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Per- and Polyfluorinated Alkyl Substances in Different Water Matrices: Nontargeted Analysis, Suspect Screening, and Targeted Analysis

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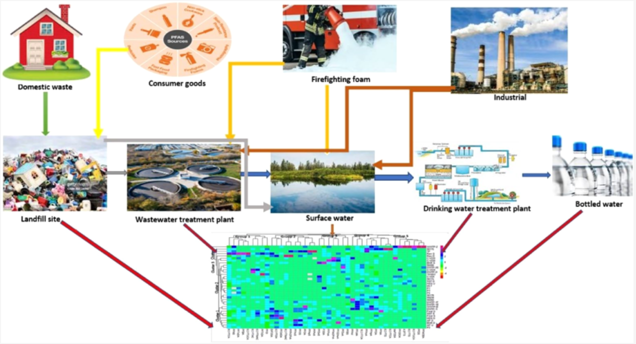
ABSTRACT: This study investigated the presence of unknown and known PFAS in wastewater treatment plants, drinking water treatment plants, bottled water, tap water, and surface water using both high-resolution and tandem mass spectrometry. The sources of PFAS in these matrices were elucidated via a multivariate statistical analysis. A total of 70 PFAS features were identified using nontargeted analysis at varying confidence levels. For the first time in South Africa, and probably on the African continent, novel PFAS (MeFOSA, EtFOSA, 6:2 FTUCA, 8:2 FTUCA, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, PFHxI, PFOI, 8:2 FTAC, 6:2 FTMAC, and 8:2 FTMAC) and emerging PFAS (PFMOPrA, PFPrOPrA, PFO2HxA, PFO3OA, and PFO4DA) were detected and reported in various water sources. The sum of $\sum_{21}$ PFAS concentrations in bottled water, tap water, surface water, DWTP, and WWTP samples ranged from <LOD-126, <LOD-363, <LOD-716, <LOD-1056, and <LOD-2304 ng/L, respectively. The average concentrations of PFOA, PFOS, PFNA, and PFHxS in drinking tap water exceeded their respective US EPA maximum contaminant levels. PFO2HxA, PFO4DA, and PFO3OA were reported for the first time in drinking water, with PFAS displaying potential similarities in sources. This study underscores the importance of PFAS regulation in drinking water in South Africa to safeguard public health.



KEYWORDS: *novel, PFAS, drinking water, bottled water, surface water, PFOS, PFOA*

1. INTRODUCTION

Water is the most essential natural resource; however, due to population growth, expansion of industrial and agricultural activities, disturbances of the water cycle, and the impact of climate change, the quality of water in some parts of the world has deteriorated, thereby constituting public health concerns.[1] In some countries, water quality deterioration is exacerbated by both chemical and biological pollution from nonpoint and point sources. For example, nonpoint and point sources of pollution such as sewage and industrial discharge, runoff from agricultural fields, and urban runoff affect water quality.[2] For proper utilization, water from the aforementioned sources must be subjected to some treatments. However, inadequate treatment of water that is contaminated with pollutants, for example, in wastewater treatment plants can lead to the discharge of effluents containing pollutants such as per- and polyfluoroalkyl substances (PFAS) and other legacy and emerging contaminants into receiving water bodies such as rivers and groundwater with negative consequences for human health and the ecosystem.[3]

PFAS are a well-known group of synthetic compounds with strong and stable carbon−fluorine bonds,[4,5] and have been widely synthesized via electrochemical fluorination and telomerization.[6−8] The unique properties of PFAS[9] are responsible for their wide applications in products such as textiles, nonstick cookware, food packaging, furnishings, and firefighting formations.[10,11] They are also used in the manufacture of semiconductors and photographic or photolithographic materials.[12] Some PFAS are known to be persistent, toxic, bioaccumulative and have a long-range transport characteristic,[7,8] hence their classification as persistent organic pollutants (POPs) by the Stockholm Convention. Perfluorohexanesulfonates (PFHxS), perfluorooctanesulfonates (PFOS), and perfluorooctanoic acid (PFOA)

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are examples of PFAS listed by the Stockholm Convention as POPs and are strongly regulated.[13] Many congeners of PFAS are still produced and used, albeit many others that are structurally similar to PFOS and PFOA or their precursors are produced at higher volumes.[14] Short-chain compounds have been used as replacements for some long-chain PFAS, although these are now considered as contaminants of emerging global concern because they have been found to be persistent and bioaccumulative similar to the discontinued long-chain PFAS.[15]

The widespread use of PFAS has led to their distribution in the environment at elevated levels in training/fire response sites, industrial sites, landfills, and wastewater treatment plants.[16] They have also been detected in some cosmetics, pharmaceuticals, electronics, and insecticides.[17−19] An increase in detectable PFAS has been reported in wastewater treatment plants that employ biological treatment processes to remove contaminants.[20,21] The increase in the detection of PFAS in wastewater is not only limited to the increasing use of PFAS in consumer and industrial products, but also from the breakdown of polyfluorinated precursors, which leads to the formation of more PFAS.[21] For example, polyfluorinated precursors such as fluorotelomer alcohol (8:2 FTOH) and 2-(*N*-ethyl-perfluorooctanesulfonamido) ethanol can biodegrade leading to the formation of perfluoroalkyl acids (PFAAs).[21] Therefore, wastewater treatment plants are recognized as significant contributors of PFAS into the aquatic environment emanating from several sources, including households. They have also been recognized as secondary point sources of PFAS to surface and groundwater.[22,23] The contamination of surface water tends to occur more often via the discharge of wastewater effluents containing PFAS into surface water bodies, such as rivers. Such water bodies are frequently abstracted, treated, and distributed as drinking water.[21,24,25]

Recently, the analysis of POPs, such as PFAS, has significantly evolved, particularly with the availability and use of sophisticated analytical instruments, for example, high-resolution mass spectrometer which can perform accurate mass identification and tandem mass spectrometry (MS−MS) for quantitative analysis of multiple PFAS in a single chromatographic analysis. While tandem mass spectrometry provides good sensitivity and selectivity for targeted analysis of PFAS, it is incapable of detecting the presence of new and emerging PFAS since it requires analyte-specific information and consequently does not give an exhaustive overview of other PFAS present in environmental matrices such as water. The use of full-spectrum acquisition techniques that provide accurate mass high-resolution spectrometry such as LC-QTOF-MS is essential to obtain information about a large number of PFAS present in various water matrices. Suspect or nontargeted screening approaches are used as forensic tools to detect the presence of potentially overlooked emerging PFAS that could be harmful and present in water. This is of high importance since these substances end up in nearby water-bodies thereby adversely affecting the health of living organisms.[26]

A number of recent studies have reported the presence of PFAS in various matrices in South Africa. However, these studies have so far focused on a target list of PFAS in different matrices such as human breast milk,[27] retail milk and infant formula,[28] farmed marine shellfish,[29] water, sediment, and fish along the Vaal River,[30] sediment from Hartbeespoort and Roodepoort dams,[31,32] dragonflies,[33] and WWTPs.[34] Only limited PFAS were targeted in the aforementioned studies and none on emerging PFAS. Hitherto, information on PFAS status in South Africa's drinking tap water, branded bottled water, and drinking water treatment plants (DWTPs) is still sparse. It is, therefore, pertinent to investigate the status of PFAS in South Africa's water sources through nontargeted analysis in order to identify legacy and emerging PFAS, followed by targeted quantification of selected PFAS. This study thus reports for the first time in South Africa, and probably in the African continent nontargeted analysis of PFAS in different water sources and identifies potential sources of PFAS in different interconnected water systems. The results of this study provide novel insights into the current status of known and unknown PFAS in different water matrices and unveil their fate and transport from one water source to another.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents. Information on the chemicals and reagents used in this study is provided in Text S1.

