Matrix Diffusion as a Key Attenuation Process for PFAS in Groundwater

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Background/Objectives. Because there is little evidence that perfluoroalkyl acids (PFAAs) degrade under natural conditions in groundwater, they have not traditionally been considered as a candidate for management using monitored natural attenuation (MNA). However, a new paradigm based on retention based PFAS MNA has been proposed and is now being explored in field and modeling studies. The objective of this presentation is to establish the scientific basis and practical guidelines for using retention based MNA for PFAS plumes, to indicate favorable and unfavorable site conditions for its application, to evaluate the prospect for significant use in the coming years, and report on current research efforts focused on PFAS MNA.

Approach/Activities. First, a literature review of natural attenuation for other contaminants (hydrocarbons, solvents, oxygenates, stabilizers, metals, and radionuclides) was conducted to understand the history of natural attenuation, the implicit "social contract" involved in its use, and the key fate and transport processes that these MNA technologies rely upon. Next, observations from key PFAS research sites where matrix diffusion processes were considered were compiled with respect to the retention of PFAS in fine-grained saturated soils. Finally, modeling studies using the REMChlor-MD model repurposed for PFAS were performed to model the behavior of an existing, well characterized PFOS plume and the behavior of a hypothetical non-degrading solute to better understand how matrix diffusion can affect the migration of PFAS plumes.

Results/Lessons Learned. The literature review first showed that plume migration was attenuated by diffusion into low-permeability geologic media was observed as far back as 1985 (Sudicky et al., 1985). Further work confirmed that as a remediation technology natural attenuation developed slowly, with several examples of incorrect conceptual models suggesting that certain contaminants would likely create very long groundwater plumes. In addition, a partial analog for retention based PFAS MNA was found in U.S. EPA guidance developed for MNA of non-degrading metals and radionuclides. Overall, this analysis suggested that there is a scientific basis for using retention as an MNA approach for PFAS rather than relying on degradation (Newell et al., 2020a) and on this basis a set of Practical Guidelines (Newell et al., 2020b) were proposed.

Concurrent research at a high-resolution PFAS plume by the U.S. Navy, GSI Environmental, Oregon State University, and the Colorado School of Mines provided key insights on the distribution of different PFAS (108 different PFAS in soils; 58 different PFAS in groundwater) in several soil types and suggested that 82% of the PFAS mass at the site had entered lower-permeability soils (Adamson et al., 2020; 2022; Nickerson et al., 2022).

The REMChlor-MD model was then applied to the PFOS plume at this site and showed that calibrating the model to site conditions was much easier when matrix diffusion was operational in the model compared to the no-matrix diffusion case, and that if matrix diffusion had not been present than the plume would have been significantly longer (Kulkarni et al., 2022). An investigation of nature of the retention process with relation to different types and amount of geologic heterogeneity was then performed by Farhat et al. (2022). This study showed that in contrast to matrix diffusion processes that impact persistent chlorinated solvent plumes, matrix diffusion into thin "layers and lenses" in saturated transmissive zones retarded the migration of non-degrading plumes like PFOS to a larger extent than thick aquitards above and/or below the transmissive geologic media.

Finally preliminary results from an on-going U.S. Air Force PFAS research project evaluating if and how the REMChlor-MD might be used to simulate the behavior of PFAS plumes will be presented. This study will be used to learn if retention-based PFAS MNA could be employed for three actual PFAS plumes or if enhanced attenuation or plume control is likely to be needed.