

Richard Jack³, Alexandria L.B. Forster¹, Ying Zhang^{1,2}, Danielle C. Westerman¹, Susan D. Richardson¹

¹Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208 USA
²Department of Environmental Science and Engineering, Nankai University, No. 38 Tongyan Road, Jinnan District, Tianjin, 300350, China
³Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

Introduction

Per- and Polyfluoroalkyl Substances (PFAS) are present in all environmental matrices, including water, soil, air, and living organisms. Since it has been estimated that there are over 6000 possible PFAS compounds, most organic Fluorine present in the sample is missed. By measuring Total Organic Fluorine (TOF) content, a more comprehensive account of PFAS contamination can be determined. Traditional LC-MS/MS approaches are limited based on the standards and PFAS compounds tested. To more comprehensively capture organic Fluorine, Combustion Ion Chromatography (CIC) can be used which converts organic Fluorine into inorganic Fluoride and is measured by ion chromatography. This CIC method involves sample extraction, concentration, combustion, collection of generated gasses in an aqueous absorbing solution, and analysis of resulting

anions by ion chromatography. However, CIC is limited in its ability to distinguish between organic and inorganic Fluorine/Fluoride, so analyte extraction methods must be optimized. For TOF, previous extraction methods include Extractable Organic Fluorine (EOF) and Adsorbable Organic Fluorine (AOF), which differ in how the samples are extracted. EOF uses Solid Phase Extraction (SPE) with a solid stationary phase while AOF uses an activated Carbon column. In this technical note, we report a new TOF method with improved recovery, detection limits, and quantity of PFAS studied (43 total) by implementing the Strata PFAS SPE cartridge.

Overview of AOF and EOF Methods



*EOF does not require the laborious extrusion needed to remove the GAC prior to combustion. This makes EOF scalable for higher throughput laboratories as EOF can readily be automated.

Table 1. Comparison of AOF and EOF Methods.

	AOF (500 mL Sample Volume)	EOF (500 mL Sample Volume)
Mean Recovery in Ultrapure Water	79 %	91 %
Mean Recovery in River Water	72 %	87 %
Inorganic Fluoride Removed	98 %	≥99 %
LOD (µg/L)	0.3	0.2
LOQ (µg/L)	1.0	0.5
Full Analysis Time (one sample in triplicate)	~11 hours	~5 hours

Discussion and Conclusion

Both AOF and EOF methods can be used to quantify TOF. Compared to AOF, EOF extractions have higher overall recoveries and lower LODs and LOQs (Table 1). Both SPE extraction methods allow for the removal of inorganic Fluoride which is crucial for the use of CIC as a PFAS screening technique. The lower LOD and LOQ using Strata PFAS is due to the use of the WAX layer that allows for better recoveries since this approach relies on acidic pKas of many PFAS compounds. As shown in Table 1, there is a significant time savings between the methods. EOF does not require the laborious extrusion needed to remove the GAC prior to combustion. This makes EOF scalable for higher throughput laboratories as EOF can readily be automated. As shown in Figures 1 and 2, AOF recoveries in river water and ultrapure water ranged from 55–98 % to 46–112 %. Trends between compounds show a slight decrease in river water compared to ultrapure water, likely due to other organics outcompeting PFAS for sorption sites on the AC. Branched ether compounds, such as PMPA (C4), HPFO-DA (C6), and PFECAG (C7) yielded somewhat lower recoveries (46, 89, and 87 %, respectively) than linear ethers, PEPA (C4), PFO4DA (C6), and PFOSDA (C7) with the same number of carbons (65, 89, and 92 %, respectively). Perfluorocarboxylic Acids (PFCA) and Perfluorosulfonic Acids (PFSA) such as PFBA (C4), PFBS (C4), PFHxA (C6), and PFHpA (C7) generally yielded higher recoveries (64, 90, 92, 92 %, respectively) when compared to ethers of similar chain length. While in general, shorter-chain PFAS compounds yielded lower recoveries compared to longer-chain PFAS, no consistent trend was observed. An LOD of 0.3 µg/L and an LOQ of 1.0 µg/L can be achieved with a 500 mL sample. This LOD value is well below those required by the EPA 1621 draft method (2.4 µg/L). The efficiency of the final EOF method was evaluated using 39 individual PFAS standards and a 39-PFAS mix (as 50 µg/L Fluorine) in ultrapure and river water (DOC of 2.4 mg/L). Two zwitterionic and two neutral PFAS compounds were also

evaluated individually (data not shown) for a total of 43. As observed for AOF, recoveries for EOF also decreased slightly in river water (66–98 %) compared to ultrapure water (72–99 %), and shorter-chain PFAS generally yielded lower recoveries compared to longer-chain PFAS, but no consistent trend was observed. Branched ether compound PMPA (C4) yielded a lower recovery (87 %) than its linear ether, PFCA, and PFSA counterparts PEPA (95 %), PFBA (88 %), and PFBS (94 %); however, branched ether compounds HPFO-DA (C6) and PFECAG (C7) yielded higher recoveries (91 and 89 %, respectively) than their linear ether, PFCA, and PFSA counterparts PFO4DA (91 %), PFHxA (89 %), PFOSDA (86 %), and PFHpA (88 %). When compared to the AOF trends, the difference in the higher recoveries of longer-chain PFAS could be explained by the extra GCB layer for extraction. An LOD and LOQ of 0.2 and 0.5 µg/L can be achieved, respectively, with a 500 mL sample.