2.2. Study Area and Sample Collection. The present study was carried out in Gauteng Province, South Africa from 2021 to 2024. Gauteng has an integrated cluster of towns and urban nodes with a population of over 15 million people (the highest in the country), even though it is the smallest province in terms of land area in the country. It is also characterized by several industrial centers.[35] Detailed information showing the map of the study area, sampling sites, descriptions, and characteristics of the WWTPs, DWTPs, and rivers in the catchment are outlined in Text S2.

2.3. Sample Extraction and Cleanup. PFAS were extracted from the samples by using USEPA Method 537.1 with slight modifications. Briefly, samples from wastewater, rivers, dams, and DWTP samples (except for effluent samples) were first filtered using a 0.45 and 0.2 μm glass fiber filter in a vacuum filtration unit. Prior to extraction, 100 μL of the 200 ng/mL surrogates (MPFNA) standard was added to 200 mL of each sample. The SPE cartridges were first conditioned with 5 mL of HPLC-grade methanol followed with 5 mL of ultrapure water. Without allowing the cartridges to dry, samples were passed through the cartridges under vacuum below 2.50 psi. Sample bottles were rinsed with 7 mL of ultrapure water and passed through the cartridge. The cartridges were then allowed to near dryness under vacuum for 1 h. Thereafter, PFAS were eluted with 10 mL of methanol under gravity in a dropwise manner. The eluates were concentrated to dryness under a gentle stream of nitrogen in a sonicator bath at temperatures between 65 and 70 °C. The dried extracts were reconstituted in 1 mL of methanol and vortexed for 1 min. The reconstituted extract was then transferred to a 2 mL centrifuge tube and centrifuged for 5 min to separate possible fine suspended particles in the extract. A 950 μL portion of the extract and a 50 μL portion of 1000 ng/L of internal standards were added to an autosampler vial. Five microliters (5 μL) of the samples was injected into the LC-QTOF/MS for nontargeted analysis.

2.4. Instrumental Analysis. *2.4.1. Nontargeted and Suspect Screening of PFAS.* Nontargeted and suspect screening of PFAS was carried out using SCIEX TripleTOF 6600 series coupled with a SCIEX ExionLC ultrahigh-performance liquid chromatography system (AB SCIEX, Framingham, USA). The QTOF was operated with electro-

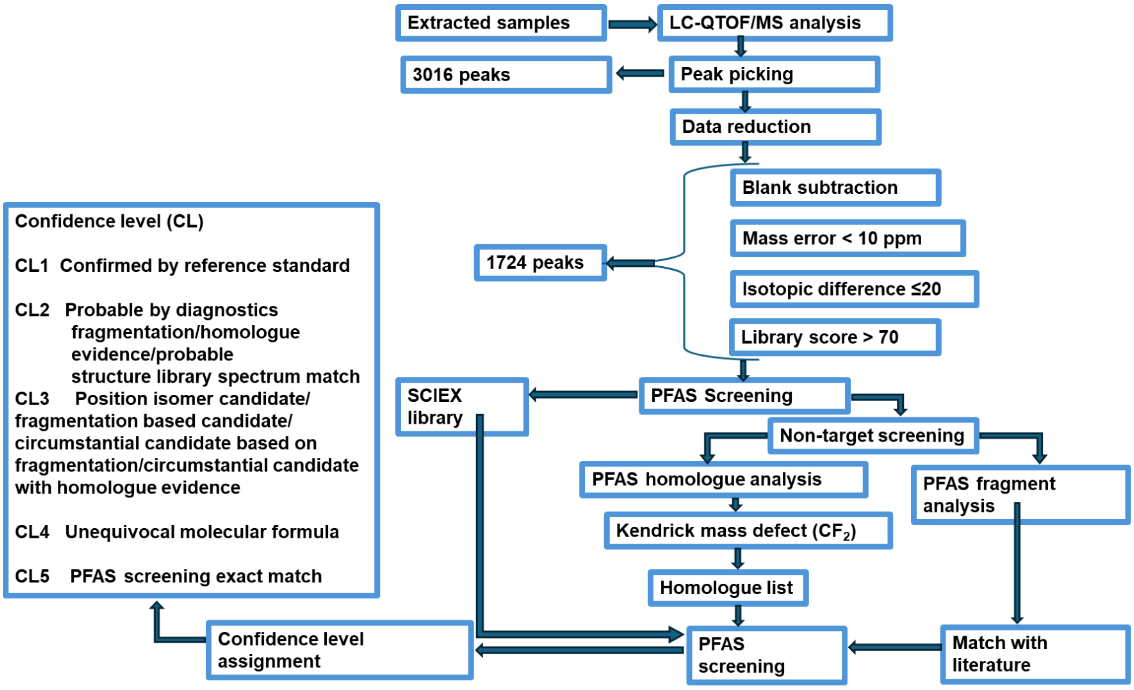

Figure 1. Workflow used for nontarget analysis of PFAS, with Kendrick mass defect based on repeating fluoroalkyl (CF_2) units.

spray ionization operated in the negative polarity mode. Dynamic background subtraction was coupled with information-dependent acquisition (IDA) for dynamic exclusion in high-resolution mode. The IDA experiment was carried out with a TOF-MS survey scan spanning 100−1000 Da (100 ms) and up to 10 dependent TOF-MS/MS scans 50−1000 Da (100 ms) per cycle. The collision energy (CE) was −35 V, with a collision energy spread (CES) of ± 15 V. Chromatographic separation was performed on a Kinetex 2.6 μm XB-C18 100 Å, LC column (50 × 4.6 mm) with a column oven temperature set at 40 °C. The mobile phase comprised 20 mM of ammonium acetate and 0.1% (v/v) of formic acid solutions in water (mobile phase A) and 100% methanol as mobile phase B. The LC gradient condition was set at 95% of mobile phase A for 16 min, which decreased to 5% and held for 4 min, and then the mobile phase A increased to 95% for 6 min. The acquisition time was 26 min. An aliquot (5 μL) of the clean sample extract was injected into the TripleTOF at a constant flow rate of 0.500 mL/min. Both data acquisition and data processing were achieved by using SCIEX OS software.

The investigation of nontargeted and suspect PFAS was designed for WWTPs, DWTPs, drinking water, and surface water samples, and the list of some legacy and emerging PFAS was screened against their molecular formulas. Features with a signal-to-noise ratio (S/N) > 3 and peak intensity >100 cps were screened for PFAS. The workflow for the identification of PFAS (shown in Figure 1) was modified from ref. 36. Compounds with positive hits were confirmed by library matching, which was automatically carried out using the SCIEX Fluorochemical HR-MS/MS library 2.0, which contains 252 PFAS compounds. These compounds include negative, positive, and zwitterionic compound classes and include legacy and novel PFAS, for example, those originating from aqueous film-forming foam (AFFF) and AFFF-impacted water. Also, library matching was performed with the SCIEX All-in-one HR-MS/MS library version 2.0 and the NIST library 2017 version (SCIEX format) which contains spectral data for 3900 and over 13 800 compounds, respectively. Confidence levels were assigned as indicated in Figure 1. Pure analytical standards were further used to confirm features at confidence level (CL) 1. Further details of the assignment of confidence levels for the identification of PFAS are presented in Text S4.

