

# Poly- and Per-fluorinated Substances in Selected Dams in South Africa

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## 1 Introduction

Poly- and perfluorinated substances (PFASs) are synthetic organic chemical that have been produced since the 1950s<sup>1</sup>. Because of their water, oil, and grease repellency, PFASs are widely applied in industrial and consumer products such as textiles, firefighting foams and floor polishes<sup>2</sup>. Of all the PFASs, PFOS and PFOA are of most concern<sup>3</sup>. In South Africa, PFASs have been detected in both river and drinking water<sup>4</sup>. However, there is still scarce information of PFASs in other water sources such as dams, particularly dams that provide water for domestic consumption, irrigation and recreational activities. In recent times, the quality of the water in some of the dams in South Africa has been of concern. For example, the water quality of Roodeplaait Dam has been of concern due to hypertrophic conditions<sup>5</sup>. Hartbeespoort Dam is another dam that has received much attention because of pollution problems. It provides water for irrigation and domestic consumption, recreation and receives drains from Crocodile River that borne pollutants from highly industrialised and urbanised areas<sup>5</sup>. The aim of the present study was, therefore, to identify the presence and concentrations of targeted PFASs in water samples from two important dams, Hartbeespoort and Roodeplaait. The present study is part of an ongoing national monitoring programme of PFASs in water sources in South Africa.

## 2 Materials and Methods

Water samples were collected from Hartbeespoort and Roodeplaait Dams, South Africa between 2020-2022. Roodeplaait Dam is located approximately 24 km north-east of Pretoria, while Hartbeespoort Dam is located in the North West Province, within the Limpopo River system. The locations of the dams and the sampling points are shown in Figure 1.

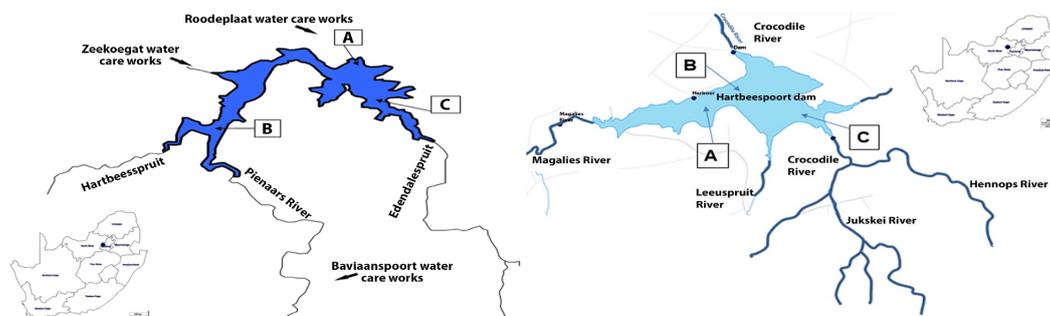


Figure 1: Location of sampling sites in the Roodeplaait (left) and Hartbeespoort (right) Dams, and sampling sites within South Africa (bottom left and top right)

In the Roodeplaait Dam, sampling Point A is located at the dam wall whereas point B is located upstream of the dam, where there is inflow from the Hartbeespoort and Pienaars Rivers. The Pienaars River drains into the central part of the Roodeplaait Dam, receiving run-off from the Mamelodi Township, and treated sewage from the Baviaanspoort sewage works. Point C is located downstream of the dam, where there is an inflow from the Edendalespruit River, which mainly drains into the agricultural area on the east side of the Roodeplaait Dam catchment. Sampling Point A in the Hartbeespoort Dam, represents the Magalies River inflow into the dam, where significant irrigation and mining activities are present. Sampling Point B is located in the middle of the dam, between Points A and C. Sampling Point C of the dam represents the Crocodile River inflow.

A 50 mg·L<sup>-1</sup> PFAS standard mix, with 20 investigated PFASs, were purchased from Wellington Laboratories, Ontario, Canada. Similarly, stable isotopically labelled PFASs standard employed as surrogates were perfluoro-n-[1,2,3, 4-<sup>13</sup>C<sub>4</sub>] octanoic acid (MPFOA), perfluoro-n-[1,2,3,4, 5-<sup>13</sup>C<sub>5</sub>] nonanoic acid (MPFNA), perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>] undecanoic acid (MPFUnDA), perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>] dodecanoic acid (MPFDoDA) and sodium perfluoro-[1,2,3,4-<sup>13</sup>C<sub>4</sub>] octanesulfonate (MPFOS). Internal standards were perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>] butanoic acid (MPFBA), perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>] hexanoic acid (MPFHxA), perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>] decanoic acid (MPFDA) and sodium perfluoro-1-hexane[<sup>13</sup>C<sub>2</sub>] sulfonate (MPFHxS) purchased in methanol from Wellington Laboratories (Ontario, Canada). LC-MS grade water, methanol and ammonium acetate were purchased from Sigma-Aldrich (Aston Manor,

