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The Challenges of PFAS Remediation

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Summary

Many military bases and their surrounding communities are impacted by contamination with per- and polyfluoroalkyl substances (PFAS) from Aqueous Film-Forming Foams (AFFFs). Soil sorption technologies provide a promising solution to immobilize PFAS in the soil and prevent groundwater and drinking water contamination. This article is the result of a collaborative effort between Battelle and the U.S. EPA's review of the most promising technologies.

Since the 1960s, Aqueous Film-Forming Foams (AFFFs) have been the standard for fighting petroleum fires and conducting firefighting training exercises at U.S. military bases. The synthetic foam's chemical properties make it ideal for quickly smothering petroleum fires. But recent studies have raised concerns about the long-term environmental and human health impact of contamination in soil and groundwater around sites where the foams were heavily used.

AFFFs contain per- and polyfluoroalkyl substances (PFAS), a class of chemicals that has come under increasing regulatory and public pressure. A 2016 report¹ documented PFAS contamination in drinking water in communities in 33 states. Most of these communities are near military bases where numerous firefighting exercises were conducted. New answers are needed to help the military clean up or contain PFAS contamination on these sites.

The Problem with PFAS

PFAS encompasses a family of thousands of individual chemicals used in many industrial and commercial products. As a group, PFAS chemicals are highly resistant to heat, water and oil, making them highly useful for many industrial applications and consumer products ranging from non-stick cookware to stain-resistant fabrics. AFFFs were developed by the U.S. Naval Research Lab in the 1960s to extinguish fuel fires fasters. At military sites, PFAS accumulation is often found near fire fighting training areas, hangers, runways and crash

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sites. High accumulation of PFAS is also associated with sludge disposal areas and oil-water separators.

The same chemical properties that make PFAS so effective in firefighting foams and other products make them particularly hard to remediate. PFAS chemicals have very limited reactivity. As a result, PFAS is both highly persistent in the environment and bioaccumulative in human and animal tissues. This is especially true for “long-chain” PFAS chemicals such as perfluorooctane sulfonate (PFOS), which was until recently commonly used in firefighting foams. Some PFAS chemicals also have the potential to travel through the environment, meaning contamination in soil can sometimes make its way into groundwater.

Toxicology studies have raised concern about potential toxic effects for humans exposed to PFAS, including possible developmental effects for fetuses and young children. Other studies have pointed to possible links to cancer, immune system disorders and fertility problems. For these reasons, the Environmental Protection Agency (EPA) has set lifetime health advisory levels for PFOS and perfluorooctanoic acid (PFOA), another long-chain PFAS chemical, at just 70 parts per trillion.

Soil Sorption Technologies for PFAS Remediation

The persistence and mobility of PFAS in the environment make it a serious long-term concern for military bases. Natural attenuation and long-term monitoring is not an effective strategy for PFAS. Active treatment strategies must be used to either clean up the contamination or contain it so that it cannot leach from contaminated soil into groundwater or drinking water reserves.

Most of these treatment strategies are in their infancy and need more research and validation in the field. One promising approach currently in use is sorption, in which a material with PFAS-adsorbent properties is introduced to the contaminated area to immobilize the PFAS (although not destroying it). While there are sorption technologies for both water and soil, because PFAS releases tend to occur on the surface and some PFAS chemicals have a strong affinity to soil, sorption technologies for PFAS in soil could be highly beneficial. The goal of these treatments is to immobilize the PFAS in the soil to prevent it from leaching into groundwater.

Battelle recently completed a literature review for the EPA to determine which soil sorption technologies, carbon based, resins, minerals, biomaterials and molecular imprinted polymers have the most promise for PFAS-contaminated sites.

Biomaterials, as a class, may be less effective for PFAS contamination than other options, as they are likely to (or have the potential to) biodegrade over time. Resins also have significant limitations for use in soil treatments and are cost prohibitive compared to other options. Carbon and mineral treatment show more promise for treatment of PFAS-contaminated soils.

Carbon

Carbon sorbents can be classified into three broad groups: granular activated carbon (GAC), powdered activated carbon (PAC), and multi-walled carbon nanotubes (CNTs). Of these CNTs, has the highest sorption capacity, followed by PAC. However, GAC has been shown to be the most applicable for treatment.

Carbon's non-polar functional groups make it highly useful for hydrophobic contaminants like PFAS. However, all forms of carbon tend to be fouled by high concentrations of organic matter in sediments or soils. Studies also suggest that they work better for low concentrations of PFAS than for higher concentrations.

Minerals

Mineral options for PFAS sorption include organoclays (organically modified phyllosilicates - e.g., montmorillonite, kaolinite and palygorskite), iron oxides (goethite, hematite), and silica.

Organoclays have been most widely studied. They have a high sorption capacity and modifications may enhance their sorption capacity. Unmodified organoclays have a surface that is hydrophilic, making them ineffective for hydrophobic compounds like PFAS. However, modification with surfactants and amine or amino groups enhances its ability to adsorb PFAS compounds like PFOA and PFOS.

Like organoclays, silica-based sorbents can be modified with surfactants to enhance sorption of PFAS. However, due to their high cost, their use is mainly limited to solid phase extraction for laboratory analysis of PFAS compounds.

Iron oxide minerals have been shown to have a strong affinity to PFAS compounds. Some studies have shown that they outperform modified organoclays in their sorption capacity, but more research is needed.

Considerations in Sorbent Selection

The overall effectiveness of a sorption treatment for PFAS compounds will be impacted by several variables. These include:

- **Media characteristics:** The efficacy of a particular sorbent is impacted by the media (e.g., soil) in which it is used. The pH and the presence of inorganic and organic ions both have an effect on sorption efficiency. PFAS sorption decreases in more alkaline environments. Natural organic matter present in the soil will greatly reduce the sorption capacity of activated carbon. Inorganic ions impact sorption capacity of organoclays by changing the charge of the sorbent.
- **PFAS characteristics:** PFAS chemicals are broadly categorized by the length of the carbon-fluoride chain that forms their backbone. Long-chain compounds (with six or more carbon atoms) tend to adsorb more strongly than shorter-chain compounds. The functional groups attached to the chain also have an impact; sulfonate functional groups lead to stronger adsorption.

- Sorbent characteristics: The physical and chemical characteristics of the sorbent material have a large effect on sorption capacity. Smaller particles or highly porous materials have higher specific surface area and higher sorption rates. More basic or positively charged sorbents tend to have better performance than more acidic or negatively charged materials.

Stabilizing PFAS at Military Bases

Soil sorption technologies are likely to be a significant part of the solution for PFAS contamination at military bases. By stabilizing PFAS compounds in the soil, we can prevent them from getting into groundwater or drinking water and limit their ability to interact with living organisms in the ecosystem.

Finding answers for military bases contaminated with PFAS is urgent. There are an estimated 26,000 PFAS contaminated sites across the U.S., and six million Americans are believed to be impacted by PFAS-contaminated drinking water². The vast majority of these communities are around military sites where AFFFs were used. While AFFFs are far from the only source of PFAS contamination in the environment, their heavy concentrations on and around the bases and the specific chemical makeup of PFASs used in firefighting foams makes these sites a priority. Stabilizing PFAS in the soil on and around these military bases will significantly reduce the potential for harm to surrounding communities.

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