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# ASSESSMENT OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN DRINKING WATER SOURCES IN ABAKALIKI, NIGERIA

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## ABSTRACT

The drinking water sources in Abakaliki, Nigeria were investigated for PFAS concentration. PFAS has been known for its bioaccumulation in the food chain, causing a detrimental health effect to humans when contaminated food is ingested. 13 targeted PFAS were analyzed using a Gas Chromatography-Mass Spectrometry (GC-MS) technique. This method allowed for the identification and quantification of specific PFAS compounds present in the sample. Perfluorohexanoate (PFHX1), N-methylperfluorooctanesulfonamide (MeFOSA), and N-ethylperfluorooctanesulfonamides (ETFOSA) were the only perfluoroakyl substances found others were fluorotelomers which are polyfluoroalkyl substance and there were the predominant PFAS obtained in this study. The mean sum of the targeted PFAS ($\sum$PFAS) across all the samples analyzed ranged from 0.22±0.06 mg/L (sample A3) to 7.20±1.82 mg/L (sample C4). The mean value of the PFAS obtained in samples A1 to A5 ranged from 0.22±0.06 mg/L (samples A3) to 0.59±0.12 mg/L (sample A1) while the mean values of samples B1-B5, C1-C5, and D1-D5 ranged from 0.35±0.08 mg/L (B1) to 1.14±0.21 mg/L (B5), 0.64±0.04 mg/L (C3) to7.20±1.82 mg/L (C4) and 0.63±0.04 mg/L (D1) to 3.61±1.08 mg/L (D4) respectively. PFAS are contaminants of emerging concern whose toxicity is of environmental and health concern. However, the detection of PFAS in water is gradually decreasing because of the restriction of PFAS and its industrial applications, which result from environmental and health-associated problems.

**Keywords:** Perfluoroaalkyl, poly-fluoroalkyl, water, PFAS, drinking

## INTRODUCTION

Water is an essential resource for human health, and the quality of drinking water is of paramount importance. Water exists as solid, liquid, and as well gas and it is very essential to both plants and animals. It can dissolve other chemical substances. Each water molecule contains 2 hydrogen atoms and 1 oxygen atom connected by a covalent bond. Water is used in industrial processes because it is an excellent solvent for various minerals and organic Ogbuewu and Nnaji (2023). Water is used for entertainment and sports such as swimming, boat racing, and diving. All these uses of water are hindered if the water is polluted. Water is said to be polluted when it is contaminated by substances such as domestic waste, industrial effluents, radioactive materials, and atmospheric deposition.

Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) refer to synthetic organo-fluorine chemical compounds that are composed of multiple fluorine atoms connected with an alkyl chain. In early 2011, PFASs were said to contain at least one perfluoroalkyl moiety $-C_nF_{2n+1}$ (Buck *et al.,* 2011; Ritscher *et al*., 2018). In 2021, the Organization for Economic Co-operation and Development (OECD) defined PFAS to be a fluorinated substance that contains at least one fully fluorinated methyl or methylene carbon atom without any hydrogen, chlorine, iodine, and or bromine atom attached or connected to it. That is, any chemical compounds with at least aperfuorinated methyl group $(CF_3)$ or perfuorinated methylene group $(CF_2)$ is regarded to be PFAS (Wang *et al*., (2021). All PFAS contain a chain of carbon atoms bonded to fluorine atoms. Some PFAS have functional groups attached at the end of the chain. These different structures entail the basis for the various chemical names and as well chemical properties of PFAS. In PFAS all carbon atoms are attached to fluorine atoms except the last carbon atom which is attached to the functional group (Buck *et al*., 2011). Some scholars describe PFAS as forever chemicals because they remain in the environment for a very long period. According to the National Academies of Sciences, Engineering, and Medicine, PFAS exposure is associated with an increased risk of hypercholesterolemia (abnormally high cholesterol), reduction of infant and fetal growth, and as well high rate of kidney cancer. Many of the products and materials such as Teflon and aqueous film foaming foam were used in mid-20th century as a result of their enhanced water-resistant properties but their environmental and human health impacts were not known as of then till of recently when more researchers embarked deeply on the study of the impacts and toxicity of PFAS (Buck *et al*., 2011).

