Advanced Materials for Environmental Remediation: Metal-Organic Frameworks (MOFs) and Emerging PFAS Destruction Technologies

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Abstract- *Per- and polyfluoroalkyl substances (PFAS) constitute a large and chemically diverse group of anthropogenic contaminants that have attracted global concern due to their extreme environmental persistence, bioaccumulative behavior, and adverse health effects. The remarkable stability of the carbon–fluorine bond renders PFAS highly resistant to conventional biological, chemical, and physical treatment processes, necessitating the development of advanced remediation technologies capable of both effective removal and complete destruction. In recent years, metal–organic frameworks (MOFs) have emerged as a highly promising class of advanced materials for environmental remediation owing to their exceptional porosity, tunable surface chemistry, modular structural design, and multifunctional capabilities. This review critically examines the role of MOFs in PFAS remediation, with a particular emphasis on adsorption mechanisms, material design strategies, and catalytic and photocatalytic degradation pathways. In parallel, emerging PFAS destruction technologies—including electrochemical oxidation, advanced oxidation processes, thermal treatment, and hybrid material systems—are comprehensively evaluated. Key structure, property, performance relationships governing PFAS interactions with MOFs are discussed, alongside the challenges associated with material stability, regeneration, scalability, and real-world deployment. Finally, future research directions are proposed, highlighting the integration of MOFs with advanced oxidation technologies, computational materials design, and systems-level engineering approaches aimed at achieving sustainable, cost-effective, and complete PFAS mineralization.*

Keywords: Metal–organic frameworks; PFAS remediation; adsorption; photocatalysis; electrochemical degradation; advanced oxidation; water treatment; environmental nanomaterials.

I. INTRODUCTION

The increasing presence of persistent and emerging contaminants in water, soil, and air systems poses one of the most pressing environmental challenges of the 21st century. Among these contaminants, per- and polyfluoroalkyl substances (PFAS) have gained unprecedented attention due to their widespread use, extreme chemical stability, and potential impacts on human health and ecosystems. PFAS are synthetic organ fluorine compounds characterized by partially or fully fluorinated carbon chains, which impart unique physicochemical properties such as hydrophobicity, oleophobicity, and thermal resistance. These properties have led to their extensive application in industrial processes and consumer products, including firefighting foams, non-stick coatings, textiles, food packaging, and electronic components. [1,2]

However, the same properties that make PFAS technologically valuable also contribute to their environmental persistence. The carbon–fluorine bond, one of the strongest single bonds in organic chemistry, significantly hinders natural degradation pathways. As a result, PFAS accumulate in groundwater, surface water, sediments, and biota, leading to long-term exposure risks. Epidemiological studies have linked PFAS exposure to adverse health outcomes such as endocrine disruption, immunotoxicity, developmental effects, and increased cancer risk. Consequently, regulatory agencies worldwide have begun implementing increasingly stringent limits on PFAS concentrations in drinking water and the environment. [3,4]

Conventional water treatment technologiessuch as granular activated carbon (GAC), ion exchange resins, and membrane filtrationare primarily effective at removing PFAS rather than destroying them. These approaches often suffer from reduced efficiency for short-chain PFAS, high operational costs, secondary waste generation, and limited regeneration capabilities. Therefore, there is a critical need for advanced materials and processes that enable both selective PFAS capture and irreversible destruction.[5]

In this context, metal–organic frameworks (MOFs) have emerged as a transformative platform for environmental remediation. MOFs are crystalline porous materials composed of metal nodes coordinated to organic linkers, forming extended three-dimensional networks. Unlike traditional adsorbents, MOFs offer unparalleled structural tunability, enabling precise control over pore size, surface chemistry, hydrophilicity, and catalytic functionality. This tunability allows MOFs to be rationally designed for targeted interactions with PFAS molecules, potentially overcoming the limitations of conventional materials.[6]

Beyond adsorption, MOFs can serve as catalytic and photocatalytic platforms capable of activating strong chemical bonds under mild conditions. Recent studies have demonstrated that certain MOFs and MOF-based composites can facilitate PFAS defluorination through redox reactions, light-driven processes, or electrochemical pathways. These multifunctional capabilities position MOFs at the forefront of next-generation PFAS remediation technologies.

