

Towards closing the mass balance on per- and polyfluorinated alkyl substances in groundwater at aqueous film forming foam impacted sites

KRISTA BARZEN-HANSON¹, SIMON ROBERTS,² CHRISTOPHER HIGGINS,² JENNIFER FIELD³

¹Department of Chemistry, Oregon State University, Corvallis, OR 97331, United States, barzenhk@onid.oregonstate.edu

²Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, United States

³Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR 97331, United States, jennifer.field@oregonstate.edu

Aqueous film-forming foams (AFFFs), containing per- and polyfluorinated alkyl substances (PFASs), were applied repeatedly at military and civilian sites to extinguish hydrocarbon-based fuel fires. Recent data on groundwater and sediment indicates that at least 50% of the PFASs at military sites remain unidentified. Identification of all PFASs present in groundwater is needed to develop appropriate remediation treatments and to fully characterize potential ecological and human exposure. Three complementary analytical approaches were combined in an attempt to close the mass balance on PFASs in groundwater at military sites. First, an orthogonal liquid chromatography tandem mass spectrometry (LC-MS/MS) system was used to quantify 62 known PFASs. Second, the total oxidizable precursor (TOP) assay was used to quantify the total picomolar concentrations of precursors present, which captures known and unknown PFASs. Third, unknown families of PFASs were identified by quadrupole time-of-flight mass spectrometry (QTOF-MS). Kendrick mass defect plots were constructed to identify and catalog known and unknown PFAS families. These three analytical approaches were then applied to representative groundwater samples from each of 14 different military sites. The classes and individual PFASs discovered include ultra-short-chained C₂ and C₃ perfluoroalkyl sulfonic acids, C₂-C₈ perfluoroalkyl sulfonamides, and the perfluoroethylcyclohexane sulfonate. Zwitterionic chemicals with one or more sulfonic acids groups and a hydroxyl group also were identified that likely originate from old (pre-1989) 3M AFFF formulations. The concentrations of newly-identified PFASs in groundwater were then estimated and added to the concentrations of previously-identified PFASs. The total picomolar concentration of PFASs determined by QTOF and LC-MS/MS was then compared to that obtained by the TOP assay for each groundwater sample. The current status on the mass balance on PFASs in groundwater as the needs for future research will be discussed.