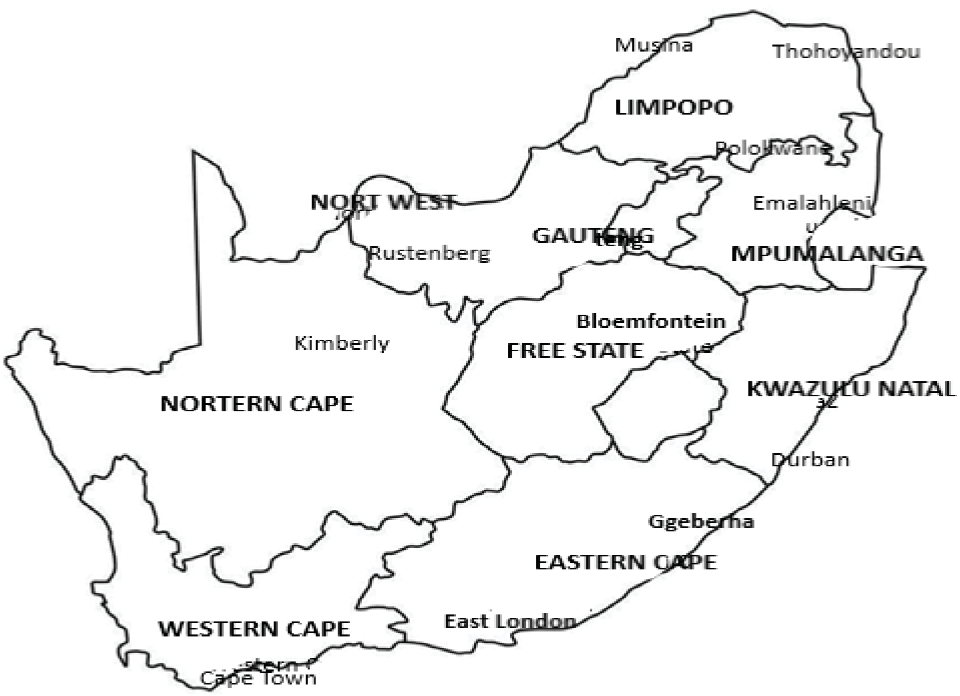

Figure 2.1: Map showing the nine provinces and sampling locations in South Africa.

Seasonal (wet and dry seasons) samples were collected from all the following provinces, Eastern Cape, Free State, Gauteng, KwaZulu-Natal, Limpopo, Mpumalanga, North west and Northern Cape except for the Western Cape where only dry season sample was collected. This was because the Western Cape Province monitoring programme was later assigned to another project. The minimal work conducted in the Western Cape, consisting of the sampling locations and available results for the Western Cape are shown in Chapter 11 in this volume. Sample collection from pristine areas was not possible because of inaccessibility of the identified areas.

The following water sample types were collected during this study:

- Wastewater
- Surface water
- Groundwater
- Treated drinking water (final water from a water treatment plant)
- Tap water – Treated drinking water collected from household taps
- Bottled water
- Rainwater

Monitoring sites were selected in nine provinces based on the criteria stated below:

- **Eastern Cape province** – Monitoring in the Eastern Cape Province was conducted in East London and Gqeberha areas. These areas were chosen because they are big metros, highly populated and industrialized. Also, the water quality within both cities has been of great concern to the municipality and, therefore, the communities living in these metropolitan areas.

- **Gauteng province** – Water samples were collected from Pretoria and the Vaal (southern of Johannesburg) in the Gauteng province during both the wet (October-April) and dry (June-August) seasons. Vaal River has, over the years, been at the centre of pollution discussion in the public space because of the various human activities surrounding the river. Pretoria is the administrative centre of South Africa with relatively small industrial activities and, therefore, it presents an important study area.

- **KwaZulu-Natal province** – Water samples were collected from Durban and Umgeni River in the KwaZulu-Natal province during both the wet (October-April) and dry (June-august) seasons. Durban is the most cosmopolitan city in KZN with many industrial and other human activities. Therefore, it represents a good study area. Furthermore, water samples were also collected from Umgeni River which has been dogged with pollution problems over the years.

- **Limpopo province** – Water samples were collected from Polokwane which is the most cosmopolitan city in the province and Musina and Thohoyandou, are fast growing urban towns in the far north in the Limpopo province during both the wet (October-April) and dry (June-August) seasons. Once again, the selected areas have been in identified as areas with serious water quality problems.

- **Mpumalanga province** – Water samples were collected from eMalahleni and surrounding areas and Oliphant and Zaalklip Rivers in the Mpumalanga province during both the wet (October-April) and dry (June-august) seasons. These areas are highly industrialized with many mining activities such as coal and energy generation.

- **Northern Cape province** – Water samples were collected from Kimberly and the surrounding area in the Northern Cape province during both the wet (October-April) and dry (June-august) seasons.

Kimberly is the most populated city in the Northern Cape and, therefore, will have a fair share of pollution problems.

- **North West province** – Water samples were collected from Rustenburg and surrounding areas in the North West province during both the wet (October-April) and dry (June-August) seasons. Rustenburg and its environ is inundated with mining activities and the mines have the potential to generate chemical pollutants such as PFAS during the various stages of mining.

- **Western Cape province** – Water samples were collected from Cape Town and Diep River in the Western Cape province during both the wet (October-April) season.

- **Free State province** – Water samples were collected from Bloemfontein and surrounding area in the Free State province during both the wet (October-April) and dry (June-August) seasons. Once again, Bloemfontein is the most populated city in the province and, therefore, presents a good sampling area.

2.3.2 Sample collection methods

Two sampling approaches were evaluated in this study; grab and passive sampling. Grab samples were collected from all the sampling sites in all 9 provinces during the dry and wet season. For investigating PFASs concentrations using a passive sampling method, Gauteng Province was used as a case study.

2.3.2.1 Grab sampling

Grab samples were collected from all the sampling sites in all 9 provinces during the dry (June-August) and wet (October-April) seasons. At each site, water samples were collected in clean high-density polyethylene bottles from the various water sources. After collection, the samples were kept in ice and transported to laboratory and prepared for analysis.

2.3.2.2 Passive sampling

Pre-cleaned Polar Organic Chemical Integrated Sampler (POCIS) containing Oasis hydrophilic-lipophilic balance (HLB) purchased from (EST – Environmental Sampling Technologies, USA) was used in the study. Before field deployment, the sampling rates were determined in the laboratory in a tapwater-filled 50-L aquarium under dark conditions, at 20.5°±2°C. The calibration study was conducted according to Gobelius et al. (2019) with minor modification, over 14 days in the laboratory using a modified flow through system consisting a test and a reservoir 20-L glass tanks. Both tanks were wrapped with aluminium foil and with a black lid to prevent UV light penetration. The two glass tanks were fitted with two air pumps to ensure uniform distribution of PFASs and continuous circulation of the water body. Water temperature was controlled by maintaining the room temperature using air conditioning. The tap water in the test and reservoir tanks was spiked with 21 mix PFASs at concentration of 100 ng/L. Before starting the uptake experiment the tank reservoir and tank passive samplers were left to equilibrate overnight to stabilize the sorption of PFASs to the glass walls of the tanks. Every day, 3 L of spiked water sample was removed from the test tank and replaced with the same volume from the reservoir on day 1, 7 and 14 using a peristaltic. In total 3 POCIS-HLB were placed in the test tank. A blank POCIS was exposed in the laboratory environment as laboratory blank. All POCIS-HLB samples were vacuum sealed in polypropylene bags and stored in the refrigerator (4°C) until analysis.

Passive samplers were deployed for 14 days in the effluent of a wastewater treatment plant in Pretoria. Passive samplers were retrieved on day 7 and 14. Grab samples were also taken from the same point on the same day. Composite samples comprising influent, aerobic digestion, secondary settlement tank and effluent was also collected. Samples were stored inside a cooler box and stored in the refrigerator (4°C) until analysis. The process of accumulation in the POCIS is essentially adsorption on the internal solid phase after contaminants passively diffuse through the hydrophilic membrane. In order to assess the time-averaged ambient concentration of POCIS-available contaminants, the POCIS is exposed during the linear-phase (phase I) regime, after which a calculation is made based on Equation 2.1:

$$C_{water} = C_{pocis} \cdot M_{pocis} / R_s.t \quad \text{(Equation 2.1)}$$

Where:
Cwater = mean contaminant concentration (over the sampling period) in the ambient water (µg/L);
Cpocis = concentration in the POCIS (µg/g);
Mpocis = mass of adsorbent phase in the POCIS (g);
Rs = sampling rate (L/d), which corresponds to the volume of water purified per unit-of-time; and
t is the total exposure time (d).

2.4 SAMPLE ANALYSIS

2.4.1 Preparation of samples for analysis

Sample extraction validation? The SPE SupelcoTM Envi18 cartridges purchased from SIGMA Aldrich Ltd were used for all PFASs extraction from all the grab water samples. Cartridges were first conditioned. Thereafter, the cartridges were then allowed to dry under vacuum for 1 h. The solvent extract was then concentrated under the gentle steam of nitrogen. The reconstituted extract was then transferred to a 2 mL centrifuge tubes and 950 µL of the extract and a 50.0 µL of internal standard added to an autosampler vial. A 10.0 µL of the samples was then injected to the LC-MS/MS.

PFASs adsorbed on POCIS-HLB retrieved from the laboratory and field set up was extracted using 6 mL SPE cartridge which was fitted with polyethylene frits at the bottom. The HLB sorbent was transferred from the POCIS into the cartridges, through a glass funnel, and rinsed using ultrapure water. Excess water was dried under vacuum for approximately 30 min and then another frit was placed on top of the sorbent. The cartridge was spiked with 100 uL of surrogate standard mixture. The HLB sorbent was eluted with 8 mL methanol. The eluent was collected in 50 mL polypropylene tubes. The POCIS-HLB field blanks underwent the same extraction procedure as the sample. The samples were concentrated under gentle nitrogen at room temperature and 950 µL of the sample was transferred into 1 mL LC glass vials and spiked with 50 µL internal standard. The samples were then analysed using liquid chromatography-tandem mass spectrometry (LC-MS/MS).

2.4.2 Target and non-target analysis of water samples

Prior to sample analysis, a liquid chromatography-mass spectrometry (LC-MS) method for PFAS analysis was optimised and validated through the analysis of calibration standards and selection of multiple reaction monitoring (MRM) to ensure sensitivity and specificity. V**olume I of this report** addresses this aspect. The optimised method was then used for sample analysis.

For target and non-target analysis of samples with suspected high concentrations of PFAS, an LC-MS-8030 triple quadrupole system (Table 2.3) and a TripleTOF 6600, SCIEX (Table 2.4) were used, respectively. The quantitation of the target compounds was based on internal standard method calibration with concentrations ranging from 1.0-1000 ng/L. An R^2=0.99 was achieved in all the calibrations with good precision of the internal standard. The method was then applied to the extracted water samples.

Table 2.3: Instrument conditions for the target analysis of high PFASs concentration samples

LC-MS/MS instrument	Shimadzu, LC-MS-8030 triple quadrupole system
Analytical column	Kinetex® 2.6 µm XB-C18 100 Å, LC Column 50 x 4.6 mm
Column temperature	40°C
Injection volume	10.00 µL
Flow rate	0.3000 mL/min
Mobile Phases	A 20 mM Ammonium Acetate B 50:50 Methanol: Acetonitrile
Gradient conditions	
Time (min)	% Mobile phase B
1	20
4	90
7	20
12	0
Acquisition time	12 min

Table 2.4: Instrument conditions for non-target PFASs identification using TOF-MSW

Instrument name	TripleTOF 6600, SCIEX
Analytical column	Luna Omega 3 µm polar C18 100Å LC column 100 x 2.1 mm, Phenomenex
Column temperature	40°C
Injection volume	10.00 µL
Flow rate	0.50 mL/min
Mobile Phases	A 2 mM Ammonium Acetate, 0.1% Formic Acid B 100% Methanol
Gradient conditions	
Time (min)	% Mobile phase B
1	5.0
16	95
20	5.0
26	0
Acquisition	Information Dependent Acquisition
Acquisition time	26 min

For the analysis of water samples with suspected low concentrations of PFASs, i.e. water samples collected from all other provinces other than Gauteng, a target analytical approach using an LC-MS/MS (LCMS-8030, Shimadzu) was used for PFASs detection and quantification. Method optimisation and validation is presented in Volume I of this report. Four different chromatographic methods comprising **A, B, C** and **D (**Table 2.5**)** were used for sample analysis to ensure good separation of PFASs compounds.

Table 2.5: Instrument and optimization conditions for targeted analysis low PFASs concentration samples

LC-MS/MS instrument	Shimadzu, LCMS-8030
Analytical column	Kinetex 2.6 um Polar C18 100 A LC Column 100 x 2.1 mm, Unit
Column temperature	40°C
Injection volume	10.00 µL
Flow rate	0.3000 mL/min
Method A	
Mobile Phases	A: 10 mM Ammonium Formate
	B: 20:80 Methanol: Acetonitrile
	Gradient Conditions
Time (min)	Mobile Phase B (%)
1	45
3	50
4	60
4.5	70
5	65
5.5	68
6	80
7.5	70
10	0
16	Stop
Method B	
Mobile Phases	A: 10 mM Ammonium Formate
	B: 50:50 Methanol: Acetonitrile
	Gradient conditions
Time (min)	Mobile Phase B (%)
1	
4	20
6.5	55
7	75
7.2	95
9	0
10	20
12	Stop
Method C	
Mobile Phases	A: 20 mM Ammonium Acetate
	B: 95:5 Methanol: Water
	Gradient Conditions
Time (Min)	Mobile Phase B (%)
1	20
2	75

3	85
4	70
6	95
7.5	100
10	90
16	Stop

	Method D	
Mobile Phases	A: 10 mM Ammonium Formate	
	B: 20:80 Methanol: Acetonitrile	
		Gradient Conditions
Time (Min)		Mobile Phase B (%)
1		20
2		55
3.5		70
4		0
5		Stop

2.4.3 Identification of emerging and legacy PFASs using non-target analysis

Identification of emerging and legacy PFASs was done using non-targeted analysis (Figure 2.2). The workflow used in this study involved suspect screening and considered evidence reported in the literature to identify legacy and emerging PFASs in different water samples, and such evidence was based on the actual mass, library score of >70%, the presence of fragment ions, homologues mass difference, mass error (mDa) and retention times.

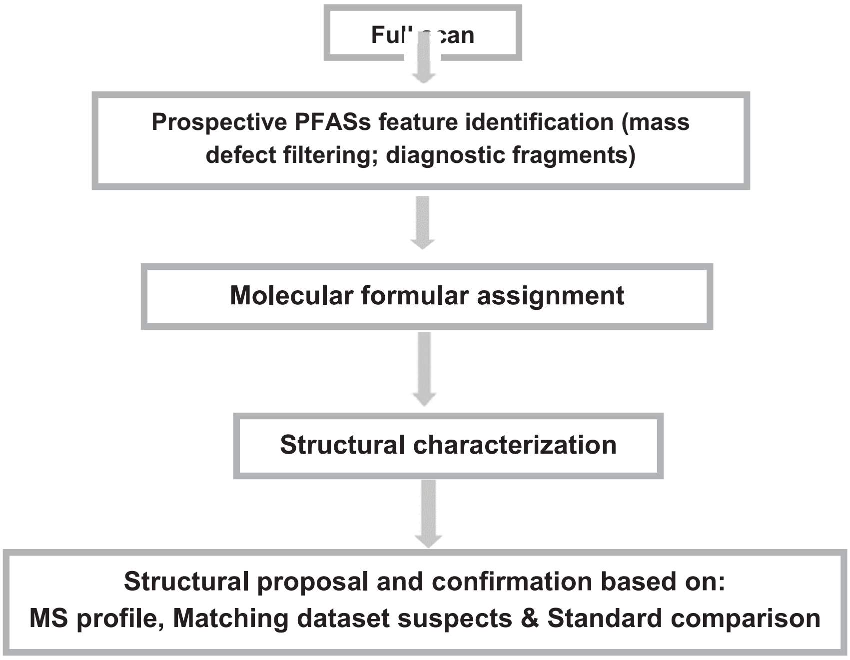

Figure 2.2: General schematic workflow for non-target PFAS by TOF-MS.

2.4.4 Quantification of PFASs using targeted analysis

The chromatographic conditions developed were used to calculate the final concentrations of PFASs in the water samples using the following formula:

$$\mathbf{A_{nat}/A_{IS} \times 1/RRT \quad x \quad M_{IS}/SS} \qquad \text{(Equation 2.2)}$$

where: A_{nat} = area of surrogate standard; A*is* = area of internal standard; M_{IS} = mass of internal standard (ng);
RRF = slope or gradient in the calibration curves; SS = sample size (mL).

The RRF is obtained when the ratio of response for the unit amount of the contaminant of interest to the response of the IS and is expressed in equation below:

$$\mathbf{RRF = A_{NAT}/A_{IS} \times C_{IS}/C_{NAT}} \qquad \text{(Equation 2.3)}$$

where:
A_{NAT} is peak area of the native ($^{13}C_2$) compound; A_{IS} is the peak area of the internal standard in the standard C_{NAT} is the concentration of the native standard; C_{IS} is the internal standard concentration.

2.5 SOURCE APPORTIONMENT

Source apportionment of PFAS is a multidisciplinary process that combines analytical chemistry, environmental science, and data analysis techniques. It is essential for understanding the origins of PFAS contamination and taking appropriate actions to manage and remediate PFAS-related environmental issues. To address Aim 2 of this project, a multivariate statistical analysis was used to establish inter-relationships between different groups of PFASs, and sample sites and to establish possible sources of PFAS. Principal Component Analysis (PCA) was used to identify patterns, potential sources of variation and relationships within the obtained datasets of PFASs concentrations in the different sampling sites. Data interpretation was done in conjunction with knowledge on the land uses within the catchment area of the sampling sites.

2.6 RISK ASSESSMENT

The monitoring data obtained was used to assess risks associated with PFAS exposure, particularly in regions with elevated PFAS concentrations. In this study, a Yeast Estrogen Screen (YES) assay was used to assess the estrogenic activity of the samples containing PFASs and their potential effects on human health. The YES assay is designed to determine whether a substance has estrogen-like properties and can bind to and activate estrogen receptors, which are relevant to various health impacts, particularly related to hormonal disruption and endocrine-disrupting compounds (EDCs). In order to account for endocrine-disrupting activity from metals, the samples were further subjected to ICP-MS analysis (Section 2.5.8).

2.6.1 Materials

Yeast was obtained from Prof JP Sumpter's laboratory, in the Department of Biology and Biochemistry, Brunel University, Uxbridge, Middlesex, United Kingdom. Potassium dihydrogen phosphate (KH_2PO_4), ferric sulphate ($Fe_2(SO_4)_3$, pantothenic acid, 17β-Estradiol, HPLC grade ethanol and pyroxidine were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Anhydrous ammonium sulphate ($(NH_4)_2SO_4$,, potassium hydroxide (KOH) pellets anhydrous magnesium sulphate ($MgSO_4$), L-leucine), L-histidine ,adenine, L-arginine, hydrochloric acid (HCL), L-methionine, L-tyrosine, L-isoleucine, L-lysine-HCl, L-phenylalanine, L-glutamic acid, L-serine, L-valine, D(+)-glucose, L-aspartic acid , L-threonine , thiamine, inositol , anhydrous, copper (II) sulphate ($CuSO_4$), ethanol (HPLC grade) , and Chlorophenol red-β-D-galactopyranoside (CPRG) were obtained from Roche Diagnostics (Mannheim, Germany), (Sigma-Aldrich), glycerol (Sigma), Agar (, Sigma), parafilm, pH indicator strips, HPLC grade MeOH and 32% hydrochloric acid (HCL) were all purchased from Merck (Darmstadt, Germany).

Cryovials and 96-well assay plates were purchased from Thermo Fisher Scientific (Denmark). Autoclave tape was from 3 M Health Care (Neuss, Germany). Polyethersulfone (PES) membrane syringe filters were from Merck (Darmstadt, Germany). Disposable serological pipettes were obtained from Corning Incorporated (Corning, New York, USA); whereas tin foil, glass wool filters were all purchased from Macherey-Nagel. Glass microfiber filter papers (0.45 µm), Supelco ENVI-18™ SPE cartridges (500 mg, 6 mL) and polypropylene bottles (1 L) were all purchased from Whatman (New jersey, United states), Sigma-Aldrich (Aston Manor, South Africa) and Plastillon (Gezina, South Africa) respectively.

2.6.2 Sample collection and preparation for analysis

Water samples collected from the Northern Cape and Gauteng provinces were used in the yeast bioassay estrogenic assay to test for potential estrogenic activities of PFASs compounds. The pH of the water samples was adjusted to 3 using pH indicator strips and 32% hydrochloric acid before extraction. Samples extraction involved the use of Supelco ENVI-18™ SPE cartridges (500 mg, 6 mL) loaded onto SPE 12-position vacuum manifold (Phenomenex, Torrance, California, USA. After preconditioning the cartridge using 5 mL of distilled water, followed by 5 mL of HPLC grade methanol, the cartridges were allowed to equilibrate with 5 mL of double distilled water (DDH_20). After extraction, the cartridges were dried for 1 h. The samples were then eluted from the cartridges with 5 mL of MeoH. Furthermore, the extracts were evaporated to dryness at 37°C using a reacti-vap and Reacti-therm unit under a mild stream of nitrogen. Afterwards, the sample residues were reconstituted in sterile glass amber vials (4 mL volume) with 1 mL ethanol and stored in a freezer at -20°C prior to bioassay analysis.

2.6.3 Yeast estrogenic bioassay analysis

Yeast bioassay analysis to determine estrogenic activity in water samples were carried out in the EDC laboratory at the University of Pretoria according to the protocols developed by Aneck-hanh et al. (2008). According to Routledge & Sumpter (1996), the Genetics Department of Glaxo Group Research Ltd created the YES bioassay to assess the estrogenic activity of compounds. Human oestrogen receptor alpha (hER) and expression plasmids carrying the reporter gene lac-Z, encoding the enzyme β-galactosidase, were genetically added to a yeast strain (Sacchromyces cerevisiae). The reporter gene Lac-Z is expressed in response to substances that bind to and activate the ER, which causes the synthesis of -galactosidase in a dose-dependent mode. The enzyme is released into a media containing the chromogenic substrate chlorophenol red-D-galactopyranoside (CPRG). CPRG is typically yellow, however, it is converted by β-galactosidase into a red product that can be detected by measuring the absorbance at a particular wavelength.

2.6.4 Preparation of Medium and Stock solution

Minimal medium was prepared by adding the following chemicals: 13.6 g KH_2PO_4, 1.98 g $(NH_4)_2SO_4$, 4.2 g KOH pellets, 0.2 g $MgSO_4$, 1 mL $Fe_2(SO_4)_3$ solution (40 mg/50 mL water), 50 mg/L-leucine, 50 mg/L-histidine, 50 mg adenine, 20 mg/L-arginine-HCl, 20 mg/L-methionine, 30 mg/L-tyrosine, 30 mg/L-isoleucine, 30 mg/L-lysine-HCl, 25 mg/L-phenylalanine, 100 mg L-glutamic acid, 375 mg L-serine and 150 mg/L-valine. About 1L of ddH_2O was added to the components and the pH adjusted to 7.1. Then the medium was sterilized by autoclaving for 20 min at 121°C and 15 psi and stored at 4°C. Thereafter, a stock solution of glucose (200 g/L), L-aspartic acid (4 g/L) and L-threonine (24 g/L) was prepared in ddH_2O. The solutions were autoclaved for 20 min at 121°C, 15 psi to sterilize and later stored at 4°C. Vitamin solution was prepared by adding 8 mg thiamine, 8 mg pyroxidine, 8 mg pantothenic acid, 40 mg inositol and 20 mL biotin solution (0.02 g/L in ddH_2O) to 180 mL ddH_2O. The solution was sterilized by filtering through a 0.2 µm syringe filter. Stock solutions of $CuSO_4$ (0.3192 g/L) and CPRG (10 g/L) were also filtered, sterilized and stored at 4°C. Thereafter, a growth medium was prepared by adding 45 mL minimal medium, 5 mL glucose, 1.25 mL L-aspartic acid, 0.5 mL vitamin solution, 0.4 mL L-threonine and 125 µL $CuSO_4$ together. A 54.58 µg/L stock solution of the E2 positive control was prepared in EtOH and stored at -20°C.

2.6.5 Preparation and Storage of Yeast Stock Cultures

Agar slopes were used to prepare long-term yeast stock cultures and a 1% agar solution was prepared in minimal medium. Thereafter, the solution was autoclaved and the following growth medium components were added to 90 mL of the agar solution once it cooled down to 50°C, and 10 mL glucose, 2.5 mL L-aspartic acid, 1 mL vitamin solution, 0.8 mL L-threonine and 250 µL $CuSO_4$ were added to the solution. Using sterilized glass tubes, the solution was poured directly into the tubes and allowed to set at 45° angle. Approximately, 2 µL of the original yeast stock was spread over the surface of the agar slopes and were incubated for 3 days at 32°C. Then, the yeast cells were resuspended in 1 mL sterile glycerol and stored in aliquots in cryovials at -80°C. Short term 10x concentrated stock cultures were prepared by adding, 125 µL of the long-term yeast stock to 50 mL growth medium and incubated at 28°C in a rotating water bath (at 155 upm). After 24 h incubation, 1 mL of the 24 h yeast culture was added to two flasks containing 50 mL growth medium each. The flasks were subsequently incubated for another 24 h in a water bath (28°C, 155 upm). After incubation, the yeast cultures were transferred to 50 mL centrifuge tubes and centrifuged for 10 min at 4°C and 2000 psi. (Sigma 4K15 centrifuge from Sigma Laborzentrifugen, Germany). The pellets were resuspended in 5 mL of 15% glycerol minimum medium after the supernatant was decanted. For a maximum of four months, aliquots of the 10x concentrated stock cultures were kept in cryovials at -20°C.

2.6.6 Yeast Assay Procedure

A volume of 125 µL of 10x concentrated short term yeast stock was inoculated into 50 mL growth medium as outlined in Section 3.6.6. Thereafter, the yeast was incubated overnight in a rotating water bath (Grant OLS 200, Grant Instruments, Cambridge, UK) at 155rpm until turbid for approximately 24 h. At 620 nm, an absorbance reading of at least 1 indicated sufficient yeast growth to proceed with the assay. In a 96 well microtiter plate, a serial dilution of the water sample extract, controls (ethanol), and E2 positive control was performed by transferring 100 µL of ethanol in well 2-12, followed by an addition of 200 µL of the sample extract/control/blank into the first well, then a serial dilution was performed by transferring 100 µL across the plate to determine estrogenic activity. Thereafter, 10 µL of the dilution series was transferred across new triplicate 96 µL plates and allowed to evaporate. Then, a growth medium was prepared as outlined earlier. Furthermore, 200 µL of the seeded assay medium containing the CPRG was dispensed into each sample well of the triplicate plate using a multichannel pipette. The plates were then sealed with an autoclave plate and kept for 3-5days in an incubator at 32°C (Scientific Series 2000 incubator from Lasec, South Africa). In order to obtain data with best contrast between positive and solvent controls and to allow for slow reacting chemicals, the plates were read over 3 days. A Multiskan Spectrum 96-well plate reader (Thermo Fisher Scientific, Vantaa, Finland) was used to determine the colour development of the medium after the plates had been incubated for three days. The absorbance was measured at 540 nm for colour change and 620 nm for turbidity of the yeast growth.

2.6.7 Data Analysis

Turbidity correction was carried out using the following equation:

Corrected value = **test absorbance** (540 nm) – [**test absorbance** (620 nm) **– median blank absorbance** (620 nm)] (Equation 2.4)

Graphpad Prism (version 4) was used to fit the E2 standard curve (sigmoidal function, variable slope), which calculated the minimum, maximum, slope, EC50 value, and 95% confidence limits. The absorbance induced by the solvent control (blank) plus three times the standard deviation was used to calculate the detection limit of the yeast test. Cytotoxic concentrations were defined as sample concentrations having absorbance values less than the solvent control minus three times the standard deviation. The samples' estradiol equivalents (EEq) were interpolated from the estradiol standard curve and corrected with the appropriate dilution factor.

2.6.8 Assessment of trace metals in water samples using inductively coupled plasma-mass spectrometry (ICP-MS)

2.6.8.1 Reagents and materials

All chemicals and reagents used were of analytical grade. Deionized water (-18MΩ-cm water) prepared using an Elga water purification system (Woodridge, USA) was used throughout the experiment for preparations and dilutions of solutions. Nitric acid was purchased from Sigma-Aldrich (St. Louis MO, USA). Indium internal standard (1000 mg/L) was purchased from Inorganic Ventures (Christiansburg, Virginia, USA). Multi standard solution (250 mg/L) was purchased from Sigm-Aldrich (St. Louis MO, USA).

2.6.8.2 Sample preparation and chemical analyses

The collected samples were analysed for 21 trace metals including Lithium (Li), Beryllium (Be), Titanium (Ti) , Vanadium (V), Chromium (Cr), Manganese (Mn), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Selenium (Se), Rubidium (Rb), Strontium (Sr), Molybdenum (Mo), Cadmium (Cd), Tin (Sn), Antimony (Sb), Tellurium (Te), Cesium (Cs), Barium (Ba), Lanthanum (La), Tungsten (W), Platinum (Pt), Thallium (Ti), Lead (Pb), Bismuth (Bi) and Uranium (U). An Inductively coupled plasma mass spectrometry (ICP-MS-7700X (Agilent Technologies Inc., Tokyo, Japan) was used to analyse the samples. The samples were introduced into the nebulizer using a peristaltic pump. Prior to analysis, the field samples were spiked with 10 ng/L of indium. Operating parameters of the instrument are presented in Table 2.6. The ICP-MS was calibrated for every set using multi standard solution (250 mg/L). Typical concentration calibration set was within a range of 5-50ppb. Indium (10 µg/L) was added to all solutions, including the calibration blank, to verify the performances of the methods. The analyte recovery was at least 90%. Nitric acid (3%) and deionized water was pumped through the nebulizer between all samples to avoid cross contamination.

Table 2.6: ICP-MS operating parameters

ICP parameters	
RF power	155W
RF matching	0.30V
Nebulising pump	0.10rps
Carrier Gas	1.03L/min
Sample depth	10.0mm
S/C Temperature	2°C
Sampling period	0.31sec

2.7 DATA MANAGEMENT

To address Aim 3 of the project, which focuses on the development and presentation of a database on PFAS levels in the different provinces, the data obtained from the analysis of samples is presented in Chapters 3 to 12.

CHAPTER 3: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE EASTERN CAPE PROVINCE

3.1 SAMPLING STRATEGY

3.1.1 Location and description of sampling sites

The sampling sites in the Eastern Cape Province were in East London and Gqeberha areas (Figure 3.1). The selected areas are highly populated and industrialized. Furthermore, the water quality within both cities has been of great concern to the municipality and, therefore, the communities living in these metropolitan areas are probably exposed to water pollutants such as PFASs. Within these two cities, samples were collected from the following sources:

- Nahoon River (NHR1 and NHR2) in East London,
- Quenera River (QR1);
- Bridle Drift Dam (BDBR);
- Tap water metropolitan area
- Loerie Dam (LD1 and LD2);
- Drinking water treatment plant (WTP);
- Gamtoos River (GR) and
- Tap water from the suburban areas

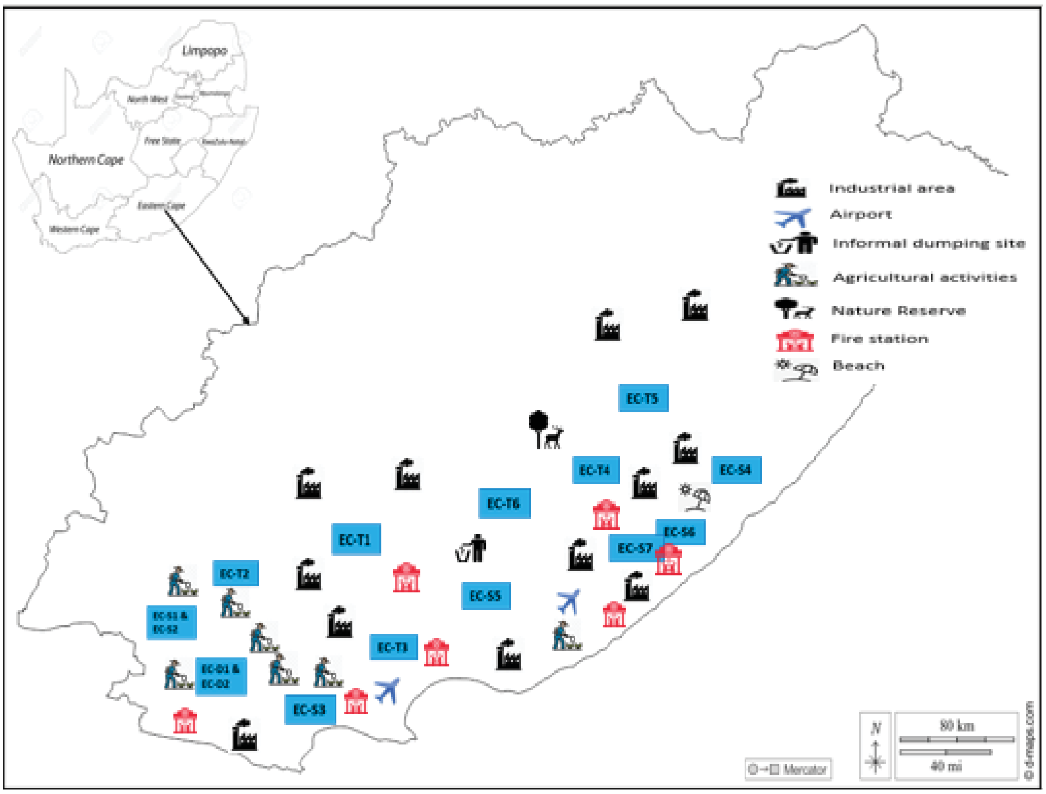

Figure 3.1: Land use map and the sampling sites in Eastern Cape Province.

3.1.2 Sample collection

Table 3.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the two cities. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 3.1: Sampling sites in Eastern Cape

DATE	SAMPLE LOCATIONS	CO-ORDINATES
29-04-2022	EC-D1	33.86803°S
		25.03790°E
29-04-2022	EC-D2	33.86803°S
		25.03790°E
29-04-2022	EC-T1	33.9340021°S
		25.5890735°E
29-04-2022	EC-T2	33.9315337°S
		25.464647°E
29-04-2022	EC-T3	33.8151447°S
		25.6064527°E
19-04-2022	EC-T4	32.9773444°S
		27.8734673°E
19-04-2022	EC-T5	32.9605391°S
		27.9154206°E
19-04-2022	EC-T6	32.9657974°S
		27.6788602°E
29-04-2022	EC-S1	33.8614616°S
		25.0395737°E
29-04-2022	EC-S2	33.8655255°S
		25.0399339°E
29-04-2022	EC-S3	33.9125709°S
		25.0249091°E
19-04-2022	EC-S4	32.9711989°S
		27.9617544°E
19-04-2022	EC-S5	32.981569°S
		27.7256933°E
19-04-2022	EC-S6	32.9761284°S
		27.9282323°E
19-04-2022	EC-S7	32.9813959°S
		27.9327534°E

3.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. The percentage recoveries of surrogate standards in blanks and samples are shown in Tables 3.2 and 3.3. From Tables 3.2 and 3.3, the recoveries ranged from 61.8-107%; 62.3-101% and 51.8-140% for the blank and samples, respectively. Generally, the recoveries were satisfactory with the exception of MPFUdA and MPFNA in Nahoon and Gamtoos Rivers.

Table 3.2: Percentage (%) recoveries and standard deviation of blanks spiked with surrogate standards in wet season

Samples – Surrogate recoveries (%) ± Standard deviation	
Surrogates	**BL**
MPFNA	78.2±8.12
MPFUdA	61.8±6.49
MPFHxS	107.3±0.62

Table 3.3: Percentage recoveries (%) of blanks and samples in wet season

SAMPLE LOCATIONS	MPFNA	MPFunDA	MPFHxS
BLANKS (n=7)	101.6	92.6	62.3
EC-D1	90.3	117.2	106.7
EC-D2	140.9	95.2	127.5
EC-S1	135.3	114.5	126.0
EC-S2	127.3	148.6	125.3
EC-S3	65.7	94.8	84.0
EC-T1	107.5	89.8	135.4
EC-T2	76.3	127.9	133.9
EC-T3	82.8	108.5	58.6
EC-T4	114.7	79.2	98.9
EC-T5	74.5	99.8	86.6
EC-T6	118.8	104.7	134.6
EC-S4	125.6	68.2	160.9
EC-S5	107.1	55.8	108.0
EC-S6	51.8	136.9	94.8
EC-S7	71.8	135.9	150.2

EC-D1=Treated water; EC-D2=Raw water, EC-T1=Aspen tap water; EC-T2=Acacia tap water; EC-T3=Motherwell tap water; EC-T4=Cambridge tap water; EC-T5=Abbortsford tap water; EC-T6=Mdantsane tap water; EC-S1=Loerie dam P1; EC-S2=Loerie dam P2; EC-S3= Gamtoos River; EC-S4= Quenera River; EC-S5= Bridle Dam; EC-S6= Nahoon River P1; EC-S7= Nahoon River P2

3.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

3.3.1 Distribution of PFASs in various water sources during the wet season

Figure 3.2 gives a pictorial view of the distribution of PFASs compounds in various water samples during the wet season. Accordingly, PFASs compounds more clustered in surface and tap water compared to drinking water treatment plant. The clustering of PFASs is more at the bottom (<25%); whereas at >25% the contribution is scattered. This may suggest that PFASs detected in surface water and tap water samples contributed more to the overall concentrations detected in this province and this is collaborated by the concentrations of PFASs in EC-S1-EC-S7 as shown in Table 3.4. The highest PFASs concentration was observed in EC-S5. It is also possible that the clustering is an indication of similar sources of PFASs influent. PFPeA, PFHxA, FOET and PFBA were the dominant PFASs compounds. It is also noteworthy that all the concentrations of PFASs compounds were below the 70 ng/L for PFOS+PFOA (horizontal line) set by the USEPA.

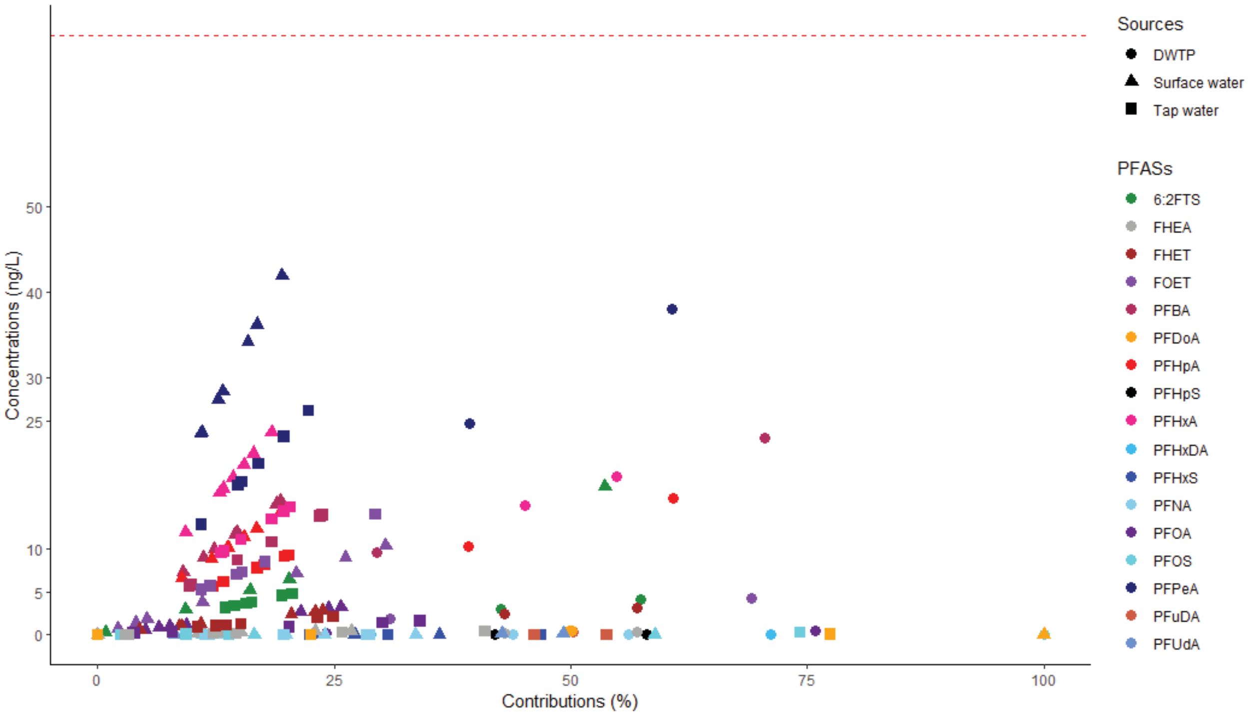

Figure 3.2: PFASs concentration distributions for various water sources in the Eastern Cape during the wet season

Sixteen PFASs were detected in tap and source water (river, dam and water treatment plant) collected (Table 3.4). The concentrations ranged from <LOD-41.92 ng/L, with PFPeA having the highest detected concentration of 41.92 ng/L in sampling EC-S5. This was followed by point EC-D1 (38.04 ng/L), EC-S2 (36.23 ng/L), EC-S4 (34.17 ng/L), EC-S6 (28.42 ng/L) and EC-S7 (27.38 ng/L).

Table 3.4: Data showing the mean concentrations of PFASs in various water samples from Eastern Cape Province in wet season

Compounds	EC-D1	EC-D2	EC-T1	EC-T2	EC-T3	EC-T4	EC-T5	EC-T6	EC-S1	EC-S2	EC-S3	EC-S4	EC-S5	EC-S6	EC-S7
L_PFBS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L_PFHpS	0.03±0.004	0.02±0.002	ND	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L_PFDS	ND	ND	ND	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L_PFHxS	0.01±0.01	<LOD	<LOD	<LOD	<LOD	0.01±0.006	0.01±0.007	0.02±0.023	0.01±0.004	<LOD	0.01±0.01	<LOD	0.01±0.001	0.02±0.019	<LOD
L_PFOS	0.13±0.05	<LOD	<LOD	<LOD	<LOD	0.04±0.01	0.06±0.02	0.29±0.11	<LOD	<LOD	<LOD	<LOD	0.03±0.02	<LOD	<LOD
PFOA	<LOD	<LOD	<LOD	<LOD	<LOD	1.58±0.53	1.4±0.84	0.94±0.03	0.64±0.65	0.83±0.23	0.97±0.12	1.19±0.41	2.74±0.49	3.28±0.49	3.11±0.73
PFHpA	**16±0.29**	**10.3±0.89**	**7.79±1.05**	**6.15±0.38**	**5.63±1.33**	**8.13±0.74**	**9.3±0.15**	**9.11±1.44**	**12.4±0.41**	**11.4±1.40**	**6.6±1.40**	**8.9±0.45**	**10.2±1.69**	**14.3±7.95**	**10.1±5.42**
PFHxA	**18.4±1.72**	**15.1±2.56**	**11.1±0.25**	**9.58±0.25**	**9.79±0.45**	**13.4±2.15**	**14.4±1.64**	**14.9±1.90**	**23.6±5.64**	**16.5±0.98**	**11.9±0.99**	**18.3±3.36**	**19.84±6.51**	**21.18±5.55**	**17.1±4.36**
PFPeA	**38±3.97**	**24.6±4.92**	**17.88±1.71**	**12.88±0.69**	**17.4±2.24**	**19.9±1.30**	**23.13±4.17**	**26.1±0.79**	**23.4±18.9**	**36.2±1.61**	**23.6±2.18**	**34.1±11.13**	**41.92±15.9**	**28.4±5.72**	**27.3±5.13**
PFNA	0.06±0.01	0.08±0.01	0.01±0.013	<LOD	0.01±0.013	0.03±0.033	0.03±0.03	0.02±0.02	0.03±0.031	ND	0.02±0.02	0.05±0.04	0.06±0.05	0.08±0.07	ND
PFDoA	0.5±0.1	0.51±0.15	ND	ND	ND	ND	<LOD	ND	ND	<LOD	<LOD	ND	ND	ND	ND
PFODA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFUdA	0.42±0.05	0.41±0.09	<LOD	ND	ND	<LOD	ND	ND	ND	<LOD	ND	ND	<LOD	<LOD	ND
PFBA	**22.9±5.22**	**9.59±8.5**	**13.9±0.38**	**10.8±0.91**	**13.8±1.14**	**5.71±0.16**	**5.82±0.43**	**8.71±0.17**	**7.32±9.89**	**9.96±6.59**	**15.2±8.15**	**15.6±3.22**	**11.75±1.75**	**11.9±1.58**	**9.05±2.17**
PFHxDA	0,03	0,08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4_2 FTS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8_2 FTS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6_2FTS	4.16±0.53	3.09±0.03	3.82±0.07	3.38±1.10	3.16±0.29	3.68±0.15	4.56±0.01	4.81±0.82	0.25±0.18	<LOD	<LOD	5.22±0.86	3.00±0.02	6.55±1.73	17.37±5.12
FHEA	0.36±0.16	0.27±0.003	0.26±0.12	0.03±0.05	0.03±0.04	0.14±0.12	0.12±0.03	0.4±0.01	<LOD	0.46±0.07	0.39±0.05	0.26±0.07	0.19±0.04	0.23±0.07	0.18±0.05
FOET	**1.9±0.25**	**4.26±0.06**	**5.7±1.07**	**5.24±0.18**	**7.04±0.46**	**8.48±0.38**	**14±0.17**	**7.33±0.83**	**1.38±0.19**	**0.74±0.09**	**1.79±0.25**	**10.4±0.32**	**7.23±0.71**	**9.02±3.13**	**3.81±0.58**
FHET	**3.21±0.31**	**2.42±0.22**	**2.1±0.29**	**1.05±0.76**	**1.28±0.14**	**1.96±0.17**	**1.15±0.18**	**0.89±0.24**	**2.75±0.15**	**2.45±0.05**	**2.85±0.85**	**1.31±0.01**	**1.06±0.12**	**1.04±0.30**	**0.53±0.06**

Compound PFHxA showed the second highest detected concentration in sampling point EC-S1 of 23.63 ng/L, followed by PFBA (22.98 ng/L) in point EC-D1. L-PFBS, L-PFDS, PFODA, 4:2 FTS and 8:2 FTS were not detected in all the samples. In order to determine if there are any pattern to the data, a scatter logbase plot as shown in Figure 3.3 was constructed. As can be seen in Figure 3.3, the data show an uphill pattern from left to right, indicating that there is clearly a strong positive relationship between contribution and concentrations in the water samples. This means that as the percentage contribution values increased, the concentration of PFASs also increased. The uphill pattern spreads from the bottom of the plot to the top where some congestion can be seen.

Figure 3.3: PFASs concentration distributions in logbase for various water sources in the Eastern Cape in wet season

In the present study, both short and long chain PFASs were detected, however, lower concentrations of C ≥ 9 were detected. Studies from the Vaal River, South Africa and Uganda also reported similar observations (Groffen et al., 2018; Dalahmeh et al., 2018). Short-chain alternatives among the perfluorocarboxylic acids (PFCAs), PFBA and PFHxA were the most detected PFASs. These short chain PFASs were detected more than the long chains. This could be attributed to their tendency to be more water soluble and have lower potential for sorption to particles than the long-chain analogues.

Figure 3.4 shows a box plot of contributions of classes of PFASs in various water sources. PFCAs had more contribution in drinking water treatment plant followed by the Fluorotelomer class, exhibited by PFPeA and 6:2 FTS, respectively. The PFCAs group had lesser contribution in both surface and tap water compared to the other groups. In surface water, the Fluorotelomers had the highest contribution as shown by 6:2 FTS followed by PFHxS which belongs to the PFSAs class. PFSAs had the highest contribution in tap water, which is represented by PFOS in the plot.

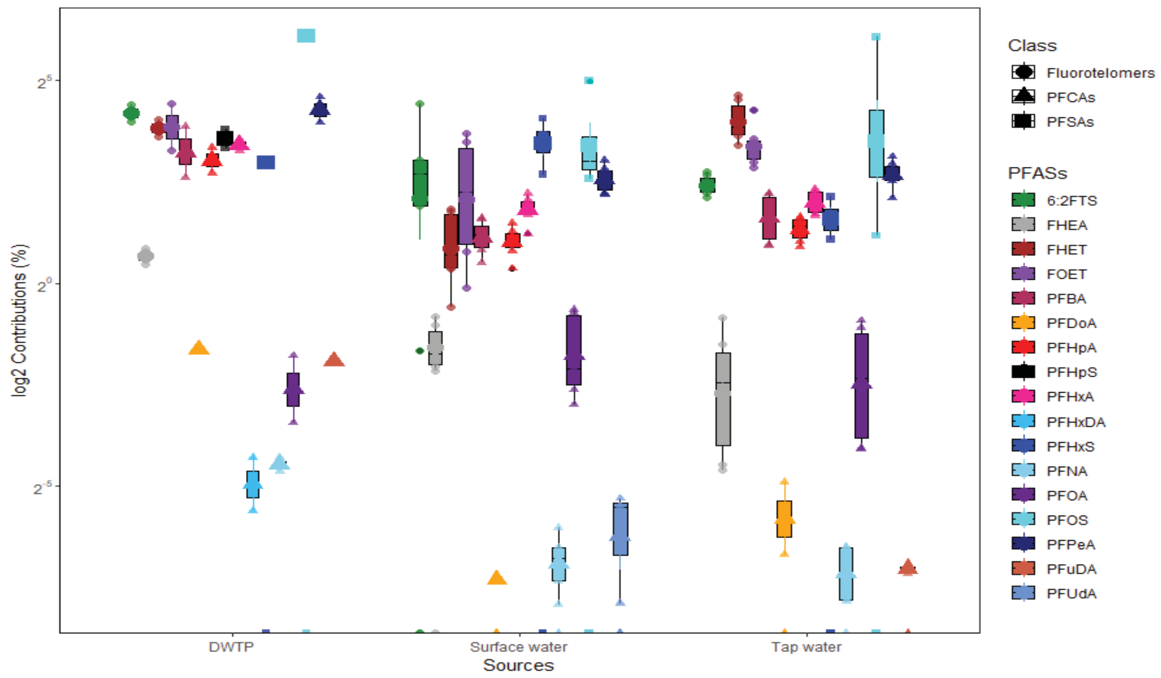

Figure 3.4: PFASs class contributions for various water sources in the Eastern Cape during the wet season.

Figure 3.5 shows the contributions of long and short chain PFASs in various water sources. The short chains had more contribution in the drinking water treatment plant. In both surface water and tap water, the long chains were observed to have more contribution and PFOA was the compound with the highest contribution. The observed pattern is indicative of either more use of short chain PFASs or the breakdown of long chains into short.

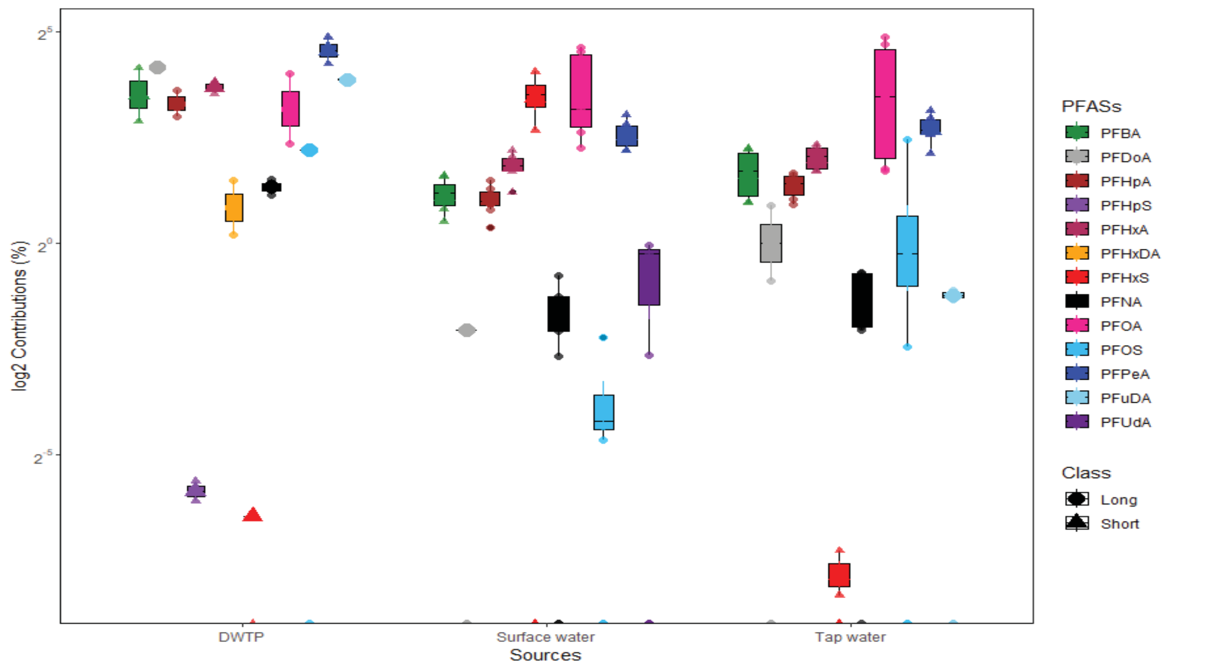

Figure 3.5: Contributions of long- and short-chain PFASs for various water sources in the Eastern Cape during the wet season.

3.3.2 Establishing the possible sources of the PFASs detected in the water

The dataset of PFASs congeners detected in the water samples were subjected to PCA. The differences between the PFAS concentrations found in the samples were statistically significant (p=0.05). All the PFASs compounds are clustered in quadrants 1 and 2 (clockwise), except FOET (Figure 3.6). PFCAs and PFSAs are more in quadrant 1 compared to quadrant 2. The PFCAs that dominated are perfluoroalkyl acids (PFAAs, i.e. PFCAs) and they tend to be formed from the transformation of polyfluorinated substances present in the environment. From Table 3.4, PFPeA was the highest detected compound followed by PFHxA and PFBA. Also a study by Groffen *et al*., (2018), reported PFPeA highest detected compound in Vaal dam whereas Batayi *et al*., (2021) reported PFPeA to be the lowest detected in Hartbeespoort and Roodeplaat Dams. Congeners PFNA, PFHpA, PFHxA, and PFPeA were positively associated with each other (Figure 3.6). Although PFOA is on the same score plot with the aforementioned PFASs, however, it is not close to others. This behaviour suggests different pattern/source. The same can be said for 6:2 FTS and FOET. On the other hand, FHEA, PFBA and FHET were negatively associated with each (Figure 3.6).

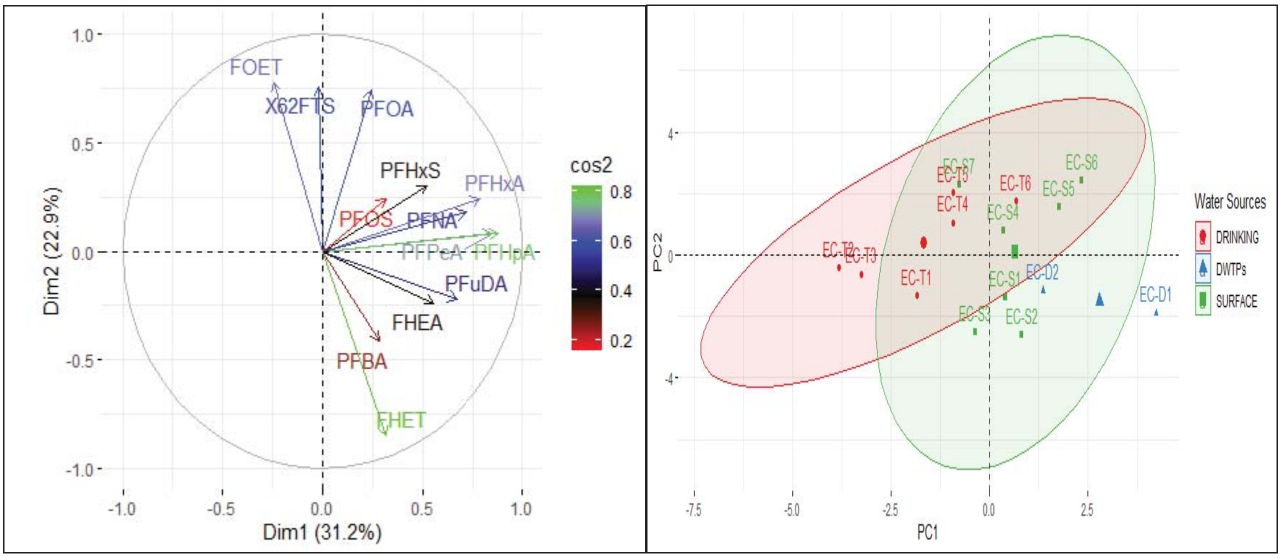

Figure 3.6: PCA of PFASs congener contributions and their relationships (a) and sampling sites and their relationships (b) in wet season

FTOH-based substances are precursors of perfluoroalkyl carboxylates (Li *et al*., 2015); their widespread application has resulted in FTOH occurrence in the environment. Moreover, according to Schenker *et al*., 2008, their high volatility enables them to travel long distances reaching remote areas where they are degraded and contribute to PFCAs contamination. Therefore, high contribution of perfluoroalkyl carboxylic acids (PFCAs) detected in sampling from EC-S5, EC-S1 and EC-D2 may be attributed to fluorotelomer transformation. The high concentrations detected for PFPeA in samples from EC-S5, EC-S4, EC-S6 and EC-S7 in the East London area, may be due to pollution since this area has a history of sewage contamination (Despatchlive, 2020; 2022). In addition, in the Mdantsane Township, four small tributaries carry domestic effluents into the Bridle dam (BDBR), resulting in water quality problems such as levels of salinity and eutrophication (WRC Report, 1993).

Quenera River (QR1) is next to Bonza Bay Beach and, therefore, any anthropogenic activity on the beach is likely to impact on the dam. Nahoon Rivers (NHR) are subject to eutrophication and water hyacinth due to domestic, industrial effluent discharge and run-off from agricultural lands (BCMM, Performance report). The concentrations detected in samples from EC-S6 and EC-S7 may also be due to the sources mentioned earlier. The high PFHxA and PFBA detected in EC-S1 and EC-D1 may be due to the extensive agricultural activities surrounding the catchment area (Ndude *et al*., 2022) (refer to Figure 3.1). The high PFBA detected at EC-D1 compared to the source water, suggested a contribution from the treatment processes as the source water had lower concentrations. As can be seen from Figure 3.6, all the other sampling sites are scattered, particularly EC-D1, with the exceptions of AP and MW on one hand and LD1 and RW on the other. This behaviour suggested different pattern from others. These were all in line with high PFASs concentrations observed at these sampling sites.

East London is the second largest industrial centre in Eastern Cape Province. The motor industry is the dominant employer. Other industries include clothing, textiles, pharmaceuticals and food processing. There are also some agricultural activities in East London. Besides the automotive and components industry, the other predominant industries in Gqeberha (Port Elizabeth) are: chemical, metal, metal products, machinery and electrical machinery, textile and clothing, and the food and beverages industries. Considering the fact that the predominant PFASs detected in the water samples were the PFAAs and these have a wide industrial applications, it is possible that the various industrial and agricultural activities around the sampling areas may have used or still using PFASs in their activities.

3.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

3.4.1 Distribution of PFASs in various water sources during the dry season

Figures 3.7 and 3.8 show the distribution of the PFAS concentrations in the various water sources collected from the Eastern Cape during the dry season. The PFASs in water samples collected from drinking water treatment plants and tap water were more clustered and along the same line in the plot. Similar trend was also observed in surface water, but above those from DWTP and tap water. This suggested that the surface water PFASs concentration contributed more to the results detected.

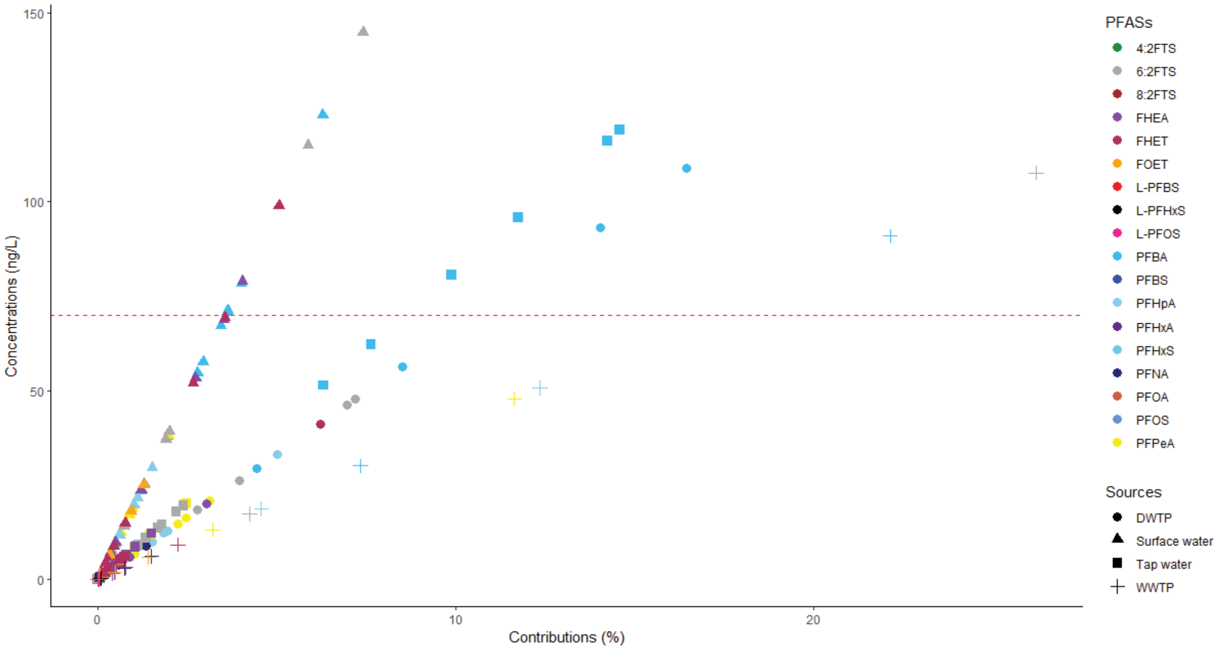

Figure 3.7: PFASs concentration distributions in various water sources in the Eastern Cape Province during the dry season.

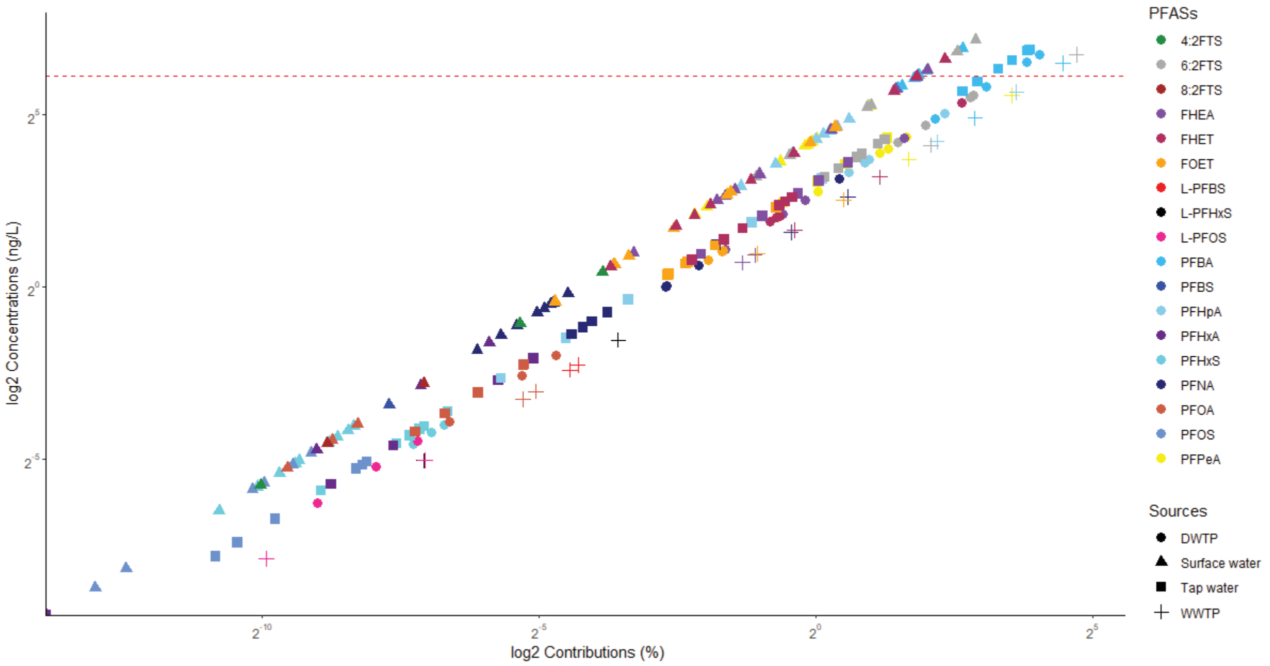

Figure 3.8: PFASs concentration distributions in various water sources in the Eastern Cape Province during the dry season.

Samples from wastewater treatment plants were a bit scattered, though along the same line in the plot and that indicated that they had less contribution to the concentrations detected. PFBA and 6:2 FTS were the compounds that had more contribution to the concentrations, as they are at the top part of the plot. Figures 3.9 and 3.10 show the contribution from the different classes of PFASs in the water sources during the dry season.

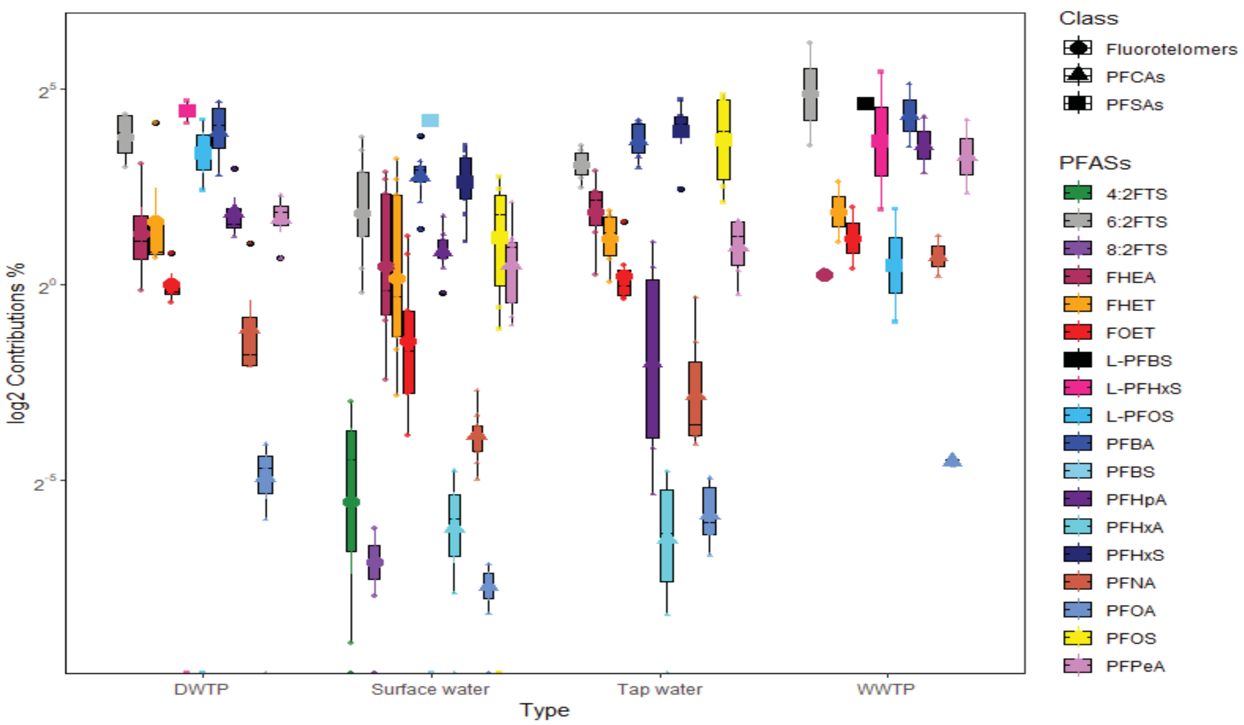

Figure 3.9: PFASs class contributions in various water sources in the Eastern Cape during the dry season.

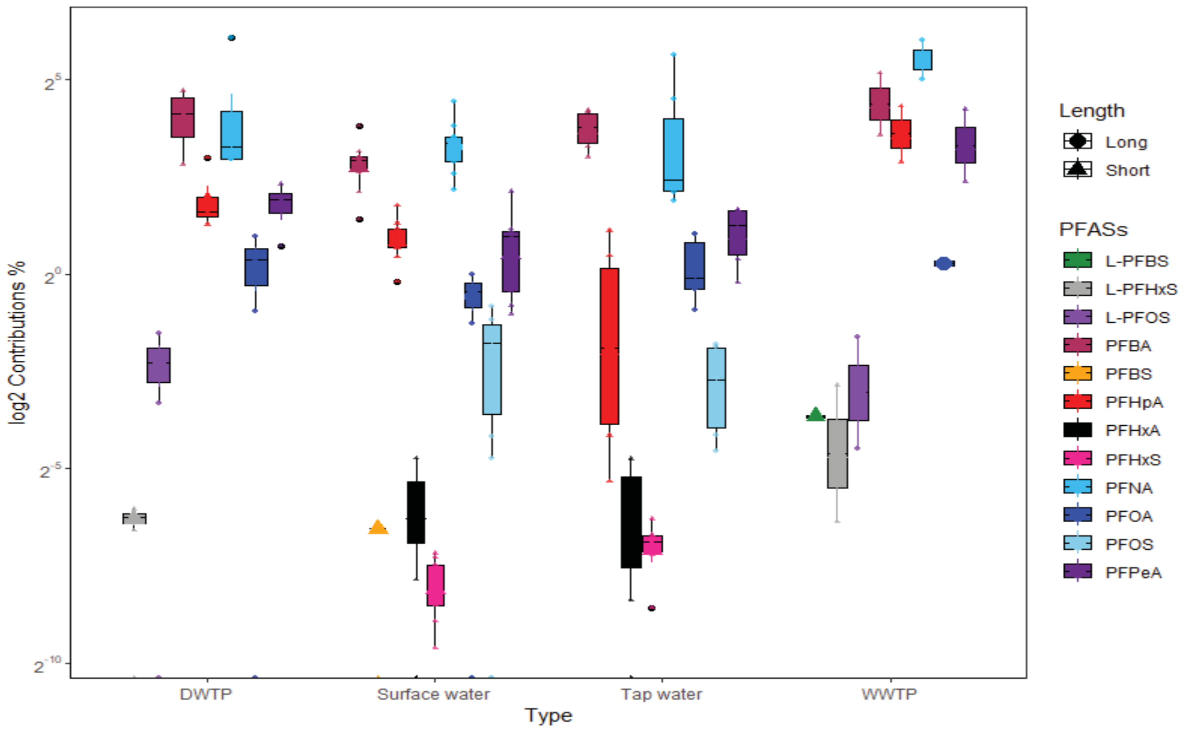

Figure 3.10: Contributions of long- and short-chain PFASs in various water sources in the Eastern Cape during the dry season.

As can be seen from Figure 3.10, the short chains had more contribution in the drinking water treatment plant and PFBA was the compound with the highest contribution. In surface water, tap water and wastewater treatment plants the long chains had more contribution and PFNA was the compound with the highest contribution.

Table 3.5 represents data showing the mean PFASs concentrations detected in surface water during the dry season. Fluorotelomers had more contributions in drinking water treatment plant, surface water and wastewater treatment and this was indicated by 6:2 FTS in Table 3.5. In tap water, however, the PFSAs had the highest contributions indicated by L-PFOS by followed by L-PFHxS.

The most dominant compounds were PFBA, 6:2 FTS, FHET, FHEA, PFHpA and PFPeA and the highest concentration was observed at site EC-S7 for 6:2 FTS (144.8 ng/L). This was followed by PFBA (122.7 ng/L) at site EC-S8, 6:2 FTS (114.8 ng/L) at site EC-S6, EC-S4 (78.9 ng/L), FHEA (78.9 ng/L) at site EC-S6 and PFBA (78.4 ng/L) at site EC-S7. Lower concentrations were detected for L-PFBS, L-PFHxS, PFHxA, PFOA, L-PFOS, PFNA, 4:2 FTS, and 8:2 FTS. The Fluorometers were the most prevalent group of PFASs detected with a sum concentration of ΣFluorotelomers=1002 ng/L, followed by perfluorocarboxylic acids (PFCAs) with sum concentration of ΣPFCAs=881 ng/L. The long chain PFASs were detected more than the short chain. In addition, the concentrations detected during the dry season were higher compared to the concentrations detected during the wet season. This might be attributed to non-dilution of high load of pollution entering the water through point and non-point sources during dry season as there is no rainfall.

A study by Chen (2017), similarly detected lower concentrations of PFASs during high water periods compared to lower water periods in Xiaoling River, Daling River, Pu River and Jiaolai River in China. PFBA was the prevalent compound detected with the highest concentration detected at site EC-T5 (118.91 ng/L).

Table 3.5: Mean PFAS concentrations (ng L^{-1}) from the Eastern Cape Province during the dry season

Sites	PFBA	PFHpA	PFPeA	PFHxA	PFOA	PFNA	L-PFBS	L-PFHxS	L-PFOS	4:2FTS	8:2FTS	6:2FTS	FHEA	FOET	FHET
EC-D1	92.9±5.84	33.2±6.45	20.7±1.5	ND	0.07±0.01	1.03±0.05	ND	0.06±0.05	0.05±0.01	ND	ND	46.1±1.04	5.79±0.15	2.05±0.04	4.22±0.31
EC-D2	108.9±5.82	12.2±1.50	14.8±0.95	ND	ND	1.01±0.47	ND	0.04±0.04	0.03±0.004	ND	ND	26.1±1.76	4.37±0.09	1.72±1.35	3.73±0.55
EC-D3	56.3±0.37	12.9±3.50	16.3±3.67	ND	0.26±0.02	1.54±0.92	ND	0.05±0.06	<LOD	ND	ND	47.7±0.44	20.1±3.25	4.09±0.59	41.1±3.37
EC-D4	29.4±3.35	10.1±3.15	6.84±0.19	ND	0.17±0.03	8.90±8.64	ND	ND	ND	ND	ND	18.5±0.29	2.12±0.19	2.08±0.27	4.06±0.23
EC-T1	62.2±5.79	1.55±0.16	20.2±5.2	<LOD	0.08±0.02	2.34±0.36	ND	0.04±0.03	0.03±0.01	ND	ND	14.62±1.04	4.19±0.55	1.60±0.04	3.28±0.17
EC-T2	116.0±11.40	13.4±3.66	19.9±2.11	<LOD	0.12±0.09	5.21±5.45	ND	0.06±0.07	0.03±0.01	ND	ND	19.5±3.00	12.3±0.54	1.65±0.16	2.60±0.16
EC-T3	95.8±0.89	4.40±0.36	19.9±3.67	<LOD	0.08±0.05	0.60±0.05	ND	0.06±0.05	0.03±0.0002	ND	ND	10.9±7.82	8.52±1.38	4.99±4.42	5.18±0.04
EC-T4	51.4±1.54	16.3±0.78	11.9±6.85	ND	0.21±0.12	0.50±0.43	ND	0.08±0.05	<LOD	ND	ND	13.6±5.92	6.56±0.93	1.30±0.89	6.10±3.57
EC-T5	118.9±1.24	42.6±13.83	8.32±4.68	ND	0.21±0.16	0.44±0.02	ND	0.05±0.02	<LOD	ND	ND	9.18±0.29	8.51±0.44	1.28±0.26	5.58±1.64
EC-T6	80.6±6.29	38.9±8.87	5.45±2.46	<LOD	0.05±0.03	0.39±0.12	ND	0.02±0.01	<LOD	ND	ND	17.9±0.51	1.95±0.16	2.32±0.29	1.74±0.78
EC-S1	57.5±1.24	29.7±0.40	19.7±2.59	ND	0	0.60±0.22	ND	0.02±0.002	0.04±0.02	ND	ND	37.1±8.27	9.72±0.09	1.88±0.47	3.39±0.26
EC-S2	71.1±9.66	14.7±0.14	17.8±2.22	ND	0.03±0.01	0.73±0.21	ND	0.06±0.06	0.03±0.01	ND	ND	39.0±1.02	6.28±0.24	1.58±1.35	5.24±0.45
EC-S3	23.4±0.66	19.7±1.72	18.8±0.26	ND	0	0.70±0.16	ND	0.05±0.04	0.02±0.003	ND	ND	25.4±6.56	53.4±5.92	3.30±0.53	8.68±0.67
EC-S4	54.6±5.59	14.05±2.35	38.2±8.40	<LOD	0	0.88±0.22	ND	0.06±0.01	ND	<LOD	ND	78.9±6.96	23.7±5.16	18.21±1.70	14.9±0.87
EC-S5	37.9±1.46	14.2±0.82	4.29±0.64	<LOD	0.06±0.02	0.28±0.08	ND	0.02±0.01	<LOD	ND	ND	9.24±2.94	68.8±3.73	0.75±0.41	1.50±0.89
EC-S6	67.1±3.03	18.2±0.14	12.6±0.63	ND	0	0.46±0.18	ND	0.04±0.04	ND	ND	ND	114.8±1.00	78.9±0.59	25.06±1.41	69.4±4.37
EC-S7	78.39±4.27	21.63±0.47	6.45±1.08	ND	0	0.38±0.06	ND	0.03±0.01	ND	1.36±1.92	<LOD	144.83±8.89	7.07±0.40	6.76±0.44	52.03±7.25
EC-S8	122.74±2.08	7.66±2.56	5.01±5.02	<LOD	0.05±0.04	1.36±1.81	0.09±0.08	0.01±0.001	<LOD	<LOD	<LOD	25.01±0.81	2.00±0.95	6.44±5.68	98.92±6.15
EC-S9	70.74±8.76	11.83±3.71	17.05±0.46	ND	0	0.65±0.11	ND	0.03±0.03	0.02±0.01	ND	ND	14.12±2.67	5.68±0.46	1.56±0.55	4.28±1.75
EC-WI1	30.12±0.73	50.67±0.44	13.17±9.51	ND	0.12±0.08	3.02±2.80	ND	0.35±0.21	0.03±0.02	ND	ND	107.61±5.87	1.64±0.75	5.81±5.19	9.18±7.08
EC-WI2	90.9±11.20	18.7±0.61	47.8±6.79	<LOD	0.11±0.003	6.15±4.57	0.21±0.02	0.03±0.03	<LOD	ND	ND	17.4±0.88	1.92±0.58	1.97±0.15	3.16±0.23

EC-D1=Treated water; EC-D2=Raw water, EC-D3=Treated water, EC-D4=Raw water; EC-T1=Aspen tap water; EC-T2=Acacia tap water; EC-T3=Motherwell tap water; EC-T4=Cambridge tap water; EC-T5=Abbortsford tap water; EC-T6=Mdantsane tap water; EC-S1=Loerie dam P1; EC-S2=Loerie dam P2; EC-S3= Gamtoos River; EC-S4= Quenera River; EC-S5= Bridle Dam; EC-S6= Nahoon River P1; EC-S7= Nahoon River P2, EC-S8=Buffalo River; EC-S9=Kowie River, EC-WI1=Influent; EC-WE1=Effluent

The second dominant compound was PFHpA followed by PFPeA and 6:2 FTS. The rest of the PFASs followed the order: FHEA (1.95-12.3 ng/L); FHET (1.74-6.1 ng/L); FOET (1.28-4.99 ng/L); PFNA (9.49 ng/L); PFOA (0.05-0.21 ng/L); PFHxA (0.89-2.10 ng/L); L-PFHxS 0.02-0.08 ng/L); L-PFOS (<LOD-0.30 ng/L); and PFHxA (<LOD).

In drinking water treatment plant (Table 3.5) PFBA was the dominant compound at point EC-D2 (108.39 ng/L), followed by site EC-D1 (92.97 ng/L). The order of detection was: PFBA (29.4-108 ng/L); 6:2 FTS (18.5-47.7 ng/L); PFHpA (10.1-33.2) ; PFPeA (6.84-20.7 ng/L); FHET (3.73-41.1 ng/L); FHEA (2.12-20.1 ng/L); PFNA (1.01-8.9 ng/L); FOET (1.72-4.09 ng/L); PFOA (0.07-0.26 ng/L); L-PFHxS (0.04-0.06 ng/L); and L-PFOS (<LOD-0.05 ng/L. The concentrations detected in EC-D1 and EC-D2 were above the 70 ng/L advisory limit from the USEPA.

3.4.2 Establishing the possible sources of the PFASs detected in the water

The dataset of PFASs congeners detected in the water samples were subjected to PCA. Positive correlation was observed for 6:2 FTS, PFHxS, and FOET suggesting similar sources (Figure 3.11). FHET was negatively associated, suggesting different sources. Since some fluorotelomers are known to be a source of PFCAs, the high detection of the fluorotelomers explains the prevalence of PFBA detected in all the water sources.

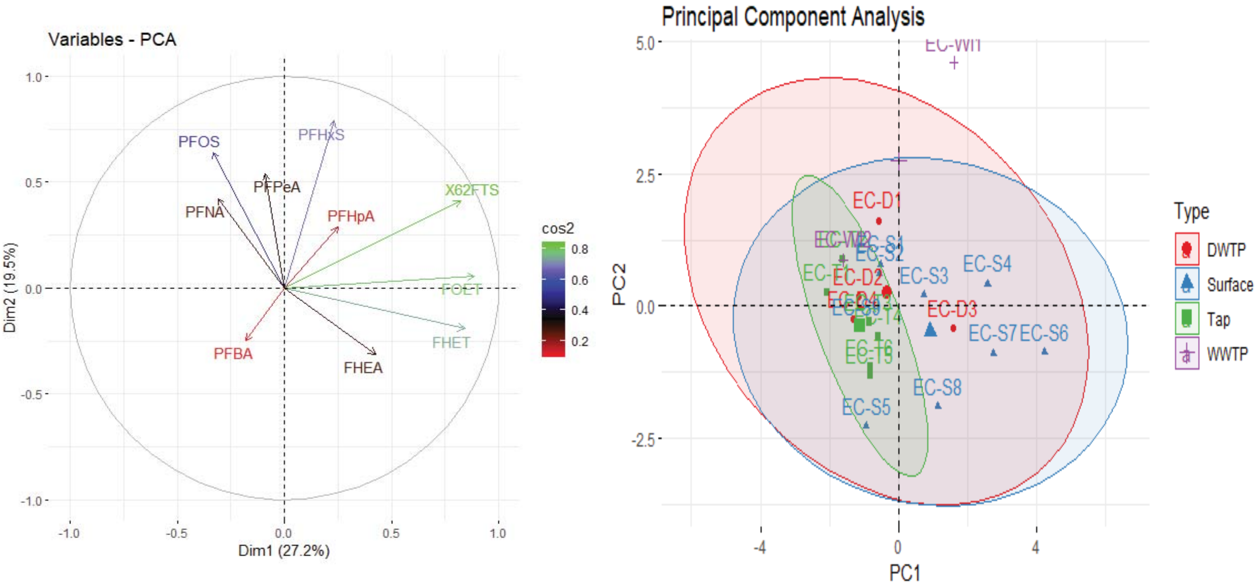

Figure 3.11: PCA of PFASs congener contributions and their relationships and sampling sites and their relationships during the dry season.

This is similar to a study by Yamazaki, 2021, where PFBA was the dominant compound. The high concentrations of 6:2 FTS detected in sites EC-S6 and EC-S7 might be due to sewage contamination, eutrophication and water hyacinth as previously mentioned.

The high PFBA in site EC-S8 could be attributed to some anthropogenic activities, as the site is very close to a beach. In addition, at the time of the sampling, there was a lot of plastic fragments observed inside the water which might also be a contributor in addition to the degradation of Fluorotelomer. As can be seen in Figure 3.11, more sampling sites for drinking water treatment plants and tap water are clustered on the left side of the quadrant, which suggests a similar pattern. Whereas surface water sites are more scattered on the right, including EC-WI1 from a WWTP. Therefore, suggesting a different pattern from the others.