This review aims to provide a comprehensive and critical assessment of MOFs and emerging PFAS destruction technologies, focusing on fundamental mechanisms, material design principles, performance evaluation, and real-world applicability. By integrating insights from materials science, environmental chemistry, and engineering, this work seeks to elucidate the current state of the field and identify pathways toward scalable and sustainable PFAS remediation solutions.[7]

1. Fundamentals of Metal–Organic Frameworks for Environmental Remediation

Structural Characteristics of MOFs

Metal–organic frameworks are defined by their modular architecture, consisting of inorganic metal nodes (single ions or metal-oxo clusters) connected by multidentate organic ligands. This coordination chemistry enables the formation of highly ordered porous networks with exceptional surface areas, often exceeding those of traditional porous materials such as activated carbon and zeolites. Surface areas of MOFs can surpass 5,000 $m^2 g^{-1}$, providing abundant active sites for contaminant interaction.[8,9,10]

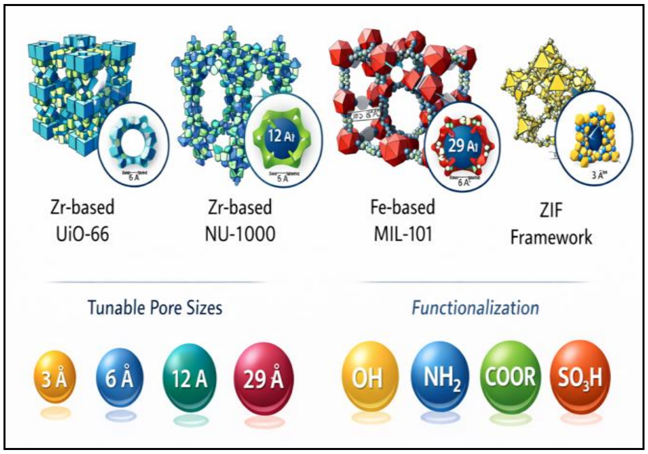

Figure 1. Structural Diversity of MOFs

The structural diversity of MOFs arises from the vast combination of metal ions (e.g., Zr, Fe, Al, Cu, Zn) and organic linkers (e.g., carboxylates, azolates, phosphonates). This diversity allows precise tuning of pore size distribution, framework flexibility, and chemical functionality-key attributes for selective adsorption and catalysis in complex environmental matrices.[11]

Physicochemical Properties Relevant to PFAS Remediation

For PFAS remediation, several MOF properties are particularly important:

Hydrolytic Stability: Many MOFs degrade in aqueous environments; therefore, water-stable frameworks such as zirconium-based (UiO-series) and aluminum-based MOFs are favored.[12]

Surface Charge and Functional Groups: PFAS typically exist as anions in water; thus, positively charged or functionalized MOFs can enhance electrostatic attraction.

Pore Geometry: The size and shape of MOF pores influence accessibility and diffusion of PFAS molecules, especially for long-chain versus short-chain species.[13,14]

2. Metal–Organic Frameworks as Adsorbents for PFAS and Persistent Organic Pollutants

Molecular Complexity of PFAS Adsorption

PFAS adsorption differs fundamentally from the adsorption of conventional organic contaminants due to the unique amphiphilic and fluorophilic nature of these molecules. PFAS are composed of a highly fluorinated alkyl chain that is both hydrophobic and oleophobic, coupled to a hydrophilic, typically anionic, terminal functional group (e.g., $–COO^-$, $–SO_3^-$). This structure results in low polarizability of the fluorinated tail, weak van der Waals interactions, and poor affinity for traditional carbonaceous adsorbents.[15,16]

Furthermore, PFAS exhibit:

- High aqueous solubility, especially short-chain PFAS;
- Low partitioning to organic matter relative to hydrocarbons;
- Strong hydration shells, reducing adsorption kinetics.

