Partitioning and Storage of Per- and Polyfluoroalkyl Substances Considering Precursors and Multi-Bilayer Supramolecular Assemblies in Unsaturated and Saturated Zones of Fire Training Areas

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Background/Objectives. There are current uncertainties regarding why AFFF impacted soils and concrete surfaces retain a significant mass of PFAS which continues to leach for decades following cessation of AFFF use. Multiple site investigations where assessment of per- and polyfluoroalkyl substances (PFAS) at fire training areas using advanced characterization tools, such as the total oxidizable precursor (TOP) assay, have determined that high concentrations of PFAS, including elevated concentrations of cationic and zwitterionic precursors are present in superficial soil and vadose zone. The results from several site investigations of Fire Training Areas using advanced analytical tools are compared and combined with a detailed understanding of the physical chemistry, partitioning and self-assembly behaviour of fluorosurfactants to potentially explain why unsaturated zone soils and concrete surfaces comprises a long-term reservoir of PFAS.

Approach/Activities. Groundwater and soil samples were characterized for PFASs at multiple sites, including fire training areas (FTAs), using advanced analytical tools. A detailed literature review of publications considering the behavior of fluorosurfactants was performed to shed light on their partitioning behavior. Self assembly phenomena exhibited by amphiphillic fluorosurfactants at higher concentrations, driven by entropic forces was assessed as the potential driving mechanism behind the observed sorption. PFAS are known to self-assemble to form large supramolecular assemblies, at interfaces and in solution via nucleation. Self-Assembled PFAS (SA-PFAS) structures have been described to be similar to crystalline solids and have been shown to grow to form 500 micron sized supramolecular assembliesover a 4-month period. These assemblies have been demonstrated to form at solid-liquid interfaces at concentrations some 5 orders of magnitude lower that PFAS critical micelle concentrations (CMC). From examination of the physical chemistry of PFAS it is considered that when they are dispensed in AFFF they coat solid surfaces with SA-PFAS, via the repeat formation of Langmuir-Blodgett films and that this mechanism is potentially responsible for storage of PFAS at interfaces in the vadose zone. In the saturated zone at FTAs relatively high concentrations (mg/L) of dissolved PFAS will concentrate at solid-liquid interfaces leading to the potential for SA-PFAS to form.The supramolecular assemblies formed by SA-PFAS are considered to be an important reservoir of PFAS at FTAs, as they can potentially comprise millions of quasi-crystalline bilayers, which slowly release PFAS over time as a result of rainwater infiltration. Electron microscopy was used to examine surfaces to visualize supramolecular structures.

Results/Lessons Learned. The vertical and horizontal delineation of PFAS at sites will be presented in relation to the site's hydrogeology and lithology. A review of publications describing the concentration of amphiphilic PFAS at the surface of concrete and on surficial soils was compared to data from several site investigations. The self-assembly behavior of fluorosurfactants is characterized by a strong tendency to form vesicles and lamellar phases rather than micelles, primarily due to the rigidity and helical nature of the perfluoroalkyl chain, which creates a cylindrical shape that tends to decrease the curvature of the aggregates they form in solution. These bulky supramolecular structures can further assemble to create a quasi-crystalline phase which can grow to micron sized structures. These reservoirs of PFAS, bound to soils, primarily adhere to surfaces, so deposits such as clays, which comprise those with greatest surface area may be primary sites for self-assembly and growth of supramolecular PFAS reservoirs, which form following repeat fire training.

The often frequent and repeat, historical applications of class B firefighting foams such as aqueous film forming foams (AFFFs) to open ground are considered to be responsible for this mass distribution, where amphiphilic PFASs are primarily stored in the vadose zone. When assessing the distribution of PFASs in soil and groundwater as a result of repeat fire training or equipment testing, the fate and behavior of all of the components of AFFF, such as glycols, hydrocarbon surfactants need to be considered, in addition to the PFAS.

Self-assembly of C8 PFASs into contiguous bilayers has been reported to occur at concentrations as low as 50 mg/L, meaning that the g/L concentrations encountered in AFFF as discharged to ground, is far greater than that needed for growth of these lamellar, vesicles and microtubules on soil surfaces. A model will be described which details the interaction of PFAS in AFFF with soils, explaining why FTAs remain as continuing source of PFAS to groundwater plumes for many decades. The formation of multiple bilayers where cationic and zwitterionic PFAS facilitate and stabilize the formation of bilayers will be discussed, which also may account for the slow rates of biotransformation of these precursors as they may not be bioavailable when located internally within multiple bilayers.