Many scholars have concluded that PFAS is among the Contaminants of Emerging Concerns (CECs). CECs refer to contaminants for which concern about their potential negative impacts is recent and which are generally not regulated in present-day environmental laws (Murnyak *et al*., 2011). PFAS when discharged as waste in the environment can enter into water cycles through the process of water runoff finding its way to the river, ocean, and or lakes by effluent discharge and eventually getting into the public water supply. PFAS is implicated as a causative agent for cancer, endocrine disruption, and other health-challenging problems (Sauvé *et al*., 2014). PFAS when discharged to the water bodies through industrial waste discharge can affect fish and other aquatic animals. PFAS can bio-accumulate in the food web thereby causing detrimental health effects to humans when contaminated food is ingested. The rising trends of emerging contaminants do not only impair the quality of water, air, and or soil but could also find their way to the food chain and affect human and animal health. PFASs include perfluorooctanesulphuric acid (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctanesulfonamide (PFOSA), fluorotelomer among others. PFAS is discharged from domestic and industrial activities like power generation, manufacturing operations, and mineral extractions. Glüge *et al*. (2020) gave a complete summary of the main historical and modern-day uses of PFAS. Based on this paper and an OECD database on PFAS (OECD, 2018), PFAS are used globally in a wide variety of industries which consist of: Fire-fighting (fire suppressants), Chemical manufacturing, Building and construction, Cabling and wiring, Metal finishing and plating, Hydraulic fluids, Fluoropolymer manufacturing, Paper products and packaging, Semiconductor Manufacturing, Textiles, leather, and apparel (such as carpets and furniture), Cleaning products (such as industrial surfactants) and Refrigeration. This study focuses on the assessment of PFAS in drinking water sources in Abakaliki, Nigeria.

## MATERIALS AND METHODS

### Study Area

Abakaliki is the capital city of Ebonyi state. It has boundaries with Cross River State through Ikwo and Izzi local government Areas, Benue State through Ohaukwu local government area, Enugu through Ohaozara, Ivo, and Ishielu local government areas, and Abia, Imo through Afikpo and Ohaozara local government areas. It was carved out of the states of Enugu and Abia. Late General Sani Abacha created it on the 1st of October 1996. Ebonyi state is majorly known for rice production. It is the major rice production in the southeastern and southern parts of Nigeria. Ebonyi State comprises thirteen (13) local government areas, but this work was focused on the Abakaliki local government area, the state's capital city Abakaliki is at longitude 8$^{o}$ 06$^{1}$ 49.25E and latitude 6$^{o}$ 19$^{1}$ 29.46N. It is about 64 km from Enugu. The figure 1 below shows the global positioning system (GPS) of the studied area. The dotted red includes the studied area.

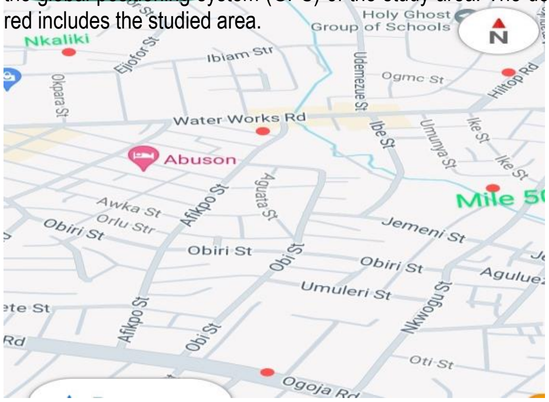

**Figure 1:** GPS of the studied area

### Sample Collection

Samples were collected from various drinking water sources such as bottled water, sachet water, tap water, and borehole water in Abakaliki metropolis. Multiple sampling campaigns were conducted for the collection of tap and borehole water samples in five (5) different locations within the Abakaliki metropolis namely; Nkaliki, Mile 50, Ogoja Road, Water Works Road, and Hill-top as indicated by the dotted reds in figure 1 above. Five (5) bottles and sachet water samples each were collected from different water production companies. Samples were collected with pre-cleaned 500 ml containers to prevent contamination. Special care was taken to avoid other forms of contamination during sample collection and handling.

### Extraction of Pfas From Water Samples (Bach *Et Al.*, 2016)

The PFAS in the water samples was extracted using solid phase extraction (SPE) techniques. SPE involves passing the water through a specialized sorbent that selectively retains PFAS components, allowing for their isolation and concentration. The extraction technique employed in this work was the United States Environmental Protection Agency (USEPA) 2005 revised Method 3510 for aqueous matrix for the analysis of semi-volatile and non-volatile organics. After filtration, a 100 ml portion of the water sample was transferred into a 2 L capacity glass-separating funnel. Then 30 ml of saturated sodium chloride (NaCl) was added to produce a salt-out effect. It was thoroughly mixed by inverting the flask three to four times. 100 ml of methanol as extraction solvent was added and this was vigorously shaken manually for 3 minutes and released the pressure intermittently. The phases were then allowed to separate for 5 min and the methanol extract (organic layer) was separated or collected from the aqueous layer. The extraction was repeated with 100 ml of methanol and the organic layers were put together and dried over anhydrous magnesium sulphate. The extracts from water samples were then concentrated on a rotary vacuum evaporator to about 2 ml and subjected to cleanup.