Consequently, adsorption materials must be engineered to overcome both thermodynamic and kinetic barriers, requiring precise control over surface chemistry and pore architecture.[17]

Design Principles for MOFs as PFAS Adsorbents

The modularity of MOFs allows rational design based on PFAS molecular characteristics. Effective MOF adsorbents typically integrate the following design elements:

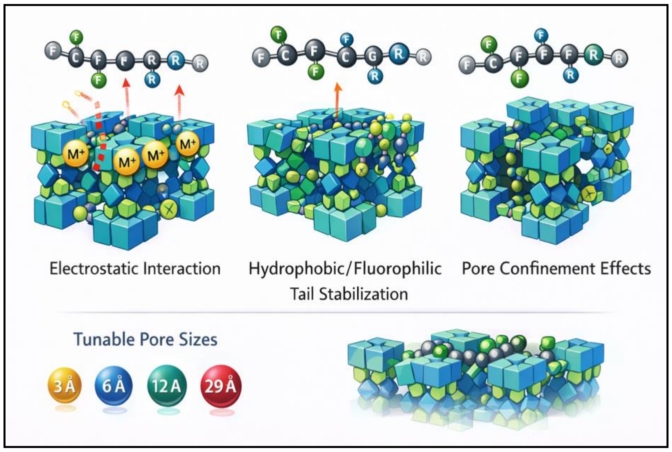

Figure 2. PFAS Adsorption Mechanisms on MOFs

Electropositive Binding Domains

Since PFAS exist predominantly as anions at environmentally relevant pH values, electrostatic attraction is a dominant adsorption driving force. MOFs containing positively charged metal clusters or cationic functional groups exhibit enhanced PFAS uptake. Strategies include:[18]

- Incorporation of quaternary ammonium-functionalized linkers;
- Introduction of open metal sites with Lewis acidity;
- Post-synthetic modification to impart permanent positive charge.

These electrostatic interactions are particularly critical for short-chain PFAS, which lack strong hydrophobic interactions.[19]

Hydrophobic and Fluorophilic Microenvironments

Hydrophobic pore interiors stabilize the fluorinated tail of PFAS molecules through weak dispersive interactions and entropy-driven desolvation effects. Fluorophilic domains-though difficult to design-can further enhance adsorption selectivity. MOFs employing aromatic linkers or fluorinated ligands have demonstrated improved affinity for long-chain PFAS.[20]

Hierarchical and Mesoporous Structures

Diffusion limitations are a significant challenge for PFAS adsorption. Hierarchical MOFs featuring micropores for strong binding and mesopores for rapid transport mitigate mass-transfer resistance. Mesoporous Zr-based MOFs such as NU-1000 exemplify this strategy, enabling high adsorption capacities under dynamic flow conditions.[21]

Thermodynamics and Kinetics of PFAS Adsorption on MOFs

Adsorption thermodynamics provide insight into PFAS–MOF interactions. Reported adsorption isotherms often follow Langmuir or Freundlich models, indicating monolayer adsorption on heterogeneous surfaces. Key observations include:[22]

- Negative Gibbs free energy ($\Delta G° < 0$), confirming spontaneous adsorption;
- Moderately exothermic enthalpy changes, suggesting physical adsorption with partial chemisorption contributions;
- Strong dependence of adsorption capacity on ionic strength and pH.[23]

Kinetically, PFAS adsorption on MOFs frequently follows pseudo-second-order models, indicating rate control by surface interactions rather than intraparticle diffusion alone.[24]

Table 1. Representative MOFs for PFAS Adsorption

MOF	Metal Node	Key Functionalization	PFAS Target	Key Advantage
UiO-66-NH_2	Zr	Amine groups	PFOA, PFOS	High stability
NU-1000	Zr	Open metal sites	Long/short-chain PFAS	Mesoporosity
MIL-101(Fe)	Fe	Redox-active nodes	PFOA	Catalytic potential
ZIF-8	Zn	Hydrophobic pores	Short-chain PFAS	Chemical stability

Influence of Water Chemistry and Competitive Adsorption

In real waters, PFAS adsorption performance is strongly affected by background constituents:

- **Competing anions** (e.g., sulfate, phosphate) reduce adsorption via site competition;
- **Natural organic matter (NOM)** can adsorb preferentially, blocking pores and reducing active sites;
- **Multivalent cations** may either enhance adsorption by charge bridging or inhibit it by site occupation.

