

Understanding PFAS Behavior in Sediment

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Per- and polyfluoroalkyl substances (PFAS) have vaulted to the forefront of interest for manufacturers, water utilities, regulators, litigators, and the wider public. With diverse applications, PFAS are in hundreds of products for residential, commercial, and industrial use. As a result, they are ubiquitous in the environment, and they are increasingly regulated by the Environmental Protection Agency and state agencies.

Contrary to “old guard” contaminants—such as PCBs and dioxins/furans—many PFAS do not sorb strongly to sediment. Nonetheless, they cause concern to the contaminated sediment practitioner due to their diversity. The expanse of PFAS, particularly larger ones, brings four notable characteristics as they relate to sediment:

1. Certain designed characteristics of larger PFAS can vastly increase their potential to sorb to sediment compared to simpler, smaller PFAS.
2. Larger PFAS compounds may incorporate or contain one or more basic PFAS, such as perfluorooctanoic acid (PFOA) or perfluorooctane sulfonic acid (PFOS). The degradation of these larger PFAS can release the incorporated PFAS into the environment.
3. Transformation- or degradation-type reactions generate different PFAS. For example, the degradation of fluorotelomer alcohols (FTOHs) forms compounds such as perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), and PFOA.
4. Analytical methods for PFAS fail to measure precursors that eventually transform into the analyzed PFAS. They also fail to detect the presence of specific PFAS when it is incorporated into a larger PFAS.



Because of these characteristics, PFAS can be released into the environment in forms that are highly sorptive (#1), contain other PFAS and PFAS precursors (#2 and #3), and remain undetectable by current analytical methods (#4). This implies that sediment can

become enriched in PFAS that are “invisible” (i.e., not measured by standard methods) until they degrade and subsequently release known, detectable, and less sorbable PFAS. Essentially, PFAS visibility and sorbability are driven by molecular changes, and a basic understanding of these changes can help explain PFAS fate and transport.

As an example, one of the largest PFAS applications is for coatings to impart water- and stain-resistant properties onto a material. Understanding the functionality of these surface applications, by way of their molecular structure, is key to understanding the potential for PFAS accumulation in sediment. Consider a common class of PFAS fabric treatments—a type of polymer, known as a side-chain fluorinated polymer, comprising three parts:

- **PFAS moiety:** The moiety is the source of the functional characteristics of stain- and water-resistance. The type of moiety is defined by the functional group (carboxylic acid or sulfonate) and chain length. Examples include a short-chain sulfonate, such as perfluorobutanesulfonic acid (PFBS), and a long-chain carboxylic acid, such as PFOA.
- **Polymer backbone:** This part provides adhesion to the fabric to ensure the durability of treatment. The polymer backbone is typically a urethane or acrylate polymer with numerous PFAS moieties attached to it.

- **Linkage:** The linkage provides the chemical bond between the PFAS moiety and the polymer backbone. The linkage-moiety combination often includes a PFAS precursor. Examples include FTOHs, such as 8:2 FTOH, and perfluorooctanesulfonamide (PFOSA).

These polymers have high molecular weights—10,000 Da or higher—that allow them to sorb or settle into sediment and biosolids. (After all, the purpose of the polymer backbone is to ensure adhesion to a textile surface.) Over time, however, these compounds degrade in the environment. The degradation rates are variable, with half-lives ranging from years to decades. Degradation rates are affected by pH and organic carbon content. Higher rates of degradation occur at high pH and at lower organic carbon content. Regardless, as these compounds degrade, PFAS or their precursors are released from the degrading structure. The base carboxylic or sulfonate molecules (e.g., PFOA and PFOS) represent the degradation endpoints. They are highly stable, readily identifiable, and substantially less sorptive than the original polymeric molecules.

The example of the side-chain fluorinated polymer demonstrates the need to evaluate larger PFAS despite their “invisibility.” There are three key strategies to do so:

- **Develop a strong conceptual model.** Analysts can create a conceptual model that includes the potential for PFAS precursors and smaller PFAS from

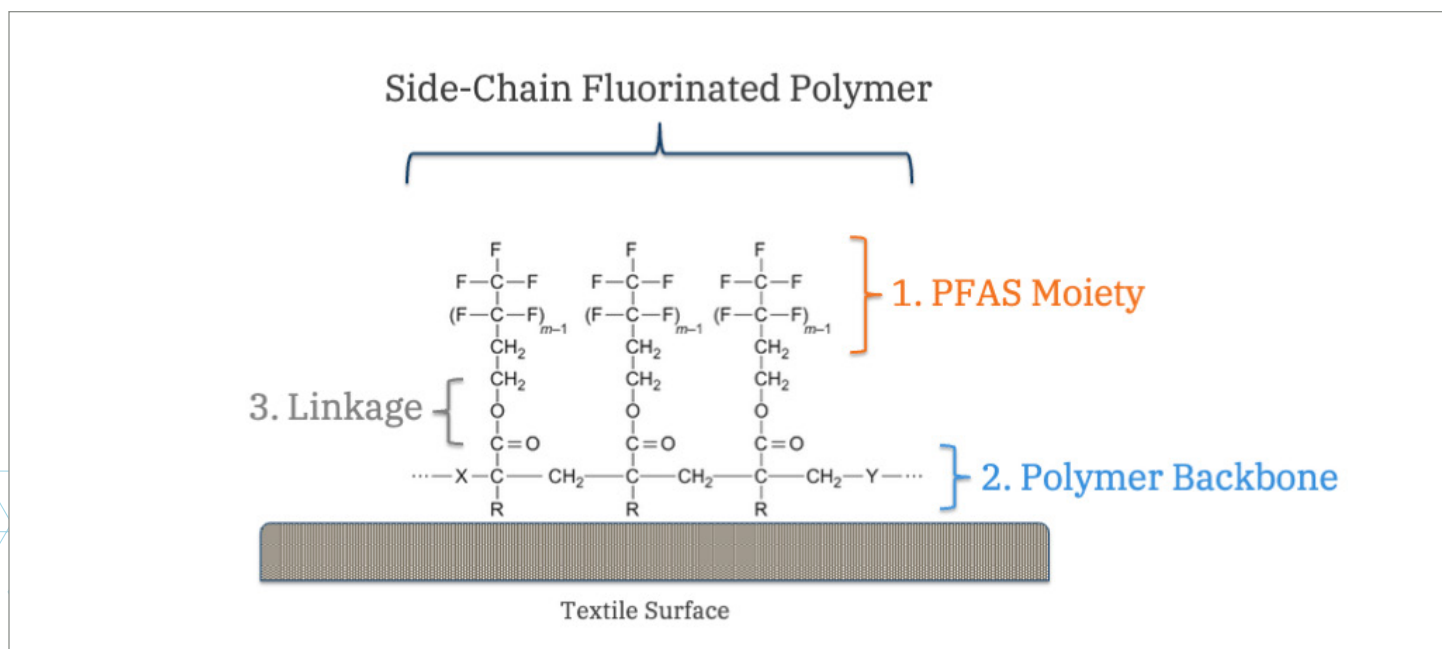


Figure 1. Side-Chain Fluorinated Polymer Molecular Structure