2.4.2. Targeted Analysis of PFAS. Targeted analysis of PFAS was carried out using Shimadzu LC-MS-8030 model (Shimadzu USA Manufacturing Inc., Canby, OR, USA), which was equipped with an electrospray ionization source (ESI). Multiple reaction monitoring (MRM) transitions were optimized using flow injection analysis (FIA) for all compounds. High-concentration standards of 1000 ng/L containing a mixture of all of the target PFAS were used for the optimization of MRM conditions. The mixture was then run under optimized LC-MS/MS conditions to obtain the retention times of each analyte. Separation was performed on a Kinetex 2.6 μm XB-C18 100 Å LC column (50 × 4.6 mm) with a column oven temperature set at 40 °C. The mobile phase comprised 20 mM of ammonium acetate in water (mobile phase A) and a 50:50 methanol: acetonitrile as mobile phase B. The gradient condition was set at 20% of mobile phase A for 3 min, which increased to 90% and held for 3 min, and then the mobile phase A decreased to 20% for 5 min. The acquisition time was 12 min. An aliquot (10 μL) of the cleaned sample extract was injected into the LC-MS-MS at a constant flow rate of 0.300 mL/min. Quantification was carried out using an internal standard calibration method.

2.4.3. Quality Assurance and Quality Control. To ensure the integrity of the results and to avoid contamination, all laboratory glassware and equipment were washed thoroughly, rinsed with methanol, and oven baked. The same procedure for sample preparation was used for the preparation of procedural blanks. Ultrapure water was used as procedural blanks and prepared for each batch of 10 samples.

The analytical method was validated for accuracy, precision, and sensitivity by using spiked samples and the European-certified reference material CRM IRMM-428 (PFAS in water).

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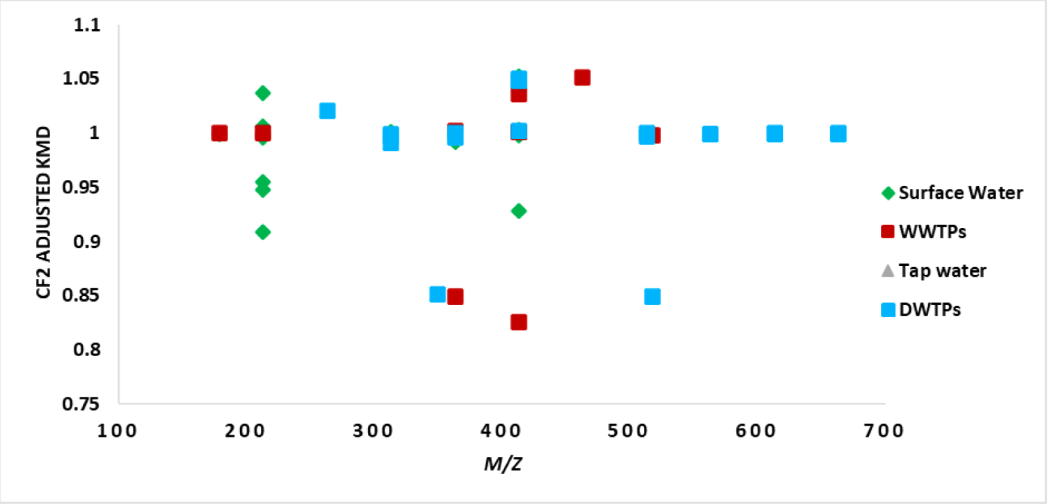

Figure 2. A plot of CF_2 adjusted Kendrick mass defect (KMD) with *m/z* in surface water, WWTPs, tap water, and DWTPs identified by homologous analysis.

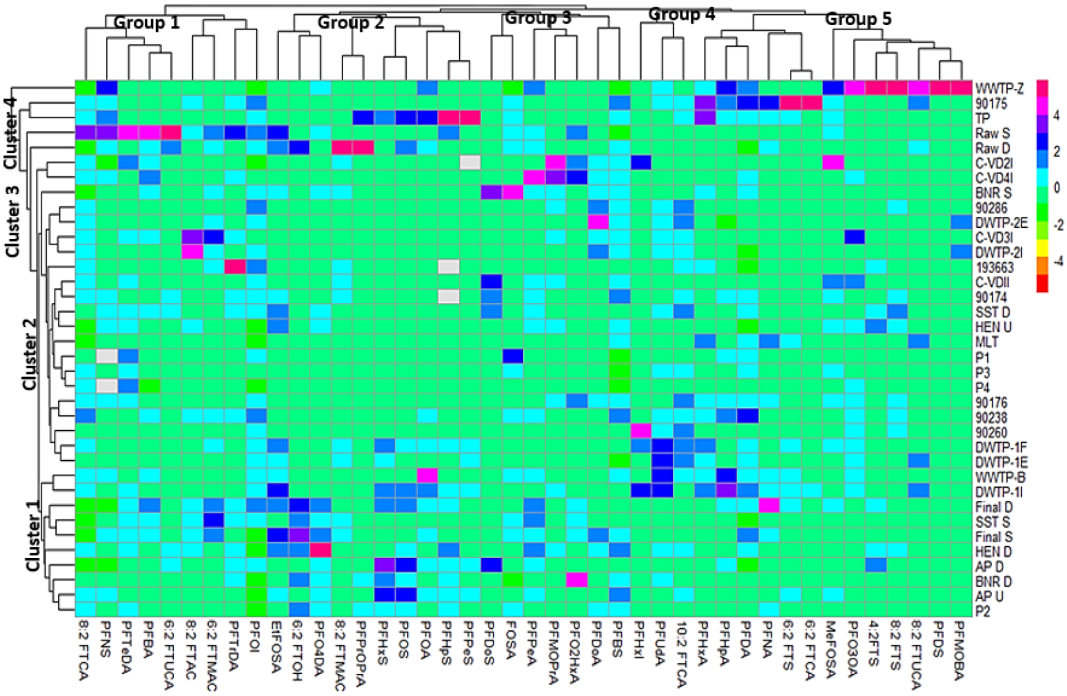

Figure 3. Occurrence of PFAS identified at confidence levels 1−3, based on intensity in various water samples.

The recoveries of PFAS were satisfactory and ranged between 59.7% and 150% (Table S3). The method's precision measured as the relative standard deviation of triplicate measurement was generally <27% (Table S3).

Full details of all quality control and assurance measures employed throughout the study are presented in Text S4.

2.4.4. Statistical Analysis. All mathematical and statistical computations were performed with Microsoft Excel 2016 (Microsoft Office), IBM SPSS (version 28.0.0.0), and R software (version 4.2.1). The data for PFAS with detection frequencies of >60% were explored in SPSS to check for their distribution, and log transformation was used for data normalization. Multivariate analysis was carried out on the normalized data. Hierarchical cluster analysis was used to identify possible sources of PFAS in different water systems.