Designing MOFs with selective binding sites and antifouling surfaces remains a major challenge for practical deployment.[25,26]

3. MOF-Based Catalytic and Photocatalytic PFAS Destruction

Necessity of Destruction-Oriented Technologies

Adsorption alone does not eliminate PFAS but merely transfers them from one phase to another, creating concentrated waste streams. Long-term sustainability requires destruction technologies capable of cleaving C–F bonds, thereby eliminating PFAS persistence.[27, 28]

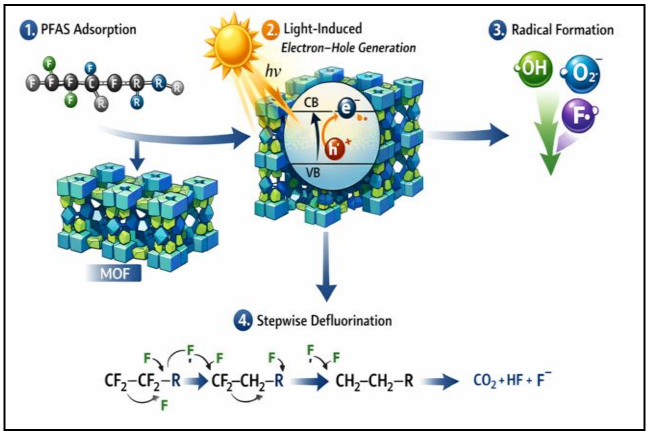

Figure 3. MOF-Based PFAS Destruction Pathways

MOFs are uniquely positioned to bridge adsorption and destruction due to their ability to:

- Pre-concentrate PFAS near reactive sites;
- Stabilize catalytic intermediates;
- Mediate redox reactions under mild conditions.[29]

Table 2. PFAS Destruction Technologies

Technology	Mechanism	Destruction Level	Maturity
Electrochemical oxidation	Electron transfer	High	Pilot
UV/Persulfate	Radical oxidation	Moderate	Pilot
Thermal incineration	Complete mineralization	Complete	Commercial
MOF photocatalysis	Redox + adsorption	Partial–High	Lab

Fundamental Challenges of C–F Bond Activation

The C–F bond has a dissociation energy exceeding 480 kJ mol^{-1}, making it resistant to thermal, biological, and chemical attack. Effective destruction pathways typically rely on:[30]

- Highly reducing environments (e.g., solvated electrons);
- Strong oxidizing radicals;
- Catalytic electron transfer processes.

MOFs can facilitate these pathways by localizing reactants and mediating electron transfer.[31]

Photocatalytic PFAS Degradation Mechanisms in MOFs

MOF-based photocatalysis involves light-induced excitation of electrons from the valence band to the conduction band (or ligand-to-metal charge transfer states), generating reactive species. Key degradation pathways include:[32,33,34]

Reductive Defluorination

Photoexcited electrons reduce PFAS molecules, initiating sequential C–F bond cleavage. This pathway is particularly effective for perfluoroalkyl carboxylates under UV irradiation.

Oxidative Pathways

Photogenerated holes or radicals oxidize PFAS head groups, destabilizing the molecule and facilitating chain shortening. However, oxidative pathways often yield short-chain PFAS intermediates, which remain environmentally problematic.

5. MOF-Based Composite Photocatalysts

To improve performance, MOFs are frequently integrated into composite systems:

- MOF–carbon hybrids improve charge separation and electron mobility;

- MOF–semiconductor composites expand light absorption into the visible region;
- MOF–metal nanoparticle systems enhance catalytic turnover.

These composites demonstrate significantly improved PFAS degradation rates and partial mineralization under laboratory conditions.[35]

Limitations and Stability Concerns

Despite promising results, MOF-based photocatalytic PFAS destruction faces significant limitations:

- Structural degradation under prolonged irradiation;
- Leaching of metal ions;
- Low quantum efficiency under solar illumination;
- Formation of persistent transformation products.

Addressing these issues requires robust framework design and system-level optimization.[36]

Electrochemical-MOF Hybrid Systems

Emerging research explores coupling MOFs with electrochemical systems, where MOFs serve as:[37]

- Electrocatalysts;
- Pre-concentration layers;
- Electron mediators.

These hybrid systems show promise for energy-efficient PFAS destruction but remain at an early developmental stage.