3.5 SUMMARY

The long chain PFASs were detected more than the short chain, although the concentrations of short chain were, in most cases, higher. In addition, the concentrations detected during dry season were higher compared to the concentrations detected in wet season. This might be attributed to non-dilution of high load of pollution entering the water through point and non-point sources during dry season with no rainfall. That long chain were generally detected at low concentrations may be due to their low solubility in water. Furthermore, the restrictions and regulations placed on the long chain PFASs and use of shorter chain as alternatives may have contributed in the observed results in the province. The Eastern Cape was mostly dominated by PFCAs. The detected PFASs results did not exceed the recommended lifetime health advisory of 70 ng/L for PFAS in all the water collected during the wet season, but exceeded during the dry season. The increased concentrations detected in drinking water compared to source water in the wet season and increased concentrations in dry season is a cause for concern. Table 3.6 shows a comparison of the concentrations of PFASs observed in the present study to other studies conducted in different parts of the world. The concentrations detected in this study are lower than the levels reported in Singapore, China, South Africa (Hartbeespoort Dam and Roodeplaat Dam, Vaal River) but higher than the levels reported in Vietnam, Uganda and India.

Table 3.6: Comparison of PFASs concentrations obtained in the current study with other studies

Location	PFAS concs. (means) (ng/L)	Number of PFASs targeted	Reference
China	5.83-120.88	17	Cao et al., 2019
Vietnam	0.09-18	11	Duong et al., 2015
Singapore	1-156		Nguyen et al., 2011
India	1.3-15.9	15	Sharma et al., 2016
Korean rivers and lakes	1.17-40.63	10	Lam et al., 2014
Vaal River, South Africa	<LOD-45.0	14	Groffen et al., 2018
Shandong Province Liaoning Province, China	13.1-69 238 22.4-26 730	19	Chen et al., 2017
Uganda	1.0-14	26	Dalahmeh et al., 2018
Hartbeespoort Dam and Roodeplaat Dam, South Africa	1.38-346.32	20	Batayi et al., 2021
Eastern Cape Province	**<LOD-38.0**	**21**	**This study**

CHAPTER 4: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE FREE STATE PROVINCE

4.1 SAMPLING STRATEGY

4.1.1 Location and description of sampling sites

Water samples were collected from Bloemfontein and surrounding area in the Free State province during both the wet (October-April) and dry (June-August) seasons. These sites were targeted because of massive industrialization and urbanization over the years in the area. The land use map and sampling sites are shown in Figure 4.1. Water samples were collected from the following water sources:

- Bloemspruit River (BF-S1 AND BF-S2);
- Wastewater treatment plant influent (BF-WI) and effluent (BF-W2);
- Drinking water treatment plant raw water (BF-DI) and final treated water (BF-D2)
- Tap water (BF-T1 and BF-T2)

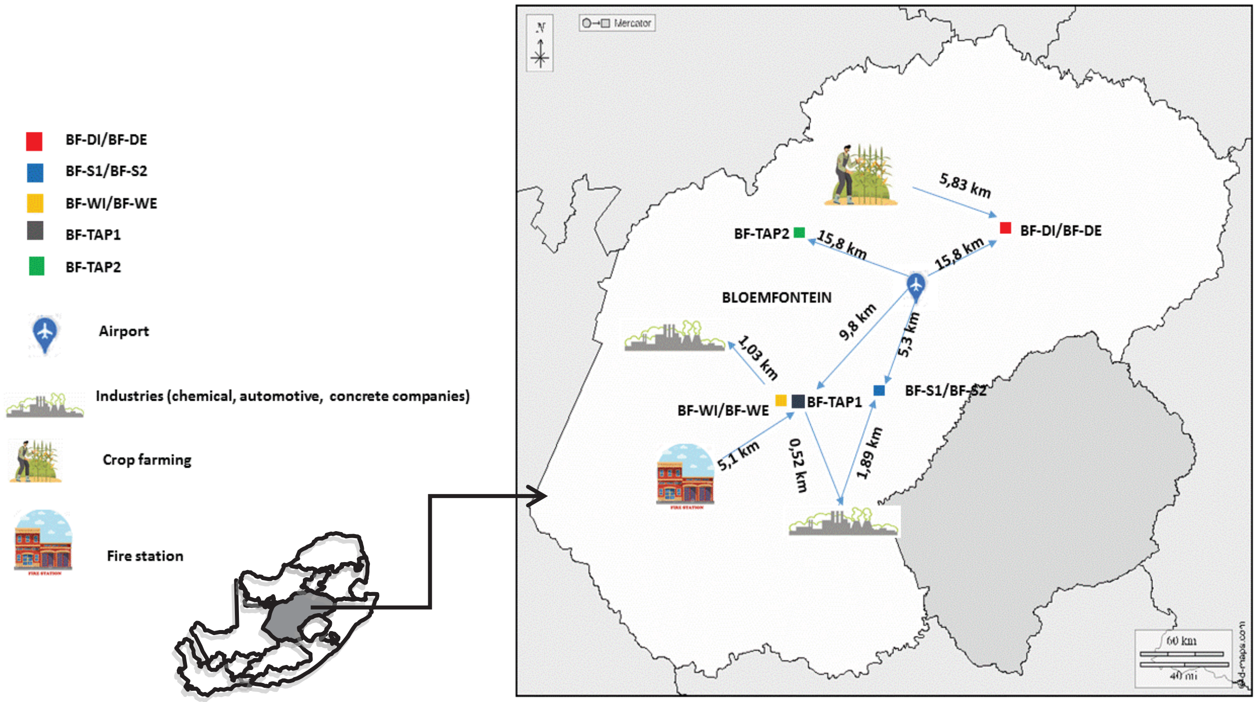

Figure 4.1: Land use map and the sampling sites in Free State Province

4.1.2 Sample collection

Table 4.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the cities. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 4.1 Sampling sites with coordinates in Bloemfontein

Location	Coding	Date	Coordinates
Bloemspruit	*BF-WI	17/05 2022	29^{O} 07^{I} 28^{II} S 29 ^{O} 07^{I} 28^{II} E
	*BF-WE	17/05/2022	
Bloemspruit	*BF-T1	17/05/2022	29.120075 ^{O} S, 26.28340^{O} E
Bloemfontein central	*BF-T2	17/05/2022	29.100000^{O} S, 26.216700^{O} E
Bloemspruit river	*BF-S1	17/05/2022	29^{O} 07^{I} 28^{II} S 29^{O} 07^{I} 28^{II} E
	*BF-S2	17/05/2022	29.12075^{O} S 26.28340 ^{O} E
Maselspoort	*BF-DI	17/05/2022	29^{O} 01^{I} 44^{II} S 26^{O} 24^{I} 26^{II} E
	*BF-DE	17/05/2022	29^{O} 01^{I} 46^{II} S 26^{O} 24^{I} 22^{II} E

4.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. The percentage recoveries of surrogate standards in blanks and samples shown in Table 4.2 ranged from 61.8-107%.

Table 4.2: Percentage recoveries and standard deviation of blanks spiked with surrogate standards in dry season

	Samples – Surrogate recoveries (%) ± Standard deviation
Surrogates	**BL**
MPFNA	78.2±8.12
MPFUdA	61.8±6.49
MPFHxS	107.3±0.62

4.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

4.3.1 Distribution of PFASs in various water sources during the dry season

Table 4.3 shows the mean concentrations of the selected 21 PFASs, which includes both long and short chain PFAS compounds. Concentrations of 6:2 FTS, FOET, and FHET were observed in four sampling locations namely, wastewater treatment plant (n=2), tap (n=2), river (n=2), and drinking water treatment plant (n=2). Furthermore, the three aforementioned compounds were the most prevalent. Mean concentrations of perfluorinated compounds (PFCs) for influent BF-WI and effluent BF-WE plant ranged from 0.132-298.1ng/L and 0.119-225.2 ng/L respectively. Tap water BF-T1 and BF-T2 had concentration ranges of 0.332-253.0 ng/L and 0.205-265.5 ng/L, respectively. This was followed by river water samples upstream and downstream BF-S1 and BF-S2 with the concentration ranges of 0.140-306.7 ng/L and 0.316-187.2 ng/L, respectively. Lastly influent

BF-DI and effluent BF-DE had a range of 0.289-307.1 ng/L and 0.352-241.1 ng/L, respectively. In this study, it was observed that the BF-WI and BF-WE, had concentrations of PFAS that ranged from <LOD-298. 1 ng/L and <LOD-225.2 ng/L, respectively. These mean concentrations were higher than the values reported by Adeleye et al. (2016) and Tavasoli et al. (2021). The observed high concentrations of PFASs in the studied BF-WI and BF-WE in this study was most likely to be attributed to anthropogenic discharges into the Bloemspruit WWTP. The plant treats both industrial and domestic wastes.

With regards to tap water (BF-T1 and BF-T2), river (BF-S1 and BF-S2) and drinking water treatment plants (BF-DI and BF-DE), their mean concentrations ranged from 0.332-265.5 ng/L, 0.140-306.7 ng/L and 0.127-07.1 ng/L respectively. The detected concentrations were higher than the concentrations reported by Guardian et al. (2020) for tap water, but lower than the level for drinking water treatment plant (99-644.6 ng/L in raw water and 6.26-493 ng/L in drinking water) reported by Kim et al. (2020).

Table 4.3: Mean concentrations of PFASs in various water sources in dry season

	BF-WI	BF-WE	BF-T1	BF-T2 (ng/L)	BF-S1	BF-S2	BF-DI	BF-DE
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpA	0.114±0.064	0.155±0.121	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	0.131±0.014	14.75±0.183	<LOD	<LOD	<LOD	8.638±2.509	<LOD	0.352±0.091
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFODA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeA	0.318±0.259	0.119±0.067	LOD	<LOD	0.1407±0.101	<LOD	0.289±0.183	<LOD
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8-2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4-2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBA	**1.37±0.378**	**0.500±0.256**	**0.332±0.052**	**<LOD**	**0.211±0.134**	**0.316±0.175**	**0.217±0.117**	**0.560±0.159**
L-PFHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFOS	<LOD	<LOD	<LOD	<LOD	LOQ	<LOD	<LOD	<LOD
PFOA	<LOd	<LOD	<LOD	<LOD	LOD	<LOD	<LOD	<LOD
L-PFBS	<LOD	<LOD	<LOD	<LOD	LOD	<LOD	<LOD	<LOD
L-PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
LPFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHEA	**1.57±8.624**	**3.41±3.4**	**1.04±0.471**	**0.205±0.071**	**<LOD**	**LOD**	**0.819±0.117**	**0.934±0.709**
6-2 FTS	**298.1±68.3**	**123.9±78.905**	**87.4±3.89**	**73.1±9.26**	**190.2±9.61**	**127.3±29.2**	**94.5±3.001**	**4.14±0.60**
FOET	**235.4±95.9**	**225.201±97.10**	**253.1±65.2**	**265.5±24.6**	**306.7±43.6**	**187.2±131.0**	**307.1±130.0**	**241.18±24.7**
FHET	**23.9±0.696**	**107.5±15.04**	**5.10±1.85**	**2.58±1.44**	**21.01±3.89**	**11.1±1.66**	**4.62±0.78[b]**	**3.94±0.60**

BF-WI/BF-WE = Waste water treatment plant influent and effluent; BF-T1/BF-T2 = Tap water; BF-S1/BF-S2 = surface water down stream and upstream; BF-DI/BF-DE = Drinking water treatment plant influent and effluent; BF=Bloemfontein, W=waste water, T=Tap water, S=River water, D=drinking treatment plant

The Bloemspruit River registered concentration ranges of 0.140-306.7 ng/L and 0.136-187.2 ng/L for both upstream and downstream respectively. These concentrations are higher than those reported by Fagbayigbo et al. (2018) for the Plankenburg River (62.3-186.4 ng/L). In the current study, 6:2 FTS and FOET and FHET were the most dominant compounds with high concentrations within the sampling points. Most of the other compounds were <LOD. Compounds that were not detected can be attributed to the prevailing weather in the sampling area. For example, it rained during the sampling period and this may have affected the non-detection of other compounds. The grab sampling method used in the current study only gives a snap shot at that particular time. (Tapie et al., 2011; Godlewska et al., 2021).

Figure 4.2 shows a scatter plot of PFASs concentrations against the contribution of PFASs congeners in various water sources. The wastewater PFASs contributed most followed by surface water. There are some clustering at <10% contribution. Furthermore, PFASs concentrations in WWTP and surface water were dominant above 70 ng/L for PFOS+PFOA set limit by the USEPA.

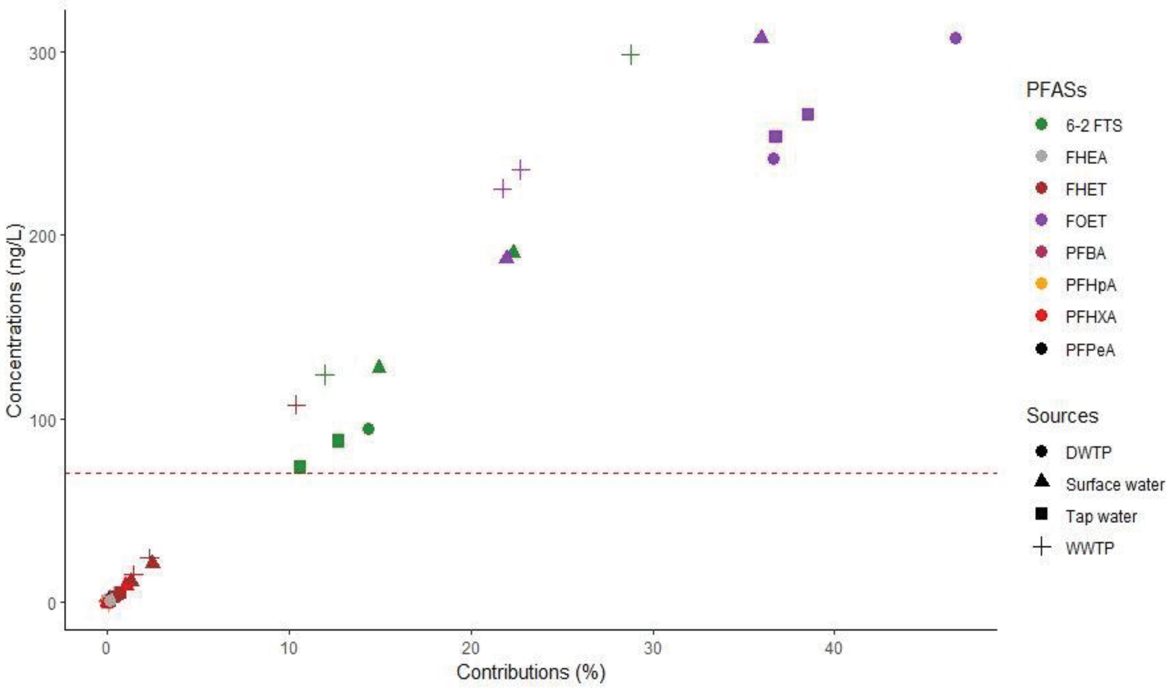

Figure 4.2: PFASs concentration distributions for various water sources in the Free Strate during the dry season

A log based Scatter plot was constructed to determine the influence of different water sources (% contribution) on the concentrations of PFASs. It can be seen in Figure 4.2 that there is a relationship between % contribution and concentration of PFASs (Positive correlation). This suggests that as the contribution of PFASs congeners in different sources increased with increase in PFASs concentration. High concentration were observed between FOET and 6-2 FTS from the four water sources with log concentration of more than 2^6. Similar trend was observed with FHET, PFBA, PFHxA which had log concentration of more than 2^1. The presence of PFASs determined in the present study may have been influenced by the anthropogenic activities taking place within the vicinity of sampled different water sources (Figure 4.1). For example, the military base, airport and firefighting stations around sampling sites may have been using fluorotelomers, especially in firefighting foams.

Figures 4.3, 4.4 and 4.5 illustrate the contributions of PFASs in different water sources, PFASs class contributions and short- and long-chain PFASs from various water sources, respectively.

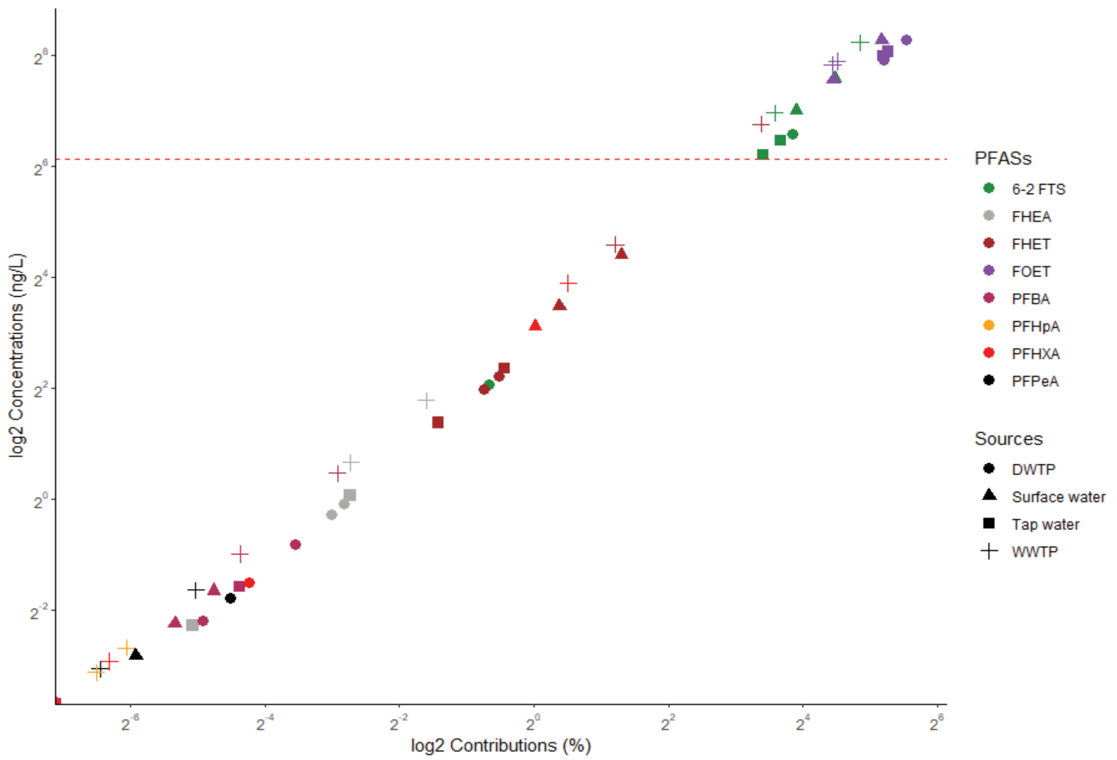

Figure 4.3: PFASs concentration distributions in log base for various water sources in the Free State during the dry season.

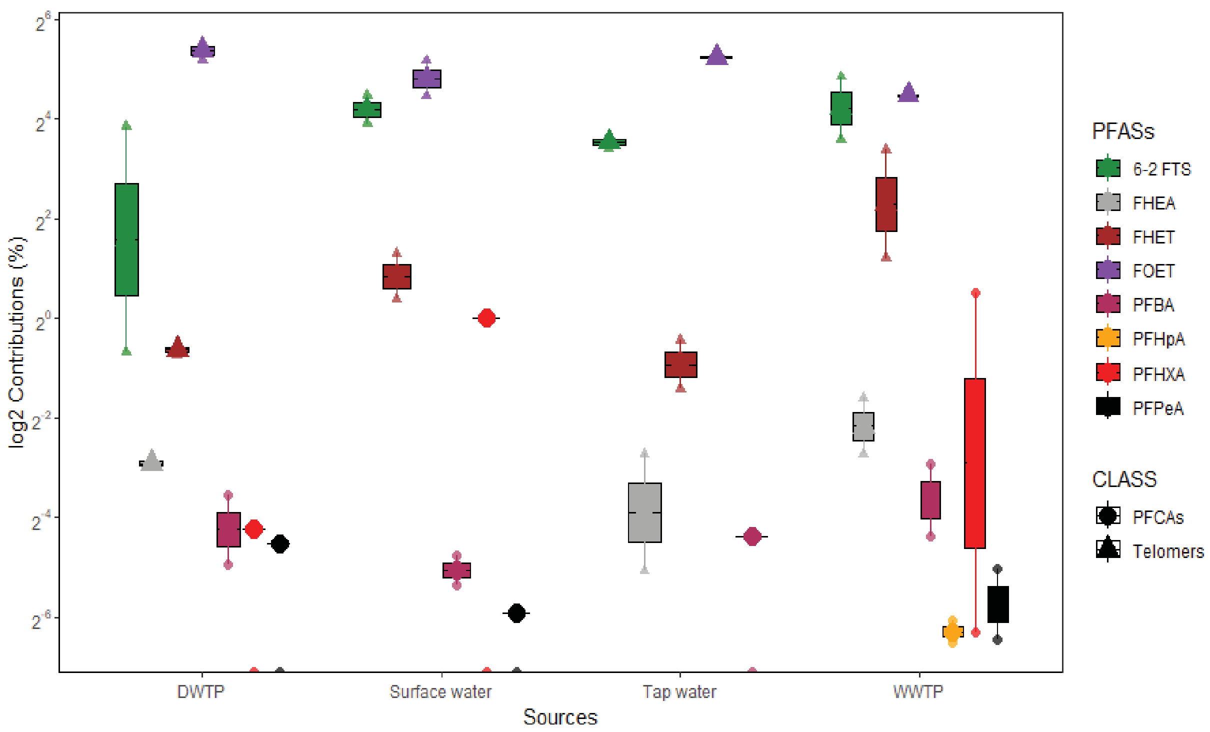

Figure 4.4: PFASs class contributions for various water sources in the Free State during the dry season.

In Figure 4.4 drinking water treatment plant (DWTP) was dominated by telomers which is represented by squares. 6-2 FTS exhibited the highest % contributing compared to other telomers. PFCAs had lower % contribution which was lower than Log 2°. In surface water, 6-2 FTS, FOET and FHET were the most dominant compared to PFCAs with log contribution of more than 2°. Similar trend was also observed with tap water and wastewater treatment plant. In Figure 4.5, it is evident that the short chain PFASs were the most dominant compared to long chain PFASs. PFHpA was the only long chain detected in wastewater treatment plant (WWTP). PFBA, PFHxA, PPFeA, were the most contributing short chain PFASs in drinking water treatment plant. Similar trend was also observed in surface water; however, the % contribution of short chain PFASs were lower in DWTP. On the other hand, in the tap water, PFBA was the only short chain detected with log contribution of 2^6.

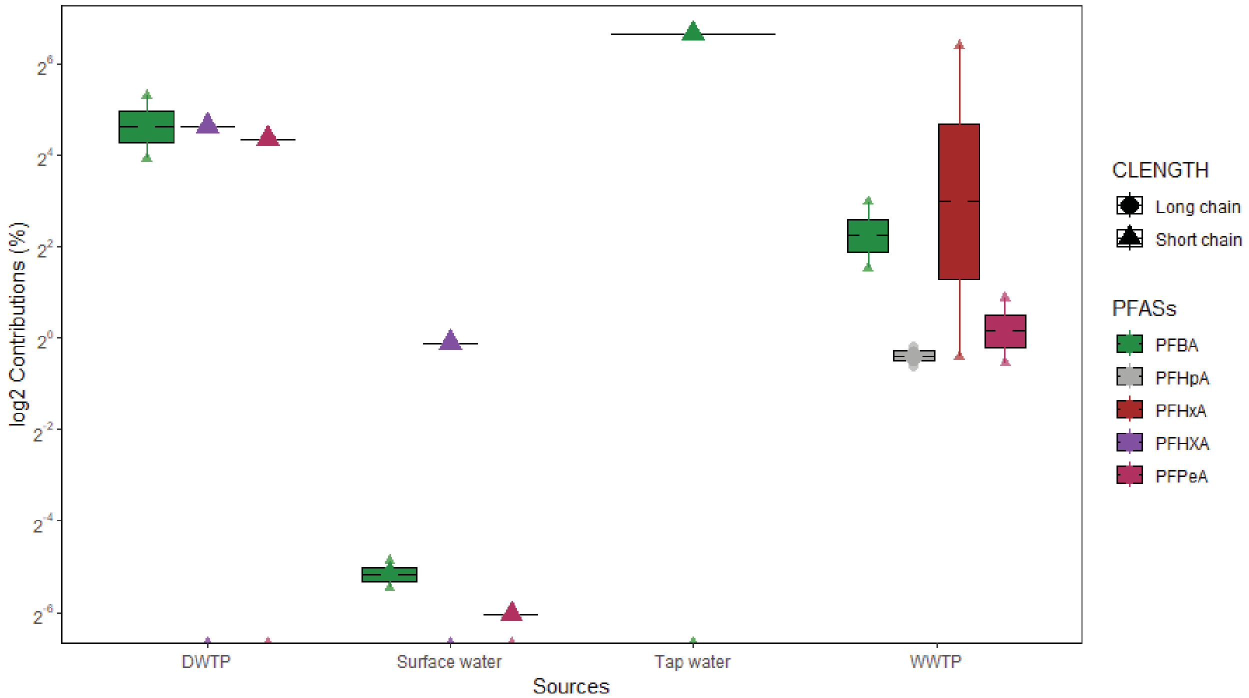

Figure 4.5: Contributions of short- and long-chain PFASs for various water sources in Free State during the dry season.

4.3.2 Establishing the possible sources of the PFASs detected in the water

Principal component analysis was constructed to evaluate any relationship between the PFASs compounds and also between the sampling sites. Figure 4.6, shows the PCA of PFASs compounds. As can be seen in Figure 4.6, the following PFASs were correlated: PFHpA, LPFOS, PFBA, 6:2 FTS, PFHxS, PFOA, PFPeA and FHEA (first quadrant – clockwise); suggesting possible similar sources; whereas PFHxA and FOET were outlayers in quadrants 2 and 4, suggesting different sources from the other PFASs. Interestingly, PFBA, a short chain is clustered with another short chain, PFPeA, and long chain PFOA and PFOS. The presence of FHEA may have contributed to the formation of PFBA as well as PFOA. The presence of 6:2 FTS may have contributed to PFOS since this is one of the precursors of sulphonic acids of PFASs.

Significant industrial sectors in Bloemfontein include retail & trade, manufacturing and transport. Sectors such as agriculture and mining contribute a small portion to the local economy (Figure 4.1). Once again, the detection of PFASs in the water samples from the sampling sources may have originated from the use of

PFASs-containing products. For example, PFBS is used as a surfactant in a variety of applications such as pesticides, textile and others. The application of PCA to the sampling sites, gives a picture of cluster formations as shown in Figure 4.6. BF-D1/ BF-S1, BF-T1/BF-T2/BF-DE, BF-S2/BF-WE, and BF-W1 formed a single cluster. This clustering suggested that the site had similar sources of contamination and it was noted that the sites had similar concentrations of PFASs, and may be receiving PFASs from the same source, storm water, domestic wastewater and others.

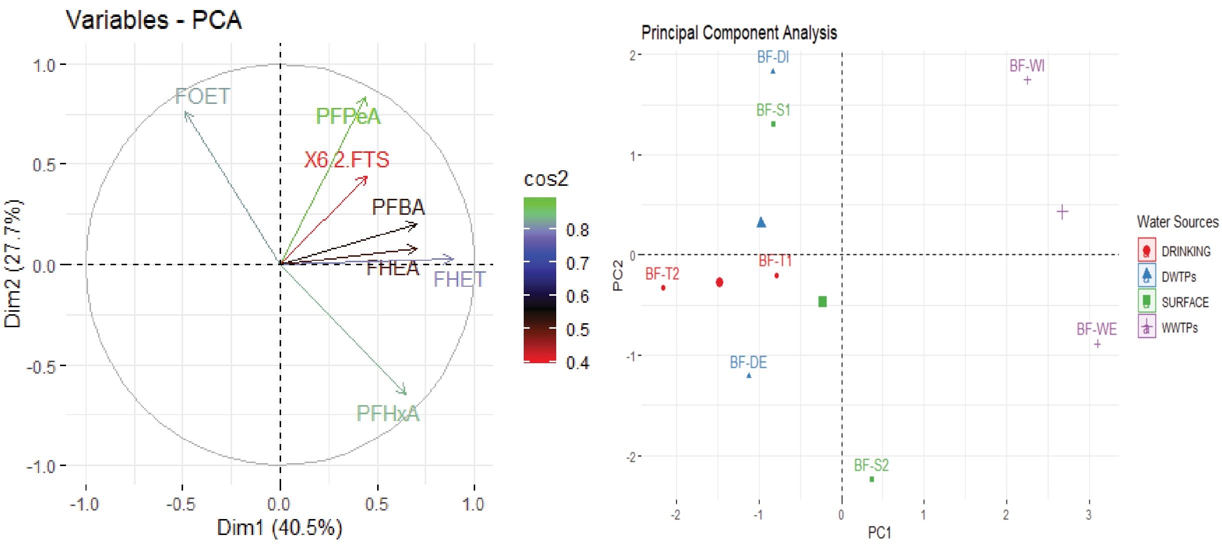

Figure 4.6: PCA of PFASs congener contributions and their relationships, and sampling sites and their relationships during the dry season.

4.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

4.4.1 Distribution of PFASs in various water sources during the wet season

Table 4.4 represents the mean concentrations of PFASs detected in different water sources in Free State (Bloemfontein) in wet season. The mean concentration levels detected from different water sources namely drinking water treatment plant(BF-DI/DE), surface water (BF-S1/S2), tap water (BF-T1/T2)) and wastewater treatment plant (BF-WI/WE) were in the following range, 0.11-82.2 ng/L, 0.14-82.3 ng/L, 0.02-94.6 ng/L and 0.28-108.5 ng/L, respectively. Furthermore, compounds detected in highest concentrations were PFPeA, PFHpA, 6-2 FTS and FHET with mean concentration of 63.9 ng/L, 82.2 ng/L, 94.6 ng/L and 108.5 ng/L, respectively for different water sources. The frequently detected compounds from all the water sources were observed with PFBA, PFNA, 6:2FTS, FHEA, FOET and FHET with detection frequency of 100%. The prevalence of these compounds is attributed to the activities taking place within the vicinity of these water sources. The activities surrounding the sampling sites were, airport, firefighting stations and military bases which have been reported to use telomers in firefighting foams.

Table 4.4: Mean concentrations (ng/L) of PFASs in various water sources during the wet season.

	BF-DI	BF-DE	BF-S1	BF-S2	BF-T1	BF-T2	BF-WI	BF-WE
PFHpA	33.81±2,23	24.64±6,73	82.24±2,89	128.33±3,84	30.93±7,31	35.55±0,91	33.93±1,08	ND
PFPeA	**63.87±2.03**	**38.84±6.73**	**26.72±2.89**	**30.27±3.84**	**45.38±7.31**	**48.06±0.91**	**33.06±1.08**	**7.38±0.45**
PFHxA	ND	0.66±0.11	ND	ND	0.27±0.07	ND	ND	ND
PFOA	ND	0.65±0.25	0.15±0.11	0.29±0.13	ND	ND	ND	ND
PFNA	**1.05±0.37**	**42.70±0.82**	**8.46±10.17**	**0.73±0.19**	**0.66±0.55**	**1.72±0.60**	**1.04±0.68**	**0.25±0.15**
L-PFBS	ND	ND	0.42±0.02	0.54±0.23	ND	ND	ND	ND
L-PFHxS	ND	0.13±0.10	0.25±0.06	0.21±0.09	ND	ND	ND	ND
L-PFOS	0.11±0.09	0.14±0.07	0.16±0.03	0.14±0.03	0.02±0.02	0.02±0.01	ND	ND
4:2FTS	ND	ND	ND	ND	ND	ND	ND	ND
8:2FTS	ND	ND	ND	ND	ND	ND	ND	ND
PFBA	**23.31±0.64**	**28.32±1.55**	**25.32±0,75**	**33.43±1.16**	**44.20±0.65**	**22.69±2.88**	**17.02±2.34**	**7.16±0.63**
6:2FTS	**31.62±10.92**	**21.72±5.65**	**45.03±4,45**	**23.27±2.90**	**94.57±8.08**	**133.70±3.09**	**90.15±7.78**	**78.05±0.04**
FHEA	**41.33±1.27**	**50.48±5.24**	**62.76±0,03**	**51.16±30.09**	**29.89±2.81**	**19.08±0.64**	**65.76±6.51**	**15.25±0.87**
FOET	**13.05±1.06**	**11.31±0.41**	**38.16±10.32**	**13.73±0.32**	**14.13±3.95**	**12.07±8.61**	**39.31±6.59**	**20.01±0.23**
FHET	**25.43±10.42**	**18.45±2.94**	**45.69±0.83**	**24.76±2.13**	**12.37±3.04**	**13.14±8.98**	**108.47±8.48**	**40.06±1.79**
PFODA	ND	ND	ND	ND	ND	ND	ND	ND
L-PFDS	ND	ND	ND	ND	ND	ND	ND	ND
LPFHpS	ND	ND	ND	ND	ND	ND	ND	ND
PFBA	ND	ND	ND	ND	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	ND	ND	ND

A translation of the mean concentrations of PFASs presented in Table 4.4, is shown as scatter and box plots in Figures 4.7 and 4.8. A linear trend can be observed in Figure 4.6 with some clustering below 100 ng/L. Once again the PFASs content in WWTP contributed most to the observed PFASs compounds followed by DWTP and surface water. A log base scatter plot was constructed to establish any relationship between source water PFASs concentrations and their contributions to the overall PFASs. A clear linear relationship between contribution and concentration of PFASs (Positive correlation) can be seen in Figure 4.8.

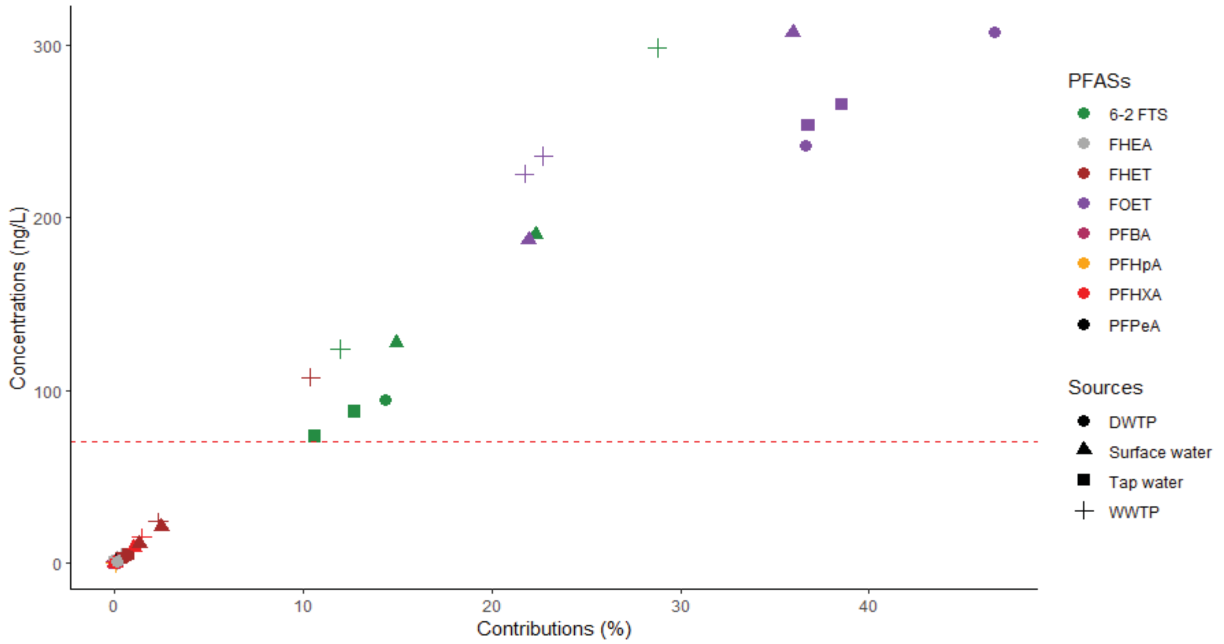

Figure 4.7: PFASs concentration distributions for various water sources in the Free Strate during the wet season.

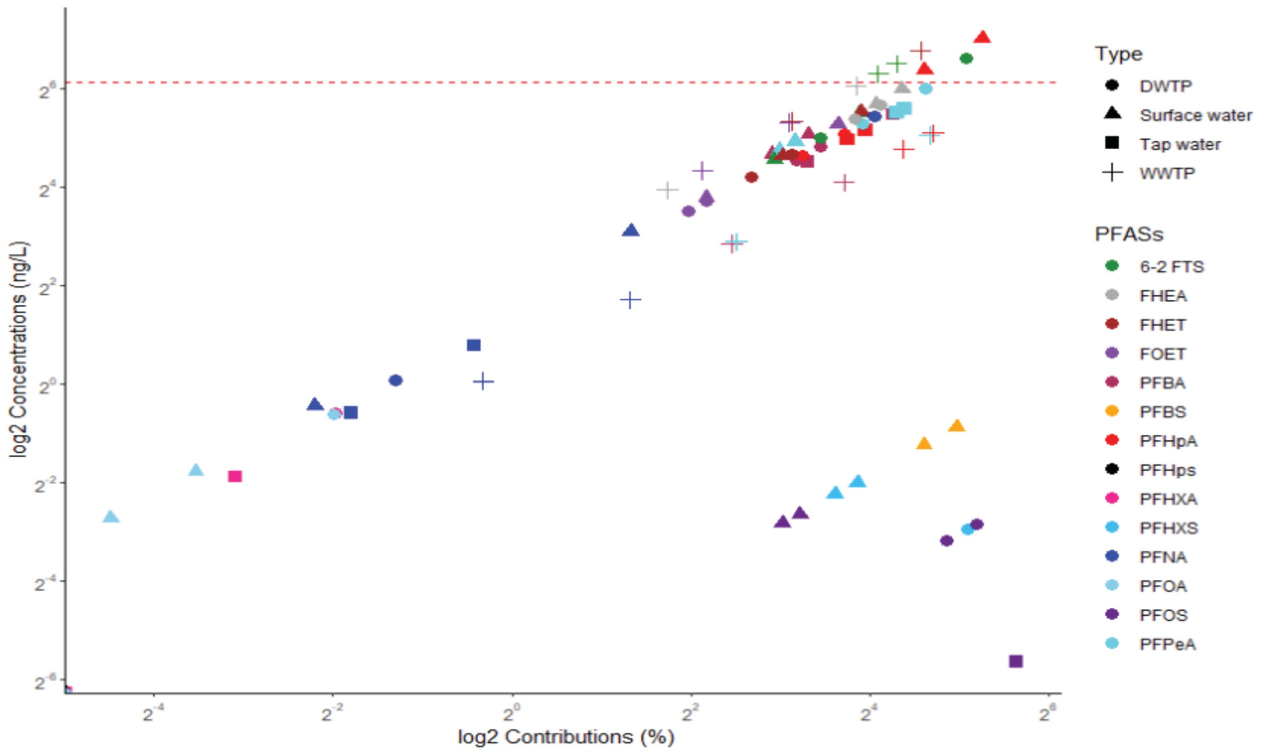

Figure 4.8: PFASs concentrations distributions for various water sources in Free State during the wet season

This suggests that PFASs concentrations increased with increase in contributions from different water sources. High concentrations were observed between PFHpA and 6-2 FTS from the three different water sources namely drinking water treatment plant, surface water and wastewater treatment plant, which had log concentration of more than 2^6. There was also a clustering of PFBS, PFOS and PFHxS in tap water, drinking water treatment plant and surface water, which are outliers.

Figures 4.9 and 4.10 illustrate the class contribution of PFASs and contributions of short and long-chain PFASs in various water sources. In Figure 5.10, drinking water treatment plant (DWTP) was mostly dominated by telomers and with equal contributions of PFCAs and PFSAs; similar trend was also observed in surface water. In tap water, PFCAs classes were dominant compared to PFASs class. PFBA and PFHpA were the highest compound detected in tap water. While wastewater treatment plant (WWTP) was dominated by PFCAs and telomers, comprising PFPeA and PFHpA and (6-2 FTS, FHET and FHEA) respectively.

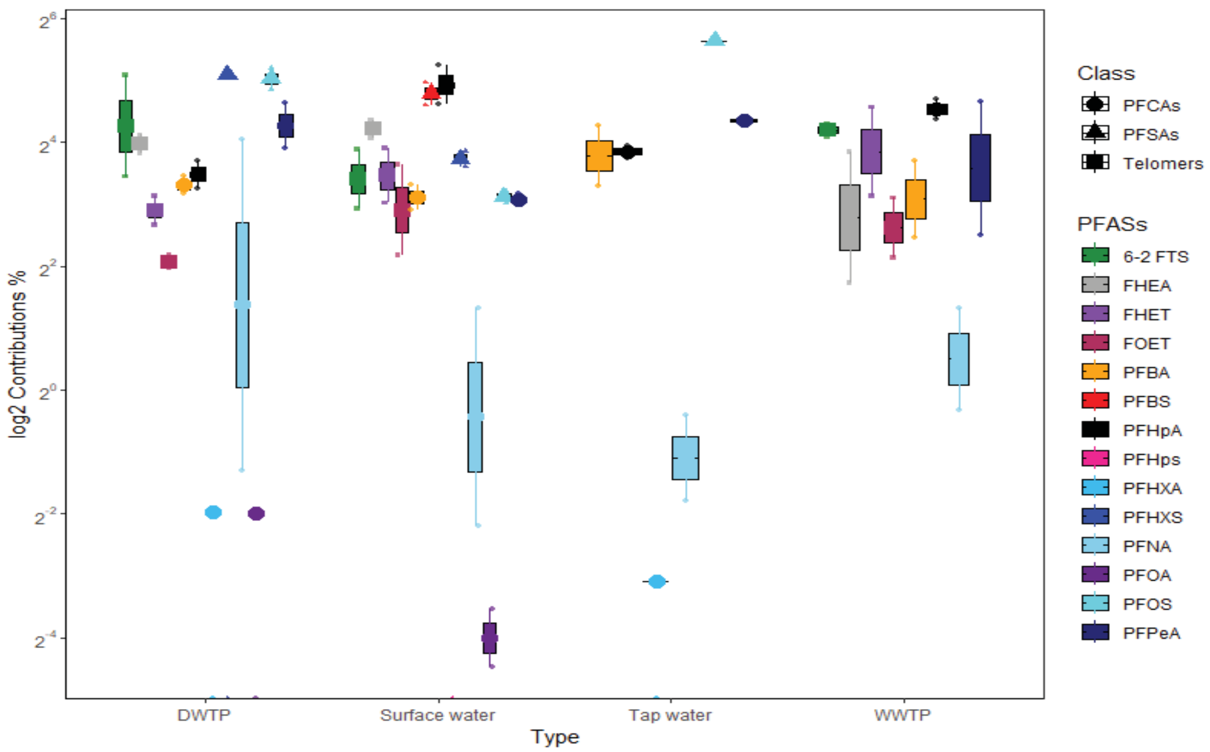

Figure 4.9: PFASs class contributions for various water sources in Free State during the wet season.

In Figure 4.9, it is evident that the short chains PFASs were detected more than long chain PFASs in drinking water treatment plant. The compounds detected were PFHxS, PFPeA and PFBA with log concentration above log 2^0 and other remaining compounds were detected in lower concentrations. Additionally, surface water was also dominated by short chain PFASs. In tap water, there was equal contribution between long and short chain. Wastewater treatment plant was dominated by short chain. The prevalence of short chain PFASs in water sources is due to their high mobility, this result in a fast distribution of these short chain compounds to water sources.

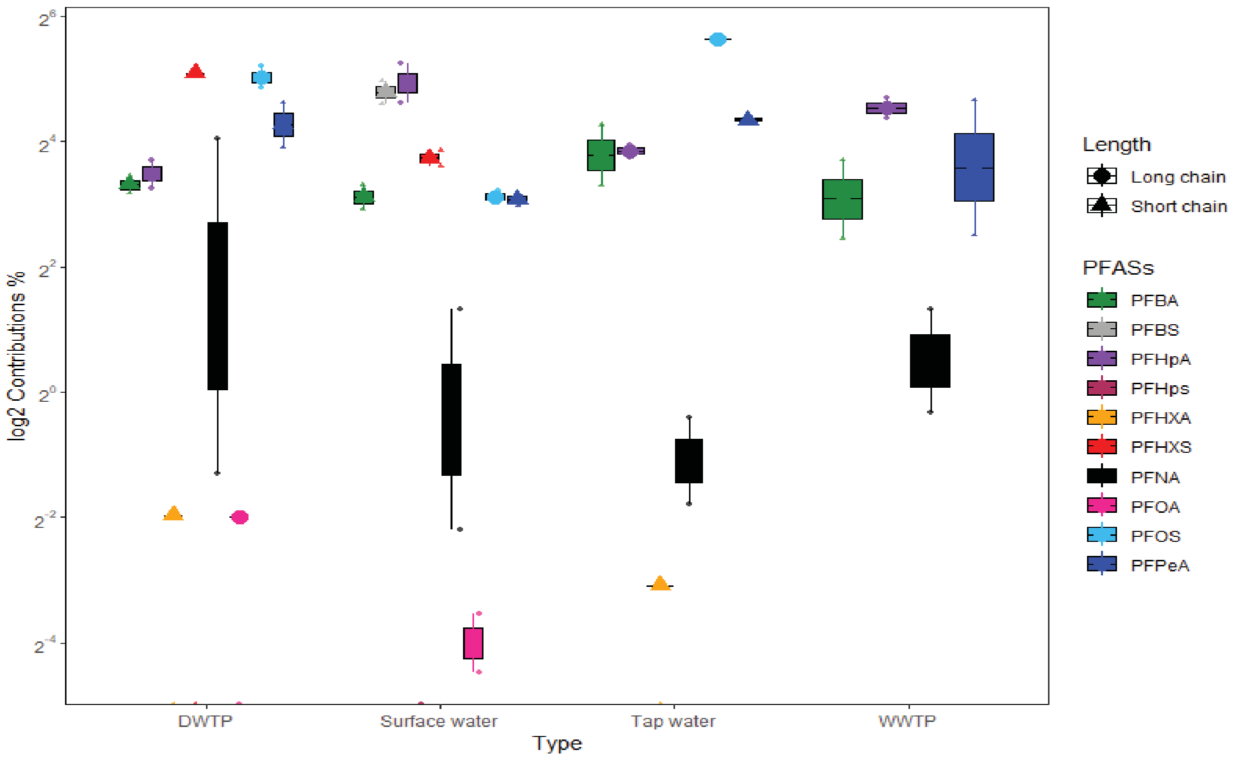

Figure 4.10: Contributions of short- and long-chain PFASs for various water sources in Free State during wet season

4.4.2 Establishing the possible sources of the PFASs detected in the water

Principal component analysis was conducted to assess any relationship among the PFASs congeners and also between the sampling sites. As can be seen in Figure 4.11, the following PFASs are correlated: PFBA and PFPeA (group 1), PFHpA and FHEA; FOET and FHET (group 2) suggesting possible similar sources; whereas PFNA and 6-2 FTS are outliers, suggesting different sources.

Significant industrial sectors in Bloemfontein include, retail and trade, finance, manufacturing and transport. Other sectors such as agriculture and mining contribute a small portion to the local economy. Once again, the detection of PFASs in the water samples from the sampling sites may have originated from the use of PFASs-containing products from any of the aforementioned sources. For example, fluorotelomers are used in firefighting foams, grease resistant food packaging, anti-fogging sprays, textile and others.

The application of PCA to the sampling sites gives a picture of cluster formations as shown in Figure 4.11. BF-D1/ BF-DE, BF-S1/BF-S2, BF-T1/BF-T2 and BF-WI/BF-WE, formed 4 separate clusters. This clustering suggests that the sites had similar sources of contamination and it was also noted that the sites had more or less the same concentrations of PFASs, which may be receiving PFASs from the same sources, storm water, domestic wastewater and others.

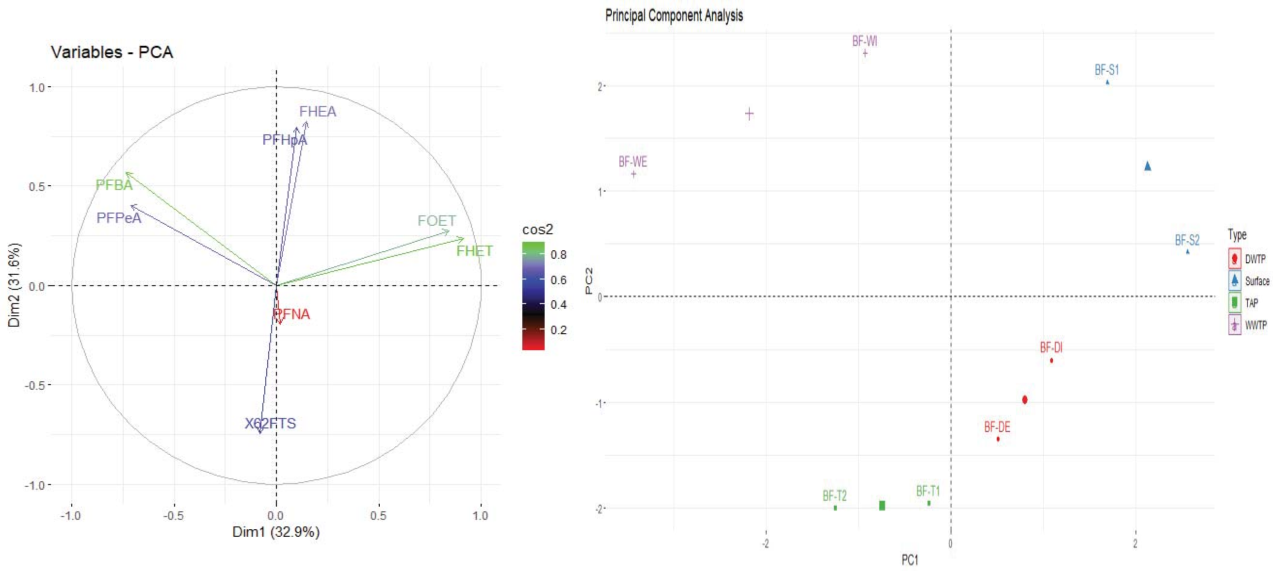

Figure 4.11: PCA of PFASs congener contributions and their relationships, and sampling sites and their relationships in wet season

4.5 SUMMARY

In dry season, fluorotelomer compounds had the highest mean concentrations with a range of <LOD-307 ng/L compared to wet season which had the mean concentrations range of 7.16-108.5 ng/L. Furthermore, 8-2 FTS and 4-2 FTS were quantified below limit of detection in dry season and in wet season were not detected. The mean concentrations from different water sources were comparable. Drinking water treatment plant(BF-DI/DE), surface water (BF-S1/S2), tap water (BF-T1/T2)) and wastewater treatment plant (BF-WI/WE) in wet season had mean concentration range of 0.11-82.2 ng/L, 0.14-82.3 ng/L, 0.02-94.6 ng/L and 0.28-108.5 ng/L, respectively. On the other hand, dry season had mean concentration range of <LOD-225 ng/L. 6-2 FTS for wastewater treatment plant (BF-WI/BF-WE), tap water (BF-T1 and BF-T2) <LOD-266 ng/L, surface water had mean concentration levels of <LOD-306 ng/L and drinking water treatment plant (BF-DI and BF-DE) <LOD-307 ng/L. Table 4.5 shows a comparison of the concentrations of PFASs observed in samples collected from the Free State to other studies conducted in different parts of the world. The concentrations detected in this study were higher than the levels reported in Singapore, China, Vietnam, Uganda and India, but lower than the levels reported in South Africa (Hartbeespoort Dam and Roodeplaat Dam, Vaal River).

Table 4.5: Comparison of PFASs concentrations obtained in the current study with other studies

Location	PFAS concentrations (means) (ng/L)	Number of PFASs targeted	Reference
China	5.83-120.88	17	Cao et al., 2019
Vietnam	0.09-18	11	Duong et al., 2015
Singapore	1-156		Nguyen et al., 2011
India	1.3-15.9	15	Sharma et al., 2016

Location	PFAS concentrations (means) (ng/L)	Number of PFASs targeted	Reference
Korean rivers and lakes	1.17-40.63	10	Lam et al., 2014
Vaal River, South Africa	<LOD-45.0	14	Groffen et al., 2018
Shandong Province Liaoning Province, China	13.1-69 238 22.4-26 730	19	Chen et al., 2017
Uganda	1.0-14	26	Dalahmeh et al., 2018
Hartbeespoort Dam and Roodeplaat Dam, South Africa	1.38-346.32	20	Batayi et al., 2021
Free State Province (WWTP)	0.132-298.1 (influent) 0.119-225.2 (effluent)	21	This study
Free State Province (Tap water)	**0.332-253.0** **0.205-265.5**	**21**	**This study**
Free State Province (River water)	**0.140-306.7** **0.316-187.2**	**21**	**This study**
Free State Province (River water)	**0.289-307.1 (influent)** **0.352-241.1(effluent)**	**21**	**This study**

CHAPTER 5: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE GAUTENG PROVINCE

5.1 SAMPLING STRATEGY

5.1.1 Location and description of sampling sites

- Water samples were collected from Pretoria and the Vaal (southern of Johannesburg) in the Gauteng province during both the wet and dry seasons. Vaal River has, over the years, been at the centre of pollution discussion in the public space because of the various human activities surrounding the river. Pretoria is the administrative centre of South Africa with relatively small industrial activities and, therefore, it presents an important study area. Figure 5.1 shows the land use map and the sampling sites. The following water systems were targeted in the province:
- Surface water (Vaal, Apies, Hennops Rivers, Zeekoegat, A2H029Q01 at Leeuwfontein on Edendalspruit, Pienaars at Moloto Road bridge downstream of Roodeplaat dam**,** A2H027Q01 Pienaars River at Baviaanspoort Klipvoor dam and Hartbeespoort dam); Rietvlei Dam**,** Centurion inlet and outlet;
- Groundwater (Garankuwa boreholes located within the vicinity of landfill site – B);
- Wastewater treatment plant in Pretoria (WWTP – influent and effluent)
- Drinking water Treatment Plant (DWTP);
- Bottled water (BW) and
- Tap water (TW)

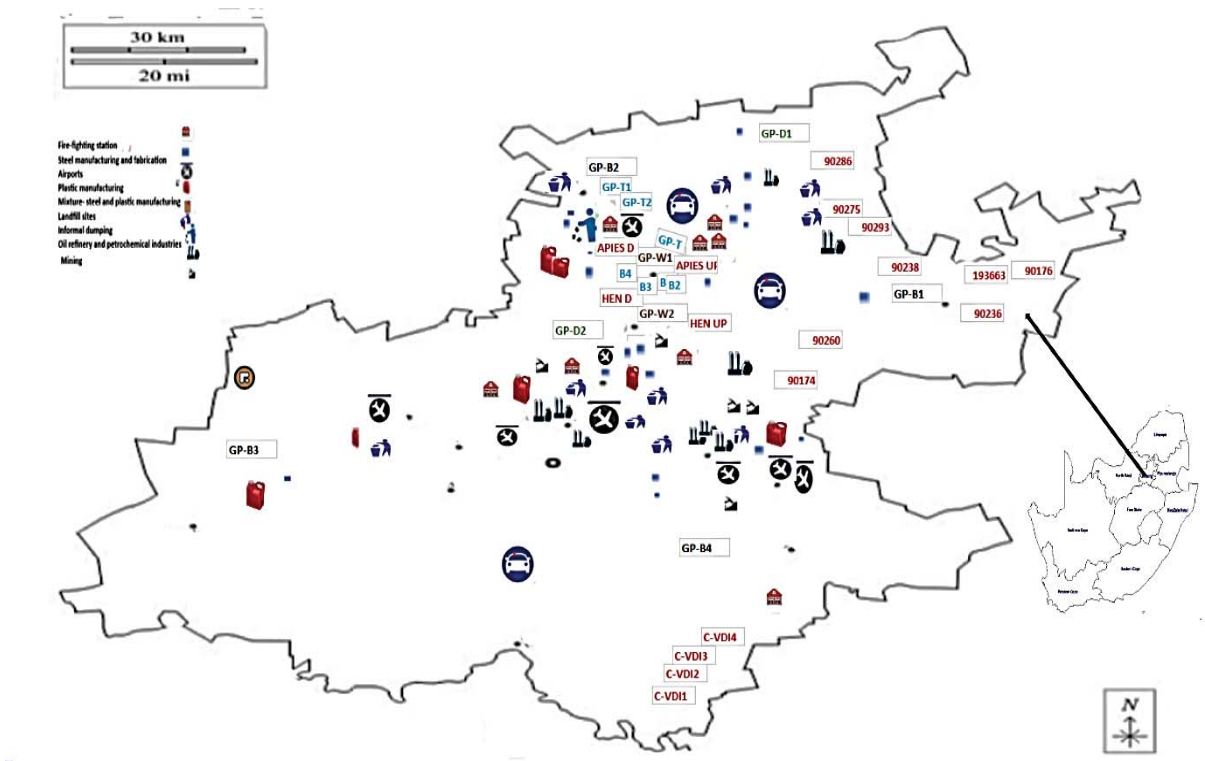

Figure 5.1: Land use map and sampling sites in Gauteng Province.

5.1.2 Sample collection

Table 5.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the cities. Grab and passive samples were collected and prepared for analysis as described in Chapter 2.

Table 5.1: Sampling sites in Gauteng province with coordinates

(Table on next page)

Sampling site	Sampling location	Sample no	Sample ID	Sampling dates	Coordinates/ barcodes
WASTEWATE TREATMENT PLANT					
GP-WWTP2	Final effluent	X2	GP-WE2	04/03/2021	
	Raw water	X2	GP-WI2	04/03/2021	
	SST	X2	GP-WS2	04/03/2021	
	BNR	X2	GP-WB2	04/03/2021	
GP-WWTP1	Final effluent	X2	GP-WE1	14/03/2021	
	Raw water	X2	GP-WI1	14/03/2021	
	SST	X2	GP-WS1	14/03/2021	
	BNR	X2	GP-WB1	14/03/2021	
RIVERS					
Hennops	Downstream	2	HEN D	04/03/2021	Lat: 25°82’88’’S Long: 28°10’28’’E
	Upstream	X2	HEN UP	04/03/2021	Lat: 25°82’70’’S Long:28°10’48’’E
Vaal	Vaal dam integrated @ Raw intake	X2	C-VD1I	26/01/2021	Lat:28ᵒ122’146’ Long:26ᵒ884’589’
				26/01/2021	4665996
	Confluence of Vaal and Wilge River (Vaal Marine Township river	X2	C-VD2I-1	26/01/2021	Lat: 28ᵒ198’882’’ Long: 26ᵒ908’064’’
				26/01/2021	
	Wilge River downstream of Oranjeville	X2	C-VD3I-1	26/01/2021	Lat: 28ᵒ211’645;; S Log:26ᵒ936’795’’ E
				26/01/2021	
	Vaal River upstream of Vaal Marine	X2	C-VD4I-1	26/01/2021	Lat: 28ᵒ286’983’’ S Long:26ᵒ922’762’’E
				26/01/2021	
Apies	Downstream	X2	API D	14/03/2021	Lat: 25°71’60’’S Long: 28°17’57’’E
	Upstream	X2	API UP	14/03/2021	Lat: 25°73’35’’S Long:28°17’76’’E
	A2H027Q01 Pinaars River at Baviaanspoort	X2	90174		
	Zeekogaart	X2	90236		
	A2H029Q01 AT LEEUWFONTEIN ON	X2	90176		

5.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. The percentage recoveries of samples and blanks spiked with surrogate standards are shown in Table 5.2. As can be seen in Table 5.2, the percentage recoveries of the labelled surrogate standards ranged between 40.62-150.10%, with the exception of two low recoveries exhibited in Zeekoegat and Inlet Centurion. It has been suggested that recoveries can and often have a wide range (50-200%), due to matrix effects which can occur in water samples. From Table 5.2, the recoveries of PFASs surrogate generally fall within the accepted range. Shown in Table 5.3 are the mean concentrations of PFASs in blanks with standard deviation. The percentage recoveries ranged from 45-131%. Apart from low percentage recoveries exhibited by samples 90260 and 195445 for MPFNA and MPFUdA respectively, the rest were within the acceptable range.

Table 5.2: Percentage recoveries of samples and blanks spiked with surrogate standards during the wet season

Sample ID	% Mean recoveries	Standard deviation
SB (blank)	77.8	15.6
C-VDI1	71.4	2.07
C-VDI2	90.4	15.0
C-VDI3	71.6	7.98
C-VDI4	67.0	14.5
MOLOTO	93.9	9.63
90174	85.6	4.15
90175	150.1	2.92
90176	90.1	3.67
90236	51.6	3.37
90260	79.0	0.00
90286	74.7	8.09
195443	40.67	7.53
195445	56.0	6.76
AP UP	75.3	4.09
APU	76.7	1.82
AP D	88.2	8.79
HEN U	70.6	25.8
HEN D	100.6	15.8
SST D	102.0	28.2

Sample ID	% Mean recoveries	Standard deviation
SST S	84.0	26.8
RAW D	87.4	5.43
RAW S	108.0	16.2
SB (blank)	96.6	1.75
I	86.9	14.7
II	104.8	17.6
III	102.82	17.2
IV	146.4	10.16
SB (blank)	122.6	0.06
V	80.5	0.68
VI	90.1	5.29
VII	60.9	8.89
VIII	75.50	6.60
USB	<LOD	-

SB = Spiked blank; USB = Unspiked blank; C-VDI1 = Vaal dam integrated @ Raw intake; C-VDI2 =Confluence of Vaal and Wilge River (Vaal Marine Township River; C-VDI3 = Wilge River downstream of Oranjeville; C-VDI4 = Vaal River upstream of Vaal Marine; MOLOTO = Pienaars @ Moloto Road bridge downstream of Roodeplaat dam; 90174 = A2H027Q01 Pienaars River at Baviaanspoort; 90175 = A2H128Q01 at Kameeldrift on Hartebeesspruit; 90176 = A2H029Q01 at Leeuwfontein on Edendalspruit; 90236 = Zeekoegat; 90286 = Klipvoor dam; 195443 = Inlet Centurion; 90260 = Rietvlei Dam; AP UP = Apies River Upstream; APU = Apies River Downstream; HEN U = Hennops River Upperstream; HEN D = ; Hennops River Downstream; SSD = SST Daspoort; SST = Sunderland Ridge; Raw D = RAW Daspoort; RAW S = RAW Sunderland ridge; I = Product A; II = Product B; III = Product C; IV = Product D; V = Tap Water; VII = Inlet Temba; VII = Filters Temba; VIII = Final. Temba.

Table 5.3: Percentage recoveries (%) of PFASs in blanks with and standard deviations in dry season

	SB	90286	90249	90260	193640	195443	193663	195445
MPFNA	78.3±8.12	131±18.8	112±14.9	45.01±12.5	108±14.7	73.6±1.79	95.7±6.09	75.8±21.8
MPFUdA	61.8±6.49	109±7.82	78.3±20.5	111±33.2	110±6.9	93.6±4.62	104±19.4	66.9±1.30
MPFHxS	107±0.61	92.7±13.6	111±6.23	113±23.4	115±17.2	117±16.0	102±9.46	130.9±8.27

5.3 IDENTIFICATION OF TARGET AND NON-TARGET OF PFASS IN VARIOUS WATER SAMPLES

Tables 5.4 to 5.8 show targeted and non-targeted PFASs identified in surface water, wastewater treatment plant, drinking water treatment plant and bottled and tap drinking water using TOF-MS. As can be seen in the Tables, new PFASs were picked up in addition to those in the mixed standard. The fluorotelomers were the prominent new compounds. It is also worth noting that unlike many other PFASs, fluorotelomer alcohols are highly volatile compounds. Consequently, volatilization is a primary transport pathway for these compounds. As they oxidize in the atmosphere, they break down into perfluorinated carboxylic acids, such as PFOA.

From the obtained data, 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) are the most dominant fluorotelomers. Their percentage detection ranged from 30-100 and 0-80 for 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) respectively. Table 5.6 shows the percentage detection of targeted and non-targeted PFASs in wastewater treatment plant. In addition, 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer sulfonate (8:2 FTSA) can be seen to be prominent. As shown in the data, 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) are the most dominant and their percentage detection range from 50-83 and 33-100 for 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer sulfonate (8:2 FTSA) respectively in drinking water treatment plant . However, in Table 5.8, their detections were less than 60% in bottled and tap drinking water.

Congeners such as 6:2 Fluorotelomer sulfonate (6:2 FTSA) and 8:2 Fluorotelomer Sulfonate (8:2 FTSA) are one of the primary and relevant subgroups of fluorotelomers. Fluorotelomer alcohols (FTOH): The n:2 fluorotelomer alcohols (n:2 FTOHs) are key raw materials in the production of n:2 fluorotelomer acrylates and n:2 fluorotelomer methacrylates. Fluorotelomer sulfonic acids (FTSA): The n:2 fluorotelomer sulfonic acids (n:2 FTSAs) are associated with aqueous film forming foam (AFFF), wastewater treatment plant effluents, and landfill leachate. Fluorotelomer carboxylic acids (FTCA). These compounds are known to form through the biodegradation of FTOHs. Other emerging PFASs identified included: perfluorooctane sulphonamide, N-Methyl perfluorooctane sulphonamide, N-Ethyl perfluorooctane sulphonamide; 6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA, 8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA, 6:2 Fluorotelomer carboxylic acid, 8:2 Fluorotelomer carboxylic acid and 10:2 Fluorotelomer carboxylic acid; Perfluorohexyl Iodide and Perfluorooctyl Iodide; 8:2 Fluorotelomer acrylate, 6:2 Fluorotelomer methacrylate and 8:2 Fluorotelomer methacrylate; Perfluoro-2-methoxyacetic acid, Perfluoro-3-methoxypropanoic acid, Perfluoro-4-methoxybutanoic acid, Perfluoro-2-propoxypropanoic acid, Perfluoro(3.5-dioxahexanoic) acid, Perfluoro(3.5.7-trioxaoctanoic) acid and Perfluoro (3.5.7.9-tetraoxadecanoic) acid.

Table 5.4: Targeted and non-targeted PFASs in surface water samples

Surface water		**API D**	**API UP**	**HEN UP**	**HEN D**	**C-VD1I**	**C-VD21**	**C-VD3I**	**C-VD4I**	**90236**	**90176**	
Compound Name	Formula	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detection frequency%
(PFBA)	$C_4HF_7O_2$	√	√	√	√	√	√	√	√	√	√	100
(PFPeA)	$C_5HF_9O_2$	√	√	√	√	√	√	√	√	√	√	100
PFHxA	$C_6HF_{11}O_2$	√	√	√	√	√	√	√	√	√	√	100
PFHpA	$C_7HF_{13}O_2$	√	√	√	√	√	√	√	√	√	√	100
PFOA	$C_8HF_{15}O_2$	√	√	√	√	√	√	√	√	√	√	100
PFNA	$C_9HF_{17}O_2$	√	√	√	√	√	√	√	√	√	√	100
PFDA	$C_{10}HF_{19}O_2$	√	√	√	√	√	√	√	√	√	√	100
PFUdA	$C_{11}HF_{21}O_2$	√	√	√	√	N/A	√	√	√	√	√	90
PFDoA	$C_{12}HF_{23}O_2$	√	√	√	√	√	N/A	√	N/A	N/A	√	70
PFTrDA	$C_{13}HF_{25}O_2$	N/A	√	√	√	√	N/A	√	N/A	N/A	√	60
PFTeDA	$C_{14}HF_{27}O_2$	√	√	√	√	√	√	√	√	√	√	100
L-PFBS	$C_4HF_9O_3S$	√	√	√	√	√	√	√	√	√	√	100
L-PFHxS	$C_6HF_{13}O_3S$	√	√	√	√	√	√	√	√	√	√	100
L-PFOA	$C_8HF_{17}O_3S$	√	√	√	√	√	√	√	√	√	√	100
L-PFDS	$C_{10}HF_{21}O_3S$	√	√	√	√	√	√	√	√	√	√	100
L-PFHpS	$C_7F_{15}SO_3H$	√	√	√	√	√	√	√	√	√	√	100
L-PFNS	$C_9F_{19}SO_3H$	√	N/A	√	√	N/A	N/A	√	√	N/A	√	60
L-PFDoS	$C_{12}HF_{25}O_3S$	N/A	√	N/A	N/A	N/A	N/A	N/A	√	N/A	N/A	20
L-PFPeS	$C_5F_{11}SO_3H$	√	√	√	√	√	√	√	√	√	√	100

Non target compounds												
4:2 Fluorotelomer sulfonic sulfonate 4:2 FTSA	$C_6H_5F_9O_3S$	√	√	√	√	N/A	√	√	N/A	√	√	80
6:2 Fluorotelomer sulfonate (6:2 FTSA)	$C_8H_5F_{13}O_3S$	√	√	√	√	√	√	√	√	√	√	100
8:2 Fluorotelomer Sulfonate (8:2 FTSA)	$C_{10}H_4F_{17}O_3S$	√	√	√	√	N/A	√	√	N/A	√	√	80
Perfluorooctane sulfonamide (FOSA)	$C_8H_2F_{17}NO_2S$	√	√	√	√	√	√	√	√	√	√	100
N-Methyl perfluorooctane sulfonamide (MeFOSA)	$C_9H_4F_{17}NO_2S$	N/A	√	N/A	√	N/A	√	√	√	√	√	70
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	$C_{10}H_6F_{17}NO_2S$	√	√	√	√	N/A	√	√	√	√	√	90
6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA	$C_8H_2F_{12}O_2$	√	√	√	√	N/A	√	√	√	√	√	90
8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA	$C_{10}H_2F_{16}O_2$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
6:2 Fluorotelomer carboxylic acid (6:2 FTCA)	$C_6F_{13}CH_2COOH$	√	√	√	√	√	N/A	N/A	N/A	N/A	N/A	50
8:2 Fluorotelomer carboxylic acid (8:2 FTCA)	$C_8F_{17}CH_2COOH$	√	N/A	√	√	√	N/A	N/A	N/A	N/A	N/A	30
10:2 Fluorotelomer carboxylic acid (10: 2 FTCA)	$C_{10}F_{21}CH_2COO H$	√	N/A	√	√	N/A	√	√	N/A	√	√	70
6:2 Fluorotelomer alcohol (6:2 FTOH)	$C_8H_5F_{13}O$	√	N/A	√	√	N/A	√	√	N/A	√	√	30
Perfluorohexyl Iodide PFHxI	$C_6F_{13}IH$	N/A	N/A		N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluorooctyl Iodide PFOI	$C_8F_{17}IH$	N/A	N/A		√	√	√	N/A	N/A	√	N/A	50
8:2 Fluorotelomer acrylate (8:2 FTAC)	$C_{13}H_7F_{17}O_2$	√	N/A	√	√	√	√	√	N/A	√	√	80

6:2 Fluorotelomer methacrylate (6:2 FTAC)	$C_{12}H_9F_{13}O_2$	√	N/A	√	√	√	√	√	N/A	√	√	80
8:2 Fluorotelomer methacrylate (8:2 FTMAC)	$C_{14}H_9F_{17}O_2$	√		√	√	√	√	√	N/A	N/A	√	80
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	√	N/A	√	√	N/A	√	√	√	√	√	80
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	√	N/A	√	√	√	√	√	√	√	√	90
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	√	N/A	√	√	N/A	√	√	N/A	√	√	70
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	√	N/A	√	√	N/A	√	√	N/A	√	√	70
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	√	N/A	N/A	√	N/A	N/A	√	N/A	√	√	50
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	√	N/A	√	√	N/A	√	√	√	√	√	80

Table 5.5: Targeted and non-targeted PFASs in surface water

Surface water		**90293**	**MLT**	**90174**	**90236**	**90286**	193663	**90260**	**195445**	**195443**	
Compound Name	Formula	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detected	Detection frequency %
(PFBA)	$C_4HF_7O_2$	√	√	√	√	√	√	√	√	√	100
(PFPeA)	$C_5HF_9O_2$	√	√	√	√	√	√	√	√	√	100
PFHxA	$C_6HF_{11}O_2$	√	√	N/A	√	√	√	√	√	√	88.89
PFHpA	$C_7HF_{13}O_2$	√	√	√	√	√	√	√	√	√	100
PFOA	$C_8HF_{15}O_2$	√	√	√	√	√	√	√	√	√	100
PFNA	$C_9HF_{17}O_2$	√	√	√	√	√	N/A	N/A	N/A	N/A	55.56
PFDA	$C_{10}HF_{19}O_2$	√	√	√	√	√	√	√	N/A	N/A	77.78
PFUdA	$C_{11}HF_{21}O_2$	√	√	√	√	√	√	N/A	√	√	88,89
PFDoA	$C_{12}HF_{23}O_2$	N/A	N/A	√	√	√	√	N/A	N/A	N/A	44.44
PFTrDA	$C_{13}HF_{25}O_2$	N/A	N/A	√	N/A	N/A	N/A	N/A	N/A	N/A	11.11
PFTeDA	$C_{14}HF_{27}O_2$	√	N/A	√	N/A	N/A	N/A	N/A	N/A	N/A	22.22
L-PFBS	$C_4HF_9O_3S$	√	√	√	√	√	N/A	√	√	N/A	77.77
L-PFHxS	$C_6HF_{13}O_3S$	√	√	√	√	√	N/A	N/A	N/A	N/A	55.56
L-PFOA	$C_8HF_{17}O_3S$	√	√	√	√	√	N/A	N/A	N/A	N/A	55.56
L-PFDS	$C_{10}HF_{21}O_3S$	√	N/A	√	√	√	N/A	√	N/A	N/A	55.56
L-PFHpS	$C_7F_{15}SO_3H$	√	√	√	N/A	N/A	N/A	√	N/A	N/A	44.44
L-PFNS	$C_9F_{19}SO_3H$	√	√	√	N/A	N/A	N/A	√	√	√	66.67
L-PFDoS	$C_{12}HF_{25}O_3S$	√	N/A	√	N/A	N/A	N/A	N/A	N/A	N/A	22.22
L-PFPeS	$C_5F_{11}SO_3H$	√	N/A	√	N/A	N/A	N/A	N/A	N/A	N/A	22.22

					Non-targeted PFASs						
4:2 Fluorotelomer sulfonic sulfonate 4:2 FTSA	$C_6H_5F_9O_3S$	N/A	√	N/A	N/A	N/A	N/A	N/A	N/A	N/A	11.11
6:2 Fluorotelomer sulfonate (6:2 FTSA)	$C_8H_5F_{13}O_3S$	√	√	√	N/A	N/A	√	√	√	√	77,77
8:2 Fluorotelomer Sulfonate (8:2 FTSA)	$C_{10}H_4F_{17}O_3S$	N/A	√	N/A	√	√	√	√	√	√	77.77
Perfluorooctane sulfonamide (FOSA)	$C_8H_2F_{17}NO_2S$	√	√	N/A	N/A	N/A	√	√	√	√	66.67
N-Methyl perfluorooctane sulfonamide (MeFOSA)	$C_9H_4F_{17}NO_2S$	√	√	N/A	N/A	N/A	N/A	N/A	N/A	N/A	22.22
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	$C_{10}H_6F_{17}NO_2S$	√	√	N/A	N/A	N/A	N/A	N/A	N/A	N/A	22.22
6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA	$C_8H_2F_{12}O_2$	√	N/A	N/A	√	√	√	√	N/A	N/A	55.56
8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA	$C_{10}H_2F_{16}O_2$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	√	√	22.22
6:2 Fluorotelomer carboxylic acid (6:2 FTCA)	$C_6F_{13}CH_2COOH$	N/A	√	N/A	√	√	N/A	√	N/A	N/A	44.44
8:2 Fluorotelomer carboxylic acid (8:2 FTCA)	$C_8F_{17}CH_2COOH$	N/A	N/A	N/A	N/A	N/A	N/A	√	N/A	N/A	11.11
10:2 Fluorotelomer carboxylic acid (10: 2 FTCA)	$C_{10}F_{21}CH_2COOH$	N/A	N/A	√	√	√	N/A	√	N/A	N/A	44.44
6:2 Fluorotelomer alcohol (6:2 FTOH)	$C_8H_5F_{13}O$	N/A	√	N/A	N/A	N/A	N/A	N/A	√	√	33.33

Perfluorohexyl Iodide PFHxI	$C_6F_{13}IH$	N/A	√	N/A	N/A	N/A	N/A	√	N/A	N/A	22.22
Perfluorooctyl Iodide PFOI	$C_8F_{17}IH$	N/A	√	N/A	√	√	√	√	√	√	22.22
8:2 Fluorotelomer acrylate (8:2 FTAC)	$C_{13}H_7F_{17}O_2$	N/A	√	N/A	N/A	N/A	N/A	√	√	√	44.44
6:2 Fluorotelomer methacrylate (6:2 FTAC)	$C_{12}H_9F_{13}O_2$	N/A	√	N/A	N/A	N/A	√	√	√	√	55,56
8:2 Fluorotelomer methacrylate (8:2 FTMAC)	$C_{14}H_9F_{17}O_2$	N/A	N/A	N/A	N/A	N/A	N/A	√	√	√	33.33
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	√	√	√	N/A	N/A	N/A	N/A	N/A	N/A	33.33
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	√	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	11.11
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	N/A	√	N/A	√	√	N/A	N/A	√	√	55.56
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	C6HF11O6	√	√	N/A	N/A	N/A	N/A	N/A	N/A	N/A	22.22

Table 5.6: Targeted and non-targeted PFASs in wastewater treatment plant

Wastewater Treatment plants		**FINAL D**	**FINAL S**	**SST D**	**SST S**	**RAW D**	**RAW S**	
Compound Name	Formula	Detected	Detected	Detected	Detected	Detected	Detected	Detection frequency %
(PFBA)	$C_4HF_7O_2$	√	√	√	√	√	√	100
(PFPeA)	$C_5HF_9O_2$	√	√	√	√	√	√	100
PFHxA	$C_6HF_{11}O_2$	√	√	√	√	√	√	100
PFHpA	$C_7HF_{13}O_2$	√	√	√	√	√	√	100
PFOA	$C_8HF_{15}O_2$	√	√	√	√	√	√	100
PFNA	$C_9HF_{17}O_2$	√	√	√	√	√	√	100
PFDA	$C_{10}HF_{19}O_2$	√	√	√	√	√	√	100
PFUdA	$C_{11}HF_{21}O_2$	√	√	√	√	√	√	100
PFDoA	$C_{12}HF_{23}O_2$	N/A	√	N/A	√	√	√	66.7
PFTrDA	$C_{13}HF_{25}O_2$	N/A	√	N/A	√	√	√	66.7
PFTeDA	$C_{14}HF_{27}O_2$	√	√	√	√	√	√	100
L-PFBS	$C_4HF_9O_3S$	√	√	√	√	√	√	100
L-PFHxS	$C_6HF_{13}O_3S$	√	√	√	√	√	√	100
L-PFOA	$C_8HF_{17}O_3S$	√	√	√	√	√	√	100
L-PFDS	$C_{10}HF_{21}O_3S$	√	√	√	√	√	N/A	83.3
L-PFHpS	$C_7F_{15}SO_3H$	√	√	√	√	√	√	100
L-PFNS	$C_9F_{19}SO_3H$	N/A	√	√	√	√	√	83.3
L-PFDoS	$C_{12}HF_{25}O_3S$	N/A	N/A	√	N/A	√	N/A	33,3
L-PFPeS	$C_5F_{11}SO_3H$	√	√	√	N/A	√	N/A	66.7

				Non-targeted PFASs				
4:2 Fluorotelomer sulfonic sulfonate 4:2 FTSA	$C_6H_5F_9O_3S$	√	√	N/A	√	√	√	83.3
6:2 Fluorotelomer sulfonate (6:2 FTSA)	$C_8H_5F_{13}O_3S$	√	√	√	√	√	√	100
8:2 Fluorotelomer Sulfonate (8:2 FTSA)	$C_{10}H_4F_{17}O_3S$	√	√	N/A	√	√	√	83.3
Perfluorooctane sulfonamide (FOSA)	$C_8H_2F_{17}NO_2S$	√	√	√	√	√	√	100
N-Methyl perfluorooctane sulfonamide (MeFOSA)	$C_9H_4F_{17}NO_2S$	√	√	√	√	√	√	100
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	$C_{10}H_6F_{17}NO_2S$	√	√	√	√	√	√	100
6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA	$C_8H_2F_{12}O_2$	√	√	√	N/A	√	√	83.3
8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA	$C_{10}H_2F_{16}O_2$	N/A	N/A	N/A	N/A	√	N/A	16.7
6:2 Fluorotelomer carboxylic acid (6:2 FTCA)	$C_6F_{13}CH_2COOH$	N/A	N/A	N/A	√	N/A	√	33.3
8:2 Fluorotelomer carboxylic acid (8:2 FTCA)	$C_8F_{17}CH_2COOH$	N/A	N/A	N/A	N/A	N/A	N/A	0
10:2 Fluorotelomer carboxylic acid (10: 2 FTCA)	$C_{10}F_{21}CH_2COO H$	√	√	N/A	N/A	N/A	N/A	16.7
6:2 Fluorotelomer alcohol (6:2 FTOH)	$C_8H_5F_{13}O$	√	√	N/A	√	N/A	N/A	50
Perfluorohexyl Iodide PFHxI	$C_6F_{13}IH$	N/A	N/A	N/A	√	N/A	N/A	16.7
Perfluorooctyl Iodide PFOI	$C_8F_{17}IH$	√	N/A	N/A	√	N/A	√	50
8:2 Fluorotelomer acrylate (8:2 FTAC)	$C_{13}H_7F_{17}O_2$	√	√	N/A	√	N/A	√	66,7
6:2 Fluorotelomer methacrylate (6:2 FTAC)	$C_{12}H_9F_{13}O_2$	√	√	N/A	√	N/A	√	66.7

8:2 Fluorotelomer methacrylate (8:2 FTMAC)	$C_{14}H_9F_{17}O_2$	√	√	N/A	N/A	N/A	√	50
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	√	√	√	√	N/A	√	83.3
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	√	√	√	N/A	N/A	N/A	50
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	N/A	N/A	N/A	N/A	N/A	N/A	0
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	√	√	N/A	N/A	N/A	√	50
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	√	√	N/A	N/A	N/A	√	50
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	√	√	N/A	√	N/A	√	66.7
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	√	√	√	√	N/A	N/A	66.7

Table 5.7: Targeted and non-targeted PFASs in drinking water treatment plant

		DWTP-I	**DWTP-F**	**DWTP-E**	
Drinking Water treatment					
Compound Name	Formula	Detected	Detected	Detected	Detection frequency %
(PFBA)	$C_4HF_7O_2$	√	√	√	100
(PFPeA)	$C_5HF_9O_2$	√	√	√	100
PFHxA	$C_6HF_{11}O_2$	√	√	√	100
PFHpA	$C_7HF_{13}O_2$	√	√	√	100
PFOA	$C_8HF_{15}O_2$	√	√	√	100
PFNA	$C_9HF_{17}O_2$	√	√	√	100
PFDA	$C_{10}HF_{19}O_2$	√	√	√	100
PFUdA	$C_{11}HF_{21}O_2$	N/A	√	√	66.7

PFDoA	$C_{12}HF_{23}O_2$	√	N/A	√	66.7
PFTrDA	$C_{13}HF_{25}O_2$	N/A	N/A	N/A	0
PFTeDA	$C_{14}HF_{27}O_2$	N/A	N/A	N/A	0
L-PFBS	$C_4HF_9O_3S$	√	√	N/A	66,.
L-PFHxS	$C_6HF_{13}O_3S$	√	√	N/A	66.7
L-PFOA	C8HF17O3S	√	√	N/A	66,7
L-PFDS	$C_{10}HF_{21}O_3S$	N/A	N/A	N/A	0
L-PFHpS	$C_7F_{15}SO_3H$	N/A	N/A	N/A	0
L-PFNS	$C_9F_{19}SO_3H$	√	N/A	N/A	33.3
L-PFDoS	$C_{12}HF_{25}O_3S$	N/A	N/A	N/A	0
L-PFPeS	$C_5F_{11}SO_3H$	√	√	N/A	66.7
			Non-targeted PFASs		
4:2 Fluorotelomer sulfonic sulfonate 4:2 FTSA	$C_6H_5F_9O_3S$	N/A	N/A	N/A	0
6:2 Fluorotelomer sulfonate (6:2 FTSA)	$C_8H_5F_{13}O_3S$	√	√	N/A	66.7
8:2 Fluorotelomer Sulfonate (8:2 FTSA)	$C_{10}H_4F_{17}O_3S$	√	√	N/A	66.7
Perfluorooctane sulfonamide (FOSA)	$C_8H_2F_{17}NO_2S$	N/A	√	N/A	33.3
N-Methyl perfluorooctane sulfonamide (MeFOSA)	$C_9H_4F_{17}NO_2S$	N/A	√	N/A	33,3
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	$C_{10}H_6F_{17}NO_2S$	√	√	N/A	66.7
6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA	$C_8H_2F_{12}O_2$	N/A	√	N/A	33.3
8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA	$C_{10}H_2F_{16}O_2$	√	N/A	N/A	33.3
6:2 Fluorotelomer carboxylic acid (6:2 FTCA)	$C_6F_{13}CH_2COOH$	N/A	√	√	66.7
8:2 Fluorotelomer carboxylic acid (8:2 FTCA)	$C_8F_{17}CH_2COOH$	√	√	N/A	66.7
10:2 Fluorotelomer carboxylic acid (10: 2 FTCA)	$C_{10}F_{21}CH_2COO\ H$	√	N/A	√	66.7
6:2 Fluorotelomer alcohol (6:2 FTOH)	$C_8H_5F_{13}O$	√	N/A	N/A	33.3

Perfluorohexyl Iodide PFHxI	$C_6F_{13}IH$	N/A	N/A	N/A	0
Perfluorooctyl Iodide (PFOI)	$C_8F_{17}IH$	N/A	√	√	66.7
8:2 Fluorotelomer acrylate (8:2 FTAC)	$C_{13}H_7F_{17}O_2$	N/A	N/A	N/A	0
6:2 Fluorotelomer methacrylate (6:2 FTAC)	$C_{12}H_9F_{13}O_2$	N/A	N/A	N/A	0
8:2 Fluorotelomer methacrylate (8:2 FTMAC)	$C_{14}H_9F_{17}O_2$	N/A	√	√	66.7
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	N/A	N/A	N/A	0
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	N/A	N/A	N/A	0
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	N/A	N/A	N/A	0
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	N/A	N/A	N/A	0
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	N/A	N/A	N/A	0
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	N/A	N/A	√	33.3
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	N/A	N/A	N/A	0

Table 5.8: Targeted and non-targeted PFASs in bottled and tap drinking water

Bottled water and tap water		**Product A**	**Product B**	**Product C**	**Product D**	**Tap water**	
Compound Name	Formula	Detected	Detected	Detected	Detected	Detected	Detection frequency (%)
(PFBA)	$C_4HF_7O_2$	√	√	√	√	√	100
(PFPeA)	$C_5HF_9O_2$	√	√	√	√	√	100
PFHxA	$C_6HF_{11}O_2$	√	√	√	√	√	100
PFHpA	$C_7HF_{13}O_2$	√	√	√	√	√	100
PFOA	$C_8HF1_5O_2$	√	√	√	√	N/A	80
PFNA	$C_9HF_{17}O_2$	√	√	√	√	√	100
PFDA	$C_{10}HF_{19}O_2$	√	√	√	N/A	√	80
PFUdA	$C_{11}HF_{21}O_2$	N/A	N/A	√	N/A	N/A	20
PFDoA	$C_{12}HF_{23}O_2$	N/A	N/A	N/A	N/A	N/A	0

PFTrDA	$C_{13}HF_{25}O_2$	N/A	√	N/A	N/A	N/A	20
PFTeDA	$C_{14}HF_{27}O_2$	N/A	N/A	N/A	√	N/A	20
L-PFBS	$C_4HF_9O_3S$	√	√	N/A	N/A	√	60
L-PFHxS	$C_6HF_{13}O_3S$	√	√	N/A	N/A	√	60
L-PFOA	$C_8HF_{17}O_3S$	√	√	N/A	N/A	√	60
L-PFDS	$C_{10}HF_{21}O_3S$	√	N/A	N/A	√	√	60
L-PFHpS	$C_7F_{15}SO_3H$	√	√	N/A	√	N/A	60
L-PFNS	$C_9F_{19}SO_3H$	√	N/A	N/A	N/A	√	40
L-PFDoS	$C_{12}HF_{25}O_3S$	N/A	N/A	N/A	N/A	N/A	0
L-PFPeS	$C_5F_{11}SO_3H$	√	√	N/A	N/A	N/A	40
			Non-targeted PFASs				
4:2 Fluorotelomer sulfonic sulfonate 4:2 FTSA	$C_6H_5F_9O_3S$	√	√	N/A	N/A	N/A	40
6:2 Fluorotelomer sulfonate (6:2 FTSA)	$C_8H_5F_{13}O_3S$	√	√	N/A	N/A	√	60
8:2 Fluorotelomer Sulfonate (8:2 FTSA)	$C_{10}H_4F_{17}O_3S$	N/A	N/A	N/A	N/A	N/A	0
Perfluorooctane sulfonamide (FOSA)	$C_8H_2F_{17}NO_2S$	N/A	N/A	√	N/A	N/A	20
N-Methyl perfluorooctane sulfonamide (MeFOSA)	$C_9H_4F_{17}NO_2S$	N/A	√	√	N/A	N/A	40
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	$C_{10}H_6F_{17}NO_2S$	N/A	N/A	N/A	N/A	N/A	0
6:2 Fluorotelomer unsaturated carboxylic acid 6:2 FTUCA	$C_8H_2F_{12}O_2$	N/A	N/A	N/A	N/A	N/A	0
8:2 Fluorotelomer unsaturated carboxylic acid 8:2 FTUCA	$C_{10}H_2F_{16}O_2$	N/A	N/A	N/A	N/A	N/A	0
6:2 Fluorotelomer carboxylic acid (6:2 FTCA)	$C_6F_{13}CH_2COOH$	N/A	N/A	N/A	√	N/A	20
8:2 Fluorotelomer carboxylic acid (8:2 FTCA)	$C_8F_{17}CH_2COOH$	N/A	N/A	N/A	N/A	N/A	0
10:2 Fluorotelomer carboxylic acid (10: 2 FTCA)	$C_{10}F_{21}CH_2COO H$	√	N/A	N/A	N/A	N/A	20
6:2 Fluorotelomer alcohol (6:2 FTOH)	$C_8H_5F_{13}O$	N/A	N/A	N/A	N/A	N/A	0

Perfluorohexyl Iodide PFHxI	$C_6F_{13}IH$	N/A	N/A	N/A	N/A	N/A	0
Perfluorooctyl Iodide PFOI	$C_8F_{17}IH$	N/A	N/A	N/A	N/A	N/A	0
8:2 Fluorotelomer acrylate (8:2 FTAC)	$C_{13}H_7F_{17}O_2$	N/A	N/A	N/A	N/A	N/A	0
6:2 Fluorotelomer methacrylate (6:2 FTAC)	$C_{12}H_9F_{13}O_2$	N/A	N/A	N/A	N/A	N/A	0
8:2 Fluorotelomer methacrylate (8:2 FTMAC)	$C_{14}H_9F_{17}O_2$	√	N/A	√	N/A	N/A	40
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	√	N/A	√	N/A	√	60
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	$C_4HF_7O_3$	N/A	√	N/A	N/A	N/A	20
Perfluoro-4-methoxybutanoic acid (PFMOBA)	$C_5HF_9O_3$	N/A	N/A	N/A	N/A	N/A	0
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	N/A	√	N/A	N/A	√	40
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	N/A	√	N/A	N/A	N/A	20
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	N/A	N/A	N/A	N/A	N/A	0
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	N/A	√	N/A	N/A	N/A	20

5.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

5.4.1 Distribution of PFASs in various water sources during the wet season

Tables 5.9 shows the mean concentrations of PFASs in surface water, wastewater, drinking water and bottled water in wet season. PFOA, PFDA, PFBA, PFPeA, PFNA, PFHxA and PFHpA were the dominant PFASs in all the water samples. The following PFASs were detected in all the surface water samples analysed: PFOA (0.372-85.192 ng/L); PFBA (233.1-412.5 ng/L); PFHxA (0.241-9.55 ng/L) and PFHpA (0.135-3.23 ng/L. PFPeA (0.293-33.13 ng/L) was detected in all but one sample. PFDA (<LOD-1.092 ng/L) and PFNA (<LOD-0.695 ng/L) were detected in 14 samples; while LPFBS and LPFdUA were detected in nine samples at <LOD-138.2 and <LOD-3.057 ng/L respectively. LPFPeS (7.02-9.44 ng/L) and LPFOS (<LOD-30.8 ng/L were detected in eighteen and nine samples respectively; while LPFDS, PFTrDA and PFTeDA were all below the LOD. PFBA exhibited the highest concentration (413 ng/L) in 90286.

