Groundwater Monitoring&Remediation

Rapid Short Communication

Demonstration of On-Site Field Monitoring for PFAS and AFFF-Impacted Groundwater

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Abstract

Remediation processes aimed at removing per- and polyfluoroalkyl substances (PFAS) from aqueous film-forming foam (AFFF)-impacted sites often suffer from delays due to the slow turnaround time of obtaining PFAS results from analytical lab services. This not only extends projects, leading to increased costs, but it also contributes to delays in the fine-tuning of remediation processes, as any modifications are made on outdated data. These off-site analytical monitoring methods are also usually limited to the list of compounds in targeted methods such as EPA method 1633, which does not include some precursors that may convert into more harmful PFAS compounds over time. The FRED-PFAS sensor is a real-time monitoring system that detects the sum of anionic PFAS species (perfluoro- and polyfluoroalkyl, >C4 chain length) present in a sample with similar sensitivity across key PFAS species, as demonstrated with perfluorooctanoic acid, the precursor 6:2 fluorotelomer sulfonate, and a commercial AFFF mixture. When deployed at AFFF-impacted groundwater and an upstream aircraft rescue and firefighting PFAS removal project, the FRED-PFAS detector was able to provide actionable same-day data that correlated with EPA 1633 methods and total organic fluorine measurements. This generates actionable PFAS data on-site, enabling faster turnaround times and reduced overall PFAS monitoring costs.

Per- and polyfluoroalkyl substances (PFAS)-containing aqueous film-forming foam (AFFF) products were first introduced in the 1960s for fire suppression and were adopted for their improved performances over previous foams (Divine et al. 2025). However, the emergence of information about PFAS-induced health problems and PFAS resistance to degradation has incentivized remediation of AFFF-impacted sites that affect groundwater and soil systems (Leeson et al. 2022; Obsekov et al. 2023). While efforts are underway to characterize and treat these sites, and to remove PFAS-containing AFFF from firefighting equipment, the inability to quickly and easily test for the presence of PFAS has slowed these efforts (Schiavone and Portesi 2023). There is currently no commercially available, small footprint, on-site testing for PFAS, requiring dependence on the shipment of samples to off-site analytical laboratories which typically have 2 to 6 weeks turnaround times from sample preparation to results. This wait time delays remediation efforts and increases the cost of projects.

To overcome these limitations, the FRED-PFAS™ sensor was developed to monitor PFAS levels in a field setting within a 4-hour window. The unit consists of a compact, easily portable, solid-phase extraction system, and a fluorometer. This sensor relies on a fluorescence assay with the capacity to bind PFAS species, resulting in a dose-dependent change in the fluorescence as a function of PFAS concentration. The detection polymer preferentially interacts with the fluorocarbon tail of the PFAS molecules and does not distinguish between anionic head groups, enabling detection of the sum of the PFAS species present within a sample as opposed to the selective, though limited, species identification of methods 533 and 1633 from the US Environmental Protection Agency (EPA) (US EPA 533 2019; US EPA 1633 2022).

To test the performance of the FRED-PFAS sensor for measuring combined PFAS species within AFFF-impacted groundwater, the assay was first validated against a legacy PFAS perfluorooctanoic acid, a fluorotelomer (6:2 fluorotelomer sulfonate), and a commercial AFFF (Chemguard C303). Figure 1a demonstrates that the sensor was able to respond to PFAS without significant discrimination between the response profiles to the three PFAS standard compositions, indicating the suitability of this sensor to produce an additive PFAS result akin to what can be estimated from total organic fluorine (TOF) measurements. The limit of detection was observed to be approximately 1 parts per billion (ppb) for all three PFAS samples, with a maximal

Article impact statement: This work demonstrates the first field implementation of a light-weight, portable PFAS monitoring system producing same-day results, confirmed by EPA 1633 and TOF.