3. RESULTS AND DISCUSSION

3.1. Nontarget Analysis. PFAS features identified in this study are presented in Tables S4 and S5. Homologues of PFAS with mass differences of 49.99 and 99.99 Da were observed among the exact masses of the PFAS identified in the samples. Overall, through nontargeted analysis, a total of seventy (70) features were identified, where forty-one (41) PFAS were identified as legacy and emerging PFAS at confidence levels (CL) 1−3, while twenty-nine (29) suspect features were identified at CL 4. PFAS identified at CL 1−3 were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFHxS, PFOS, PFDS, PFHpS, PFNS, PFDoS, PFPeS, 4:2 FTS, 6:2 FTS, 8:2 FTS, FOSA, MeFOSA, EtFOSA, 6:2 FTUCA, 8:2 FTUCA, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTOH, PFHxI, PFOI, 8:2

FTAC, 6:2 FTMAC, 8:2 FTMAC, PFMOPrA, PFPrOPrA, PFO2HxA, PFO3OA, and PFO4DA, and are listed in Table S4. Suspect features that were identified at CL 4 are presented in Table S5. Representative examples of extracted ion chromatogram (XIC), MS, and MS/MS spectral for identified PFAS are shown in Figures S1−S4.

In this study, most of the legacy PFAS were confirmed at CL1 through suspect screening. PFSAs were mostly characterized by those fragment ions that are reported in the literature.[28] Among those characteristic fragment ions observed were $C_3F_7O^-$, $C_5F_5^-$, $O_3F_7^-$, O_3S^-, FO_3S, and others as shown in Table S4. The CF_2 Kendrick mass defects (KMD)[37] were successfully computed for PFCAs with $m/z < 699$ as shown in Figure 2. Among the characteristic mass differences, the ethoxy repeating units were the most identified, followed by methoxy repeating units and hydrogen double bonds. Features for perfluoro-2-methoxyacetic acid (PFMOAA) were observed in all blanks and samples, including the analytical standard reference materials, which were known not to contain the compound; hence, the results of PFMOAA were not included in the study.

Figure 3 shows hierarchical cluster analysis (HCA), highlighting similarities in PFAS patterns between the sites. For clarity, PFAS were grouped into groups 1−5, and samples into clusters 1−4. On the horizontal bottom x-axis are the PFAS detected, whereas the sample codes/sites are shown on the vertical right of the heat map. The colour of each cell represents the scaled intensity of each PFAS, increasing from red to dark pink. These groups presented PFAS with different carbon chain lengths, with groups 1 and 4 comprising mostly those with a carbon length ($n \geq 7$). Cluster 1 is characterized by WWTP effluents (Final S and D) that are discharged into rivers (Hen D and AP D), which are in the same cluster 1, as well as DWTP-1I (raw water abstracted from AP D). From this clustering, it can be deduced that the WWTP effluent can be accounted as the source of pollution[38] in these rivers, as well as the DWTP downstream. Three of the bottled water samples are clustered together with a mixture of surface water samples in cluster 2, while clusters 3 and 4 show a complete mixture of samples. However, in these clusters, it can be observed that WWTP influent (Raw S and D), Vaal River (C-VD) samples and DWTP-2 samples are closely associated. This can be as a result of similar source of pollution. Similar to this study, Liu et al.[39] used HCA to establish if groundwater was impacted by PFAS from the landfill leachate. This group found that landfill leachate was a major source of PFAS in the groundwater within the landfills and downstream sites.

3.1.1. Occurrence of PFAS in WWTP. Of the 41 legacy and emerging PFAS detected in this study, perfluorocarboxylic acids (PFCAs) with carbon chain length of C4−C14, C4−C9 perfluorosulfonic acids (PFSAs), fluorotelomer sulfonates (X:2 FTS), *N*-methyl sulfonamide (*N*-methyl FASAA), *N*-ethyl FASAA, fluorotelomer unsaturated carboxylic acid (6:2 FTUCA), fluorotelomer methacrylate (X:2 FTMAC), and perfluoroalkyl ether carboxylic acid (PFECA) were frequently detected in WWTP samples. The detection frequencies of PFAS in WWTP samples ranged from 23% to 100%, with PFBA, PFPeA, PFHpA, PFOA, L-PFBS, L-PFHxS, L-PFOS, L-PFHpS, 6:2 FTS, 6:2 FTUCA, and 6:2 FTMAC detected in all the samples. Similarly, PFHxA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, L-PFDS, L-PFNS, L-PFDoS, L-PFPeS, 4:2 FTS, 8:2 FTS, FOSA, MeFOSA, EtFOSA, 8:2 FTUCA, 6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTOH, PFOI, 8:2 FTAC, 8:2 FTMAC, PFMOPrA, PFPrOPrA, PFO2HxA, and PFO3OA were frequently detected.

The presence of PFCAs, PFSAs, and X:2 FTS in WWTPs in South Africa has been reported by Morethe et al.[40] (C4−17), Kibambe et al.[34] (C4−C10), and Adeleye[41] (C7−C11). *N*-methyl FASAAs, *N*-ethyl FASAA, 6:2 FTUCA, X:2 FTMAC, perfluorooctane sulfonamide (FOSA), perfluorooctly iodide (PFOI), fluorotelomer carboxylic acids (X:2 FTCAs), and PFECAs detected in this study are reported for the first time in WWTPs in South Africa.

As shown in Figure 3, influent samples (Raw S and Raw D) that are clustered together had similar PFAS signatures, suggesting similar sources of contamination. The distinction that exists between the two samples is as a result of PFAS in group 2 (8:2 FTMAC, perfluoro-2-propoxypropanoic acid (PFPrOPrA), PFOS, PFOA, PFDoA, and PFBS). This could imply that in addition to the similar sources of pollution, both WWTPs may have other sources of pollution. The influents (Raw S and Raw D), BNR (BNR S and BNR D), and SST and final effluents (Final S and Final D) from two WWTPs showed distinct patterns in PFAS distribution (Figure 3), where PFAS that were not observed in the influent samples were detected in subsequent WWTP process units and the effluent. For instance, while most of the PFCAs and PFSAs, 6:2 fluorotelomer methacrylate (6:2 FTMAC), 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA), *N*-methyl sulfonamide (MeFOSA), and 6:2 fluorotelomer sulfonate (6:2 FTS) were detected frequently across various points in the WWTPs, 6:2 fluorotelomer (6:2 FTOH), 8:2 fluorotelomer acrylate (8:2 FTAC), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA), perfluoro(3,5-dioxahexanoic) acid (PFO2XA), and perfluoro-2-propoxypropanoic acid (PFPrPrA) were detected from the BNR, SST, and effluent only.

While the detection of PFAS in both influent and effluent of WWTP samples may suggest that these treatment plants are inefficient in removing PFAS, their detection in the effluent may indicate some sort of transformation in the WWTPs during secondary treatment (BNR and SST) and tertiary treatment processes (photolysis due to UV treatment).[42] The transformation or degradation may also be explained by the PFAS composition profiles across the treatment plant process. All WWTPs investigated in this study utilized the activated sludge process (ASP) as the biological nutrient removal process (BNR) with different configurations and showed different patterns in PFAS profiles. This could account for the variability in PFAS composition between BNR D and BNR S as shown in Figure 3. Similar variations were also observed for the SST samples. Additionally, this variation was further observed with features identified at CL 4 (Table S5). The same is true for the SST and effluent samples. A previous study by Coggan et al.[20] also indicated that the increase of PFOA from the influent to the effluent may reflect PFAS transformation in the WWTP. These observations provide valuable insights into the transformations taking place within the WWTP systems.