Table 5.9: Concentrations of PFASs in various water samples from Gauteng collected during the wet season

Compds	LPFPeS	PFOA	PFDA	PFBA	L-PFOS	LPFHpS	LPFNS	L-PFBS	PFdUA	PFTrDA	PFTeDA	PFPeA	PFNA	PFHxDA	PFHxA	PFHpA	PFDS	LPFHxS
Samples								**Mean concentrations (ng/L) and standard deviations (±)**										
API D	**7.03** ±3.24	**3.30** ±0.01	**0.138** ±0.05	**312** ±21.45	**8.54** ±0.45	<LOD	<LOD	**138** ±22.95	<LOD	<LOD	<LOD	**10.4** ±0.02	**0.266** ±0.12	<LOD	**1.33** ±0.53	**0.996** ±0.08	<LOD	**19.0** ±0.76
API UP	**7.58** ±1.79	**2.29** ±0.08	**0.146** ±0.01	**306** ±1.41	**30.8** ±1.04	<LOD	<LOD	**6.39** ±0.03	<LOD	<LOD	<LOD	**8.89** ±1.46	**0.381** ±0.07	<LOD	**2.95** ±0.04	**1.50** ±0.29	<LOD	35.3 ±1.4
HEN UP	**8.80** ±0.02	**1.05** ±0.19	**0.376** ±0.06	**333** ±20.93	<LOD	<LOD	<LOD	**132** ±14.69	<LOD	<LOD	<LOD	**8.74** ±0.9	**0.695** ±0.37	<LOD	**2.87** ±0.59	**1.38** ±0.39	<LOD	<LOD
HEN D	**9.45** ±0.47	**1.26** ±0.79	**0.191** ±0.09	**326** ±89.94	<LOD	<LOD	<LOD	**100** ±3.48	<LOD	<LOD	<LOD	**5.90** ±1.95	**0.618** ±0.07	<LOD	**3.75** ±0.01	**1.67** ±0.36	<LOD	<LOD
C-VDI1	<LOD	**0.372** ±0.13	**0.216** ±0.03	**337** ±14.71	<LOD	<LOD	<LOD	<LOD	**2.05** ±0.05	<LOD	<LOD	**10.1** ±0.02	**0.271** ±0.02	<LOD	**9.56** ±0.29	**1.10** ±0.33	<LOD	<LOD
C-VDI2	<LOD	**0.402** ±0.24	**0.401** ±0.11	**329** ±3.91	<LOD	<LOD	<LOD	<LOD	**1.68** ±0.47	<LOD	<LOD	**6.64** ±3.39	**0.228** ±0.18	<LOD	**0.946** ±0.42	**1.06** ±0.2	<LOD	<LOD
C-VDI3	<LOD	**0.458** ±0.09	**1.09** ±0.49	**383** ±9.67	<LOD	<LOD	<LOD	<LOD	**3.07** ±1.36	<LOD	<LOD	**14.4** ±2.31	**0.561** ±0.05	<LOD	**2.16** ±0.37	**1.54** ±0.08	<LOD	<LOD
C-VDI4	<LOD	**0.705** ±0.11	**0.465** ±0.02	**296** ±7.50	<LOD	<LOD	<LOD	<LOD	**0.939** ±0.81	<LOD	<LOD	**33.1** ±5.06	**0.535** ±0.03	<LOD	**1.64** ±0.18	**1.33** ±0.07	<LOD	<LOD
90236	<LOD	**1.22** ±0.11	**0.311** ±0.07	**334** ±9.92	<LOD	<LOD	<LOD	**9.62** ±2.83	**1.05** ±0.69	<LOD	<LOD	**5.18** ±0.25	**0.425** ±0.08	<LOD	0.918 ±0.01	**3.24** ±0.09	<LOD	<LOD
90176	<LOD	**0.922** ±0.12	**0.239** ±0.00	**405** ±24.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**4.60** ±0.18	**0.262** ±0.02	<LOD	**0.757** ±0.01	**1.27** ±0.21	<LOD	<LOD
90293	<LOD	**2.77** ±0.05	**0.325** ±0.03	**349** ±19.19	<LOD	<LOD	<LOD	61.2 ±8.36	**1.11** ±0.19	<LOD	<LOD	**30.8** ±5.41	**0.382** ±0.11	**0.343** ±0.07	**1.60** ±0.56	**2.94** ±0.23	<LOD	**7.79** ±0.28
MLT	<LOD	**0.906** ±0.02	**0.397** ±0.08	**361** ±18.26	<LOD	<LOD	<LOD	**11.8** ±3.67	**2.45** ±0.6	<LOD	<LOD	**3.21** ±1.38	**0.362** ±0.07	<LOD	**1.33** ±0.09	**1.785** ±0.97	<LOD	<LOD
90174	<LOD	**0.965** ±0.2	**0.268** ±0.09	**320** ±32.28	<LOD	<LOD	<LOD	**55.5** ±4.16	**0.886** ±0.25	<LOD	<LOD	**6.87** ±2.15	**0.544** ±0.04	<LOD	**1.34** ±0.06	**1.37** ±0.14	<LOD	<LOD
90238	<LOD	**85.2** ±0.00	**0.206** ±0.01	**382** ±9.04	<LOD	<LOD	<LOD	**5.74** ±1.59	**1.78** ±0.02	<LOD	<LOD	**7.33** ±1.31	**0.184** ±0.00	<LOD	**0.920** ±0.19	**2.03** ±0.19	<LOD	<LOD
90286	<LOD	**0.370** ±0.06	<LOD	**413** ±0.59	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.413** ±0.03	<LOD	<LOD	**0.241** ±0.06	**0.288** ±0.02	<LOD	<LOD
193663	<LOD	**0.655** ±0.03	<LOD	**333** ±4.27	<LOD	<LOD	<LOD	<LOD	**11.8** ±6.17	<LOD	<LOD	**0.865** ±0.57	<LOD	<LOD	**0.473** ±0.07	**0.500** ±0.08	<LOD	<LOD
90260	<LOD	**0.542** ±0.18	<LOD	**294** ±8.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.293** ±0.01	<LOD	<LOD	**0.309** ±0.25	**0.295** ±0.12	<LOD	<LOD
195445	<LOD	**0.685** ±0.21	<LOD	**276** ±13.2	<LOD	<LOD	<LOD	<LOD	**21.3** ±3.31	<LOD	<LOD	<LOD	<LOD	<LOD	**0.500** ±0.09	**0.135** ±0.04	<LOD	6.12 ±0.75

195443	<LOD	**0.427**	<LOD	**233**	<LOD	<LOD	<LOD	<LOD	**20.7**	<LOD	<LOD	**0.48**	<LOD	<LOD	**0.409**	**0.492**	<LOD	<LOD
		±0.09		±48.2					±5.92			±0.26			±0.08	±0.02		
B1	**10.6**	**2.19**	**0.490**	**72.54**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.21**	**0.197**	<LOD	**1.29**	**1.68**	<LOD	<LOD
	±1.41	±1.48	±0.11	±9.03								±0.51	±0.12		±0.38	±0.94		
B2	**26.1**	1.23	0.326	10.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**2.22**	**0.435**	**0.823**	**5.86**	**3.55**	<LOD	<LOD
	±6.18	±0.21	±0.01	±3.64								±0.66	±0.05	±0.36	±3.49	±1.24		
B3	**14.8**	**0.656**	**0.528**	**22.0**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.53**	**0.251**	<LOD	**2.40**	**3.75**	<LOD	<LOD
	±0.25	±0.09	±0.05	±3.55								±0.61	±0.09		±0.29	±0.63		
B4	**13.7**	**0.334**	**0.465**	**51.3**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.707**	<LOD	<LOD	**0.713**	**0.816**	<LOD	<LOD
	±4.62	±0.09	±0.31	±0.99								±0.09			±0.12	±0.09		
GP-T1	**18.8**	**30.6**	<LOD	**51.0**	**17.5**	<LOD	<LOD	**57.0**	**1.723**	<LOD	<LOD	**2.31**	**0.357**	<LOD	**3.16**	**6.58**	<LOD	**34.1**
	±5.63	±9.88		±27.55	±3.97			±15.84	± 0.09			±0.12	±0.19		±2.48	±0.00		±4.53
GP-DI	**11.9**	**7.04**	**0.638**	**127**	**45.1**	<LOD	<LOD	**135**	**1.65**	<LOD	<LOD	**0.672**	**0.191**	<LOD	**3.21**	**1.83**	<LOD	**25.8**
	±8.42	±5.31	±0.32	±13.93	±0.49			±41.06	±0.89			±0.09	±0.06		±0.13	±1.14		±0.25
GP-DF	**9.46**	**5.66**	**0.205**	**90.5**	**23.4**	<LOD	<LOD	**179**	**1.15**	<LOD	<LOD	**0.453**	**0.384**	<LOD	**5.29**	**1.22**	<LOD	**36.9**
	±1.59	±0.36	±0.05	±10.23	±2.68			± 8.43	±1.01			±0.05	±0.16		±0.16	±0.15		±8.18
GP-DE	**10.5**	**3.68**	**0.838**	**66.3**	**11.3**	<LOD	<LOD	**80.4**	**0.868**	<LOD	<LOD	**0.381**	**0.422**	<LOD	**250**	**0.824**	<LOD	**30.9**
	±1.53	±0.93	±0.34	±1.41	±2.04			±1.07	±0.42			±0.04	±0.08		±1.32	±0.23		±1.39
GP-WE1	**13.4**	**1.575**	0.485	**267**	**12.8**	<LOD	<LOD	**153**	**3.91**	<LOD	<LOD	**11.3**	**0.962**	**0.536**	**2.65**	**1.44**	<LOD	**9.62**
	±1.63	±0.17	±0.05	±13.15	±2.31			±31.29	±0.06			±0.10	±0.23	±0.28	±0.15	±0.70		±0.87
GP-WE2	**18.0**	**1.13**	**0.543**	**283**	<LOD	<LOD	<LOD	**132**	**2.62**	<LOD	<LOD	**14.0**	**0.832**	**0.380**	**11.5**	**1.91**	<LOD	**4.67**
	±0.73	±0.31	±0.12	±33.81				±1.29	±0.35			±0.30	±0.16	±0.17	±1.78	±0.53		±1.56
GP-WS1	**9.96**	**1.60**	**0.626**	**280**	**12.4**	<LOD	<LOD	**315**	**1.03**	<LOD	<LOD	**6.40**	**0.474**	<LOD	4.269	**3.86**	<LOD	**13.5**
	±0.20	±0.6	±0.09	±29.15	±2.36			±28.02	±0.12			±1.00	± 0.06		±0.18	±1.09		±0.67
GP-WS2	**14.5**	**1.04**	**0.782**	**266**	<LOD	<LOD	<LOD	**403**	**6.93**	<LOD	<LOD	**2.9**	**0.727**	<LOD	**7.66**	**2.56**	<LOD	**7.76**
	±0.73	±0.09	±0.49	±6.75				±79.04	±2.29			±0.97	±0.03		±1.73	±0.41		±0.45
GP-WI1	**12.0**	**1.09**	**0.609**	**331**	**17.5**	**15.2**	<LOD	**60.0**	**2.23**	<LOD	<LOD	**5.1**	**0.910**	<LOD	**1.42**	**1.87**	<LOD	**6.59**
	±0.96	±0.43	±0.38	±11.98	±3.01	±6.31		±12.21	±0.84			± 0.71	±0.22		±0.68	±0.26		±0.38
GP-WI2	**12.3**	**1.05**	**1.04**	**305**	<LOD	**20.1**	<LOD	**76.4**	**8.07**	<LOD	<LOD	**20.0**	**1.25**	<LOD	**3.63**	**4.25**	<LOD	**12.0**
	±0.26	±0.11	±0.09	±23.66		±2.57		±12.51	±3.74			±3.29	±0.05		±0.14	±1.71		±0.47

nd=non-detectable, LOD= Limit of quantification, LOQ=limit of quantification

Figures 5.2 and 5.3 show the scatter and box plots of PFASs in various water sources. These were constructed in order to establish if there is any relationship/pattern from the observed PFASs concentrations. In Figure 5.2, most of the PFASs congeners are congested below 500 ng/L. The lowest concentration recorded for PFBA was 10.3 ng/L in sample B2. PFOA (85.19 ng/L); PFHxS (35.29 ng/L); PFPeA (33.13 ng/L); LPFOS (30.83 ng/L). PFHpA and PFNA exhibited the following concentration range of <LOQ-4.45 ng/L and <LOQ-0.695 ng/L and LPFdUA (21.29 ng/L). Other PFASs compounds ranged between <LOD-9.55 ng/L). The highest concentration was detected at Klipvoor dam (413 ng/L), followed by 90176 (405 ng/L); C-VDI3 (383 ng/L); C-VDI1 (337 ng/L); Franspoort Road Bridge on Edendalspruit (85.19 ng/L); Apies River Upstream (35.29 ng/L); Vaal River upstream of Vaal Marine 33.13 ng/L) and Outlet Centurion (21.29 ng/L). Groffen et al. (2018) reported PFPeA as the most detected PFASs in the Vaal River. However, Batayi et al. (2021) reported PFPeA as the least detected PFASs in water samples from Hardebeespruit and Roodeplaat dams.

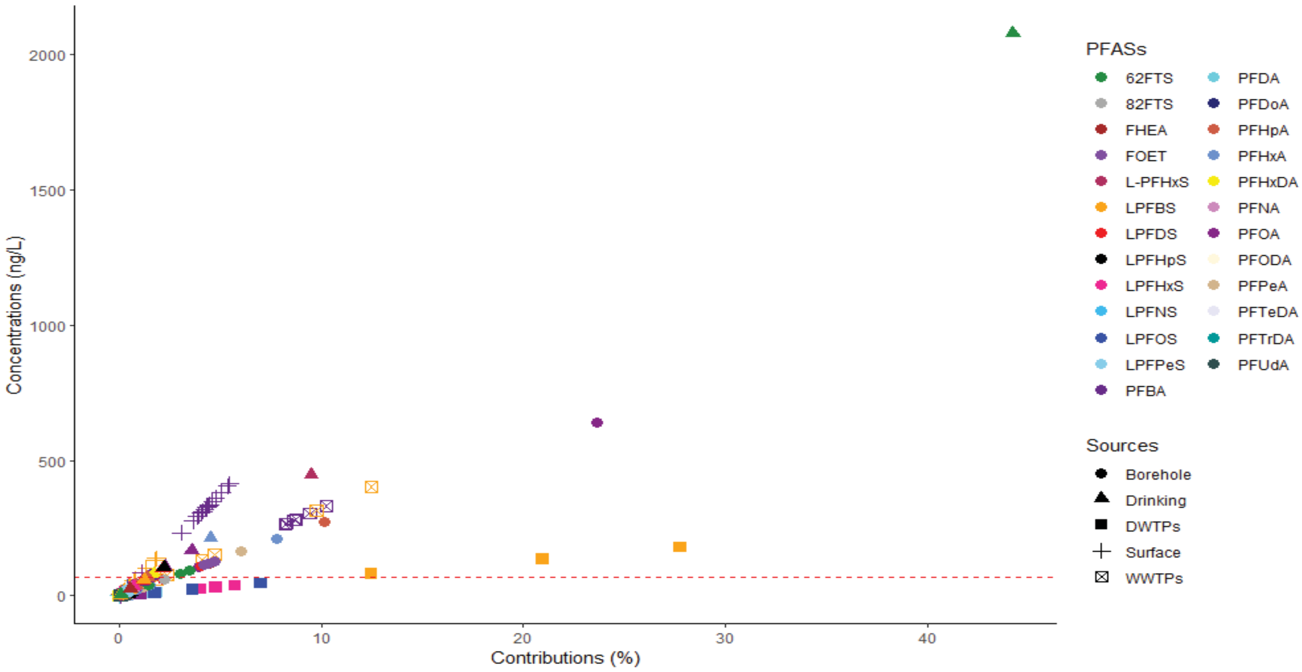

Figure 5.2: PFASs concentration distributions in various water sources in Gauteng province during the wet season.

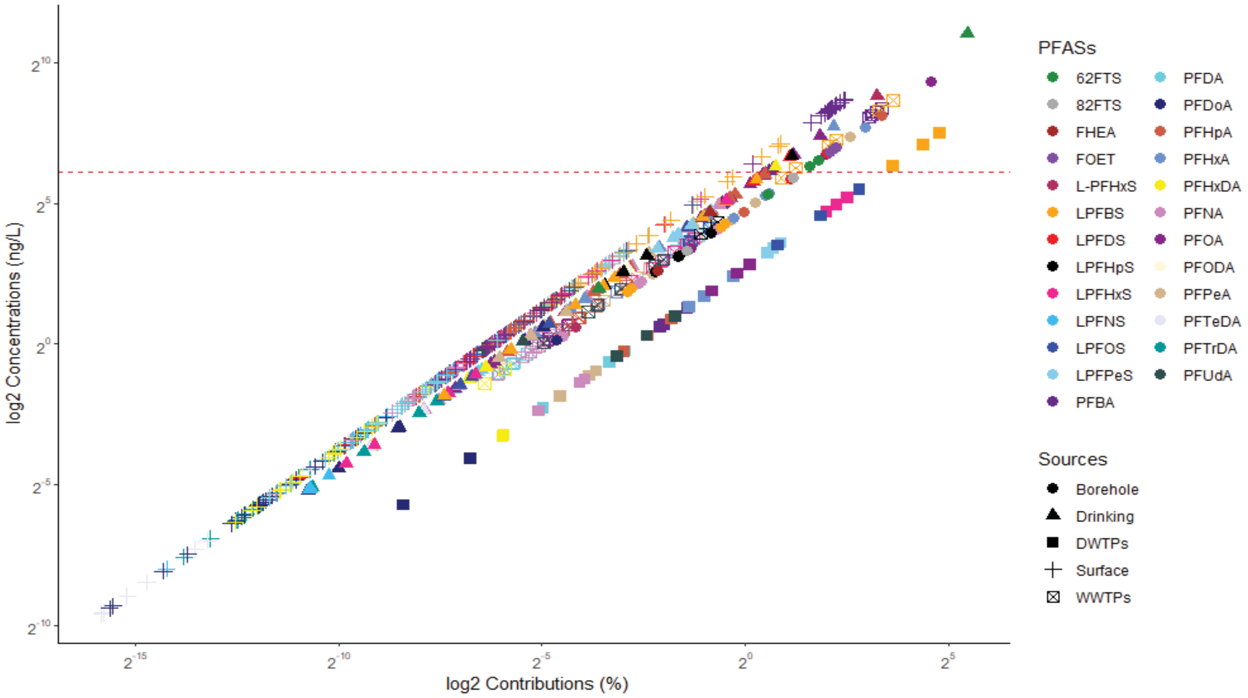

Figure 5.3: PFASs concentrations distributions for various water sources Gauteng during the wet season.

According to Groffen et al. (2018), the mean PFASs concentrations in water samples ranged from <LOQ-38.5 ng/L and that the PFASs concentrations in water samples were similar or lower compared to other studies in Europe, Asia and America. In the present study, PFBA exhibited the highest concentration followed by PFOA (90238) and PFPeA (90293).

In the wastewater treatment samples, the order of detection were: LPFBS (59.9-403.10 ng/L); PFBA (265.8-331.4 ng/L); PFPeA (2.91-20.2 ng/L); LPFPeS (9.95-13.3 ng/L); PFHxS (4.67-13.5 ng/L); PFHxA (1.41-11.5 ng/L); LPFdUA (1.03-8.06 ng/L); PFHpA (1.43-4.24 ng/L); PFOA (1.04-1.57 ng/L); PFDA (0.485-1.03 ng/L0; PFHxA (0.380-0.536 ng/L), while PFTrDA, PFTeDA and PFDoA were not detected.

In the case of drinking water treatment plant samples, the following PFASs were detected: LPFPeS (9.45-11.94 ng/L); PFOA (3.68-7.04 ng/L); PFDA (0.205-0.838 ng/L); PFBA (66.3-127 ng/L); PFPeA (0.381-0.672 ng/L; PFNA 191-0.422 ng/L); PFHxA (2.49-5.29 ng/L); PFHpA (0.824-1.83 ng/L) and PFHxS (25.8-36.8 ng/L) except LPFHpS, LPFDS, PFTrDA, PFTeDA, LPFHxDA and LPFDoA which were all <LOD.

The following PFASs compounds were detected in bottled water: PFHpA (0.860-6.57 ng/L); PFPeS (10.5-2.05 ng/L); PFOA (0.33-30.5 ng/L); PFBA (10.2-72.4 ng/L); PFPeA (0.707-2.30 ng/L) and PFHxA (0.713-5.86 ng/L) except LPFHpS, LPFDS, PFTrDA, PFTeDA and PFDoA. Although not mandated by law, the International Bottled Water Association (IBWA) requires its members to test for PFASs in all the bottled water products sold. The IBWA operational limits for its members are 5 ng/L for a single PFASs and 10 ng/L for more than one PFASs (IBWAs, 2019). The PFASs detected in the bottled drinking water in the present were generally much lower than the IBWA operational limits except PFBA, PFOA, PFBS and LPFPeS.

The concentrations of PFASs detected in borehole and tap water samples are shown in Table 5.10. The concentrations ranged from <LOD-2077 ng/L, with the highest concentration recorded for 6:2 FTS. Interestingly, LPFOS was not detected in any of the samples. This was also the same with PFUdA and 4:2

FTS. The second highest concentration was recorded for PFOA (641 ng/L), followed by PFHpA (275 ng/L), all in GP-BT1. With the exception of PFODA, PFOS, FHET, PFUDA, 4;2 FTS, PFHxDA and L-PFHxs, all the other PFASs congeners were detected in sample GP-BT1.The detected 6: 2 FTS at a high concentration of 2077 ng/L in GP-T2 is rather surprising considering the fact that this was tap water. Compared to the health advisory levels at 70 ng/L, by the USEPA to protect its sensitive populations, from a lifetime of exposure to PFOA+PFOS from drinking water, the values in Table 5.10 for GP-BT1 is much higher. This is of concern. The concentrations of PFOA+PFOS in the other samples are far lower than the 70 ng/L.

The concentrations observed in the present study were, in some cases, higher than the values reported by other researchers in surface water. The PFASs detected in the bottled drinking water in the present study were higher than the IBWA operational limits of 5 ng/L for a single PFASs and 10 ng/L for more than one PFASs. Compared to the health advisory levels at 70 ng/L, by the USEPA to protection its sensitive populations, from a lifetime of exposure to PFOA and PFOS tap water, the concentrations of PFASs in the present study are much higher.

Table 5.10: Mean concentrations of PFASs in borehole and tap water samples in wet season

Samples	GP-BT1	GP-BT2	GP-BL1	GP-BL2	GP-T1	GP-T2
Compounds		**Mean concentrations (ng/L) and standard deviations (±)**				
PFODA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeA	**21.2 ±0.82**	**163 ±2.30**	**32.2 ±2.6**	**5.59 ±1.85**	**19.2 ±0.22**	**17.0 ±3.6**
L-PFBS	**17.9 ±0.60**	**19.2 ±0.70**	**3.62 ±1.10**	**3.91 ±1.10**	**5.07 ±0.13**	**33.6 ±18.20**
PFOA	**641 ±72.35**	**10.7 ±6.32**	**17.3±3.0**	**106.8 ±2.4**	**63.8 ±18.12**	**0.611 ±0.08**
PFBA	**8.19 ±1.70**	**7.69 ±2.65**	**0.127 ±0.02**	**1.20± 0.328**	**0.165 ±0.02**	**0.114 ±0.01**
L-PFOS	<LOQ	<LOQ	ND	<LOQ	<LOQ	<LOQ
L-PFHpS	**15. 2 ±3.35**	**8.62 ±0.87**	**8.79 ±0.92**	**5.88 ±0.78**	**4.28 ±1.70**	**104 ±20.9**
FHET	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFDS	58.7 ±15.71	110 ±27.04	<LOD	<LOQ	100 ±12.65	54.1 ±4.20
PFUDA	ND	ND	<LOD	<LOD	ND	<LOD
4:2 FTS	ND	ND	<LOD	ND	<LOD	<LOD
6:2 FTS	**80.9±4.47**	**ND**	**39.6±5.00**	**93.7±4.90**	**3.87±0.98**	**2077±861.38**
8:2 FTS	60.78 ±10.16	ND	ND	10.1 ±3.20	<LOD	<LOD
FHEA	120 ±35.67	6.09 ±0.52	<LOQ	<LOQ	<LOQ	25.9 ± 0.46
FOET	127 ±9.16	118.7316±9.4 65	ND	114.0±7.2	<LOD	<LOD
PFNA	**4.39 ±0.66**	**4.63 ±0.23**	**1.20±0.24**	**17.0±3.6**	**3.16±1.1**	**6.82±1.2**
PFHxDA	ND	ND	<LOD	<LOD	ND	<LOD
PFHxA	**211 ±9.16**	**22.4 ±4.70**	**38.5 ±8.70**	**41.0 ±6.3**	**35.2 ±1.5**	**24.5 ±3.30**
PFHpA	**275 ±6.98**	**26.24 ±1.02**	**39.8 ±3.16**	**5.59 ±0.07**	**23.7 ±0.27**	**26.4±5.8**
PFDoA	<LOD	<LOD	<LOD	1.09 ±0.22	<LOD	<LOQ
L-PFHxS	ND	<LOQ	<LOD	1.50±0.38	<LOQ	446 ±5.3

The PFASs detected in water samples were grouped into short and long chain PFASs in other to evaluate the detection frequencies of each group. Table 5.11 shows the number of detections, percentage detection frequencies and concentration ranges (ng/L) of short and long chain PFASs in water samples. In the blank samples, PFPeA and PFDA exhibited 83% and 33% detection frequencies. Other PFASs were <LOD. The following short chain PFASs were detected at 100%: PFHxA, PFBA and PFHpA; PFPeA was at detected frequency of 94% and the other short chains PFASs, PFHxS and PFBS frequency detection were below 50% in surface water samples (Table 5.11). In comparison to the detection frequency of long chain PFASs, only PFOA showed 100% detection frequency; while the detection frequencies of other long chain PFASs ranged from <LOD-74%. The high detection frequency exhibited by PFBA, PFHxA, PFHpA and PFPeA suggests widely occurrence of these PFASs in the surface water analysed.

With respect to wastewater treatment plant, all the short chain (six) PFASs (Table 5.12) exhibited 100% detection frequency compared with five of long chains. The detection frequencies of the other long chain PFASs ranged from 33-50%. Similar trend was observed in drinking water treatment plant (Table 6.4) where all the detection frequencies of all the short chain (six) PFASs were 100%. Furthermore, six long chain PFASs exhibited 100% detection frequencies while the rest ranged from <LOD-67%. In the borehole water samples, PFPeA short chain exhibited the only 100% detection frequency. Other short and long chain PFASs showed detection frequency of 50%.

As for bottled and tap drinking water, all the short chain PFASs namely, PFHxA, PFBA, PFpeA and PFHpA showed detection frequency of 100%; while the detection frequencies of PFHxS and PFBS were 20%. In contrast with long chain PFASs, only PFOA showed 100% detection frequency and the detection frequencies others ranged from <LOD-80%. Although the number of short chain PFASs in Table 5.11 is smaller than the number of long chains, however, the detection frequency of short chains is more than that of long chain suggesting a bigger contribution to the water samples than long chains. Furthermore, the fact that the short chain PFASs were detected at a comparable level or even higher level than the long chain PFASs in the water samples suggests the use and, therefore, prevalence of short chain-containing materials/chemicals in the country. Their presence may have originated from discharge/leaching from short chain-containing materials.

In addition to the direct products, short-chain PFAS can result from decomposition of long-chain PFAS. For instance, Vaalgamaa et al. (2011) stated that PFOA can be photochemically transformed to short-chain PFHxA and PFHpA by UV irradiation with the natural sensitizers such as dissolved organic matter (DOM), ferric iron (Fe^{3+}), and nitrate in surface water. Furthermore, 6:2 Fluorotelomer sulfonic acid (6:2 FTS, C8 long-chain PFSA) was reported to be aerobically bio-transformed to shorter-chain products by activated sludge from wastewater treatment plants. During the 90-day treatment, 63.7% of 6:2 FTS remained in the activated sludge system, while typical short-chain byproducts including PFBA (0.14 wt %), PFHpA (1.5 wt %), and PFHxA (1.1 wt %) were detected.

Figures 5.4 and 5.5 illustrate the class contribution of PFASs and contributions of short and long-chain PFASs in various water sources in Gauteng during the wet season.

Table 5.11: Number of detections and concentration ranges (ng/L) of short and long chain PFASs in water samples

	Blanks (n=6)		Surface water (n=19)		Wastewater treatment plant (n=6)		Water treatment plant (n=3)		Borehole (n=2)		Bottled and Tap drinking water (n=5)	
	No of detection	range	No of detection	range	No of detection	range	No of detection	range	No of detection	range	No of detection	range
Short-chain PFASs												
PFBS	<LOD	<LOD	9(47%)	<LOD-138.2	**6(100%)**	59.970-403.10	**3(100%)**	80.44-135.0	ND	ND	1(20%)	<LOD-54.04
LPFPeS	<LOD	<LOD	4(21%)	7.029-9.445	6**(100%)**	9.956-13.360	**3(100%)**	9.45-11.94	ND	ND	5	10.55-26.05
PFHxA	<LOD	<LOD	**19(100%)**	0.241-9.559	**6(100%)**	1.419-11.530	**3(100%)**	2.497-5.294	ND	ND	**5(100%)**	0.713-5.86
PFBA	<LOD	<LOD	**19(100%)**	233.10-412.50	**6(100%)**	265.80-331.40	**3(100%)**	66.31-126.90	ND	ND	**5(100%)**	10.29-72.54
PFPeA	5 (83%)	0.239-0.924	18(94%)	0.293-33.13	**6(100%)**	2.910-20.23	**3(100%)**	0.381-0.672	**2(100%)**	0.54-0.79	**5(100%)**	0.707-2.306
PFHpA	<LOD	<LOD	**19(100%)**	0.135-3.235	**6(100%)**	1.438-4.246	**3(100%)**	0.824-1.834	1(50%)	<LOD-0.65	**5(100%)**	0.860-6.577
Long-chain PFASs												
PFOA	<LOD	<LOD	**19(100%)**	0.372-85.192	**6(100%)**	1.040-1.575	**3(100%)**	3.68-7.04	ND	ND	**5(100%)**	0.33-30.58
PFOS	<LOD	<LOD	2(11%)	<LOD-30.834	3(50%)	<LOD-17.47	**3(100%)**	11-31-45.11	ND	ND	1(20%)	<LOD-17.47
PFNA	<LOD	<LOD	14(74%)	<LOD-0.695	**6(100%)**	0.475-1.251	**3(100%)**	0.191-0.422	1(50%)	<LOD-0.16	4(80%)	<LOD-0.435
PFDA	2 (33%)	<LOD-2.87	14(74%)	<LOD-1.092	**6(100%)**	0.485-1.035	**3(100%)**	0.205-0.838	1(50%)	<LOD-0.15	4(80%)	<LOD-0.528
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1(50%)	<LOD-0.38	<LOD	<LOD
PFUdA	<LOD	<LOD	12(63%)	<LOD-3.057	**6(100%)**	1.033-8.065	**3(100%)**	<LOD-1.723	1(50%)	<LOD-0.38	1(20%)	<LOD-1.723
PFHxDA	<LOD	<LOD	1(5%)	<LOD	2(33%)	<LOD-0.536	2(67%)	<LOD-0.823	ND	ND	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	ND	ND	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	ND	ND	<LOD	<LOD
PFHpS	<LOD	<LOD	<LOD	<LOD	2(33%)	<LOD-20.11	<LOD	<LOD	1(50%)	<LOD-0.30	<LOD	<LOD
LPFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	ND	ND	<LOD	<LOD
PFHxS	<LOD	<LOD	4(21%)	<LOD-6.116	**6(100%)**	4.676-13.51	**3(100%)**	25.820-36.860	1(50%)	<LOD-0.53	1(20%)	<LOD-34.09

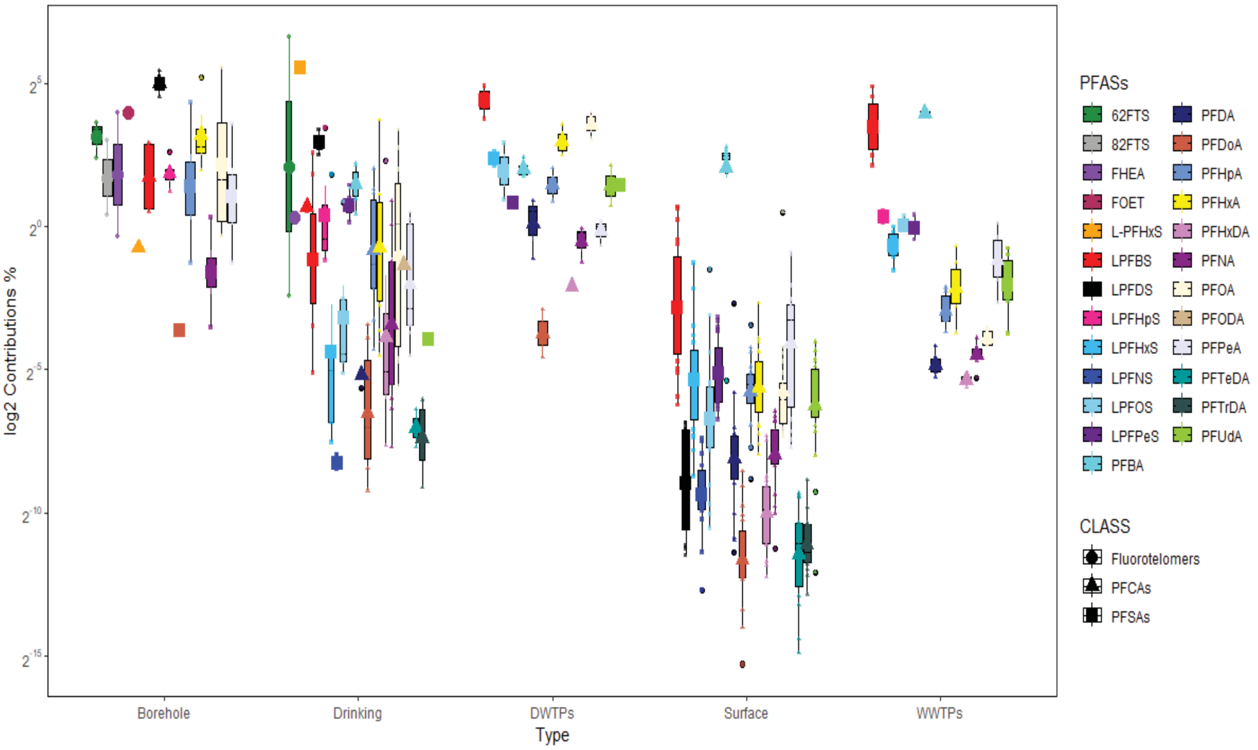

Figure 5.4: PFASs class contributions for various water sources in Gauteng during the wet season.

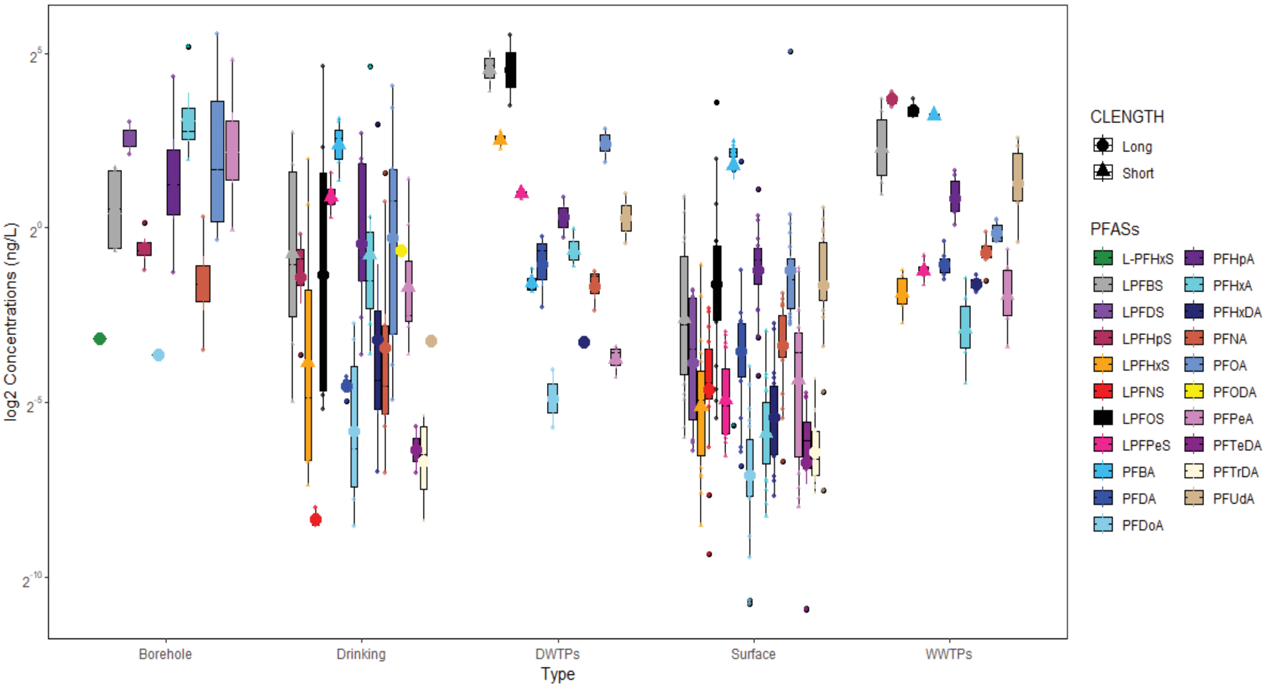

Figure 5.5: Contributions of long- and short-chain PFASs for various water sources in Gauteng during the wet season.

5.4.2 Establishing the possible sources of the PFASs detected in the water

Multivariate analysis was conducted using the PFASs dataset generated from analysis of water samples from various sampling sites in Gauteng. Shown in Figure 5.6 are the contributions of PFASs compounds detected in the water samples during the wet season. The results showed detectable concentrations especially for the short chain PFASs. Lower to none detectable levels were detected for the long chain PFAS, suggesting that they were less produced and consumed. Another reason could be due to the low water solubility of the long chain. (Onghena et al., 2012). Compounds LPFPeS, PFDA, FHEA, PFPeA, PFNA and PFOA, all show positive strong contributions in the first quadrant (clockwise). The same applied to FOET, PFDoA, PFTrDA and 8:2 FTS in the second score plot, albeit in the negative quadrant. PFBA is in its own in the third score plot; whereas the sulphonates are dominant in the fourth score plot. The clustering of PFASs in different may suggest different sources for different groups in different score plots.

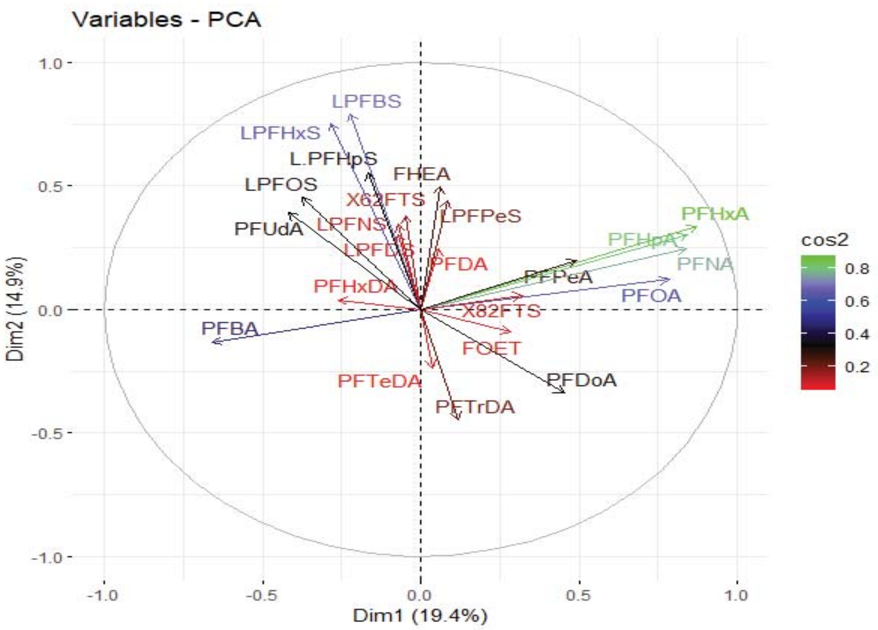

Figure 5.6: PCA of PFASs congener contributions and their relationships during the wet season.

Figure 5.7 shows the PCA of the sampling sites. As can be seen in Figure 5.7, GP-T1, GP-BL2 and GP-BT1 are clearly the outlayers compared to the other sites. The surface samples are clustered. This suggested that the sources of PFASs may be different for these sites. These PFASs may have originated from any of the following: 1) Chemical industry (application of fluorochemicals in production of materials); 2) Wastewater treatment plant (PFASs-containing domestic cookware and food raps that are flushed into the sewerage system thereby ending in wastewater treatment plants); 3) Landfill sites (dumping of PFASs-containing wastes); 4) Waste dump sites (PFASs-containing wastes that are dumped indiscriminately that can be washed into water bodies); 5) Use of fire-fighting foams that may contain PFASs – airport, fire-fighting stations and others); 6) Storm water and 7) mining sources. The major industries in Gauteng are appliances and electrical supplies, basic iron and steel, chemical products, electrical machinery, fabricated and metal products, food, machinery, motor vehicle parts and mining. There are also agricultural activities within the province. All these industries may be using or may have used PFASs compounds in their various industrial processes.

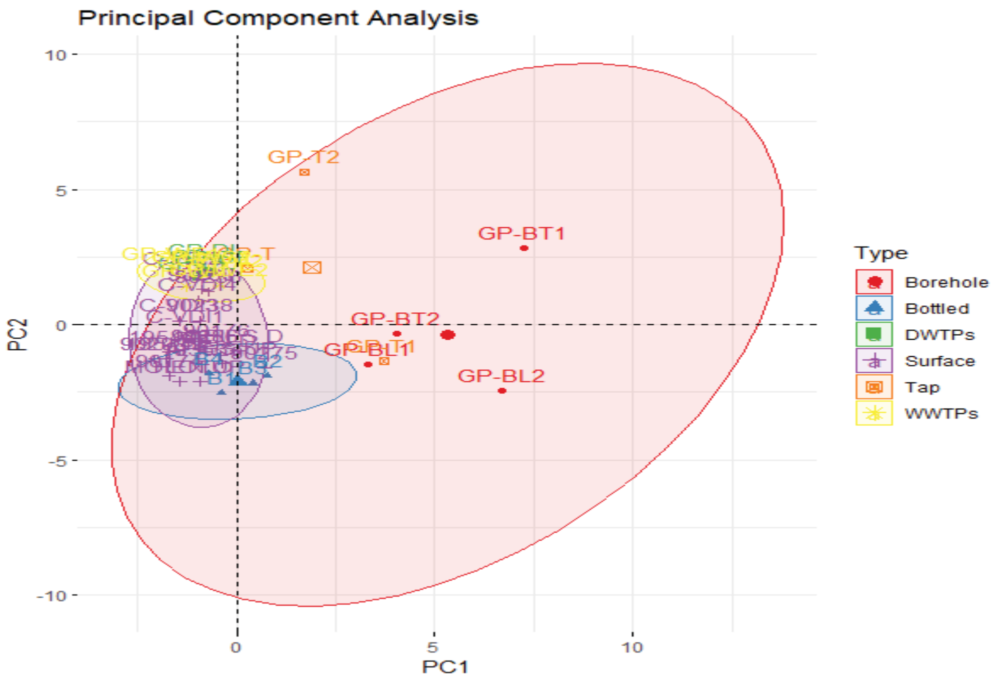

Figure 5.7: PCA of sampling sites and their relationships during the wet season.

5.5 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

5.5.1 Distribution of PFASs in various water sources during the dry season

The mean concentrations of PFASs in water samples are shown in Table 5.12. The following samples were detected in all the samples: PFBS, PFHxS, PFHxA, PFOA, PFOS, PFHpA, and PFNA. Of all the PFASs congeners detected in all the samples, PFHxA exhibited the highest concertation of 364 ng/L in GP-BT2, followed by PFHpS (170 ng/L) in GP-BL1, PFOA (169 ng/L) in GP-T1; A concentration of 106 ng/L was also recorded for PFOS this time in 193640 and 90247. The high concentrations observed for the sulphonate group of PFASs may be linked with the breakdown of fluorotelomer sulphonates (8:2FTS, 6:2 FTS and 4:2 FTS) which are volatile and are precursors of the sulphonate group of PFASs. Furthermore, PFBA was detected in all the samples except in 193640 and 195443. High concentrations of PFBA were also observed in the following samples: GP-BT1 (471.9 ng/L); GP-BL1 (383 ng/L); GP-BT2 (337 ng/L) and GP-BL2 (289 ng/L). 8: 2 FTS and 6:2 FTS was also observed in all the samples except in samples GP-BT1 and GP-BT2 and 90260 and 195445 respectively. FOET was detected only in the borehole and tap water.

In order to translate the observed concentrations into visual perspective, scatter and box plots were constructed and these are shown in Figures 5.8 and 5.9. As can be seen in Figure 5.8, the points are most clustered <100 ng/L, with some signs of linear pattern. An improved plot of Figure 5.8, which is shown in Figure 5.9 which is a log base plot. A clear linear pattern can been seen suggesting strong correlation of PFASs contributions and their concentrations.

Table 5.12: Mean concentrations of PFASs in various water samples during the dry season

Samples	90286	90249	90260	193640	195443	193663	195445	GP-BT1	GP-BT2	GP-BL1	GP-BL2	GP-T1	GP-T2
Compounds	Mean concentrations (ng/L) and standard deviations (±)												
PFBS	20.8±10.8	32.5±0.52	14.7±3.80	20.9±2.67	27.3±4.38	19.8±2.31	8.41±1.78	17.2 ±12.86	62.3±2.78	4.86 ±0.82	2.46 ±0.17	30.3 ±15.6	22.8 ±1.52
PFHxS	7.68±1.41	21.8±4.92	9.61±1.46	30.7±0.69	47.8 ±13.9	10. 5±0.39	1.07±0.10	95.0 ±15.19	4.47 ±0.13	170 ±3.4	0.167±0.05	0.0876±0.02	13.8±8.99
PFHxA	6.55±0.40	6.80±1.18	1.59 ±0.04	4.14 ±0.24	1.65 ±0.34	1.48 ±0.41	0.77±0.254	18.69 ±5.83	364 ±143.7	12.1 ±0.64	161 ±82.2	212 ±49.50	3.05 ±1.03
PFBA	45.6±9.05	26.0±5.13	50.7 ±11.0	<LOD	<LOD	20.8±0.479	19.7±4.00	471.9 ±107.9	337 ±36.40	383 ±12.30	289.3±31.80	71.1 ±33.22	31.7±5.30
PFPeA	0.489±0.03	0.467±0.100	0.432 ±0.04	0.391 ±0.01	0.497 ±0.10	0.438±0.10	0.345±0.10	<LOQ	50.2 ±2.08	2.67 ±1.70	13.8 ±2.40	22.8 ±19.7	9.19±0.21
PFOA	4.90±0.37	4.59±0.76	3.12 ±1.19	9.39 ±1.55	2.86±0.23	9.58 ±1.97	6.96 ±0.56	3.49 ±0.06	76.8 ±22.00	1.44 ±0.05	140 ±2.10	169 ±49.4	32.0 ±17.2
PFOS	20.0±1.33	106±7.16	44.4±11.90	106±6.17	60.3±13.00	52.7±4.32	5.92 ±2.05	94.3 ±8.33	121 ±13.4	77.6 ±1.60	201 ±39.90	247 ±67.70	50.1±5.71
PFHpA	0.847±0.141	1.36 ±0.17	1.37 ±0.05	2.21 ±0.27	0.872 ±0.05	1.11±0.07	0.241±0.04	39.4 ±0.24	42.3 ±0.37	0.893 ±0.37	41.9 ±7.80	65.6±0.46	36.2 ±6.18
PFNA	9.12±2.82	4.10±1.28	3.66 ±0.08	4.32 ±1.57	2.64±0.223	3.14±0.88	0.156±0.01	14.83±19.30	9.71 ±5.10	6.15 ±0.29	84.1±16.90	30.1±14.12	1.45±0.36
PFUdA	0.190±0.056	0.0392±0.01	<LOD	0.110 ±0.01	0.122 ±0.00	0.0280±0.01	<LOD	<LOD	<LOD	1.47 ±1.30	<LOD	<LOD	2.67 ±0.71
PFHpS	111 ±5.87	1.54 ±0.05	1.61 ±0.188	4.64 ±0.74	87.6 ±14.80	1.62 ±0.79	7.05±1.81	2.24 ±0.89	<LOD	<LOD	9.10±6.80	5.12 ±1.50	0.806±0.07
PFDoA	0.547±0.04	0.0222±0.01	0.0100±0.001	0.0225±0.01	0.0123±0.001	0.0822±0.01	<LOD	ND	<LOD	30.4 ±1.0	7.60±1.30	<LOD	1.50±0.65
PFHxDA	1.47±0.11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	10.8 ±1.30	78.6 ±5.40	78.6±5.40	0.419 ±0.05
L-PFDS	<LOD	<LOD	5.56±1.83	<LOD	<LOD	<LOD	<LOD	<LOD	ND	<LOD	ND	<LOD	0.410±0.06
4:2 FTS	<LOD	<LOD	<LOD	0.41 ±0.40	<LOD	<LOD	<LOD	<LOQ	ND	<LOD	ND	0.542 ±0.49	15.6±3.39
6:2 FTS	0.39±0.37	0.211±0.02	<LOD	0.126 ±0.02	0.222 ±0.16	0.230 ±0.01	<LOD	7.69 ±4.71	38.8 ±2.6	163 ±24.70	64.4 ±7.6	126±7.58	<LOD
8:2 FTS	24.0±0.27	7.54 ±0.47	1.11± 0.10	6.82 ±0.59	10.4 ±1.15	4.44 ±0.57	0.301±0.13	ND	ND	5.88 ±1.10	45.8 ±6.64	115±89.7	15.2±1.00
FHEA	41.3±12.10	12.2±0.13	<LOD	7.52±0.41	7.33±2.54	8.85±0.94	11.2 ±0.29	119 ±10.50	154 ±31.90	169±16.60	96.4 ±6.83	218 ±12.14	25.9±0.58
FOET	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.472±0.95	19.57 ±4.12	4.32 ±3.50	9.79 ±1.10	1.08 ±0.08	16.50±0.46
FHET	<LOD	0.0511±0.07	<LOD	0.0527±0.00	0.694±0.24	0.0364 ±0.01	<LOD	0.3296 ±0.14	0.657 ±0.03	0.187± 0.00	0.152±0.02	0.210 ±0.15	ND
PFODA	nd	nd	nd	nd	nd	nd	nd	<LOQ	<LOQ	1.76 ±0.03	<LOQ	<LOQ	6.36±0.44

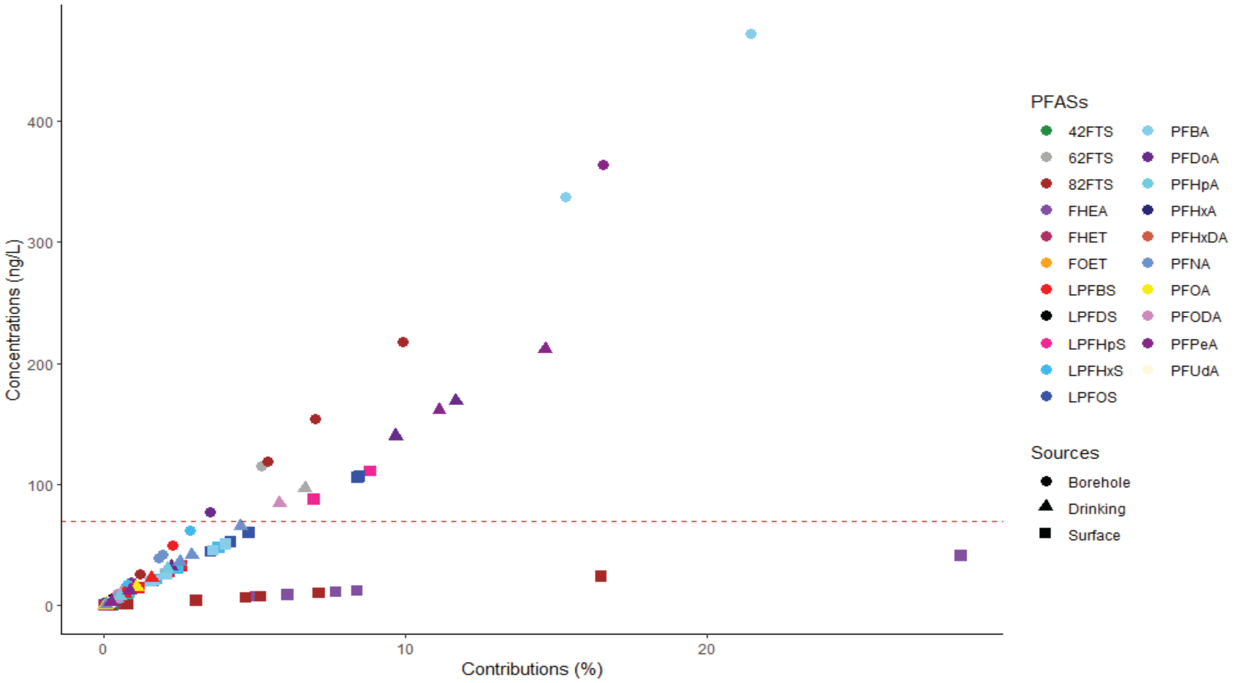

Figure 5.8: PFASs concentration distributions in various water sources in Gauteng province during the dry season.

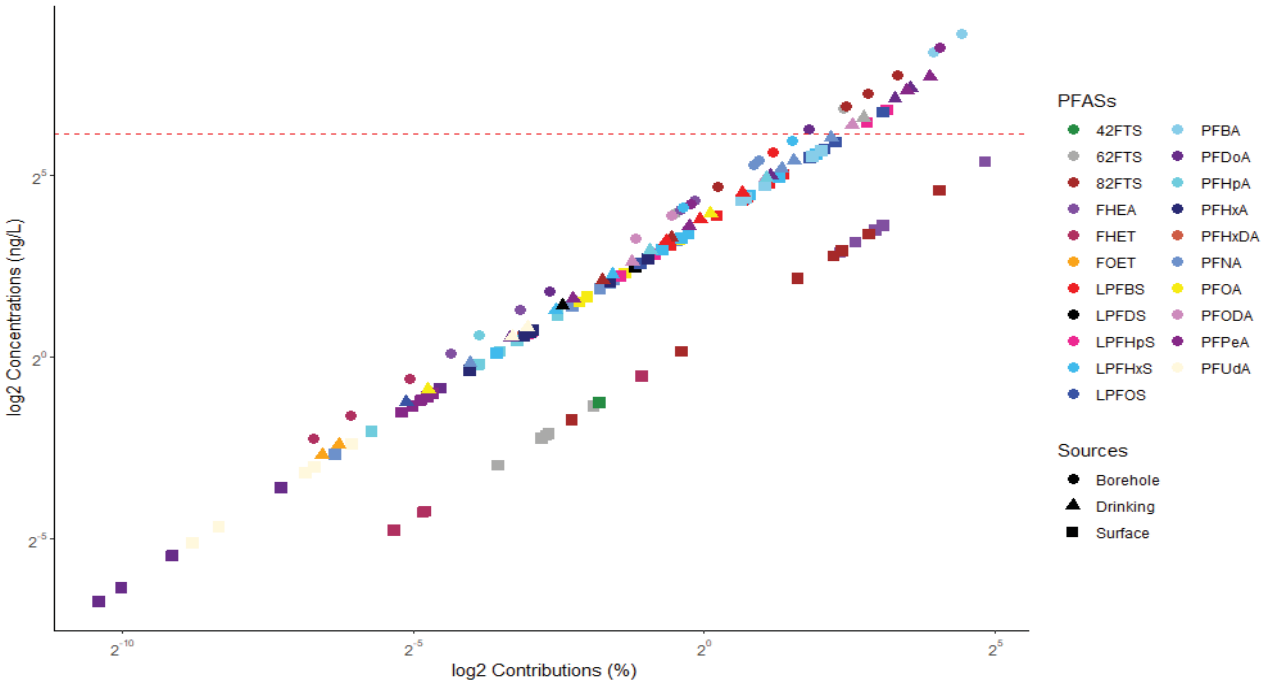

Figure 5.9: PFASs concentrations distributions for various water sources Gauteng during the dry season.

The contributions of the various classes of PFASs in different water sources can be seen in Figure 5.10. All the classes are most present in drinking and surface water and scattered in borehole samples. However, the PFCAs appear to be the most dominant PFASs compared to the PFSAs and fluorotelomers. The contributions of short and long-chain PFASs in various water sources are shown in Figure 5.11. Both short and long chains feature prominently in drinking water compared to borehole and surface water samples. However, long chains appear to have contributed more than short chains.

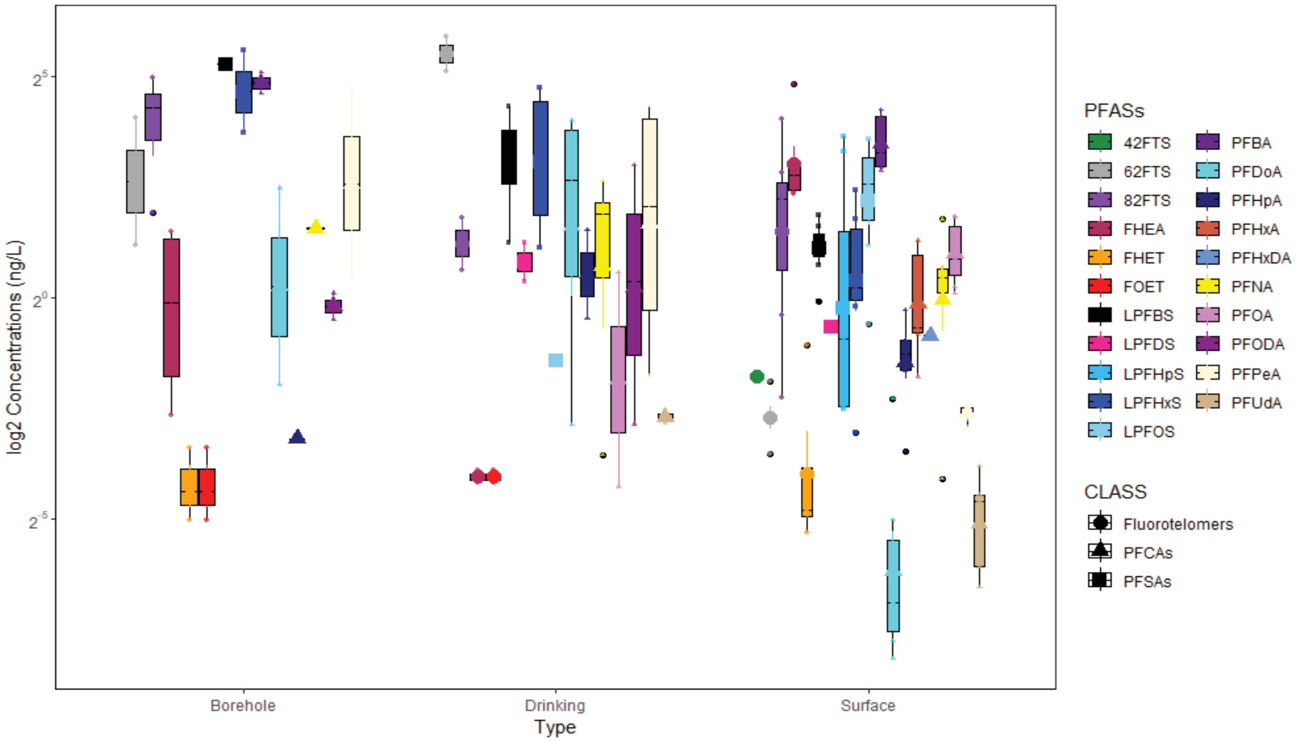

Figure 5.10: PFASs class contributions for various water sources in Gauteng in dry season

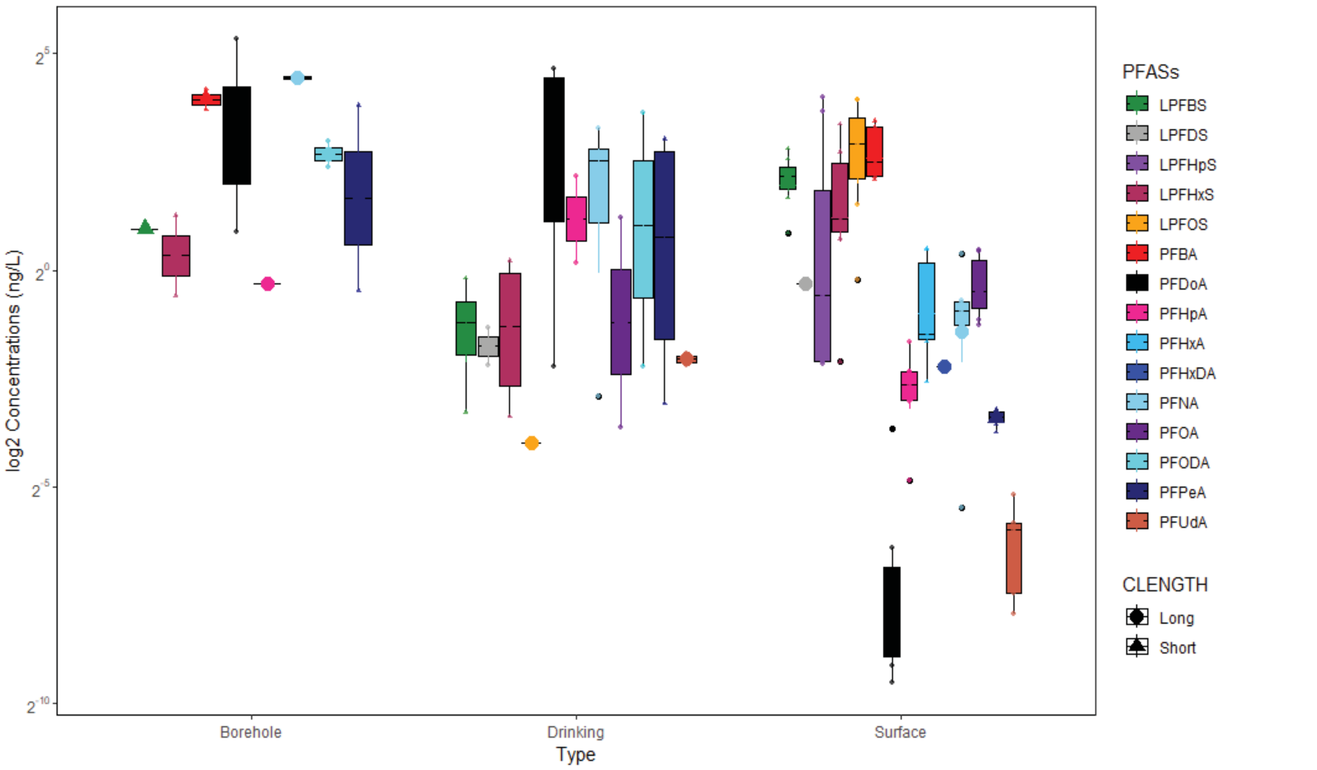

Figure 5.11: Contributions of short and long-chain PFASs for various water sources in Gauteng during the dry season.

5.5.2 Establishing the possible sources of the PFASs detected in the water

An attempt was made to establish if any relationship existed between the PFASs congeners, i.e. whether they share common sources. A principal component analysis was constructed to assess PFASs congener contributions and their relationships and this can be seen in Figure 5.12. The first quadrant (clockwise) shows a mix of fluorotelomers, PFCAs and PFSAs. The same also applies to the second quadrant. However, the third and fourth quadrants are dominated by the sulfonates. PFASs in the same quadrants would suggest similar sources. PFASs. With respect to samples and their relationships, a PCA plot was constructed and it is shown in Figure 5.13. The surface samples are clustered and well isolated from the other samples. Some of the borehole samples are also clustered, whereas the tap water are well separated. The clustering may suggest share of the same sources of PFASs contamination. On the other hand, non-clustering would suggest different sources.

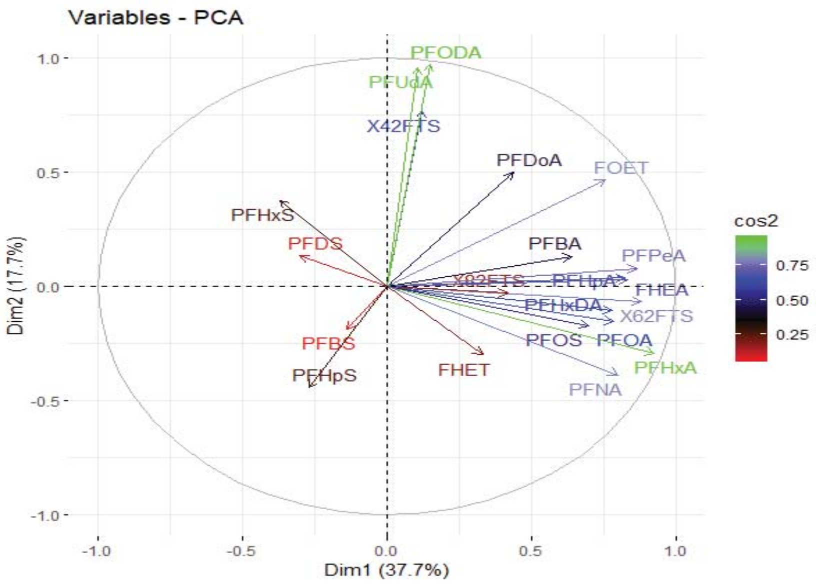

Figure 5.12: PCA of PFASs congener contributions and their relationships during the dry season.

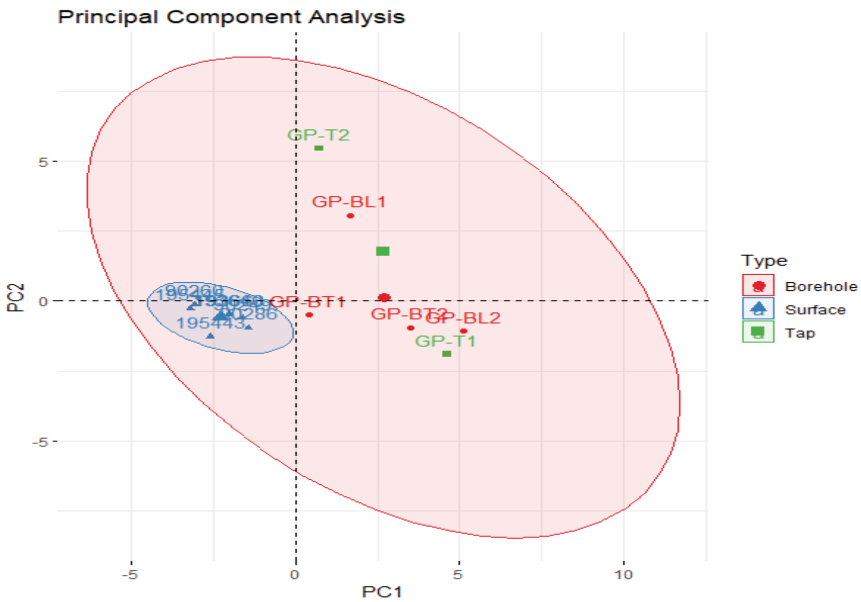

Figure 5.13: PCA of sampling sites and their relationships during the dry season.

5.6 DISTRIBUTION OF PFASS IN RAINWATER

As seen in Table 5.13, good recoveries (74-128%) were obtained and this was within the percentage recovery range of 50-200%. This validated the extraction method.

Table 5.13: Percentage recoveries (%) and standard deviations for rainwater samples (2021).

Surrogates	February	November	December
MPFNA	84.03 ±4.10	109.1±0.49	128.4±3.24
MPFUdA	80.9±0.71	75.92±15.83	75.9±15.83
MPFHxS	100.3±0.82	74.02±16.21	91.1±40.37

Table 5.14 shows the mean PFASs concentrations in rainwater collected in February, November and December 2021. The PFASs concentrations ranged from <LOD-38.5 ng/L. PFBA exhibited the highest concentration (173.9 ng/L) in the rainwater sample collected in February 2021, followed by FOET with a concentration of 67.9 ng/L. PFHxA, PFPeA, 8:2 FTS, PFHpA, LPFBS, PFOA, 6:2 FTS, FOET, FHET and PFBA were all detected in the rainwater samples collected in February, November and December 2021. Rainwater sample collected in February exhibited the highest number of PFASs compounds. It was possible that the stench that clouded Gauteng Province for some days in February 2021 may have contributed to the observed high PFASs compounds detected. FOET and PFBA showed high concentrations in all the rainwater samples.

Table 5.14: Mean concentrations (ng/L) of PFASs and standard deviations in rainwater (February, November and December 2021)

Compounds	February	November	December
PFUdA	0.333±0.12	<LOD	0.593±0.13
PFHxA	38.5±13.59	3.70±0.69	3.29±1.27
PFPeA	2.65±0.09	1.201±0.17	1.064±0.01
4:2 FTS	0.08 ±0.01	<LOD	<LOD
8:2 FTS	6.25±0.70	0.128±0.62	0.787±1.09
PFHpA	0.881±0.83	0.728±0.11	0.438±0.07
PFNA	2.48±0.62	<LOD	0.832±0.08
L-PFBS	21.9±4.74	0.122±0.05	0.062±0.03
L-PFHxS	0.0957±0.11	<LOD	2.83±2.59
L-PFOS	10.5±0.74	9.20±1.45	<LOD
PFHpS	<LOD	<LOD	<LOD
PFOA	31.2±1.69	1.02±0.46	3.28±1.02
PFDoA	<LOD	<LOD	<LOD
PFODA	<LOD	<LOD	<LOD
L-PFDS	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD
FHEA	<LOD	<LOD	2.487±1.05
6:2 FTS	1.62±0.02	11.6±0.66	5.62±0.27
FOET	67.9±7.28	37.6±11.66	52.1±6.429
FHET	0.283±0.02	0.107±0.01	0.177±0.03
PFBA	173.9±42.14	17.6±2.01	38.7±11.01

5.7 USING PASSIVE SAMPLING TO MONITOR PER- AND POLYFLUOROALKYL SUBSTANCES (PFASS) IN WASTEWATER

5.7.1 Calibration of the passive sampler

Before deployment, the Polar Organic Chemical Integrative Sampler (POCIS) containing Oasis hydrophilic-lipophilic balance (HLB) was calibrated in using 21 PFASs mix standards compounds for 14 days. The sampling rates were calculated using the following equation:

$$C_w = C_s M_s / R_s t \qquad \text{(Equation 5.1)}$$

where C_w and C_s are the concentrations of PFASs the water (ng/L) and in the POCIS (ng/g) respectively, M_s is the mass of the sorbent in the POCIS (g), Rs is the sampling rate (L/day) and t is the sampling period (days) .

The calibration plots of POCIS-HLB adsorption of PFASs are shown in Figure 5.14. As can be seen, the uptake of PFASs are linear. From the linear plots, the sampling rates were determined as reported (Arditsoglou and Voutsa, 2008; Morin et al., 2012; Weiss et al., 2015). The determined sampling rates were in the following range 0.0029-0.099 L/day as can be seen in Table 5.15.

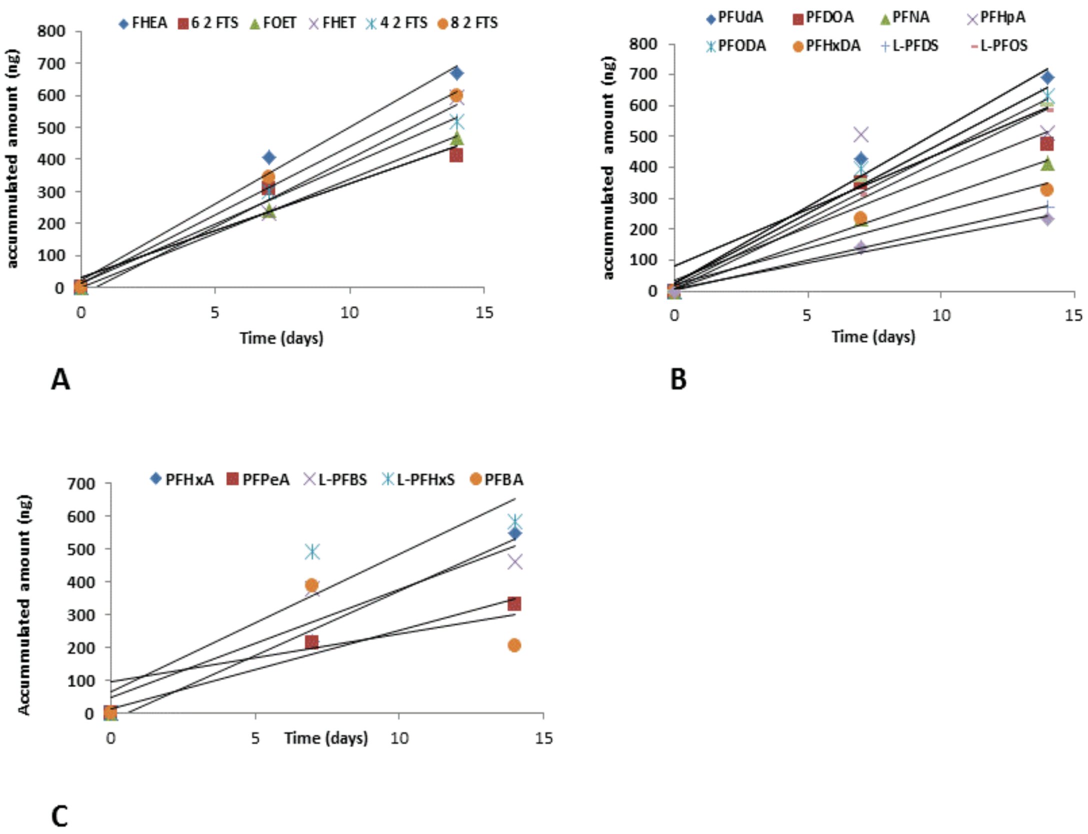

Figure 5.14: Uptake profile of individual PFASs for POCIS-HLB samplers over 14-day period (A) Fluorotelomers, (B) Long chain and (C) short chain PFASs.