6. Comparative Assessment of PFAS Remediation Technologies

Removal vs. Destruction Paradigm

PFAS remediation technologies can be broadly categorized into removal-based and destruction-based approaches. Removal technologies transfer PFAS from water to another phase (solid or concentrate), while destruction technologies aim to break the C–F bond, permanently eliminating PFAS.[38,39]

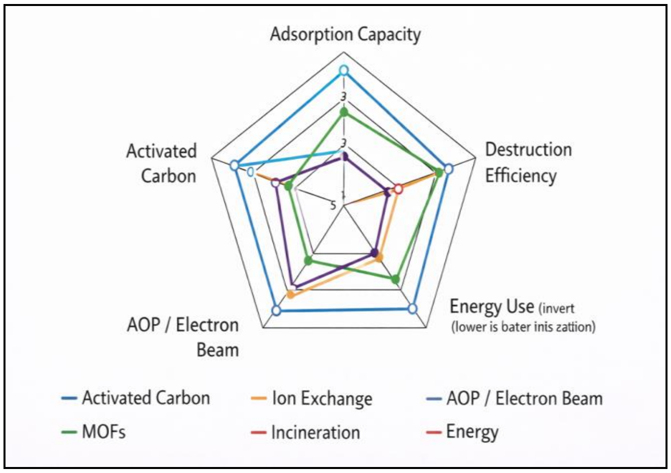

Figure 4. Comparative PFAS Remediation Technologies

MOFs uniquely occupy an intermediate position: they can act as high-performance adsorbents, pre-concentration platforms, and catalytic materials capable of initiating PFAS degradation. This multifunctionality distinguishes MOFs from conventional technologies such as activated carbon or ion exchange resins.[40, 41]

Table 3: Comparison of Major PFAS Treatment Technologies

Technology	PFAS Removal	PFAS Destruction	Energy Demand	Scalability	Key Limitations
Activated Carbon	High (long-chain)	None	Low	High	Poor short-chain removal, regeneration waste
Ion Exchange	High	None	Low	High	Expensive resins, fouling
Membrane Filtration	Very high	None	Moderate–High	High	Concentrate disposal
Electrochemical Oxidation	Moderate	High	High	Moderate	Energy cost, electrode fouling
Advanced Oxidation (AOPs)	Low–Moderate	Partial	High	Moderate	Incomplete mineralization
Thermal/Plasma	Complete	Complete	Very High	Low	Capital cost
MOFs (Adsorption)	High	None	Low	Low–Moderate	Stability, scale-up
MOFs (Catalytic)	Moderate	Partial–High	Moderate	Low	Reaction efficiency

MOF-based systems excel in selectivity and tunability, but currently lag behind mature technologies in scalability and robustness. [42]

Performance Against Short-Chain PFAS

Short-chain PFAS (e.g., PFBS, PFHxA) are especially challenging due to high solubility and weak hydrophobic interactions. Conventional adsorbents perform poorly, whereas cationic and functionalized MOFs demonstrate significantly enhanced uptake via electrostatic binding. However, complete destruction of short-chain PFAS remains unresolved, highlighting a critical research gap.[43]

7. Reaction Pathways and Chemical Equations for PFAS Destruction

Reductive Defluorination Reactions[44]

Reductive PFAS degradation proceeds via electron injection into antibonding orbitals of the C–F bond. A generalized reaction scheme for perfluoroalkyl carboxylates (PFCAs) is:

$$\mathrm{C}_n\mathrm{F}_{2n+1}\mathrm{COO}^- + e^- \rightarrow \mathrm{C}_n\mathrm{F}^{\cdot}_{2n+1} + \mathrm{CO}_2$$
$$\mathrm{C}_n\mathrm{F}^{\cdot}_{2n+1} \rightarrow \mathrm{C}_{n-1}\mathrm{F}^{\cdot}_{2n-1} + \mathrm{CF}_2$$
$$\mathrm{CF}_2 + 2e^- + 2H^+ \rightarrow \mathrm{CHF}_2 \rightarrow \mathrm{HF} + \mathrm{CO}_2$$

MOFs stabilize radical intermediates by:

- Coordinating PFAS head groups to metal nodes
- Restricting diffusion, increasing reaction probability
- Providing localized electron-rich environments

Oxidative PFAS Degradation Reactions[45]

Oxidative degradation typically initiates at the head group:

$$\mathrm{C}_n\mathrm{F}_{2n+1}\mathrm{COO}^- + \cdot\,\mathrm{OH} \rightarrow \mathrm{C}_n\mathrm{F}^{\cdot}_{2n+1} + \mathrm{CO}_2 + \mathrm{OH}^-$$