Our results demonstrate the development of two new sensitive methods (AOF and EOF) to quantify TOF in river water. Compared to previous methods, we achieved higher recoveries for a larger mix of 43 PFAS compounds, and our AOF method utilizes commercial pre-packed ACs rather than manual packing in a clean room. Our EOF method also utilizes a new type of SPE cartridge, Strata PFAS, which combines benefits of a WAX phase with GCB to more efficiently extract a wide range of PFAS classes with varying size and polarity. Larger samples (up to 1200 mL) can be used with larger Strata PFAS cartridges to achieve 0.1 µg/L LOD and 0.3 µg/L LOQ (data not shown). Another benefit of EOF is that a sample of SPE eluent can be saved for future LC-MS/MS analysis to identify specific PFAS compounds in samples with high TOF.

Results

Figure 1. Mean Organic Fluorine Recovery of 39 Individual PFAS Standards Spiked into Ultrapure Water.

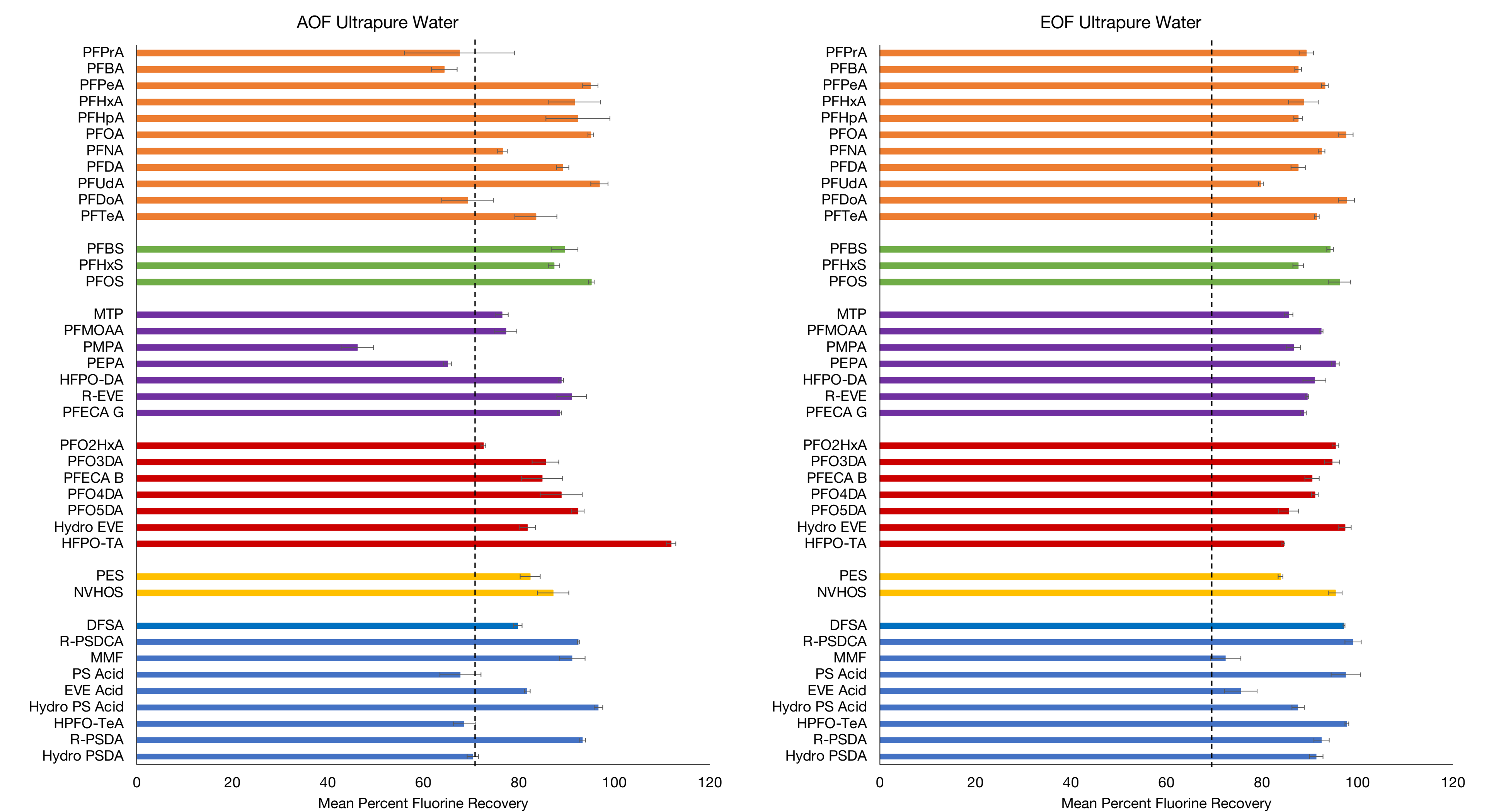
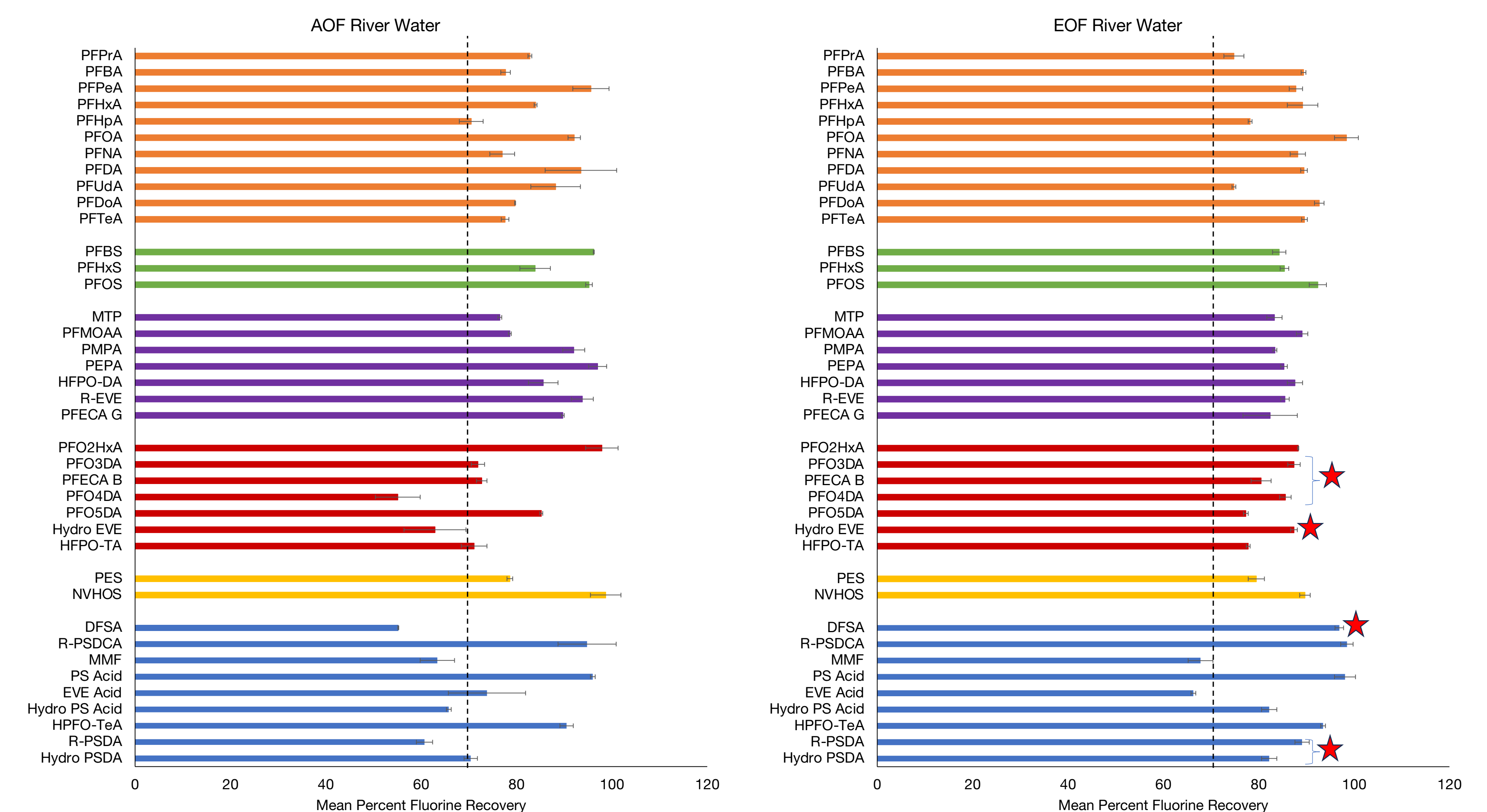


Figure 2. Mean Organic Fluorine Recovery of 39 Individual PFAS Standards Spiked into River Water.



Starred PFAS highlight significant improvement of recoveries using Strata PFAS.