3.1.2. Occurrence of PFAS in Surface Water. Nontargeted analysis of PFAS in surface water ($n = 17$) investigated in this study resulted in the identification of widely reported PFAS in surface water samples, with the detection frequency of 12−100%. PFCAs including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTeDA, and PFTrDA were more frequently detected, followed by C4−C10 PFSAs, e.g., PFBS, PFHxS, L-PFOS, L-PFNS, L-PFDS, L-PFHpS, and PFPeS; X:2 FTS (C8−10) (6:2 FTS and 8:2

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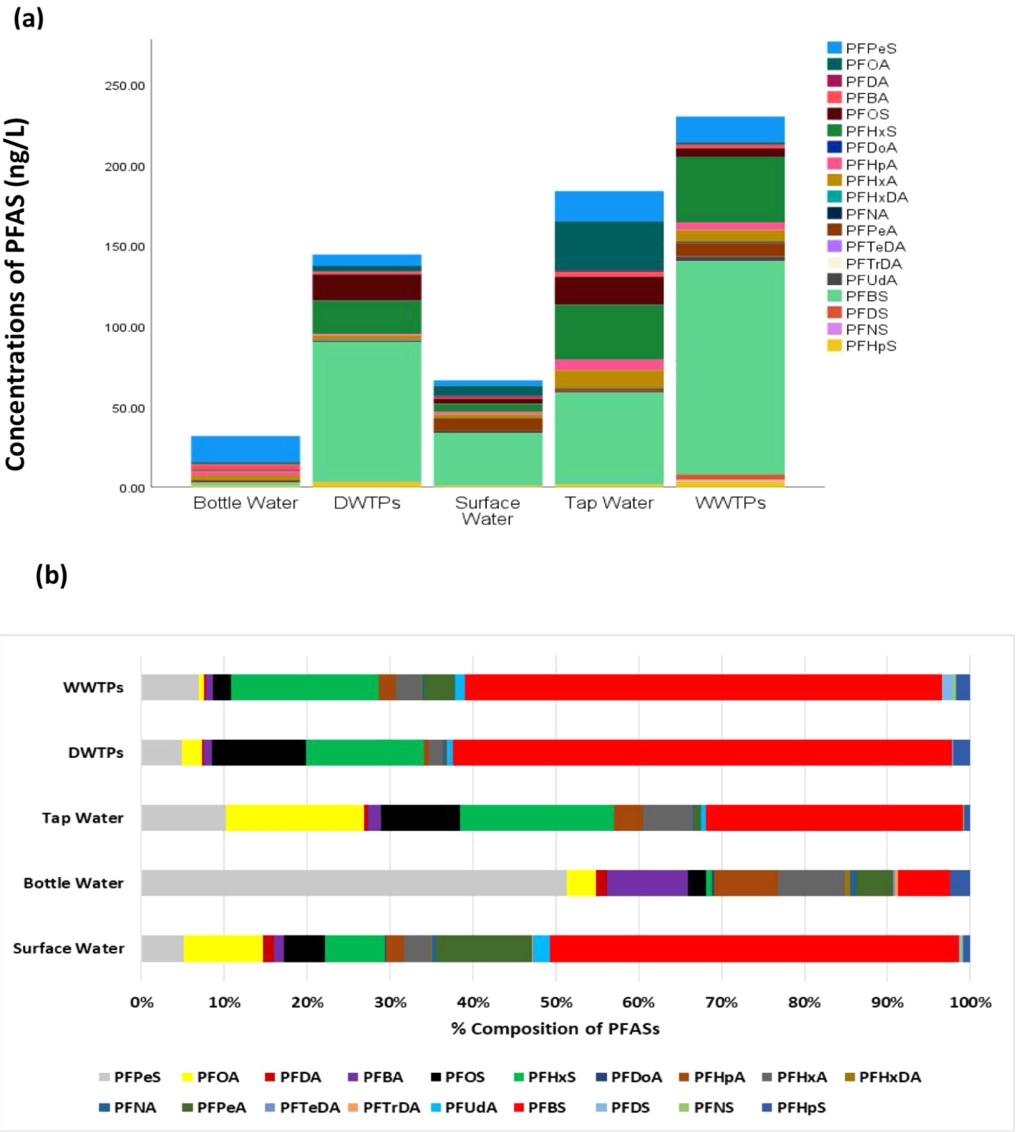

Figure 4. (a) Mean concentrations of PFAS in various water matrices and (b) % composition profiles of PFAS in bottled water, DWTPs, surface water, tap water, and WWTPs.

FTS), FOSA (C8), MeFOSA (C9), EtFOSA (C10), 6:2 FTUCA (C8), X:2 FTCA (C8−10) (6:2 FTCA, 8:2 FTCA, and 10:2 FTCA), 8:2 FTAC (C13), X:2 FTMAC (C12−14) (6:2 FTMAC and 8:2 FTMAC), and PFECAs (C3−C5) (PFMOAA, PFMOPrA, PFPrOPrA, PFO2HxA, and PFO3OA). Only FOSA was detected in all of the samples.

Surface water samples exhibited a wide range of features compared to other matrices, with 1−7 suspect features identified at confidence level 4 (Table S5). Legacy PFAS have been widely reported in surface water[43−45] including in South Africa.[30,31,46] Similar to those PFAS reported in the WWTPs in this study, *N*-methyl FASAAs, *N*-ethyl FASAA, 6:2 FTUCA, X:2 FTMAC, X:2 FTAC, X:2 FTCA, PFOI, and PFECAs are reported for the first time in South African surface water. Figure 3 shows the clustering of surface water (Hen D and AP D) in the same cluster with WWTP effluent samples. It is noteworthy that Final S and Final D are discharged into Hen D and AP D, respectively, while AP U receives discharge from WWTP-B via 90174. Surface water collected downstream of WWTPs showed higher numbers of PFAS compared to those of upstream samples. This suggests that WWTPs could account for the contamination of these surface water.

Studies of PFAS in South Africa's surface water have so far focused on targeted analysis with a few lists of PFAS. For the first time in South Africa, we reported the occurrence of perfluoroalkyl ether carboxylic acids (PFECAs) in surface water. PFECAs have been reported previously in surface water from North Carolina.[47] The presence of these long-chain PFAS may be attributed to their environmental persistence as well as the fact that they may still be in use. The detection of short-chain and emerging PFAS suggests, in part, a response to current legislations on PFOA and other long-chain PFAS, or due to degradation. PFAS in surface water pose a risk not only to aquatic living organisms but also to terrestrial organisms. Surface water has a long range of transportation, and since most surface waters serve as abstraction points for DWTPs, end-users are most likely to be exposed to PFAS through the ingestion of drinking water.

3.1.3. Occurrence of PFAS in DWTP. The detection of PFAS in the DWTPs mostly comprised PFCAs (C4−10, 14), PFSAs (C4−10), X:2 FTS (C8−10), FOSA, EtFOSA, X:2

FTCA (C6−10), X:2 FTUCA (C8−10), 6:2 FTOH, PFOI, PFHxI, 8:2 FTAC, X:2 FTMAC (C12−14), and PFECAs (C3−5) in 60% to 100% of the samples. FOSA, MeFOSA, *N*-Ethyl perfluorooctane sulfonamide (EtFOSA), 6:2 FTUCA, 8:2 FTUCA, 10:2 FTCA, 6:2 fluorotelomer alcohol (FTOH), perfluorohexyl iodide (PFHxI), 8:2 FTAC, 8:2 FTMAC, perfluoro-3-methoxypropanoic acid (PFMOPrA), PFPrOPrA, PFO2HxA, and PFO3OA were detected in DWTPs, at confidence levels, CL2−3. We reported for the first time the occurrence of PFAS in DWTPs in South Africa. PFBA, PFPeA, PFHxA, PFOA, PFNA, PFHxS, and PFOS confirmed in the present study have been previously reported in DWTP samples from other parts of the world.[48] The detection of these PFAS in all DWTP samples, specifically from the raw intake (influent), filters, and effluent indicate that these PFAS are not efficiently removed by conventional DWTPs. Based on the discussions in Subsections 3.1.1 and 3.2, it can be deduced that both WWTP effluents and surface water influence the detection of PFAS in DWTPs. These arguments are corroborated by the results reported by Boiteux et al.[49], and this poses a problem for end-users, especially because risk assessments have not been conducted to evaluate the extent of the health risk associated with exposure to these emerging contaminants in the South African context.