Table 5.15: Sampling rates for the calibration of POCIS-HLB samplers

Compound	*R_S (L days^{-1})	*R^2
FHEA	0.099±0,023	0.9842
6 2 FTS	0.010±0,002	0.9239
FOET	0.044±0,184	0.9997
FHET	0.054±0,046	0.9843
PFUdA	0.012±0,901	0.9817
PFDOA	0.052±0,006	0,9299
PFHxA	0.020±0,036	0.985
PFNA	0.076±1,10	0.9941
PFPeA	0.084±0,045	0.2824
4 2 FTS	0.0523±0,066	0.9923
8 2 FTS	0.041±0,033	0.9921
PFHpA	0.077±0,043	0.7576
PFODA	0.061±0,061	0.9806
PFHxDA	0.050±0,056	0.941
L-PFBS	0.036±0,043	0.8759
L-PFDS	0.0029±0,023	0.9995
L-PFHxS	0.031±0,01	0.8654
L-PFOS	0.0081±0,14	0.9984
L-PFHpS	0.018±0,632	0.9886
PFOA	0.087±0,001	0.9892
PFBA	0.004±0,14	0.9755

*R_S= sampling rate, R^2 = regression

5.7.2 Mean concentrations of PFASs using passive and grab sampling methods for 14 days

Shown in Table 5.16 are the mean concentrations of PFASs detected in GP-W, a domestic wastewater treatment plant in Pretoria. The passive samplers were deployed at the effluent of the GP-W for 14 days. Thereafter, the samplers were retrieved and grab samples collected at the same intervals on day 7 and 14. The mean concentrations of PFASs recorded on 7 day were in the range of 0.51 to 81.67 ng/L. All PFASs targeted were detected except 6:2 FTS, PFDOA, 8:2 FTS, and PFHxDA. 4-2 FTS had the highest concentration of 81.67 ng/L. The same trend was also observed in grab samples, although FOET exhibited the highest concentration of 22.36 ng/L in this case. Furthermore, FHET and PFHpA were not detected in the grab samples. Generally, on day 7, the PFASs concentrations recorded for POCIS higher than the grab samples except for FOET. On 14 day, the mean PFASs concentrations for POCIS-HLB ranged 0.94-98.86 ng/L. PFNA had the highest concentration of 94.04 ng/L. On the other hand grab sample had mean concentration range of LOD-30.55 ng/L. PFHxA had the highest concentration of 30.55 ng/L. Once again, 6:2 FTS, 8:2 FTS, PFODA and PFHxDA were not in POCIS samples. This trend was seen in grab samples in addition to PFDOA.

It can be seen from Table 5.16, that the PFASs concentrations in POCIS were significantly higher than that of grab samples. The difference between the concentrations recorded for the two sampling method was because grab samples provided only snap shot concentrations, while POCIS-HLP provided time weighted average concentrations (Godlewska, Stepnowski and Paszkiewicz, 2021). The PFASs concentrations detected in the current study are higher than the concentrations reported by Gobelius et al. (2019) with total sum of all PFASs of 7.1 ng/L in drinking water treatment samples. The higher PFASs concentrations observed in POCIS-HLB indicated the ability of the sampler to adsorb more PFASs compounds compared to grab samples.

Table 5.16: Mean concentrations of PFASs in POCIS-HLB and grab samples.

PFASs (ng/L)	Day 7		Day 14	
	POCIS HLB sampler	Grab sample	POCIS HLB sampler	Grab sample
FHEA	32.61±0.123	1.61±1.02	38.14±0.09	0.63±0.075
6 2 FTS	ND	ND	ND	ND
FOET	8.67±0.11	22.36±0.03	75.10±0.05	7.50±0.25
FHET	57.98±0.15	ND	35.17±0.125	14.93±0.36
PFUdA	25.60±0.002	3.00±0.05	73.29±0.96	0,18±0.46
PFDOA	ND	ND	0.94±0.05	ND
PFHxA	14.23±0.01	21.13±0.521	55.96±0.09	30.55±0.65
PFNA	38.84±0.23	0.34±0.56	94.04±0.36	2.96±0.09
PFPeA	13.04±0.3650	5.62±048	20.58±0.06	6.31±0.02
4 2 FTS	81.67±0.15	0.31±0.03	9.86±0.09	5.16±0.05
8 2 FTS	ND	ND	ND	ND
PFHpA	0.51±0.655	LOD	3.07±1.5	LOD
PFODA	ND±0.35	ND	ND	ND
PFHxDA	ND	ND	ND	ND
L-PFBS	29.77±0.100	10.56±0.05	47.56±0.02	0.99±0.08
L-PFDS	36.16±1.05	0.56±0.125	54.42±0.06	4.20±0.156
L-PFHxS	48.52±0.80	2.91±0.89	64.55±0.05	0.51±0.03
L-PFOS	7.58±0.92	0.80±02.712	23.18±0.65	15.08±0.06
L-PFHpS	36.42±0.15	0.03±0.14	46.53±0.985	0.08±0.089
PFOA	12.79±0.02	4.64±0.125	33.73±0.062	0.83±1.01
PFBA	7.1±0.05	0.68±0.05	15.84±0.03	5.8±0.46

5.8 SUMMARY

The PFASs were grouped into categories of telomers, short and long chains and the concentrations exhibited by each groups are discussed in the sections above. FHEA was the dominant telomere except in 90260. All the short and long chains were detected in most of the samples. However, the highest concentration was observed for PFOS and this may be attributed to the breakdown of the sulphonate telomers. More long chain were detected in wet season than in dry season. However, the concentrations of PFASs in dry season were generally higher than in wet season. Table 5.17, shows comparison of the concentrations of PFASs observed in this study to other studies conducted from different parts of the world. As seen in Table 5.5, the concentrations detected in this study were much lower than the levels reported in Shandong and Liaoning Provinces in China. However, higher levels are seen in German Rivers in Ruhr area.

Table 5.17: Comparison of PFASs concentrations obtained in current study with other studies

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.88	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area) 2-61 (Rhine River)	Skutlarek et al., 2006
Shandong Province	13.1-69,238	Chen et al., 2017
Liaoning Province	22.4-26,730	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
Gauteng Province South Africa (Dam Surface)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al., 2014,
South Africa (River water)	<LOQ to 38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
Gauteng Province South Africa (Surface water)	**<LOQ-412.5**	**This study**
Gauteng Province South Africa (Wastewater treatment plant)	**<LOD-403**	**This study**
Gauteng Province South Africa (Drinking water treatment plant)	**<LOD-179.0**	**This study**
Gauteng Province South Africa (Bottled drinking water)	**<LOD-72**	**This study**
Gauteng Province South Africa (Borehole water)	**LOD-383**	**This study**
Gauteng Province South Africa (rainwater)	**<LOD-38.7**	**This study**
Gauteng Province South Africa (Tap water)	**<LOD-2077**	**This study**

CHAPTER 6: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE KWAZULU-NATAL PROVINCE

6.1 SAMPLING STRATEGY

6.1.1 Location and description of sampling sites

Water samples were collected from Durban and Umgeni River in the KwaZulu-Natal province during both the wet and dry seasons. Figure 6.1 shows the land use map around the sampling sites. Durban is the most cosmopolitan city in KZN with many industrial and other human activities. Therefore, it represents a good study area. Furthermore, water samples were also collected from Umgeni River which has been dogged with pollution problems over the years. The following water systems were targeted in the province:

- Tap water;
- Wastewater;
- River water and
- Reserviour water

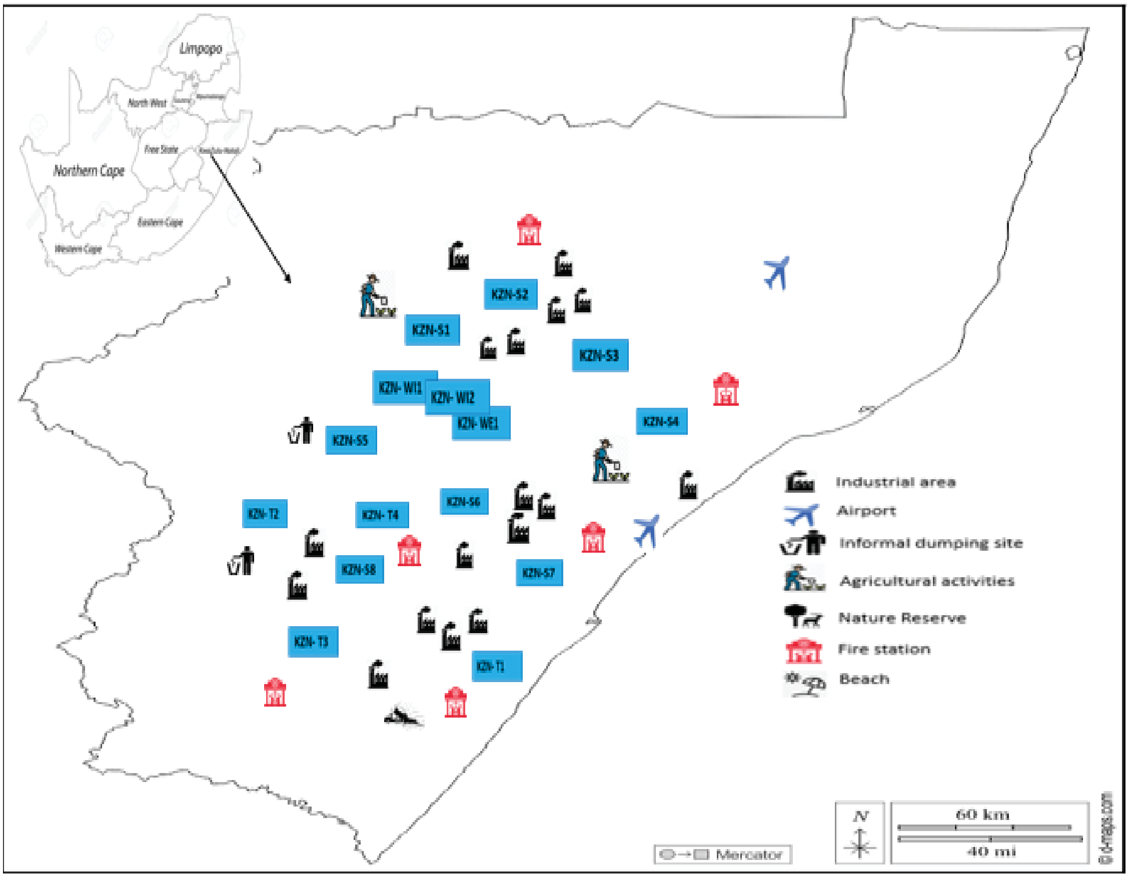

Figure 6.1: Land use map and the sampling sites in KwaZulu-Natal Province.

6.1.2 Sample collection

Table 6.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the Durban and surrounding areas and Umgeni River in wet October-April) and dry (June-August) seasons. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 6.1: Sampling sites in KwaZulu-Natal province with coordinates

Dry Season			Wet Season		
LOCATION/SAMPLE NAME	COORDINATES	pH	LOCATION/SAMPLE NAME	COORDINATES	pH
KZN-T1	-29.86723, 30.99102	7.8	KZN-T1	-29.86723, 30.99102	7.6
KZN-T2	-29.81478, 30.94959	7.4	KZN-T2	-29.81478, 30.94959	7.8
KZN-T3	-29.81187, 30.95418	7.5	KZN-T3	-29.81187, 30.95418	7.6
KZN-T4	-31.94895, 28.36657	7.1	KZN-T4	-31.94895, 28.36657	7.6
KZN-S1	-29.67236, 31.02982	7.5	KZN-S1	-29.67236, 31.02982	7.6
KZN-S2	-29.67557, 31.02657	7.2	KZN-S2	-29.67557, 31.02657	7.6
KZN-S3	-29.67675, 31.02788	6.8	KZN-S4	-29.69516, 31.07604	7.6
KZN-S4	-29.69516, 31.07604	6.9	KZN-S6	-29.80345, 30.99277	7.6
KZN-S5	-31.9555, 28.35129	7.3	KZN-S7	-29.80845, 31.00102	7.6
KZN-S6	-29.80345, 30.99277	6.4	KZN-S8	-29.80554, 30.96565	7.6
KZN-S7	-29.80845, 31.00102	6.4	KZN-WE1	-29.77389, 30.97453	7.6
KZN-S8	-29.80554, 30.96565	6.1	KZN-WE2	-29.77389, 30.97454	7.6
KZN-WE1	-29.77389, 30.97453	7.4	KZN-WI1	-29.77389, 30.97453	7.6
KZN-WI1	-29.77389, 30.97453	7.3	KZN-WI2	-29.77389, 30.97453	7.6
KZN-WI2	-29.77389, 30.97453	7.8			

KZN-T2=Glenwood/Tap water; KZN-T2=Reservoir Hill 1/Tap water; KZN-T3=Claire Estate/Tap water; KZN-T4=Reservoir Hill/Tap water 2; KZN-S1=Phoenix (Ohlanga) River 1; KZN-S2=Phoenix (Ohlanga) River 2; KZN-S3=Phoenix (Ohlanga) 3; KZN-S4=Umgeni River 1; KZN-S5=Umgeni River 2; KZN-S6=Umgeni River 3; KZN-S7=Umgeni River 4; KZN-S8=Phoenix (Ohlanga) River 4; KZN-WE1=Dewats effluent; KZN-WE2=Dewats effluent before gravel filtration, KZN-WI1=Dewats influent/Ciphon Chamber; KZN-WI2=Dewats influent ABR Train 1

6.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. The percentage recoveries of blanks and samples in drinking water, river water and wastewater treatment plant samples spiked with surrogate standards are shown in Tables 6.2 to 6.5. As can be seen in Table 6.2, the percentage recoveries of the labelled surrogate standards were 99.6±23.74 76.5±2.82% and 88.6±10.61 for MPFNA, MPFUdA and MPFHxS respectively. Recoveries for drinking water, river water and wastewater treatment plants ranged from 54-89%, 44-113% and 32-127% respectively, as can be seen in Tables 6.2-6.5. It has been suggested that recoveries can and often have a wide range (50-200%), due to matrix effects which can occur in water samples. From Tables 6.2-6.5, the recoveries of PFASs surrogate generally fall within the accepted range.

Table 6.2: Percentage recoveries and standard deviation of blanks spiked with surrogate standards during the dry season

Samples – Mean (n=6) surrogate recoveries (%) ± Standard deviation	
Surrogates	**Blanks**
MPFNA	99.6±23.7
MPFUDA	76.5±2.8
MPFHxS	88.6±10.6

Table 6.3: Percentage recoveries and standard deviations for drinking water samples during the dry season

	Samples – Surrogate recoveries (%) ± Standard deviation			
Surrogates	**KZN-T1**	**KZN-T2**	**KZN-T3**	**KZN-T4**
MPFNA	77.5±4.41	71.7±22.7	89.2±11.6	87.8±11.2
MPFUDA	74.2±2.13	66.9±13.0	88.5±14.4	76.1±7.60
MPFHxS	87.8±21.2	46.5±0.74	64.0±19.7	54.8±9.94

KZN-T = KwaZulu-Natal Tap water

Table 6.4: Percentage recoveries and standard deviations for surface water samples during the dry season

	Samples Surrogate recoveries (%) ± Standard deviation							
Surrogates	**KZN-S1**	**KZN-S2**	**KZN-S3**	**KZN-S4**	**KZN-S5**	**KZN-S6**	**KZN-S7**	**KZN-S8**
MPFNA	113.1±5.06	102.3±1.53	87.46±13.46	66.61±18.56	71.1±3.67	103.3±8.59	72.4±3.64	44.4±9.88
MPFUDA	69.5±3.59	78.6±25.5	58.1±9.38	69.6±8.51	57.6±0.93	92.3±9.73	72.4±22.9	38.8±4.51
MPFHxS	52.8±4.97	73.2±0.81	63.4±16.0	52.7±8.19	49.4±1.44	68.5±13.36	75.7±11.3	32.7±3.70

KZN-S = KwaZulu-Natal Surface water

Table 6.5: Percentage recoveries and standard deviations for wastewater treatment plant samples during the dry season

	Surrogate recoveries (%) ± Standard deviation		
Surrogates	**KZN-WE1**	**KZN-WI1**	**KZN-WI2**
MPFNA	64.8±8.99	127.1±24.67	110.1±27.4
MPFUDA	55.1±8.45	32.8±2.49	68.76± 5.08
MPFHxS	48.2±6.32	64.4±5.84	59.9±1.37

KZN-W-WE = KwaZulu-Natal wastewater effluent; KZN-WI = KwaZulu-Natal wastewater influent

The mean concentrations of PFASs detected in the blanks are shown in Table 6.6. As can be seen in Table 6.6, the mean concentrations of PFASs in blank samples ranged from <LOD-29.46 ng/L. From Table 6.6, FHEA exhibited the highest concentration. PFHxA, PFPeA, PFHpA, PFNA, PFOA, FHEA and 6:2 FTS were detected in the blank at a very low concentration except the concentration exhibited by FHEA.

Table 6.6: Mean concentrations of PFASs compounds in field blank samples during the dry season

	Samples – Mean concentrations (ng/L) ± standard deviation
Compounds	**Blanks (n=6)**
PFUdA	<LOD
PFHxA	0.112±0.10
PFPeA	0.463±0.08
4:2 FTS	<LOD
8:2 FTS	<LOD
PFHpA	0.107±0.01
PFNA	0.052±0.003
L-PFBS	<LOD
L-PFHxS	<LOD
L-PFOS	<LOD
PFHpS	<LOD
PFOA	0.135±0.03
PFDoA	<LOD
PFODA	<LOD
L-PFDS	<LOD
PFHxDA	<LOD
FHEA	29.4±8.95
6:2 FTS	0.247±0.061
FOET	<LOD
FHET	<LOD
PFBA	3.49±1.21

6.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

6.3.1 Distribution of PFASs in various water sources during the dry season

Table 6.7 shows the concentrations of PFASs compounds in different water samples in dry season. Congeners PFBA, PFHpA, PFPeA, PFHxA, PFOA, PFNA, L-PFHxS, 6:2 FTS, 8:2 FTS, PFUdA, FOET, FHET were detected in all the samples at concentrations ranging from 0.0279-42.05 ng/L; while PFOS was detected in only one sample. LPFBS, 4:2 FTS, PFDoA, PFODA, L-PFDS, PFHxDA and FHEA were all below the LOD. The highest concentration (42.05 ng/L) was detected in KZN-T4 water and this was exhibited by FOET. FOET exhibited the highest concentrations across all the drinking tap water samples. L-PFOS was detected in all the samples except in three tap water. PFHxDA, PFHpS and 4:2 FTS were detected in five, four and two sites respectively and PFDoA, PFODA and L-PFDS were either not detected or <LOD in all the sites. The PFASs concentrations in surface water (river water) obtained in KZN river water are far less than the PFASs concentrations reported by Skutlarek et al., (2006) in Rhine river, Mudumbi et al. (2014) in Western Cape, Batayi et al. (2018) in Hartbeespoort and Roodeplaat Dams; but higher than concentrations in sea water reported by Ojemaye et al. (2019). Water samples were collected after the flooding in KZN, and this may have affected the concentration of PFASs observed. Generally, the concentrations of PFASs detected in drinking water are extremely low and well below the 70 ng/L advisory limit.

Figure 6.2, shows the PFASs concentration distributions in water sources collected in KZN during the dry season. Clustering of PFASs can be observed in the plot. The PFASs compounds also showed similar influence, with the exception of PFUdA which showed more scattering for all the water sources.

Figure 6.3 shows the log base contributions of PFASs from various water sources. Contributions from WWTP and surface water were more than tap water. In both surface water and tap water the long chains were observed to have more contribution and PFOA was the compound with the highest contribution.

In Figure 6.4, the PFSAs class had more contribution in the results detected in surface water and wastewater treatment plant collected from KZN. The compounds that contributed the most to class of PFSAs were PFOS in surface water and PFBS in WWTP. This was followed by the Fluorotelomer class in both water sources. In tap water, however, the Fluorotelomers had more contribution with FOET contributing more followed by PFSAs. PFCAs had less contribution to the results in all the water sources collected.

In all the water sources represented in Figure 6.5, the long chain PFASs had more contribution than the short chains. PFOS contributed the most in surface water and in wastewater treatment plant samples and in tap water PFNA had the most contribution.

Table 6.7: Mean concentrations and standard deviations of PFASs in various water samples in dry season

Compounds	KZN-T1	KZN-T2	KZN-T3	KZN-T4	KZN-S1	KZN-S2	KZN-S3	KZN-S4	KZN-S5	KZN-S6	KZN-S7	KZN-S8	KZN-WE1	KZN-WI1	KZN-WI2
PFBA	**1.17±0.56**	**0.85±0.33**	**1.00±0.55**	**1.09±0.16**	**4.40±1.75**	**0.37±0.18**	**0.26±0.08**	**4.13±0.01**	**0.45±0.24**	**4.30±2.25**	**0.32±0.17**	**0.68±0.22**	**4.81±1.71**	**6.02±3.15**	**5.89±1.23**
PFHpA	**0.70±0.2**	**0.37±0.11**	**0.25±0.16**	**0.38±0.18**	**6.60±2.52**	**0.39±0.03**	**0.68±0.28**	**0.39±0.1**	**0.7±0.26**	**0.51±0.004**	**0.50±0.06**	**1.39±0.14**	**0.54±0.05**	**0.65±0.23**	**0.45±0.25**
PFPeA	**0.27±0.13**	**0.38±0.06**	**0.40±0.17**	**0.27±0.09**	**0.55±0.23**	**0.33±0.02**	**0.49±0.23**	**0.43±0.08**	**0.05±0.03**	**0.53±0.1**	**0.66±0.02**	**0.42±0.08**	**0.33±0.1**	**0.51±0.04**	**0.87±0.55**
PFHxA	**0.53±0.45**	**0.35±0.17**	**0.53±0.08**	**0.28±0.12**	**1.45±0.2**	**0.97±0.25**	**1.64±0.04**	**0.87±0.03**	**0.89±0.14**	**1.08±0.1**	**1.13±0.25**	**1.16±0.3**	**1.88±1.32**	**2.32±0.15**	**5.38±3.96**
PFOA	**0.31±0.08**	**0.11±0.05**	**0.14±0.07**	**0.30±0.15**	**0.65±0.29**	**0.42±0.08**	**0.41±0.08**	**0.40±0.23**	**0.70±0.22**	**0.27±0.01**	**0.50±0.25**	**0.97±0.83**	**0.45±0.04**	**0.49±0.09**	**0.38±0.25**
PFNA	**0.42±0.34**	**0.62±0.63**	**0.87±0.33**	**0.50±0.14**	**3.45±3.55**	**0.66±0.01**	**1.97±0.10**	**0.47±0.17**	**1.31±0.86**	**2.36±0.41**	**1.42±0.13**	**1.54±0.19**	**3.07±0.02**	**0.71±0.06**	**3.40±2.21**
PFUdA	**0.03±0.02**	**0.03±0.01**	**0.09±0.1**	**0.03±0.001**	**0.04±0.01**	**0.05±0.02**	**0.10±0.05**	**0.04±0.03**	**0.01±0.02**	**0.04±0.02**	**0.09±0.04**	**0.09±0.01**	**0.08±0.05**	**0.24±0.24**	<LOD
PFODA	ND	ND	ND	ND	<LOD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	ND	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	ND	ND	ND	ND	ND	ND	**1.36±1.91**	**2.91±4.11**	**0.81±1.14**	**3.08±4.36**	**1.32±1.86**	ND	ND	ND	**0.42±0.59**
L_PFBS	ND	ND	ND	<LOD	**0.09±0.08**	**0.14±0.08**	**1.68±0.04**	**3.79±0.46**	**0.12±0.04**	**0.49±0.17**	**0.80±0.89**	**3.43±1.14**	**20.5±0.65**	**4.04±0.71**	**13.89±5.45**
L_PFHpS	ND	ND	ND	**0.08±0.11**	**0.09±0.13**	ND	ND	ND	ND	**0.09±0.1**	**0.1±0.01**	**0.25±0.16**	**0.02±0.003**	**5.66±1.93**	**14.65±9.28**
L_PFHxS	**0.27±0.16**	**0.03±0.03**	**0.22±0.02**	**0.11±0.1**	**0.66±0.25**	**0.37±0.16**	**0.40±0.18**	**0.30±0.16**	**0.61±0.02**	**0.25±0.03**	**0.17±011**	**1.13±0.66**	**0.37±0.19**	**1.37±0.41**	**6.7±3.44**
L_PFOS	ND	ND	**0.24±0.23**	ND	**4.11±2.07**	**2.19±0.68**	**2.43±1.21**	**1.13±0.12**	**5.63±0.73**	**2.29±0.82**	**1.52±1.37**	**8.46±5.9**	**4.31±5.25**	**0.28±0.2**	**5.19±0.47**
L_PFDS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**1.32±0.95**
4:2FTS	ND	ND	ND	ND	ND	ND	ND	**0.02±0.003**	ND	ND	ND	**0.01±0.01**	**0.05±0.07**	**0.88±0.24**	**0.44±0.004**
6:2FTS	**1.88±0.53**	**2.91±2.02**	**1.50±0.08**	**1.61±0.09**	**1.51±0.24**	**1.50±0.18**	**1.44±0.003**	**1.53±0.05**	**1.50±0.23**	**1.43±0.05**	**1.59±0.3**	**1.44±0.01**	**1.60±0.11**	**1.46±0.09**	**0.70±0.99**
8:2FTS	**2.00±0.98**	**3.99±2.13**	**2.26±1.5**	**1.65±0.7**	**4.70±2.22**	**4.38±0.76**	**7.63±2.41**	**4.75±0.13**	**1.95±0.23**	**2.60±0.32**	**3.37±1.68**	**5.90±0.93**	**3.35±0.61**	**12.04±2.53**	**20.43±4.92**
FOET	**26.17±3.85**	**42.05±2**	**22.17±0.79**	**33.89±0.15**	**22.71±0.14**	**22.48±4.16**	**20.83±0.22**	**23.23±1.66**	**24.4±0.49**	**20.72±4.35**	**25.58±3.32**	**26.32±7.81**	**19.04±5.47**	**10.41±0.03**	**10.49±0.14**
FHET	**0.50±0.01**	**0.76±0.05**	**0.41±0.01**	**0.47±0.002**	**0.68±0.15**	**0.54±0.02**	**0.23±0.33**	**2.85±1.01**	**1.52±2.16**	**0.61±0.86**	**0.96±0.15**	**0.65±0.91**	**1.41±1.01**	ND	ND
FHEA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

KZN-T =Tap water; KZN-S = surface river water; KZN-WE1= wastewater effluent; KZN-WI1= wastewater influent; ND = not detected; <LOD = less than the detection limit.

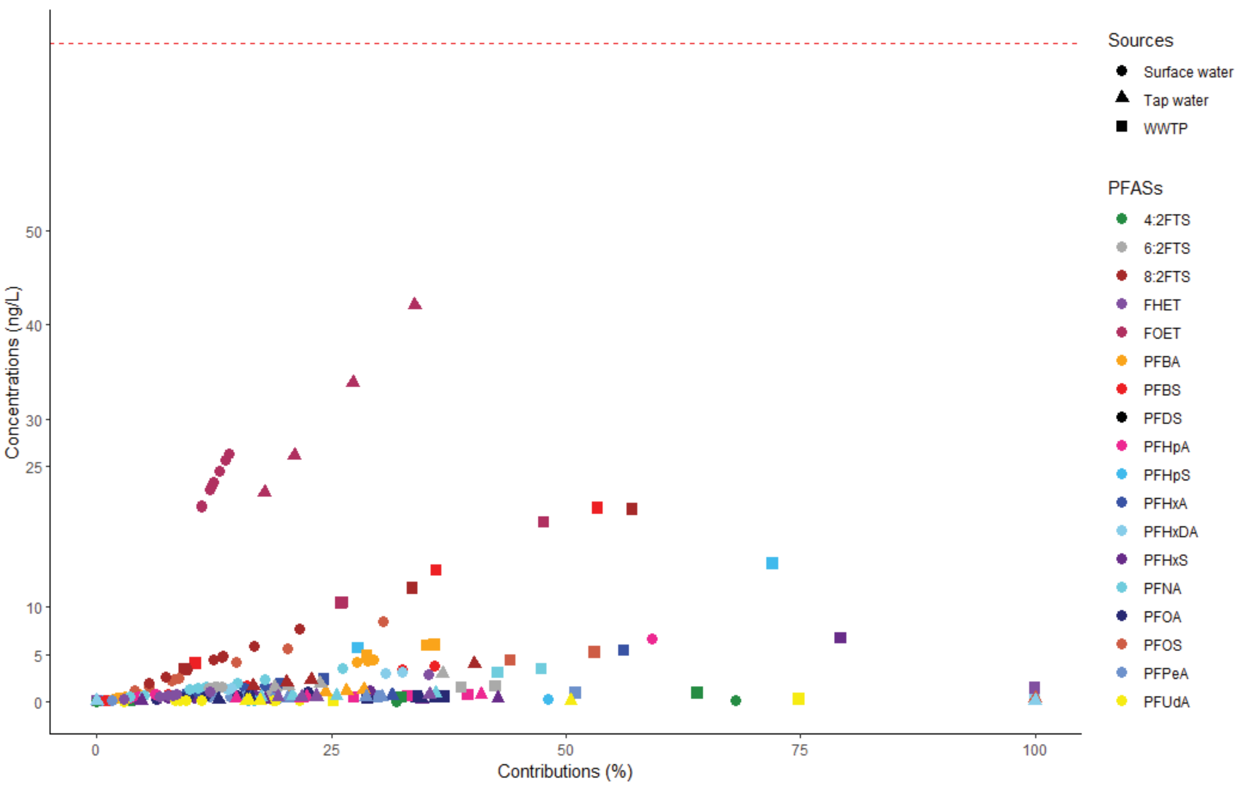

Figure 6.2: PFASs concentration distributions in various water sources in Kwa-Zulu Natal during the dry season.

Figure 6.3: PFASs concentration distributions in log base in various water sources in Kwa-Zulu Natal during the dry season.

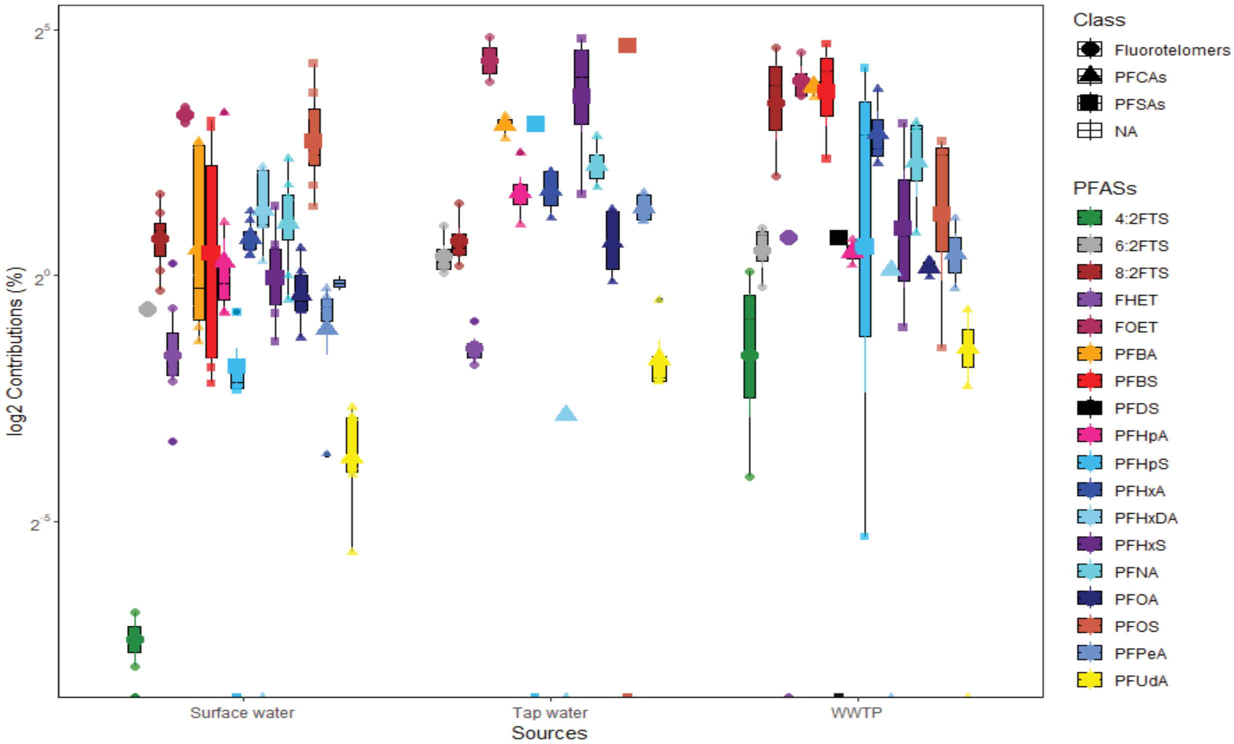

Figure 6.4: PFASs class contributions in various water sources in Kwa-Zulu Natal during the dry season.

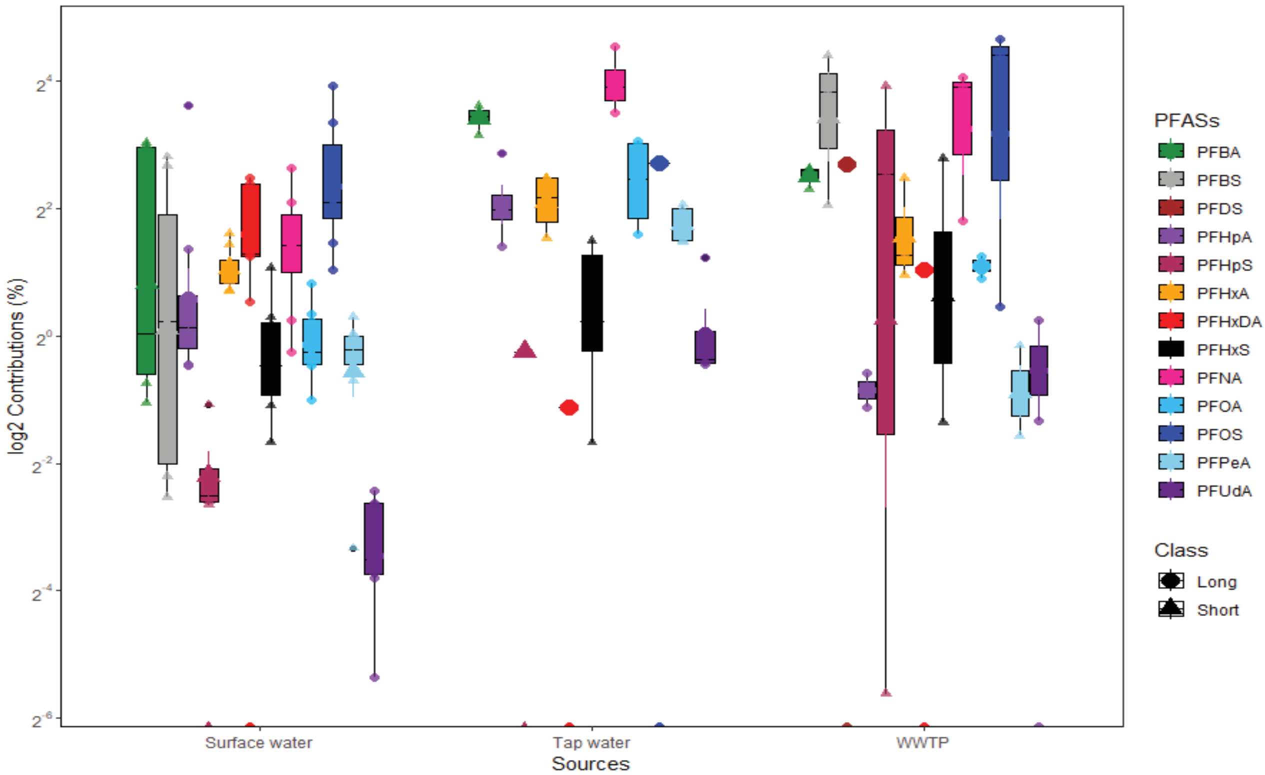

Figure 6.5: Contributions of long- and short-chain PFASs in various water sources in Kwa-Zulu Natal during the dry season.

6.3.2 Octanol/water partitioning coefficient (K_{OW}) of the PFASs

Water samples from KZN was used to evaluate the influence of octanol-water characteristics of the PFASs and their detectability in water. Octanol-water partition coefficient (K_{ow}) is a very valuable parameter with numerous environmental applications, where it is used as a primary characterizing parameter since it represents a measure of the tendency of a compound to move from the aqueous phase into lipids. Table 6.8 shows the K_{ow} of most of the PFASs determined in the present study. For drinking water/tap water, PFOA, L-PFHxS, PFHxA, PFHeA, 8:2 FTS, PFNA, PFHpA, PFUdA, 6:2 FTS, FOET, FHET and PFBA were detected in all the samples. These PFASs compounds have K_{OW} values of 2.82-6.82, indicating their tendency to move from the aqueous phase to the organic phase, hence their detection in most of the water samples. The highest concentration recorded in the river water (26.30 ng/L) was exhibited by FOET with low K_{ow} value of 4.31. On the other hand, PFBS with K_{OW} value of 3.90 exhibited the highest concentration in wastewater samples. PFDoA and PFODA, were not detected in any of the samples and this can be attributed to their high K_{OW} values of 5.65-11.51. This trend is repeated in the case of wastewater treatment where PFHxA, PFPeA, 4:2 FTS, 8:2 FTS, PFHpA, PFNA, L-PFBS, LPFHxS, L-PFOS, PFHpS, PFHxS , PFOA, 6:2 FTS, FOET, FHET and PFBA with low K_{OW} values were frequently detected; whereas PFDoA and PFODA, which were not detected in any of the samples have high K_{OW} values. The aforementioned observation infers that PFASs compounds with low K_{OW} are expected to be detected most frequently.

Table 6.8: K_{OW} of PFASs compounds

	STANDARDS	
PFAS compound	**K_{ow} value**	**Reference**
M2PFOA PFOA	4.67	Xiang et al., 2018
MPFDA PFDA	5.44	Xiang et al., 2018
MPFHxA PFHxA	3.26	Arp, Niederer & Goss, 2006
MPFUnDA PFUnDA	5.65	Xiang et al., 2018
MPFHxS PFHxS	5.17	Concawe, 2016
MPFNA PFNA	5.02	Xiang et al., 2018
	PFASs compounds	
PFHxDA	10.17	Gałęzowska et al., 2021
PFHxA	3.26	Niederer & Goss, 2006
PFNA	5.02	Xiang et al., 2018
PFDoDA	5.65	Xiang et al., 2018
PFODA	11.51	Gałęzowska et al., 2021
PFUdA	6.82	Gałęzowska et al., 2021
PFPeA	3.19	Xiang et al., 2018
PFHpA	4.40	Xiang et al., 2018
PFBA	2.82	Concawe, 2016
PFOA	4.30	Arp, Niederer & Goss, 2006
L_PFHpS	N\A	N\A
L_PFBS	3.90	Concawe, 2016
L_PFDS	7.66	Concawe, 2016
L_PFHxS	5.17	Concawe, 2016
L_PFOS	5.25	Arp, Niederer & Goss, 2006
Fluorotelomer carboxylic acids	N\A	N\A
Fluorotelomer acrylate	N\A	N\A
	Fluorotelomer sulfonic acids	
4:2 FTS	3.21	Concawe, 2016
6:2 FTS	4.44	Concawe, 2016
8:2 FTS	5.66	Concawe, 2016
10:2 FTS	6.91	Concawe, 2016
	Fluorotelomer Alcohols	

4:2 FTOH	2.31	Arp, Niederer & Goss, 2006
6:2 FTOH	3.32	Arp, Niederer & Goss, 2006
8:2 FTOH	4.31	Arp, Niederer & Goss, 2006
10:2 FTOH	5.39	Arp, Niederer & Goss, 2006

6.3.3 Establishing the possible sources of PFASs detected in the water

Statistical analyses was performed using Principal Component Analysis (PCA) for the PFASs concentrations detected in KwaZulu-Natal Province water samples (Figure 6.6). A p-value ≤ 0.05 was considered statistically significant for all datasets. PFOA, PFOS, PFDoA, PFNA, PFBS and PFHxA all show positive strong contributions in the first quadrant (clockwise). The observed pattern suggests similar sources. PFBA, PFHxS, 8:2 FTS, PFHpS, PFPeA and PFUdA also showed similar behaviour in the second quadrant. 6:2 FTS, FOET and FHET are in the third and fourth quadrants respectively. The compound that had the highest concentrations detected in most of the sampling sites was FOET. A study by Chen et al., 2020 reported FOET as the major FTOH homolog released into the environment in China (Chen et al., 2020). Proposed sources of FTOH into the aquatic environment so far are wastewater treatment plants (WWTPs) discharging into water bodies (Chen et al., 2020).

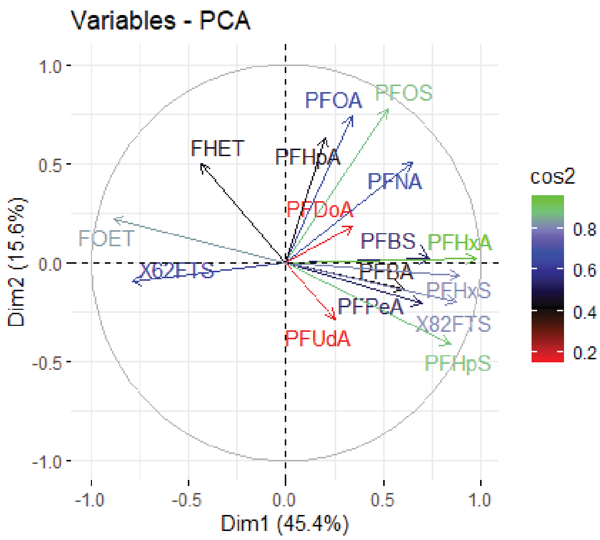

Figure 6.6: PCA of PFASs congener contributions and their relationships for the dry season.

Shown in Figure 6.7 is the PCA plot of sampling sites and their relationships. The water sources are all clustered indicating similar sources of PFAS. The concentrations detected in these sites may also be due to the discharge from WWTPs into river samples, since a high concentration was also detected at point KZN-S8. Although the wastewater sites are not clustered as observed for tap and river water, they occupy the second quadrant suggesting similar sources.

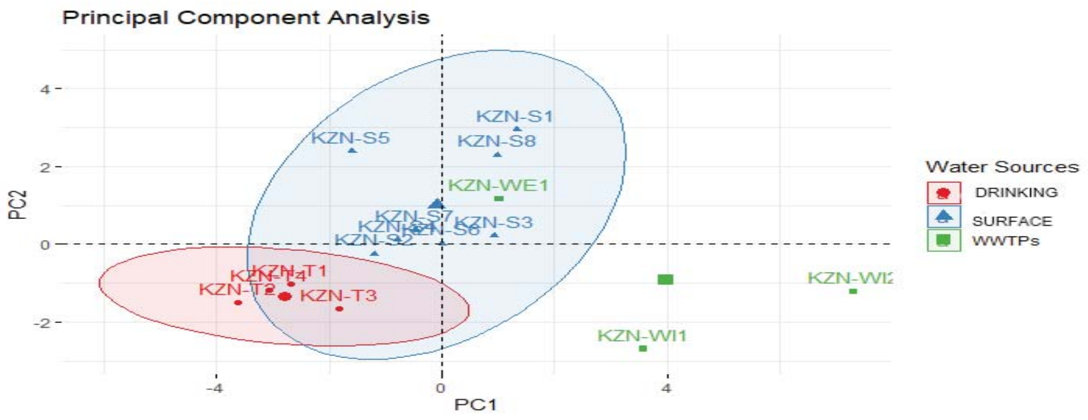

Figure 6.7: PCA of sampling points and their relationships during the dry season.

6.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

6.4.1 Distribution of PFASs in various water sources during the wet season

Table 6.9 shows the concentrations of PFAS compounds in various water sources. The detected compounds in drinking water were PFBA, PFHpA, PFPeA, PFHxA, PFOA, PFNA, L-PFBS, L-PFHpS, L-PFHxS, L-PFOS, 6:2 FTS, FHEA, FOET and FHET. The most dominant compound was PFBA, followed by PFHpA, with concentrations of 57.1 ng/L and 41.5 ng/L, respectively. The highest concentration for both compounds was detected at site KZN-T2. The concentrations of PFASs detected in drinking water were low and well below the 70 ng/L advisory limit. With respect to surface water, the highest concentration was detected at site KZN-S8 for PFBA (68.5 ng/L) and this was followed by PFHpA (49.5 ng/L) at site KZN-S4. L-PFBS and PFPeA were <LOD in all the sites. This was a similar pattern observed in drinking water samples.

PFBA, PFPeA, PFHpA, L-PFBS, L-PFHxS, L-PFOS, PFHpS, PFOA, 6:2 FTS, FOET, and FHET were all detected in all the samples; whereas PFNA, PFHxA and FHEA were detected only in one sample. PFOA was below LOD for all the samples. 6:2 FTS exhibited the highest concentration of 52.5 ng/L at KZN-WE1. This was followed by PFBA with a concentration of 48.5 ng/L at KZN-WI1. L-PFBS was detected in only two samples at KZN-WI2 and KZN-WE1.

Figures 6.8 and 6.9, show the PFASs concentration distributions for the water sources collected in KZN during the wet season. Surface water and wastewater treatment plant water contributed more to the concentrations detected which is shown by the clustering observed in the plot (Figure 6.8). Tap water showed more scattering, suggesting less contribution to the concentrations detected in the province. A very clear relationship between contributions and PFASs concentrations can be seen in Figure 6.9.

Table 6.9: Mean PFAS concentrations (ng L^{-1}) in various water sources in wet season

Sites	L-PFBS	L-PFHxS	L-PFHpS	L-PFOS	PFBA	PFHpA	PFPeA	PFHxA	PFNA	PFOA	6:2FTS	FHEA	FOET	FHET
KZN-T1	ND	<LOD	ND	<LOD	34.5±2.54	22.7±3.51	<LOD	ND	ND	<LOD	2.65±0.15	ND	0.35±0.05	2.54±0.04
KZN-T2	ND	<LOD	ND	<LOD	57.1±6.51	41.5±0.54	<LOD	ND	ND	<LOD	2.66±0.19	ND	0.73±0.14	2.60±0.19
KZN-T3	ND	ND	ND	<LOD	20.8±2.74	12.8±3.02	<LOD	ND	ND	<LOD	3.37±0.04	ND	0.50±0.02	3.26±0.01
KZN-T4	ND	<LOD	ND	<LOD	52.4±4.87	25.7±1.28	<LOD	ND	ND	ND	2.75±0.36	2.07±0.84	0.20±0.01	2.24±0.06
KZN-S1	<LOD	0.02±0.004	0.01±0.001	0.05±0.003	29.9±3.30	11.4±0.27	<LOD	ND	ND	<LOD	5.67±0.48	2.90±0.50	0.16±0.03	4.50±0.24
KZN-S2	<LOD	<LOD	<LOD	<LOD	24.8±0.52	34.1±1.04	<LOD	ND	ND	<LOD	11.6±1.50	2.44±0.14	0.14±0.03	5.41±0.14
KZN-S4	<LOD	<LOD	ND	<LOD	20.9±10.22	49.5±1.14	<LOD	ND	1.44±0.61	<LOD	8.34±0.03	0.65±0.02	0.24±0.03	7.30±0.25
KZN-S6	<LOD	0.03±0.005	0.01±0.003	0.06±0.01	15.2±3.63	1.70±0.09	<LOD	ND	0.23±0.18	<LOD	18.1±0.83	ND	2.07±1.30	13.3±0.50
KZN-S7	ND	<LOD	<LOD	<LOD	26.6±0.66	14.0±1.32	<LOD	ND	0.29±0.07	<LOD	3.06±0.23	ND	0.32±0.05	3.44±0.08
KZN-S8	<LOD	0.01±0.001	<LOD	0.02±0.006	68.5±8.69	40.±2.96	<LOD	ND	ND	<LOD	6.61±0.17	ND	0.37±0.04	5.14±0.09
KZN-WI1	<LOD	0.08±0.004	0.04±0.001	0.02±0.001	48.5±8.27	26.9±10.62	<LOD	ND	ND	<LOD	41.2±5.45	ND	1.19±0.05	26.29±0.47
KZN-WI2	0.17±0.004	0.30±0.03	0.06±0.01	0.03±0.004	45.1±8.00	25.8±4.76	<LOD	<LOD	<LOD	<LOD	23.5±1.69	ND	1.77±0.44	15.4±0.55
KZN-WE1	0.13±0.01	0.38±0.004	0.04±0.004	0.04±0.01	16.9±5.56	34.6±0.46	<LOD	ND	ND	<LOD	52.5±2.35	ND	1.05±0.14	27±1.54
KZN-WE2	<LOD	<LOD	<LOD	<LOD	25.4±0.80	ND	ND	ND	ND	<LOD	8.87±0.12	4.48±1.31	0.32±0.03	6.14±0.32

KZN-T2=Glenwood/Tap water; KZN-T2=Reservoir Hill 1/Tap water; KZN-T3=Claire Estate/Tap water; KZN-T4=Reservoir Hill/Tap water 2; KZN-S1=Phoenix (Ohlanga) River 1; KZN-S2=Phoenix (Ohlanga) River 2; KZN-S3=Phoenix (Ohlanga) 3; KZN-S4=Umgeni River 1; KZN-S5=Umgeni River 2; KZN-S6=Umgeni River 3; KZN-S7=Umgeni River 4; KZN-S8=Phoenix (Ohlanga) River 4; KZN-WE1=Dewats effluent; KZN-WE2=Dewats effluent before gravel filtration, KZN-WI1=Dewats influent/Ciphon Chamber; KZN-WI2=Dewats influent ABR Train 1.

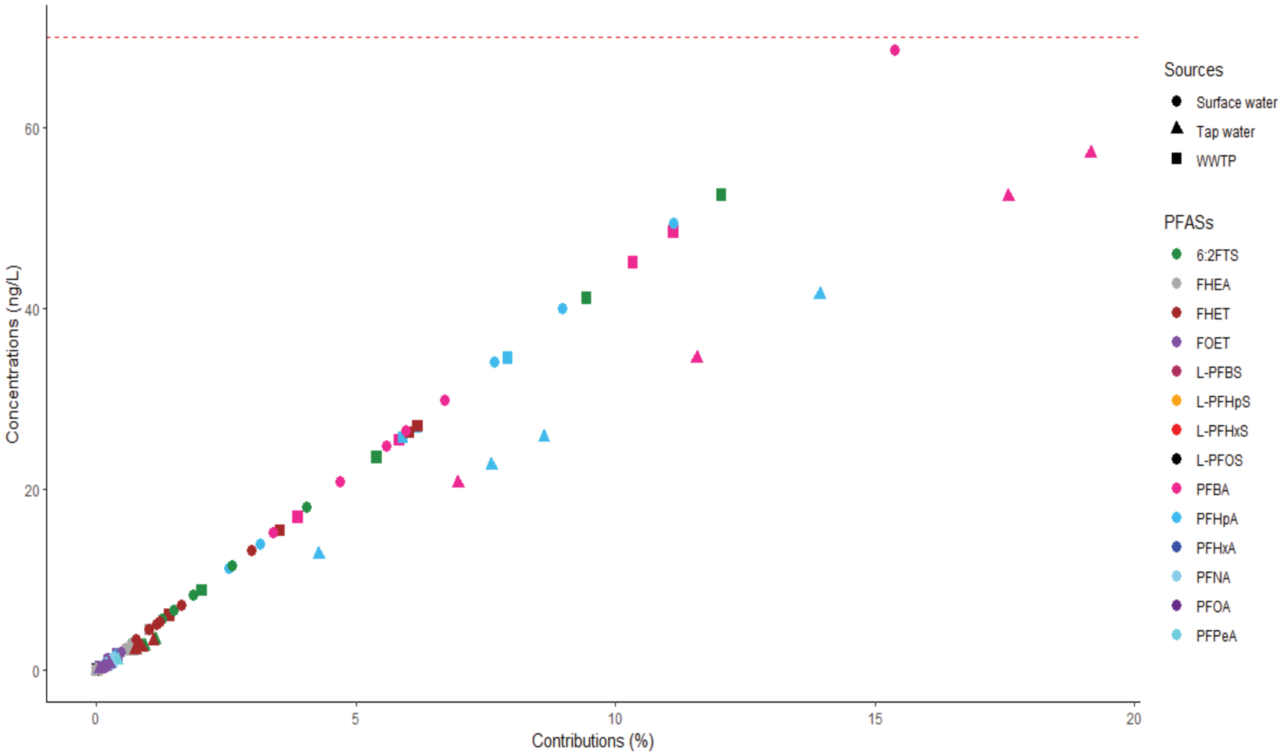

Figure 6.8: PFASs concentration distributions in various water sources in Kwa-Zulu Natal during the wet season.

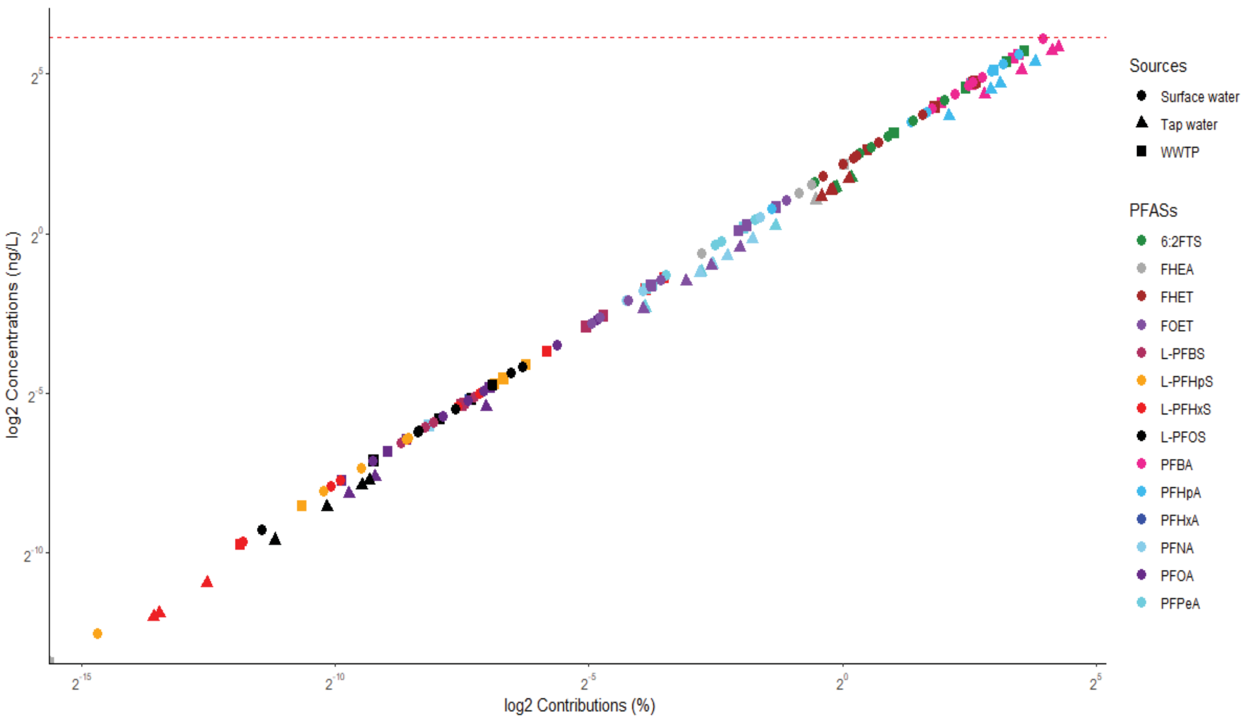

Figure 6.9: PFASs concentration distributions in various water sources in Kwa-Zulu Natal during the wet season.

In Figure 6.10, the Fluorotelomer contributed most in surface water collected from KZN during the dry season. The compound that contributed the most to the class was 6:2 FTS. This was followed by the PFSAs class indicated by L-PFOS. In tap water and wastewater treatment plants, the PFSAs had more contribution with L-PFOS and L-PFHxS, respectively. PFCAs had less contribution to the results in all the water sources collected. In all the water sources represented in Figure 6.11, the long chain PFASs had more contribution than the short chains. PFNA contributed most in surface water and in tap water. In wastewater treatment plant samples, L-PFOS had the most contribution.

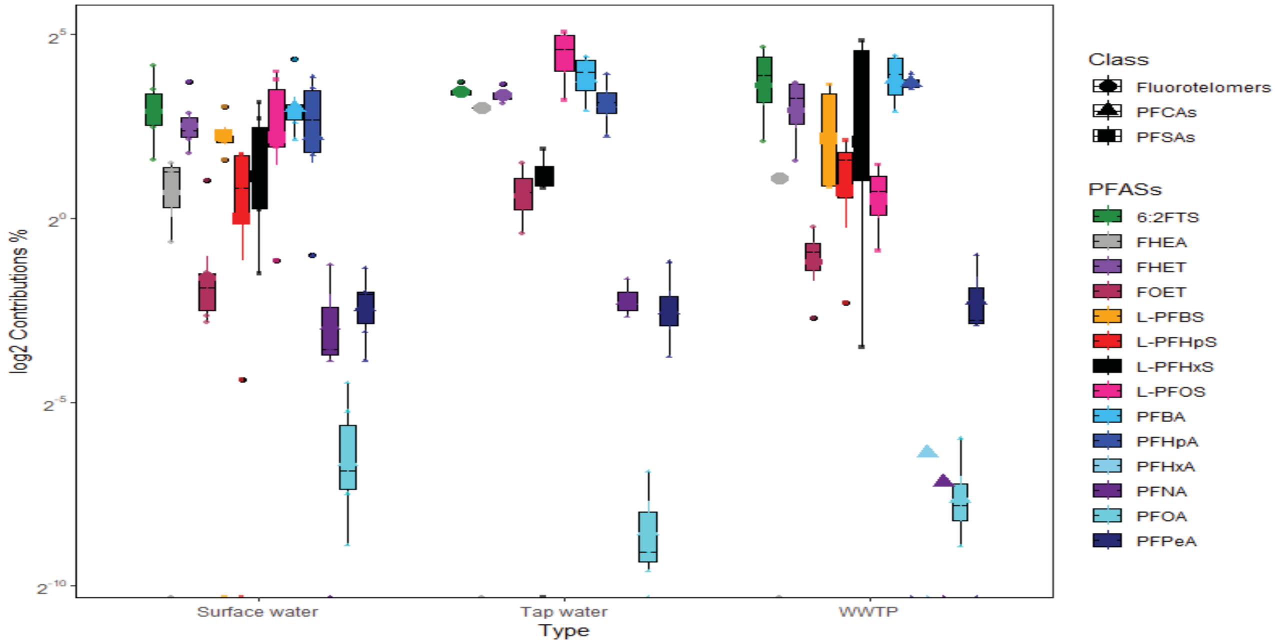

Figure 6.10: PFASs class contributions in various water sources in Kwa-Zulu Natal during the wet season.

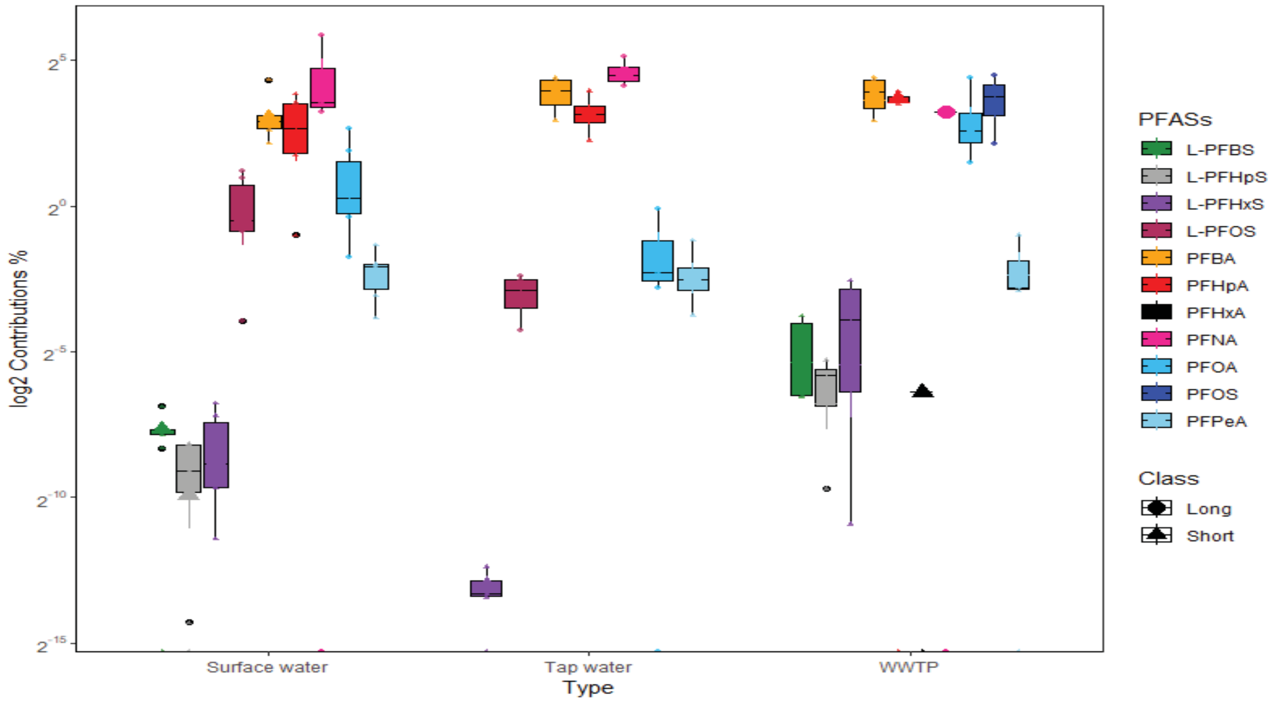

Figure 6.11: Contributions of long- and short-chain PFASs in various water sources in Kwa-Zulu Natal during the wet season.

6.4.2 Establishing the possible sources of PFASs detected in the water

Figure 6.12 shows the statistical analyses performed using Principal Component Analysis (PCA) for the concentrations detected in KwaZulu-Natal Province water samples during the wet season. A p-value ≤ 0.05 was considered statistically significant for all datasets. L-PFHpS, L-PFHxS, L-PFBS, 6:2 FTS and FHET showed a positive strong contributions. PFHpA, PFBA and PFPeA also showed similar behaviour. PFHpA and PFBA had the highest concentrations detected in most of the sampling sites. The high detection of perfluoroalkyl carboxylic acids (PFCAs) detected in these samples might be attributed to the degradation of fluorotelomers.

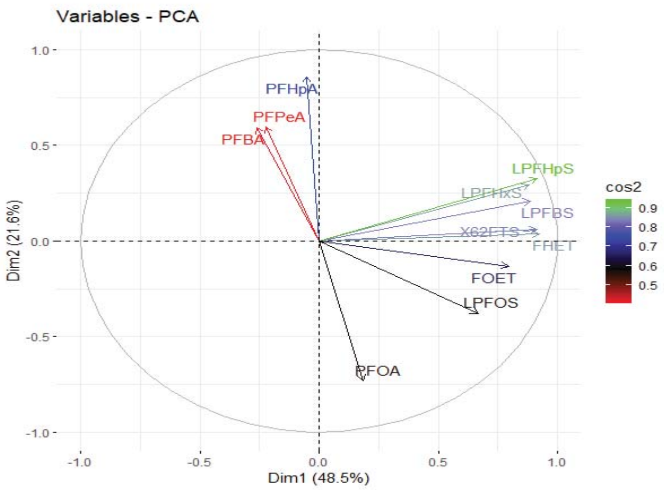

Figure 6.12: PCA of PFASs congener contributions and their relationships during the wet season.

The high concentrations detected at KZN-S4 may be due to the agricultural activities as there are sugar cane field around the site and the concentration at KZN-S8 may be due to the discharge of WWTPs into the Umgeni River as mentioned during dry season. Figure 6.13 shows the observation of the sampling sites. Samples from surface water and tap water were clustered together, suggesting a similar sources of PFASs contamination excluding KZN-S6. Wastewater treatment plant samples also showed similar sources for the PFAS concentrations detected, except for KZN-WE2.

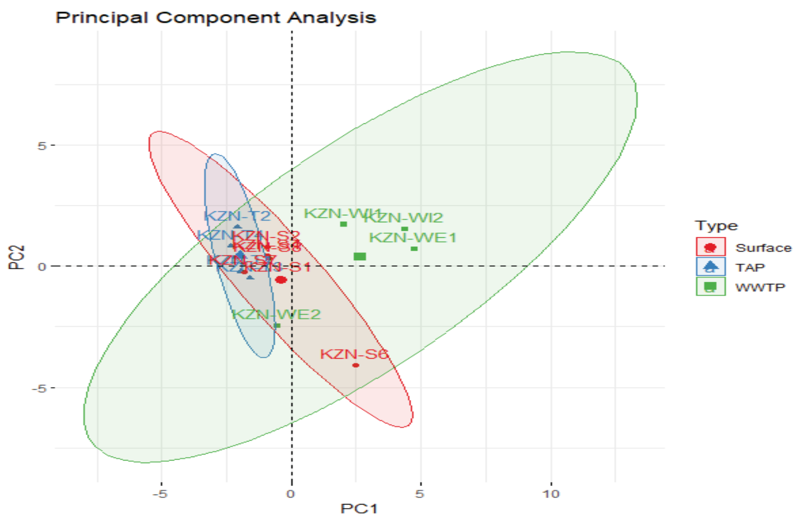

Figure 6.13: PCA of sampling sites and their relationships during the wet season.

6.5 SUMMARY

All the short and long chains were detected in most of the samples. However, the highest concentration was observed for PFBA and this may be attributed to the breakdown of the sulphonate telomers. More long chain were detected in wet season than in dry season. However, the concentrations of PFASs in wet season were generally higher than in dry season. Fluorotelomers, PFCA and PFSA classes of PFAS were all detected in dry and wet seasons. PCA plots indicated that some of the PFASs may have originated from the same sources. Table 6.10 shows comparison of the concentrations of PFASs observed in the present study to other studies conducted in different parts of the world. As can be seen in Table 6.10, the concentrations detected in Umgeni River in the present study is much lower than the levels reported in Shandong and Liaoning Provinces in China and German Rivers in Ruhr area; but higher than others.

Table 6.10: Comparison of PFASs concentrations obtained in the current study with other studies

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.8	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area)	Skutlarek et al., 2006
	2-61 (Rhine River)	
Shandong Province	13.1-69.23	Chen et al., 2017
Liaoning Province	22.4-26.73	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
Gauteng Province South Africa (Dam Surface)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al., 2014,
South Africa (River water)	<LOQ to 38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
KwaZulu-Natal Province South Africa (drinking water/Tap water)	**<LOQ-42.05**	**This study**
KwaZulu-Natal Province South Africa (river water)	**<LOD-26.30**	**This study**
KwaZulu-Natal Province South Africa (wastewater treatment plant)	**<LOD-20.50**	**This study**

CHAPTER 7: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE LIMPOPO PROVINCE

7.1 SAMPLING STRATEGY

7.1.1 Location and description of sampling sites

Water samples were collected from Polokwane which is the most cosmopolitan city in the province and Musina and Thohoyandou, two fast growing urban towns in the far north in the Limpopo province during both wet (October-April) and dry (June-August) seasons. Once again, the selected areas have been identified as areas with serious water quality problems. Figure 7.1 shows the land use map within the vicinity of sampling sites. The following water systems were targeted in the province:

- Wastewater treatment plant (W-primary and secondary treatment effluent and influent;
- Tap water (LP-T);
- Surface water (LP-S) and
- Landfill borehole (LP-B)
- Wastewater primary and secondary influent and effluent (LP-WE; LP-WS, LP-WI)

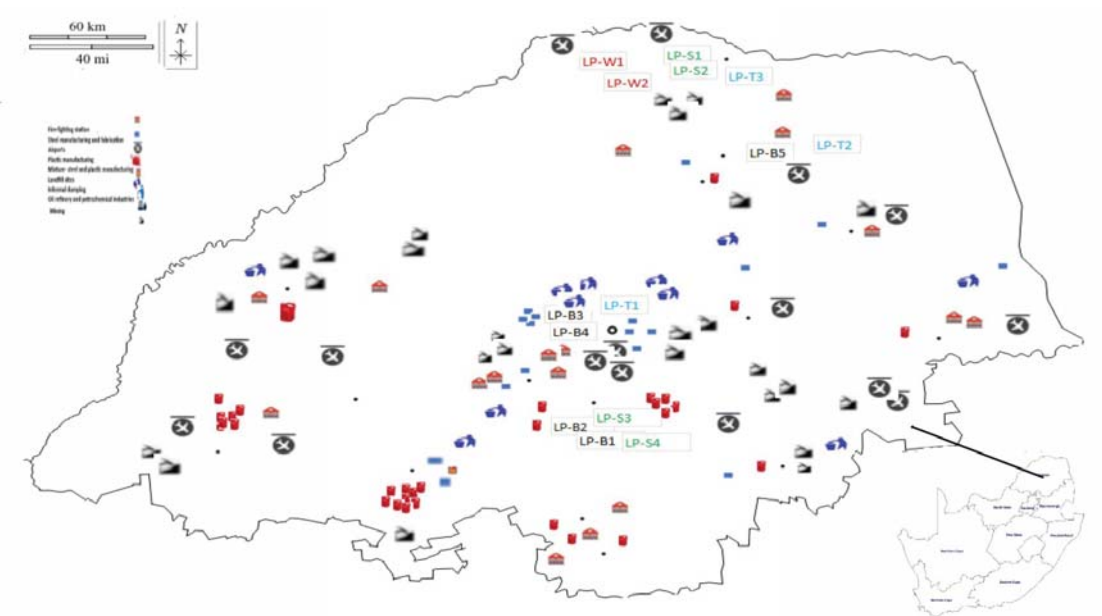

Figure 7.1: Land use map and sampling sites in Limpopo Province.

7.1.2 Sample collection

Table 7.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the 2 cities. Grab samples were collected and prepared for analysis as described in Chapter 3.

Table 7.1 Sampling sites in Limpopo province with coordinates

Sample code	Sampling sites	Sampling dates	Coordinates
LP-B1	Landfill borehole 1	10/05/2021	
LP-B2	Landfill borehole 2	10/05/2021	
LP-B3	Borehole 3	02/06/2021	23°56’46”S, 29°29’47”E
LP-B4	Landfill Borehole 2	02/06/2021	23°56’49”S, 29°29’35”E
LP-S1	Surface 1	03/06/2021	22°37’54”S, 30°23’51”E
LP-S2	Surface 1	03/06/2021	22°37’54”S, 30°23’50”E
LP-S3	Surface 3	10/05/2021	
LP-T1	Limpopo tap-water 1	10/05/2021	23°91’11”S, 29°45’54”E
LP-S4	Surface 4		
LP-T2	Limpopo tap water 2	07/05/2021	22°58’34”S, 30°27’33”E
LP-B5	Landfill borehole	10/05/2021	23°0’07”S, 30°28’13”E
LP-T3	Limpopo taps water 3	03/06/2021	22°21’29”S, 30°03’04”E
LP-WS1	WWTP1 secondary effluent	03/06/2021	22°21’29”S, 30°03’04”E
LP-WE1	WWTP1 effluent	03/06/2021	22°21’26”S, 30°03’13”E
LP-WP1	WWTP1 final effluent primary	03/06/2021	22°21’29”S, 30°03’04”E
LP-WI1	WWTP1 influent	03/06/2021	22°21’26”S, 30°03’13”E
LP-WP1	WWTP2 primary influent	03/06/2021	22°19’15”S, 30°02’18”E
LP-WE2	WWTP2 final effluent	03/06/2021	22°19’31”S, 30°02’30”E
LP-WS2	WWTP2 secondary effluent	03/06/2021	22°19’15”S, 30°02’18”E
LP-WI2	WWTP2 influent	03/06/2021	22°19’31”S, 30°02’30”E

7.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. Tables 7.2 and 7.3 show the mean percentage recoveries of blanks and surrogates respectively for dry season. The recoveries ranged from 61.8-107.3% and 71.1-96.7% respectively. This range is within the acceptable recovery range of 50-200%. Table 7.4 show the mean concentrations of PFASs in blank samples, where the concentrations ranged from <LOD-7.59 ng/L with 8:2 FTS showing the highest concentration.

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Table 7.2: Percentage recoveries and standard deviations of PFASs in blanks during the dry season

Samples – Surrogate recoveries (%) ± Standard deviation	
Surrogates	**BL**
MPFNA	78.2±8.12
MPFUdA	61.8±6.49
MPFHxS	107.3±0.62

Table 7.3: Percentage recoveries and standard deviations of PFASs in different water source in dry season

	Samples – Surrogate recoveries (%) ± Standard deviation									
Surrogates	**BH1**	**BH2**	**PLK B1**	**PLK B2**	**LNF**	**LNR**	**LM**	**PTW**	**MW**	**TTW**
MPFNA	83.7±7.95	91.1±3.80	96.6±0.60	92.9±0.71	92.7±1.66	81.3±0.96	89.1±7.20	89.6±8.27	91.4±3.04	91.4±1.19
MPFUdA	82.9±4.91	73.2±7.96	77.7±5.44	96.7±3.24	83.8±4.60	88.0±0.74	74.1±1.04	89.5±4.99	91.1±0.72	82.1±5.18
MPFHxS	94.5±3.35	94.5±6.71	86.6±0.43	82.4±4.18	71.1±7.48	82.6±1.94	93.6±2.52	86.6±11.49	77.8±0.01	83.4±1.03

Table 7.4: Mean concentrations of PFASs and standard deviations in blanks during the dry season

	Samples – Mean concentrations (ng/L) ± standard deviation
Compounds	**BL**
PFUdA	<LOD
PFHxA	3.29±1.6
PFPeA	0.115±0.01
4:2 FTS	0.0451±0.02
8:2 FTS	7.51±5.76
PFHpA	<LOD
PFNA	0.702±0.35
L-PFBS	0.187±0.12
L-PFHxS	0.200±0.03
L-PFOS	3.37±0.64
PFHpS	<LOD
PFOA	1.52±0.56
PFDoA	0.615±0.40
PFODA	<LOD
L-PFDS	4.59±2.07
PFHxDA	<LOD
FHEA	<LOD
6:2 fts	<LOD
FOET	<LOD
FHET	<LOD
PFBA	<LOD

7.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

7.3.1 Distribution of PFASs in various water sources during the dry season

Table 7.5 shows the PFASs concentrations in various water sources in Limpopo province. L-PFBS, PFOA, PHEA, FOET, FHET and PFBA were detected in all the samples; whereas PFPeA and FHxS were detected in all the samples except in LP-B3. PFHxA was not detected in LP-S3 and LP-T3. L-PFOS was detected in all the samples except in LP-B2. The detection of other congeners varied. PFOA exhibited 1028 ng/L and 24.4 ng/L in LP-WP2 effluent and LP-WE2 respectively, 1063 ng/L in LP-W12 influent, 658.8 ng/L in LP-WS2 effluent and 604.9 ng/L in LP-WI1. PFDoA, PFODA, PFUdA and PFHxDA were not detected in any of the samples. L-PFBS exhibited concentrations greater than 10 ng/L in all the samples. The same trend was also observed for PFBA except in LP-W12 final effluent. The overall concentration range was <LOD-1063 ng/L.

In order to identifying other patterns in the data in Table 7.5, a scatter plot was constructed as can be seen in Figure 7.2. The plot clearly shows that WWTP contributed the highest concentration and this is in line with the observed data in Table 7.5. Without drawing a line of best fit, there is already a linear trend between concentrations and PFASs congener contributions. To show more clarity, a log base scatter plot was carried out and this is shown in Figure 7.3.

Figure 7.3 depicts clearly a linear relationship between contributions of different PFSAs in various water sources and their concentrations in various water samples. Shown in Figure 7.4 are the PFASs class contributions for various water sources. PFCAs can be seen to be the most dominant in all the water sources, particularly in the WWTP samples where they are clustered compared to surface water. PFSAs also follow the same trend. The Fluorotelomers are much more in landfill borehole, drinking water and surface water.

The contributions of short and long chain PFASs are shown in the box scatter plot in Figure 7.5. Short chains are more dominant in all the water sources. This cam be attributed to 1) discontinued use of long chain PFASs in products 2) the possble break down of long chain into short chains and 3) more use of short chains in products.

Table 7.5: Mean concentrations of PFAS in various water samples during the dry season

Samples	LP-B1	LP-B2	LP-B3	LP-B4	S1	S2	S3	LP-T1	LP-S4	LP-B5	LP-T2	LP-T3	LP-WS1	LP-WE1	LP-WP1	LP-WI1	LP-WP2	LP-WE2	LP-WS2	LP-WI2
Compounds									Mean concentrations (ng/L) and standard deviations (±)											
PFUdA	0.044 ±0.16	<LOD	<LOD	<LOD	0.229 ±0.01	0.131 ±0.09	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	0.276 ±0.21	7.82 ±1.49	3.27 ±0.81	15.7 ±11.14	2.01 ±2.84	<LOD	0.0142 ±0.01	0.367 ±0.21	0.762 ±0.18	0.0173 ±0.03	0.0102 ±0.07	<LOD	9.30 ±6.58	69.6 ±9.49	4.84 ±1.80	14.6 ±2.75	25.5 ±1.81	2.90 ±1.34	40.6 ±8.78	43.5 ±2.89
PFPeA	0.855 ±0.23	1.43 ±1.00	<LOD	1.56 ±0.85	0.170 ±0.02	0.148 ±0.02	1.41 ±0.93	0.745 ±0.42	0.920 3±0.04	0.400 ±0.04	3.22 ±0.63	0.663 ±0.07	0.808 ±0.08	0.246 ±0.06	1.737 ±0.63	0.901 ±0.22	1.67 ±0.48	1.05 ±0.32	0.697 ±0.21	0.201 ±0.16
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.0500 ±0.07	<LOD	<LOD	0.085 ±0.02	<LOD	0.0506 ±0.03	<LOD	0.0543 ±0.04	<LOD	0.412 ±0.10	<LOD	<LOD	<LOD	<LOD
8:2 FTS	0.577 ±0.22	<LOD	0.727 ±0.62	14.7 ±10.43	2.74 ±0.66	<LOD	<LOD	3.24 ±2.35	2.24 ±3.18	1.68 ±2.14	0.447 ±0.63	9.78 ±1.27	1.59 ±2.26	0.555 ±0.27	<LOD	15.9 ±0.77	2.87 ±2.09	10.2 ±8.47	0.257 ±0.36	1.03 ±0.94
PFHpA	0.100 ±0.02	2.90 ±1.37	1.35 ±0.47	1.15 ±0.37	0.792 ±0.31	<LOD	<LOD	<LOD	<LOD	0.0517 ±0.02	0.294 ±0.13	5.50 ±0.60	3.52 ±0.77	4.92 ±0.31	1.06 ±0.30	0.358 ±0.22	5.26 ±0.25	0.185 ±0.04	4.57 ±1.60	6.88 ±0.01
PFNA	0.236 ±0.29	3.95 ±2.66	1.18 ±0.10	2.24 ±0.01	2.06 ±0.49	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	21.1 ±0.00	31.8 ±8.85	1.41 ±1.70	<LOD	37.5 ±4.76	<LOD	16.9 ±1.94	34.7 ±6.11
L-PFBS	10.0 ±0.22	11.2 ±0.17	18.6 ±0.08	35.1 ±0.54	21.8 ±0.12	45.5 ±0.23	22.8 ±0.34	10.5 ±0.23	11.1 ±0.09	32.3 ±0.21	17.2 ±0.01	38.9 ±0.19	243 ±3.38	27.0 ±0.34	158 ±3.61	111 ±2.25	208 ±6.97	48.0 ±0.56	80.6 ±2.62	213 ±7.62
L-PFHxS	0.0913 ±0.04	0.0265 ±0.00	0.448 ±0.16	2.38 ±0.20	1.30 ±0.12	<LOD	<LOD	<LOD	<LOD	0.0521 ±0.00	0.641 ±0.17	3.40 ±0.51	0.704 ±0.06	1.52 ±0.17	0.137 ±0.02	45.8 ±3.44	1.14 ±0.37	8.52 ±0.01	10.5 ±9.75	3.81 ±0.23
L-PFOS	0.608 ±0.34	<LOD	1.76 ±0.06	13.2 ±2.05	5.34 ±1.59	2.21 ±0.05	0.229 ±0.03	1.78 ±0.35	0.644 ±0.31	1.614 ±0.18	8.95 ±1.51	6.87 ±0.65	4.41 ±1.45	12.9 ±4.47	0.398 ±0.11	181 ±64.3	3.60 ±0.17	35.6 ±18.6	3.42 ±2.06	17.5 ±12.51
PFHpS	<LOD	<LOD	0.0660 ±0.03	0.672 ±0.24	0.301 ±0.24	<LOD	0.0700 ±0.01	<LOD	<LOD	0.212 ±0.01	0.318 ±0.18	6.47 ±2.52	0.667 ±0.58	5.19 ±2.80	0.214 ±2.17	52.63 ±13.0	35.32 ±2.31	19.9 ±9.98	0.785 ±0.07	7.58 ±6.16
PFOA	0.636 ±0.01	122 ±43.8	2.76 ±0.02	3.81 ±0.88	51.2 ±11.6	1.34 ±0.06	0.510 ±0.05	0.120 ±0.04	0.107 ±0.01	0.398 ±0.04	0.579 ±0.06	0.484 ±0.03	236.7 ±185.0	51.0 ±24.09	131.8 ±5.83	605 ±11.7	1028 ±215	24.4 ±12.2	659 ±44.3	1063 ±86.00
PFDoA	<LOD	<LOD	<LOD	0.0850 ±0.06	<LOD	<LOD	<LOD	<LOD	<LOD	0.0270 ±0.02	0.775 ±0.50	<LOD	<LOD	0.015 ±0.00	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFODA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFDS	<LOD	<LOD	<LOD	0.626 ±0.31	<LOD	<LOD	0.0957 ±0.05	<LOD	<LOD	1.62 ±0.81	3.41 ±1.63	1.17 ±0.90	17.7 ±3.55	13.7 ±0.46	0.215 ±0.13	39.8 ±18.06	0.823 ±0.12	1.31 ±0.33	1.47 ±0.72	2.25 ±1.90
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHEA	5.01 ±1.35	6.63 ±1.34	5.89 ±0.19	7.48 ±0.47	4.51 ±0.61	18.4 ±3.46	8.68 ±2.01	18.1 ±3.28	11.2 ±0.76	4.76 ±0.09	15.4 ±9.26	11.8 ±0.011	35.9 ±6.92	25.5 ±3.68	14.78 ±2.11	4.76 ±13.3	11.9 ±3.58	35.2 ±4.97	18.6 ±4.97	125 ±67.22
6:2 FTS	2.57 ±0.14	0.757 ±0.03	3.76 ±0.57	8.24 ±2.61	3.25 ±0.08	<LOD	<LOD	<LOD	<LOD	2.09 ±0.10	0.965 ±1.27	2.12 ±0.20	1.10 ±0.05	1.80 ±0.05	0.806 ±0.06	21.1 ±1.62	1.46 ±0.02	5.18 ±0.01	0.928 ±0.05	0.902 ±0.03
FOET	0.752 ±0.17	1.39 ±1.93	1.04 ±0.40	1.32 ±0.32	0.484 ±0.00	2.49 ±1.91	1.18 ±0.54	1.58 ±0.53	0.422 ±0.03	0.314 ±0.39	1.76 ±1.92	3.87 ±6.017	2.92 ±1.77	1.89 ±0.534	8.394 ±0.63	3.91 ±3.57	2.95 ±0.12	1.33 ±2.50	0.370 ±0.49	8.58 ±7.56
FHET	0.0tap 128 ±0.00	0.0215 ±0.01	0.0172 ±0.01	0.0258 ±0.00	0.0119 ±0.00	0.0434 ±0.01	0.0190 ±0.01	0.0434 ±0.01	0.0257 ±0.00	0.0143 ±001	0.0460 ±0.02	0.215 ±0.06	0.235 ±0.12	0.117 ±0.02	0.0273 ±0.01	0.406 ±0.04	0.055 ±0.01	0.132 ±0.01	0.0353 ±0.02	0.292 ±0.26
PFBA	13.8 ±2.11	19.7 ±2.99	13.0 ±0.14	19.2 ±3.19	4.90 ±1.42	22.4 ±6.56	10.9 ±2.50	21.1 ±2.07	7.53 ±0.00	13.5 ±2.31	15.9 ±2.71	10.2 ±2.58	35.0 ±4.69	13.7 ±1.25	14.8 ±2.95	14.7 ±0.77	11.5 ±1.54	7.25 ±0.50	11.7 ±5.29	34.8 ±2.30

LP-B = landfill bore, LP-S = surface water, LP-T = tap water, LP-WI = wastewater influent, LP-WE = wastewater effluent; LP-WP = wastewater primary treatment; LP-WS = wastewater secondary treatment; nd=non-detectable, LOD= Limit of quantification, LOQ=limit of quantification

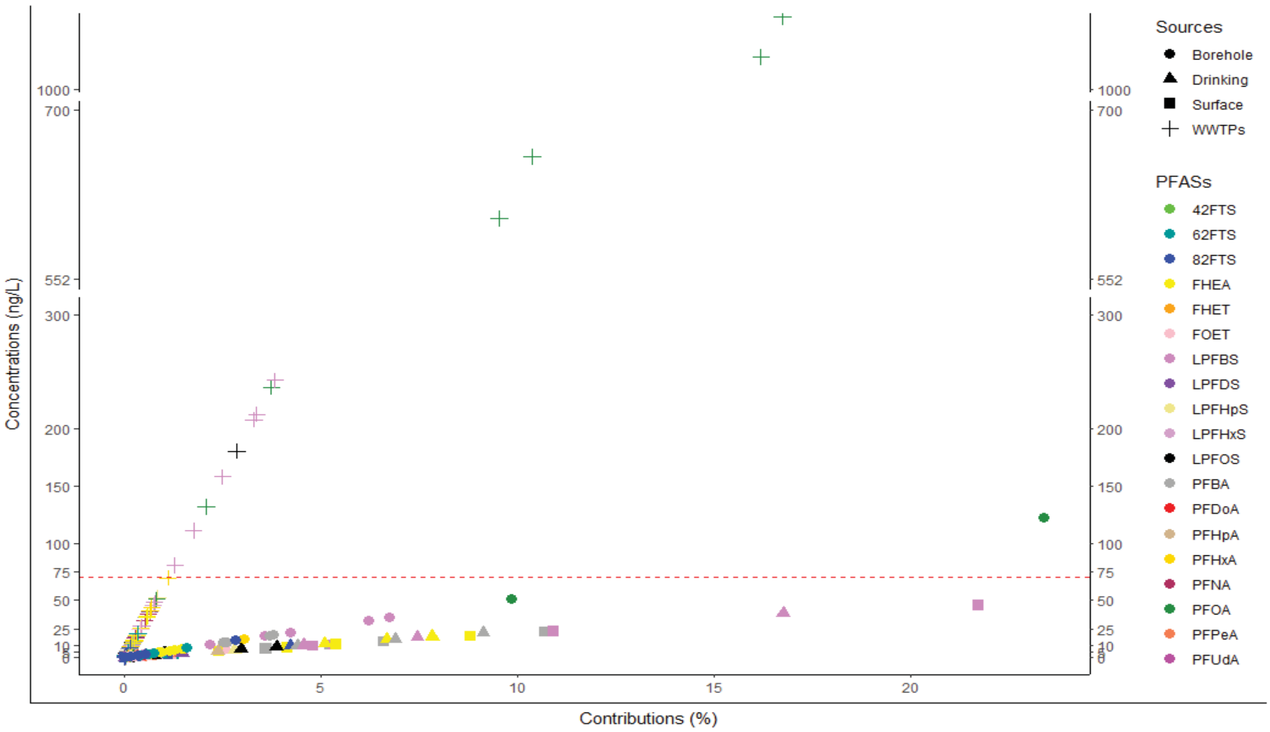

Figure 7.2: PFASs concentration distributions for various water sources in Limpopo during the dry season.