### Clean-Up of Extract (Purification Using Silica Spe Cartridge)

One gram of silica gel that had been previously activated at 130 ºC for 5 h was carefully packed into a 10 mL polypropylene cartridge column and 6 mL methanol was used to condition the cartridge. The concentrated extract was then loaded onto the column and a 50 mL pear-shaped flask was placed under the column to collect the eluate. A 10 mL methanol was used to elute the column afterward, and the total filtrate collected concentrated to just dryness using the rotary evaporator set at 38ºC. The residue was re-dissolved in 1 mL methanol and transferred into a 2 mL standard vial prior to quantification by Gas Chromatography. The instrument system configuration for the application consisted of an Agilent GC/MS model Agilent 6890 and a multifunctional auto-sampler equipped with an SPME module and a split/splitless inlet. HP-5MS column (30 m in length × 250 μm in diameter × 0.25 μm in thickness of film). Spectroscopic detection by GC–MS involved an electron ionization system that utilized high-energy electrons (70 eV). Pure helium gas (99.995%) was used as the carrier gas with a flow rate of 1 mL/min. The initial temperature was set at 50 °C with an increasing rate of 3 °C/min and a holding time of about 10 min. Finally, the temperature was increased to 300 °C at 10 °C/min. One microliter of the prepared sample diluted with methanol was injected in asplitless mode. The relative quantity of the chemical compounds present in each of the extracts was expressed as ppm based on the peak area produced in the chromatogram.

### Analysis

The extracted samples were analyzed using a Gas Chromatography Mass Spectrometry (GC-MS) technique. This method allowed for the identification and quantification of specific PFAS compounds present.

### Standards and Reagents

The PFAS target list consists of PFIs, FTIs, FTACs, FTIMACs, FTOHs and FASAs. Internal standards were FTOHs, FASAs, and FTAC mass-labeled compounds. A stock of each analyte 50 ppm was prepared in methanol. This stock was further diluted to make an intermediate stock of 10 ppm. They were stored at 4degree. An internal calibration curve was prepared in 10ml of methanol. Sodium chloride was added to each vial to achieve a final salinity concentration of 2 % NaCl (w/v). The sample was vortex for 30 seconds and then plated on the AOC-625 plus vortex auto sampler rack for HS-SPME analysis.

### Quantification of Pfas Residues

Quality control measures including the use of appropriate blank samples, calibration standards, and quality assurance protocols were obtained to ensure accuracy and reliability of the analytical results. The residue levels of PFA were quantitatively determined by the external standard method using peak area. Measurement was carried out within the linear range of the detector. The peak areas whose retention times coincided with the standards were extrapolated on their corresponding calibration curves to obtain the concentration.

### Statistical Analysis

The means and standard deviations of triplicate determinations were calculated, and the values obtained were analyzed using single-factor analysis of variance (ANOVA). A comparison of means was done using the New Duncan Multiple Range Test. Data was analyzed with SPSS software (Version 22.0).

## RESULTS AND DISCUSSION

Perfluoroalkyl substances are among the contaminants of emerging concern known for their persistence and potential adverse effects on human when ingested. They are resistance to environmental degradation and as such referred to as 'forever chemicals'. The total number of samples analyzed for PFAS concentration in drinking water samples sourced from Abakaliki in Ebonyi State was twenty (n=20) which were labeled as A1-A5, B1-B5, C1-C5, and D1-D5 respectively for bottled water, sachet water, borehole water and tap water samples. Table 1 and Figure 2 shows the mean percentage concentrations of PFAS in the various studied samples, 13 targeted PFAS chemicals were analyzed using GC-MS model Agilent 6890 and a multifunctional auto sampler equipped with SPME module and a split inlet. This method allowed for identification and quantification of specific PFAS compounds present. From the results obtained both perfluoroalkyl and poly-fluoroalkyl substances were detected but poly-fluoroalkyl substances were the most predominant PFAS obtained which include the fluorotelomers; fluorotelomer iodide (FTI), fluorotelomer alcohol (FTOH), fluorotelomer carboxylic acid (FTAC) while Perfluorohexanoate (PFHX1), N-methylperfluorooctane sulfonamide (MeFOSA), N-ethylperfluorooctane sulfonamides (ETFOSA) were the poly-