3.1.4. Occurrence of PFAS in Tap and Drinking Bottled Water. Legacy PFAS detected in drinking tap water were PFCA and PFSAs both with carbon chain length (C4−10). X:2 FTS (C8−10), FOSA, MeFOSA, 6:2 FTUCA, X:2 FTCA (C8−10), X:2 FTAC (C6−10), X:2 FTMAC (C12−14), 8:2 FTAC, PFOI, and PFECAs (C4−5) were also identified. Among the PFECAs, perfluoro (3,5-dioxanoic) acid (PFO2HxA), perfluoro-3,5,7,9-butaoxadecanoic acid (PFO4DA), and perfluoro-2-propoxypropanoic acid (PFPrOPrA), and perfluoro (3,5,7-trioxaoctanoic) acid (PFO3OA) were frequently detected in drinking tap water samples. PFPrOPrA is a short-chain PFAS, also known as Gen-X, and a replacement of PFOA. It has been used as an alternative due to its high-water solubility and a reduced toxicity compared to PFOA. To date, little is known about PFPrOPrA toxicity[50] as well as the toxicity of other PFECAs. However, PFPrOPrA has been suspected to present negative health effects to humans if consumed, inhaled, or exposed to the skin.[51] To the best of our knowledge, this study provides the first evidence of the occurrence of PFAS in South African tap water and reports for the first time the presence of PFO2HxA, PFO4DA, and PFO3OA in drinking tap water, globally.

Similar to the results observed in drinking tap water samples, PFAS identified at CL 1 in all bottled water samples consisted of PFCAs (C4−10, 14), PFSAs (C4−8, 10), and 6:2 FTS (Table S4). These included PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS, which have also been reported previously by refs.[52−55] and 56. Other legacy and emerging PFAS not reported in the literature were also identified in bottled water samples at CL 2−3. Of these, 6:2 FTCA, 8:2 FTCA, and FOSA were frequently detected in bottled water samples with PFMOPrA, PFO2HxA, and PFO3OA detected in all bottled water samples, while PFPrOPrA and PFO4DA were detected in one bottled water sample. MeFOSA was also detected in two of the water samples. Bottled water samples, P1, P2, and P3, were clustered together, with similar PFAS fingerprints from group 1. Bottled water sample (P2) was further distinguished from the other three bottled water samples, characterized by PFAS in group 2, whereas other samples were characterized by PFAS in group 1, as shown in Figure 3. 6:2 FTUCA, 6:2 FTCA, and 8:2 FTCA, fluorotelomer acrylates and methacrylates, perfluorohexyl iodide, and perfluorooctyl iodide were identified in some bottled water samples, and to the best of our knowledge, this is the first time these PFAS are reported in drinking bottled water worldwide.

3.2. Targeted Analysis and Quantification of PFAS in Different Water Matrices. At least thirteen (13) PFAS were detected in WWTPs, DWTPs, surface water, tap water, and bottled water at concentrations ranging from 0.540−403, 19.2−179, 1.14−138, 45−68.2, and 0.028−26.1 ng/L, respectively (Figure 4a) andTable S6. For bottled water, PFPeS exhibited the highest mean concentration that ranged from 10.6 to 26.1 ng/L. The concentrations of most of the long-chain PFAS such as PFTrDA, PFTeDA, PFHxDA, and L-PFDS were <LOQ, while short-chain PFAS dominated in composition profiles. This may be attributed to a shift in the use of long-chain PFAS and other PFAS alternatives, and in part to the high water solubility of short-chain PFAS compared to their long-chain counterpart.

3.2.1. Concentration of PFAS in WWTPs. Different trends were observed in two WWTPs between the influent, BNR, SST, and the final effluent after disinfection. Figure S5a presents the variations of PFAS in treatment processes and the effluent (Final D, Final-S, WWTP-Z, and WWTP-B). Of the 21 PFAS investigated in wastewater samples, 16 PFAS were detected in all samples. PFBS was the major contributor to the total PFAS concentrations in the wastewater samples (Figure 4b). This was followed by PFHxS, PFPeS, PFHxA, PFPeA, PFHpS, PFOS, and PFHpA with sum concentrations of 408, 160, 84.5, 71.0, 54.3, 47.0, and 44.3 ng/L, respectively.

The trends in concentrations between WWTP D and S are somewhat similar but different with some PFAS, consistent with the observation in nontarget analysis. For instance, PFBS concentrations were lower in the influent of WWTP D and S (60.0 and 76.4 ng/L, respectively), higher in the SST (314 and 403 ng/L, respectively), and, thereafter, decreased in the final effluent (153 and 132 ng/L, respectively). This observation was similar to the trend reported by Wang et al.[57] The concentration of PFHxS in WWTP D increased from 6.58 ng/L (influent, Raw D) to 304.2 ng/L (BNR D), followed by a sharp decrease to 13.5 and 9.62 ng/L in SST and final effluent (Final D), respectively. The opposite was observed for WWTP S. This can be due in part to the different operational conditions of each treatment plant.

Short-chain PFAS (PFBS, PFHxS, PFHxA, PFBA, PFPeA, and PFPeS) were more frequently detected and at higher concentrations than the long-chain PFAS. This could be due in part to the high-water solubility and mobility of short chain,[58] and their extensive use in manufacturing processes as replacement for long-chain PFAS. The low concentrations and detections of long-chain PFSA may be due to their hydrophobicity and sorption affinity.[59] Long-chain PFAS have lower water solubility compared to short-chain PFAS and may prefer partitioning into hydrophobic surfaces than remaining in the aqueous phase.[60]

3.2.2. PFAS Concentrations in Surface Waters. At least 14 targeted PFAS were detected in all surface water samples. PFBS, PFOA, PFHxS, and PFOS exhibited mean concentrations (Figure S5b) ranging from 1.14 to 138 ng/L, 0.370 to 85.2 ng/L, <LOD-35.3 ng/L, and <LOD-30.2 ng/L, respectively. High concentrations of short-chain PFAS may