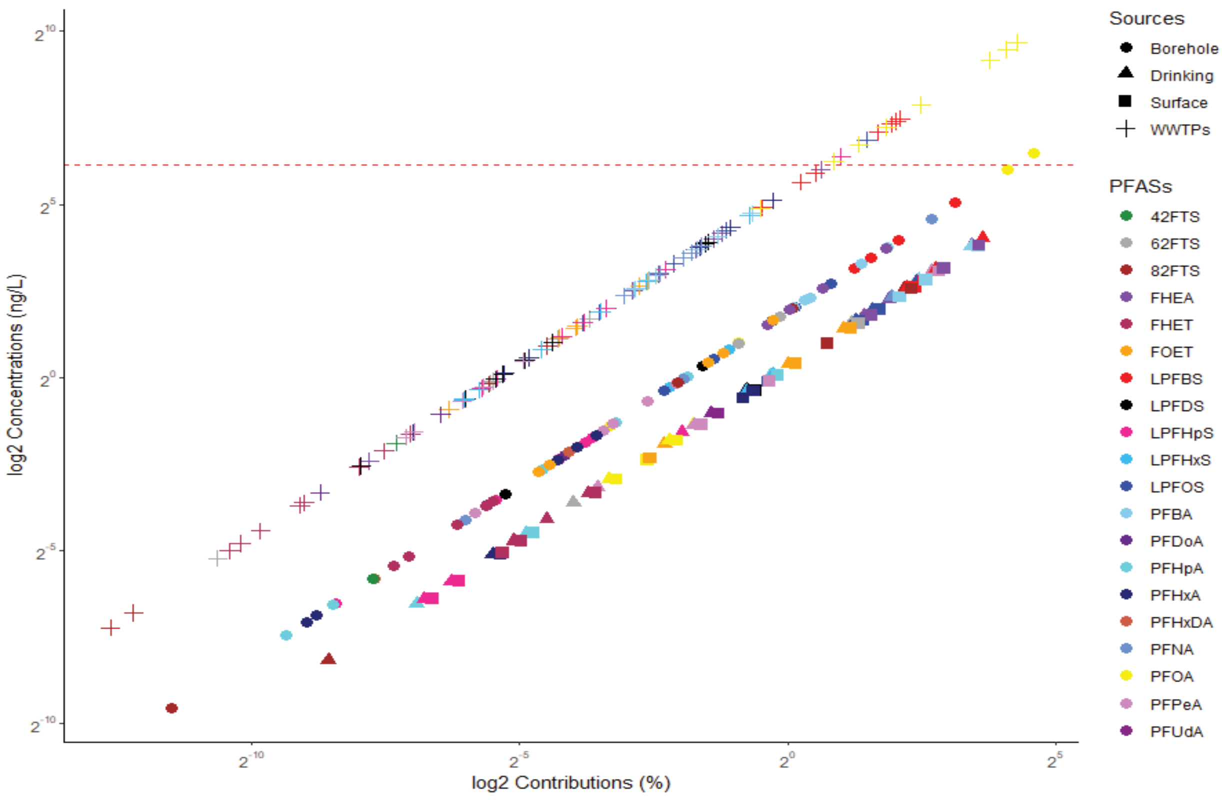

Figure 7.3: PFASs concentration distributions in log base for various water sources in in Limpopo during the dry season.

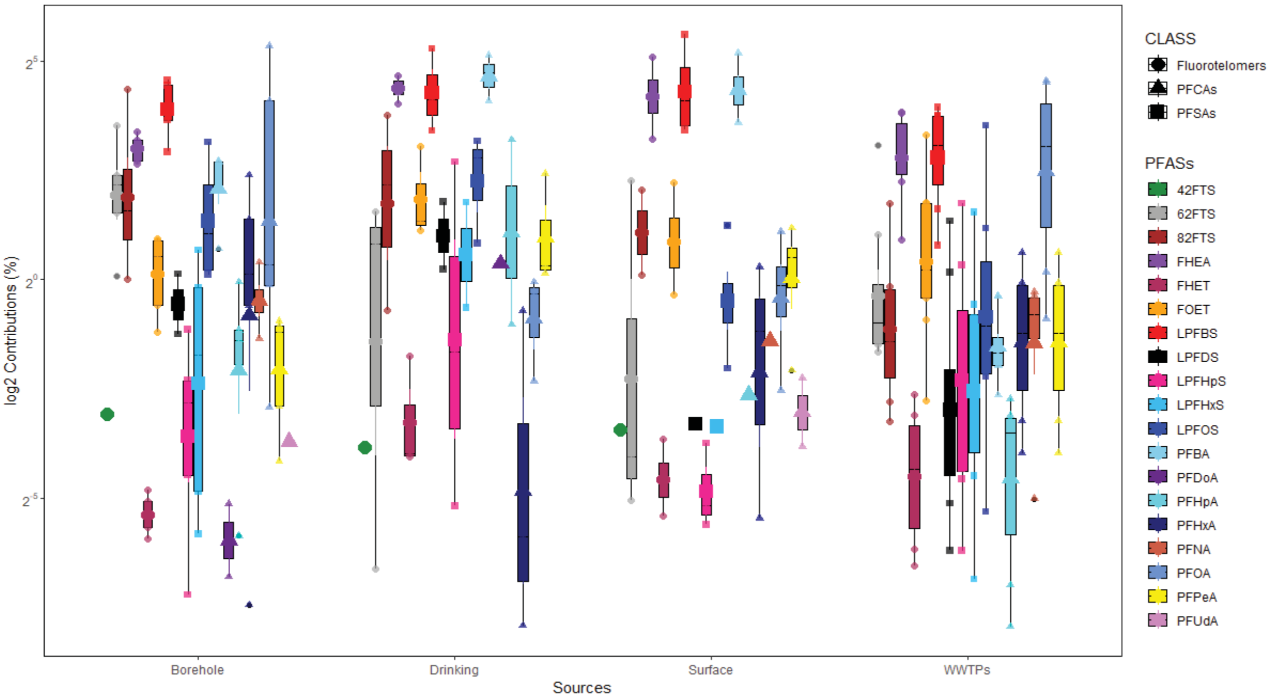

Figure 7.4: PFASs class contributions for various water sources in Limpopo during the dry season.

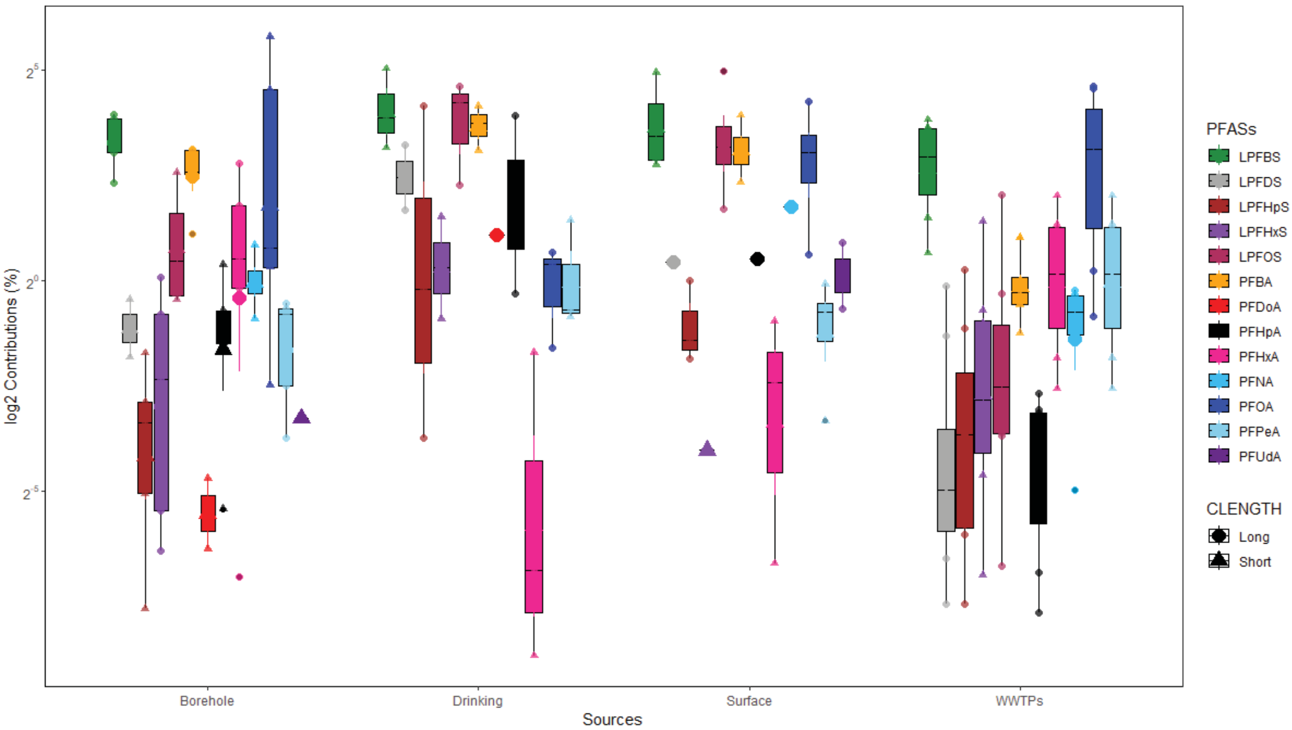

Figure 7.5: Contributions of short- and long-chain PFASs for various water sources in Limpopo during the dry season.

7.3.2 Establishing the possible sources of PFASs detected in the water

Principal component analysis (PCA) was conducted using the PFASs dataset generated from analysis of water samples from various sampling sites in Limpopo. Shown in Figure 7.6 are the contributions of PFASs compounds detected in the water samples during the dry season shown in Table 8.5. There is a strong correlation between 8:2 FTS, 6:2 FTS, L-PFOS, L-PHET, L-PFHxS, PFHpS and L-PFDS, all found in the same quadrant, suggesting that these compounds have similar pattern/ sources. Same applies for PFBA, PFNA, PFHPA, L-PFBS, FHEA, FOET and PFOA. Figure 7.7 shows the PCA of the sampling sites. As can be seen, most of the sampling sites are clustered in the 1st, 2nd and 3rd quadrants of the score plot. This suggests that the sources of PFASs are similar for these sites. However, LP-WI1 showed different sources from the rest.

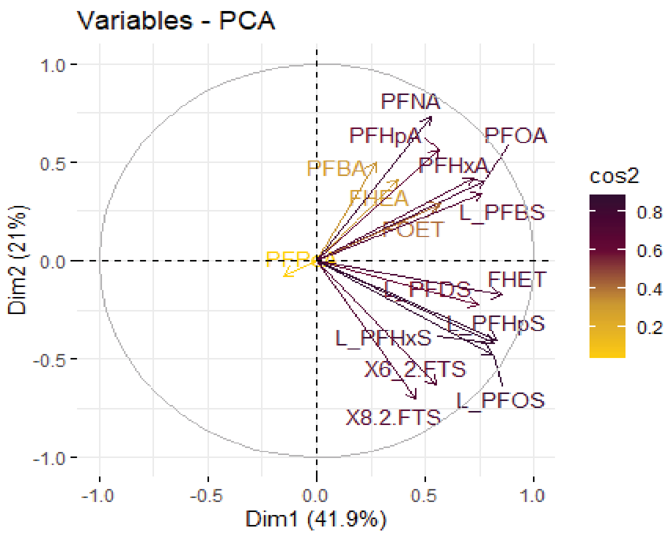

Figure 7.6: PFASs congener contributions and their relationships during the dry season.

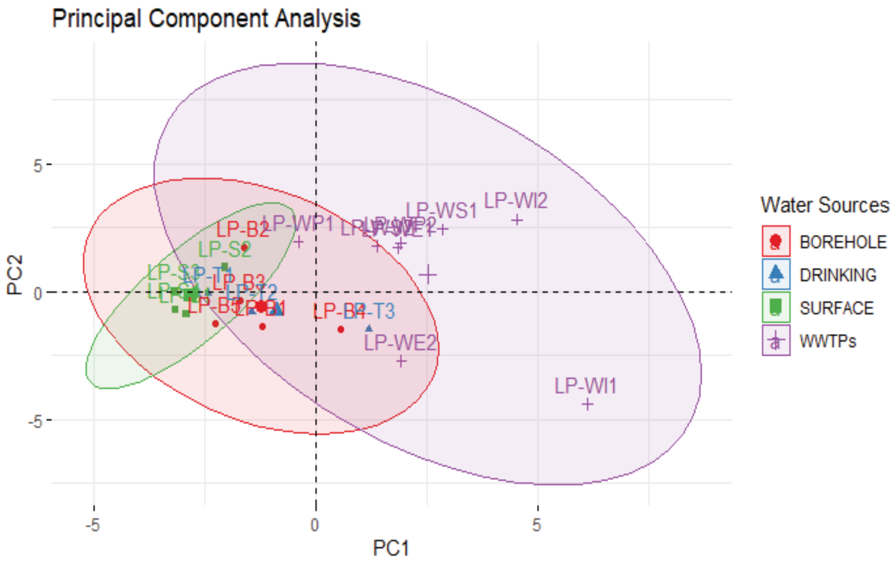

Figure 7.7: Sampling points and their relationships during the dry season.

7.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

7.4.1 Distribution of PFASs in various water sources during the wet season

Shown in Table 7.6 shows the concentrations of PFASs in different water sources in Limpopo. Congener PFPeA was detected in all the samples except in LP-WS1, LP-WP1 and LP-WE2, whereas PFODA was detected only in LP-WP2, PFNA in seven samples, PFHxDA in three and PFUdA in two samples. FHET was detected in all the samples but at a very low concentration range of 0.022-0.164 ng/L. LPFBS was also detected in all the samples except in LP-WI1. It is worth noting that the concentration range (<LOD-178.6 ng/L) exhibited by PFBS was far higher than that of FHET which was detect in all the samples. Congeners LPFDS, L-PFHXS, L-PFHpS recorded low concentration range. L-PFOS was also detected in all the samples except in LP-WE1. The highest concentration recorded for L-PFOS was 116.9 ng/L which is second to the concentration recorded for L-PFBS. PFOA was detected in all the samples except LP-WS1 and LP-WP1 as can be seen in Table 8.5. In fact, PFOA exhibited the highest concentration of 709.8 ng/L compared to the other PFASs. PFBA concentration ranged from <LOD (LP-WE1) to 26.5 ng/L (LP-WS2). PFDoA, PFHpA and PFHxA were detected at low concentrations.

Figure 7.8 shows a scatter plot of PFASs concentrations and their contributions in various water sources. Some linear trend can be seen, although not clearly defined. Clustering of PFASs can be seen at the foot of x-axis with linear tendencies. However, a logbase plot in Figure 7.9 clearly shows linear trend for PFASs in all the water sources. This trend suggest strong positive correlation existed between PFASs and their concentrations in different water sources. Shown in Figures 7.10 and 7.11 are the contributions of classes of PFASs compounds in various water sources and a contributions of short and long chain PFASs in various water sources respectively. It can be clearly seen in Figure 7.10 that the PFCAs are the dominant PFASs in all the water sources, although they are most clustered in WWTP.

This is indicative of use of PFASs products containing PFOA which belongs to PFCAs class of PFASs. It is used in several industrial applications, including carpeting, upholstery, apparel, floor wax, textiles, firefighting foam and sealants. Once again, short chain PFASs are dominant than the long chain as shown in Figure 7.11. Their frequency of detection can be attributed to their ability to be more soluble in water than their long chain analogues.

Table 7.6: Mean concentrations of PFAS in different water samples during the wet season

Samples	LP-B1	LP-B2	LP-B3	LP-B4	LP-S1	LP-S2	LP-T1	LP-S3	LP-T2	LP-B5	LP-T3	LP-WS1	LP-WE1	LP-WI1	LP-WP1	LP-WP2	LP-WE2	LP-WS2	LP-WI2
Compounds									**Mean concentrations (ng/L) and standard deviations (±)**										
PFHxDA	<LOD	<LOD	**0.0170** ±0.00	**0.222** ±0.00	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.0410** ±0.01	<LOD
PFNA	<LOD	**24.0** ±3.12	**0.974** ±0.02	**0.057** ±0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**4.96** ±0.00	<LOD	<LOD	<LOD	<LOD	**0.920** ±0.01	**10.8** ±2.98	**5.09** ±0.54	**7.97** ±3.54
PFODA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.368 ±0.01	<LOD	<LOD	<LOD
PFPeA	**0.343** ±0.14	**0.880** ±0.03	**0.611** ±0.12	**0.391** ±0.00	**1.78** ±0.14	**0.538** ±0.02	**0.384** ±0.00	**0.925** ±0.00	**0.110** ±0.04	**0.0660** ±0.26	**8.30** ±0.09	<LOD	**0.299** ±0.182	**0.622** ±27.90	<LOD	**12.7** ±0.01	<LOD	**36.3** ±0.04	**0.823** ±0.02
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.481 ±0.038	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.76 ±0.33	<LOD	<LOD	<LOD
L-PFBS	15.7 ±2.98	**10.9** ±0.74	**8.86** ±0.75	**10.8** ±1.64	**2.64** ±0.65	**12.6** ±0.74	8.85 ±0.98	**6.87** ±0.95	**16.0** ±2.96	**32.7** ±0.88	**6.08** ±3.87	**179** ±28.60	**12.9** ±2.96	**135** ±19.6	<LOD	**159.6** ±6.74	**29.9** ±1.98	**49.8** ±8.78	<LOD
L-PFDS	<LOD	<LOD	<LOD	**0.096** ±0.02	<LOD	<LOD	<LOD	<LOD	**1.06** ±0.04	**1.24** ±0.54	**0.765** ±0.03	**1.39** ±0.04	**14.9** ±1.85	**0.954** ±0.00	<LOD	**0.168** ±0.00	**1.05** ±0.05	**0.653** ±0.01	**2.00** ±0.36
L-PFHxS	**0.969** ±0.03	**0.809** ±0.15	**0.984** ±0.03	**1.75** ±0.09	<LOD	<LOD	<LOD	<LOD	**1.06** ±0.04	1.23 ±0.54	**0.765** ±0.03	**0.637** ±0.02	**0.773** ±0.22	**0.639** ±0.01	<LOD	**1.74** ±0.02	**6.96** ±1.45	**6.76** ±0.00	**3.74** ±0.00
L-PFOS	**3.05** ±0.08	**0.754** ±0.01	**4.09** ±2.97	**6.53** ±1.90	**0.638** ±0.26	**2.32** ±0.87	**3.87** ±0.79	**0.908** ±0.70	**6.83** ±1.04	**1.42** ±0.32	**3.09** ±2.85	<LOD	**9.68** ±3.87	**3.66** ±0.65	**117** ±19.8	**4.00** ±1.75	**29.7** ±0.85	**2.96** ±0.00	**18.9** ±0.00
L-PFHpS	**0.193** ±0.01	**0.010** ±0.00	**0.0850** ±0.01	**0.297** ±0.07	**0.020** ±0.00	<LOD	**0.016** ±0.01	**0.195** ±0.00	**0.330** ±0.28	**0.271** ±0.05	**0.011** ±0.01	<LOD	**3.98** ±0.94	**2.26** ±0.38	**8.06** ±3.87	**2.98** ±0.78	**0.799** ±0.03	**0.974** ±0.00	**8.63** ±0.00
FHET	**0.083** ±0.02	**0.0270** ±0.02	**0.0750** ±0.00	**0.0220** ±0.00	**0.101** ±0.01	**0.100** ±0.03	**0.097** ±0.00	**0.029** ±0.01	**0.057** ±0.00	**0.052** ±0.00	<LOD	**0.164** ±0.00	**0.100** ±0.02	**0.320** ±0.21	**0.030** ±0.0	**0.0450** ±0.01	**0.226** ±0.02	**0.0350** ±0.01	**0.0760** ±0.00
PFOA	**63.8** ±12.9	**89.6** ±19.70	**1.98** ±0.54	**1.99** ±0.01	**0.606** ±0.00	**1.28** ±0.39	**0.279** ±0.05	**0.190** ±0.03	**0.379** ±0.04	**0.378** ±0.14	**0.128** ±0.02	<LOD	**190** ±41.70	**34.9** ±8.95	<LOD	**816** ±32.90	**310** ±75.80	**575** ±54.80	**710** ±52.70
PFBA	**4.02** ±0.95	**13.6** ±1.75	**4.63** ±0.86	**9.64** ±2.96	**13.7** ±1.76	**17.7** ±1.43	**13.8** ±0.54	**4.98** ±0.33	**6.78** ±1.61	**4.96** ±0.04	**7.02** ±2.76	**16.8** ±2.74	**27.6** ±2.98	**13.7** ±3.15	<LOD	**6.95** ±1.65	**5.75** ±1.78	**5.87** ±0.65	**26.5** ±4.76
PFDoA	<LOD	**0.0770** ±0.00	**0.209** ±0.00	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.471** ±0.54	<LOD	**3.87** ±0.65	**<LOD**	**0.099** ±0.07	<LOD	<LOD
PFHpA	**0.158** ±0.01	**0.401** ±0.37	**1.02** ±0.10	**0.0100** ±0.00	**0.100** ±0.00	<LOD	**0.044** ±0.00	<LOD	**0.010** ±0.01	**0.0100** ±0.00	**1.03** ±0.08	<LOD	**1.70** ±1.12	**1.94** ±0.24	**15.9** ±0.21	**2.89** ±1.00	**3.35** ±0.00	**2.03** ±0.37	**0.240** ±0.04
PFHxA	**0.191** ±0.05	**0.245** ±0.02	**0.314** ±0.06	**0.0100** ±0.00	**0.143** ±0.04	<LOD	**0.0280** ±0.01	**0.658** ±0.0	**0.016** ±0.00	**0.0100** ±0.00	**0.753** ±0.23	<LOD	1.47 ±0.75	0.332 ±0.03	**6.83** ±1.22	**19.9** ±0.38	**1.07** ±0.43	**13.3** ±1.25	**34.4** ±6.98
4:2 FTS	**0.0170** ±0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.186** ±0.07	<LOD	**0.267** ±0.02
6:2 FTS	<LOD	**3.40** ±2.12	<LOD	**1.96** ±0.33	**0.071** ±0.02	**0.057** ±0.00	<LOD	<LOD	**0.080** ±0.00	**1.34** ±0.03	**2.93** ±0.21	**0.893** ±0.00	**2.14** ±0.31	0.966 ±2.41	<LOD	**1.02** ±0.02	**3.22** ±2.49	**0.920** ±0.01	**0.318** ±0.27
8:2 FTS	0.906 ±0.06	3.98 ±0.65	<LOD	<LOD	<LOD	<LOD	<LOD	**1.95** ±0.06	<LOD	<LOD	**5.83** ±0.95	<LOD	<LOD	<LOD	**3.87** ±0.65	**2.76** ±0.87	**0.367** ±0.01	**0.368** ±0.01	**8.85** ±1.87
FHEA	**2.86** ±0.00	13.3 ±0.00	**5.89** ±0.02	**3.85** ±0.02	<LOD	**2.42** ±0.01	**3.45** ±0.03	**8.86** ±0.75	**4.78** ±0.00	<LOD	**14.01** ±0.02	**17.8** ±0.00	<LOD	**0.186** ±0.00	**15.9** ±0.21	**7.87** ±0.01	**15.9** ±0.21	**12.7** ±0.01	**1.64** ±0.00
FOET	**0.148** ±0.01	**3.11** ± 0.15	**1.34** ±0.21	**1.63** ±0.59	**0.0900** ±0.05	**0.523** ±0.10	**1.30** ±0.02	**0.197** ±0.08	**0.263** ±0.03	**0.171** ±0.02	**2.66** ±0.79	<LOD	**2.19** ±0.56	<LOD	**6.83** ±1.22	**2.68** ±0.36	**6.20** ±1.04	**2.76** ±0.33	**0.522** ±0.01

Figure 7.8: PFASs concentrations distributions for various water sources in Limpopo during the wet season.

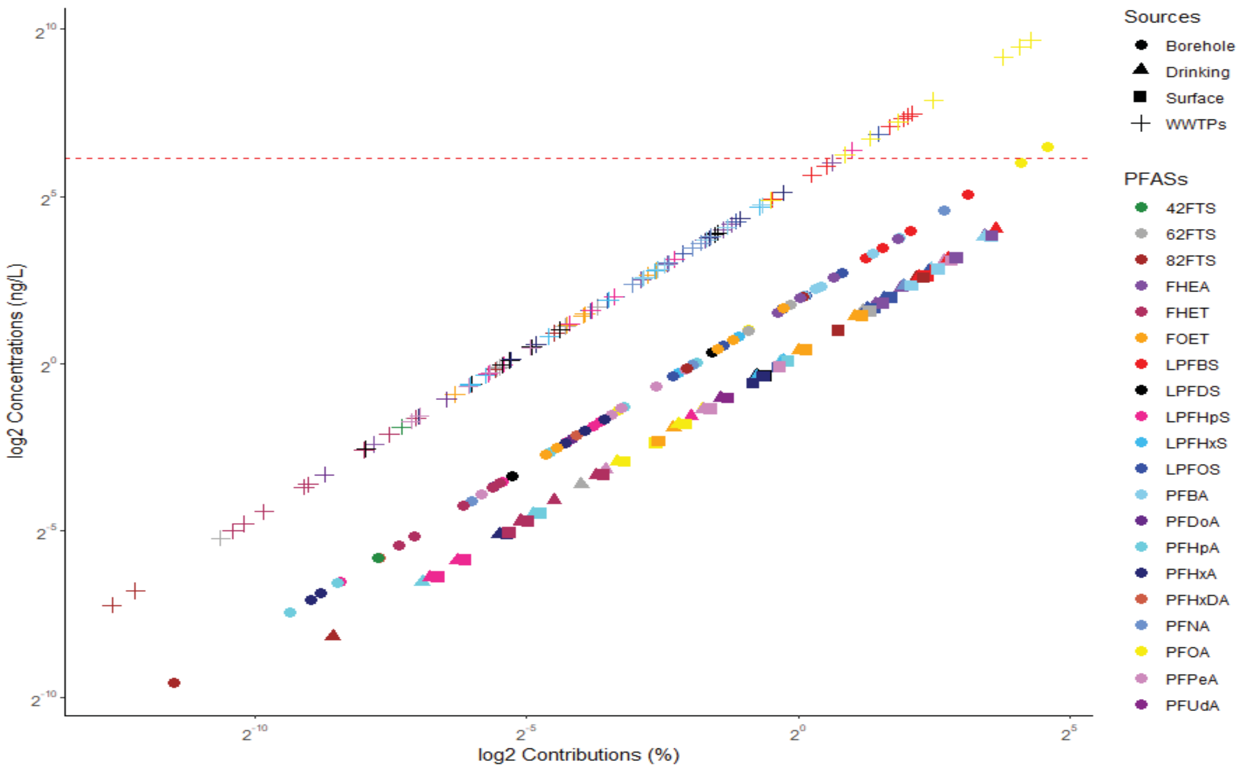

Figure 7.9: PFASs concentration contributions in various water sources in Limpopo during the wet season.

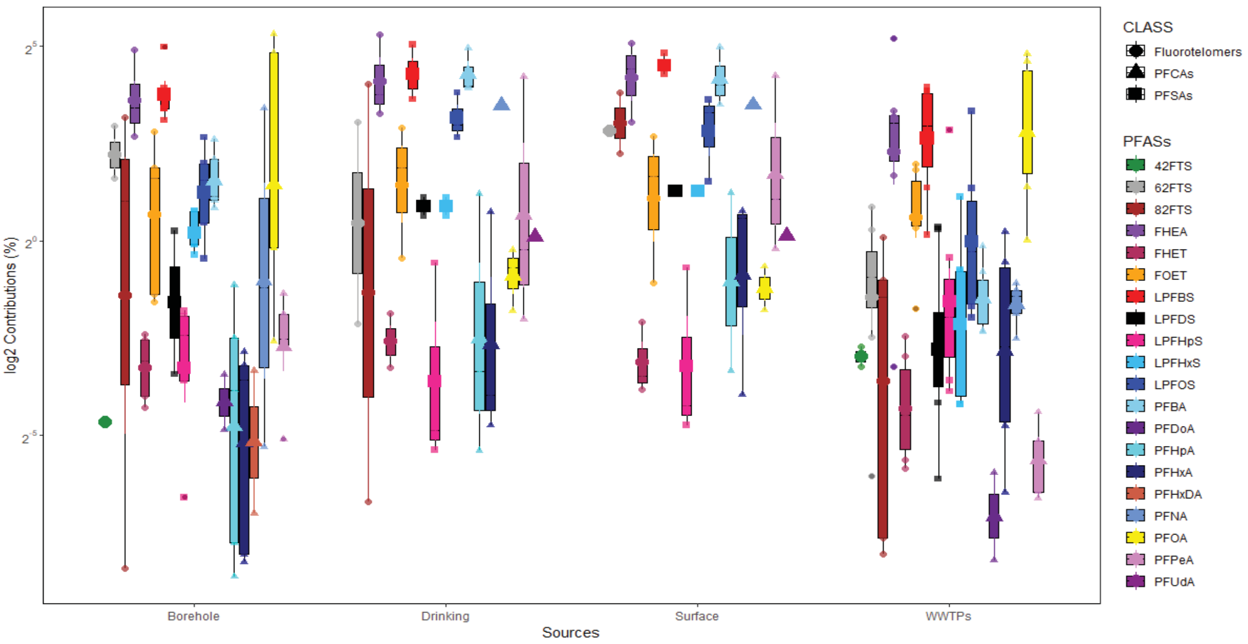

Figure 7.10: PFASs class contributions in various water sources in Limpopo during the wet season.

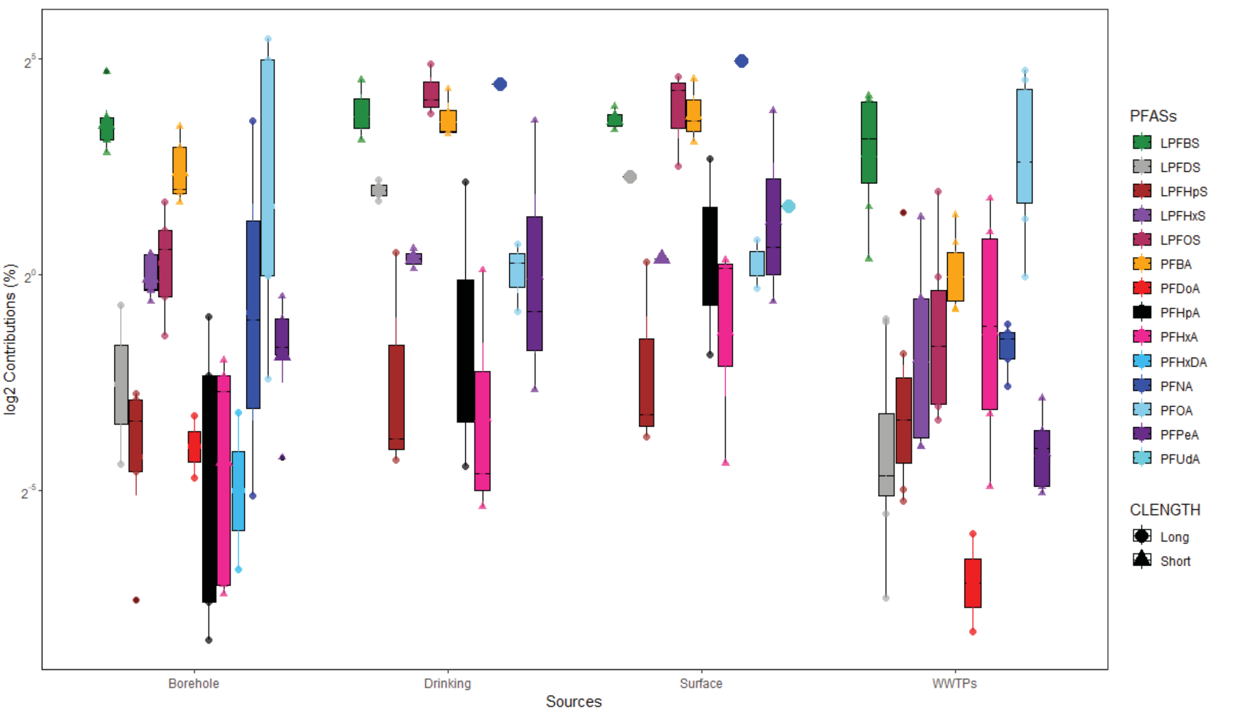

Figure 7.11: Contributions of short- and long-chain PFASs for various water sources in Limpopo during the wet season.

7.4.2 Establishing the possible sources of PFASs detected in the water

Shown in Figure 7.12 are the contributions of PFASs compounds detected in the water samples during the wet season represented in Table 7.6. Similarly, congeners in the same score plot, probably receive PFASs from similar sources. Figure 7.13 shows the PCA of the sampling sites. Similarly, the sites that are in the same cluster might have similar sources of PFAS contamination. Sample LP-WI2 and LP-WI2 are expressed similar to PCA observed during the dry season. LP-B5 and LP-B2 showed a negative correlation. The PCA of the sampling sites is represented in Table 7.6. Similarly, the sites that are in the same cluster might have similar sources of PFAS contamination, except for site PLK BH2.

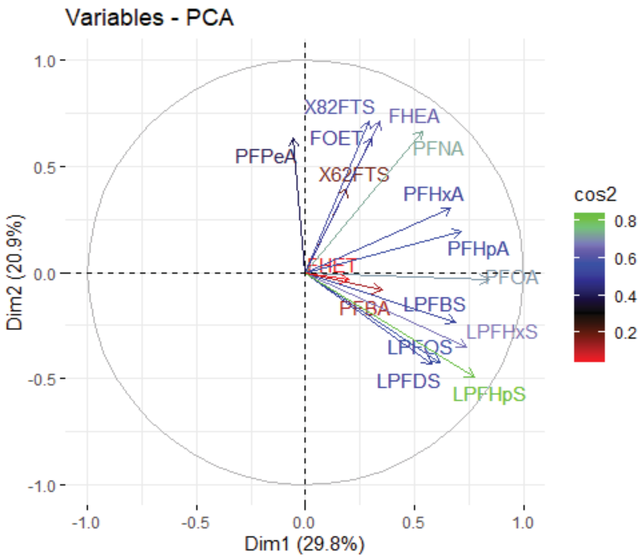

Figure 7.12: PCA of sampling points and their relationships during the wet season.

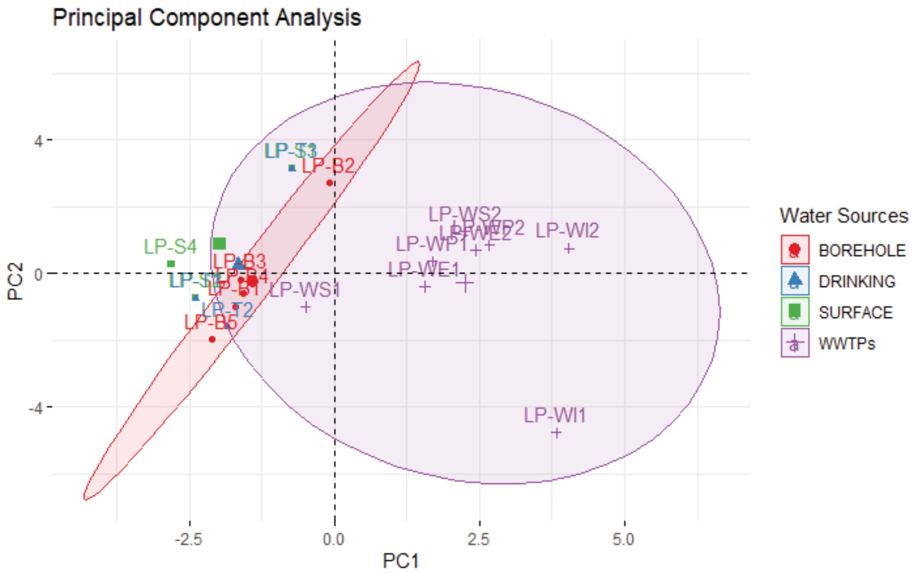

Figure 7.13: PCA of sampling points and their relationships during the wet season.

7.5 SUMMARY

The general trend in the concentrations of PFASs obtained in dry and wet seasons indicates higher concentrations in dry season compared to wet season. Because there is hardly any rain during dry season, the concentrations of contaminants are expected to be more concentrated than in wet season which comes with heavy rain. Table 7.7 compares the range of PFASs concentrations obtained in the present study with the values reported in other studies in and outside South Africa. The levels shown in Table 7.7 compares with other studies where the concentration levels are lower in some cases and higher in others.

Table 7.7: Comparison of PFASs concentrations obtained in the current study with other studies

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.8	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area) 2-61 (Rhine River)	Skutlarek et al., 2006
Shandong Province	13.1-69,23	Chen et al., 2017
Liaoning Province	22.4-26,73	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
KwaZulu-Natal Province South Africa (drinking water/Tap water)	<LOQ-42.05	This study
Gauteng Province South Africa (Dam river)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al., 2014,
Vaal River South Africa (River water)	<LOQ -38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
Limpopo Province South Africa (river water)	**<LOD-11**	**This study**
Limpopo Province South Africa (wastewater treatment plant)	**<LOD-1063**	**This study**
Limpopo Province South Africa (Drinking water)	**<LOD-18**	**This study**
Limpopo Province South Africa (Dam water)	**<LOD-45**	**This study**

CHAPTER 8: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE MPUMALANGA PROVINCE

8.1 SAMPLING STRATEGY

8.1.1 Location and description of sampling sites

Water samples were collected from eMalahleni and surrounding areas and Oliphant and Zaalklip Rivers in Mpumalanga province during both wet (October-April) and dry (June-august) seasons. These areas are highly industrialized with many mining activities such as coal and energy generation. Figure 8.1 shows the land use map within the vicinity of sampling sites. The following water systems were targeted in the province:

- Tap water (MP-T)
- Wastewater (MP-WI and MP-WE)
- Borehole (MP-B)
- Surface water (MP-S)

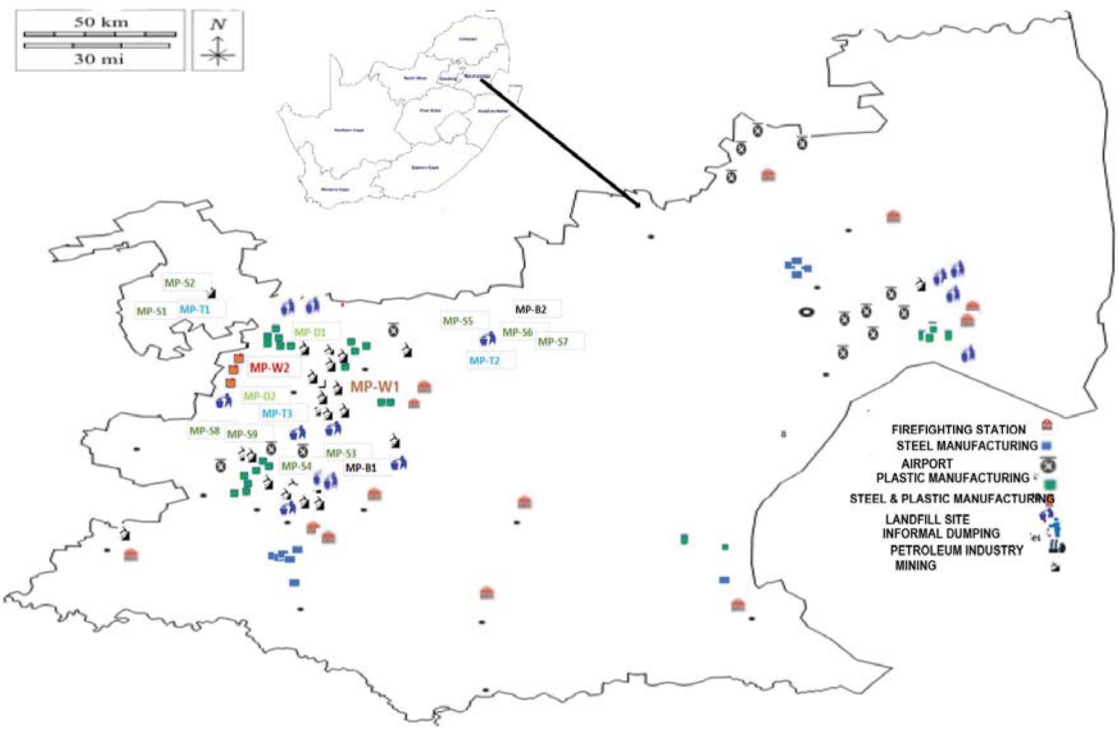

Figure 8.1: Land use map with sampling sites in Mpumalanga Province.

8.1.2 Sample collection

Table 8.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 8.1: Sampling sites in Gauteng province with coordinates

Sampling point	Sample IDs	Coordinates
Zaalklip River	MP-S1	25°86'95.14" S, 29°01'01.36" E
Kwa-Guqa stream	MP-S2	25°87'04" S, 29°12'99" E
Kwa-Guqa tap water	MP-T1	25°87'02" S, 29°12'89" E
Olifants River point 1	MP-S3	25°81'80" S, 29°29'45" E
Olifants River point 2	MP-S4	25°81'77" S, 29°29'31" E
Olifants borehole	MP-B1	25°81'83" S, 29°29'29" E
Pine Ridge, eMalahleni (tapwater)	MP-T2	25°81'63" S, 29°19'19" E
Nkangala Blesbokspruit on R544 Catchment 2	MP-T3	25°81'64" S, 29°21'17" E
Nkangala Blesbokspruit on R544 catchment 1	MP-S5	25°80'61" S, 29°17'58" E
Klipspruit River Point 1	MP-S6	25°78'37" S, 29°13'68" E
Klipspruit River point 2	MP-S7	25°78'39" S, 29°13'57" E
Klipspruit borehole	MP-B2	25°78'35" S, 29°13'70" E
Kromdraai River before discharge	MP-S8	25°77'55" S, 29°02'34" E
Kromdraai River after discharge	MP-S9	25°87'04" S, 29°02'30" E
MP-DWTP1-Effluent	MP-DE1	
MP-DWTP2-Effluent	MP-DE2	
MP-DWTP1-Influent	MP-DI1	
MP-DWTP2-Influent	MP-DI2	
MP-WWTP1-Effluent	MP-WE1	
MP-WWTP2-Effluent	MP-WE2	
MP-WWTP1-Influent	MP-WI1	
WWTP2-Influent	MP-WI2	
BLANK	BL	

8.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. Tables 8.2, 8.3 and 8.4 show the percentage recoveries of blanks and water samples respectively for dry season. The recoveries ranged from 61.8-107.3% and 51.2-150% for blank and water samples respectively. These recovery values are within the acceptable range of 50-150%.

Table 8.2: Percentage recoveries and standard deviations of PFASs in blanks during the dry season

Samples – Surrogate recoveries (%) ± Standard deviation	
Surrogates	**BL**
MPFNA	78.2±8.12
MPFUdA	61.8±6.49
MPFHxS	107.3±0.62

Table 8.3: Percentage recoveries of PFASs standards in samples during the dry season.

	Samples Recoveries (%) ± Standard deviation							
Surrogate	**MP-DE1**	**MP-DE2**	**MP-DI1**	**MP-DI2**	**MP-WE1**	**MP-WE2**	**MP-WI1**	**MP-WI2**
MPFNA	84.3±0.80	107±3.10	82.5±4.60	106±11.6	93.2±3.80	109±13.1	88.7±12.2	99.1±4.70
MPFHxS	63.7±4.40	86.5±18.9	79.8±2.7	72.3±6.0	97.5±23.7	65.0±8.50	55.6±11.8	119.4±15.9
MPFUdA	85.4±5.9	94.9±6.5	76.1±4.5	86.2±12.8	98.3±1.30	85.1±3.80	60.0±9.90	83.1±10.5

8.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

8.3.1 Distribution of PFASs in various water sources during the dry season

As shown in Table 8.5, only PFHxA, PFPeA, PFHpA, PFNA, LPFOS, PFOA, 6:2 FTS, LPFBS and PFBS were detected in all the water samples, whereas 8:2 FTS was detected in all the samples except in MP-T2. PFBA were not present in only two samples, MP-T3 and MP-S7. The highest PFASs concentration (92.4) ng/L) was found in Nkangala Blesbokspruit water sample and this was exhibited by PFOS. PFOS also exhibited a high concentration of 73.9 ng/L in Olifant borehole water sample. 6:2 FTS recorded a concentration of 51.5 ng/L in Kwa-Guqa tap water. PFDS and 8:2 FTS showed 34.0 ng/L and 17.3 ng/L respectively in the same Kwa-Guqa tap water. From Table 9.4, the sulphonate group of PFASs were most prominent. That PFOS showed the highest concentration could be due to some contribution from 8:2 and 6:2 telomers degradation. Once again, the short chain PFASs were detected in most of the samples suggesting their prevalence in the water samples. High concentrations of 73.9 ng/L was observed for PFOS in MP-B1. This suggests some leaching of PFASs from surface water to groundwater.

Table 8.4: Percentage recoveries of PFASs standards in blanks and samples during the dry season

	Samples ─ Recoveries (%) ± Standard deviation														
Surrogates	**BL (n=4)**	**MP-S1**	**MP-S2**	**MP-T1**	**MP-S3**	**MP-S4**	**MP-B1**	**MP-T2**	**MP-T2**	**MP-S5**	**MP-S6**	**MP-S7**	**MP-B2**	**MP-S8**	**MP-S9**
MPFNA	139±29.3	116±42.3	64.2±14.1	96.9±5.69	57.1±19.5	92.7±23.0	150±40.3	89.6±35.4	136±12.2	87.2±14.9	80.5±1.90	69.3±25.5	119±1.24	65.0±11.5	91.7±9.58
MPFUDA	121±19.4	66.6±2.83	94.7±23.2	118±14.4	109±25.8	112±7.61	72.2±4.37	61.±7.99	116±13.0	82.3±8.23	111±18.1	110±0.486	61.8±8.33	99.1±33.3	79.7±3.43
MPFHXS	114±15.8	57.2±1.34	51.2±0.612	63.2±18.9	111±6.10	64.5±7.89	103±20.7	79.±15.0	62.3±11.4	66.8±4.25	103±4.26	79.2±17.5	73.6±2.87	59.5±3.24	80.3±24.4

Table 8.5: Mean concentrations of PFASs in various water samples in dry season

Compounds	**PFUdA**	**PFHxA**	**PFPeA**	**4:2 FTS**	**8:2 FTS**	**PFHpA**	**PFNA**	**L-PFBS**	**L-PFHxS**	**L-PFOS**	**PFHpS**	**PFOA**	**L-PFDS**	**FHEA**	**6:2 FTS**	**FOET**	**FHET**	**PFBA**
Samples	Mean concentrations (ng/L) and standard deviations (±)																	
MP-S1	<LOD	**3.52**	**1.57**	ND	**8.99**	**0.699**	**1.43**	**2.63**	**0.249**	**20.19**	<LOD	**0.366**	**59.4**	**1.19**	**9.68**	**0.668**	**0.439**	**7.98**
		±0.40	±0.11		±2.49	±0.27	±0.30	±1.01	±0.03	±4.62		±0.20	±5.02	±0.751	±3.31	±0.0214	±0.0423	±3.023
MP-S2	<LOD	**3.29**	**5.75**	**1.43**	**18.6**	**0.86**	**0.49**	**14.4**	**0.755**	**3.82**	**0.751**	**1.2**	<LOD	**1.08**	**16**	**0.53**	**1.74**	**13.5**
		±0.23	±2.59	±0.71	±3.54	±0.17	±0.03	±4.62	±0.35	±1.01	±0.14	±0.27		±0.362	±1.26	±0.12	±1.43	±0.356
MP-T3	**0.314**	**3.71**	**4.94**	**1.06**	**17.3**	**2.60**	**1.33**	**1.92**	**1.23**	**1.51**	**0.507**	**1.05**	**34.0**	**4.45**	**51.5**	**3.38**	**0.411**	**9.94**
	±0.065	±0.040	±2.92	±0.0436	±2.23	±0.82	±0.46	±0.11	±0.615	±0.14	±0.37	±0.16	±0.507	±3.14	±5.14	±2.48	±0.0555	±2.92
MP-S3	<LOD	**12**	3.**12**	<LOD	**19.7**	**1.12**	**2.95**	**1.45**	**1.25**	**5.88**	<LOD	**1.55**	**165**	<LOD	**10.4**	**1.18**	**0.105**	**18.5**
		±2.49	±1.70		±1.13	±0.24	±2.46	±0.26	±1.10	±0.10		±0.60	±16.5		±0.489	±0.15	±0.00	±0.80
MP-S4	**2.23**	**29.2**	**1.85**	<LOD	**54.7**	**1.16**	**14.8**	**3.45**	**3.13**	**27.9**	**0.850**	**2.11**	**7.64**	**2.36**	**21.1**	**5.58**	**0.23**	**13.2**
	±0.281	±3.68	±0.242		±17.9	±0.58	±0.94	±0.26	±0.78	±0.13	±0.00	±0.70	±0.69	±2.58	±2.59	±0.619	±0.05	±5.22
MP-B1	<LOD	**2.04**	**1.55**	**6.46**	**30.1**	**0.41**	**19.2**	**0.896**	**8.25**	**73.9**	**1.85**	**3.94**	**21.8**	<LOD	**14.4**	**2.24**	**0.170**	**2.68**
		±0.06	±0.0534	±0.03	±2.65	±0.04	±0.733	±0.27	±0.43	±9.59	±0.81	±1.53	1.44		±0.82	±0.96	±0.04	±0.69
MP-T1	<LOD	**0.805**	**1.15**	<LOD	**8.72**	**1.29**	**2.51**	**1.51**	**1.25**	**7.16**	<LOD	**0.873**	<LOD	0.912	**8.58**	<LOD	<LOD	**4.05**
		±0.35	±0.46		±3.09	±0.342	±0.222	±0.13	±0.17	±4.93		±0.426		±0.41	±3.16			±0.44
MP-T2	<LOD	**0.386**	**2.04**	<LOD	<LOD	**0.0336**	**0.493**	**0.614**	**0.845**	**4.81**	<LOD	**0.902**	**26.1**	<LOD	**1.99**	<LOD	<LOD	<LOD
		±0.02	±0.48			±0.02	±0.02	±0.53	±0.21	±2.87		±0.72	±2.73		±0.54			
MP-S5	**23.8**	**8.75**	**2.00**	**0.14**	**39.7**	**1.97**	**6.42**	**0.099**	**0.823**	**92.4**	<LOD	**2.83**	**41.2**	<LOD	**31.1**	**0.285**	<LOD	**26.0**
	±1.27	±1.48	±0.336	±0.0105	±4.67	±0.76	±4.02	±0.14	±0.10	±5.15		±1.29	±1.73		±6.59	±0.04		±4.90
MP-S6	<LOD	**0.608**	**0.230**	<LOD	**2.24**	**0.149**	**1.69**	**1.65**	<LOD	**1.72**	<LOD	**0.747**	**14.5**	<LOD	**1.16**	**11.3**	<LOD	**33.5**
		±0.15	±0.01		±1.73	±0.05	±0.04	±0.433		±0.17		±0.64	±0.60		±0.28	±0.747		±0.31
MP-S7	<LOD	**1.36**	**1.83**	<LOD	**6.31**	**0.276**	**0.330**	**2.38**	**0.123**	**4.51**	<LOD	**0.851**	<LOD	<LOD	**7.44**	**1.88**	<LOD	<LOD
		±0.25	±0.925		±1.02	±0.06	±0.08	±1.97	±0.02	±1.80		±0.00			±1.92	±0.39		
MP-B2	<LOD	**5.20**	**2.35**	**0.724**	**12.0**	**0.789**	**18.3**	**2.71**	**0.400**	**27.5**	<LOD	**5.86**	<LOD	<LOD	**28.4**	**21.6**	<LOD	**6.49**
		±0.51	±1.56	±0.2	±1.72	±0.234	±0.897	±1.27	±0.03	±6.17		±4.34			±7.00	±1.17		±1.04
MP-S8	<LOD	**0.63**	**0.725**	**0.236**	**0.940**	**0.401**	**1.22**	**0.133**	<LOD	**6.52**	<LOD	**0.880**	**36.3**	<LOD	**19.8**	**1.47**	<LOD	**4.28**

Compounds	**PFUdA**	**PFHxA**	**PFPeA**	**4:2 FTS**	**8:2 FTS**	**PFHpA**	**PFNA**	**L-PFBS**	**L-PFHxS**	**L-PFOS**	**PFHpS**	**PFOA**	**L-PFDS**	**FHEA**	**6:2 FTS**	**FOET**	**FHET**	**PFBA**
Samples								**Mean concentrations (ng/L) and standard deviations (±)**										
		±0.16	±0.34	±0.06	±0.08	±0.16	±0.00910	±0.19		±1.03		±0.23	±1.10		±1.66	±0.100		±0.30
MP-S9	**0.610**	**13.4**	**1.93**	**0.0952**	**29.9**	**2.83**	**22.6**	**2.77**	**0.205**	**7.25**	<LOD	**0.390**	<LOD	**0.660**	**16.7**	**8.75**	<LOD	**9.31**
	±0.05	±2.24	±0.79	±0.010	±8.12	±0.92	±0.71	±0.312	±0.10	±0.373		±0.17		±0.05	±0.50	±2.05		±2.51
MP-DE2	nd	**11.2**	**4.12**	nd	**177**	**2.99**	**7.1**	**1.03**	**0.34**	**1.21**	**2.99**	**11.2**	nd	**2.09**	**2.65**	**7.36**	**0.350**	**122**
		±1.46	±0.1		±0.99	±0.20	±2.87	±0.12	±0.02	±0.04	±0.93	±3.64		±0.05	±0.26	±0.55	±0.05	±6.26
MP-DE1	nd	**3.92**	**1.38**	nd	**61.4**	**1.14**	**1.41**	**0.48**	**0.46**	**1.72**	nd	**35.9**	nd	**2.82**	**1.72**	**8.25**	**0.390**	**96.4**
		±1.92	±0.38		±11.35	±0.30	±0.26	±0.06	±0.16	±0.69		±2.3		±0.07	±0.45	±0.57	±0.12	±9.00
MP-DI2	nd	**9.99**	**6.04**	nd	**19.6**	**10.2**	**2.84**	**3.52**	**4.90**	**2.35**	**4.75**	**12.0**	nd	**5.91**	**4.66**	**40.5**	**6.07**	**47.3**
		±0.02	±1.31		±3.00	±2.07	±1.16	±0.61	±3.88	±0.44	±0.31	±3.94		±0.22	±0.15	±9.96	±0.55	±3.17
MP-DI1	nd	**6.14**	**2.16**	nd	**10.3**	**2.80**	**3.73**	**0.490**	**1.10**	**3.41**	**0.400**	**16.5**	nd	**1.28**	**4.34**	**22.7**	**2.03**	**205**
		±0.67	±0.99		±2.63	±0.95	±2.04	±0.10	±0.11	±0.28	±0.02	±4.79		±0.15	±0.98	±8.97	±1.14	±32.42
MP-W2E	nd	**63.7**	**6.12**	nd	**99.1**	**4.78**	**5.11**	**153**	**3.41**	**5.38**	**1.27**	**23.7**	nd	**5.32**	**14.2**	**1670**	**16.4**	**116**
		±9.89	±1.74		±9.27	±1.19	±0.09	±22.77	±0.88	±0.02	±0.33	±2.08		±0.17	±2.74	±20.05	±3.64	±11.10
MP-W1E	nd	**16.9**	**3.11**	nd	**40.9**	**6.31**	**5.55**	**356**	**8.77**	**6.56**	**208**	**228**	nd	**12.16**	**23.0**	**60.75**	**8.12**	**134**
		±2.35	±0.75		±0.15	±1.54	±0.38	±58.3	±0.89	±3.41	±28.65	±27.33		±2.35	±1.51	±7.52	±0.57	±5.00
MP-W21	nd	**29.35**	**6.11**	nd	**99.27**	**1.85**	**4.34**	**67.6**	**9.06**	**2.77**	**419**	**199**	nd	**27.89**	**11.0**	**713**	**64.5**	**285**
		±0.94	±0.3		±3.25	±0.09	±0.34	±3.74	±1.10	±0.08	±107.40	±8.67		±1.15	±0.03	±127.73	±23.8	±36.27
MP-W1I	nd	**37.7**	**5.97**	nd	**79.2**	**5.62**	**7.89**	**103**	**21.4**	**6.16**	**341**	**52.7**	nd	**26.7**	**9.00**	**172**	**9.65**	**80.79**
		±8.10	±2.01		±3.00	±1.18	±0.57	±5.02	±3.060	±0.50	±96.74	±10.68		±2.95	±0.04	±46.1	±3.36	±5.3

In a study, three main sources of pollution that impact on the quality of the Upper Olifants River and its tributaries were identified as 1) the acidification of parts of the system and inputs of metal ions and sulphates via acid mine drainage; 2) industrial effluent containing a variety of potential pollutants and genotoxicants; and 3) excessively high nutrient inputs from wastewater treatment works and agriculture, and microbial pollution from wastewater treatment works (CSIR 2009). These pollutants result in widespread eutrophication (nutrient enrichment) of the river, increased potential for bioaccumulation of metals, and human health effects related to microbial pollution. It is, therefore, possible that PFASs may be among the pollutants from industry, agriculture and wastewater effluent discharges.

The highest mean concentrations in influent and effluent samples were observed for PFBA in MP-DE2 at 121 ng/L, M-DE1 at 96.4 ng/L, MP-DI2 at 47.3 ng/L and MP-DI1 at 204 ng/L. PFBA increased from the influent, MP-DI2 to MP-DE2, and the opposite was observed between MP-DI1 and MP-DE2. A contrasting pattern was observed between the two DWTPs for 8:2 FTS and PFOS. 8:2 FT increased from the influent (MP-DI1) to the effluent (MP-DE1) DWTP1, while a slight increase in PFOS was observed in influent of DWTP2. There was no significant change in the concentration of PFOA in influents and effluents of both DWTPs. The highest concentration observed in WWTPs from Mpumalanga was for FOET at 713 ng/L, followed by PFHpS at 418 ng/L in MP-W1E and PFBA at 285 ng/L in MP-W2I. The concentrations of PFBS, PFBA and FOET increased from MP-W1I to MP-W1E while the opposite was observed for FOET and PFBA in MP-W2I to MP-W2E. However, PFHxA increased from MP-W2E, which was different for WWTP1. Overall, both WWTPs exhibited different behaviour in PFASs removal.

A scatter plot in Figure 8.2, shows the contributions of source water PFASs contents in the observed PFASs concentration in various water sources. There is linear relationship although not obvious at the lower end of the scale. A log base plot was, therefore, constructed (Figure 8.3) and it can be seen very clearly a well-developed linear relationship between PFASs contributions and their concentrations.

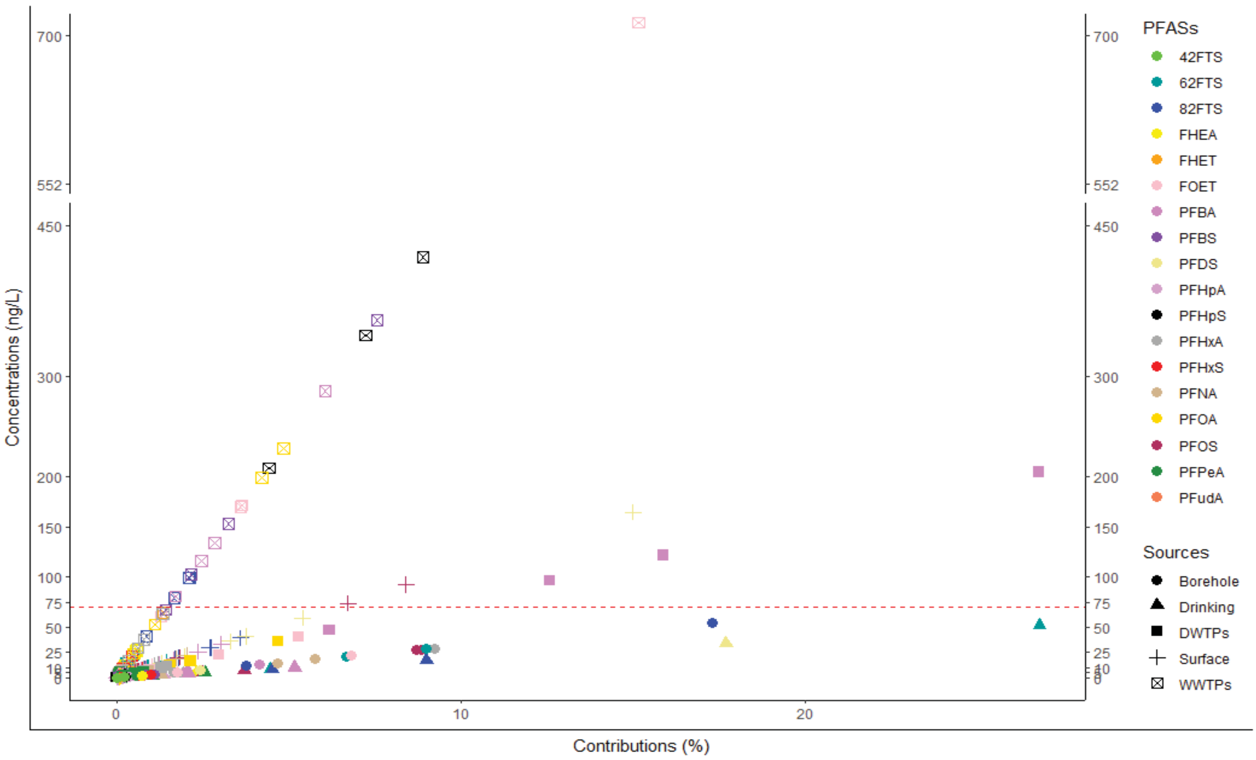

Figure 8.2: PFASs concentrations distributions for various water sources in Mpumalanga during the dry season.

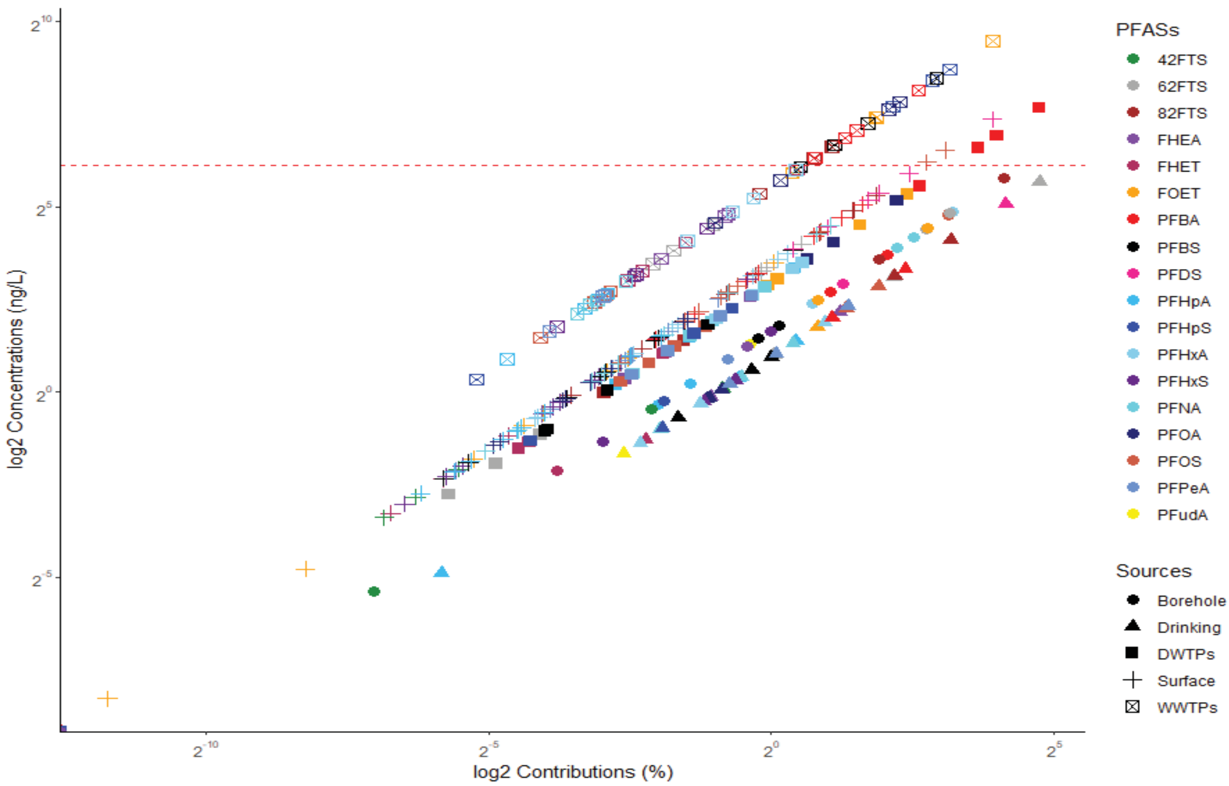

Figure 8.3: PFASs concentration contributions for various water sources in Mpumalanga during the dry season.

The three major class of PFASs, Fluorotelomer, PFCAs and PFSAs were detected in all the water sources as can be seen in Figure 8.4, although PFCAs appear to be most dominant. Furthermore, the PFASs classes are more congested in drinking water, DWTP, surface water and WWTP compared to borehole. This is probably expected since contaminants will have to travel through soil before polluting groundwater. Figure 8.5 shows the contributions of short and long chain PFASs to the observed concentrations. The short chains appear to be more prominent.

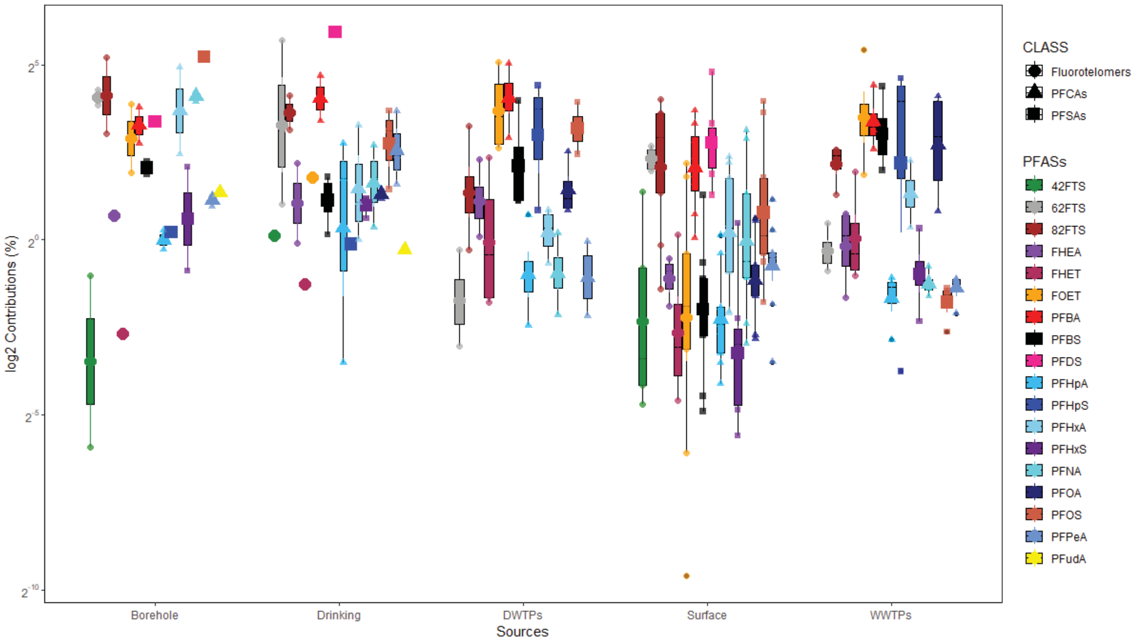

Figure 8.4: PFASs class contributions for various water sources in Mpumalanga during the dry season.

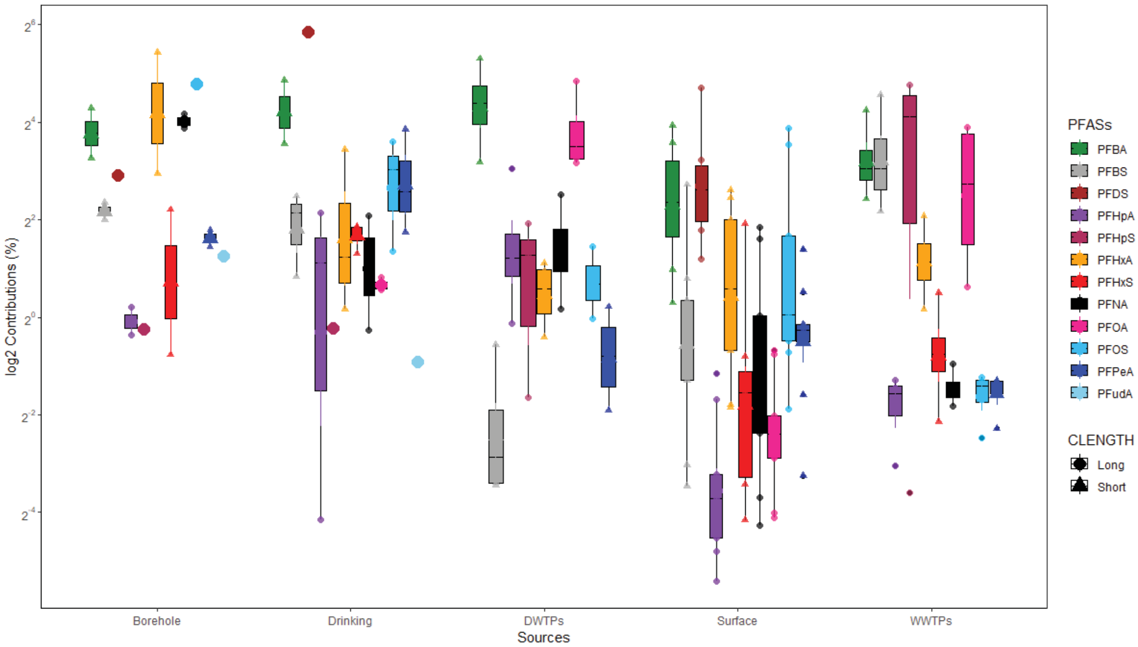

Figure 8.5: Contributions of short- and long-chain PFASs for various water sources in Mpumalanga during the dry season.

8.3.2 Establishing the possible sources of the PFASs detected in the water

The fingerprints are used to compare the composition profiles (pattern) of PFASs between different samples and can be helpful in tracking the source of the PFASs. Principal Component Analysis (PCA) was used to examine for correlations of PFASs patterns and to see how samples were related to each other. Samples that have pattern (fingerprint) similarities are located near each other in the score plot, and samples that differ are further apart. The arrows in the loading plot represent the most varying direction of the data set and thereby which PFASs are mainly contributing to separation of the samples. The data were normalized before analyses by dividing each individual PFASs concentration with the ∑PFASs concentration for each sample.

Figures 8.6 and 8.7 show the PCA plots of PFASs congeners and the sampling sites respectively. PFPeA, FHET, PFBS, FHEA, 8:2 FTS and PFHpS are all located on the top right of the score plot close to each; whereas the long chain PFASs, PFHxS, PFNA, and PFOS are located on the bottom right of the score plot close to each other (Figure 8.6). This observation suggests similar pattern/sources. The arrows in this diagram show that PFOS, PFHxS, 8:2 FTS, PFNA and PFPeA are the variables that explain the separation among the samples.

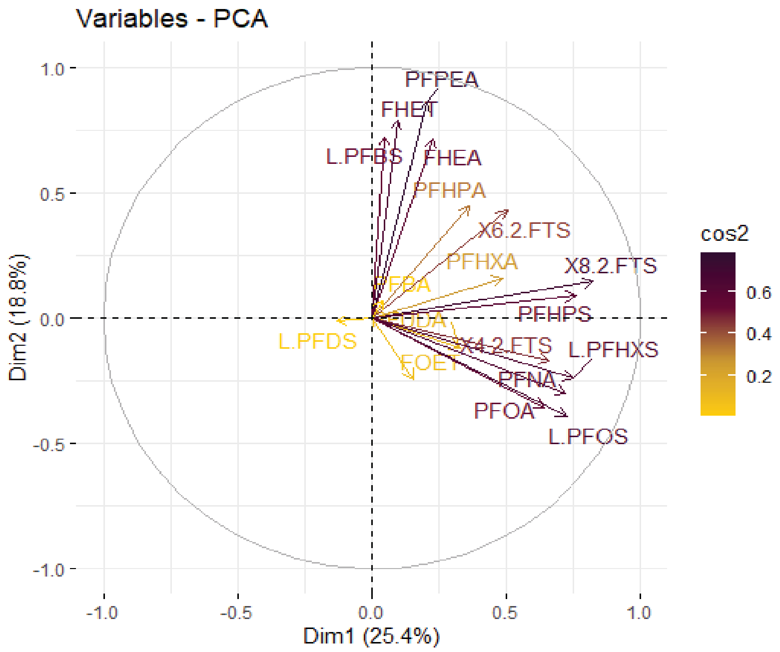

Figure 8.6: PCA of PFASs congener contributions and their relationships during the dry season.

With respect to the sampling sites (Figure 8.7), sampling sites, MP-S8 and MP-S2 showed no correlation, and this may be as a result of their distance and their sources of pollution. This suggests that the contamination in the analysed water samples from these sites have different pattern/sources. The same suggestion can also be extended to sampling sites MP-T3 and MP-T2. MP-T2 and MP-T4 are negatively correlated. MP-B1, MP-B2 and MP-S5 showed positive correlation. It is important to note that MP-B1 and MP-B2 were collected from different areas but were clustered together. This could be used to explain the behaviour of groundwater system. These groups: MP-S3, S4 and T3, MP-S6, S7, T4 and S8, DWTPs and WWTPs samples were grouped together, suggesting similar sources of pollution within these groups.

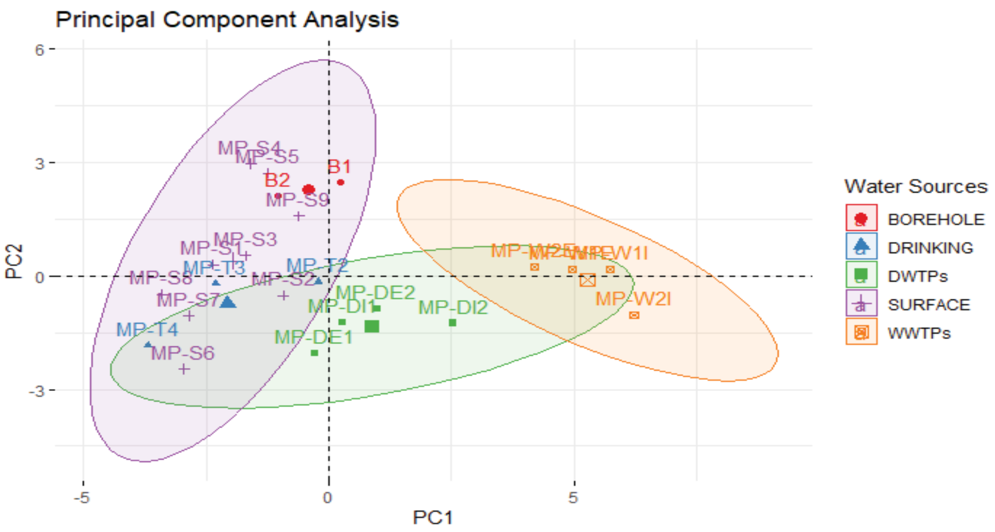

Figure 8.7: PCA of sampling sites and their relationships during the dry season.

8.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

8.4.1 Distribution of PFASs in various water sources during the wet season

Table 9.5 shows the concentrations of PFASs in wet season. For DWTPs, PFNA was observed at high concentration (490 ng/L) in the effluent MP-DE1, an increase from 206 ng/L of MP-DI1. Similar to trend. A different pattern was observed for influent MP-DI2 and effluent MP-DE2. PFOS, PFHxDA, PFBA, PFudA and PFODA increased from the influent to the effluent. Overall, total concentrations of PFSAs, PFCAs and fluorotelomers observed in effluent MP-DE1 were higher than those found in effluent MP-DE2. Similar to the observations during dry seasons, the two DWTPs exhibited different behaviour in the removal of PFASs in their systems. PFBA exhibited a concentration of 331 ng/L in MP-T3, followed by 8:2 FTS, 6:2 FTs and PFHxS at 158 ng/L (MP-T1), 70.5 ng/L (MP-T2) and 63.3 ng/L. 6:2 FTS was also observed at 56.8 ng/L in MP-T1 sample. Detection of these compounds at these concentrations in drinking water is a great concern.

Groundwater samples were collected from two boreholes which are used for drinking and domestic activities. These boreholes were located close to some of the surface PFNA behaviour; PFHxA, 8:2 FTS, FHET, 6:2 FTS, PFBS, PFHxS, PFdoA and PFOS followed the same waters investigated in this study. At least 12 PFASs were detected in all borehole water samples. The highest mean concentration in borehole water samples was observed for 8:2 FTS at 67.3 ng/L and 42.1 ng/L for MP-B1 and MP-B2, respectively. This was followed by PFHxS at 33.3 ng/L in MP-P2 and PFdoA at 32.8 ng/L. It is worth noting that PFdoA was detected in low detection frequencies and concentrations in almost all samples reported in this study. PFHxS was detected at a high of 31.8 ng/L in MP-B2. Concentrations of PFOA were observed at 2.28 ng/L and 8.92 ng/L in MP-B1 and MP-B2, respectively while PFOS was observed at 2.78 and 23.2 ng/L, respectively.
As shown in Table 9.5, PFBA exhibited high concentrations at 740 ng/L and 616 ng/L in MP-S3 and MP-S2 samples, respectively, followed by PFNA at 380 ng/L in MP-S3, 8:2 FTS at 211 ng/L in MP-S1 and 6:2 FTS at 194 ng/L in MP-S3. Long-chain PFASs; PFHxDA, PFudA, PFdoA and PFODA, and fluorotelomers; 4:2 FTS, FOET and FHEA were not frequently detected in surface water samples. These were only detected in MP-S1, S2 and S3.