Subsequent reactions yield shorter-chain PFAS and fluoride ions:

$$\mathrm{C}_n\mathrm{F}^{\cdot}_{2n+1} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{C}_{n-1}\mathrm{F}_{2n-1}\mathrm{COO}^- + \mathrm{HF}$$

MOF photocatalysts enhance oxidative reactions by:

- Promoting charge separation
- Generating reactive oxygen species (ROS)
- Anchoring PFAS near reactive sites

Mechanistic Pathways for PFAS Defluorination

Thermodynamic Barriers to C–F Bond Cleavage

The extraordinary strength of the C–F bond (>480 kJ mol^{-1}) underlies PFAS persistence. Successful defluorination pathways must overcome both:

- Bond dissociation energy barriers
- Stabilization of fluorinated intermediates

PFAS destruction typically proceeds via stepwise chain-shortening, generating progressively shorter fluorinated intermediates before complete mineralization.[46]

Reductive Defluorination Pathways

Reductive pathways rely on highly energetic electrons (e.g., solvated electrons) that attack PFAS molecules, initiating C–F cleavage:

1. Electron injection into PFAS antibonding orbitals
2. C–F bond scission
3. Release of fluoride ions
4. Formation of shorter-chain perfluoroalkyl radicals

MOFs can facilitate this process by stabilizing reduced intermediates and concentrating PFAS near electron-rich sites.[47]

Oxidative Defluorination Pathways

Oxidative mechanisms involve:

- Hydroxyl radicals (•OH)
- Sulfate radicals ($\mathrm{SO}_4^{\bullet-}$)
- Photogenerated holes

These species preferentially attack the functional head group, often leading to decarboxylation or desulfonation. While effective at initiating degradation, oxidative pathways frequently stall at short-chain PFAS, emphasizing the need for combined oxidative–reductive systems.[48]

Role of MOFs in Mechanistic Control

MOFs offer several mechanistic advantages:

- Spatial confinement, increasing local PFAS concentration
- Controlled redox environments
- Stabilization of transition states
- Sequential adsorption–reaction cycles

Computational studies suggest that linker functionalization and metal-node selection critically influence defluorination energetics.[49]

8. Engineering and Scale-Up Considerations

MOF Synthesis at Scale

Despite impressive laboratory performance, MOFs face challenges in large-scale production:

- High solvent consumption
- Long synthesis times
- Batch-to-batch variability

Recent advances in continuous flow synthesis, green solvent systems, and spray-drying techniques show promise for industrial-scale MOF fabrication.[50]

Reactor Design for MOF-Based PFAS Treatment

Key reactor configurations include:

- Fixed-bed adsorption columns
- Fluidized-bed reactors
- Photocatalytic slurry reactors
- Electrochemical flow-through systems

Design considerations must address:

- Mass transfer limitations
- Light penetration (for photocatalysis)
- Pressure drop and fouling
- Regeneration strategies

Regeneration and Lifecycle Performance

MOF regeneration methods include:

- Solvent washing
- Thermal treatment
- Electrochemical desorption

Repeated regeneration often leads to framework degradation, highlighting the importance of designing mechanically and chemically robust MOFs.[51,52]

9. Techno-Economic and Sustainability Analysis

Cost Considerations

The economic feasibility of MOF-based PFAS remediation depends on:

- Raw material cost (metal salts, organic linkers)
- Synthesis scalability
- Regeneration efficiency
- Operational lifetime

While MOFs are currently more expensive than activated carbon, their higher selectivity and multifunctionality may justify costs in high-value or high-risk applications.[53]

Environmental and Lifecycle Impacts

Potential environmental concerns include:

- Metal leaching
- Disposal of spent MOFs
- Energy intensity of destruction processes

Lifecycle assessments suggest that hybrid systems, combining MOF adsorption with centralized destruction technologies, may offer optimal sustainability.[54,55]

II. CONCLUSIONS

This review demonstrates that metal-organic frameworks represent a paradigm shift in environmental remediation materials. Their tunable chemistry enables selective PFAS capture, catalytic activity, and integration with emerging destruction technologies. However, significant scientific and engineering barriers remain. Bridging molecular-level understanding with system-level implementation will determine whether MOFs can become a cornerstone of sustainable PFAS remediation.

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