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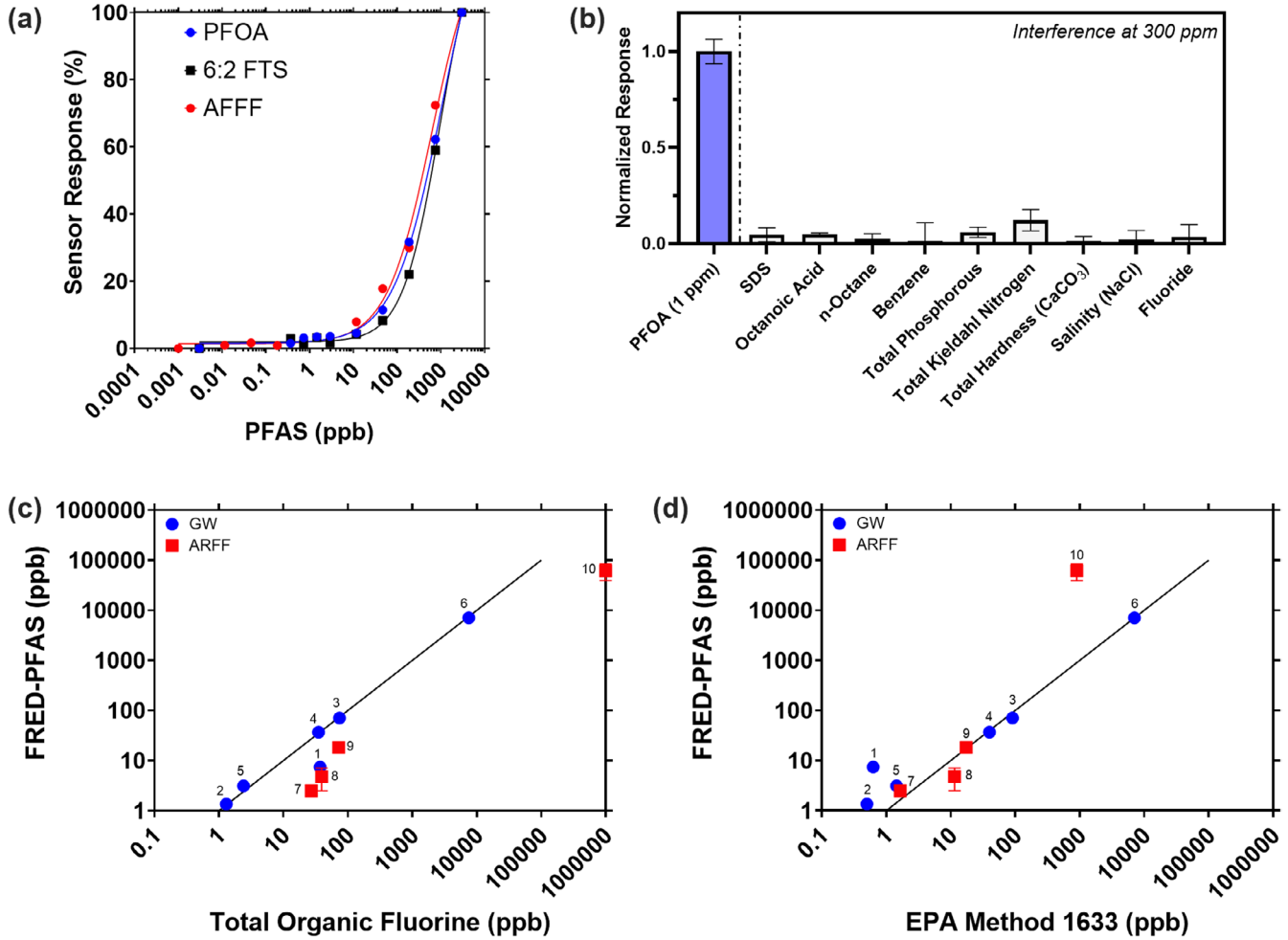