Table 8.6 Mean concentrations of PFASs in various water samples in wet season

Compounds	PFUdA	PFdoA	PFHxA	PFNA	PFPeA	42FTS	82FTS	PFHpA	FHET	FOET	62FTS	FHEA	PFDS	PFBS	PFHxS	PFOS	PFHpS	PFOA	PFODA	PFHxDA	PFBA
Samples	Mean concentrations (ng/L) and standard deviations (±)																				
MP-B1	2.43	25.5	15.4	14.1	2.02	0.0300	170	0.950	0.200	22.4	22.9	4.18	7.15	19.3	28.0	27.8	0.85	2.79	nd	nd	nd
	±2.03	±4.68	±2.02	±1.68	±1.68	±0.02	±13.15	±0.62	±0.26	±6.02	±3.64	±0.54	±8.13	±3.27	±2.58	±3.68	±0.85	±1.61			
MP-B2	nd	32.9	17.6	18.9	3.45	0.890	42.1	1.57	nd	20.8	23.4	nd	nd	33.3	31.9	23.2	nd	8.93	nd	nd	nd
		±5.71	±3.45	±1.24	±1.24	±0.55	±10.72	±0.75		±5.14	±1.81			±3.61	±0.42	±0.37		±2.6			
MP-DE2	5.34	5.27	44.6	98.1	4.85	nd	108	6.06	22.4	6.82	49.4	7.93	5.57	39.1	30.6	1.64	25.5	59.6	4.43	4.40	232
	±0.08	±0.68	±3.19	±18.54	±0.55		±7.29	±1.55	±0.52	±3.45	±1.19	±0.37	±0.56	±1.59	±2.60	±0.26	±5.83	±2.38	±0.81	±1.93	±13.63
MP-DI2	150	1.90	339	118	8.44	nd	245	9.16	28.2	4.02	121	5.40	71.3	218	142	0.42	99.3	78.6	0.820	3.05	134
	±3.69	±0.63	±0.98	±2.51	±0.62		±11.97	±1.9	±4.75	±1.34	±6.00	±0.65	±11.16	±8.43	±0.55	±0.00	±10.27	±1.89	±0.02	±0.39	±12.95
MP-DI1	1.14	1.35	43.1	306	7.58	nd	45.5	3.90	3.98	137	5.66	16.2	1.51	41.9	77.0	0.200	26.2	162	0.160	0.580	289
	±0.46	±0.28	±3.19	±16.34	±0.05		±15.27	±0.56	±1.80	±24.89	±1.06	±6.98	±0.18	±2.57	±12.59	±0.06	±4.05	±17.84	±0.23	±0.82	±38.73
MP-DE1	2.62	0.20	65.6	490	8.33	nd	90.3	6.32	43.6	928	62.8	4.65	6.18	76.6	38.7	0.610	202	99.1	nd	nd	202
	±0.88	±0.03	±0.02	±2.01	±0.92		±16.7	±0.59	±15.43	±61.56	±6.90		±3.19	±30.68	±2.87	±0.08	±4.05	±30.71			±32.56
MP-T1	8.45	20.0	53.9	28.1	7.67	nd	159	7.65	1.74	0.41	59.7	3.99	26.8	29.9	65.3	2.62	69.7	37.7	7.28	3.88	332
	±1.56	±2.00	±4.57	±5.58	±2.34		±2.17	±1.87	±1.69	±0.43	±0.06	±0.01	±0.24	±3.55	±7.35	±0.21	±13.72	±2.95	±1.87	±2.62	±28.27
MP-T2	nd	nd	3.42	nd	1.18	nd	nd	nd	nd	nd	70.5	nd	nd	0.710	0.450	0.210	nd	0.590	nd	nd	5.91
			±0.35		±0.96						±21.75			±0.67	±0.39	±0.12		±0.15			±2.77
MP-T3	nd	nd	2.93	nd	0.350	nd	nd	nd	nd	nd	3.72	nd	nd	0.860	0.520	2.63	nd	0.300	nd	nd	3.67
			±2.50		±0.16						±1.92			±0.18	±0.20	±1.47		±0.09			±0.78
MP-S1	14.1	19.3	208	381	6.33	2.17	211	3.57	1.04	2.07	89.2	4.66	3.55	26.2	10.5	0.0500	10.3	7.84	2.16	0.320	84.3
	±1.93	±2.98	±3.63	±18.59	±0.10	±0.25	±22.4	±0.06	±0.07	±0.50	±16.18	±0.17	±2.47	±1.27	±1.26	±0.01	±2.58	±0.26	±1.15	±0.46	±13.71
MP-S2	8.1	9.28	58.3	202	6.62	1.41	101	4.79	2.58	5.55	9.85	0.470	35.2	47.7	22.7	63.1	29.6	8.93	0.230	3.28	616
	±1.64	±1.25	±8.33	±6.17	±1.63	±0.24	±2.64	±1.15	±1.40	±4.82	±3.26	±0.09	±4.95	±7.91	±2.00	±16.72	±3.25	±0.29	±0.33	±1.74	±4.15
MP-S3	7.14	11.7	106	580	5.63	1.03	143	7.84	35.1	nd	195	3.37	28.8	58.0	47.7	1.33	136	42.3	2.25	5.33	740
	±1.19	±5.43	±18.84	±17.03	±1.58	±0.31	±18.23	±2.65	±22.13		±33.12	±0.01	±5.54	±4.49	±18.98	±0.22	±13.26	±9.45	±2.12	±1.96	±36.87
MP-S4	nd	nd	2.57	nd	1.69	nd	nd	0.570	0.380	nd	3.5	nd	nd	1.31	0.200	3.53	nd	0.0900	nd	nd	0.480
			±0.78		±0.26			±0.00	±1.19		±0.72			±0.00	±0.04	±1.43		±0.04			±0.18
MP-S5	nd	nd	2.36	nd	1.48	nd	nd	0.640	0.690	nd	7.52	nd	nd	2.82	0.41	33.4	nd	0.450	nd	nd	4.05
			±0.60		±0.00			±0.00	±0.37		±3.30			±0.00	±0.39	±18.36		±0.39			±1.56
MP-S6	nd	nd	3.34	nd	0.28	nd	nd	0.500	nd	nd	6.87	nd	nd	1.17	0.340	49.9	nd	0.460	nd	nd	13.9
			±2.36		±0.32			±0.00			±0.45			±0.00	±0.05	±24.61		±0.05			±0.57
MP-S7	nd	nd	0.390	nd	0.400	nd	nd	nd	nd	nd	10.6	nd	nd	nd	5.68	8.40	nd	nd	nd	nd	21.4
			±0.03		±0.00						±0.30				±0.00	±1.30					±1.57
MP-S8	nd	nd	nd	nd	1.93	nd	10.8	nd	nd	nd	6.62	nd	nd	1.09	0.750	1.87	nd	0.310	nd	nd	0.590
					±0.00		±3.36				±1.14			±0.00	±0.29	±0.39		±0.29			±0.43
MP-S9	nd	nd	nd	nd	0.420	nd	9.46	1.13	nd	nd	3.05	nd	nd	nd	0.280	0.390	nd	0.650	nd	nd	3.58
					±1.15		±1.73	±0.00			±0.35				±0.46	±0.21		±0.46			±0.42
MP-W1E	0.340	0.280	11.6	21.6	0.460	0.330	55.0	0.380	19.7	442	1.17	0.660	57.3	36.4	0.950	2.84	3.85	1.42	0.180	nd	137
	±0.30	±0.10	±0.42	±1.97	±0.03	±0.06	±24.23	±0.19	±8.86	±156.31	±0.17	±0.33	±15.44	±0.06	±0.20	±0.17	±2.95	±0.19	±0.02		±7.37
MP-W1I	26.9	30.0	562	140	1.30	2.18	572	8.88	9.86	7.85	353	11.9	425	267	439	293	31.4	0.380	0.860	nd	99.4
	±6.65	±3.63	±217.30	±2.40	±0.02	±0.10	±171.97	±1.26	±1.91	±0.12	±27.1	±2.40	±107.62	±22.37	±26.47	±15.349	±7.84	±0.30	±0.07		±20.58

Compounds	PFUdA	PFdoA	PFHxA	PFNA	PFPeA	42FTS	82FTS	PFHpA	FHET	FOET	62FTS	FHEA	PFDS	PFBS	PFHxS	PFOS	PFHpS	PFOA	PFODA	PFHxDA	PFBA
Samples	Mean concentrations (ng/L) and standard deviations (±)																				
MP-W2E	6.60	2.02	45.2	124	5.12	0.290	470	4.08	45.3	24.0	7.41	161	813	509	40.4	7.35	17.0	12.1	2.70	nd	515
	±2.89	±0.55	±0.47	±40.14	±0.6	±0.32	±18.23	±0.64	±16.39	±4.28	±3.70	±12.95	±205.67	±10.83	±24.49	±0.02	±0.47	±4.88	±3.82		±16.92
MP-W2I	13.0	31.6±6.27	108	1498	20.3	29.4	182	6.39	3.49	0.0900	59.2	69.0	173	101	797	3.83	124	59.5	nd	nd	1405
	±0.00		±50.72	±211.09	±7.09	±7.24	±21.2	±0.54	±2.83	±0.13	±24.3	±36.83	±30.61	±53.88	±189.22	±0.54	±32.36	±27.19			±22.05

Figures 8.8 and 8.9 show scatter plots of the concentrations in Table 8.6. While some linearity can be seen in Figure 8.8, a logbase plot in Figure 8.9 shows clearly linear relationship between the PFASs concentrations and their contributions. With respect to PFASs classes contribution (Figure 8.10), it can be seen clearly that all the three classes, Fluorotelomers, PFCAs and PFSAs are well clustered in DWTP, surface water and WWTP and scattered in borehole and drinking water. This trend is repeated with respect to contributions of short and long chain PFASs in Figure 8.11.

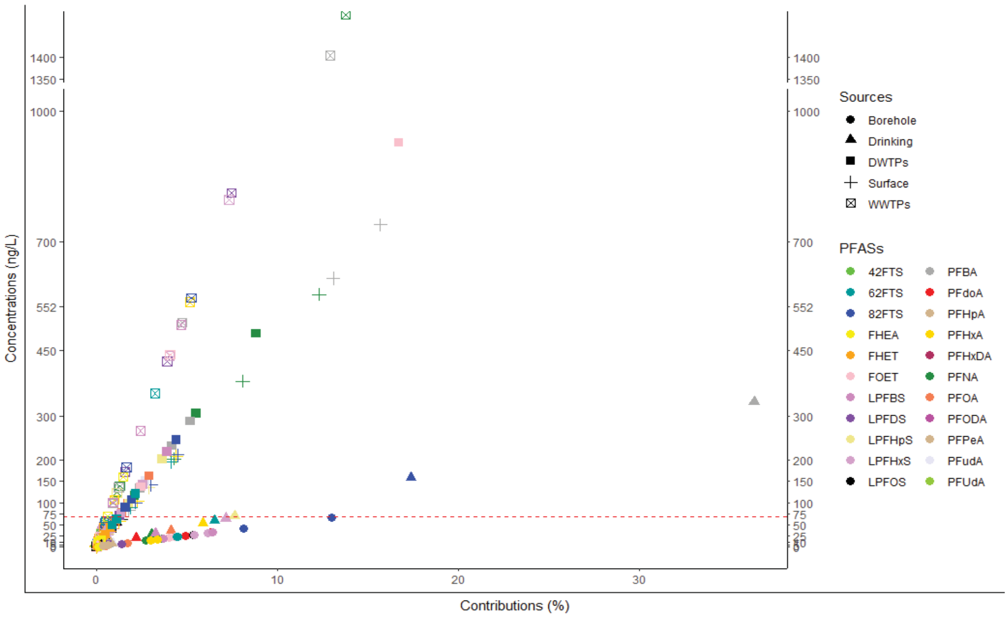

Figure 8.8: PFASs concentrations distributions for various water sources in Mpumalanga in wet season

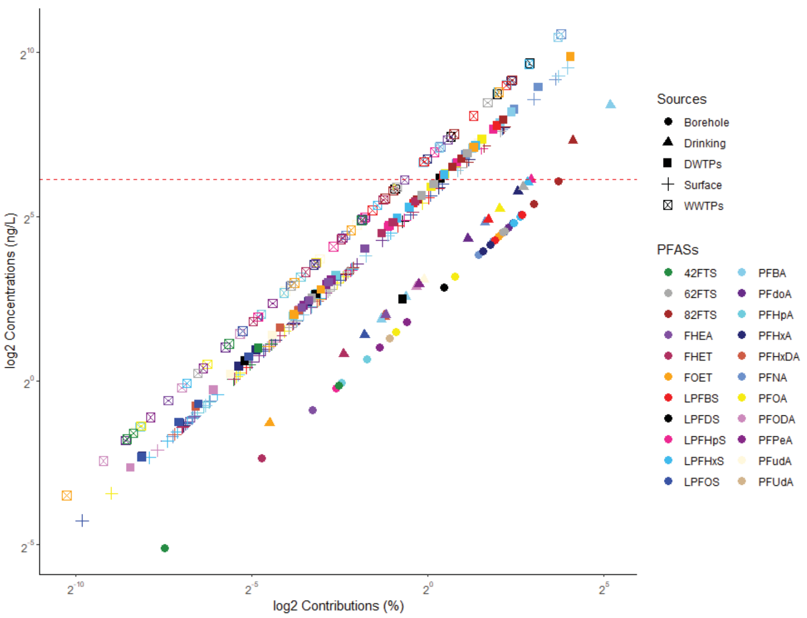

Figure 8.9: PFASs concentration contributions for various water sources in Mpumalanga in wet season

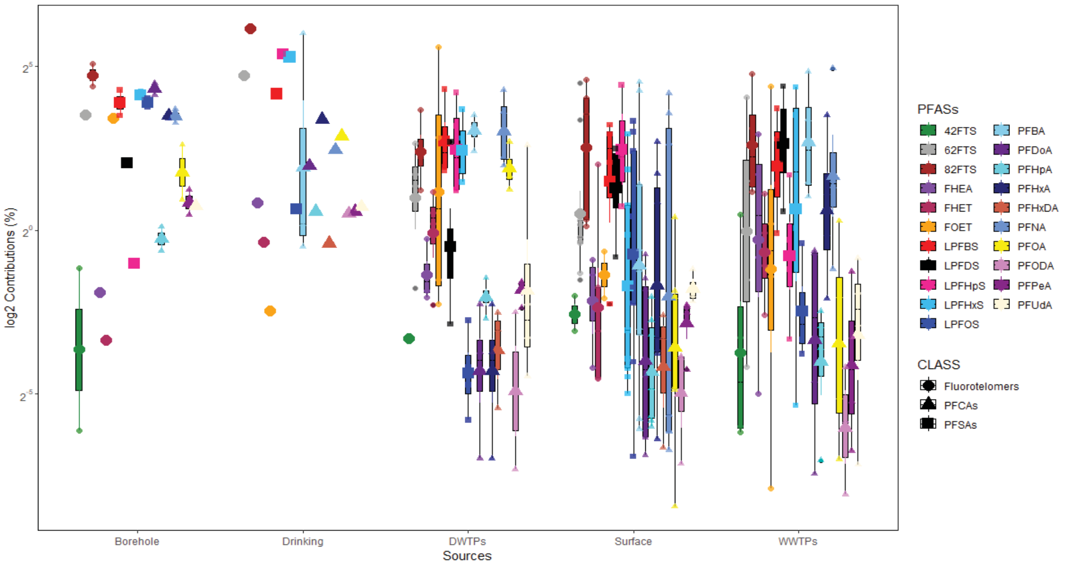

Figure 8.10: PFASs class contributions for various water sources in Mpumalanga in wet season

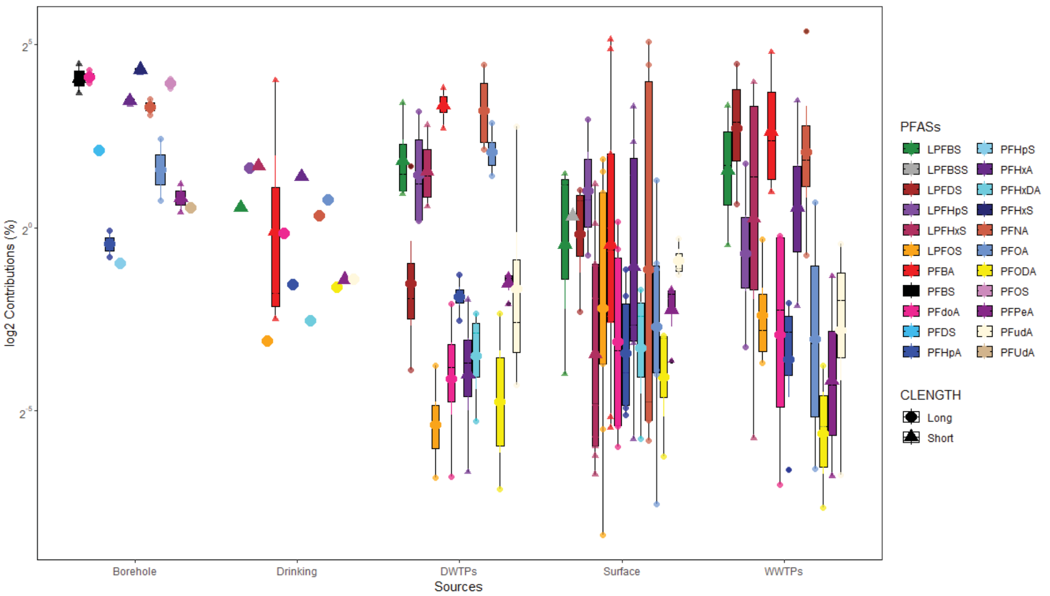

Figure 8.11: Contributions of short- and long-chain PFASs for various water sources in Mpumalanga in wet season

8.4.2 Establishing the possible sources of the PFASs detected in the water

Figure 8.12 shows the PCA plot for PFASs congeners in water samples collected in WWTPs, DWTPs, surface, boreholes and drinking water samples collected during wet season. All the PFASs congeners in the same quadrants are correlated to one another and, therefore, share similar sources. PFOS is in the 4th quadrant on its own suggesting difference sources from the other PFASs congeners. Figure 8.13 shows the PCA plot for samples in various water samples. Clusters can be observed on the plot with borehole samples clustered closely showing a strong correlation which could be as a result of similar behavioural patterns of PFASs or similar sources. The same was observed between MP-T2 and MP-T3. Surface water samples showed a strong and negatively association with each other, except MP-S2. MP-W2E and MP-W2I were clustered while MP-W1E and MP-W1I were responsible for stretching the WWTPs ellipses on to overlap. These samples show a great variation in PFASs sources of pollution or behavioural patterns.

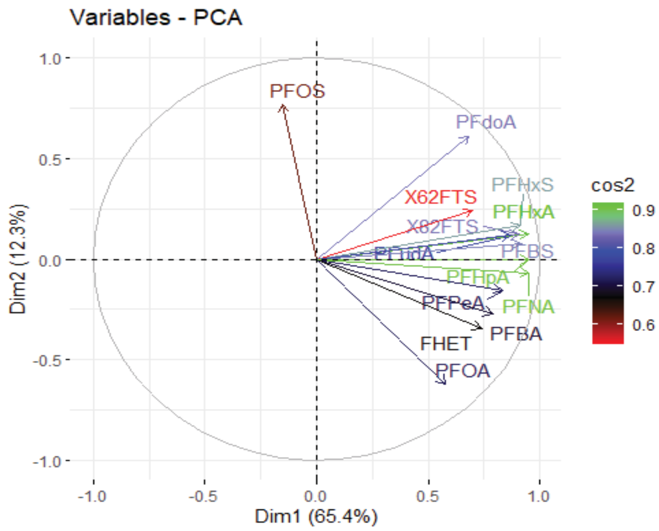

Figure 8.12: PCA of PFASs congener contributions and their relationships in wet season

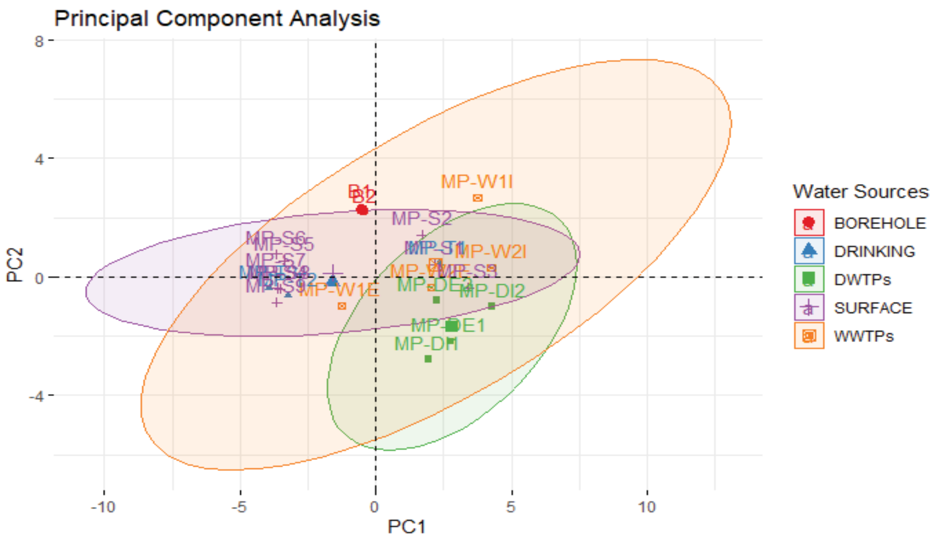

Figure 8.13: PCA of sampling sites and their relationships in wet season

8.4.3 SUMMARY

Generally, PFASs concentrations obtained in dry were higher than in wet season. The observed difference can be explained as follows: wet season comes with heavy rain which, albeit can transport contaminants from one point to another, but can at the same time dilute contaminants. In dry season, contaminants concentrations are expected to concentrate due to lack of rain. Shown in Table 8.7 is a comparison of the PFASs concentrations obtained in the present study with concentrations reported in other countries around the world. The concentration ranges for river water in the present report is lower than that from Germany (Skutlarek et al., 2006) and South Africa (Batayi et al., 2020); but higher than the concentrations reported by

Groffen et al. (2018) and Korea (Sharma et al., 2016). With respect to drinking tap water, the concentration obtained in the present is higher than that from KwaZulu-Natal.

Table 8.7 Comparison of PFASs concentrations obtained in current study with other studies

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.8	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area) 2-61 (Rhine River)	Skutlarek et al., 2006
Shandong Province	13.1-69,23	Chen et al., 2017
Liaoning Province	22.4-26,73	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
KwaZulu-Natal Province South Africa (drinking water/Tap water)	<LOQ-42.05	This study
Gauteng Province South Africa (Dam river)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al.,m 2014,
Vaal River South Africa (River water)	<LOQ -38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
Mpumalanga Province South Africa (river water)	**<LOD-92.4**	**This study**
Mpumalanga Province South Africa (Drinking water)	**0.314-51.5**	**This study**
Limpopo Province South Africa (Borehole)	**<LOD -73.9**	**This study**

CHAPTER 9: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE NORTHERN CAPE PROVINCE

9.1 SAMPLING STRATEGY

9.1.1 Location and description of sampling sites

Water samples were collected from Kimberly and the surrounding area in the Northern Cape province during both wet (October-April) and dry (June-august) seasons. Kimberly is the most populated city in the Northern Cape and, therefore, will have a fair share of pollution problems. Figure 9.1 shows the land use map within the vicinity of sampling sites. The following water systems were targeted in the province:

- Wastewater influent and effluent (WI and WE)
- Borehole drinking water influent and effluent (DI and DE)

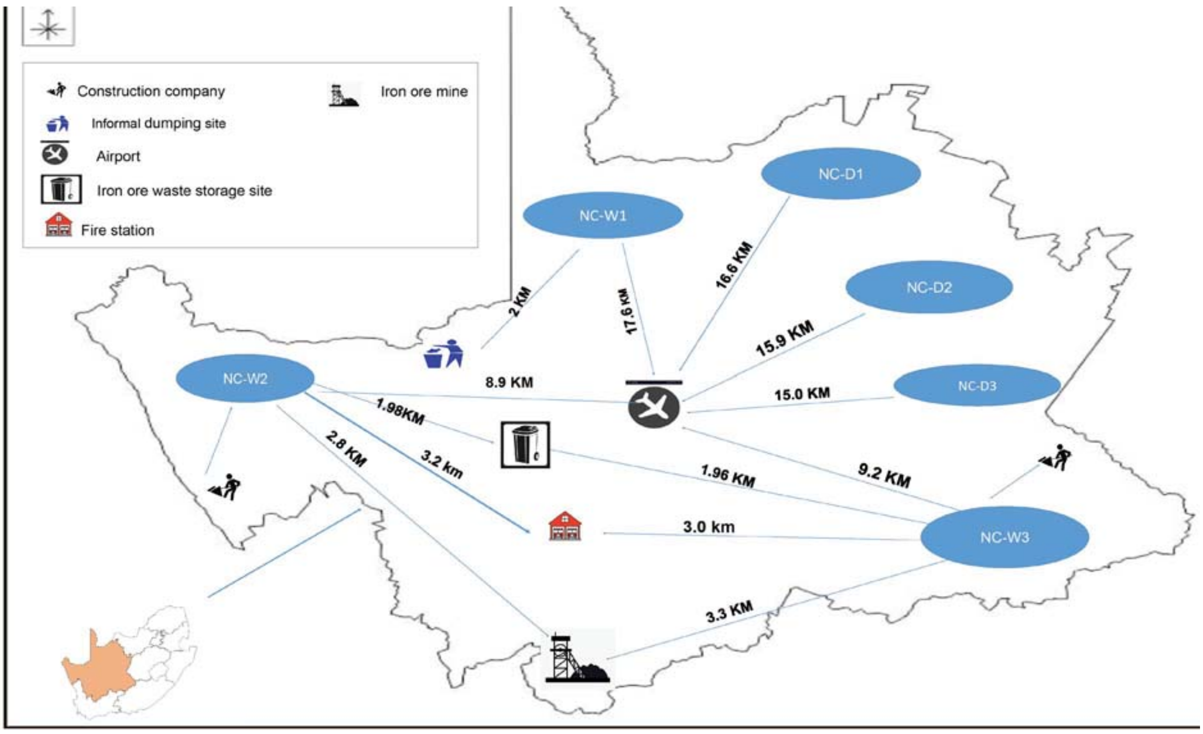

Figure 9.1: Land use map with sampling sites in Northern Cape Province.

9.1.2 Sample collection

Table 9.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 9.1: Sampling sites in Northern Cape with coordinates and dates

Sampling date	Coordinate	Sample ID	Matrice
2021/06/10	Lat:27◦36’02” S Long:22◦51’54” E	NC-WI1	Wastewater influent
2021/06/10	Lat:27◦36’02” S Long:22◦51’54” E	NC-WE1	Wastewater effluent
2021/06/10	Lat:34◦06’11’’N Long:117◦41’37’’W	NC-WI2	Wastewater influent
2021/06/10	Lat:27◦42’46” S Long:23◦00’47” E	NC-WE2	Wastewater effluent
2021/07/10	Lat:27◦42’46” S Long:23◦00’47” E	NC-DI1	Borehole drinking water inlet
2021/07/10	Lat:27◦42’44” S Long:23◦00’52” E	NC-DE1	Borehole drinking water outlet
2021/07/10	Lat:27◦42’38” S Long:23◦00’43” E	NC-DI2	Borehole raw water
2021/07/10	Lat:27◦42’38’’S Long:23◦00’43” E	NCDE2	Borehole purified water
2021/07/10	Lat:27◦35’22” S Long:22◦53’14” E	NC-DE3	Borehole pump station water

9.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. Tables 9.2 and 9.3 show the mean percentage recoveries of blank and surrogate standards for dry and wet season samples, respectively. The recoveries of compounds of interest ranged from 49.9-119.6% for the dry season and was withing a range of 49.9-119.9% for the wet season. Although low percentage recoveries were observed in some samples, high recoveries were recorded generally for the surrogate for most of the samples.

Table 9.2: Percentage recoveries of blank and surrogate standards during the dry season

	% Mean recoveries + SD		
Sample ID	MPFNA	MPFUDA	MPFHxS
NC-WI1	54.4±2.08	84.3±2.87	83.6±30.22
NC-WE1	103.1±8.09	84.02±13.29	102.1±3.22
NC-WI2	69.7±7.87	79.2±15.23	59.9±8.16
NC-WE2	68.5±10.53	67.3±4.06	98.0±3.24
SB	112.2±16.2	73.8±6.6	82.9±19.2
NC-DI1	80.8±0.08	63.1±14.76	62.3±15.93
NC-DE1	49.9±9.79	106.0±15.93	55.5±8.53
NC-DE2	65.7±11.5	42.7±2.60	62.7±14.26
SB	83.2±3.3	90.8±6.8	72.2±16.5
SB	87.4±6.8	82.3±5.6	54.6±4.23
NC-DI2	73.1 ±76	62.7±6.97	50.6±4.23
NC-DE3	51.8±2.45	99.1±5.69	54.9±20.14

Table 9.3: Percentage recoveries of blank and surrogate standards during the wet season.

	Mean concentration + SD		
Sample ID	**MPFNA**	**MPFUDA**	**MPFHxS**
SB	84.1±17.3	108.0 ±20.3	102.2±5.8
NC-WI1	54.4±10.8	56.1±2.8	98.3±2.82
NC-WE2	103.1±8.7	67.5±0.9	119.9±10.3
NC-WI2	60.0±12.3	87.2±7.2	89.9±21.2
NC-WE2	69.7±10.8	87.3±9.5	110.9±15.2
SB	122.6±3.2	80.5±2.3	75.5±10.2
NC-DI1	68.5±20.5	100.2±14.2	136.4±28.6
NC-DE1	80.8±12.4	69.1±2.32	101.2±23.9
NC-DE2	49.9±7.2	73.1±11.5	97.1±4.23
SB	65.7±0.18	61.8±20.5	96.2±13.4
NC-DI2	73.1±0.22	52.3±17.2	95.1±15.45
NC-DE3	112.7±4.6	89.2±3.2	92.2±9.6

9.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

9.3.1 Distribution of PFASs in various water sources during the dry season

The concentrations of PFASs in various water samples are presented in Table 9.4. The following PFASs congeners were detected in all the water samples analysed: PFHxA, L-PFBS, L-PFHxS, PFOA, PFHxDA, PFNA, L-PFHpS, L-PFOS, 6:2 FTS, FHEA, FOET and FHET. PFBA and PFHxS exhibited high concentrations of 740 ng/L and 675 ng/L at NC-DE3 and NC-DE2 respectively. These high concentrations observed in drinking water are matched by 659 ng/L and 662.5 ng/L shown by L-PFOS and FHEA respectively in wastewater influent. The high concentration observed for PFBA may have been influenced by the degradation of telomers, although this cannot be said for PFOA which showed 262 ng/L in wastewater influent. Previous studies have reported that biodegradation of fluorotelomers (FTOHs) to perfluoro carboxylic acids (PFCAs) during the treatment process (Just et al., 2022; Chen et al., 2017; Chen et al., 2020). Therefore, the observed maximum concentration of PFBA in NC-DE3 and NC-DE2 drinking water effluent may have originated from the degradation of fluorotelomers. It is noticeable that the concentrations exhibited by PFBA and FHEA were fairly high across all water samples. The same can be said for PFOS. L-PFDS was not detected in any of the samples. Generally, more than 50% of PFASs targeted were detected in all the samples.

Table 9.4: Mean concentrations of PFASs in various water sources in dry season

	Mean concentrations (ng/L) + SD								
	Sample ID								
Analyte	NC-WI1	NC-WE1	NC-WI2	NC-WE2	NC-DI1	NC-DE1	NC-DI2	NC-DE2	NC-DE3
PFBA	134±5.6	111±16.3	111.3±16.3	95.4±1.3	69.7±0.58	ND	223±34.0	599±112	740±74
PFHxA	20.8±6.7	77.1±19	77.12±18.5	47.0±4.6	50.5±15	4.09±1.9	5.70±0.40	11.4±1.9	3.25±1.2
PFPeA	31.8±6.5	1.51±1.6	1.509±1.6	36.3±10.6	3.05±0.53	<LOQ	1.45±0.50	6.37±2.3	9.19±1.6
L-PFBS	100±2.8	35.0±1.5	35.03±1.5	100.1±10.4	59.2±5.2	5.63±0.59	6.98±4.2	90.1±39.0	25.7±1.9
L-PFHxS	1.20±0.086	0.456±0.20	0.4564±0.20	0.212±0.012	14.6±0.16	98.9±16	0.0807±0.010	675±35.1	0.338±0.0010
4:2 FTS	2.85±1.6	2.26±1.40	2.259±1.4	154±4.2	<LOD	ND	<LOD	2.021±2.7	<LOD
PFOA	262±18.8	178±42	177.5±41.8	239±59	10.2±0.40	0.241±0.038	25.7±1.9	7.19±2.5	9.34±0.53
PFDOA	<LOQ	4.04±2.5	4.041±2.5	87.8±31	19.1±5.2	<LOQ	<LOD	5.77±4.2	11.4±1.5
PFHpA	4.748±0.50	5.02±2.2	5.016±2.16	2.41±0.33	1.37±0.41	<LOQ	<LOQ	8.63±2.2	11.2±7.3
PFHxDA	40.87±1.23	45.1±0.180	45.10±0.180	21.7±5.8	18.1±2.6	15.6±1.00	15.7±3.1	26.0±5.2	16.6±3.2
PFNA	4.501±0.81	37.6±13	37.63±12.65	8.46±0.19	14.00±0.29	1.95±0.34	3.58±0.15	10.5±1.9	18.6±0.57
PFODA	78.37±10.45	<LOQ	<LOQ	<LOQ	<LOD	ND	<LOQ	1.03±0.0050	6.73±0.87
FUDA	0.660±0.16	<LOD	<LOD	3.46±0.60	0.628±0.22	0.517±0.22	<LOD	0.582±0.15	0.624±0.27
L-PFDS-	<LOD	<LOQ	<LOQ	<LOD	ND	<LOD	ND	<LOD	<LOD
L-PFHpS	20.8±14	8.48±4.7	8.480±4.74	1.50±0.39	<LOD	9.98±5.6	13.7±1.4	2.07±1.4	10.6±0.28
L-PFOS	659±58	156±68	155.9±68.04	384±4.7	567±170	47.4±0.54	28.4±13.7	97.7±7.8	103±5.7
6:2 FTS	79.8±32	79.2±23	79.15±23.12	219±8.3	13.1±0.79	75.8±11.6	23.1±0.050	292±85.4	212±37.5
8:2 FTS	24.6±14	5.15±0.680	5.149±0.68	19.0±4.6	<LOQ	<LOQ	3.36±0.68	12.9±0.81	12.2±0.61
FHEA	509±90	66.3±20	662.5±19.58	156±11.2	48.2±3.9	302±48	246±13.0	624±45.6	202±12
FOET	62.3±4.6	14.8±11	14.79±10.56	91.1±13.1	72.1±28	6.48±0.30	2.37±1.7	11.2±3.0	9.72±1.9
FHET	3.76±1.0	0.995±0.26	0.9945±0.26	2.95±0.15	0.394±0.020	0.0940±0.0067	0.0372±0.0070	0.252±0.0066	0.236±0.024

NC-WI-Northern Cape wastewater influent; NC-WE- Northern Cape wastewater effluent; NC-DI1- Northern Cape drinking water influent; NC-DE 2- Northern Cape drinking water outlet

A scatter plot was constructed to establish any relationship between PFASs congeners contribution in different water sources and their concentrations (Figure 9.2). The points on the plot are diverged but in linear form. In order to elaborate on the observed linear relationship, a log base was plotted as shown in Figure 9.3. There is clearly a positive relationship between the percentage contribution of PFASs in different water sources and their concentrations. The study also found high concentrations of PFOA, PFDOA, FHEA, and L-PFHPs in both the DW and WWTP sources, with log concentrations exceeding 2^6. The same trend was observed for PFHpA, PFBS, FHET, and PFBA, with log concentrations higher than 2^1.

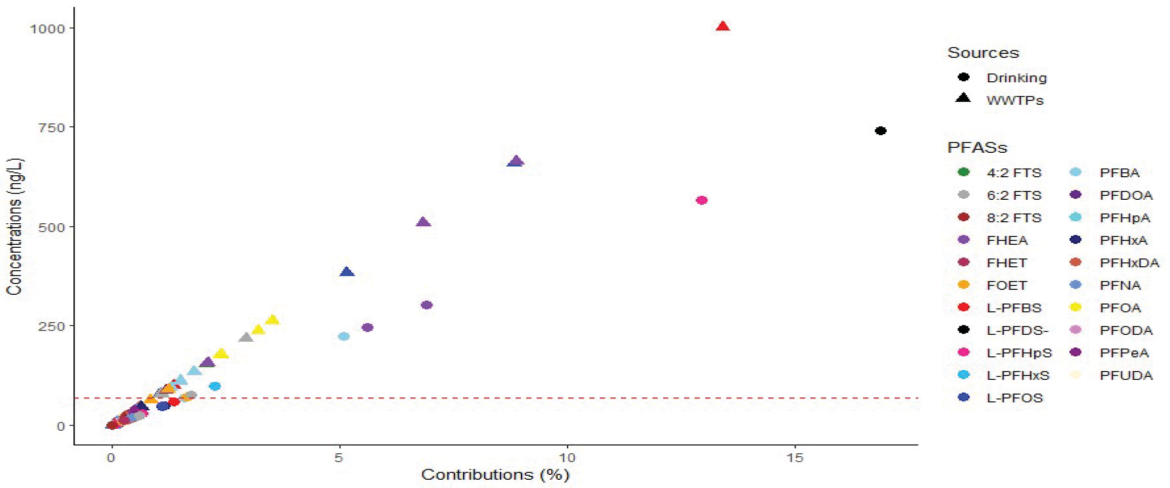

Figure 9.2: PFASs concentrations distributions for various water sources in Northern Cape during the dry season.

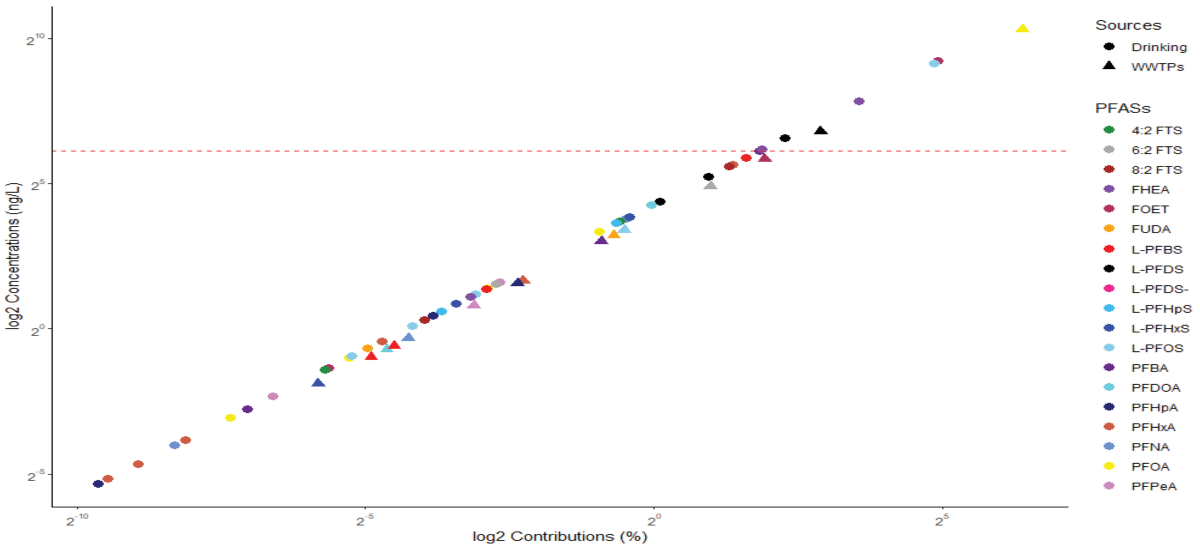

Figure 9.3: PFASs concentration contributions for various water sources in Northern Cape during the dry season.

Figure 9.4 presents the PFASs classes contribution in various water sources. The telomers class exhibited the highest contribution, followed by PFSA. Figure 9.5 presents the contributions of short and long chain PFASs in different water sources. The findings revealed that long chain PFASs were more prevalent in drinking water treatment. In contrast, short chain PFASs were found in higher proportions in wastewater treatment plants, likely due to their lower affinity to bind to solid particles and their greater mobility in water.

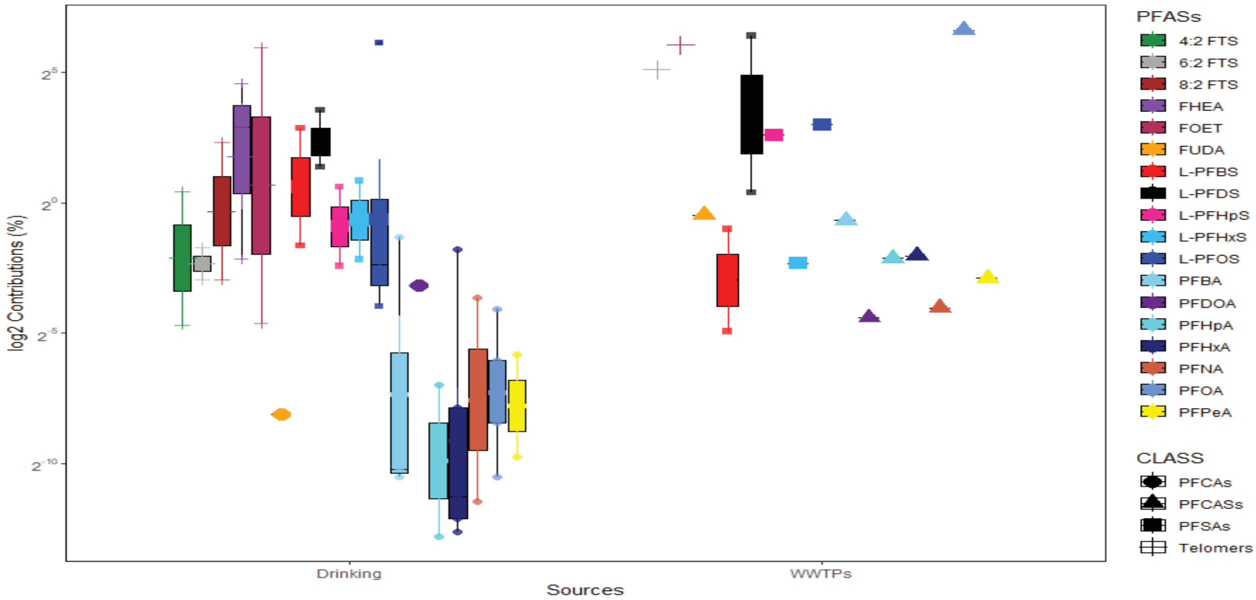

Figure 9.4: PFASs class contributions for various water sources in Northern Cape during the in dry season

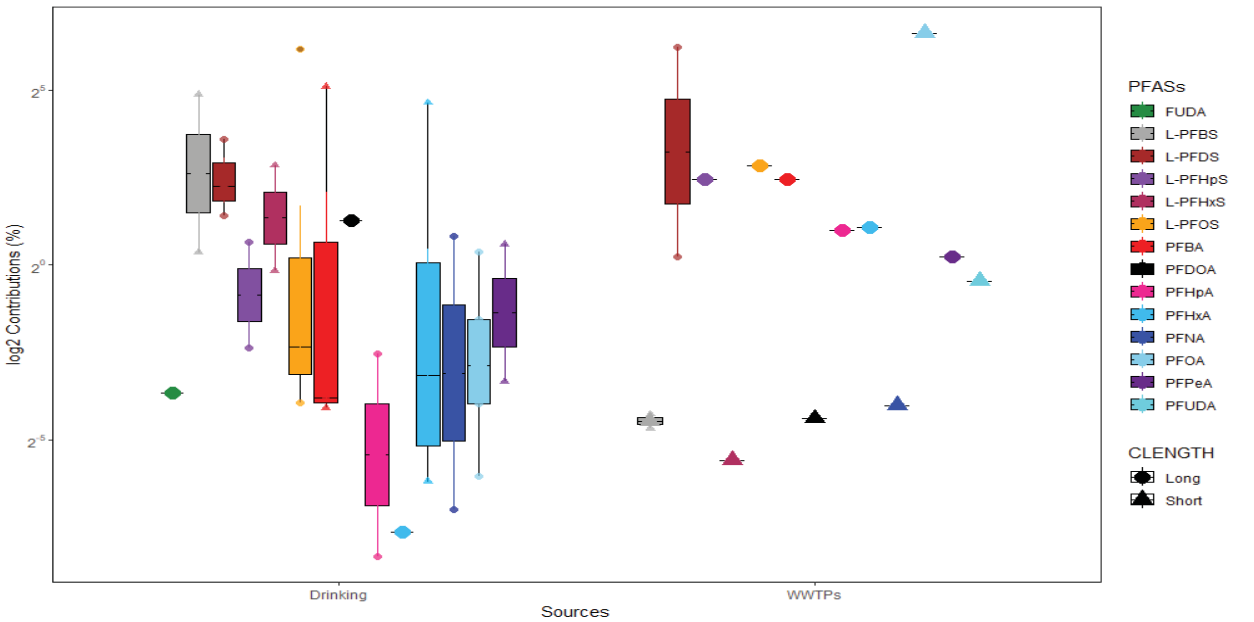

Figure 9.5: Contributions of short- and long-chain PFASs for various water sources in Northern Cape during the dry season.

9.3.2 Establishing the possible sources of the PFASs detected in the water

Shown in Figure 9.6 is the principal component analysis of contributions and their relationship in dry season. FHEA, PFHXDA, PFODA, PFHPA, PFBA, 8:2 FTS, PFOA, 6:2 FTS, PFNA, FHET AND PFPeA are all clustered in the first quadrant, suggesting positive correlation and hence similar source. About 60% of the PFASs compounds in the first quadrant were detected in all the samples. A possible similar source of contamination was also indicated by the grouping of NC-DW2 and NC-DW1; NC-W2 and NC-WW1 (Figure 9.7). This indicated shared source of contamination. NC-DW5, NC-DW4, NC-DW3 and NC-WW4 are staggard and this pattern suggests different sources of contamination. Each of these locations is close to an airport, a mine, a landfill and a firefighting station, all of which have been connected with the use of PFASs in their operations.

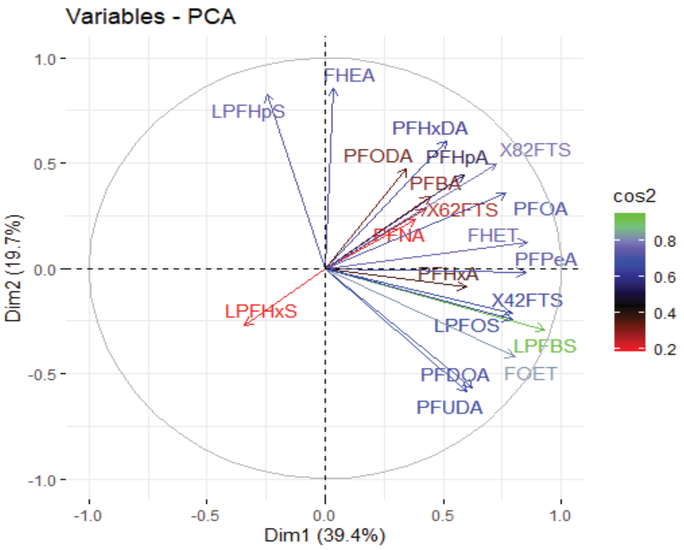

Figure 9.6: PCA of PFASs congener contributions and their relationships during the dry season.

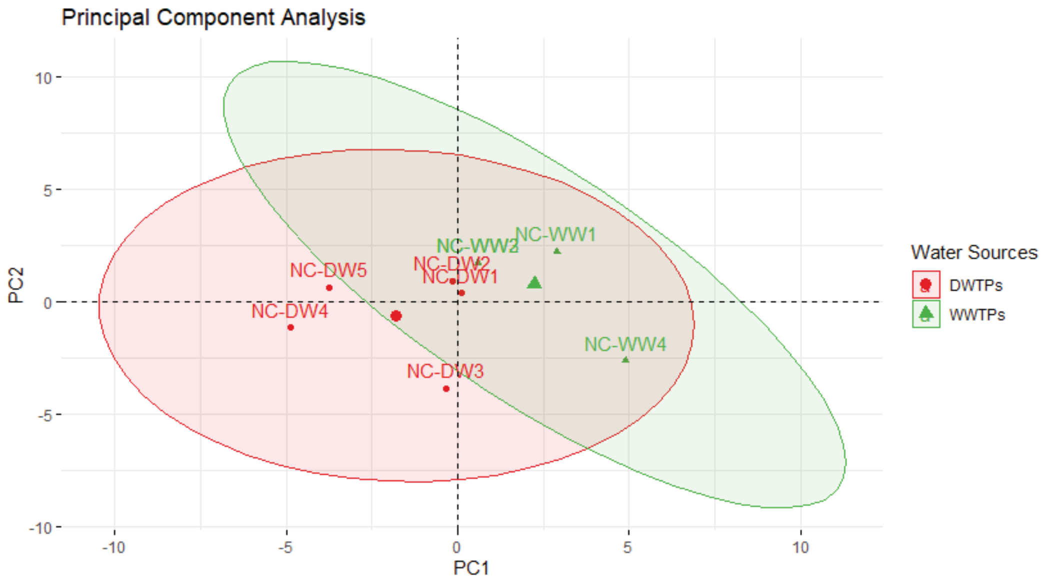

Figure 9.7: PCA of sampling sites and their relationships during the dry season.

9.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

9.4.1 Distribution of PFASs in various water sources during the wet season

Table 9.5 shows the mean concentrations of PFASs in water samples in wet season. During the wet season, PFASs were detected in both wastewater influent and effluent, with concentrations ranging from <LOD-342.0

ng/L and <LOD-1268 ng/L, respectively. The higher concentration range in the effluent suggests either poor removal from the wastewater treatment plants or transformation of PFASs precursors into more persistent forms during treatment (Petrović, Gonzalez and Barceló, 2003). Of the 21 targeted PFASs, PFOA was found to be the most prevalent compound, with a maximum concentration of 1268 ng/L observed in the effluent at sampling point NC-WE2. Similarly, PFASs in drinking water treatment plants exhibited concentrations ranging from <LOD-567 ng/L in the untreated (influent) water and <LOD-595 ng/L in the treated water (effluent), with PFOS exhibiting the highest concentration in NC-DI1. The increase in concentration from input to outflow could again be attributed to poor removal of PFASs during the treatment process or transformation of telomers into long and short chain PFASs (Tabtong, Boontanon and Boontanon, 2015). FOET was found to be the most prevalent PFAS at sampling point NC-WE1 during the high-water period, with a concentration of 690 ng/L. The presence of PFASs in DWTPs may be attributed to the wastewater treatment plant located 1.8 km away from the drinking water treatment (Tabtong et al., 2015; Kissas, 2001; Julianne et al., 2020).

The data in Table 9.5 was used to construct scatter plots of PFASs concentrations and contributions. As can be seen in Figure 9.8, most PFASs congeners congested below 70 ng/L. A sign of linearity can be seen, although not well developed. An improvement of Figure 9.8 led to the logbase scatter plot in Figure 9.9, which shows very clear linear pattern. This suggested the existence of positive correlation between PFASs contributions and their concentrations from WWTP and DWTP. Furthermore, PFDS, PFHps, PFOA, and FHEA had higher prevalence; whereas 8:2 FTS, PFPeA, and PFHxS were found to have the lowest concentration. These observations are very much in line with the data in Table 9.5.

Table 9.5: Mean concentrations of PFASs in water samples during the wet season.

				Mean concentration (ng/L) + SD					
Analyte	**NC-WI1**	**NC-WE1**	**NC-WI2**	**NC-WE2**	**NC-DI1**	**NC-DE1**	**NC-DI2**	**NC-DE2**	**NC-DE3**
PFBA	<LOD	**0.0845**±0.0064	**0.144**±0.026	**8.05**±1.8	**69.7**±0.58	<LOQ	<LOQ	0.147±0.012	**0.120**±0.016
PFHxA	<LOD	**0.116**±0.081	**0.461**±0.092	**3.15**±0.39	**50.46**±15.4	**0.0405**±0.0090	**0.0708**±0.0064	**0.0278**±0.0073	**0.747**±0.16
PFPeA	<LOQ	<LOQ	**1.63**±0.0026	**1.74**±0.27	**3.05**±0.53	<LOD	<LOD	<LOD	**0.202**±0.022
L-PFBS	**0.506**±0.24	**0.633**±0.34	**0.828**±0.22	**0.667**±0.11	**59.2**±5.2	<LOD	<LOD	2.60±0.87	<LOD
L-PFHxS	**0.268**±0.050	**0.661**±0.027	**25.4**±2.5	ND	**14.6**±0.16	<LOD	**1.82**±0.22	<LOQ	ND
4:2 FTS	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOQ	<LOQ	<LOQ
PFOA	**0.612**±0.075	**0.517**±0.0018	**342**±2.5	**1268±**43	**10.2**±0.4	**0.120**±0.064	**1.08**±0.26	**2.66**±0.093	**0.504±**0.070
PFDOA	<LOD	<LOD	<LOQ	<LOQ	**19.1**±5.2	<LOD	<LOD	<LOD	<LOD
PFHpA	<LOD	**0.0785**±0.070	**2.01**±0.0032	**2.95**±0.79	**1.37**±0.41	0.0247±0.0061	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	**18.1**±2.6	<LOD	<LOD	<LOD	ND
PFNA	<LOD	<LOD	<LOD	**0.793**±0.058	**13.9**±0.29	0.0619±0.012	<LOD	<LOD	<LOD
PFODA	**9.35**±3.8	**16.3**±0.54	ND	ND	<LOD	<LOD	<LOD	<LOD	<LOD
FUDA	<LOD	<LOD	ND	<LOD	**0.628**±0.22	<LOD	<LOD	<LOD	<LOD
L-PFDS-	**112**±21	**73.8**±11	**0.875**±0.015	**1.76**±0.089	ND	ND	**95.0**±4.0	21.0±3.9	**37.7**±.5.9
L-PFHpS	8.06±0.57	<LOD	<LOD	<LOD	<LOD	<LOD	**12.4**±2.9	<LOQ	**1.52**±0.54
L-PFOS	<LOD	<LOD	**4.55**±0.25	**10.6**±1.5	**567**±170	ND	**1.08**±0.26	**2.28**±0.21	**0.520**±0.081
6:2 FTS	<LOQ	<LOQ	**2.85**±0.36	**30.3**±3.3	**13.0**±0.79	**0.377**±0.10	<LOD	1.25±0.011	<LOQ
8:2 FTS	<LOQ	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD
FHEA	<LOQ	<LOQ	<LOD	ND	**48.2**±3.9	**1.24**±0.08	**2.93**±0.52	<LOQ	**2.15**±0.23
FOET	<LOD	**690**±55	<LOD	**57.5**±6.6	**72.05**±27.9	**231**±65	<LOD	**197**±3.4	**596±39.3**
FHET	<LOD	<LOD	<LOD	<LOD	**0.394**±0.02	<LOD	<LOD	<LOD	<LOD

*NC-WI = Northern Cape wastewater influent; NC-WE = Northern Cape wastewater effluent; NC-DI1 = Northern Cape drinking water influent; NC-DE 2 = Northern Cape drinking water effluent

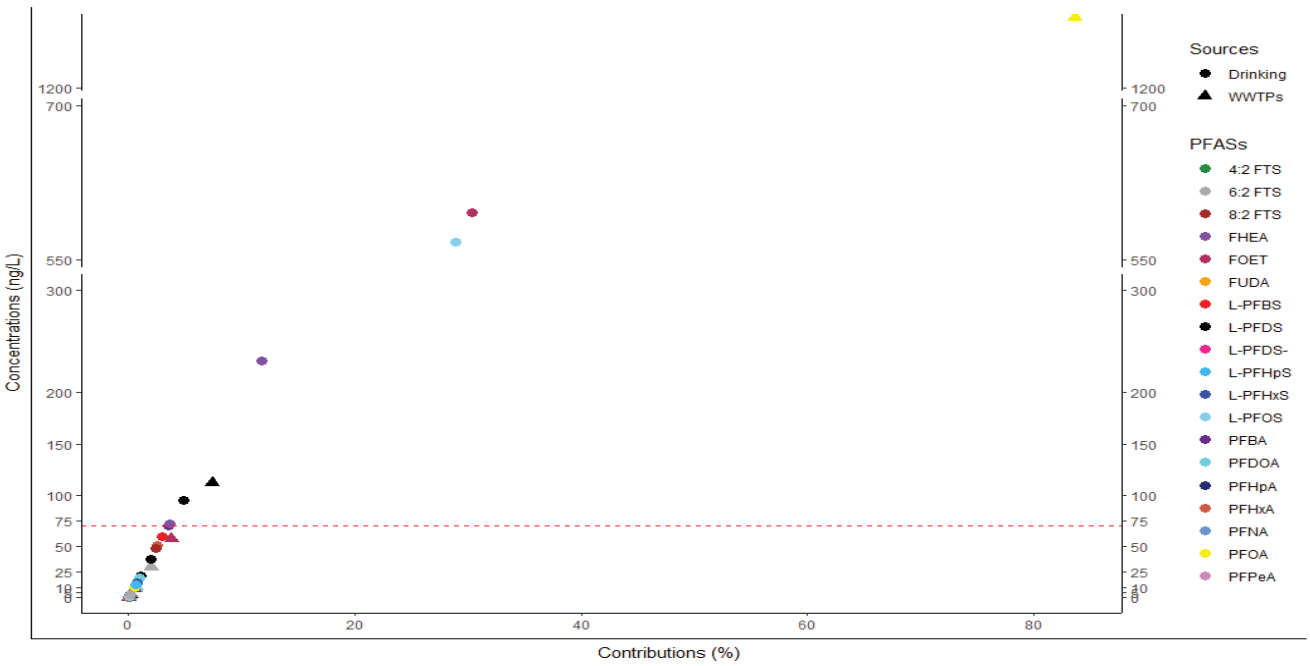

Figure 9.8: PFASs concentrations distributions for various water sources in Northern Cape during the wet season.

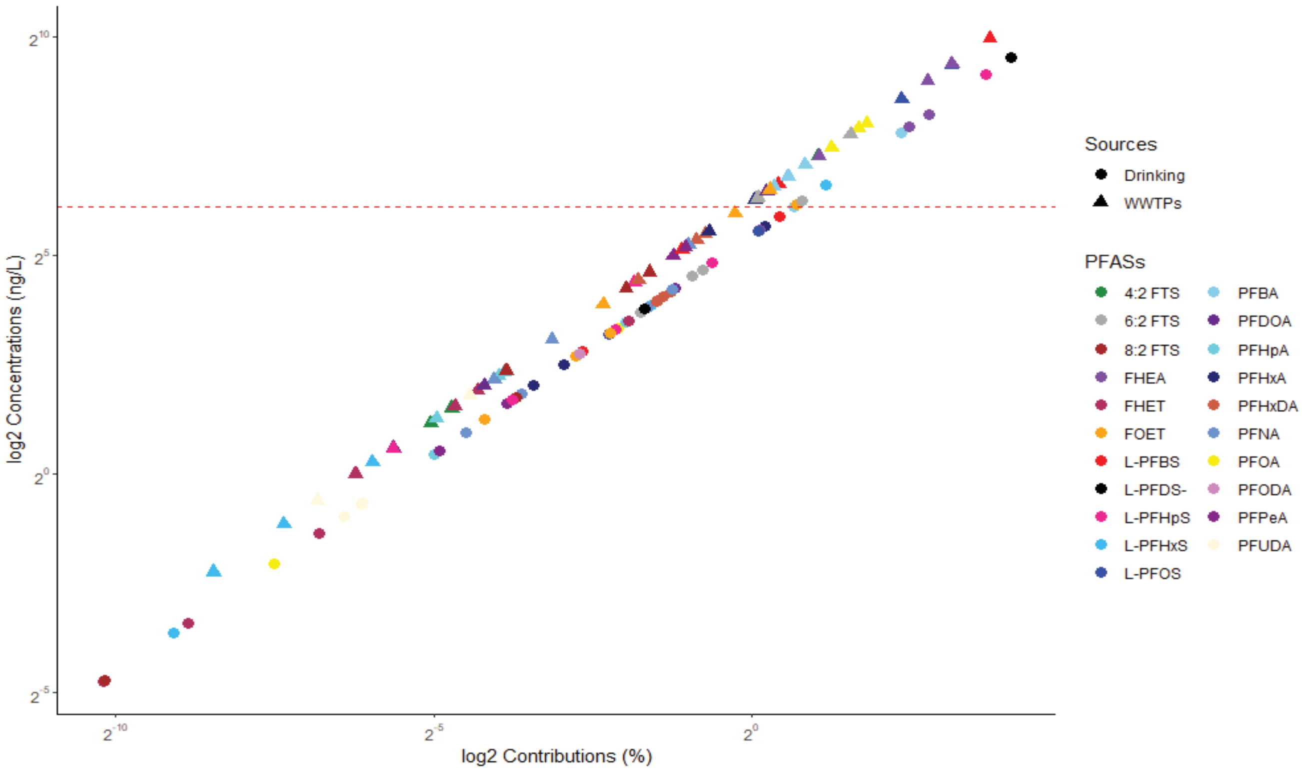

Figure 9.9: PFASs concentrations distributions in various water sources in Northern Cape during the wet season.

Figure 9.10 shows the class contribution of PFASs during the wet season, with a focus on the concentration of specific compounds in both DWTPs and WWTPs. The data revealed that PFSA was the most dominant class in both DWTPs and WWTPs, while PFCAs had a lower contribution. Furthermore, in WWTPs, telomers were more prevalent than PFCA. The contributions of long and short chain PFASs was investigated and these are shown in Figure 9.11. The results showed that long chains were more prevalent than short chains in both DWTPs and WWTPs. This may be due to the fact that long chain PFASs are more stable and resistant to degradation, making them more likely to persist in the environment. Similarly, short chain PFASs have a greater mobility in water and a lower affinity to bind to solid particles, resulting in a higher proportion in WWTPs.

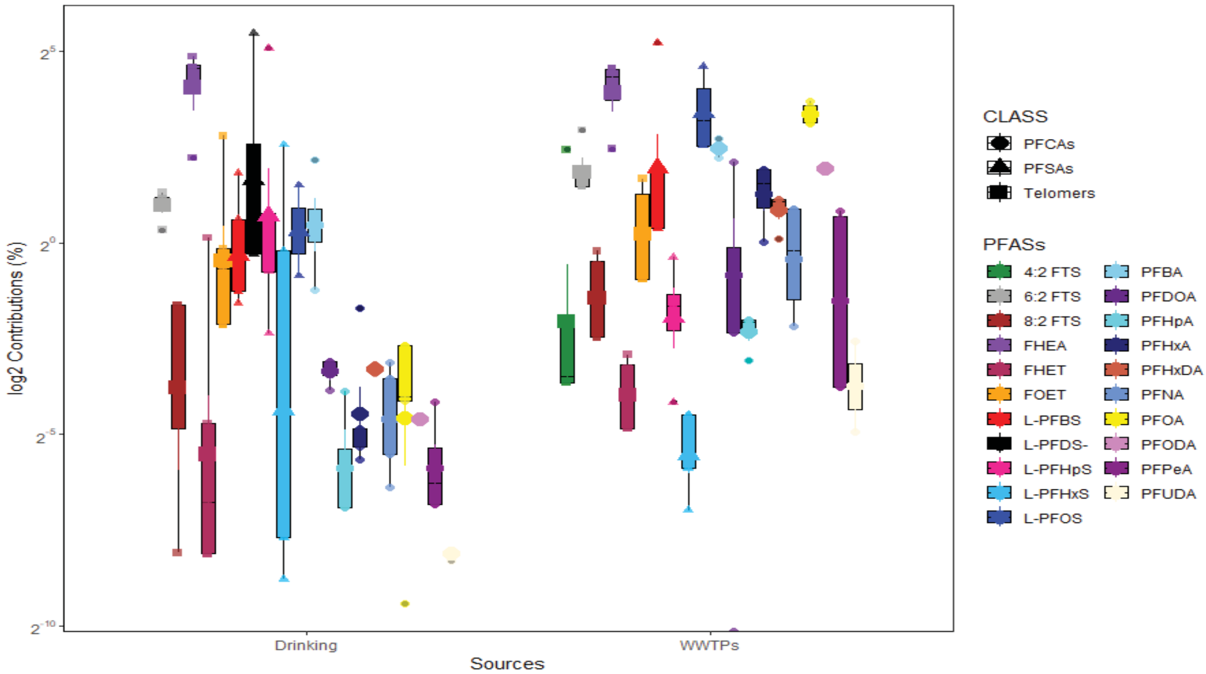

Figure 9.10: PFASs class contributions in various water sources in Northern Cape during the wet season.

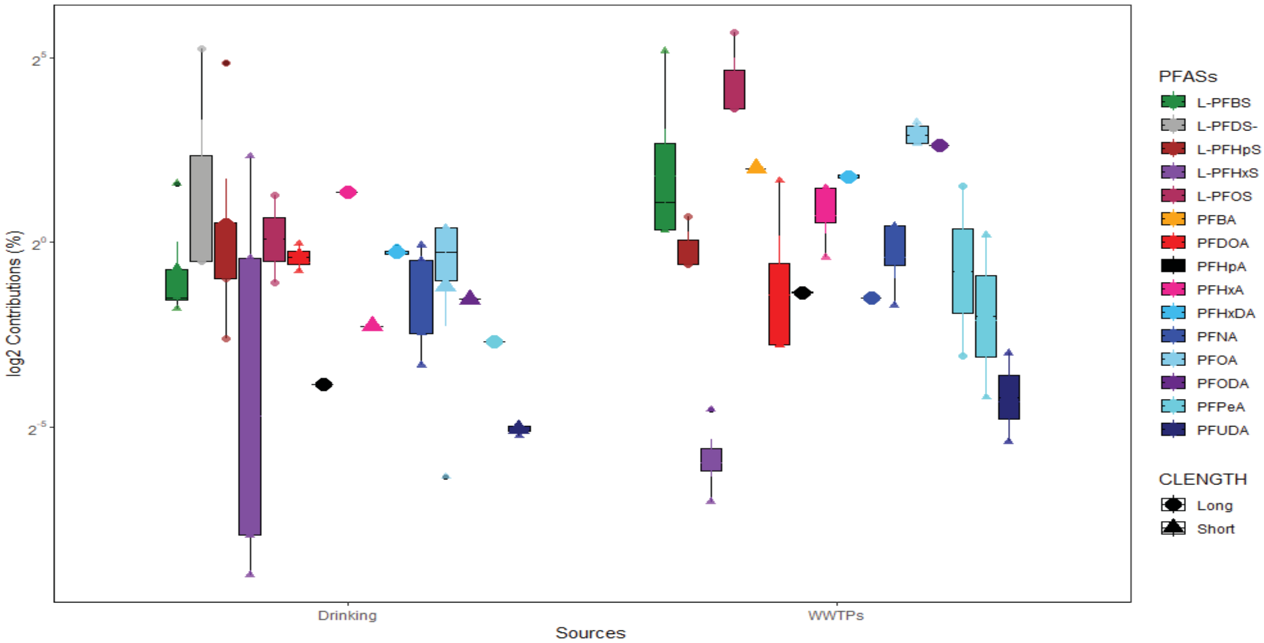

Figure 9.11: Contributions of short- and long-chain PFASs for various water sources in Northern Cape during the wet season.

9.4.2 Establishing the possible sources of the PFASs detected in the water

To establish any relationship between the various PFAS compounds detected in water samples and their respective sampling sites, principal component analysis (PCA) was employed. The analysis revealed that L-PFBS, PFHxA, PFBA, and L-PFOS in the first quadrant (clockwise) had a shared occurrence source (Figure 9.12). These compounds were found to cluster heavily with short-chained compounds, which may suggest a preference for shorter-chained compounds over longer ones. Another group comprising 6:2 FTS, PFHpA, PFOA, PFPeA, and PFHxS also showed a similar origin. The dominance of PFCA in this group is attributed to its frequent use in carpentry, surfactants, and firefighting foams. Principal Component Analysis (PCA) was conducted on the water samples collected from different sites to identify the relationship between the PFAS compounds and the sampling sites. The findings are presented in Figure 9.13. The clustering of NC-WW4 and NC-WW3 suggested that they had a comparable source of contamination, possibly from the same industrial activity. Similarly, the grouping of NC-DW1, NC-DW2, NC-WW1, and NC-WW2 indicated a possible shared source of contamination. The close proximity of these sites to an airport, a mine, a landfill, and a firefighting station, all of which are known to use PFASs in their operations, could explain the contamination.

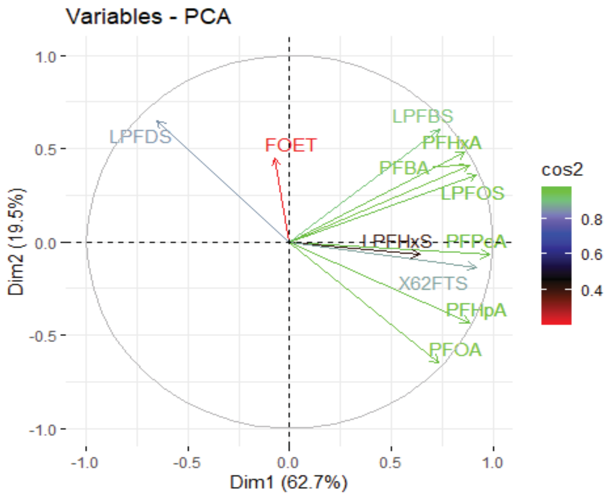

Figure 9.12: PCA of PFASs congener contributions and their relationships during the wet season.

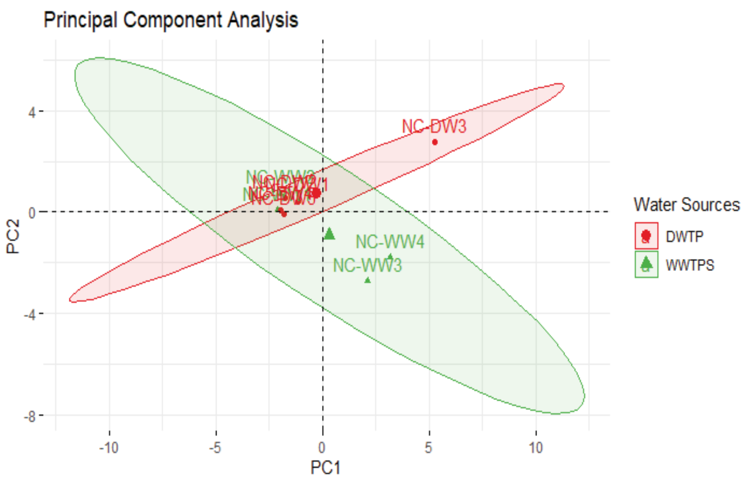

Figure 9.13: PCA of sampling sites and their relationships during the wet season.

9.5 SUMMARY

In general, higher concentrations were recorded during dry season compared to wet season, which could be related to the fact that pollutant concentrations often increase during low water periods, because of lack of precipitation, causing the concentration to increase dramatically (An et al. 2021). However, the highest concentration was recorded in wet and this was exhibited by PFOA (1268 ng/L) at sampling point NC-WW4 (effluent). Biodegradation of Fluorotelomers (FTOHs) to perfluoro carboxylic acids (PFCAs) during the treatment process has been proposed as a potential contributor to the increase of PFCAs in WWTPs (Just et al. 2022; Chen et al., 2017; Chen et al., 2020). Therefore, the observed concentration of FHEA in NC-WW3 wastewater influent, may have originated from degradation to form a higher concentration of PFOA (1268 ng/L) in wastewater effluent at sampling point NC-WW4. Over the course of the two seasons, the most abundant concentrations of PFASs were, PFBA, PFHxS, FHEA, PFOS and FOET. A very distinct seasonal pattern was noticed, demonstrating that the average concentration of PFASs in the winter (dry season) was higher than that for the summer (wet season). As previously mentioned, the low concentrations during the wet season could be as a result of precipitation diluting PFASs.

Table 9.6 shows the range of PFASs obtained in the present study and compares it to the reports from other parts of the world. As can be seen in Table 9.6, the range in the present study are higher in previous reports from South Africa and some parts of the US.

Table 9.6: Comparison of PFASs concentrations obtained in current study with other studies.

Study location	Matrix	ΣPFASs ng/L	Reference
South Africa	Influent	13.49-73.5	Adeleye, 2016
	Effluent	6.16-35.28	
	Influent	62.6-129.3	Kibambe et al., 2020
	Effluent	35.8-224.2	Kibambe et al., 2020
United States	Influent	3730	Masoner et al.,2020
	Effluent	6950	
Washington	Effluent	62.3-418	Furl et al., 2011
New Hampshire	Influent	31-132	Tavasoli et al., 2021
	Effluent	30-198	
This study	**Influent**	**0.456-662.5**	
This study	**Effluent**	**0.0785-1268**	
This study (DWTP)	**Inlet**	**0.252-675**	
This study (DWTP)	**Outlet**	**0.025-739**	
This study (DWTP)	**Inlet**	**0.393-567**	
This study (DWTP)	**Outlet**	**0.0939-302**	

CHAPTER 10: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE NORTH WEST PROVINCE

10.1 SAMPLING STRATEGY

10.1.1 Location and description of sampling sites

Water samples were collected from Rustenburg and surrounding areas in the North West province during both the wet (October-April) and dry (June-August) seasons. Rustenburg and its environ is inundated with mining activities and the mines have the potential to generate chemical pollutants such as PFAS during the various stages of mining. The following water systems were targeted in the province:

- Borehole (B);
- Wastewater (NW-WI influent and NW-WE effluent);
- Drinking water treatment (NW-DWI influent and NW-DWE effluent);
- Wastewater BNR (NW-W2A);
- Wastewater SST-WWTP (NW-W2S)
- Wastewater Influent (NW-W1I)
- Wastewater (BNR (modified UCT-NW-W1U) and
- Waster (UCT-WWTP1 NW-W1A)

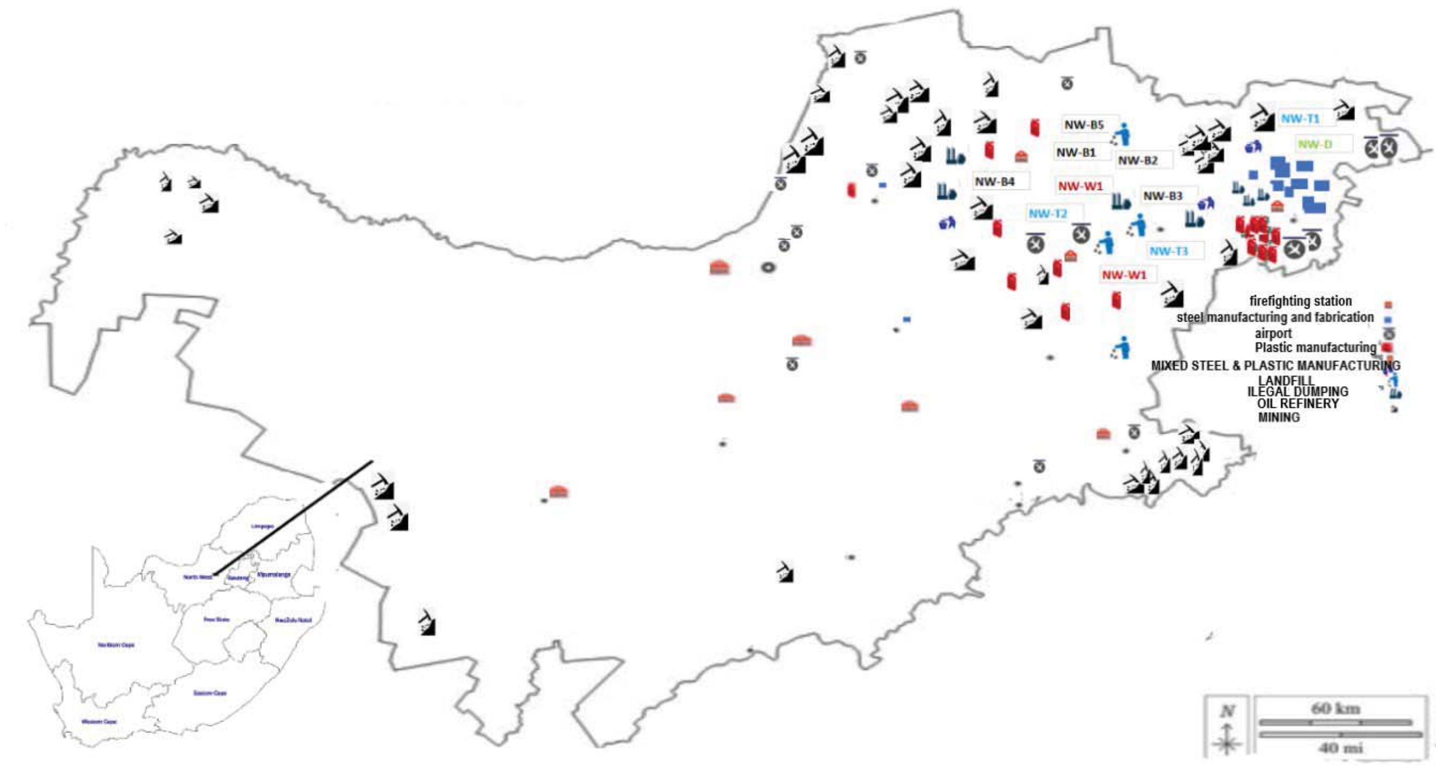

Figure 10.1: Land use map and sampling sites in North West Province.

10.1.2 Sample collection

Table 10.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection. Grab samples were collected and prepared for analysis as described in Chapter 2.

Table 10.1: Sampling sites in North West province with coordinates and dates

Sample ID	Sample Name	Date	Coordinates
FB	Field Blank	November2022(Wet season)	
NW-W2E	Final- WWTP2		
NW-W1E	Final- WWTP1		
NW-DI	INFLUENT- DWTP		
NW-DF	FILTERS- DWTP		
NW-DE	FINAL- DWTP		
NW-W2S	SST- WWTP2		
NW-W2I	INFLUENT- WWTP2		
NW-W1B	Biofilters- WWTP1		
NW-W1SU	SST (From UCT Modified)- WWTP1	June 2021 (DrySeason)	
NN-W2A	BNR- WWTP2		
NW-W1I	INFLUENT-WWTP1		
Blank 2			
NW-W1U	BNR (Modified UCT)- WWTP1		
NW-W1A	BNR (UCT)- WWTP1		
NW-W1S	SST from BNR- WWTP1		
BH	Borehole high		
BL	Borehole low		
BL1	Borehole low 1		
BL2	Borehole low 2		
BH1	Borehole high 2		
BH2	Borehole high 2		
BH3	Borehole high 3		

10.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. Table 10.2 shows the mean recoveries and standard deviations for blanks. As shown in Table 10.2, the percentage recoveries ranged from 76.9-109.3%. This range is within the acceptable range. Table 10.3 and 10.4 show the mean surrogate recoveries in various water samples.

Table 10.2: Percentage recoveries and standard deviations in blanks during the dry season.

	Samples – Mean Surrogate recoveries (%) ± Standard deviation			
Surrogates	**Blanks (n=4)**	**FB (n=2)**	**BL (n=2)**	**FB (n=2)**
MPFNA	86.2±16.6	99.0±7.45	99.6±23.7	109±3.01
MPFUdA	91.9 ±6.97	93.6±7.39	80.0±2.18	76.9±3.48
MPFHxS	84.5±17.2	100.4±13.4	90.4±13.2	91.1±7.10

Table 10.3: Percentage recoveries of isotope-labelled compounds in drinking and tap water samples during the dry season.

	Samples – Surrogate recoveries (%) ± Standard deviation							
Surrogates	**MP-T1**	**NW-B1**	**NW-B2**	**NW-B3**	**NW-B4**	**NW-B5**	**NW-T2-**	**NW-T3**
MPFNA	82.7±3.6	107±34.3	112±24.1	90.3±4.7	88.5±8.0	111±5.10	102±1.9	138±23.6
MPFudA	118±17.3	87.1±11.2	79.1±0.20	98.9±38.8	97.3±1.20	108.3±1.10	78.6±26.9	106±2.2
MPFHxS	61.1±10.3	112±21.4	69.4±3.4	95.2±17.3	94.3±4.80	63.8±4.40	65.1±16.2	109±17.5

10.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – DRY SEASON

10.3.1 Distribution of PFASs in various water sources during the dry season

Presented in Table 10.5 are the PFASs concentrations in drinking water, wastewater and groundwater (borehole) samples collected from North-West in dry season. Of the 21 PFASs investigated in this study, at least 14 PFASs were detected in all drinking water treatment plant samples (influent (NW-DI), filters (NW-DF) and effluent (NW-DE)). A wide range of short-chain (PFBS, PFHxS, PFHxA, PFBA and PFPeA), long-chain (PFOA, PFOS, PFHpA, PFNA, PFUdA and PFHpS), 6:2 FTS and 8:2 FTS were detected during dry season sampling campaign.

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Table 10.4: Percentage recoveries of isotope-labelled compounds in drinking and wastewater treatment plant samples during the dry season.

	Samples												
	Surrogate recoveries (%) ± Standard deviation												
Surrogate	**NW-W1E**	**NW-W2E**	**NW-DI**	**NW-DF**	**NW-W2S**	**NW-W2R**	**NW-W1B**	**NW-W1SU**	**NW-W2A**	**NW-W1R**	**NW-W1U**	**NW-W1A**	**NW-W1S**
MPFNA	106±28.2	101±29.5	105±9.36	95.9±22.8	101±18.2	131±17.7	84.0±9.12	106±17.1	116±33.3	104.1±5.1	98.3±8.71	69.56±1.86	98.4± 5.22
MPFUdA	77.9±4.97	104±5.20	93.3±3.32	92.2±2.85	92.6±5.84	95.9±13.7	98.6±15.5	110±29.3	82.82±23.9	114±1.06	62.5±1.58	68.1±6.58	101±13.0
MPFHxS	64.9±2.56	85.6±26.9	66.0±0.48	108±2.16	80.1±1.69	85.5±35.5	89.1±12.4	103±5.47	80.2±0.58	89.2±16.5	110±28.9	59.5±5.75	88.6±17.5

Table 10.5: Mean concentrations of PFASs in various water samples during the dry season.