**Table 1:** PFAS concentrations in mg/L obtained in the various water samples

| **S/N ID's** | **Sample** | **Analyte Concentration** | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PFHXI | PFOI | 4:2FTI | 6:2FTI | 8:2FTOH | 6:2FTAC | 8:2FTI | 10:2FTOH+ | 6:2FTMAC | 8:2FTAC | 8:2FTMAC | MeFOSA | EtFOSA | Mean |
| 1 | A1 | ND | ND | ND | ND | 0.14 | 0.93 | ND | ND | 0.69 | ND | ND | ND | ND | 0.59±0.12 |
| 2 | A2 | ND | ND | ND | ND | ND | ND | ND | 0.15 | ND | 0.47 | ND | ND | ND | 0.31±0.09 |
| 3 | A3 | ND | ND | ND | ND | ND | 0.30 | 0.40 | 0.05 | 0.43 | ND | 0.01 | ND | ND | 0.22±0.06 |
| 4 | A4 | 0.74 | ND | ND | ND | 0.99 | 0.38 | 0.08 | ND | ND | ND | ND | ND | ND | 0.55±0.10 |
| 5 | A5 | 0.16 | 0.07 | 0.81 | 0.766 | ND | 0.04 | 0.36 | 0.07 | ND | ND | ND | ND | ND | 0.32±0.07 |
| 6 | B1 | ND | ND | ND | ND | 0.07 | 1.32 | 0.01 | 0.02 | ND | ND | ND | ND | ND | 0.35±0.08 |
| 7 | B2 | ND | ND | ND | 0.435 | 0.56 | 1.17 | 0.06 | ND | 0.69 | ND | ND | ND | ND | 0.59±0.15 |
| 8 | B3 | ND | ND | ND | ND | 0.34 | 1.19 | ND | ND | ND | 0.19 | 0.41 | ND | 1.895 | 0.80±0.09 |
| 9 | B4 | ND | ND | ND | 0.237 | ND | ND | 0.10 | ND | ND | 1.81 | 1.05 | ND | ND | 0.79±0.08 |
| 10 | B5 | ND | ND | ND | 0.406 | 2.79 | ND | ND | ND | ND | 0.573 | 0.79 | ND | ND | 1.14±0.21 |
| 11 | C1 | 0.31 | 1.65 | 4.65 | 7.994 | 7.15 | 2.22 | 0.41 | 0.76 | 0.83 | 1.52 | 0.19 | 8.67 | 2.79 | 3.01±0.26 |
| 12 | C2 | 0.02 | 5.57 | 5.33 | ND | 0.22 | ND | 0.06 | 0.08 | 0.22 | 0.39 | 0.25 | ND | 0.20 | 1.23±0.15 |
| 13 | C3 | ND | ND | ND | ND | 0.29 | 0.28 | 0.16 | 0.12 | 0.18 | 0.37 | 0.45 | 0.23 | 3.05 | 0.64±0.04 |
| 14 | C4 | 0.03 | 60.16 | 7.62 | 0.203 | 0.29 | 1.87 | 0.21 | 0.10 | 0.73 | 0.76 | ND | ND | ND | 7.20±1.82 |
| 15 | C5 | ND | 1.08 | 2.61 | 0.659 | 0.75 | 1.80 | 0.32 | 0.10 | 0.90 | 0.20 | 5.68 | 3.86 | 4.16 | 1.85 ±0.25 |
| 16 | D1 | ND | ND | 0.35 | 0.333 | 0.21 | 1.96 | 5.45 | 0.05 | 0.670 | 0.35 | 1.91 | 0.41 | ND | 0.63±0.04 |
| 17 | D2 | 0.16 | 5.29 | 1.47 | 2.817 | 0.55 | 0.69 | 6.64 | 0.07 | 0.89 | 0.31 | 0.62 | 0.65 | 5.52 | 1.98±0.24 |
| 18 | D3 | 0.05 | 1.89 | 6.78 | 4.795 | 0.21 | 0.40 | 0.50 | 5.44 | 0.55 | 0.14 | 0.41 | 0.63 | ND | 0.96±0.90 |
| 19 | D4 | 1.67 | ND | 2.85 | 2.282 | 18.24 | 6.45 | 0.07 | ND | 0.28 | 0.34 | 0.49 | 5.45 | 1.62 | 3.61±1.08 |
| 20 | D5 | ND | ND | 0.21 | 1.697 | 0.82 | 0.45 | 0.100 | 0.10 | 0.21 | 0.18 | 0.34 | 0.84 | 3.03 | 0.72±0.52 |