Figure 1. Lab verification and in-field results of the FRED-PFAS sensor. (a) Comparative sensor response to perfluorooctanoic acid ("PFOA"), 6:2-fluorotelomersulfonic acid ("6:2 FTS"), and a commercial AFFF (Chemguard C303, "AFFF") dilution series in 25% v/v methanol and ultrapure water, with percent of the maximal sensor response plotted as a function of PFAS concentration. PFAS concentration is represented as values after correcting for sample concentration and assuming full recovery of the input sample via solid-phase extraction. AFFF PFAS concentration was estimated as 3% w/v PFAS concentration, as per product documentation. (b) Comparative sensor response to interferences tested with the FRED-PFAS fluorescence assay. The set includes candidate molecules with alkyl tails and head groups resembling PFAS such as octanoic acid and sodium dodecyl sulfate (SDS) as analogues to PFOA and PFOS respectively, as well as common water matrix interferences. Comparison of (c) total organic fluorine (TOF) and (d) EPA Method 1633 targeted anionic PFAS species results obtained from third-party laboratories compared to FRED-PFAS results for AFFF-impacted groundwater samples (GW, blue circles) and samples directly taken from ARFF changeouts (ARFF, red squares). The black diagonal line represents 1:1 parity between the methods. The FRED-PFAS data for Samples 1 to 4 were analyzed in a laboratory setting, whereas data for Samples 5 to 10 were collected during field deployments. The FRED-PFAS measurements were performed in triplicate. All EPA 1633 and TOF measurements were from split samples collected at the same time and sent to a third-party analytical laboratory, with all error bars representing standard deviations.

response seen at ca. 3,000 ppb. The sensor was also tested with non-PFAS contaminants and showed minimal response at concentrations of 300 ppm (Figure 1b).

The sensor was then challenged with AFFF-impacted groundwater collected from a series of sites and compared against results from TOF (Figure 1c) and EPA 1633 measurements (Figure 1d). To compare these methods to FRED-PFAS, the concentrations of each PFAS species reported within the EPA 1633 analysis were summed, whereas the TOF measurements were converted to PFAS concentrations based on approximate fluorine mass ratios (Bureau Veritas 2021).

Prior to field testing, we analyzed groundwater samples in a laboratory setting with the FRED-PFAS sensor (Samples 1 to 4). Results correlated with the third-party analytical techniques (Figure 1c and 1d), often reporting between TOF results and the targeted EPA 1633 method. This suggests the detection of PFAS species or precursors present within these samples that were beyond the scope of the targeted EPA 1633 method but are known to exist in many AFFF formulations (Leeson et al. 2022). The observed discrepancy between EPA 1633 and TOF has been previously reported (Dixit et al. 2024).

Based on these early results, the sensor was deployed at a series of airports and surrounding groundwater infrastructure in late 2024 across three sites in Canada and the US (Samples 5 to 10). Samples were taken from groundwater wells and directly from aircraft rescue and firefighting (ARFF) trucks before and during the transition from PFAS-containing AFFF to fluorine-free foams. All samples were split and sent to third-party analytical

laboratories for non-targeted total organofluorine analysis (TOF) and targeted EPA 1633 analysis to estimate PFAS content in the sample. As can be seen in Figure 1c and 1d, the FRED-PFAS sensor was able to estimate the PFAS concentrations in the samples during the field deployment. A similar trend to the in-lab samples (Samples 1 to 4) was identified, with the FRED-PFAS sensor reporting concentrations between that of TOF and EPA 1633, suggesting detection of non-EPA 1633 PFAS species in these complex real world samples. Groundwater samples produced the strongest correlations ($R^2 > 0.95$ for both TOF and EPA 1633), with ARFF rinsates producing predictable trends ($R^2 = 0.88$ for both TOF and EPA 1633).

In summary, the FRED-PFAS detection system provides a sum PFAS estimate with a 4-hour window, comparing favorably to longer reporting times associated with lab-based analytical methods. The system typically produces concentration values between these two laboratory-based analysis methods, possibly reflecting that AFFF has unique PFAS species that are not identified with EPA 1633. Considering the rapid results and the comparability to lab-based methods when demonstrated on real world samples in a field setting, the FRED-PFAS system represents an alternative to relying exclusively on off-site analyses. This enables real-time monitoring, facilitating faster decision making for the protection of groundwater systems from PFAS moving forward.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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