

# Detailed Site Investigation for Per- and Polyfluoroalkyl Substances (PFASs) Using Advanced Analytical Tools

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**Background/Objectives.** Assessments of multiple areas associated with fire training activities using high resolution sampling methods and employing the total oxidizable precursor (TOP) assay in the unsaturated zone are presented to show the relevance of precursors in developing conceptual site models for sites impacted with firefighting foams. Preliminary assessment of one site showed that per- and polyfluoroalkyl substances (PFASs) were present in groundwater, at mg/L levels, due to frequent historical applications of aqueous film forming foams (AFFFs). At this location multiple long and short chain perfluoroalkyl acids (PFAAs) and 6:2 fluorotelomer sulfonate are regulated in drinking water. Thus, the distribution of AFFF-derived PFAA precursor that may form 6:2 fluorotelomer sulfonate and PFAAs are considered of significant importance at this site. The objectives of the investigations were to characterize the area to determine the distribution of both PFAAs and PFAA precursors in soil and groundwater in relation to biogeochemical parameters, lithology and distribution of other organic compounds. In order to develop a more robust site conceptual model, further objectives were to determine if the presence of organic materials enhanced PFAA precursor sorption and to determine the extent to which redox conditions have influenced PFAA precursor transformation.

**Approach/Activities.** Groundwater and soil samples were characterized for PFASs using a targeted analyte list as well as the total oxidizable precursor (TOP) assay and adsorbable organofluorine (AOF) to indirectly measure total PFASs. The PFAS distribution in soils was assessed in relation to total organic carbon and particle size distribution. Groundwater was characterized for major anions, including fluoride, cations, total organic carbon and biogeochemical parameters. The PFAS distribution was measured in the lithology at multiple horizons to target distinctly different zones such that both migratory and non-migratory horizons were assessed for PFAS content.

**Results/Lessons Learned.** The vertical and horizontal delineation of PFASs at this site will be presented in relation to the site's hydrogeology and lithology. The results showed that nearly 98 percent of total PFAS mass in soils was estimated to occur within the top 1.8m of unsaturated soils. It's clear that unsaturated soils as many sites will likely represent ongoing sources of PFAAs as precursors transform, with seasonal rainwater increases and fluctuations in the groundwater facilitating table leaching of PFASs from source areas.

Field derived partitioning coefficients were determined for individual PFASs and total PFAA precursors in relation to localized biogeochemical conditions. Ratios of PFAA precursor concentrations to PFAAs were determined in different redox zones of the site and, after controlling for mass flux, were used to determine PFAA precursor susceptibility to biotransformation in the presence of multiple types of terminal electron acceptors. Lessons learned on how to selectively utilize advanced characterization tools to provide the most value in determining the location of contaminant mass will be discussed. The use of TOP assay was important to identify contaminant mass location and concentrations. The data quality objectives for TOP assay data interpretation will be detailed, as described in the draft Queensland DEHP guidance documents, to enable an understanding of how and why to potentially apply the TOP assay.