South Africa). For extraction, the Supelco ENVI-18 SPE cartridges were preconditioned with 2 mL methanol followed by 2 mL Milli-Q water. Prior to the extraction, the samples were spiked with 500  $\mu\text{L}$  of 100  $\text{ng}\cdot\text{mL}^{-1}$  labelled surrogate standard (MPFOA, MPFNA, MPFUnDA, MPFDoDA, and MPFOS) and allowed to equilibrate for about 1 h. Thereafter, 500 mL water samples were loaded into the SPE cartridges and at a flow rate of a drop per sec. After extraction, the SPE cartridge was vacuumed dry for 1 h and eluted with 2 x 5 mL methanol into 10 mL polyethylene tubes. Thereafter, the cleaned extracts were blown to incipient dryness under a gentle stream of nitrogen gas and reconstituted to 1 mL with methanol and 100  $\mu\text{L}$  of 2  $\text{mg}\cdot\text{L}^{-1}$  internal standards (MPFBA, MPFDA, MPFHxS, MPFHxA), and then centrifuged and transferred to 1 mL amber vials prior to instrument analysis. The PFASs were determined using liquid chromatography-tandem mass spectrometry (Shimadzu LC-MS 8030 triple quadrupole system, Kyoto, Japan). The instrument was equipped with an electrospray ionization (ESI) source and the target compounds were separated on an InertSustain C18 (3  $\mu\text{m}$ , 2.1 i.d. x 150 mm) HPLC column (Kyoto, Japan). The injection volume was 10  $\mu\text{L}$ . The mobile phases consisted of (A) 20 mM ammonium acetate, and (B) 100 % methanol. The mobile phase was initially maintained at 20% B, ramped to 80% B over 7 min, and thereafter increased to 100% B over 20 min, returned to 20% over 22 min, and maintained at 20% over 30 min. The flow rate of 0.2  $\text{mL}\cdot\text{min}^{-1}$  was maintained throughout the analysis. The quantitation of the target compounds was based on internal standard method calibration with concentrations ranging from 1.0–250  $\text{ng}\cdot\text{mL}^{-1}$ . A correlation co-efficient ( $R^2 \geq 0.99$ ) was achieved in all the calibrations with good precision of the internal standard. The method was developed and optimized through the analysis of the calibration standards employing the highly selective and sensitive multiple reaction monitoring (MRM) mode of analysis. During the analysis of samples, solvent blanks were run in between samples to check for possible carryovers and a quality control standard (100  $\text{ng}\cdot\text{L}^{-1}$ ) was analysed in each batch to check consistency during instrumental analysis. To assess the accuracy of the extraction method, samples were spiked with the surrogate standard and the recoveries of each compound calculated.

### 3 Results

Recoveries ranged from 84–115% MPFOS, 116–124% MPFNA, 113–119% MPFUnDA, 108–116% MPFDoA, and 108–114% MPFOA. LOD and LOQ were calculated at 3x and 10x the S/N ratio, respectively. Figure 2 shows the total ion chromatogram (TIC) of some of the targeted compounds (overlaid). Of the 20 targeted PFASs, only 9 PFASs were detected (PFBA, PFHpA, PFPeA, PFHxA, PFOA, PFNA, PFBS, PFHxS, PFOS).

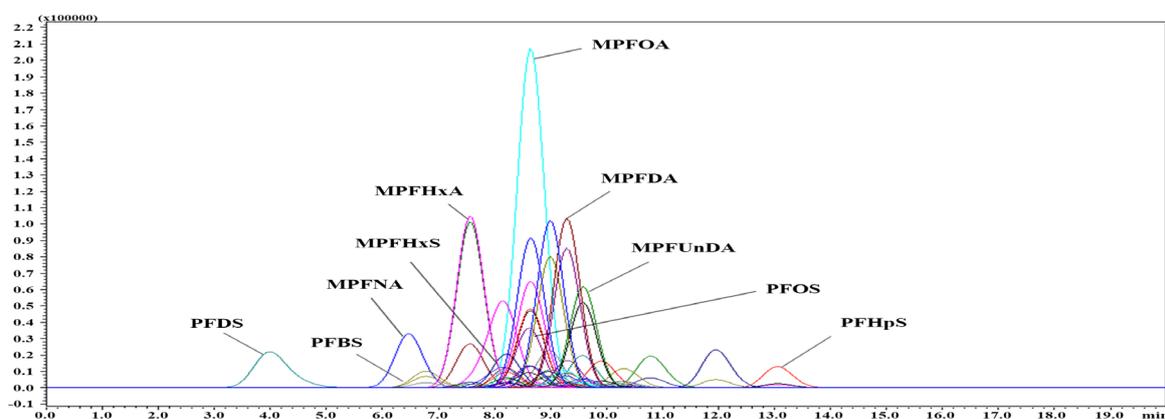


Figure 2: TIC chromatogram of overlaid peaks of the compounds after MRM selection