Samples	**NW-DI**	**NW-DF**	**NW-DE**	**NW-WE1**	**NW-WB1**	**NW-W1SU**	**NW-W1I**	**NW-W1U**	**NW-W1A**	**NW-W1S**	**NW-W2S**	**NW-W2R**	**NW-W2A**	**NW-WE2**	**NW-T1**	**NW-T2**	**NW-T3**	**NW-B1**	**NW-B2**	**NW-B3**	**NW-B4**	**NW-B5**
PFASs	**Mean concentrations (ng/L) and standard deviations (±)**																					
PFUdA	**0.10** ±0.029	nd	nd	**0.0645** ±0.01	nd	nd	nd	**0.0404** ±0.01	**0.137** ±0.06	**0.159** ±0.04	**0.250** ±0.21	**2.82** ±0.71	nd	nd	nd	nd	nd	**10.8** ±1.57	**30.6** ±5.78	**10.0** ±2.95	**9.27** ±1.00	*1.75* ±0.18
PFHxA	**11.1** ±0.13	**10.0** ±0.94	**10.5** ±0.86	**21.7** ±2.54	**21.3** ±9.32	**24.2** ±1.86	**8.36** ±4.38	**210** ±1.56	**157** ±19.38	**15.0** ±0.03	**13.2** ±2.89	**65.0** ±3.14	**359** ±29.92	**17.9** ±4.69	**15.7** ±0.83	**21.8** ±2.29	**6.85** ±3.51	**2.83** ±0.23	**4.94** ±1.95	**2.01** ±1.15	**3.05** ±0.96	**0.560** ±0.01
PFPeA	**4.30** ±0.59	**2.21** ±0.27	**1.54** ±0.31	**4.51** ±0.35	**2.63** ±0.07	**1.65** ±0.17	**0.929** ±0.32	**3.62** ±0.06	3.44 ±0.06	**3.26** ±0.61	**2.26** ±0.18	**1.26** ±0.09	**1.367** ±0.01	**4.00** ±0.58	**0.930** ±1.87	**1.87** ±2.83	11.3 ±8.71	nd	nd	nd	nd	nd
4:2 FTS	nd	nd	nd	<LOD	nd	<LOD	3.21 ±1.57	**0.326** ±0.10	**0.201** ±0.03	**0.167** ±0.11	nd	**1.29** ±0.04	<LOD	nd	nd	nd	nd	**1.10** ±1.41	**1.75** ±2.43	**1.73** ±1.28	**1.58** ±1.86	**1.85** ±0.64
8:2 FTS	**6.69** ±0.76	**17.8** ±0.87	**21.7** ±0.75	**14.5** ±1.42	**17.6** ±1.51	**25.9** ±0.78	**53.5** ±0.68	**29.6** ±1.35	**12.5** ±1.719	**11.5** ±1.05	**21.7** ±0.29	**123** ±1.41	**14.1** ±0.81	**10.7** ±0.53	**13.4** ±2.99	**22.9** ±2.20	**7.98** ±0.85	**2.91** ±1.34	**3.13** ±0.33	**0.940** ±0.02	**3.82** ±2.02	**0.550** ±0.11
PFHpA	2.55 ±0.37	0.123 ±0.03	**1.83** ±0.64	**3.87** ±1.18	**2.92** ±0.62	**3.14** ±0.00	**1.42** ±0.23	4.31 ±0.60	**5.49** ±0.78	**2.16** ±0.33	**0.672** ±0.82	**3.73** ±0.80	9.497 ±0.01	**3.54** ±0.05	**5.51** ±3.75	**2.39** ±0.42	**5.16** ±0.8	8.20 ±3.55	**5.54** ±0.86	**3.01** ±0.98	**1.40** ±0.17	**1.93** ±0.40
PFNA	**3.15** ±0.17	**0.629** ±0.07	**2.81** ±1.60	**1.15** ±0.09	**0.158** ±0.06	**0.916** ±0.07	0.901 ±0.21	53.11 ±5.81	**15.1** ±1.78	**0.218** ±0.06	**2.52** ±0.65	**3.51** ±0.98	**38.42** ±4.89	**3.45** ±1.66	**1.92** ±0.51	**5.14** ±1.1	**0.630** ±0.07	4.23 ±0.03	**21.9** ±4.36	**19.5** ±1.05	**5.18** ±2.46	**2.97** ±0.19
L-PFBS	**0.323** ±0.18	**1.23** ±1.01	**0.105** ±0.02	**3.45** ±0.58	**6.69** ±2.64	4.25 ±0.12	**12.4** ±0.44	**6.29** ±0.92	**8.29** ±1.27	**5.57** ±0.54	**4.94** ±1.24	**9.47** ±1.96	**29.3** ±4.83	**15.2** ±1.72	**5.12** ±0.70	**9.69** ±5.49	**5.72** ±0.14	**3.87** ±0.07	**4.13** ±1.23	**2.93** ±0.40	**2.01** ±1.08	**2.64** ±0.09
L-PFHxS	**1.83** ±0.01	**0.0239** ±0.02	**3.68** ±0.91	**2.54** ±0.17	**2.72** ±0.10	**1.71** ±0.41	**15.6** ±7.40	**0.235** ±0.04	**0.219** ±0.08	**4.24** ±0.34	**0.544** ±0.67	**27.0** ±15.16	**0.331** ±0.02	**5.28** ±0.65	**2.05** ±0.87	**2.38** ±0.40	**1.76** ±0.47	**2.40** ±0.63	**9.61** ±2.72	**1.78** ±0.19	**3.18** ±0.34	**2.81** ±0.58
L-PFOS	**18.5** ±3.10	**10.6** ±0.52	**6.59** ±0.56	**4.23** ±1.88	**6.12** ±0.07	**10.9** ±4.09	41.0 ±22.01	**42.1** ±11.12	**24.7** ±2.47	**5.41** ±2.13	**6.13** ±1.01	**63.1** ±19.26	**32.15** ±10.63	**6.499** ±2.92	**13.4** ±1.64	**17.7** ±7.71	**18.9** ±6.08	**1.24** ±0.78	**8.41** ±2.04	nd	**0.78** ±0.44	nd
PFHpS	**0.281** ±0.09	**0.251** ±0.02	**0.297** ±0.12	**0.169** ±0.06	nd	**0.240** ±0.03	**33.5** ±2.76	**3.86** ±3.77	**0.548** ±0.15	nd	**0.627** ±0.25	**72.4** ±10.02	**0.739** ±0.44	**1.52** ±0.16	**5.51** ±3.75	**2.39** ±0.42	**5.16** 0±0.8	**26.9** ±1.87	**69.6** ±3.97	**55.0** ±2.66	**19.4** ±4.68	**171** ±35.20
PFOA	**5.76** ±0.53	**4.54** ±0.21	**4.67** ±1.02	**3.14** ±0.50	**3.37** ±1.68	**2.76** ±0.09	**7.08** ±0.35	**976** ±90.85	**987** ±107.30	**11.2** ±4.5	**6.72** ±1.02	**93.5** ±9.14	**850** ±333.88	**6.83** ±0.30	**5.47** ±1.21	**3.19** ±2.01	**1.44** ±0.46	**50.6** ±5.97	**32.9** ±1.9	**60.9** ±18.41	**59.2** ±16.24	**26.5** ±9.03
PFBA	**2.95** ±1.22	**145** ±5.98	**230** ±14.41	**158** ±5.87	**33.9** ±4.19	**97.3** ±13.61	**82.0** ±4.63	**51.2** ±1.83	**56.0** ±20.22	**42.4** ±2.92	**13.6** ±3.72	**45.3** ±8.25	**101** ±6.39	**65.8** ±8.16	**76.3** ±14.22	**21.3** ±0.54	nd	**2.10** ±0.10	**3.46** ±0.03	**2.63** ±0.82	**2.89** ±0.26	**2.30** ±1.40

Samples	NW-DI	NW-DF	NW-DE	NW-WE1	NW-WB1	NW-W1SU	NW-W1I	NW-W1U	NW-W1A	NW-W1S	NW-W2S	NW-W2R	NW-W2A	NW-WE2	NW-T1	NW-T2	NW-T3	NW-B1	NW-B2	NW-B3	NW-B4	NW-B5
PFASs	**Mean concentrations (ng/L) and standard deviations (±)**																					
6:2 FTS	**12.96** ±0.37	**12.27** ±2.67	**0.131** ±0.01	**16.7** ±2.89	**30.0** ±2.74	**0.131** ±0.01	nd	**1.45** ±0.00	**3.53** ±0.19	**25.6** ±0.10	nd	**175** ±5.23	**3.13** ±0.14	17.4 ±0.74	nd	nd	nd	**3.38** ±0.24	4.**22** ±0.19	**5.81** ±0.66	**3.71** ±0.90	**1.00** ±0.31
FHEA	**62.3** ±1.07	**1.64** ±0.25	**0.520** ±0.01	**87.2** ±3.74	**5.89** ±1.09	nd	**5.67** ±1.14	nd	nd	nd	nd	**1.30** ±0.95	nd	**52.6** ±3.43	**0.490** ±0.12	nd	nd	**116** ±8.69	**25.2** ±3.78	197 ±21.12	**47.0** ±3.37	**51.6±** 2.82
FOET	**91.2** ±1.35	**127** ±7.35	**61.3** ±8.07	**91.2** ±1.35	**127** ±7.35	**0.131** ±0.01	**40.3** ±2.98	**1.45** ±0.00	**3.53** ±0.19	**25.6** ±0.10	nd	nd	**3.13** ±0.14	**24.2** ±2.04	nd	nd	nd	**11.7** ±1.17	**4.96** ±0.58	34.5 ±12.73	**11.5** ±3.23	**9.04** ±0.59
FHET	**0.247** ±0.01	**0.202** ±0.03	**0.711** ±0.01	**0.264** ±0.03	**0.405** ±0.23	**0.440** ±0.04	**7.43** ±4.58	**2.06** ±0.96	**1.58** ±0.47	**0.448** ±0.04	**0.871** ±0.76	**9.71** ±3.10	**4.95** ±1.15	**0.383** ±0.06	**82.9** ±24.8	**30.0** ±5.66	**32.7** ±2.44	nd		nd	nd	nd

As shown in Table 10.5, the concentrations of short-chain PFASs concentrations ranged from 0.110-1.23 ng/L, 0.024-3.68 ng/L, 10.1-11.1 ng/L, 2.95-240.4 ng/L,1.54-4.30 ng/L for PFBS, PFHxS, PFHxA, PFBA and PFPeA, respectively. PFBA concentration increased from the influent to the effluent. Samples collected from filters and the effluent contributed to high concentration of PFBA and FOET. FHET, 8:2 FTS, PFOS and PFBA were prevalent in drinking tap water samples, however, PFBA was not detected in NW-T3. The concentrations of long-chain PFASs ranged from 4.54-5.76 ng/L, 6.39-18.5 ng/L, 0.120-2.55 ng/L, 0.630-3.15 and 0.250-0.300 ng/L for PFOA, PFOS, PFHpA, PFNA and PFHpS, respectively.

While all investigated short-chain PFASs were detected in all samples collected from the DWTP, the detection for long-chain PFASs decreased with an increase in carbon-chain length (PFDoA, PFODA, PFDS and PFHxDA were not detected). For long-chain PFASs, high concentrations of PFOS with 11.3 ng/L, 10.1 ng/L and 7.23 ng/L and PFOA with 21.2 ng/L, 13.3 ng/L and 3.38 ng/L were found in NW-DI, NW-DF and NW-DE, respectively. The concentrations of some of the short-chain and long-chain PFASs observed for DWTP influent and effluent samples during dry season showed similar concentrations, except for PFBA (SD= 115) and PFOS (SD= 6.05), explaining low removal efficiencies of PFASs by conventional DWTPs.

Wastewater treatment plants samples were also collected from different treatment units for better understanding of the trend and removal of all PFASs. From the two WWTPs investigated (Table 10.5), it is notable that amongst the concentrations of short-chain PFASs, PFHxA concentrations in the BNR/activated sludge process sample 210 ng/L, 157 ng/L and 359 ng/L for NW-W1A, NW-W1U and NW-W2A, respectively, were higher than the concentrations observed in the influent (65.0 ng/L and 8.36 ng/L for NW-W2R and NW-W1R) respectively, as well as the effluent (17.9 ng/L and 21.7 ng/L for NW-W2E and NW-W1E) respectively. The concentrations of PFBA in WWTP 2 were 45.3 ng/L in the influent NW-W2R, and an increase was observed in the BNR NW-W2A (101 ng/L). A sharp decrease was observed after the SST effluent NW-W2S (13.6 ng/L), followed by an increase in concentration after the chlorine contact tank (65.8 ng/L). The trend in the concentrations of PFBA observed for WWTP 1 was different from that of WWTP 2. The concentration of PFBA was 82.0 ng/L in the influent NW-W1R, a decrease in each activated sludge was observed at 56.0 ng/L and 51.2 ng/L for NW-W1Aand NW-W1U respectively. However, a decrease in secondary settling tank (NW-W1S) for NW-W1A had an increase of PFBA (97.3 ng/L) while a decrease was observed in the secondary settling tank (NW-W1SU) for NW-W1U. Final effluent treated from NW-W1A had PFBA concentrations twice as high as that of the influent NW-W1R. The effluent treated through biofilters NW-W1B had concentrations of PFBA at 33.7 ng/L. The concentrations of PFBS, PFHxS and PFPeA were less than 30.0 ng/L for all samples collected in the two WWTPs.

Each long-chain PFASs were detected in concentrations less than 10.0 ng/L with an exception to PFOA and PFOS. The concentrations of PFOA and PFOS ranged from 2.76-987 ng/L and 4.23-42.1 ng/L, respectively. The individual concentrations of PFOA and PFOS were 7.08 ng/L and 41.0 ng/L for WWTP 1 and 93.5 ng/L and 63.1 ng/L for WWTP 2 influent. However, high concentrations of PFOA were observed in the BNR/activated sludge processes (850 ng/L, 976 ng/L, 987 ng/L of PFOA in NW-W2A, NW-W1A and NW-W1U), and low concentrations were observed in all final effluent samples. PFASs precursors, i.e. fluorotelomer sulfonates, acrylates, and alcohols, contributed to high concentrations of PFASs during this sampling campaign. The concentrations of 8:2 FTS were found in all wastewater samples at a range of 1 0.7-123 ng/L, and its concentration decreased from the influent. A similar trend was observed for 4:2 FTS and 6:2 FTS. Concentrations of 4:2 FTS and 6:2 FTS ranged from <LOD-3.21 ng/L and <LOD-175 ng/L, respectively, in WWTP 2 and WWTP 1. For fluorotelomer alcohols, FOET (8:2 FTOH), was not detected in the influent, activated sludge and secondary settling tank NW-W2S of WWTP 2, but was observed at a concentration of 24.2 ng/L in the NW-W2R influent. WWTP 1 showed a different trend. FOET concentrations increased from the influent (NW-W1R) to the effluent. The concentrations were twice as high in the effluent treated through activated sludge process (NW-W1E) and three times more in the effluent treated by trickling filters (NW-W1B). FHET (6:2 FTS) was detected at low concentrations (0.260-9.71 ng/L). The concentration of fluorotelomer acrylate, FHEA (6:2 FTA), also increased from the influent to the effluent.

Table 10.5 also shows the concentrations of PFASs in borehole water samples collected during dry season. FOET was predominant in all borehole water samples, with the highest concentrations observed at 197 ng/L and 117 ng/L in NW-B5 and NW-B3, respectively, followed by PFOA at 171 ng/L in NW-B2. FOET was also observed at 69.5 ng/L in NW-B3 and 55.0 ng/L in NW-B2. NW-B1 was dominated by PFBA and FOET at 59.1 ng/L and 46.9 ng/L, respectively. Concentrations of PFSAs were considerably lower than concentrations of PFCAs and fluorotelomers.

In order to show the contributions of PFASs in different water sources, scatter plots were constructed and these are shown in Figure 10.2. As can be seen, different PFASs are clustered at the bottom of the plot with WWTP as outliers. A clear pattern was observed when a log base scatter plot was constructed as shown in Figure 10.3. A clear linear relationship between PFASs contributions and their concentrations can be seen in Figure 10.3. This indicated that the PFASs concentrations observed were related to their respective contributions.

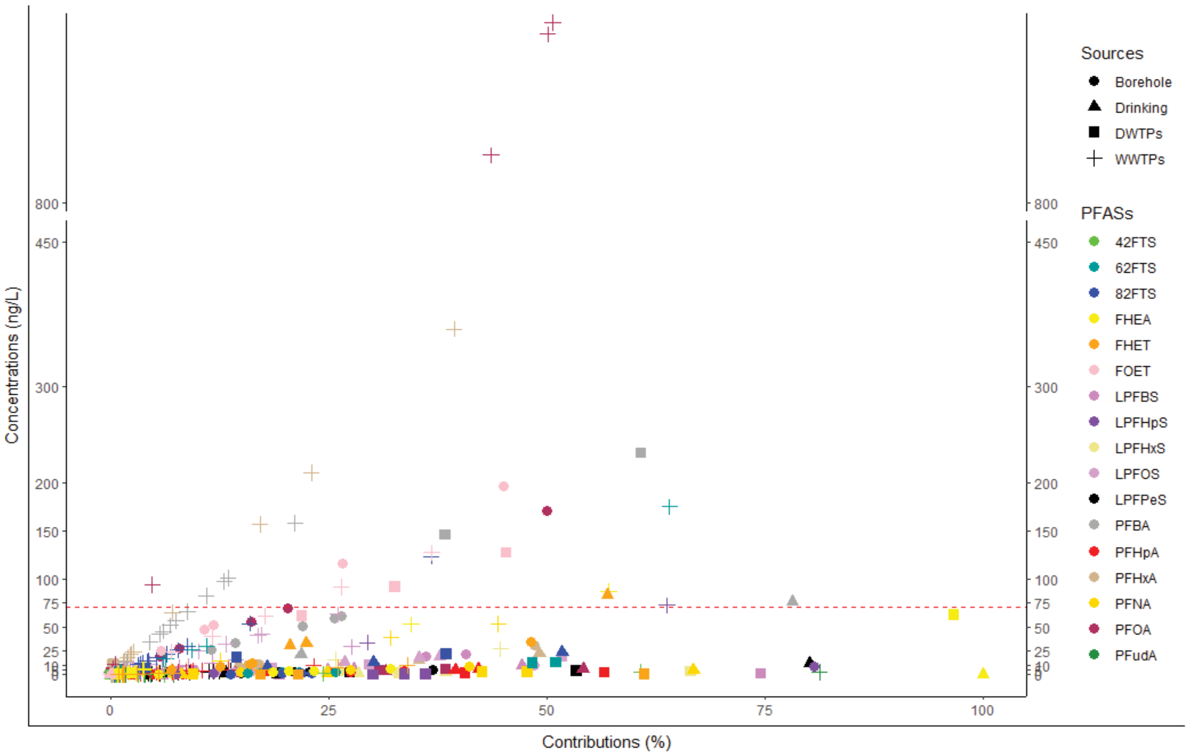

Figure 10.2: PFASs concentrations distributions for various water sources in North West during the dry season.

The three classes of PFASs, PFCAs, PFSAs and Fluorotelomers were all present in the different sourced of water analysed (Figure 10.4). FOET, a telomer, was prominent in all borehole water samples. This was followed by PFOA, a PFCA. Generally, PFCAs were most prevalent in WWTPs and borehole samples, while fluorotelomers contributed to high concentrations in DWTPs, and drinking water samples.

Figure 10.5 shows the contributions of short and long chain PFASs. Long-chain PFASs dominated the WWTPs and borehole water samples at 65% and 52%, respectively. However, they show similar contributions in DWTP influent and effluent, indicating low removal efficiencies of PFASs by conventional DWTPs.

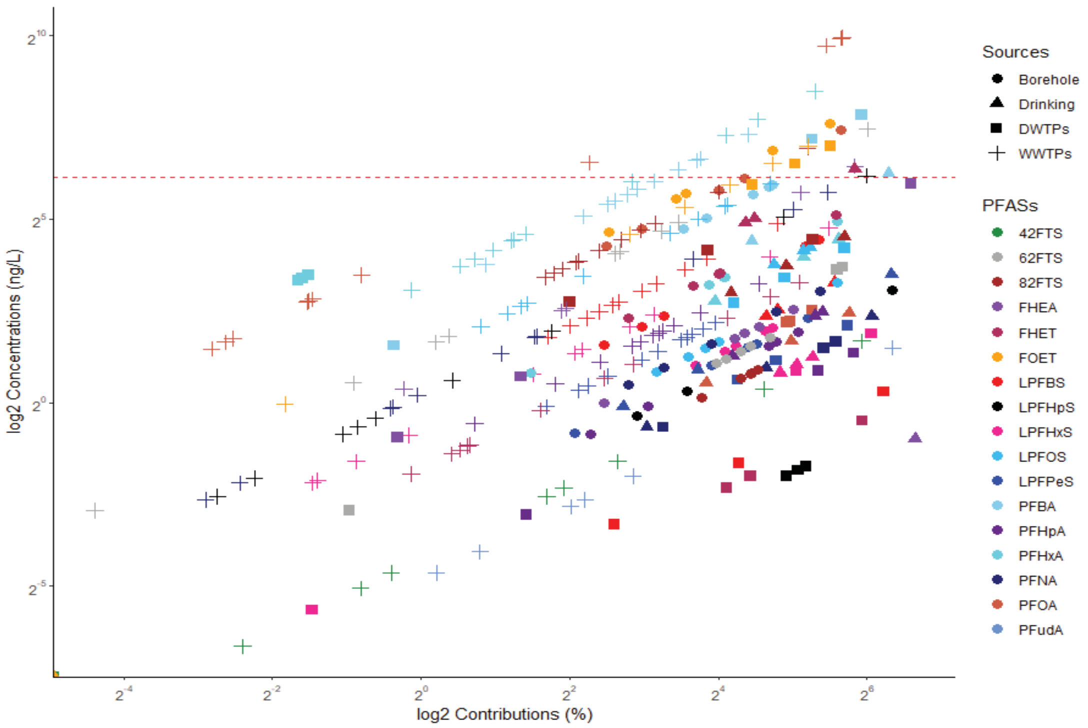

Figure 10.3: PFASs concentration contributions in various water sources in North West during the dry season.

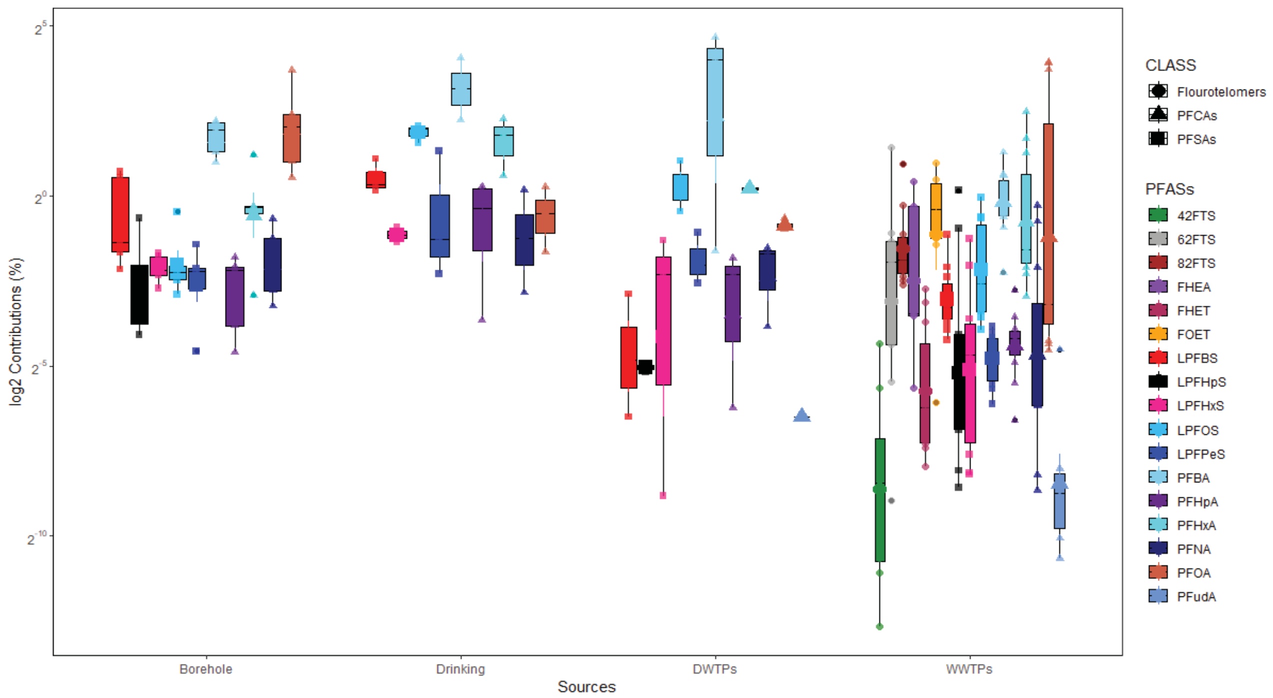

Figure 10.4: PFASs class contributions for various water sources in North West during the dry season.

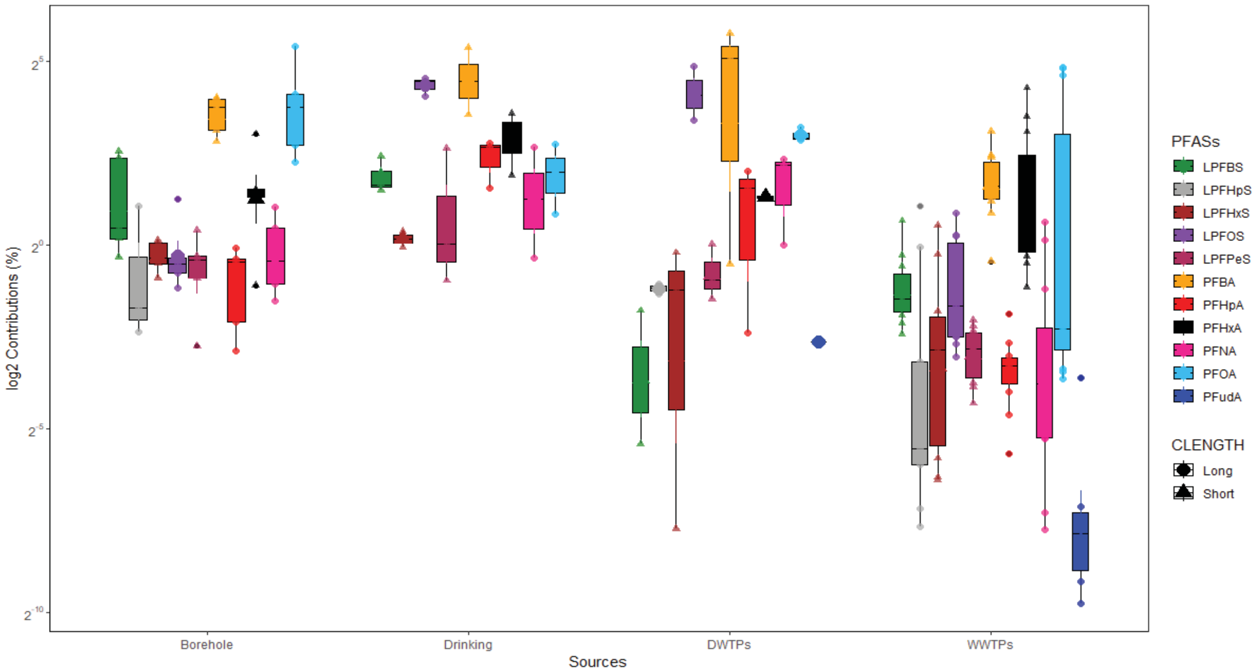

Figure 10.5: Contributions of short- and long-chain PFASs for various water sources in North West during the dry season.

10.3.2 Establishing the possible sources of PFASs detected in the water

In this study, PCA analysis was used to understand the cycle of PFASs between groundwater, drinking water and wastewater. Figures 10.6 to 10.7 show the PCA of PFAS congeners and the sampling sites respectively. As can be seen in Figure 10.6, PFBS, PFHxA, PFOS, PFHpS, PFBA and 8:2 FTS were strong and positively associated. These high loadings in quadrant 1 (clockwise) are associated with medical devices such as endoscopes and woven and non-woven surgical drapes and gowns, radio-opaque ethylene tetraethylene copolymer uses, metal plating, paints, waxes, inks and industrial coatings, metal plating, polyvinylidene fluorides, coatings, carpets, couches and food packaging. Their association, therefore, suggested the same source.

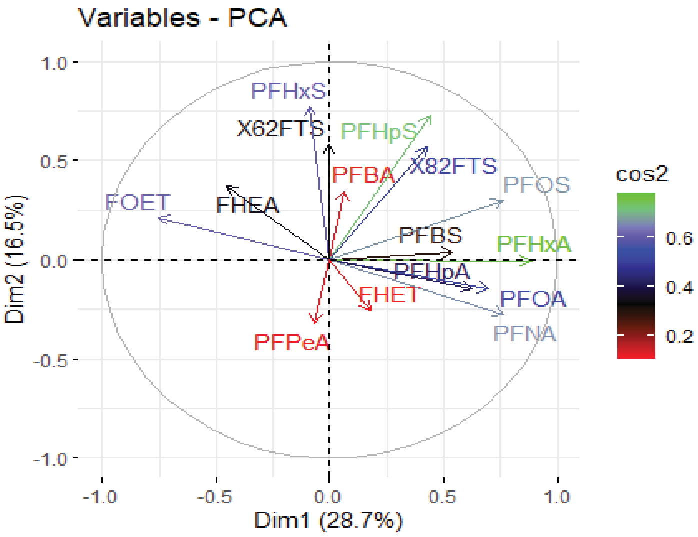

Figure 10.6: PCA of PFASs congener contributions and their relationships.

Quadrant 2 is populated with PFHpA, PFOA, FHET and PFNA. The content of the quadrant is mainly used in textile, coatings, fluorinated surfactants fields and food packaging industries. PFPeA is the only occupant of quadrant 3, suggesting different sources from the other PFASs. Quadrant 4, was characterised by PFHpS, PFHxS, 6:2 FTS and FOET. These compounds are used in stain-resistant fabrics, coatings, firefighting foams, fabrics and food packaging.

NW-W2R and NW-2R are responsible for the variability as shown in Figure 10.7. However, the groupings of samples collected from different samples within the WWTPs show that PFASs follow a particular pattern which may be similar between the two WWTPs. Borehole water samples: NW-B1, B2, B3 and B5 were negatively correlated with NW-B4. DWTP samples were grouped all together, and this could suggest less variability in the PFASs behaviour in and out of the treatment plant system. NW-T1 and NW-T2 were closely related, which could suggest they share similar sources of PFASs packaging industries and firefighting, while 8:2 FTS in coatings, paper and carpets and cleaning agents industries.

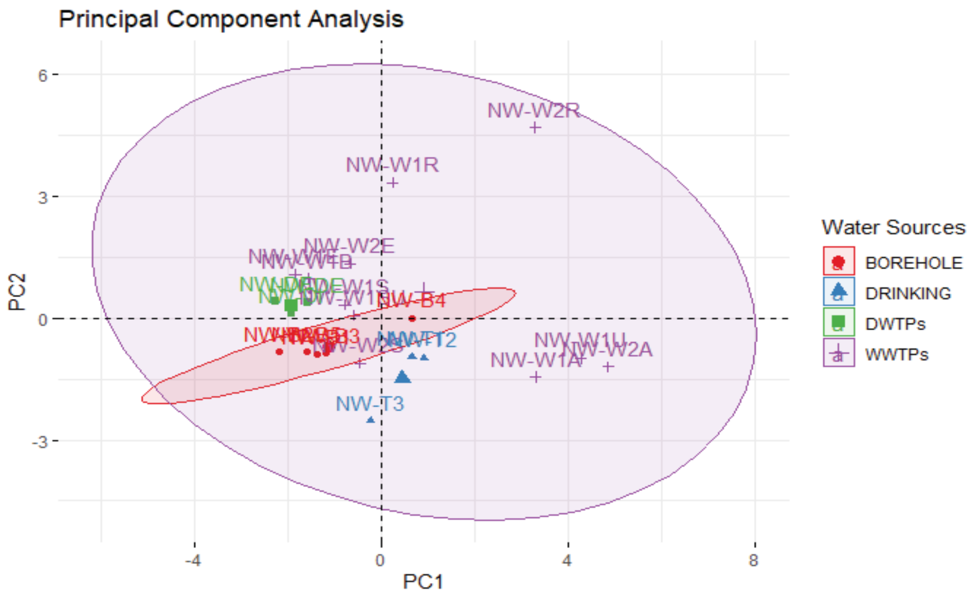

Figure 10.7: PCA of sampling sites and their relationships.

10.4 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER – WET SEASON

10.4.1 Distribution of PFASs in various water sources during the wet season

Table 10.6 shows the mean recoveries for isotope-labelled compounds in drinking and wastewater treatment plant samples collected in wet season. Amongst the short-chain PFASs, PFBA contributed high concentrations in drinking tap water samples at a range of 7.60-50.5 ng/L. In DWTP samples, PFBA was found at a range of 8.17-21.7 ng/L, and it showed an increase from the influent NW-DI to the effluent NW-DE. PFBS and PFHxS were not detected in tap water samples, while they were detected in low concentrations in the drinking water treatment plant (0.171-1.40 ng/L and 0.748-2.06 ng/L, respectively). Though the concentration of PFHxS increased in the filters, lower concentration was observed in the final effluent.

Table 10.6: Mean concentrations of PFASs in various water sources during the wet season.

Compounds	PFBS	PFHxS	PFHxA	PFBA	PFPeA	PFOA	PFOS	PFHpA	PFNA	PFHpS	42FTS	62FTS	82FTS	FHEA	FOET	FHET
Samples							**Mean concentrations (ng/L) and standard deviations (±)**									
NW-W2R	**336** ±38.19	**6.09** ±1.60	**34.8** ±2.15	48.3 ±20.48	7.25 ±0.64	43.2 ±8.01	11.6 ±0.43	2.10 ±0.35	6.80 ±1.15	51.0 ±0.68	nd	**1405** ±70.00	84.6 ±3.14	34.1 ±0.17	**2201** ±331.47	153 ±20.73
NW-W1SU	1.92 ±0.23	0.75 ±0.21	3.56 ±0.15	18.0 ±0.64	0.28 ±0.01	9.86 ±9.87	5.49 ±0.89	1.12 ±0.36	1.56 ±1.29	nd	nd	**16.5** ±2.85	5.91 ±0.99	nd	nd	nd
NW-W2S	88.5 ±3.24	3.94 ±1.73	8.67 ±0.85	35.0 ±6.54	3.24 ±0.00	1.87 ±0.14	38.0 ±1.94	7.09 ±1.83	0.230 ±0.09	**2.33** ±0.12	nd	**4899** ±1072.97	3.60 ±0.53	3.64 ±0.11	**2166** ±251.96	43.7 ±2.39
NW-W2A	678 ±23.01	7.08 ±1.07	267 ±31.79	111 ±19.7	3.77±1.08	**65.1** ±2.26	**165** ±35.68	20.1 ±8.53	3.46 ±1.01	11.6 ±3.31	nd	**2351** ±134.09	186 ±14.82	68.9 ±25.63	**1627** ±60.07	250 ±52.23
NW-W1A	1.34 ±0.54	0.310 ±0.15	7.45 ±3.16	7.32 ±0.01	0.190 ±0.00	1.94 ±0.64	3.59 ±1.19	1.70± 0.21	2.36 ±1.47	nd	nd	**8.99** ±0.06	5.09 ±0.85	nd	31.8±3.83	nd
NW-W1U	0.920 ±0.18	0.430 ±0.33	3.24 ±1.36	11.3 ±3.51	0.430 ±0.23	1.14 ±0.31	3.37 ±2.18	1.34 ±0.66	0.450 ±0.21	nd	nd	**11.0** ±1.53	6.74±3.93	nd	121 ±1.24	nd
NW-W1S	2.24 ±0.09	0.200 ±0.11	2.50 ±0.15	12.0 ±3.23	0.200 ±0.12	1.86 ±0.33	4.96 ±0.31	0.340 ±0.12	0.310 ±0.20	nd	nd	**12.1** ±1.06	9.45±0.02	nd		nd
NW-W1E	5.09 ±0.68	0.200± 0.01	3.60 ±1.83	10.9 ±6.93	0.390 ±0.02	0.630 ±0.28	3.06 ±0.15	0.400 ±0.178	1.00 ±0.26	nd	nd	**11.0** ±0.32	7.27±2.01	nd	34.4 ±6.24	nd
NW-W2E	87.9 ±13.95	6.99 ±2.63	28.5 ±1.28	27.2 ±1.80	2.88 ±0.27	3.21 ±0.46	16.4 ±4.93	15.1 ±5.36	4.12 ±2.13	8.93 ±0.01	nd	**1950** ±490.01	17.4 ±0.47	1.51 ±0.09	903 ±94.31	145 ±16.82
NW-W1B	0.930 ±0.44	0.170 ±0.02	1.85 ±0.02	11.0 ±1.80	0.290 ±0.15	2.97 ±0.99	14.1 ±5.59	0.350 ±0.08	0.630 ±0.50	nd	nd	**9.67** ±2.51	6.46 ±1.66	nd	nd	nd
NW-W1R	1.58 ±0.80	1.36 ±0.14	10.9 ±5.92	27.3 ±1.07	3.22 ±3.80	1.44 ±0.31	14.0 ±5.57	9.90 ±4.85	1.33 ±0.38	0.10 ±0.01	0.05 ±0.02	**46.0** ±4.9	10.8 ±1.49	nd	597 ±13.53	nd
NW-DI	**0.170** ±0.01	**0.990** ±0.24	**1.55** ±0.09	**8.18** ±0.57	**0.510** ±0.22	**3.39** ±0.76	**7.24** ±5.24	**1.03** ±0.16	**3.64** ±0.88	nd	nd	**11.6** ±2.05	**11.6** ±4.35	**4.64**±0.13	**25.6** ±3.09	nd
NW-DF	**0.630** ±0.18	**2.06** ±0.24	**1.82** ±0.87	**21.5** ±4.82	**0.730** ±0.19	**13.3** ±1.57	**10.1** ±2.06	**1.30** ±0.19	**0.740** ±0.44	nd	nd	**8.11** ±1.42	**6.57** ±1.81	nd	**49.7** ±5.65	nd
NW-DE	**1.40** ±0.13	**0.750** ±0.01	**3.75**±1.38	**15.8** ±5.15	**0.48** ±0.14	**21.2** ±3.28	**11.3** ±0.70	**0.900** ±0.10	**0.360** ±0.05	nd	nd	**9.55** ±0.95	**6.79** ±1.54	nd	**37.3** ±2.58	nd
NW-T1	nd	nd	1.36 ±0.23	**7.60** ±1.57	0.210 ±0.10					0.280 ± 0.11						
NW-T2	nd	nd	7.35 ±3.38	**8.33** ±1.71	<LOD	0.75 ±0.41	4.87 ±3.28	0.360 ±0.36	7.70 ±1.88	nd	nd	32.3 ±10.01	nd	nd	nd	**22**.9 ±6.66
NW-T3	nd	nd	8.19 ±1.90	**50.6** ±0.62	5.60 ±2.19	1.74 ±0.23	nd	nd	0.680 ±0.36	nd	nd	nd	5.62 ±2.10	1.28 ±0.02	nd	**7.27** ±4.24
NW-B5	**0.150** ±0.13	**0.330** ±0.15	**2.00** ±1.64	**12.2** ±0.82	**4.35** ±0.30	**4.34** ±1.88	**8.98** ±1.47	**1.55** ±0.81	nd	nd	nd	nd	7.23 ±3.05	nd	nd	nd

Compounds	PFBS	PFHxS	PFHxA	PFBA	PFPeA	PFOA	PFOS	PFHpA	PFNA	PFHpS	42FTS	62FTS	82FTS	FHEA	FOET	FHET
Samples	**Mean concentrations (ng/L) and standard deviations (±)**															
NW-B2	**0.160** ±0.02	**0.520** ±0.08	nd	**10.7** ±4.03	**4.14** ±1.38	**0.74** ±0.24	**1.43** ±0.02	**0.900** ±0.02	**0.360** ±0.05	nd	nd	**7.52** ±0.79	**8.40** ±4.87	nd	nd	nd
NW-B1	**14.5** ±1.25	**7.23** ±2.23	**8.89** ±2.63	**42.7** ±1.38	**1.84** ±0.33	**4.41±** 0.10	**21.7** ±1.01	**11.7** ±1.76	**1.80** ±0.17	**0.180** ±0.00	nd	**1097** ±115.36	**4.70** ±1.65	**6.10** ±0.01	**543** ±3.66	**50.7** ±4.97
NW-B3	**2.90** ±0.10	**2.32** ±0.43	**5.60** ±0.24	nd	0.210 ±0.38	**0.890** ±0.06	**34.8** ±1.67	**2.09** ±0.42	**1.56** ±0.40	nd	nd	**96.7** ±30.94	**1.39** ±0.18	**0.390** ±0.07	**386** ±29.82	**24.3** ±6.52
NW-B4	**5.99** ±3.60	**7.62** ±1.68	**4.55** ±1.20	nd	nd	**2.45** ±0.94	**17.5** ±6.77	**0.890** ±1.04	**6.45** ±1.65	nd	nd	nd	**1.70** ±0.23	**5.80** ±1.81	**102** ±39.18	**14.0** ±2.99

The concentrations of most of the short-chain PFASs in tap water were similar to those found in final effluent of the drinking water treatment plant. PFOA and PFOS contributed high concentrations of PFASs amongst long-chain PFAS at concentration ranges of 0.592-13.3 in DWTP samples, and 0.749-21.2 ng/L in drinking tap water samples and 4.86-11.3 ng/L in drinking tap water and 0.872-10.1 ng/L in DWTPs, respectively. The results indicate a significant removal of PFOA (from 13.3 to 0.592 ng/L) in the influent to the effluent, while PFOS increased from 0.872 ng/L to 10.1. ng/L. PFHpS was detected only in the effluent and at very low concentrations. There was no great variation of PFHxA concentrations in the tap and drinking water treatment plant samples. For fluorotelomers, FOET contributed the highest concentration of PFAS precursors at concentration of 53.1 ng/L, 25.6 ng/L, 49.7 ng/L and 37.3 ng/L in NW-DI, NW-DF, NW-DE and NW-T3, respectively. 4:2 FTS was only detected NW-DI at a concentration of 0.107 ng/L. There was no great variation of concentrations observed for each individual 6:2 FTS (SD=2.72), 8:2 FTS (SD=2.52) and FHEA (2.99) in the samples.

The concentrations of PFASs measured in wastewater in wet season are shown in Table 10.6. As can be seen from the Table, the concentrations of short-chain PFASs during wet season in WWTP 1 were lower than those observed for WWTP 2,and ranged from 0.920-5.08 ng/L, , 0.01-0.230 ng/L, 1.85-10.9 ng/L, nd-12.2, 0.190-3.22, 0.620-9.86 ng/L for PFBS, PFHxS, PFHxA, PFBA and PFPeA, respectively. The concentrations of PFBA and PFHxA contributed to high concentrations of PFASs. For both compounds, the concentrations decreased from the influent (NW-W1R) to the effluent (NW-W1E). The PFHxA and PFBA concentrations in the attached growth treatment plant effluent (NW-W1B) were lower than those from the effluent (NW-W1R) from the activated sludge treatment plant (NW-W2U). Short-chain PFASs were observed at a high concentration in WWTP 2 ranged from 3.00-3.93 ng/L, 87.9-88.5 ng/L, 27.2-111 ng/L, 8.67-266 ng/L and 2.88-7.24 ng/L for PFHxS, PFBS, PFBA, PFHxA and PFPeA. Activated sludge plant/ BNR (NW-W2A) was high with concentrations of PFHxS, PFBs, PFBA and PFHxA. For long chain PFASs PFOA and PFOS were found at concentrations lower than 15.0 ng/L in all samples collected from WWTP 2. Scatter plots of the PFASs concentrations in Table 10.6 are shown in Figures 10.8 and 10.9. In Figure 10.8, most of the points are spread our horizontally, while some are scattered. Since no clear pattern could be deduced from Figure 10.8, a log base plot was constructed and this is shown in Figure 10.9. A clear linear pattern can be seen, although there are some congestions at the midpoint of plot.

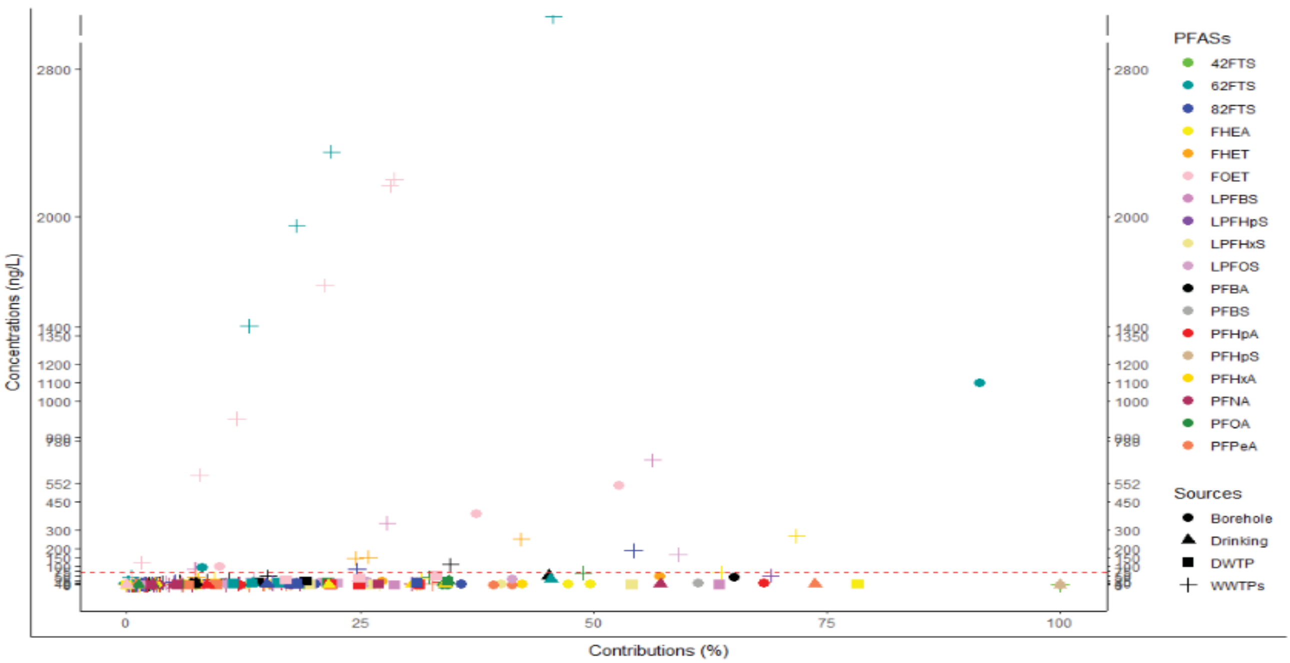

Figure 10.8: PFASs concentrations distributions for various water sources in North West during the wet season.

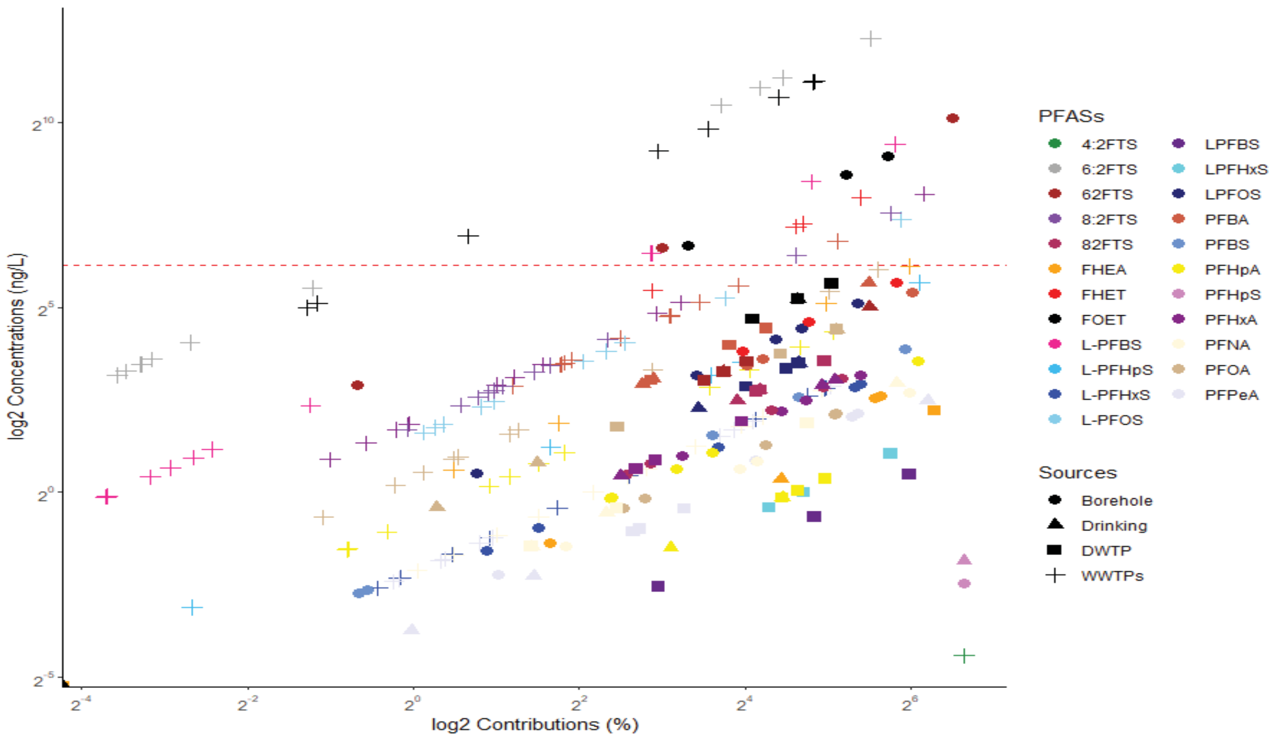

Figure 10.9: PFASs concentration contributions in various water sources in North West during the wet season.

An increase in PFOA concentration was observed in the final effluent from the attached growth plant (NW-W1B), while a decrease was observed in the final effluent treated (NW-W1E). However, the concentration of PFOA was observed to be high in the secondary settling tank (NW-W1S) of the activated sludge plant 1 (NW-W1A). Activated sludge showed no removal of PFOS, while a decrease was observed in the effluent growth treated through attached growth. For long chain PFASs PFOA and PFOS were found at concentrations lower than 15.0 ng/L in all samples collected from WWTP 2. For the telomers, the concentrations of fluorotelomer sulfonates 4:2 FTS and 8:2 FTS were significantly lower than 6:2 FTS, while FHEA and FHET were not detected in the WWTP 2 samples. Concentrations of FOET were observed to be higher in the influent, and there was no detection of this compound in the effluent treated through activated sludge plant 1 (NW-W1A). Again, the concentrations of 4:2 FTS and 8:2 FST were extremely lower than those observed for WWTP 2. The highest concentration was observed for 6:2 FTS in NW-W2S and NW-W2A, at concentrations of 4899 ng/L and 2351 ng/L followed by FOET in NW-W2S and NW-W2R at concentrations of 2166 ng/L and 2201 ng/L, respectively.

The concentrations of PFOA and PFOS in WWTP 2 ranged from 0.62-65.1 ng/L and 3.05-165 ng/L, respectively. Higher concentrations were observed in NW-W2A followed by NW-W2R. From Table 11.5, PFOA and PFOS contributed high concentrations of PFASs amongst long-chain PFAS at concentration ranges of 0.592-21.2 ng/L and 0.870-11.3 ng/L. The results indicate a significant removal of PFOA (from 21.2-3.39 ng/L) in the influent to the effluent, while PFOS decreased from 11.3 ng/L to 7,24 ng/L. PFHpS was detected only in the effluent and at very low concentrations. There was no great variation of PFHxA concentrations in the tap and drinking water treatment plant samples.

The observed linear pattern is an indication of positive correlation between PFASs contributions and their concentrations. Shown in Figures 10.11 and 10.12 are the box plots of contributions of PFASs classes and short and long chain PFASs to PFASs concentrations respectively. All the classes, PFCAs, PFSAs and telomers were present in the water sources analysed. As can be seen in Figure 11.1, the three classes are most prevalent in the WWTP. This is not surprising since WWTP receives wastewater from domestic and storm water discharged which may contain PFASs compounds leached from PFASs-containing products. Some congestion of the PFASs classes can also be seen in the borehole samples. PFCAs are the most prevalent, although telomers such as FOET exhibited the highest concentration in one of the wastewater samples, NW-W2S. That PFASs classes were detected in borehole samples suggested pollution probably from the use of WWTP effluent to recharge the aquifer or via transport of landfill leachate from unlined landfill sites.

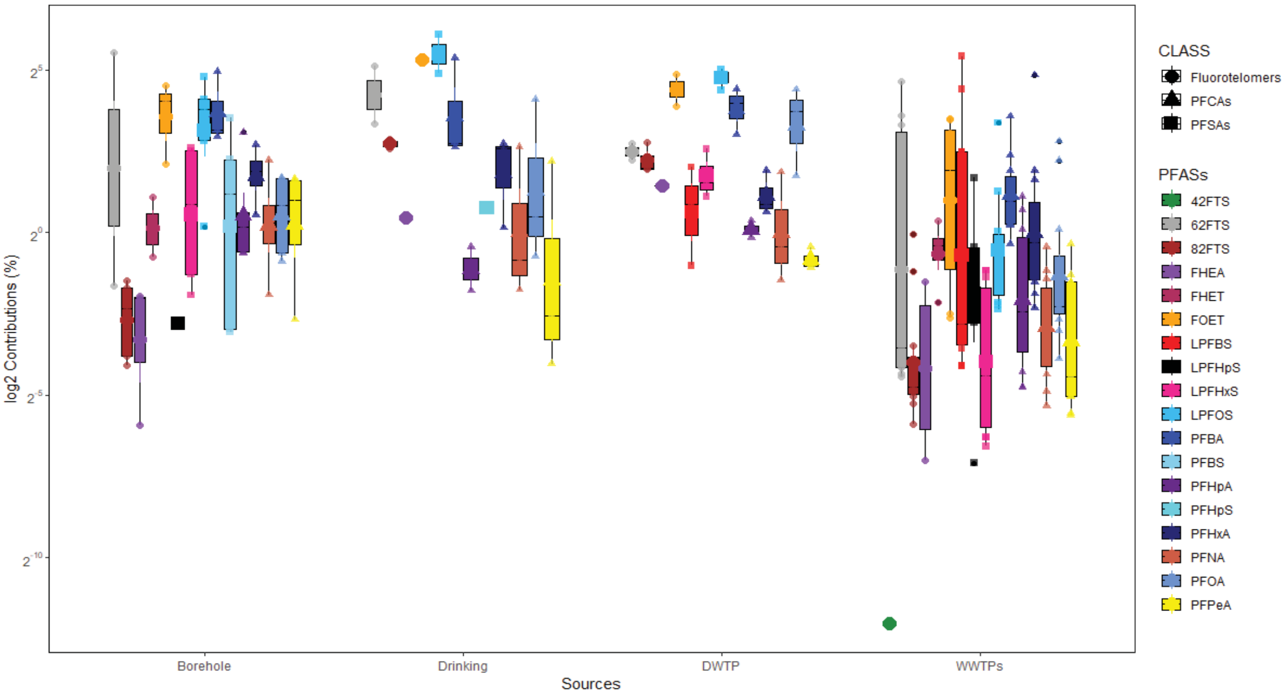

Figure 10.10: PFASs class contributions for various water sources in North West during the wet season.

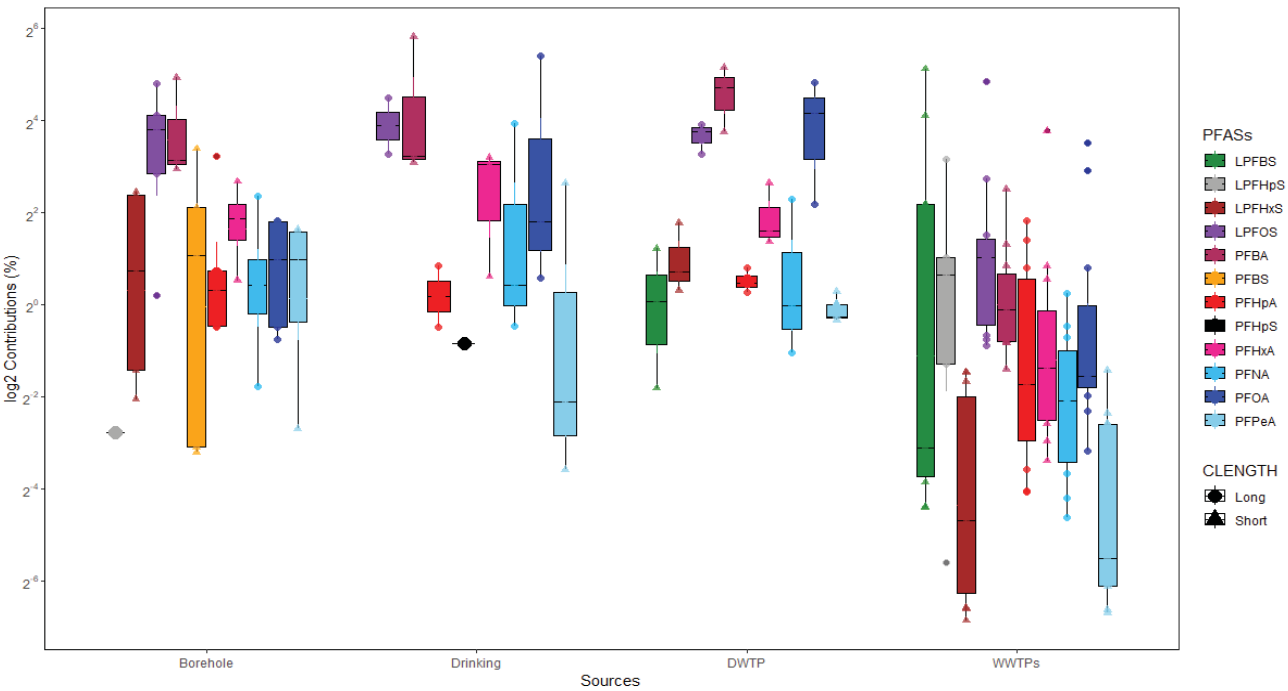

Figure 10.11: Contributions of short- and long-chain PFASs for various water sources in North West during the wet season.

Figure 10.11 shows the contributions of short and long chain PFASs to the concentrations of PFASs compounds. Short chains were more in the samples compared to long chain. Nearly all the short chains were detected in all the samples. The dominance of short chains may be due to 1) break down of telomers and long chain PFASs into short chains and 2) use of more short chain-containing products. Furthermore, long chains are less soluble in water and tend to adhere to solids than short chain and as a result, they are not readily available in water. However, PFOA and PFOS which are PFASs chain were detected in almost all the samples. PFOA and PFOS contributed high concentrations of PFASs amongst long-chain PFASs.

10.4.2 Establishing the possible sources of the PFASs detected in the water

As shown in Figure 10.12, quadrants 1 and 2 explained show high loadings of PFPeA, PFBA, 8:2 FTS, PFOA, PFHxA, PFBS and PFHpA and FHEA, 6:2 FTS, FOET, FHET, PFHxS, PFOS, and PFNA respectively. A component with high loadings of so much of PFASs could suggest a mixture of pollutants. This can be justified by the precipitation and storm-water run-off during the wet season, resulting in a mixture of sources. As shown in Figure 10.13, NW-B3 and NW-B4 were closely related. This pattern can also be seen with NW-T3 and NW-B5; NW-W2B and NW-W2A; NW-B1 and NW-2S. These closely related may share similar sources

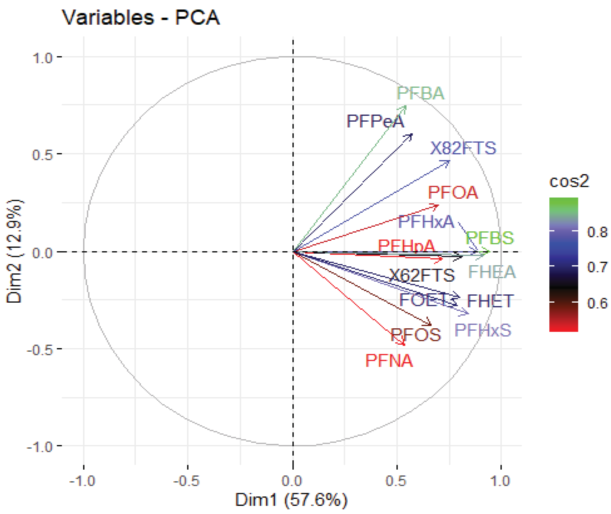

Figure 10.12: PCA of PFASs congener contributions and their relationships

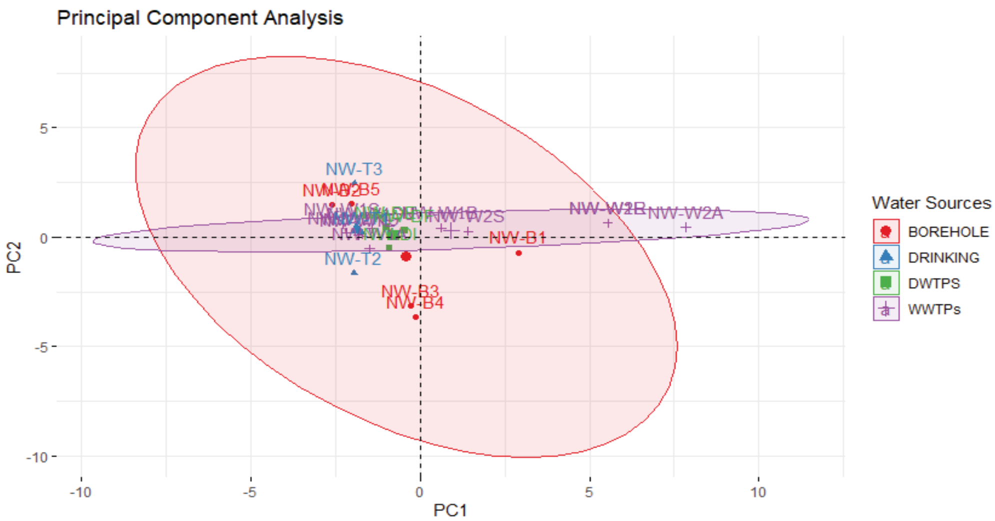

Figure 10.13: PCA of sampling sites and their relationships.

10.5 SUMMARY

Noticeable variations of PFASs were observed for PFBA, PFOA, 8:2 FTS, FHEA, FOET and FHET in both dry and wet seasons for DWTP. Similar pattern was observed for WWTP samples collected in dry and wet seasons. Huge variations were observed for concentrations of PFOA and PFOS in activated sludge plant 1 and 2. Wang et al. (2020) reported PFBA, PFOS and PFBS and PFBS, PFOS and PFHxA as the main contributors of PFASs concentration in surface water and sediments in dry and wet seasons, respectively. In the current study, PFBA, PFHxA, and PFOA, including PFASs precursors (6:2 FTS, 8:2 FTS, FHEA, FOET and FOET) contributed more in dry season; whereas PFOS, PFOA and PFHpA, PFBA, PFHxA and FOET were the main contributors during wet season. Short chain PFASs were detected in all the samples in both dry and wet seasons; whereas long chain PFASs were detected in dry season more than the wet. The telomers featured fairly well in other samples except groundwater. PFASs were detected at higher concentrations in dry season than in the wet, probably because of dilution effect of precipitation during dry season. Compared with reports on the levels of PFASs in South African waters, the levels obtained in the present report are higher, albeit lower than the levels from Germany (Table 10.7).

Table 10.7: Comparison of PFASs concentrations obtained in current study with other studies.

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.8	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area) 2-61 (Rhine River)	Skutlarek et al., 2006
Shandong Province	13.1-69,23	Chen et al., 2017
Liaoning Province	22.4-26,73	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
Gauteng Province South Africa (Dam river)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al., 2014,
Vaal River South Africa (River water)	<LOQ -38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
Northwest Province South Africa (groundwater)	**<LOD-1097**	**This study**
Northwest Province South Africa (wastewater treatment plant)	**<LOD-4899**	**This study**
Northwest Province South Africa (Drinking water)	**<LOD-50**	**This study**

CHAPTER 11: PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER IN THE WESTERN CAPE PROVINCE

11.1 SAMPLING STRATEGY

11.1.1 Location and description of sampling sites

Water samples were collected from Cape Town and Diep River in the Western Cape province during the wet season. Figure 11.1 shows the land use map within the vicinity of sampling sites. The water samples were collected during wet months (October-April). The following water systems were targeted in the province

- Tap water (WC-BT)
- Surface water (river water) and
- Wastewater treatment plant (WC-SE effluent)

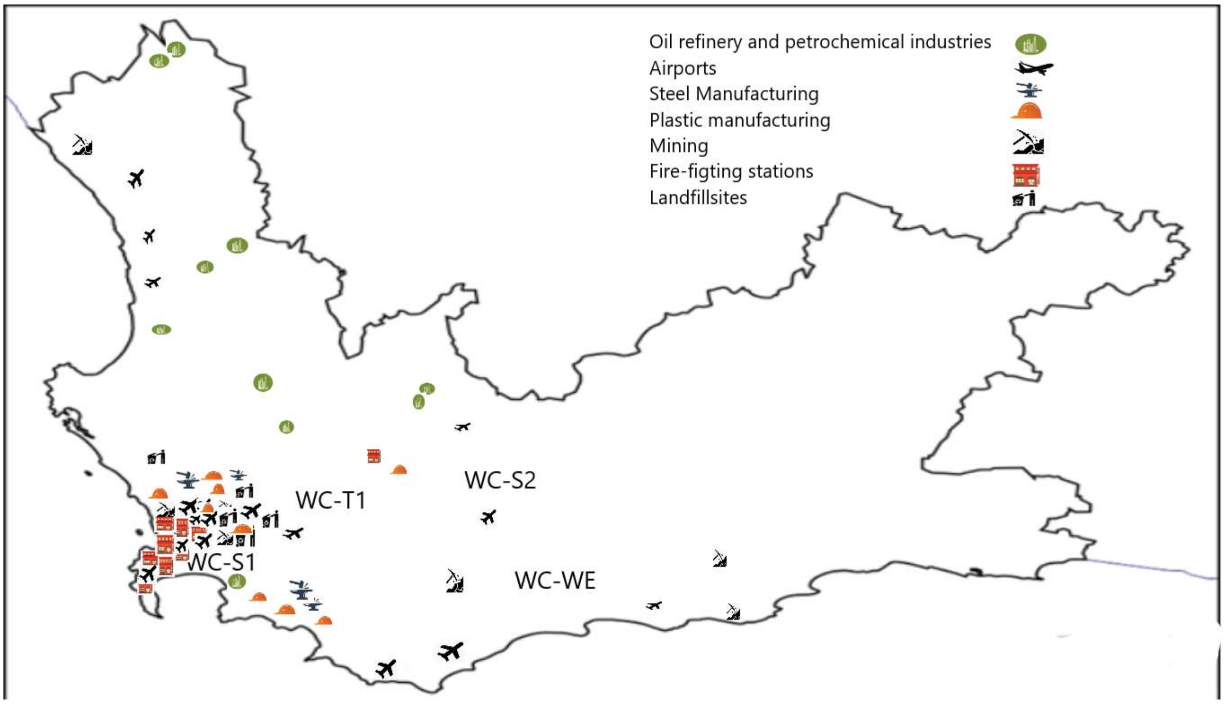

Figure 11.1: Land use map and sampling sites in Western Cape.

11.1.2 Land use map and sample collection sites

Table 11.1 provides details on the list of sampling points, water sample types collected and the timing of sample collection in the Western Cape. Grab samples were collected and prepared for analysis as described in Chapter 3.

Table 11.1: Sampling sites in Western Cape with coordinates

Site No	Site location	Site coordinates
1	WC-BT	-33.930051, 18.637753
2	Diep River	-33.88156, 18.4895
3	Plankenburg River	-33.93125, 18.85181
4	WC-SE	-33.946234, 18.822940

11.2 SAMPLE ANALYSIS AND SAMPLE EXTRACTION METHOD VALIDATION

The samples collected were analysed as described in Chapter 2. Table 11.2 shows the mean recoveries and standard deviations for blanks. The recoveries range from 66.10-111.6%. Apart from blank 2 with 66.10% and 66.72% the recoveries for the other blanks are within the acceptable range of 70-150%. In Table 11.3 are the mean recoveries and standard deviations for tap and river water and WWTP effluent. As can be seen in Table 11.3, the recoveries range from 66.10-138.4%. Apart from p11 with 66.10% for MPFHxS the recoveries for the other blanks are within the acceptable range of 70-120%. Table 11.4: shows the mean concentrations and standard deviations of PFASs in blanks. The mean concentrations range from <LOD-7.78 ng/L. PFHxA was detected in all the blanks with blank 4 exhibiting the highest concentration (Table 14.4). The following PFASs were not detected in any of the blanks: PFHxA. PFUDA, 4:2FTS, L-PFOS, PFHpS, PFDoA, PFODA, L-PFDS and PFHxDA.

Table 11.2: Percentage recoveries of surrogate standards in blanks

	Samples – Surrogate recoveries (%) ± Standard deviation				
Surrogates	**Blank 1**	**Blank 2**	**Blank 3**	**Blank 4**	**FB**
MPFNA	90.18 ±6.00	66.72 ±11.19	111.2±41.39	77.05 ±5.21	99.06 ±7.45
MPFUdA	93.52±18.37	102.6 ±0.55	84.62 ±8.17	86.94 ±6.22	93.66 ±7.39
MPFHxS	99.25±23.83	66.10 ±0.92	104.2 ±8.99	68.66 ±1.39	100.4 ±13.48

Table 11.3: Percentage recoveries of surrogate standards in tap and river water and WWTP effluent.

Surrogates	Blankenburg River	WC-BT	WC-SE	Diep River
MPFNA	107.4±6.38	134.7±10.47	116.8±2.04	107.9±9.76
MPFUdA	106.8±10.32	105.0±7.73	137.6±5.51	138.4±17.26
MPFHxS	159.1±2.31	69.66±13.03	86.39±8.55	97.75±12.15

Table 11.4: Mean concentrations and standard deviations of PFASs in blanks

	Samples – Mean concentrations (ng/L) ± standard deviation				
Compound	**Blank 1**	**Blank 2**	**Blank 3**	**Blank 4**	**FB**
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	0.721 ±0.44	0.443 ±0.06	1.59 ±1.14	7.78±2.37	0.219±0.11
PFPeA	1.00 ±0.45	0.498 ±0.48	0.789 ±0.20	<LOD	0.470 ±0.02
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTS	<LOD	<LOD	<LOD	0.559±3.14	<LOD
PFHpA	<LOD	<LOD	0.522±0.052	4.90±0.51	<LOD
PFNA	<LOD	<LOD	<LOD	<LOD	0.0485±0.015
L-PFBS	<LOD	<LOD	<LOD	0.0255±0.010	<LOD
L-PFHxS	<LOD	<LOD	<LOD	<LOD	0.391±0.42

	Samples – Mean concentrations (ng/L) ± standard deviation				
Compound	**Blank 1**	**Blank 2**	**Blank 3**	**Blank 4**	**FB**
L-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD
PFOA	0.665±0.08	<LOD	<LOD	<LOD	8.70±1.23
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD
PFODA	<LOD	<LOD	<LOD	<LOD	<LOD
L-PFDS	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD

11.3 DISTRIBUTION AND POSSIBLE SOURCES OF PER- AND POLYFLUOROALKYL SUBSTANCES IN WATER

11.3.1 Distribution of PFASs in various water sources

As can be seen in Table 11.5, PFDoA, PFODA, L-PFDS and PFHxDA were not detected in any of the samples. The overall range of concentrations observed ranged from <LOD-123 ng/L with 8:2 FTS showing the highest concentration of 123.2 ng/L in Stellenbosch WWTP.

Table 11.5: Mean concentrations (ng/L) of PFASs in tap and river water, WWTP effluent

Compds	Plankenburg River	WC-BT	WC-SE	Diep River
PFUdA	0.270 ±0.06	<LOD	2.82±0.71	0.0269±0.02
PFHxA	24.7±1.89	5.95±1.33	64.9±3.14	35.05±1.04
PFPeA	3.30±0.80	0.528±0.11	1.25±0.09	2.51±0.08
4:2 FTS	<LOD	<LOD	1.29±0.04	<LOD
8:2 FTS	15.61±1.14	0.662±1.03	123.2±1.41	14.7±1.34
PFHpA	<LOD	1.04±0.17	3.72±0.79	14.8±0.58
PFNA	4.23±0.09	<LOD	3.51±0.98	12.8±0.50
L-PFBS	<LOD	<LOD	9.47±1.96	2.43±0.76
L-PFHxS	<LOD	3.21±1.60	27.0±15.15	42.8±8.71
L-PFOS	<LOD	<LOD	63.06±19.26	24.3±0.44
PFHpS	<LOD	<LOD	72.43±10.02	<LOD
PFOA	<LOD	3.77±1.14	93.4±9.14	34.3±0.75
PFDoA	<LOD	<LOD	<LOD	<LOD
PFODA	<LOD	<LOD	<LOD	<LOD
L-PFDS	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD

11.4 SUMMARY

Shown in Table 11.6 are the ranges of PFASs concentrations in different water samples compared to other studies. The ranges for Cape Town are relatively lower than the PFASs concentrations in other studies. However, PFASs detected in drinking water is still cause for concern.

Table 11.6: Comparison of PFASs concentrations obtained in current study with other studies

Location	PFASs concentration (ng/L)	Reference
Shangai and Kunshan	39-212	Lu et al., 2015
Zheijiang Province	0.68-146	
China	5.83-120.8	Cao et al., 2019
Vietnam	0.09-18	Duong et al., 2015
Singapore	1-156	Nguyen et al., 2011
India	1.3-15.9	Sharma et al., 2016
Korean Rivers and Lakes	1.17-40.63	Lam et al., 2014
Germany Rivers	2-4,385 (Ruhr Area)	Skutlarek et al., 2006
	2-61 (Rhine River)	
Shandong Province	13.1-69,23	Chen et al., 2017
Liaoning Province	22.4-26,73	
Uganda	1.0-14	Dalahmeh et al., 2018
Maltese (rainwater)	ND-16	Sammut et al., 2017
China (rainwater)	13.4-542.2	Guo Hi Lu et al., 2018
Gauteng Province South Africa (Dam river)	1.38-346.32 and 2.31-262.29	Batayi et al., 2020
Cape Town South Africa (River water)	47-314	Mudumbi et al., 2014,
Vaal River South Africa (River water)	<LOQ -38.5	Groffen et al., 2018
South Africa (Sea water)	0.01-1.06	Ojemaye et al., 2019
Cape Town South Africa (River)	**<LOD-42.8**	**This study**
Cape Town South Africa (wastewater treatment plant)	**<LOD-93.4**	**This study**
Cape Town South Africa (Drinking water)	**<LOD-5.95**	**This study**

CHAPTER 12: EVALUATING THE TOXICITY OF WATER SOURCES AND IMPLICATIONS FOR WATER SAFETY AND HUMAN HEALTH

12.1 SAMPLING STRATEGY

Water samples collected from the Northern Cape and Gauteng provinces during both the wet (October-April) and dry (June-August) seasons was used for this evaluation. Sampling was conducted as described in Chapter 3.

12.2 USING THE YES ASSAY TO SCREEN ESTROGENIC ACTIVITY IN WATER SAMPLES

Sample preparation for screening estrogenic activity was conducted as described in Chapter 3. As shown in Table 12.1, estrogenic activity was assessed using YES in 14 samples collected from various matrices in the Northern Cape and Gauteng provinces. As can be seen in Table 12.1 the following samples were <LOD for both the dry and wet seasons, NC-DW5, NC-WW2; whereas samples NC-DW2 and GP-BTW2 were also below the <LOD in wet season. Additionally, only GP-BW1 was < LOD throughout the dry season.

Table 12.1: Estrogenic activity of water extracts collected from selected sites in Northern Cape and Gauteng using Yeast estrogenic Bioassay

Province	Sample code	Sample type	Dry season	Wet season
			Estradiol equivalents (EEq) in ng/L	
Northern Cape	NC-WW1	Raw Wastewater	117±1.4*	150.6±35.8*
	NC-WW2	Treated wastewater	<LOD	<LOD/<LOQ
	NC-WW3	Raw wastewater	593±23*	718±15.8*
	NC-WW4	Treated wastewater	5.451±1.0*	5.8±0.22
	NC-DW1	Raw Drinking water	0.329±0.008	0.712±0.090
	NC-DW2	Treated drinking water	0.163±0.026	<LOD/<LOQ
	NC-DW3	Raw water	0.154±0.02*	0.543±0.033
	NC-DW4	Treated drinking water	2.374±0.35*	13.32±3.09*
	NC-DW5	Treated drinking water	<LOD/<LOQ	<LOD/<LOQ
	Blank	Control	<LOD/<LOQ	<LOD/<LOQ
Gauteng	GP-BTW1	Borehole tap	0.179±0.020*	0.149±0.016
	GP-BTW2	water	0.584±0.044	0.890±0.125

Province	Sample code	Sample type	Dry season	Wet season
			Estradiol equivalents (EEq) in ng/L	
	GP-TW1	Tap water	0.334±0.0078	<LOD/<LOQ
	GP-TW2		5.00±.0.5*	0.500±0.023
	GP-BW1	Landfill borehole	<LOD/<LOQ	3.26±0.37
	GP-BW2	monitoring water	0.608±0.053*	0.357±0.015
	Blank	Control	<LOD/<LOQ	<LOD/<LOQ

*Cytotoxicity observed; below limit of detection(<DL)

All blank samples did not show any estrogenic activity as shown in Table 13.1. A trigger value for endocrine disrupting chemicals (EDCs) in drinking water, a framework guideline of 0.7 ng/L for estrogenic activity has been recommended in South Africa (Genthe et al., 2010). Samples GP-BTW1, GP-TW1, and GP-BW2 did not exceed the trigger value during the wet and dry seasons. While during the dry season, samples GP-BTW2 and GP-BW1 exceeded the trigger value.

Estrogenic activity in raw wastewater for samples NC-WWI (150.6±35.8 ng/L) and NC-WW3 (718±15.8 ng/L) was higher in wet season, compared to the dry season which had EEq values of 117±1.4 ng/L (NC-WW1) and 593±23 ng/L (NC-WW3). A similar pattern was seen in treated wastewater (NC-WW4), with a concentration of 5.451±1.0 ng/L (dry season) and 5.8±0.22 ng/L (wet season). In general, estrogenic activity was higher in influent than in effluents. Bistan et al. (2013) observed a similar pattern. The decrease of EDC in effluents can possibly be attributed to the removal of estrogens and xenoestrogens during treatment processes in WWTPs (Bistan et al., 2013).

Increase in estrogenic activity was observed in raw drinking water samples, NC-DW1 (from 0.329±0.008 to 0.712±0.090 ng/L) and NC-DW3 (from 0.154±0.02 to 0.543±0.033 ng/L) during the wet season. Similarly, estrogenic activity increased in treated drinking water for samples NC-DW4 (from 2.374±0.35 to 13.32±3.09 ng/L) during the wet season. In contrast, a decrease in treated drinking water was detected for sample NC-DW2 (0.163±0.026-<LOD). The decrease of estrogen activity in the final treated drinking water possibly indicates the ability of some treatment plant to remove EDC. Dias et al., (2015) reported that chlorination was effective in reducing EDCs in water treatment plants.

For sample GP-BTW1 (0.1490±.016 ng/L), a decrease was seen in borehole tap drinking water samples compared to the dry season. In contrast to the dry season, there was an increase at sampling site GP-BTW2 (from 0.584±0.044 to 0.890±0.125 ng/L) during the rainy season. Additionally, a decline in estrogenic activity was recorded for samples GP-TW1 and GP-TW2 in the tap water sample. An increase in estrogenic activity was observed in the landfill monitoring borehole samples at sampling site GP-BW1 (from <LOD to 3.26±0.37 ng/L), whereas the estrogenic activity in sample GP-BW2 (from 0.608±0.053 to 0.357±0.015 ng/L) declined in wet season. Zhai et al. (2010); Beck et al. (2005) also observed higher estrogenic activity during the dry season compared to the wet season.

The highest EEq value was measured in wastewater for sample NC-WW2 (718±15.8 ng/L). While a prevalent EEq value of 13.32±3.09 ng/L was measured as in drinking water at for sample NC-DW4. In tap water a dominant EEq value of 5.00±.0.5 ng/L*(GP-TW2) and in landfill monitoring borehole water a greater EEq value of 3.26±0.37 ng/L was observed at sampling point GP-BW1.

Out of the 14 samples, five water samples from the Northern Cape and one from Gauteng both exhibited some cytotoxicity, which resulted in an inhibition of yeast growth within a range of 8.3-50% (Table 12.2). Per-and polyfluorene alkyl substances present in the sample may be the cause of the inhibition. It is noteworthy that cytotoxicity may conceal or cause estrogenic activity to be underestimated (Beck et al., 2006; Bistan et al., 2012; de Jager et al., 2013). Because of the cytotoxicity, estrogenic activity exhibited by samples NC-WW1 (dry and wet), NC-WW3 (dry and wet), NC-WW4 (dry), NC-DW3 (dry), NC-DW5 (dry), and GP-TW2 (dry) may have been underestimated.

Table 12.2: Inhibition growth of yeast in water samples

Sample code	Cytotoxicity (inhibition %)	
	Dry season	Wet season
NC-WW1	42	33
NC-WW3	50	50
NC-WW4	8.3	
NC-DW4	8.3	
NC-DW5	17	
GP-TW2	25	

12.3 USING THE YES BIOASSAY FOR SCREENING THE TOXICITY OF PER- AND POLYFLUOROALKYL SUBSTANCES TOXICITY

Estrogenic activity and cytotoxicity were evident in most of the samples subjected to bioassay test. Over time of the two sampling periods, estrogenic activity, was detected in 12 of the 14 samples. Whereas cytotoxicity was determined in 9 of the 14 samples. In order to ascertain whether the observed estrogenic and cytotoxic activities in the samples was caused by PFASs chemicals, 19 PFASs standards (Table 12.3) were subjected to YES bioassay test.

Table 12.3: List of per- and polyfluoroalkyl substances used in this study

ANALYTES	ACRONYMS
PERFLUOROALKYLCARBOXYLIC ACIDS	PFCA
Perfluoro-n-butanoic acid	PFBA
Perfluoro-n-octanoic acid	PFOA
Perfluoro-n-dodecanoic acid	PFDoA
Perfluoro-n-heptanoic acid	PFHpA
Perfluoro-n-hexanoic acid	PFHxA
Perfluoro-n-hexadecenoic acid	PFHxDA
Perfluoro-n-nonanoic acid	PFNA
Perfluoro-n-pentanoic acid	PFPeA
Perfluoro-n-undecanoic acid	PFUdA
PERFLUOROALKYLSULFONATES	
Sodium perfluoro-1-hexanesulfonate	L-PFHxS
Potassium perfluoro-1-butanesulfonate	L-PFBS
Sodium perfluoro-1-decanesulfonate	L-PFDS
Sodium perfluoro-1-octanesulfonate	L-PFOS

ANALYTES	ACRONYMS
Fluorinated telomer sulfonates	
1H, 1H, 2H, 2H-perfluorohexane sulfonic acid	4:2 FTS
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid	6:2 FTS
FLOUROTELMERS ALCOHOLS	
2-perfluorohexyl ethanoic acid	FHEA
2-perflouroooctyl ethanol	FOET
2-Perflourohexyl ethanol (6:2)	FHET

The target chemicals shown in Table 12.3 were assessed in the YES bioassay. Out of all the compounds shown in Table 12.3, only PFOS showed estrogenic activity (Figure 12.1). In contrast, Sonthithai et al., (2016) found that PFOS did not possess estrogenic activity when exposed to T47D human breast cancer cells. Moreover, none of the compounds showed toxicity at the tested concentrations. Plots of positive estrogenic responses of PFOS is shown in Figure 12.2 and an example of the non-responsive curve in Figure 14.3 using 4:2 FTS.

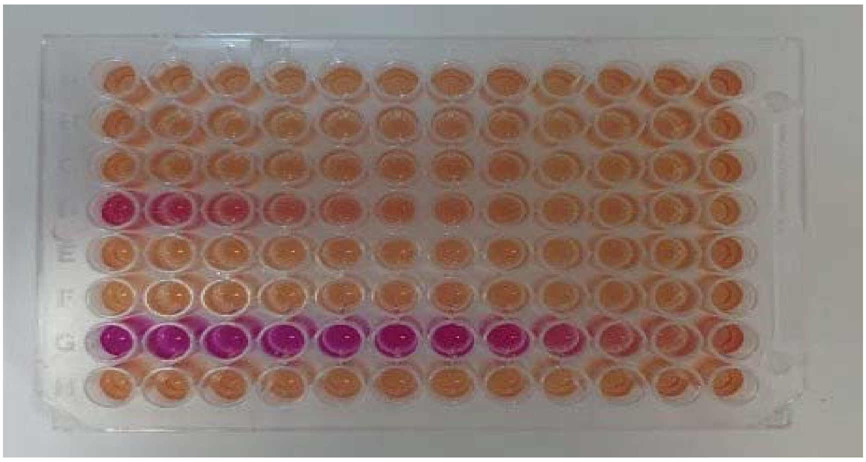

Figure 12.1: Plate showing response of the yeast screen to PFASs (Row D = PFOS, row G = estradiol used as positive control).

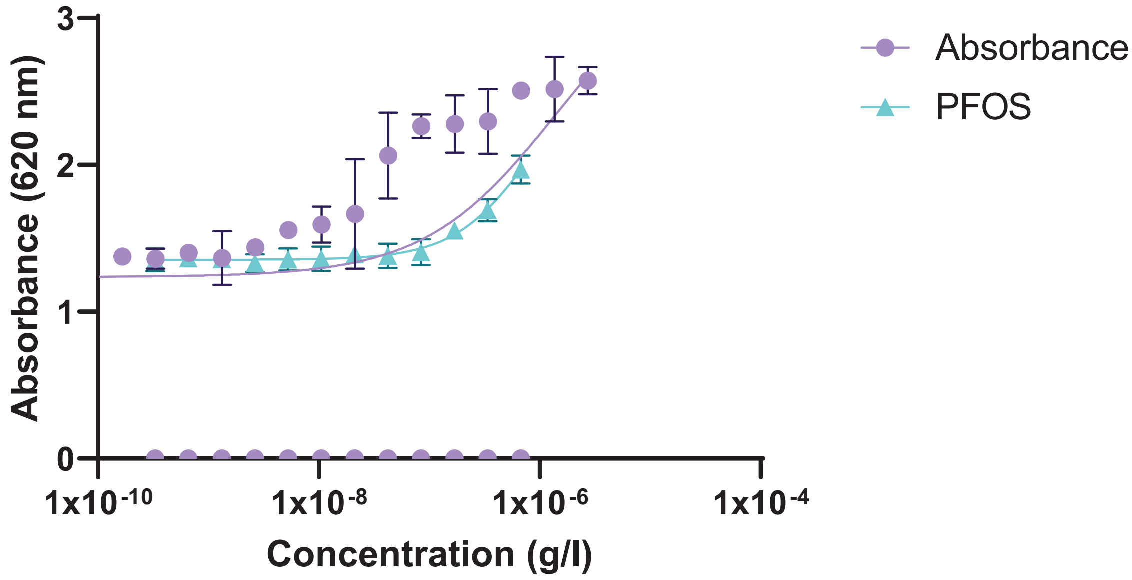

Figure 12.2: Estrogenic response of PFOS in the YES bioassay (Data points represent the average ± SD (n=3).

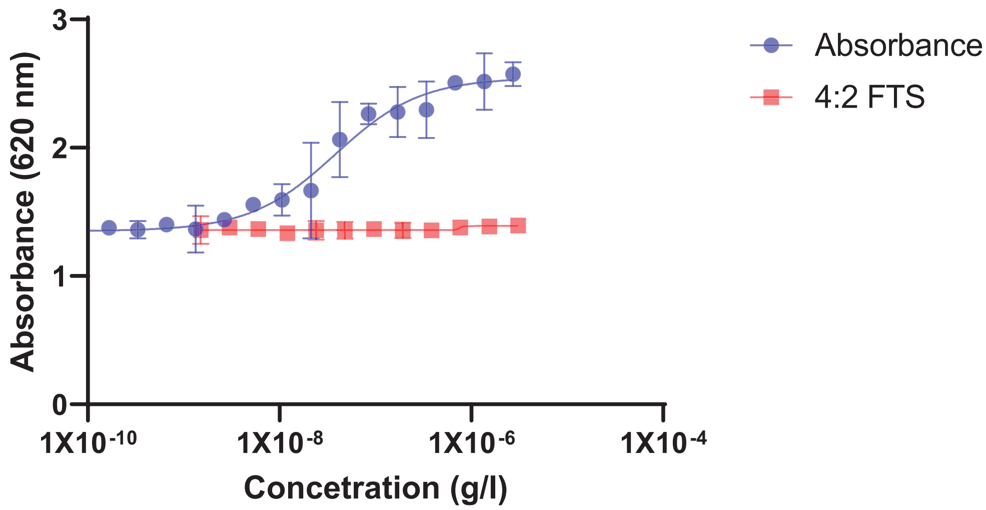

Figure 12.3: Estrogenic response of 4:2 FTS in the YES bioassay (Data points represent the average ± SD (n=3).