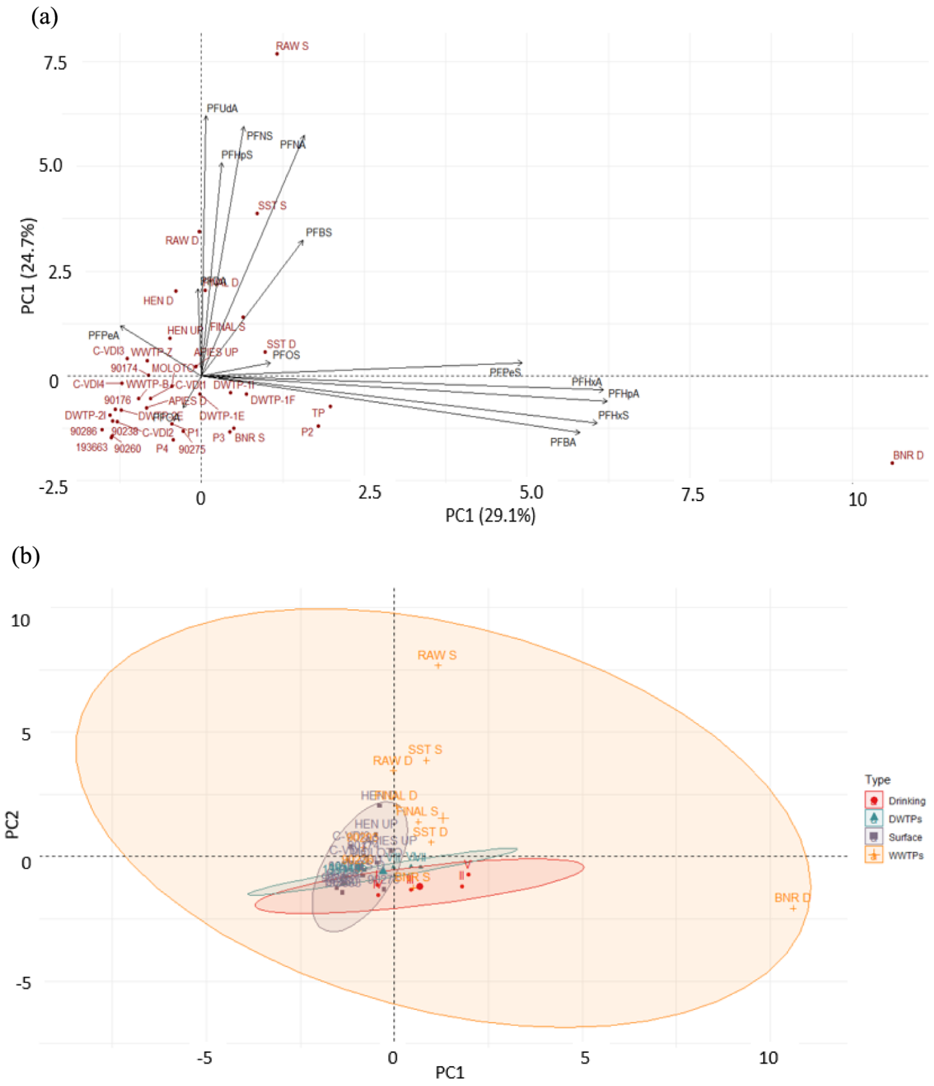

Figure 5. Multivariate analysis of various water samples showing (a) loadings of principal components analysis (PCA) and (b) ellipses of sampling sites.

be as a result of their partitioning to water, as they are highly soluble in water and mobile, while the detection of long-chain PFAS at low concentrations, especially the sulfonates, may be as a result of their preferential sorption to sediment rather than water in the aquatic environment. However, PFBS and PFOA fall somewhere in between the above-mentioned examples in terms of solubility and mobility, and are reported to be present in all environmental samples because of their combination of carbon length and functional group.[61] PFHpA and PFPeA were detected in all surface water samples, consistent with other studies.[47]

3.2.3. PFAS Concentrations in DWTPs, Drinking Tap and Bottled Water Samples. Most drinking water treatment plants in South Africa receive raw water from surface (rivers and dams) water, which are often prone to effluents from WWTPs, hence, PFAS are hypothesized to be present in DWTPs, and eventually reach drinking tap water. Some of the PFAS may end up in bottled water depending on the source of the water.

DWTPs samples showed (Figure S5c) the highest concentrations of PFBS, PFHxS, and PFOS ranging from 19.2−135, 21.3−80.4, 3.43−25.8 ng/L, 6.11−30.9, 0.78−45.1 ng/L, and 0.938−11.3 ng/L in the influent and effluent, respectively. The results indicate that DWTPs are inefficient in removing PFAS.

Fifteen (15) targeted PFAS were detected in drinking tap water with PFBS presenting the highest concentrations in this matrix, with a mean concentration of 57 ng/L. This was followed by PFHxS (34.1 ng/L), PFOA (30.6 ng/L), PFPeS (18.8 ng/L), PFOS (17.5 ng/L), and PFNA (10.9 ng/L). These concentrations exceeded the US EPA maximum contaminant levels (MCL) of 4 ng/L for PFOA and PFOS, and 10 ng/L for PFHxS and PFNA.[62] The detection and concentrations of these PFAS have also been reported in other studies.[55,63,64]

Four different brands of bottled water (brands 1, 2, 3, and 4 = P1, P2, P3, and P4, respectively) were investigated for the presence of PFAS (Figure S5d). Numerous PFAS, i.e., 15, 16, 14, and 13 PFAS, were detected in P1, P2, P3, and P4, respectively. Consistent with other matrices and similar studies,[65,66] the short-chain PFAS contributed more to the composition profiles, with the highest concentration observed for PFPeS in P1, with a mean concentration of 26.1 ng/L.

Because PFAS are reported to be bioaccumulative, their levels in the human body may be elevated after years of continued exposure. It is also reported that infants are frequently exposed to PFAS via formula milk or breastfeeding,[67] therefore, more susceptible to PFAS than old people. Liver damage, immune system suppression, adverse reproductive and developmental effects, cancer, increased serum cholesterol levels, and decreased antibody response to vaccinations have been associated with exposure to PFAS.[60]

3.2.4. Comparison with Other Studies. The results obtained in this study were compared with those reported across the world (Table S7). The concentrations of most of the short-chain PFAS in the WWTPs in this study were higher, but lower for long-chain PFAS reported by refs. 68 and 69. Even though most of the treatment plants compared in this study utilized the activated sludge process (ASP), the variation in concentrations of PFAS may be owed to different ASP configurations, the type of wastewater received by each WWTP as well as spatial variabilities.

The concentrations of PFAS in surface water reported in this study were similar to those reported in surface water from the USA for PFOS (<LOD −38.0 ng/L), PFPeS (nd −9.3 ng/L), PFBA (nd − 2.18 ng/L), PFHxS (nd −33.9 ng/L),[61] and from Poland for PFHpA (0.02−0.67 ng/L).[74] Higher concentrations were reported by Sun et al.[70] in the range of 14.0−276, 21.9−105, and 7.40−59.2 for PFBS, PFOA, and PFPeA, respectively in surface water from Shanghai (China). The concentrations of PFHxS, PFHxA, PFBA, and PFPeA in the influent and effluent of DWTP samples reported by Jiao et al.[71] were significantly higher than those reported in this study.

The levels of PFBS in drinking tap water were significantly higher than those reported by Chow et al.[66] (nd −0.65 ng/L), (0.092−18.8 ng/L), and (0.15−1.48 ng/L).[72] Compared with a study carried out by ref. 67, PFOS and PFOA were reported at 16.0 and 9.70 ng/L in drinking tap water, respectively, while Rostkowski et al.[68] reported levels of 14.8 and 45.0 ng/L for PFOS and PFOA, respectively. The concentrations of PFOS reported by both studies are similar to the levels reported in this present study, while PFOA reported by Lenka et al.[67] was lower and the concentrations reported by Rostkowski et al.[68] was higher than those reported in this study.

PFBS concentrations in bottled water observed in this study (max = 4.16 ng/L) were significantly lower than the concentration reported for PFBS in bottled water investigated by ref. 56 (max = 51.0 ng/L) in Irish bottled water. Jurivoka et al.[69] reported nondetection of long-chain PFAS, including PFDS, in bottled water samples, which was also not detected in bottled water samples investigated in this study. However, PFNS, PFTrDA, and PFTeDA were detected in the bottled water samples investigated in this study, while Pan et al.[69] reported nondetection of these PFAS.

