

Factors Influencing Fate and Transport of Perfluoroalkyl Acids in Groundwater: An Empirical Demonstration

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Background/Objectives. Groundwater fate and transport of perfluoroalkyl acids (PFAAs), a class of per and polyfluorinated alkyl substances (PFAS), are influenced by 1) chemical characteristics of individual PFAAs, 2) chemistry of the solution in which PFAAs occur, and 3) nature and type of aquifer matrix. PFAAs are recalcitrant in the environment and prone to sorption to organic carbon, oil-coated surfaces, and positively charged mineral surfaces due to a negatively charged functional group (“head”) when dissolved in water. Lower pH, increased calcium ion activity, and ionic strength of solution tend to promote sorption of PFAAs to aquifer matrices. The relative proportion and mobility of PFAAs in groundwater may also be influenced by, 1) the degradation of precursor compounds to terminal PFAAs, 2) whether the molecule is a carboxylate or sulfonate, and 3) whether the molecule is a branched or straight chain. The objective of this study is to present an analytical, statistical, and spatial evaluation of PFAAs in soil and groundwater to empirically demonstrate the factors that influence PFAA fate and transport.

Approach/Activities. The physico-chemical properties that influence PFAA behavior in groundwater were empirically evaluated by combining data from multiple sites affected by Class B fluorine-containing firefighting foams. PFAA concentrations in soil and groundwater were statistically compared, novel fractionation analysis of PFAA groups, homologues, and isomers were conducted, and PFAA concentrations were evaluated relative to salinity and turbidity, as potential co-factors influencing groundwater concentrations and distribution.

Results/Lessons Learned. Collocated soil and groundwater perfluorooctane sulfonate (PFOS) concentrations from multiple sites demonstrate a strong correlation by location ($R^2 = 0.97$). Fractionation of PFAAs by groups, homologues, and isomers occurs along the advective flow path, especially as dissolved PFAAs approach a salinity gradient in a coastal setting. PFOS concentrations for filtered groundwater samples (≤ 5 NTU per U.S. EPA National Primary Drinking Water Regulations) are demonstrated to be as much as 800 times less than unfiltered (73 NTU) low-flow purge sample results, reducing concentrations to less than the U.S. EPA Health Advisory Level of 70 ppt (0.070 $\mu\text{g/L}$) for PFOS. Understanding the collective influence of these compounds and site-specific characteristics allows for the development of fate and transport models, better assessment of PFAS migration relative to potential receptors, appropriate comparison to health-based criteria, and design of potential in situ remedies.