ND= not detected

fluoroalkyl substance obtained. The mean sum of the targeted PFAS (∑PFAS) across all the samples analyzed ranged from 0.22±0.06 mg/L (sample A3) to 7.20±1.82 mg/L (sample C4). The mean value of the PFAS obtained in samples A1 to A5 ranged from 0.22±0.06 mg/L (samples A3) to 0.59±0.12 mg/L (sample A1) while the mean values of samples B1-B5, C1-C5, and D1-D5 ranged from 0.35±0.08 mg/L (B1) to 1.14±0.21 mg/L (B5), 0.64±0.04 mg/L (C3) to7.20±1.82 mg/L (C4) and 0.63±0.04 mg/L (D1) to 3.61±1.08 mg/L (D4) respectively. Bach *et al*. (2016) investigated perfluoroalkyl iodide, perfluoroalkyl sulfonamides, fluorotelomer alcohols, fluorotelomer iodide, and fluorotelomer acrylates in water and sediments using solid-phase microextraction and gas chromatography/mass spectrometry. They obtained 8:2 FTOH and 10:2 FTOH which is also obtained in this study. Heidi *et al* (2022) studied PFAS and precursor bioaccumulation in freshwater recreational fish and detected N-EtFOSA and N-MeFOSA in water which were also detected in this study. Table 1 above showed the PFAS concentrations in the various water samples studied while figure 2 below showed the mean percentage concentration of PFAS in the various studied samples. Poly-fluoroalkyl substances were the most predominant PFAS obtained and the concentration is higher in borehole water (sample C's) followed by the tap water (sample D's). Both bottled and sachet water samples had low concentrations of PFAS. The detection of PFAS in water is gradually decreasing as a result of the restriction of PFAS and its industrial application due to environmental and human health concerns.

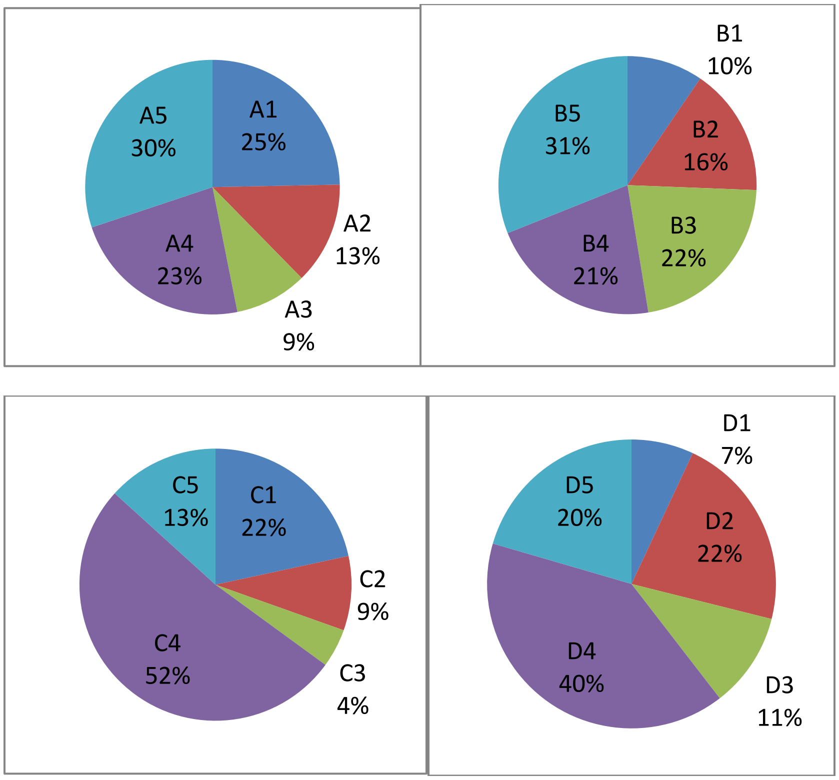

**Figure 2:** Mean percentage concentrations of PFAS in the various water samples

## Conclusion

This study assessed PFAS in drinking water sources in Abakaliki Ebonyi State, Nigeria. PFAS is among the contaminants of emerging concern whose toxicity is an environmental problem. From the result obtained samples C's and D's had the highest concentration of PFAS and poly-fluoroalkyl substances were the major PFAS obtained. The detection of PFAS in water is decreasing gradually as a result of the restriction of PFAS and its industrial applications due to environmental and human health challenges.

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