12.4 TRACE METAL ANALYSIS TO EVALUATE METAL TOXICITY IN SAMPLES

Because PFOS was the only PFAS chemicals with positive estrogenic response, it was deemed necessary to subject the water samples to trace metal analysis. A number of trace metals such as cadmium (Cd), arsenic (As), lead (Pb) and others are known to have estrogenic/cytotoxic characteristics and therefore, their presence in the water samples may have also contributed to the observed estrogenic/cytotoxic activities in the samples. Sample preparation for trace metal analysis is as described in Chapter 3.

Table 12.4 shows the concentrations of the targeted trace metals in the samples. The concentration range across all the sample was 0.01-513 ug/L. WHO trace metals concentrations considered safe in drinking water range up to 0.003-3.0 ug/L (WHO 2006). Although not all the water source samples analysed were for drinking purposes, the concentrations for most of the trace metals exceeded the WHO range.

Trace metal concentrations across all the samples, was in the following descending order: Sr<Zn<Ba<Mn<Rb<Ni<Cr<Li<Cu<Vn<Ti<Se<Ar<As<Pb<La<Pt<Mo<U<Co<Sn<Ti<Te<W<Sb<Cs<Bi<Cd<Be. For examples, trace metals such as cadmium, antimony, barium, chromium, copper, zinc, lead, mercury, nickel, arsenic, aluminium, cobalt, and mercury, have shown to exert metalloestrogens with estrogenic activity (Denier et al. 2009). Due to the presence of trace metals in the water samples, it is possible that the estrogenic activity identified in the water samples as mentioned in Table 12.1, may have also been caused by the trace metals. A number of these trace metals are used for nanoparticle production and are found in a variety of consumer products such as cosmetics, household items, and processed foods and others. These metals can be released into the water environmental via several routes such as disposal of trace metal containing wastes, illegal dumping of trace metal-containing waste on river banks and others. Of the “representative metals” listed in Table 12.4, cadmium has been shown to be estrogenic and is equipotent to the effects elicited by estradiol (Byrne et al., 2013).

Table 12.4: Concentrations (µg/L) of heavy metals in environmental water samples

	NC-WW4	NC-DW1	NC-DW2	NC-WW3	NC-WW1	NC-DW3	NC-DW4	GP-TW4	GP-BW2	GP-BW1	GP-TW1	GP-TW2
Elements												
Lithium (Li)	5.31	4.86	4.98	18.2	10.9	3.28	3.38	1.91	0.912	5.58	1.90	1.81
Beryllium (Be)	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Titanium (Ti)	2.53	0.31	0.30	6.36	6.00	1.00	1.54	0.83	< 0.1	< 0.1	< 0.1	< 0.1
Vanadium (V)	3.28	1.43	1.62	8.14	4.13	13.0	5.47	3.88	0.128	0.235	3.72	3.55
Chromium (Cr)	9.61	6.51	4.90	7.88	6.35	4.31	6.02	4.56	6.83	6.99	3.89	3.03
Manganese (Mn)	116	1.29	1.70	30.08	9.00	1.34	1.34	1.46	1.57	4.68	1.36	0.701
Cobalt (Co)	0.556	0.238	0.193	0.448	0.874	0.146	0.153	0.149	0.496	0.272	0.132	0.125
Nickel (Ni)	6.79	3.41	2.78	7.61	11.3	11.7	8.29	3.17	4.91	3.54	5.36	6.64
Copper (Cu)	3.33	5.54	1.40	6.62	7.81	4.31	11.2	6.02	2.27	3.30	1.77	1.82
Zinc (Zn)	39.4	182	19.3	42.5	86.7	47.7	36.8	43.2	11.7	5.44	12.0	11.1
Arsenic (Ar)	0.797	1.78	1.19	0.442	1.00	0.275	0.241	0.764	0.290	< 0.1	0.311	0.364
Selenium (Se)	< 1.4	< 1.4	< 1.4	< 1.4	1.53	1.75	5.35	< 1.4	< 1.4	< 1.4	< 1.4	< 1.4
Rubidium (Rb)	10.0	1.72	1.68	28.5	29.0	2.26	1.99	1.92	3.87	3.09	1.44	1.55
Strontium (Sr)	209	163	34.2	350	268	378	513	88.5	138	48.3	85.8	83.9
Molybdenum (Mo)	0.376	0.165	0.137	0.768	0.982	0.0743	0.101	0.691	0.616	0.359	0.672	0.609
Cadmium (Cd)	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07
Tin (Sn)	0.191	0.179	< 0.09	0.507	0.286	0.222	0.345	0.174	0.306	0.301	< 0.09	0.174
Antimony (Sb)	0.140	< 0.03	< 0.03	0.181	0.212	0.043	< 0.03	0.111	0.0767	0.0676	0.0789	0.101
Tellurium (Te)	< 0.09	0.145	< 0.09	0.148	0.285	0.342	0.175	0.165	0.265	0.285	0.374	0.171
Cesium (Cs)	0.134	0.127	0.116	0.156	0.144	0.0674	0.0407	0.119	0.0404	0.0617	0.0182	0.0353
Barium (Ba)	56.5	45.5	15.1	41.5	21.4	57.8	79.7	52.0	34.8	< 0.08	13.2	29.1
Lanthanum (La)	0.400	0.318	0.098	0.660	0.0574	0.870	0.130	2.96	0.0224	0.291	0.0157	0.390
Tungsten (W)	0.296	0.0408	0.0511	0.324	0.231	0.077	0.120	0.0775	0.146	0.0935	0.104	0.0587
Platinum (Pt)	0.406	0.379	0.784	0.725	0.325	0.500	0.347	0.778	0.406	0.543	0.654	0.264
Thallium (Ti)	0.286	0.209	0.199	0.201	0.225	0.165	0.167	0.173	0.254	0.236	0.161	0.133
Lead (Pb)	0.704	0.414	0.222	1.040	0.819	0.774	0.818	0.722	0.405	0.245	0.172	0.256
Bismuth (Bi)	0.0126	0.0101	0.0154	0.0292	0.0224	0.0189	0.0178	< 0.01	0.0203	0.0106	0.0116	0.0201
Uranium (U)	0.528	0.607	< 0.01	0.841	0.213	1.01	1.51	0.102	0.0732	0.0139	0.107	0.102

12.5 SUMMARY

Over the two sampling periods, estrogenic activity, was detected in 12 out of 14 samples tested. Whereas cytotoxicity was observed in 9 out of 14 samples. In order to ascertain whether the observed estrogenic and cytotoxic activities in the samples was caused by PFASs chemicals, 19 PFASs standards were subjected to YES bioassay test. Out of all the compounds tested for estrogenic activity, only PFOS showed positive estrogenic activity. Due to the presence of trace metals in the water samples, it is possible that the estrogenic activity identified in the water samples, may have also been caused by the trace metals. A number of these trace metals are used for nanoparticle production and are found in a variety of consumer products such as cosmetics, household items, and processed foods and others.

CHAPTER 13: CONCLUSION AND RECOMMENDATION

13.1 CONCLUSIONS

The nationwide study on PFASs in water resources generated information on:

- Emerging PFASs such as sulphonate and alcohol telomers among others using water samples collected from Gauteng province as benchmark;
- Target analytical method for the identification of some emerging and legacy PFASs;
- Concentrations of PFASs in the following water samples collected across the provinces using a target approach for:
    - Wastewater treatment plants;
    - Drinking water treatment plants;
    - Groundwater (boreholes);
    - Rivers and dams
    - Bottled water;
    - Tap water and
    - Rainwater

- Use of multivariate statistical analysis (PCA) to establish inter-relationships between different groups of FASs, and sample sites and to establish possible sources.

- Yeast bioassay method to test for estrogenic and cytotoxicity in the water samples collected from Northern Cape as a benchmark.

The conclusions for each province are as follows:

Eastern Cape

The results from Eastern Cape Province, show detectable concentrations especially for the short chain PFASs. Long chain PFASs were detected at lower levels, suggesting that they are less prevalent in the samples collected. Another reason for non-detection of long chain may be due to their low solubility in water. The impact of the restrictions and regulations placed on long chain PFASs and use of shorter chain as alternatives was visible in the results reported in the province. The Eastern Cape was mostly dominated by PFCAs. The detected PFASs results did not exceed the recommended lifetime health advisory of 70 ng/L for PFAS in all the water collected. However, the increased concentrations detected in drinking water compared to source water is a cause for concern.

Free State

Four water sampling sources namely, wastewater treatment plant, tap water, river and drinking water treatment plant were studied for presence of selected 21 PFASs. Of the 21 PFASs, only three compounds 6:2 FTS, FOET and FHET were found to be prevalent throughout the sampling locations. The following compounds PFDoA, PFUdA, 8-2 FTS, 4-2 FTS, PFHxDA, PFNA, PFODA, L-PFHxS, L-PFOS, PFOA, L-PFBS, L-PFDS,LPFHpS were <LOD. PCA depicted clustering of PFASs and as well the sampling sources, thus suggesting different origins of contaminations.

Gauteng

PFASs were present in water samples including rainwater collected in Gauteng Province. The following PFASs were detected in all the surface water samples analysed: *PFBA*, **PFOA**, PFPeA, PFHxA *and PFHpA*. PFDA and **PFNA**) were detected in 14 samples; while LPFBS and LPFdUA were detected in nine samples.

LPFPeS and LPFOS were detected in four and two samples respectively; while LPFHpS, LPFDS, PFTrDA and PFTeDA were all below the LOD. PFBA exhibited the highest concentration in surface water. The wastewater samples exhibited the highest concentrations. High concentrations were also recorded for river, drinking water treatment plant and rainwater. The PFASs detected in the branded bottled drinking water in the present study are higher than the IBWA operational limits of 5 ng/L for a single PFASs and 10 ng/L for more than one PFASs. Compared to the health advisory levels at 70 ng/L, by the USEPA to protection its sensitive populations, from a lifetime of exposure to PFOA and PFOS from drinking water, the concentrations of PFOS and PFOA in drinking water in the present study are generally much lower.

KwaZulu-Natal

The PFASs concentrations found in various water sources range from <LOQ-42.05 ng/L; <LOD-26.30 ng/L and <LOD-20.50 ng/L for drinking, river and wastewater treatment plant water samples respectively. These ranges are relatively lower than the concentrations reported in studies conducted in South Affrica as well as China and Germany. The water samples were collected just after the heavy flooding in KwaZulu-Natal. This extreme condition may have influenced the concentrations observed and caused some dilution. Plans are underway to sample for the winter season.

Limpopo

Of the 21 PFASs measured, only four were not detected in all the water samples. The highest concentration was recorded for wastewater treatment plant, particularly the influent water samples. PFOA exhibited the highest concentration. These PFASs detected may have originated from domestic waste from the use of PFASs-containing products that are flushed into the sewerage system ending up in wastewater treatment plants, as most of the sites were observed to have similar sources in the PCA.

Mpumalanga

Both short and long chain PFASs were detected in river and borehole samples collected from Mpumalanga. The following compounds, PFHxA, PFPeA, PFHpA, PFNA and PFBS were detected in all the samples. Whereas, 8:2 FTS and PFBA were also detected in all samples except two samples. Similarly PFHxS, PFOS, PFOA and 6:2: FTS were detected in only one sample for each congener. PFOS showed the highest concentration of 92.4 ng/L for water sample obtained from Nkangala Blesbokspruit. PCA analysis showed that most PFASs shared similar pattern/sources, i.e. tendency to originate from the same source. No conclusion can be drawn at this stage until more samples have been analysed. However, with respect to sampling sites, a number of the sampling sites showed diverse sources compared to others. It is worth mentioning that water samples have recently been collected from two wastewater and drinking water treatment plants and their extractions and analysis are in progress.

Northern Cape

The presence of PFASs in wastewater treatment facilities, drinking water treatment facilities, landfill monitoring borehole water, borehole drinking water, and tap water was the main focus of this investigation. In order to look at seasonal trends of PFASs, samples were collected during the dry and rainy seasons. The study revealed a variation in concentration between the two seasons, with higher concentrations recorded during the dry season compared to the wet season. The observed difference is most likely due to differences in environmental factors, such as rainfall. 6:2 FTS, PFOA, PFOS, FOET, PFBA, PFHxS and FHEA were the most abundant compound, with very high concentrations across all the sampling stations. Principal component analyses show that the observed PFASs are clustered indicating some relationship with their sources. This also applies to the different water sources with the origin of the PFASs observed in them.

North West

The PFASs concentrations found in various water sources range from <LOQ-15.8 ng/L; <LOD-986 ng/L and <LOD-230.50 ng/L for groundwater, wastewater and drinking respectively. These ranges are relatively higher than the concentrations reported in studies conducted in South Affrica. The concentrations of PFASs in dry

season were significantly higher than the wet season. In addition to the traditional PFASs commonly found in water, the telomers, particularly 8:2 FOET exhibited high concentrations in some water samples. Short chain PFASs were more dominant than the long chains in both dry and wet seasons. It is cause for concern that a wide range of PFASs were detected in drinking tap water.

Western Cape
The levels of PFASs detected in Cape Town is relatively lower than the levels reported in other studies. Further information on PFASs in Western Cape will no long appear in our report since monitoring of PFASs in the Western Cape has been allocated to the group in Stellenbosch University.

Bioassay
Estrogenic activity and cytotoxicity were fully evident in the bioassay. Over time of the two sampling periods, estrogenic activity, was detected in 12 of the 14 samples. Whereas cytotoxicity was determined in 9 of the 14 samples. The water samples EEq ranged from below limit of quantification to a maximum of 718 ng. These are significantly higher than the recommended trigger value for drinking water. Compared to the dry season, a higher EDC concentration was observed during the wet season, notably in wastewater and drinking water treatment facilities. This suggested that current treatment techniques are unable to remove EDC chemicals.
Of the 18 standard PFASs chemicals subjected to bioassay test, only PFOS exhibited cytotoxicity. Therefore, the observed estrogenic activity and cytotoxicity in the water samples may have been caused by PFOS, which demonstrated estrogenic action in yeast bioassays. However, other contaminants in the water samples such as trace metals may have also contributed to the concern observed estrogenic action since metals that exert metalloestrogens were detected in the water samples. In order to determine the cause of estrogenic activity and cytotoxicity in the water samples, extensive chemical monitoring should be done. Furthermore, the biological effects of EDCs on a living subject should also be evaluated by in vivo experiments.

13.2 RECOMMENDATIONS

The current nationwide exercise has shown that these chemicals are in our water system. The importance of monitoring of POP chemicals such as PFASs, without any doubt, is an expensive exercise. However, regular monitoring of these chemicals is extremely important, particularly in water system because it is via this process that proper informed decision can be made to regulated and control the presence of these in water systems.

REFERENCES

3M Company. (2000). Voluntary Use and Exposure Information Profile: Perfluorooctanoic Acid and Salts. pp. 1-28.

3M Company. (2005). A 28-day oral (gavage) toxicity study of T-7485 in Sprague-Dawley rats. Study no. 132-007, 3M Corporate Toxicology, St Paul, MN. P-00-1085.

Adeleye A.P., 2016, Perfluorinated Compounds, Bisphenol A Acetaminophen in Selected Waste Water Treatment Plants in and around Cape Town, South Africa. Master of Technology (Chemistry) thesis. Cape Peninsula University of Technology.

Ahrens L., Siebert U., Ebinghaus, R. 2009. Total body burden and tissue distribution of polyfluorinated compounds in harbour seals (Phoca vitulina) from German Bight, Mar. Pollut. Bull., (58): pp.520-525.

Ahrens L., Yeung LWY., Taniyasu S., Lam PKS., Yamashita N. 2011. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment, Chemosphere, 85(5): pp.731-737.

Ahrens L., Bundschuh M. 2014. Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: A review, Environ. Toxicol. Chem., (33): pp. 1921-1929.

Ahrens L., Norström K., Tomas Viktor T., Cousins AP., Josefsson S. 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish, Chemosphere, (129): pp. 33-38.

Ahrens L., Gashaw H., Sjöholm M., Gebrehiwot SG., Getahun A., Derbe E., Bishop K ., Åkerblom S. 2016. Poly- and perfluoroalkylated substances (PFASs) in water, sediment and fish muscle tissue from Lake Tana, Ethiopia and implications for human exposure, Chemosphere, (165): pp.352-357.

Alexander BH. 2001a. Mortality study of workers employed at the 3M Cottage Grove facility. Final Report. April 26, 2001. Division of Environmental and Occupational Health, School of Public Health, University of Minnesota, US EPA Administrative Record, AR-226-1030a018.

Alexander BH., Olsen GW., Burris JM., Mandel JH., Mandel JS. 2003. Mortality of employees of a perfluorooctanesulfonyl fluoride manufacturing facility, Occup. Environ. Med., (60): pp. 722-729.

Alexander BH., and Grice M. 2006. Self-Reported medical conditions in perfluorooctanesulfonyl fluoride manufacturing workers. Final Report. USEPA Administrative Record, AR-226-3677.

An W., Duan L., Zhang Y., Wang B., Liu CS., Wang F., Sui Q., Xu D. 2021. Occurrence, spatiotemporal distribution, seasonal and annual variation, and source apportionment of poly- and perfluoroalkyl substances (PFASs) in the northwest of Tai Lake Basin, China. Journal of Hazardous Materials, 416:125-144.

Andersen ME., Butenhoff JL., Chang SC., Farrar DG., Kennedy GL., Lau C., Olsen GW., Seed J., Wallace KB. 2008. Perfluoroalkyl acids and related chemistries-toxicokinetics and modes of action, Toxicol. Sci., 102(1), 3-14.
ATSDR. (2018). Toxicological Profile for Perfluoroalkyls Draft for Public Comment, U.S. Department of Health and Human Services.

Arditsoglou, A. and Voutsa, D. (2008) 'Passive sampling of selected endocrine disrupting compounds using polar organic chemical integrative samplers', Environmental Pollution, 156(2), pp. 316-324..

Arinaitwe K., Keltsch N., Taabu-Munyaho A., Reemtsma T. and Berger U., 2021. Perfluoroalkyl substances (PFASs) in the Ugandan waters of Lake Victoria: Spatial distribution, catchment release and public exposure risk via municipal water consumption. Sci Total Environ. 78: pp.146-170.

Arp HPH., Niederer C. and Goss K. 2006. Predicting the portioning behaviour of various highly fluorinated compounds. Environ. Sci. Technol, 40(23): pp. 7298-7304.

Banks RE., Tatlow JC. 1994. Organofluorine chemistry: nomenclature and historical landmarks. In: Organofluorine Chemistry. Boston: Springer US, 1994: pp.1-24

Barber JL., Berger U., Chaemfa C., Huber S., Jahnke A., Temme C., Jones KC. 2007 Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. J Environ Monit 9: pp.530-541.

Batayi B., Okonkwo, OJ., Daso, AP. 2021. Poly- and perfluoroalkyl substances in environmental water from the Hartbeespoort and Roodeplaat Dams, South Africa, Water SA, (1): pp.54-66.

Becker AM., Gerstmann S., Frank H. 2008. Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main river, Bayreuth, Germany, Environ. Pollut, (156): pp. 818-820.

Beck IC., Bruhn R., and Gandrass J. 2006. Analysis of estrogenic activity in coastal surface waters of the Baltic Sea using the yeast estrogen screen. *Chemosphere*, *63*(11), 1870-1878. https://doi.org/10.1016/J.CHEMOSPHERE.2005.10.022

Bistan, M., Podgorelec, M., R. L.-F. T., & 2012, undefined. (2012). Yeast estrogen screen assay as a tool for detecting estrogenic activity of waters. *Researchgate.Net*. https://www.researchgate.net/profile/RomanaMarinsekLogar/publication/267382363_Yeast_Estrogen_Screen_Assay_as_a_Tool_for_Detecting_Estrogenic_Activity_of_Waters/links/545b7e0e0cf28779a4dd8f5f/Yeast-Estrogen-Screen-Assay-as-a-Tool-for-Detecting-Estrogenic-Activity-of-Waters.pdf

Begley TH., White K., Honigfort P., Twaroski ML., Neches R., Walker RA. 2005. Perfluorochemicals: potential sources of and migration from food packaging, Food Addit. Contam, (22): pp. 1023-1031.

Belle G., and Fossey A. and Esterhuizen L., 2018, Use of multiple indicators to assess the pollution condition of urban streams: a case study of Bloemspruit, Free State Province, South Africa, Water and Environment Journal. 34. 10.1111-12444

Beškoski VP., Takemine S., Nakano T., Beškoski LS., Gojgić-Cvijović G., Ilić M., Miletić S., Vrvi ć MM. 2013. Perfluorinated compounds in sediment samples from the wastewater canal of Pančevo (Serbia) industrial area, Chemosphere, (91): pp.1408-1415.

Berger U., Langlois I., Oehme M., Kallenborn R. 2004. Comparison of three types of mass spectrometers for HPLC/MS analysis of perfluoroalkylated substances and fluorotelomer alcohols, Eur.J.Mass Spectrom., (10): pp.579-588.

Bistan M., and Podgorelec M. 2012,. Yeast estrogen screen assay as a tool for detecting estrogenic activity of waters. *Researchgate.Net*. https://www.researchgate.net/profile/Romana-Marinsek-Logar/publication/267382363_Yeast_Estrogen_Screen_Assay_as_a_Tool_for_Detecting_Estrogenic_Activity_of_Waters/links/545b7e0e0cf28779a4dd8f5f/Yeast-Estrogen-Screen-Assay-as-a-Tool-for-Detecting-Estrogenic-Activity-of-Waters.pdf

Bjermo H., Darnerud PO., Pearson M., Barbieri HE., Lindroos AK., Nälsén C., Lindh CH., Jönsson BAG., Glynn A. 2013 Serum concentrations of perfluorinated alkyl acids and their associations with diet and personal characteristics among Swedish adults. Mol Nutr Food Res 57: pp.2206-2215.

Bolan N., Sarkar B., Yan Y., Li Q., Wijesekara H., Kannan K., Tsang DCW., Schauerte M., Bosch J., Noll H., Ok Y. S., Scheckel K., Kumpiene J., Gobindlal K., Kah M., Sperry J., Kirkham MB., Wang H., Tsang YF., Rinklebe J., 2021, Remediation of poly- and perfluoroalkyl substances (PFAS) contaminated soils – To mobilize or to immobilize or to degrade? J. Haz. Mat., 401(September 2020). https://doi.org/10.1016/j.jhazmat.2020.123892

Bossi R., Strand J., Sortkjær O., Larsen MM. 2008. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments, Environ. Int., 34 (4): pp. 443-450.

Bowman JS. 2015. Fluorotechnology is critical to modern life: the FluoroCouncil counterpoint to the Madrid Statement. Environ. Health Perspect, (123): pp. 112-128.

Bradley EL., Read WA., Castle L. 2007. Investigation into the migration potential of coating materials from cookware products. Food Addit Contam 24: pp.326-338

Buck RC., Franklin J., Berger U., Conder JM., Cousins IT., de Voogt P., Jensen AA., Kannan K., Mabury SA., van Leeuwen SPJ. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins, Integr. Environ. Assess. Manag, (7): pp. 513-541.

Buffalo City Metropolitan Municipality (BCMM), Service Delivery Report (Performance Report Part 1).

Byrne C.; Divekar SD.; Storchan GB.; Parodi DA.; Martin MB. 2013. Metals and breast cancer. J. Mamm. Glan. Biol. Neoplas. 18: pp. 63-73.

Cai MH., Yang H.Z., Xie ZY., Zhao Z., Wang F., Lu ZB., Sturm R., Ebinghaus R. 2012. Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica, Journ. Hazard Mater, (209-210): pp. 335-342.

Campo J., Pérez F., Masiá A., Picó Y., Farré, MI., Barceló D. 2015. Perfluoroalkyl substance contamination of the Llobregat River ecosystem (Mediterranean area, NE Spain), Sci. Total Environ, (503-504): pp. 48-57.

Campo J., Lorenzo M., Pérez F., Picó Y., Farré MI., Barceló, D. 2016. Analysis of the presence of perfluoroalkyl substances in water, sediment and biota of the Jucar River (E Spain). Sources, partitioning and relationships with water physical characteristics. Environmental Research, 147: pp. 503-512.

Cao X., Wang C., Lu Y., Zhang M., Khan K., Song S., Wang P., Wang C. 2019. Occurrence, sources and health risk of polyfluoroalkyl substances (PFASs) in soil, water and sediment from a drinking water source area, Ecotoxicology and Environmental Safety, (174): pp. 208-217.

Che, C., Wang J., Li L., Xu W., Liu J. 2020. Comparison of fluorotelomer alcohol emissions from wastewater treatment plants into atmospheric and aquatic environments, Environ. Inter, (139): pp.105718.

Chen MH., Ha EH., Wen TW., Su YN., Lien GW., Chen CY., Chen PC., Hsieh WS. 2012a. Perfluorinated compounds in umbilical cord blood and adverse birth outcomes. PLoS ONE, 7(8), 424-444. doi:10.1371/journal.pone.0042474.

Chen H., Zhang C., Han JB., Sun RJ., Kong XY., Wang XM., He X. 2015. Levels and spatial distribution of perfluoroalkyl substances in China Liaodong Bay basin with concentrated fluorine industry parks, Mar. Pollut. Bull, (101): pp. 965-971.

Chen S., Jiao XC., Gai N., Li XJ., Wang XC., Lu GH., Piao HT., Rao Z., Yang YL. 2016. Perfluorinated compounds in soil, surface water, and groundwater from rural areas in eastern China, Environ. Pollut, (211): pp.124-131.

Chen H., Wang, X., Zhang, C., Sun R., Han J., Han G., Yang W., He, X. 2017. Occurrence and inputs of perfluoroalkyl substances (PFASs) from rivers and drain outlets to the Bohai Sea, China, Environ. Pollut, (221): pp.234-243.

Chirikona F., Filipovic M., Ooko S., Orata F. 2015. Perfluoroalkyl acids in selected wastewater treatment plants and their discharge load within the Lake Victoria basin in Kenya, Environ. Monit. Assess, 187 (5): pp. 238-250.

Christensen K., Raymond M., Blackowicz M., Liu Y-J., Thompson B., Anderson H. 2017. Perfluoroalkyl substances and fish consumption, Environ Res, (154): pp. 145-51.

Clement RE., Taguchi VY. 1991. Techniques for the gas chromatography-mass spectrometry identification of organic compounds in effluents, Laboratory Services Branch, ISBN 0-7729-59834.

Codling G., Hosseini S., Corcoran MB., Bonina S., Lin T., Li A., Sturchio NC., Rockne KJ., Ji K., Peng H. 2018. Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes-Superior, Huron, and Michigan, Environmental Pollution, (236): pp. 373-381.

Concawe, 2016. Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS).

Costa G. (2004). Report on the meeting held on Friday 20th and Saturday 21st 2004 at the Inn at Montchanin Village (Wilmington, USA) with 3M and DuPont delegations. DuPont. Submitted to the U.S., Environmental Protection Agency, AR226-1866.

Costa G., Sartori S., Consonni D. 2009. Thirty years of medical surveillance in perfluooctanoic acid production workers, Journ al of Occup. Environ. Med., 51(3): pp. 364-372.

CTDPH. Per- and Polyfluoroalkyl Substances. https://portal.ct.gov/DPH/Drinking-Water/DWS/Per--and-Polyfluoroalkyl-Substances (accessed 23 July 2022).
MADEP. https://www.mass.gov/info-details/per-and-polyfluoroalkyl-substances-pfas> [Accessed 27 July 2022].

Dalahmeh S., Tirgani S., Komakech AJ., Niwagaba CB., Ahrens L. 2018. Per- and polyfluoroalkyl substances (PFASs) in water, soil and plants in wetlands and agricultural areas in Kampala, Uganda, Sci Total Environ, (631-632): pp. 660-667.

Daly ER., Chana BP., Talbot EA., Nassif J., Bean C., Cavalloa SJ., Metcalf E., Simonec K., Woolf AD. 2018. Per- and polyfluoroalkyl substance (PFAS) exposure assessment in a community exposed to contaminated drinking water, New Hampshire, 2015, Int. Journ. Hygiene and Environ. Health, (221): pp. 569-577.

Danish EPA. Risk assessment of fluorinated substances in cosmetic products. 2018. https://mst.dk/service/publikationer/ publikationsarkiv/2018/nov/risk-assessment-of-fluorinatedsubstances-in-cosmetic-products/

Darrow LA., Stein CR., Steenland K. 2013. Serum perfluorooctanoic acid and perfluorooctane sulfonate concentrations in relation to birth outcomes in the Mid-Ohio Valley, 2005-2010, Environ. Health Perspect, 121(10): pp. 1207-1213.

Darrow LA., Howards PP., Winquist A., Steenland K. 2014. PFOA and PFOS serum levels and miscarriage risk, Epidemiology, 25(4): pp. 505-512.

Darrow LA., Groth AC., Winquist A., Shin HM., Bartell SM., Steenland K. 2016. Modeled perfluorooctanoic acid (PFOA) exposure and liver function in a mid-Ohio Valley community, Environ. Health Perspect, 124(8): pp.1227-1233.

de Cock M., de Boer MR., Lamoree M., Legler J., van de Bor M. 2014. First year growth in relation to prenatal exposure to endocrine disruptors – a Dutch prospective cohort study, Int. Journal of Environ. Res. Public Health, 11(7): pp. 7001-7021.

De Jager C., Aneck-Hahn NH., Barnhoorn IEJ., Bornman MS., Pieters R., van Wyk JH., and van Zijl C. 2011. The Compilation of a Toolbox of Bio-assays for Detection of Estrogenic Activity in Water. WRC report number 1816/1/10. Pretoria: Water Research Commission of South Africa.

De Jager C., Aneck-Hahn NH., Swart P., Truebody B., and Zijl V. 2013. Estrogenic activity and endocrine disrupting chemical (EDC) status in water obtained from selected distribution points in Pretoria and Cape Town. *Wrc.Org.Za*. https://www.wrc.org.za/wp-content/uploads/mdocs/KV%20317-13.pdf

Denier X., Hill EM., Rotchell J. and Minier C. 2009. Estrogenic activity of cadmium, copper and zinc in the yeast estrogen screen. Toxicology in vitro, 23(4): pp.569-573.

D'Eon JC., Mabury SA. 2011. Exploring in direct sources of human exposure to per-fluoroalkyl carboxylates (PFCAs): evaluating uptake, elimination, and biotrans-formation of polyfluoroalkyl phosphate esters (PAPs) in the rat, Environ. Heal. Perspect, (119): pp. 344-350.

Ding N., Harlow SD., Batterman S., Mukherjee B., Park SK. 2020. Longitudinal trends in perfluoroalkyl and polyfluoroalkyl substances among multiethnic midlife women from 1999 to 2011: the Study of Women's Health Across the Nation. Environ Int 135: pp.105-381.

Dinglasan MJ., Yeh Y., Edwards EA., Mabury SA. 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. Environ. Sci. Technol., (38): pp. 2857-2864.

Domingo JL., Jogsten IE., Eriksson U., Martorell I., Perelló G., Nadal M., Bavel van B. 2012. Human dietary exposure to perfluoroalkyl substances in Catalonia. Spain Temporal trend Food Chem 135: pp.1575-1582

Domingo JL., Nadal M. 2017. Per- and polyfluoroalkyl substances (PFASs) in food and human dietary intake: a review of the recent scientific literature. J Agric Food Chem 65: pp.533-543.

Domingo JL., Nadal M. 2019. Human exposure to per- and polyfluoroalkyl substances (PFAS) through drinking water: a review of the recent scientific literature. Environ Res 177: pp.108-648.

Dufková V., Ĉabala R., Ševčík V. 2012. Determination of C5-C12 perfluoroalkyl carboxylic acids in river water samples in the Czech Republic by GC-MS after preconcentration, Chemosphere, (87): pp. 463-469.

Duong HT., Kadokami K., Shirasaka H., Hidaka R., Chau HTC., Kong L., Nguyen TQ., Nguyen TT. 2015. Occurrence of perfluoroalkyl acids in environmental waters in Vietnam, Chemosphere, (122): pp. 115-124.

EFSA. (2008). Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts scientific opinion of the panel on contaminants in the food chain, EFSA J., (653): pp. 1-131.

Ellis DA., Martin JW., De Silva AO., Mabury SA., Hurley MD., Sulbaek Andersen MP., Wallington TJ. 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids, Environ. Sci. Technol., (38): pp. 3316-3321.

Environmental Health Canadian. (2006). Perfluorinated carboxylic acids (PFCAs) and precursors: a proposed action plan for assessment and management. http://www.environmentaldefence.ca.

Eriksson U., Kärrman A., Rotander A., Mikkelsen B., Dam M. 2013. Perfluoroalkyl substances (PFASs) in food and water from Faroe Islands. Environ Sci Pollut Res 20: pp.7940-7948.

Essumang DK., Eshun A., Hogarh JN., Bentum JK., Adjei JK., Negishi J., Nakamichi S., Habibullah-Al-Mamun M., Masunaga S. 2017. Perfluoroalkyl acids (PFAAs) in the Pra and Kakum River basins and associated tap water in Ghana, Sci. Total Environ., (579): pp. 729-735.

European Commission. 2002. Commission decision of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Off. J. Eur. Union 2002; L221/8.

European Union. 2006. Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC. Official Journal of the European Union L 372/32.

European Union. 2013. Official Journal of the European Union, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

Falk EB., O'Donnell MB., Cascio CN., Tinney F., Kang Y., Lieberman MD., Taylor SE., An L., Resnicow K., Strecher VJ. 2015. Self-affirmation alters the brain's response to health messages and subsequent behavior change. Proc Natl Acad SciUSA 112: pp.1977-1982.

Fasano WJ., Sweeney LM., Mawn MP., Nabb DL., Szostek B., Buck RC., Gargas ML. 2009. Kinetics of 8-2 fluorotelomer alcohol and its metabolites, and liver glutathione status following daily oral dosing for 45 days in male and female rats, Chem. Biol. Interact., (180): pp. 281-295.

Fraser AJ., Webster TF., Watkins DJ., Mark J., Strynar MJ., Kato K., Calafat KM., Vieira VM., McClean MD. 2013. Polyfluorinated compounds in dust from homes, offices, and vehicles as predictors of concentrations in office workers 'serum, Environ. Int, (60): pp. 128-136.

Fromme H., Tittlemier SA., Völkel W., Wilhelm M., Twardella D. 2009. Perfluorinated compounds-exposure assessment for the general population in Western countries, Int. Journ. Hyg. Environ. Health, (212): pp.239-270.

Furl CV., Meredith CA., Strynar MJ. and Nakayama, SF. 2011. Relative importance of wastewater treatment plants and non-point sources of perfluorinated compounds to Washington State rivers. Sci Total environment. 409(15): pp.2902-2907.

Gałęzowska G., Rogowska J., Olkowska E., Ratajczyk W. and Wolska, L. 2021. Environmental risk assessment resulting from sediment contamination with perfluoroalkyl substances. Molecules, 26(1): pp. 116-135.

Gellrich V., Brunn H and Stahl T. 2013. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in mineral water and tap water. J*ournal of Environ Sci and Health*, Part A. 48(2): pp.129-135.

Genthe B., Steyn M., Aneck-Hahn NH., Van Zijl C. and De Jager C. 2010 The Feasibility of A Health Risk Assessment Framework to Derive Guidelines for Oestrogen Activity in Treated Drinking Water. WRC Report No. 1749/1/09. Water Research Commission of South Africa.

Gewurtz SB., Bhavsar SP., Crozier PW., Diamond ML., Helm PA., Marvin CH., Reiner EJ. 2009. Perfluoroalkyl contaminants in window film: indoor/outdoor, urban/rural, and winter/summer contamination and assessment of carpet as a possible source, Environmental Science & Technology, (43): pp.7317-7323.

Giesy J., Kannan K. 2001. Global distribution of perfluoroctane sulfonate in wildlife, Environ Sci Technol., (35): pp.1339-42.

Gobelius, L. et al. (2019) 'Calibration and application of passive sampling for per- and poly fluoroalkyl substances in a drinking water treatment plant', *Journal of Hazardous Materials*, 362(August 2018), pp. 230-237. doi:10.1016/j.jhazmat.2018.09.005.

Godlewska, K., Stepnowski, P. and Paszkiewicz, M. (2021) Pollutant analysis using passive samplers : principles , sorbents , calibration and applications . A review, Environmental Chemistry Letters. Springer International Publishing. doi:10.1007/s10311-020-01079-6.

González-Barreiro C., Martínez-Carballo E., Sitka A., Scharf S., Gans O. 2006. Method optimization for determination of selected perfluorinated alkylated substances in water samples, Anal Bioanal.Chem, (386): pp.2123-2132.

Goosey E., Harrad S. 2012 Perfluoroalkyl substances in UK indoor and outdoor air: spatial and seasonal variation, and implications for human exposure. Environ Int 45: pp.86-90.

Groffen T., Wepener V., Malherbe W. 2018. Distribution of Perfluorinated Compounds (PFAAs) in an aquatic food chain in the Vaal River, South Africa. Sci Total Environ 627: pp.1334-1344.

Guardian MGE., Boongaling EG., Bernardo-Boongaling, VRR., Gamonchuang J., Boontongto T., Burakham R., Arnnok P. and Aga DS., 2020. Prevalence of per-and polyfluoroalkyl substances (PFASs) in drinking and source water from two Asian countries. Chemosphere, 256: pp.127115

Guo R., Sim WJ., Lee ES., Lee JH., Oh JE. 2010. Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants, Water Res., (44): pp.3476-3486.

Guo Hui Lu, Xiao-Chun Wang, Shu Chen, Ke-Yan Tan, Nan Gai, Xiao-Cai Yin, Yong-Liang Yang & Jing Pan et al. (2018) The Extent of the Impact of a Fluorochemical Industrial Park in Eastern China on Adjacent Rural Areas. Arch Environ Contam and Toxico 74: pp.484-491

Habibullah-Al-Mamun M., Ahmed MK., Raknuzzaman M., Islam MS., Negishi J., Nakamichi S., Sekine M., Tokumura M., Masunaga S. 2016. Occurrence and distribution of perfluoroalkyl acids (PFAAs) in surface water and sediment of a tropical coastal area (Bay of Bengal coast, Bangladesh), Sci. Total Environ., (571): pp.1089-1104.

Halldorsson TI., Rytter D., Haug LS., Bech BH., Danielsen I., Becher G., Henriksen TB., Olsen SF. 2012. Prenatal exposure to perfluorooctanoate and risk of overweight at 20 years of age: A prospective cohort study, Environ. Health Perspect, 120(5): pp.668-673.

Haug LS., Thomsen C., Brantsaeter AL., Kvalem HE., Haugen M., Becher G., Alexander J., Meltzer HM., Knutsen HK. 2010. Diet and particularly seafood are major sources of perfluorinated compounds in humans, Environ. Int., (36): pp.772-778.

Haug LS., Huber S., Becher G., Thomsen C. 2011. Characterisation of human exposure pathways to perfluorinated compounds – comparing exposure estimates with biomarkers of exposure, Environ Int., (37): pp.687-93.

Haug LS., Salihovic S., Jogsten IE., Thomsen C., van Bavel B., Lindström G., Becher G. 2010. Levels in food and beverages and daily intake of perfluorinated compounds in Norway. Chemosphere 80: pp.1137-1143

Haug LS., Huber S., Becher G., Thomsen C. 2011a. Characterisation of human exposure pathways to perfluorinated compounds – comparing exposure estimates with biomarkers of exposure. Environ Int 37: pp.687-693.

Haug LS., Huber S., Schlabach M., Becher G., Thomsen C. 2011b. Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes. Environ Sci Technol 45: pp.7991-7998.

Hess KA., Chen L., Larsen WJ. 1998. The ovarian blood follicle barrier is both charge- and size-selective in mice. Biol Reprod 58: pp.705-711.

Hill PJ., Taylor M., Goswami P., Blackburn RS. 2017. Substitution of PFAS chemistry in outdoor apparel and the impact on repellency performance. Chemosphere 181: pp.500-507

Hu XC., Andrews DQ., Lindstrom AB., Bruton TA., Schaider LA., Grandjean P., Lohmann R., Carignan CC., Blum A., Balan SA. 2016. Detection of poly- and perfluoroalkyl substances (PFASs) in U.S. drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants. Environ Sci Technol Lett 3: pp.344-350

Hamm MP., Cherry NM., Chan E., Martin JW., Burstyn I. 2010. Maternal exposure to perfluorinated acids and fetal growth. Journal of Exposure Science and Environment Epidemiology, (20): pp.589-597.

Han X., Snow TA., Kemper RA., Jepson GW. 2003. Binding of perfluorooctanoic acid to rat and human plasma proteins. Chem Res Toxicol 16: pp.775-781.

Hansen K.J., Clemen LA., Ellefson ME., Johnson HO. 2001. Compound-specific, quantitative characterization of organic: fluorochemicals in biological matrices, Environ. Sci. Technol., (35), pp.766-770.

Hansen KJ., Johnson HO., Eldridge JS., Butenhoff JL., Dick LA. 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River, Environ. Sci. Technol, (36), pp.1681-1685.

Hanssen L., Röllin H., Odland J.Ø., Moe MK., Sandanger TM. 2010. Perfluorinated compounds in mertenal serum and cord blood from selected areas of South Africa: results from a pilot study, Journ. Environ. Monit, (12), pp.1355-1361.

Hansen S., Vestergren R., Herzke D., Melhus M., Evenset A., Hanssen L., Brustad M., Sandanger T. M. 2016. Exposure to per- and polyfluoroalkyl substances through the consumption of fish from lakes affected by aqueous film-forming foam emissions – A combined epidemiological and exposure modelling approach. The SAMINOR 2 Clinical Study, Environ. Int., (94): pp.272-282.

Harada K., Inoue K., Morikawa A., Yoshinaga T., Saito N., Koizumi A. 2005. Renal clearance of perfluorooctane sulfonate and perfluorooctanoate in humans and their species-specific excretion. Environ Res 99: pp.253-261.

Hedlund, J. 2016. Per-and polyfluoroalkyl substances (PFASs) in Swedish waters. Available from: https://stud.epsilon.slu.se/9187/.

ITRC. 2017. *History and Use of Per- and Polyfluoroalkyl Substances (PFAS)*.

Heffernan AL., Cunningham TK., Drage DS., Aylward LL., Thompson K., Vijayasarathy S., Mueller JF., Atkin SL., Sathyapalan T. 2018. Perfluorinated alkyl acids in the serum and follicular fluid of UK women with and without polycystic ovarian syndrome undergoing fertility treatment and associations with hormonal and metabolic parameters. Int J Hyg Environ Health 221: pp.1068-1075

Hemat H., Wilhelm M., Völkel W., Mosch C., Fromme H., Wittsiepe J. 2010. Low serum levels of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and perfluorohexane sulfonate (PFHxS) in children and adults from Afghanistan, Science of the Total Environ., (408): pp.3493-3495.

Higgins CP., Field JA., Criddle CS., Luthy RG. 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge, Environ. Sci. Technol., (39): pp.3946-3956.

Houtz EF., Sutton R., Park JS., Sedlak M. 2016. Poly-and perfluoroalkyl substances in wastewater: significance of unknown precursors, manufacturing shifts, and likely AFFF impacts, Water Res., (95): pp.142-149.

Hundley SG., Sarrif AM., Kennedy GL. 2006. Absorption, distribution, and excretion of ammonium perfluorooctanoate (APFO) after oral administration to various species, Drug Chem. Toxicol., (29): pp.137-145.

Kaserzon, S.L. et al. (2019) ‘Calibration and validation of a novel passive sampling device for the time integrative monitoring of per- and polyfluoroalkyl substances (PFASs) and precursors in contaminated groundwater’, Journal of Hazardous Materials, 366(November 2018), pp. 423-431. doi:10.1016/j.jhazmat.2018.12.010.

Karásková P., Venier M., Melymuk L., Becanová J., Vojta S., Prokes R., Diamond ML., Klánová J. 2016. Perfluorinated alkyl substances (PFASs) in household dust in Central Europe and North America. Environ Int 94: pp. 315-324.

Kibambe M., Momba M., Daso A., Coetzee M 2020. Evaluation of the efficiency of selected wastewater treatment processes in removing selected perfluoroalkyl substances (PFASs). *J of Environ. Managt*. 255: pp.1099-2015.

Kim KY., Ekpe OD., Lee HJ. and Oh JE., 2020, Perfluoroalkyl substances and pharmaceuticals removal in full-scale drinking water treatment plants. J. Haz. Mat. 400: pp.123-235.

Kissa, E. (Ed.). (2001). Fluorinated surfactants and repellents (Vol. 97). CRC Press.

Kotthoff M., Müller J., Jürling H., Schlummer M., Fiedler D. 2015. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. Environ Sci Pollut Res 22: pp. 14546-14559.

Kubwabo C., Stewart B., Zhu J., Marro L. 2005. Occurrence of perfluorosulfonates and other perfluorochemicals in dust from selected homes in the city of Ottawa, Canada. J Environ Monit 7: pp.1074-1078.

IARC. (2017). Agents classified by the IARC Monographs, Volumes 1-117. Lyon, France: International Agency for Research on Cancer. http://monographs.iarc.fr/ENG/Classification/List_of_Classifications.pdf. February 28, 2017.

Ingelidoa AM., Abballe A., Gemma S., Dellatte, E., Iacovella N., De Angelis G., Zampaglioni F., Marra V., Miniero R., Valentini, S., Russo F., Vazzoler M., Testai E., De Felip E. 2018. Biomonitoring of perfluorinated compounds in adults exposed to contaminated drinking water in the Veneto Region, Italy, Environ. Int., (110): pp.149-159.

International Bottled Water Association (2019). International Bottled Water Association. [Online] Available at: bottledwater.org/and-polyfluoalkyl-substances-pfas-and-bottled-water.

Jahnke A., Berger U. 2009. Trace analysis of per- and polyfluorinated alkyl substances in various matrices – How do current methods perform? J. Chrom. A, (1216): pp.410-421.

Jian J-M., Guo Y., Zeng L., Liang-Ying L., Lu X., Wang F., Zeng EY. 2017. Global distribution of perfluorochemicals (PFCs) in potential human exposure source – a review. Environ Int 108: pp.51-62.

Jin YH., Liu W., Sato I., Nakayama SF., Sasaki K., Saito N., Tsuda S. 2009. PFOS and PFOA in environmental and tap water in China, Chemosphere, (77): pp.605-611.

Jogsten IE., Nadal M., van Bavel B., Lindström G., Domingo JL.2012. Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: Implications for human exposure, Environ. Int., (39): pp.172-180.

Jones PD., Hu W., De Coen W., Newsted J. L., Giesy JP. 2003. Binding of perfluorinated fatty acids to serum proteins. Environ. Toxicol. Chem. 22: pp.2639-2649.

Karásková P., Venier M., Melymuk L., Becanova J., Vojta S., Prokes R., Diamond ML., Klanova J. 2016. Perfluorinated alkyl substances (PFASs) in household dust in Central Europe and North America, Environ. Int., (94): pp.315-324.

Kärrman A., Domingo JL., Llebaria X., Nadal M., Bigas E., van Bavel B., Lindström G. 2010. Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples, Environ. Sci. Pollut. Res., (17): pp.750-758.

Kim SK., Kho YL., Shoeib M., Kim KS., Kim KR., Park JE., Shin YS. 2011. Occurrence of perfluorooctanoate and perfluorooctanesulfonate in the Korean water system: implication to water intake exposure, Environ. Pollut., (159): pp.1167-1173.

Kim SK., Shoeib M., Kim KS., Park JE. 2012. Indoor and outdoor poly- and perfluoroalkyl substances (PFASs) in Korea determined by passive air sampler, Environ. Pollut, (162): pp.144-150.

Kissa E. (2001). Fluorinated Surfactants and Repellents. Marcel Dekker Inc., New York.

Kotthoff M., Müller J., Jürling H., Schlummer M., Fiedler D. 2015. Per- and Polyflu-oroalkyl Substances in Consumer Products, Environ. Sci. Pollut. Res., 22 (19): pp.14546-14559.

Kröfges P., Skutlarek D., Färber H., Baitinger C., Gödeke I., Weber R. 2007. PFOS/PFOA contaminated megasites in Germany polluting the drinking-water supply of millions of people. Organohalogen Compd. 69: pp. 877-880. <http://www.dioxin20xx.org/pdfs/2007/07-634.pdf>.

Kudo N., Suzuki-Nakajima E., Mitsumoto A., Kawashima Y. 2006. Responses of the liver to perfluorinated fatty acids with different carbon chain length in male and female mice: In relation to induction of hepatomegaly, peroxisomal b-oxidation and microsomal 1-acylglycerophosphocholine acyltransferase, Biol. Pharm. Bull., (29): pp.1952-1957.

Labadie P., Chevreuil M. 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France), Environ. Pollut, (159): pp.1452-1453.

Lam NH., Cho CR., Lee JS., Soh HY., Lee BC., Lee JA., Tatarozako N., Sasaki K., Saito N., Iwabuchi K., Kannan K., Cho, HS 2014. Perfluorinated alkyl substances in water, sediment, plankton and fish from Korean rivers and lakes: a nationwide survey. Sci Total Environ, 491-492: pp.154-162.

Langer V., Dreyer A., Ebinghaus R. 2010. Polyfluorinated compounds in residential and non-residential indoor air, Environ. Sci. Technol., (44): pp.8075-81.

Lau C., Anitole K., Hodes C., Lai D., Pfahles-Hutchens A., Seed J. 2007. Perfluoroalkyl acids: A review of monitoring and toxicological findings, Toxicol. Sci., (99): pp.366-394.

Lau C., Thibodeaux JR., Hanson RG., Rogers JM., Grey BE., Stanton ME., Butenhoff JL., Stevenson LA. 2003. Exposure to perfluorooctane sulfonate during pregnancy in rat and mouse. II. Postnatal evaluation. Toxicol. Sci., (74): pp.382-392.

LC, GC's Chromacademy, Theory and Instrumentation of GC Introduction. Crawford Scientific. www.chromacademy.com, accessed: 11.06.2019.

Lee JH., Lee CK., Suh C-H., Kang H-S., Hong C-P., Choi S-N. 2017. Serum concentrations of per- and poly-fluoroalkyl substances and factors associated with exposure in the general adult population in South Korea. Int J Hyg Environ Health 220: pp.1046-1054.

Lein NP., Fujii S., Tanaka S., Nozoe M., Tanaka H. 2008. Contamination of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan), Desalination, (226): pp.338-347.

Lehmler H.-J. 2005. Synthesis of environmentally relevant fluorinated surfactants – A review, Chemosphere, (58): pp.1471-1496.

LHWA. 2005. Notice of contamination. Little Hocking's current activities. http://www.littlehockingwater.org/.

Li L., Zihan Z., Jianguo L., Jianxin H. 2015. Estimating industrial and domestic environmental releases of perfluorooctanoic acid and its salts in China from 2004 to 2012, Chemosphere, (129): pp.100-109.

Li X., Fatowe M., Cui D. Quinete N. 2022. Assessment of per-and polyfluoroalkyl substances in Biscayne Bay surface waters and tap waters from South Florida. Sci Total Environ. 806: pp.1503-1513

Lin AYC., Panchangam SC., Lo CC. 2009c. The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers, Environ. Pollut. 157 (4): pp.1365-1372.

Lin AYC., Panchangam SC., Ciou PS. 2010. High levels of perfluorochemicals in Taiwan's wastewater treatment plants and downstream rivers pose great risk to local aquatic ecosystems, Chemosphere, 80 (10): pp.1167-1174.

Lindstrom AB., Strynar MJ., Delinsky AD., Nakayama SF., McMillan L., Libelo EL., Neill M., Thomas L. 2011. Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA, Environ. Sci. Technol., (45): pp.8015-8021.

Lieder PH., Chang S., Ehresman DJ., Roy RR., Otterdijk F., Butenhoff JL. 2007. Twenty-eight-day oral toxicity study of perfluorobutyrate in rats, Toxicologist, (96): pp.193-205.

Llorca M., Farré M., Picó Y., Müller J., Knepper TP., Barceló D. 2012. Analysis of perfluoroalkyl substances in waters from Germany and Spain, Sci. Total Environ., (431): pp.139-150.

Loganathan BG., Lam PKS. 2012. Global contamination Trends of Persistent Organic Chemicals, ISBN-13:978-1-43983831-0.

Loos R., Wollgast J., Huber T., Hanke G. 2007. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy, Anal. Bioanal. Chem., (387): pp.1469-1478.

Loos R., Wollgast J., Huber T., Hanke G. 2008. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy. Anal. Bioanal. Chem., (387): pp.1469-1478.

Lorenzo M., Campo J., Farré M., Pérez F., Picó Y., Barcelód D. 2016. Perfluoroalkyl substances in the Ebro and Guadalquivir river basins (Spain), Science of the Total Environment, (540): pp.191-199.

Lu Z., Song L., Zhao Z., Ma Y., Wang J., Yang H., Ma H., Cai M., Codling G., Ebinghaus R., Xie Z., Giesy JP. 2015. Occurrence and trends in concentrations of perfluoroalkyl substances (PFASs) in surface waters of eastern China, Chemosphere, (119): pp.820-827.

Martin JW., Mabury SA., Solomon KR., Muir DCG. 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss), Environ. Toxicol. Chem., (22): pp.196-204.

Martin D., Munoz G., Mejia-Avendaño S., Duy SV., Yao Y., Volchek K., Brown CE., Liu, J. and Sauvé, S., 2019, Zwitterionic, cationic, and anionic perfluoroalkyl and polyfluoroalkyl substances integrated into total oxidizable precursor assay of contaminated groundwater. Talanta, 195(September 2018), 533-542. https://doi.org/10.1016/j.talanta.2018.11.093.

Masunaga S. (2017) Perfluoroalkyl acids (PFAAs) in the Pra and Kakum River basins and associated tap water in Ghana. Sci Total Environ (579): pp.729-735.

MDH. (2007). Health risk assessment unit. In: Proceedings of the Workshop on Public Health Response to Perfluorochemical Contamination in Minnesota. Minnesota Department of Health.

Meng J., Wang T., Wang P., Giesy JP., Lu Y. 2014. Perfluoroalkyl substances and organochlorine pesticides in sediments from Huaihe watershed in China, J Environ. Sci, (26): pp.2198-2206.

Moeti L. 2013. Towards the Effective Implementation of the Expanded Public Works Programme in South Africa Municipalities: A Case Study of the City of Tshwane Metropolitan Municipality (Doctoral dissertation, University of South Africa).

Monroy R., Morrison K., Teo K., Atkinson S., Kubwabo .C, Stewart B., Foster WG. 2008. Serum levels of perfluoroalkyl compounds in human maternal and umbilical cord blood samples. Environ Res 108: 56-62.

Morin, N. et al. (2012) ‘Chemical calibration, performance, validation and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments’, TrAC – Trends in Analytical Chemistry, 36, pp. 144-175. doi:10.1016/j.trac.2012.01.007.

Mudumbi JBN., Ntwampe SKO., Muganza FM., Okonkwo JO. 2014. Perfluorooctanoate and perfluorooctane sulfonate in South African river water, Water Sci. Technol., 69 (1): pp.185-194.

Mudumb, JBN., Ntwampe SKO., Muganza M and Okonkwo O., 2014. Susceptibility of Riparian Wetland plants to perfluoroctanoic acid (PFOA) accumulation. International Journal of Phytoremediation DOI: 10.1080/15226514.2013.810574.

Murakami M., Adachi N., Saha M., Morita C., Takada H. 2011. Levels, temporal trends, and tissue distribution of perfluorinated surfactants in freshwater fish from Asian countries, Arch. Environ. Contam. Toxicol, (61): pp.631-641.

Munoz G., Giraudel JL., Botta F., Lestremau F., Dévier MH., Budzinski H., Labadie P. 2015. Spatial distribution and partitioning behavior of selected poly- and perfluoroalkyl substances in freshwater ecosystems: A French nationwide survey, Sci. Total. Environ, (517): pp.48-56.

Munoz G., Labadie P., Botta F., Lestremau F., Lopez B., Geneste E., Pardon P., Dévier MH., Budzinski H. 2017. Occurrence survey and spatial distribution of perfluoroalkyl and polyfluoroalkyl surfactants in groundwater, surface water, and sediments from tropical environments, Sci. Total. Environ. (607-608): pp.243-252.

Mylchreest E., Munley SM., Kennedy GL. 2005. Evaluation of the developmental toxicity of 8-2 telomer B alcohol, Drug Chem. Toxicol., (28): pp.315-328.

Naile JE., Khim JS., Wang T., Chen C., Luo W., Kwon B-O., Park J., Koh C-H., Jones P., Lu Y., Giesy JP. 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea, Environ. Pollut, (158:, pp.1237-1244.

Nakata H., Kannan K., Nasu T., Cho HS., Sinclair E., Takemura A. 2006. Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat areas of the Ariake Sea, Japan: environmental fate of perfluorooctane sulfonate in aquatic ecosystems, Environ. Sci. Technol., (40): pp.4916-4921.

Nascimento RA., Nunoo DBO., Bizkarguenaga E., Schultes L., Zabaleta I., Benskin JP., Spanó S., Leonel J. 2018. Sulfluramid use in Brazilian agriculture: A source of per- and polyfluoroalkyl substances (PFASs) to the environment, Environmental Pollution, (242): pp.1436-1443.

Ndude MA., Gwena KR., Hamandawana H. 2022. The Nature, Causes and Extent of Land cover Changes in gamtoos River Estuary, Eastern Cape Province, South Africa: 1991-2017, Sustainability, (14): pp.7859-7877.

Nguyen VT., Reinhard M., Karina GYH. 2011. Occurrence and source characterization of perfluorochemicals in an urban watershed, Chemosphere, (82): pp.1277-1285.

Noorlander CW., van Leeuwen SPJ., Biesebeek JD., Mengelers MJB., Zeilmaker MJ. 2011. Levels of perfluorinated compounds in food and dietary intake of PFOS and PFOA in the Netherlands. J Agric Food Chem 59: pp.7496-7505.

NTP. (2016b). NTP Monograph on immunotoxicity associated with exposure to perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Research Triangle Park, NC: U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program. https://ntp.niehs.nih.gov/ntp/ohat/pfoa_pfos/pfoa_pfosmonograph_508.pdf. December 21, 2017.

OECD. (2002). Hazard assessment of perfluorooctane sulfonate (PFOS) and its salts. Organization for Economic Co-operation and Development; November 21.

OECD. (2005). Results of survey on production and use of PFOS, PFAS and PFOA, relates substances and products/mixtures containing these substances. ENV/JM/MONO(2005)1.

Olsen GW., Burris JM., Burlew MM., Mandel JH. 2000. Plasma cholecystokinin and hepatic enzymes, cholesterol and lipoproteins in ammonium perfluorooctanoate production workers. Drug Chem. Toxicol., (23): pp.603-620.

Olsen GW., Zobel LR. 2007. Assessment of lipid, hepatic, and thyroid parameters with serum perfluorooctanoate (PFOA) concentrations in fluorochemical production workers, Int. Arch. Occup. Environ. Health, (81): pp.231-246.

Olsen GW., Butenhoff JL., Zobel LR. 2009. Perfluoroalkyl chemicals and human fetal development: an epidemiologic review with clinical and toxicological perspectives, Reprod. Toxicol. (27): pp.212-230.

Park SK., Peng Q., Ding N., Mukherjee B., Harlow SD. 2019 Determinants of per- and polyfluoroalkyl substances (PFAS) in midlife women: evidence of racial/ethnic and geographic differences in PFAS exposure. Environ Res 175: pp.186-199.

Pérez F., Nadal M., Navarro-Ortega A., Fàbrega F., Domingo JL., Barceló D., Farré M. 2013. Accumulation of perfluoroalkyl substances in human tissues. Environ Int, 59: pp.354-362.

Petro EML., D'Hollander W., Covaci A., Bervoets L., Fransen E., De Neubourg D., De Pauw I., Leroy JLMR., Jorssen EPA, Bols PEJ. 2014. Perfluoroalkyl acid contamination of follicular fluid and its consequence for in vitro oocyte developmental competence. Sci Total Environ, 496: pp.282-288.

Piekarz AM., Primbs T., Field JA., Barofsky DF., Simonich S. 2007 Semivolatile fluorinated organic compounds in Asian and Western U.S. air masses. Environ Sci Technol, 41: pp.8248-8255.

Pétré MA., Genereux DP., Koropeckyj-Cox L., Knappe DR., Duboscq S., Gilmore TE., Hopkins ZR., 2021. Per-and Polyfluoroalkyl Substance (PFAS) Transport from Groundwater to Streams near a PFAS Manufacturing Facility in North Carolina, USA. Environ Sci & Technol. 55(9): pp. 5848-5856.

Post GB., Louis JB., Cooper KR., Boros-Russo BJ., Lippincott RL. 2009. Occurrence and potential significance of perfluorooctanoic acid (PFOA) detected in New Jersey public drinking water systems. Environ Sci Technol, 43: pp.4547-4554.

Post GB., Louis JB., Lippincott RL., Procopio NA. 2013. Occurrence of perfluorinated compounds in raw water from New Jersey public drinking water systems, Environ. Sci. Technol, 47 (23), pp.13266-13275.

Powley CR., George SW., Ryan TW., Buck RC. 2005. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes, Analytical Chemistry, (77): pp. 6353-6358.

Prevedouros, K, Cousins, IT, Buck, RC & Korzeniowski, SH. 2006. *Sources, fate and transport of perfluorocarboxylates*. V. 40. American Chemical Society. doi.org/10.1021/es0512475.

Prevedouros K., Cousins IT., Buck RC., Korzeniowski SH. 2006. Sources, fate and transport of perfluorocarboxylates, Environ. Sci. Technol., (40): pp.32-44.

Qazi MR., Nelson BD., DePierre JW., Abedi-Valugerdi M. 2012. High-dose dietary exposure of mice to perfluorooctanoate or perfluorooctane sulfonate exerts toxic effects on myeloid and B-lymphoid cells in the bone marrow and these effects are partially dependent on reduced food consumption, Food Chem. Toxicol, 50(9): pp.2955-2963.

Qian X., Guoqiang S., Wei W., Hangbiao J and Lingyan, Z. 2018. Measuring log Kow coefficients of neutral species of perfluoroalkyl carboxylic acids using reversed-phase high-performance liquid chromatography. Environ. Pollut, 242(2): pp. 1283-1290.

Quiñones O., Snyder SA. 2009. Occurrence of perfluoroalkylcarboxylates and sulfonates in drinking water utilities and related waters from the United States, Environmental Science and Technology, (43): pp.9089-9095.

Rostkowski P., Yamashita N., So IMK., Taniyasu S., Lam PKS., Falandysz J., Lee KT., Kim SK., Khim JS., Im SH., Newsted JL., Jones PD., Kannan K., Giesy JP. 2006. Perfluorinated compounds in streams of the shihwa industrial zone and Lake Shihwa, South Korea. Environ. Toxicol. Chem, (25): pp.2374-2380.

Routledge EJ., and Sumpter JP. 1996. Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. Environmental Toxicology and Chemistry, *15*(3): pp. 241-248. https://doi.org/10.1897/1551-5028(1996)015<0241:EAOSAS>2.3.CO;2

Saito N., Harada K., Inoue K., Sasaki K., Yoshinaga T., Koizumi A. 2004. Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan, Journ. Occup. Health, (46): pp.49-59.

Sammut G., Sinagra E., Helmus R., de Voogt P. 2017. Perfluoroalkyl substances in the Maltese environment – (I) surface water and rain water, Sci Total Environ, 589: pp.182-190.

Sharma BM., Bharat G.K., Tayal S., Larssen T., Becanov J., Karaskov P., Whitehead P.G., Futter MN., Butterfield D., Nizzetto L. 2016. Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: Emissions and implications for human exposure. Environ Pollut 208: pp.704-713.

Savitz DA., Stein CR., Elston B., Wellenius GA., Bartell SM., Shin HM., Vieira VM., Fletcher T. 2012b. Relationship of perfluorooctanoic acid exposure to pregnancy outcome based on birth records in the Mid-Ohio Valley, Environ. Health Perspect, 120(8): pp.1201-1207.

Schenker U., Scheringer M., Macleod M., Martin JW., Cousins IT., Hungerbühler K. 2008. Contribution of Volatile Precursor Substances to the Flux of Perfluorooctanoate to the Arctic, Environ. Sci. Technol., (42): pp.3710-3716.

Schlummer M., Gruber L., Fiedler D., Kizlauskas M., Müller J. 2013. Detection of fluorotelomer alcohols in indoor environments and their relevance for human exposure, Environ. Int, (57-58): pp.42-49.

Sepulvado JG., Blaine AC., Hundal LS., and Higgins C.P. 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ Sci & technol, *45*(19): pp. 8106-8112.

Shoemaker JA. 2009. Method 537. Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS).

Schröder HF. 2003. Determination of fluorinated surfactants and their metabolites in sewage sludge samples by liquid chromatography with mass spectrometry and tandem mass spectrometry after pressurised liquid extraction and separation on fluorine-modified reversed-phase sorbents, Journal of Chrom.A, (1020):pp.131-151.

Schwanz TG., Llorca M., Farré M., Barceló D. 2016. Perfluoroalkyl substances assessment in drinking waters from Brazil, France and Spain, Sci Total. Environ, (539): pp.143-152.

Schweigert FJ., Gericke B., Wolfram W., Kaisers U., Dudenhausen JW. 2006. Peptide and protein profiles in serum and follicular fluid of women undergoing IVF. Hum Reprod, 21: pp.2960-2968.

Shafique U., Schulze S., Slawik C., Kunz S., Paschke A., Schüürmann G. 2017. Gas chromatographic determination of perfluorocarboxylic acids in aqueous samples: A tutorial review, Analytica Chimicaica Acta, (949): pp.8-22.

Shao M., Ding G., Zhang J., Wei L., Xue H., Zhang N., Li Y., Chen G., Sun Y. 2016. Occurrence and distribution of perfluoroalkyl substances (PFASs) in surface water and bottom water of the Shuangtaizi Estuary, China, Environ Pollut, (216): pp.675-681.

Sharma BM., Bharat GK., Tayal S., Larssen T., Becanov J., Karaskov P., Whitehead PG., Futter MN., Butterfield D., Nizzetto L. 2016. Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: Emissions and implications for human exposure, Environmental Pollution, (208): pp.704-713.

Shimadzu Corporation. 2013. Liquid Chromatograph Mass Spectrometer LCMS-8030,

www.shimadzu.com/an/

Shimadzu. 2019. Fundamental Guide to Liquid Chromatography Mass Spectrometry (LCMS).

Sinclair E., Kannan K. 2006. Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants, Environ. Sci. & Technol., 40 (5): pp.1408-1414.

Schaider LA., Balan SA., Blum A., Andrews DQ., Strynar MJ., Dickinson ME., Lunderberg DM., Lang JR., Peaslee GF. 2017. Fluorinated compounds in U.S. fast food packaging. Environ Sci Technol Lett 4: pp.105-111

Shoeib T., Hassan Y., Rauert C., Harner T. 2016. Poly and perfluoroalkyl substances (PFASs) in indoor dust and food packaging materials in Egypt: Trends in developed and developing countries, Chemosphere, (144): pp.1573-1581.

Skutlarek D., Exner M., Farber H. 2006. Perfluorinated surfactants in surface and drinking waters, Environ. Sci. Pollut. Res., 23: pp.299-307.

Smart BE. 1994. Characteristics of C-F systems in: Banks RE, Smart BE, Tatlow JC, editors. Organofluorine chemistry: Principles and commercial applications. New York (NY): Plenum. pp. 57-88.

Smith JWN., Beuthe B., Dunk M., Demeure S., Carmona JMM., Medve A., Spence MJ., Pancras T., Schrauwen G, Held T. 2016, Environmental fate and effects of polyand perfluoroalkyl substances (PFAS), CONCAWE, 8: pp. 1-107.

Sonthithai P., Suriyo T., Thiantanawat A., Watcharasit P., Ruchirawat M. and Satayavivad J. 2016. Perfluorinated chemicals, PFOS and PFOA, enhance the estrogenic effects of 17β-estradiol in T47D human breast cancer cells. Journal of Applied Toxicology, 36(6): pp.790-801.

Ssebugere P., Sillanpää M., Matovu H., Wang Z., Schramm KW., Omwoma S., Wanasolo W., Ngeno EC. and Odongo, S., 2020, Environmental levels and human body burdens of per- and poly-fluoroalkyl substances in Africa: A critical review. Sci Total Environ, 739: 1399-1414. https://doi.org/10.1016/j.scitotenv.2020.139913

Steenland K., Zhao L., Winquist A. 2015. A cohort incidence study of workers exposed to perfluorooctanoic acid (PFOA), Occup. Environ. Med., 72(5): pp.373-380.

Steenland K., Tinker S., Shankar A., Ducatman A. 2010. Association of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) with uric acid among adults with elevated community exposure to PFOA, Environ. Health Perspect, (118): pp.229-233.

Stein CR., Savitz DA., Dougan M. 2009. Serum levels of perfluorooctanoic acid and perfluorooctane sulfonate and pregnancy outcome, Am. Journ. Epidemiol, 170(7): pp.837-846.

Stockholm Convention (2009). Stockholm Convention on persistent organic pollutants (POPs) as amended in 2009. http://chm.pops.int/Portals/0/download.aspx?d= UNEP-POPS-COP-CONVTEXT-2009.En.pdf.

Stubleski J., Salihovic S., Lind PM., Lind L., Dunder L., McCleaf P., Eurén K., Ahrens L., Svartengren M., van Bavel B., Kärrmana A. 2017. The effect of drinking water contaminated with perfluoroalkyl substances on a 10-year longitudinal trend of plasma levels in an elderly Uppsala cohort, Environ. Res., (159): pp.95-102.

So MK., Miyake Y., Yeung WY., Ho YM., Taniyasu S., Rostkowski P., Yamashita N., Zhou BS., Shi XJ., Wang JX., Giesy JP., Yu H., Lam PKS. 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China, Chemosphere, (68): pp.2085-2095.

Strynar MJ., Lindstrom AB. 2008). Perfluorinated compounds in house dust from Ohio and North Carolina, USA. Environ Sci Technol 42: pp.3751-3756.

Sunderland EM., Hu X.C., Dassuncao C., Tokranov AK., Wagner CC., Allen JG. 2018. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects, Journal of Expos. Sci. & Environ. Epid., https://doi.org/10.1038/s41370-018-0094-1.

Tabtong, W., Boontanon, S. K., & Boontanon, N. (2015). Fate and risk assessment of perfluoroalkyl substances (PFASs) in water treatment plants and tap water in Bangkok, Thailand. *Procedia Environ Scis*, *28*: pp. 750-757.

Takagi S., Adachi F., Miyano K., Koizumi Y., Tanaka H., Mimura M., Watanabe I., Tanabe S., Kannan K. 2008. Perfluorooctanesulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan, Chemosphere, (72): pp.1409-1412.

Taniyasu S., Kannan K., So MK., Gulkowska A., Sinclair E., Okazawa T., Yamashita N. 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short-and long-chain perfluorinated acids in water and biota, Journal of Chrom.A, (1093): pp.89-97.

Taniyasu S., Kannan K., Wu Q., Kwok K.Y., Yeung LWY., Lam PKS., Chittime B., Kida T., Takasuga T., Tsuchiya Y., Yamashita N. 2013. Inter-laboratory trials for analysis of perfluorooctanesulfonate and perfluorooctanoatein water samples: performance and recommendations, Anal. Chimica. Acta, (770): pp111-120.

Tavasoli E., Luek JL., Malley JP. and Mouser, PJ., 2021, Distribution and fate of per-and polyfluoroalkyl substances (PFAS) in wastewater treatment facilities. Environmental Science: Processes & Impacts, Environ. Sci.: Processes Impacts, 23, 903-913.

Thompson J., Eaglesham G., Mueller J. 2011. Concentrations of PFOS, PFOA and other perfluorinated alkyl acids in Australian drinking water. Chemosphere 83: pp.1320-1325.

Tittlemier SA., Pepper K., Seymour C., Moisey J., Bronson R., Cao X-L., Dabeka RW. 2007. Dietary exposure of Canadians to perfluorinated carboxylates and perfluorooctane sulfonate via consumption of meat, fish, fast foods, and food items prepared in their packaging. J Agric Food Chem, 55: pp.3203-3210

Trier X., Granby K., Christensen JH. 2011. Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environ Sci Pollut Res, 18: pp.1108-1120.

Trudel D., Horowitz L., Wormuth M., Scheringer M., Cousins IT., Hungerbühler K. 2008b. Estimating consumer exposure to PFOS and PFOA. Risk Anal, 28:251-269

Taylor KW., Hoffman K., Thayer KA., Daniels JL. 2014. Polyfluoroalkyl chemicals and menopause among women 20-65 years of age (NHANES). Environ Health Perspect, 122: pp.145-150.

UNEP. (2010). New POPs SC-4/17: Listing of Perfluorooctane Sulfonic Acid, its Salts and Perfluorooctane Sulfonyl Fluoride. United Nations Environment Programme: Stockholm Convention on Persistent Organic Pollutants (POPs), Geneva, Switzerland.

USEPA, Method 8327. Per- and polyfluoroalkyl substances (PFAS) using external standard calibration and multiple reaction monitoring (MRM) liquid chromatography/ tandem mass spectrometry (LC/MS/MS).

USEPA. (2001). Analysis of PFOS, FOSA, and PFOA from Various food Matrices Using HPLC Electrospray/Mass Spectrometry. 3M Study Conducted by Centre Analytical Laboratories. United States Environmental Protection Agency.

USEPA. (2009). Provisional Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS). http://water.epa.gov/action/advisories/ drinking/upload/2009_01_15_criteria_drinking_pha-PFOA_PFOS.pdf.

USEPA. (2012). Perfluorochemical Contamination of Biosolids Near Decatur. <http://www.epa.gov/region4/water/PFCindex.html> (accessed 15.09.12).

USEPA. (2016). Lifetime health advisories and health effects support documents for perfluorooctanoic acid and perfluorooctane sulfonate. Washington, DC: Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016 05/documents/pfoa_pfos_prepub_508.pdf [Accessed 31 August 2018].

USEPA. (2016a. Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS). EPA Document Number: 822-R-16-004. U.S. Environmental Protection Agency Office of Water (4304T) Health and Ecological Criteria Division, Washington, DC, p. 20460.

USEPA. (2016b. Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA). EPA Document Number: 822-R-16-005. U.S. Environmental Protection Agency Office of Water (4304T) Health and Ecological Criteria Division, Washington, DC, p. 20460

USEPA. (2016e). Drinking water health advisory for perfluorooctanoic acid (PFOA). U.S. Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final-plain.pdf. March 3, 2017.

USEPA. (2016f). Drinking water health advisory for perfluorooctane sulfonate (PFOS). U.S. Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016-05/documents/pfos_health_advisory_final-plain.pdf. March 3, 2017.

Vaalgamaa S; Vähätalo AV., Perkola N; Huhtala S. (2011) Photochemical reactivity of perfluorooctanoic acid (PFOA) in conditions representing surface water. Sci. Total Environ., 409: pp. 3043-3048

Van Leeuwen SPJ., de Boer J. 2007. Extraction and clean up strategies for the analysis of poly- and perfluoroalkyl substances in environmental and human matrices, Journal of Chromatography A, (1153), 172-185.

Vestergren R., Cousins IT. 2009. Tracking the pathways of human exposure to perfluorocarboxylates. Environ Sci Technol 43: pp.5565-5575.

Vestergren R., Berger U., Glynn A., Cousins IT. 2012. Dietary exposure to perfluoroalkyl acids for the Swedish population in 1999, 2005 and 2010, Environ. Int, (49): pp.120-127.

Vierker L., Staude C., Biegel-Engler A., Drost W., Schulte C. 2012. Perfluorooctanoic (PFOA) – main concerns and regulatory developments in Europe from an environmental point of view, Environ. Sci. Europe, (24): pp. 16.

Wallace DR. 2015. Nanotoxicology and metalloestrogens: Possible involvement in breast cancer. Toxics, 3(4): pp.390-413.

Wang T., Wang Y., Liao C., Cai Y., Jiang G. 2009. Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm convention on persistent organic pollutants 1, Environ. Sci. Technol., (43): pp. 5171-5175.

Wang T., Lu Y., Chen C., Naile JE., Khim JS., Park J., Luo W., Jiao W., Hu W., Giesy JP. 2011. Perfluorinated compounds in estuarine and coastal areas of north Bohai Sea, China, Marine Pollution Bulletin, (62): pp. 1905-1914.

Wang T., Khim JS., Chen C., Naile JE., Lu Y., Kannan K., Park J., Luo W., Jiao W., Hu W., Giesy JP. 2012a. Perfluorinated compounds in surface waters from Northern China: comparison to level of industrialization, Environ. Int, (42): pp. 37-46.

Wang Y., Adgent M., Su PH., Chen HY., Chen PC., Hsiung CA., Wang SL. 2016. Prenatal exposure to perfluorocarboxylic acids (PFCAs) and fetal and postnatal growth in the Taiwan maternal and infant cohort study, Environ. Health Perspect, 124(11): pp. 1794-1800.

Wang W., Liu JX.; Buck RC., Korzeniowski SH., Wolstenholme, BW., Folsom, PW., Sulecki LM. (2011) 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants Chemosphere, 82: pp. 853-858

Washington JW., Yoo H., Ellington JJ., Jenkins TM., Libelo EL. 2010. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA, Environ. Sci. Technol., (44), 8390-6.

Washburn ST., Bingman TS., Braithwaite SK., Buck RC., Buxton LW., Clewell HJ. 2005. Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles, Environ. Sci. Technol, 39(11): pp. 3904-3910.

Water Research Commission (WRC) Report. (1993). A Situation Analysis of Water Quality In The Catchment Of The Buffalo River, Eastern Cape, With Special Emphasis On The Impacts Of Low Cost, High-Density Urban Development On Water Quality, WRC Report No. 40S/2/96, ISBN NO. 1 86845 287 5, (2): pp.1-11.

Weiss, J. et al. (2015) 'Global Monitoring Plan on Persistent Organic Pollutants PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention Set-up and guidelines for monitoring PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convent', (April).

West Virginia Department of Environmental Protection (WVDEP). (2002). Ammonium Perfluorooctanoate (C8) Assessment of Toxicity Team (CATT) Final Report. West Virginia Department of Environmental Protection.

White SS., Calafa AM., Kuklenyik Z., Villanueva L., Zehr RD., Helfant L., Strynar MJ., Lindstrom AB., Thibodeaux JR., Wood C. 2007. Gestational PFOA exposure of mice is associated with altered mammary gland development in dams and female offspring, Toxicol. Sci, (96): pp. 133-144.

Wille K., Vanden Bussche J., Noppe H., De Wulf E., Van Caeter P., Janssen CR., De Brabander HF., Vanhaecke L. 2010. A validated analytical method for the determination of perfluorinated compounds in surface-, sea- and sewagewater using liquid chromatography coupled to time-of-flight mass spectrometry, Journ. Chromatogr. A, http://dx.doi.org/10.1016/j.chroma.2010.03.054.

Wolf CJ., Fenton SE., Schmid JE., Calafat AM., Kuklenyik Z., Bryant XA., Thibodeaux JR., Das KP., White SS., Lau CS., Abbott BD. 2007. Developmental toxicity of perfluorooctanoic acid in the CD-1 mouse after cross-foster and restricted gestational exposure, Toxicol. Sci, (95): pp. 462-473.

Xia W., Wan Y., Li YY., Zeng H., Lv Z., Li G., Wei Z., Xu S.Q. 2011. PFOS prenatal exposure induce mitochondrial injury and gene expression change in hearts of weaned Sprague Dawley rats, Toxicology, (282)(1-2): pp. 23-29.

Xiang Q., Guoqiang Shan., Wei Wu., Hang. (2018) Measuring log Kow coefficients of neutral species of perfluoroalkyl carboxylic acids using reversed-phase high-performance liquid chromatography. Environmental Pollution, 242, (Part B): pp. 1283-1290

Xiao F., Halbach TR., Simcik MF., Gulliver JS. 2012. Input characterization of perfluoroalkyl substances in wastewater treatment plants: source discrimination by exploratory data analysis, Water Res, (46): pp. 3101-3109

Yamashita N., Kannan K., Taniyasu S., Horii Y., Petrick G., Gamo T. 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawaterusing liquid chromatography-tandem mass spectrometry, Environ. Sci.Technol,(38): pp. 5522-5528.

Yamashita N., Kannan K., Taniyasu S., Horii Y., Petrick G., Gamo T. 2005. A global survey of perfluorinated acids in oceans, Mar. Pollut. Bull, (51): pp. 658-668.

Yang Q., Xie Y., Eriksson AM., Nelson BD., DePierre JW. 2001. Further evidence for the involvement of inhibition of cell proliferation and development in thymic and splenic atrophy induced by the peroxisome proliferator perfluorooctanoic acid in mice, Biochem. Pharmcol, (62): pp. 1133-1140.

Yang Q., Abedi-Valugerdi M., Xie Y., Zhao XY., Moller G., Nelson BD., DePierre JW. 2002a. Potent suppression of the adaptive immune response in mice upon dietary exposure to the potent peroxisome proliferator, perfluorooctanoic acid, Int. Immunopharmacol, (2): pp. 389-397.

Yang Q., Xie Y., Alexson SEH., Nelson BD., DePierre JW. 2002b. Involvement of the peroxisome proliferator-activated receptor alpha in the immunomodulation caused by peroxisome proliferators in mice, Biochem. Pharmacol, (63): pp. 1839-1900.

Yang L., Zhu L., Liu Z. 2011. Occurrence and partition of perfluorinated compounds in water and sediment from Liao River and Taihu Lake. China, Chemosphere, (83), 806-814.

Yao Y., Zhao Y., Sun H., Chang S., Zhu L., Alder AC., Kannan K. 2018. Per- and Polyfluoroalkyl Substances (PFASs) in Indoor Air and Dust from Homes and Various Microenvironments in China: Implications for Human Exposure, Environ. Scien. Technol., (52): pp. 3156-3166.

Ylinen M., Auriola S. 1990. Tissue distribution and elimination of perfluorodecanoic acid in the rat after single intraperitoneal administration. Pharmacol Toxicol 66: pp.45-48

Yoo H., Washington JW., Ellington JJ., Jenkins TM., Neill MP. 2010. Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA, Environ. Sci. Technol, (44): pp. 8397-8402.

Yuan G., Peng H., Huang C., Hu J. 2016. Ubiquitous Occurrence of Fluorotelomer Alcohols in Eco-Friendly Paper-Made Food-Contact Materials and Their Implication for Human Exposure, Environ. Sci. Technol, (50): pp.942-950.

Yu N., Shi W., Zhang B., Su G., Feng J., Zhang X., Wei S., Yu H. 2013. Occurrence of perfluoroalkyl acids including perfluorooctane sulfonate isomers in Huai River Basin and Taihu Lake in Jiangsu Province, China, Environ. Sci. Technol, (47): pp. 710-717.

Zafeiraki E., Costopoulou D., Vassiliadou I., Bakeas E., Leondiadis L. 2014. Determination of perfluorinated compounds (PFCs) in various foodstuff-packaging materials used in the Greek market, Chemosphere, (94): pp. 169-176.

Zeng C., Atkinso, A., Sharma N., Ashani H., Hjelmstad A., Venkatesh K. and Westerhoff P. 2020. Removing per-and polyfluoroalkyl substances from groundwaters using activated carbon and ion exchange resin packed columns. *AWWA* Water Science, *2*(1):pp. 172-182.

Zhang W., Zhang Y., Taniyasu S., Yeung LW., Lam PK., Wang J., L, X., Yamashita N. and Dai J. 2013. Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China. Environ pollut. *176*: pp.10-17.

Zhang T., Sun HW., Wu Q., Zhang XZ., Yun SH., Kannan K. 2010. Perfluorochemicals in meat, eggs and indoor dust in China: assessment of sources and pathways of human exposure to perfluorochemicals. Environ Sci Technol, 44:pp.3572-3579.

Zhang Z., Sarkar D., Biswas J. K. and Datta, R., 2022, Biodegradation of per- and polyfluoroalkyl substances (PFAS): A review. Bioresource Technology, 344(PB), 126223. https://doi.org/10.1016/j.biortech.2021.126223.

Zushi Y., Hogarh J.N., Masunaga S. 2012. Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes, Clean Technol. Environ, 14 (1): pp. 9-20.