The mean PFAS concentrations found were in the range of 1.38–346.32  $\text{ng}\cdot\text{L}^{-1}$  during the months of February, March, May and June. At Sampling Point A of Hartbeespoort Dam, the PFAS concentrations detected were higher in summer than in winter. In February and March, the highest compounds exhibited concentration ranges of 213.04  $\text{ng}\cdot\text{L}^{-1}$  (PFOA) and 320.50  $\text{ng}\cdot\text{L}^{-1}$  (PFOS), with contribution factors of 55.07% and 46.35%, respectively (Fig. 3). In May and June, PFHxS showed marginally higher concentrations 41.22 and 67.32  $\text{ng}\cdot\text{L}^{-1}$  than the other compounds, respectively. At Sampling Point B, the detected concentrations of PFASs were also higher in summer than in winter. In February and March, PFOA (202.90  $\text{ng}\cdot\text{L}^{-1}$ ) and PFOS (200.19  $\text{ng}\cdot\text{L}^{-1}$ ) exhibited the highest concentration detected. In May and June, PFHxS was detected at higher concentrations, with mean concentration of 40.62 and 49.82  $\text{ng}\cdot\text{L}^{-1}$ , respectively. PFHxS also contributed 25.94% and 29.67% in May and June, respectively (Fig. 4). At Sampling Point C, the PFASs detected were observed to be higher in summer than in winter. In February and March, PFOA (275.92  $\text{ng}\cdot\text{L}^{-1}$ ) and PFOS (346.33  $\text{ng}\cdot\text{L}^{-1}$ ) had the highest concentration detected. PFHxS showed higher concentrations in winter with mean concentrations of 56.24  $\text{ng}\cdot\text{L}^{-1}$  in May and 81.18  $\text{ng}\cdot\text{L}^{-1}$  in June. The trends showed high concentrations of the PFASs in February, followed by March, and decreased from March to June at all sampling points. Sampling Point C showed the highest concentrations detected, followed by Point A and Point B. The same trend was observed in summer and winter. PFPeA showed the lowest concentrations detected at all the sampling points across all the months, except in June for Sampling Point B.

