

In Situ Carbon-Based PFAS Immobilization and Beyond: Case Study at a Suspected AFFF Site in Alpena, Michigan

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Background/Objectives. Perfluorooctane sulfonate (PFOS) is one of several per- and polyfluoroalkyl substances (PFAS) detected at elevated levels in soil and groundwater at a former tannery located along the Thunder Bay River in Alpena, Michigan (Site). Tannery operations ceased in the 1950s. The Site buildings burned to the ground in 2005. Aqueous film-forming foam (AFFF) use is suspected during the 2005 fire. Investigations of PFAS in soil, groundwater, surface water and river foam were initiated in 2017. Near the former building, residual PFOS in soil extend from the capillary fringe (0.5 feet below grade [ft bg]) to the base of the shallow aquifer (up to 8 ft bg). PFAS-impacted groundwater in the source area migrates into the Site's decaying storm water infrastructure and is conveyed to the river and, seasonally, vents to the ground surface. Pilot tests to mitigate PFAS impacts to surface water, including carbon-based (biochar) immobilization pilots, were initiated in December 2018. Immobilization is not destruction and bioaugmentation bench and pilot studies were initiated in 2020 and 2021 to assess the effectiveness of bioaugmentation to further reduce PFOS in Site groundwater.

Approach/Activities. The selected biochar product was assessed in a bench top test, prior to performing the 2018 injection pilot test (46 injection points advanced over a 2,250 square foot area), and soil mixing pilot test (excavator blended in a 100 square foot area). In March 2020 a bench top study to culture endemic microbes that may breakdown PFAS "precursor" compounds was performed. The study included the use of laboratory controls and bioenhancement (e.g., nutrients, aeration, etc.) to assess factors that may enhance PFOS breakdown. Performance monitoring during the tests included a combination of qualitative and analytical methods to assess mechanisms and changes in PFAS (including total oxidizable precursor assay and modified toxicity characteristic leaching procedure [TCLP]), metals, soil cation exchange capacity, total organic and inorganic fluoride (i.e., for mass balance/mineralization assessment) and organic carbon.

Results/Lessons Learned. Soil mixing with biochar reduced PFOS levels in groundwater from 2,130 nanograms per liter (ng/L) to 23.3 ng/L at 28 days and 179 ng/L (a 92% reduction) at 1 year. Less reduction is observed in short chain PFAS (PFBA=39% and PFBS=57% at 1 year). Injection pilot test results indicate a 35% and 100% reduction in PFOS in groundwater (depending on injection array spacing/loading rate and media distribution). A temporary, local increase in arsenic in groundwater was observed in each biochar pilot test area. PFOS in TCLP leachate decreased from 414 ng/L (untreated soil) to 8.2 ng/L (treated soil) at 1 year.

In the bioaugmentation bench top study endemic microbes from the Site demonstrated a 70% reduction in PFOS levels in groundwater at 8 weeks. Reductions in PFAS concentrations varied in microbially-treated samples but was greatest in the reactor that included aeration. Qualitative analyses indicate free fluoride was produced by two of the candidate PFAS-degrading microbe colonies. In 2020 the biochar soil mixing pilot was expanded to include bioaugmentation and oxygenation. During the initial two weeks of the bio-pilot test PFOS levels in groundwater decreased by over 50% in the microbe/oxygen treated area. In an oxygen-only buffered area, PFOS levels increased by over 20%. Additional steps to enhance oxygen delivery (aeration) and extend the bio-pilot test are being implemented at the Site in fall 2021.