3.3. Multivariate Analysis. *3.3.1. Sample Variance and Correlations of PFAS in Samples.* To establish whether there was any relationship between the sampling sites and PFAS patterns within the samples for possible source identification, different tests including variance, correlations, and PCA were conducted. There was no statistical difference ($p > 0.05$) between the mean concentrations of PFAS in WWTP, DWTP, and drinking tap water samples, but differs significantly ($p < 0.05$) from surface and bottled water samples. Table S8 shows Pearson's correlations between different PFAS in samples collected from various sources. Long-chain PFSAs (PFNS, PFHpS, PFUdA, and PFNA) were strongly and positively correlated ($r > 0.800$) with each other except for PFOS and PFOA. However, PFOS was moderately correlated with PFBS ($r = 0.382$). Strong correlation was also observed between short-chain PFAS. PFOA was only negatively and weakly correlated with PFNA ($r = -0.127$). The observed strong and positive correlations between long-chain PFSA may suggest a common source and predictability, whereas moderate correlation suggests a weak linear relationship. On the other hand, the weak and negative correlation observed between PFOA and PFNA may indicate different sources.

3.3.2. Source Apportionment of PFAS: PCA and Cluster Analysis. Five (5) components were extracted with eigenvalues >1, explaining 79% of the total variance (Additional information on HCA plot, extracted components, and loadings is provided in Tables S9 andS10). As shown in Figure 5a, principal component 1 (PC1) resulted in 29.1% variance and had high positive loadings of short-chain PFAS (PFPeS, PFBA, PFHxS, PFHxA) and long-chain PFHpA. Principal component 2 had 24.7% of variance with high loadings of long-chain PFAS (PFNA, PFudA, PFNS, and PFHpS).

Most of the surface water samples as shown in Figure 5a on the second and third quadrants were characterized by high loadings of PFOA, PFDA, and PFPeA, thus indicating similar sources of PFAS. The same is observed in HCA (Figure S6) which gave distinct groupings of samples and PFAS as variables which separate each sample from the other. HCA further distinguished groups within clusters according to the PFAS signatures. It is notable that Raw D and Raw S are distinguished from this subcluster by PFHpS, PFUdA, PFNA, and PFNS, indicating the probability of similar sources of PFAS. Similarly, Final D and Final S samples are distinctively grouped together in one subcluster and are dominated by long-chain PFNA. BNR S and BNR D showed different PFAS signatures, and this could be owed to their different activated sludge plant configurations; however, PFPeS was abundant in both samples. DWTPs and drinking water (tap and bottled water) samples were distributed along the 3 clusters obtained through HCA, with bottled water (P1, P3, and P4) showing similar PFAS signatures.

Results obtained from PCA and HCA could indicate the activities from upstream and downstream of the sampled areas or within each water body. For example, activities upstream of the river, where HEN UP, HEN D, and WWTP S samples were collected including plastic manufacturing and food processing industries as described by Nawn.[73] Upper Vaal (upstream C-VDI1, C-VDI2, C-VDI3, and C-VDI4) is characterized by industrial activities such as mineral processing plants, steel and petrochemical industries, fertilizer, pulp, and paper.[74]

Two samples from WWTPs (BNR D and RAW S) stretch the ellipses (Figure 5b) as a result of high concentrations and their variability. Samples grouped near each other have similar PFAS profiles or sources of pollution. Wastewater samples (WWTP-Z and RAW D) and surface water (HEN U, HEN D, 90174, APIES U, and C-VDI3) were characterized mostly by PFCAs, which are known to originate from industrial and environmental sources, consumer products, and potential breakdown products of polyfluoroalkyl phosphoric acid diesters (diPAPS),[75] their occurrence in WWTP effluent may have been influenced by the degradation of these compounds or the inability of WWTPs to remove them. Fiedler et al.[76] used PCA to assess differences between PFOA, PFOS, and PFHxS in human milk, water, and air on regional and matrices basis, and all three matrices overlapped. Similarly, ref. 77 carried out a multivariate analysis on 15 PFAS from different environmental matrices and used PCA to investigate the differences between PFOS, PFOA, and PFHxS in national samples from global monitoring plan projects. Bugsel et al.[75] investigated various PFAS in impregnated paper and soil samples to establish if the paper samples were a source of pollution to the soil, using PCA and HCA. Similar to this study, the link between sources of contamination was established and variability was observed between samples.

4. CONCLUSION

Nontargeted and suspect screening approaches used in the present study identified seventy (70) PFAS in WWTPs, surface water, DWTPs, tap water, and different brands of bottled water. PFAS were reported for the first time in South African DWTPs, bottled water, and drinking tap water. Most of the legacy PFSAs were detected at confidence level, CL 1, and emerging PFAS such as PFO2HxA, PFO3OA, PFO4DA, PFMOPrA, and PFPrOPrA were also identified in WWTPs, drinking tap water, and bottled water for the first time in South Africa. Additionally, legacy PFAS, detected at CL 2−3, such as FOSA, 6:2 FTCA, 6:2 FTUCA, and 8:2 FTCA, have not been reported in South African water sources, and their detection in the present study suggests the need to increase the number of PFAS investigated in different water sources. Legacy short-chain PFAS (PFBA, PFHxA, L-PFPeA, PFBS, L-PFHxS, L-PFPeS, and 4:2 FTS) were frequently detected in the samples, suggesting a proliferation of this group of PFAS in South African water systems.

This study suggests that WWTPs potentially contribute to the burden of PFAS in DWTPs and rivers in South Africa. Similarly, we observed that PFAS fingerprints in both treatment plants were different, and this may be due in part to the different biological nutrient removal (BNR) configurations for the WWTPs. Though only six short-chain PFAS were targeted, their concentrations were higher than those of long-chain PFAS in this study, suggesting a shift from the use of long-chain PFAS to short-chain PFAS or transformation within the water systems. The composition profiles of PFAS observed in this study are similar to those observed in studies across the globe. Though statistical analyses such as correlations, PCA, and HCA clustering are useful for identifying potential sources, the information is inadequate to account for the magnitude of PFAS discharged from various industries, the PFAS precursors as well as factors contributing to increase in PFAS levels

The presence of these PFAS in water causes a great concern as a result of their long-range transportation, bioaccumulation, and significant human health risks. The average concentrations of PFHxS, PFOA, PFOS, and PFNA in drinking tap water in this study exceeded the US EPA maximum contaminant levels, raising concerns over public health implications of PFAS. Human exposure to PFAS has been linked to several negative health outcomes including different types of cancer, reproductive defects, and thyroid diseases. Our results provide important experimental evidence for policymakers to legislate for PFAS in drinking water in South Africa, to minimize human exposure to these toxic group of chemicals.

Finally, we recommend that future investigations of PFAS contamination should be interactive and integrative to better understand the pattern of each PFAS in different environmental matrices and samples.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.5c00145.

Details of chemicals, analytical standards and reagents used in this study; Optimized mass spectrometry parameters and method performance characteristics; List of abbreviation of studied PFAS; Location, map and description of sampling sites; Detailed sample extraction and cleanup protocols; Quality Control and Assurance protocol; Details of nontargeted analysis and performance characteristics; Figures and Tables of Results of nontargeted and targeted analysis of PFAS (PDF)

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Notes

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