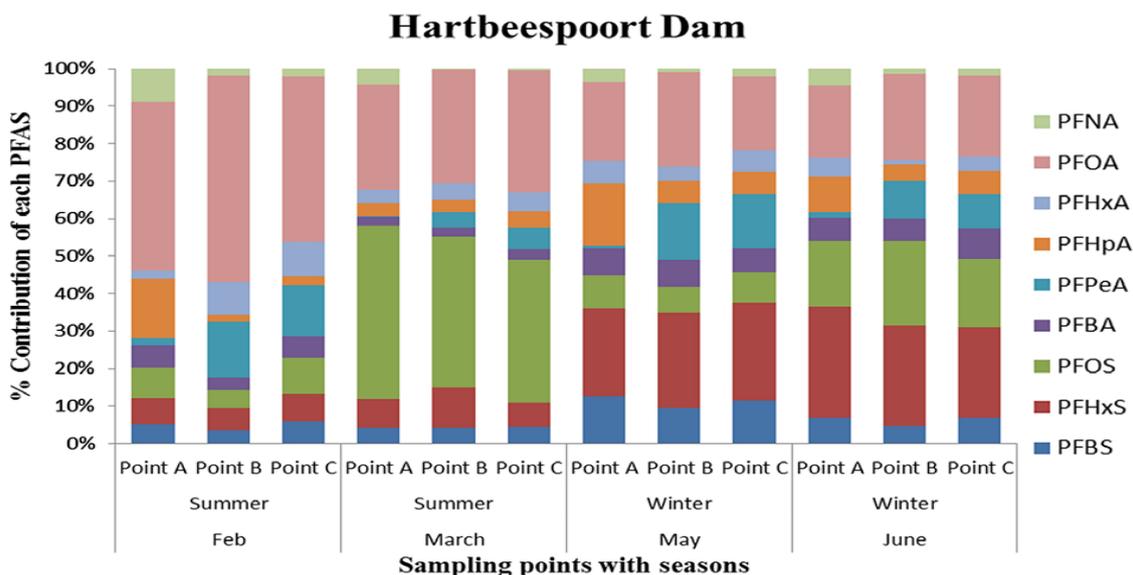


Figure 3: Percent contributions per PFAS in Hartbeespoort Dam

In the Roodeplaat Dam, the mean concentrations of PFASs detected were in the range of 2.31–262.29 ng L<sup>-1</sup>. The results showed that PFOA was the compound detected at the highest concentrations in February and March for Sampling Points A (163.58 and 187.44 ng·L<sup>-1</sup>), B (174.80 ng·L<sup>-1</sup> and 262.30 ng·L<sup>-1</sup>) and C (151.13 and 235.71 ng·L<sup>-1</sup>). PFOA contributed 31.11–43.91% to the total PFASs detected (Fig. 4). In May and June, PFHpA exhibited higher concentrations at all sampling points (25.83–72.21 ng·L<sup>-1</sup>), also contributing the most to the total PFASs detected (Fig. 4). The overall trend showed high PFASs concentrations in February and March at Points A, B, C and lower concentrations in May and June. However, in February, PFHxS was lower at Point A, while PFHpA and PFPeA were lower in March than in May and June. PFHxS was also lower in February and PFPeA lower in March at Point C. Sampling Point B in the Roodeplaat Dam had the highest levels of PFASs in all sampled months, followed by Point C and Point A in all sampled months. There were no significant differences ( $p < 0.05$ ) recorded between the dams, sampling points or seasons for PFAS concentrations.

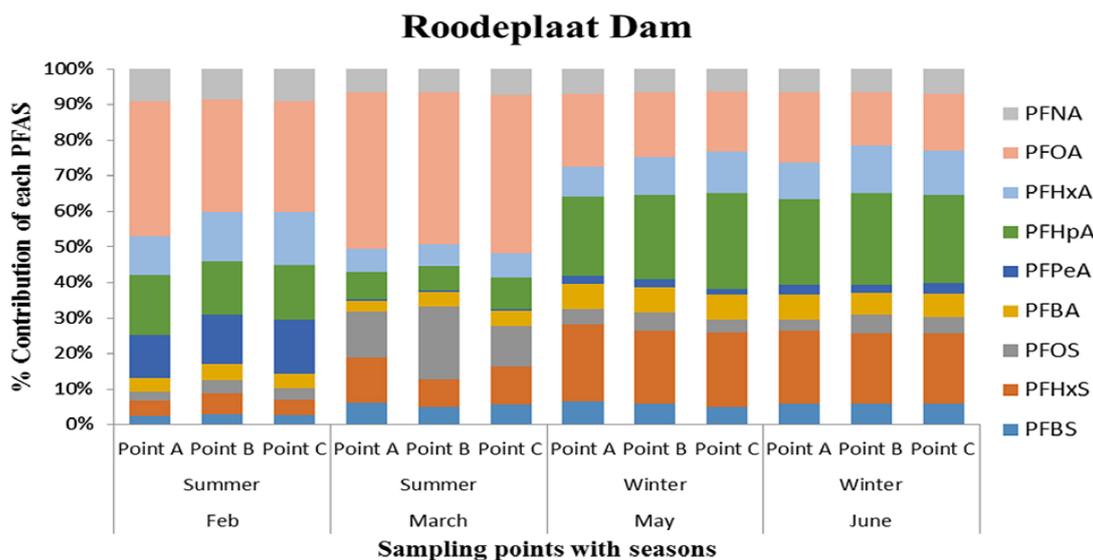


Figure 4: Percent contributions of PFAS in Roodeplaat Dam

#### 4 Conclusions

The present study confirmed the presence of PFASs compounds in Hartbeespoort and Roodeplaat Dams, South Africa. Out of the 20 PFASs investigated, 9 PFASs were detected in both dams. PFOA, PFOS, PFHxS and PFHpA were the most predominant compounds. The PFASs concentration levels were higher in summer months and decreased in winter months. The concentrations of PFASs detected in the present study are higher than the levels reported in other developing countries such as Uganda, Singapore and Vietnam, but lower than the levels reported in developed countries such as Germany, Japan and China. The PFOA and PFOS concentrations are also higher than

the lifetime health advisory issued by the USEPA. Since PFASs are not produced in South Africa, the possible main source of these compounds is most likely from use of PFASs-containing products.

## 5 Acknowledgements

The authors are indebted to the Water Research Commission of South Africa for financing this project.

## 6 References

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