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The Hydrogeological Implications and Management of Per- and Polyfluoroalkyl Substances (PFAS) in Aquifer Systems: A Critical Review

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Abstract

This is a critical review of how Per- and Polyfluoroalkyl Substances (PFAS) also referred to as forever chemicals in colloquial terms, widely contradict groundwater resources around the world, with a particular focus on the complicated hydrogeological processes of contamination. The discussion confirms that the unprecedented retention of PFAS plumes is essentially the result of the unusual retention processes at the subsurface level. These mechanisms involve a process of matrix diffusion where mass storage in low-permeability areas has been demonstrated to contribute up to 82 per cent of the total contaminant load and a process of substantial air-water interface (AWI) partitioning in the unsaturated zone which stores an estimated 50 per cent to 75 per cent of the mobile mass. The resulting mass sequestration is a source of chronic back-diffusion and makes the traditional models of remediation non-existent. Existing technologies are also under review: whilst physical sequestration using state of the art Ion Exchange Resins (IXR) have high capacity mass concentration, true destructive sequestration, especially Electrochemical Oxidation (EO), is limited by the prohibitive energy usage, and the highly detrimental, reportedly documented liability of producing acutely toxic secondary byproducts, such as chlorate, many thousands of times above drinking water levels. The review ends with a call to action of the world to abandon reactive management of plumes to a compulsory requirement of upstream elimination of sources and the deployment of risk-managed hybrid treatment trains to traverse the radical difference between global regulatory standards.

Keywords: Per- and polyfluoroalkyl substances (PFAS); groundwater remediation; matrix diffusion; air-water interface; electrochemical oxidation; aquifer management.

1. Introduction: The Global Threat of Per- and Polyfluoroalkyl Substances (PFAS)

Rampant Per- and Polyfluoroalkyl Substances (PFAS) pollution of the world water resources is an environmental and social health crisis of the planetary scale. The chemicals initially introduced in industry and in the hands of consumers during the 1940s, this group of anthropogenic chemicals has created a ubiquitous presence across the ecosystem of Earth (EPA, 2024). The severity of this crisis is based on the two characteristics of the chemicals: one of a chemical structure that offers it an almost permanent ability to resist environmental decay, and the other of a high level of mobility to propagate quickly across critical aquifer systems, which are the main sources of drinking water (EPA, 2024). As a consequence, PFAS pollution management ceased to be a local issue, as it has now become a global regulatory necessity. The dynamics of this common pollution are described in Figure 1 that shows how the plumes move out of the surface sources to the drinking water receiving points.

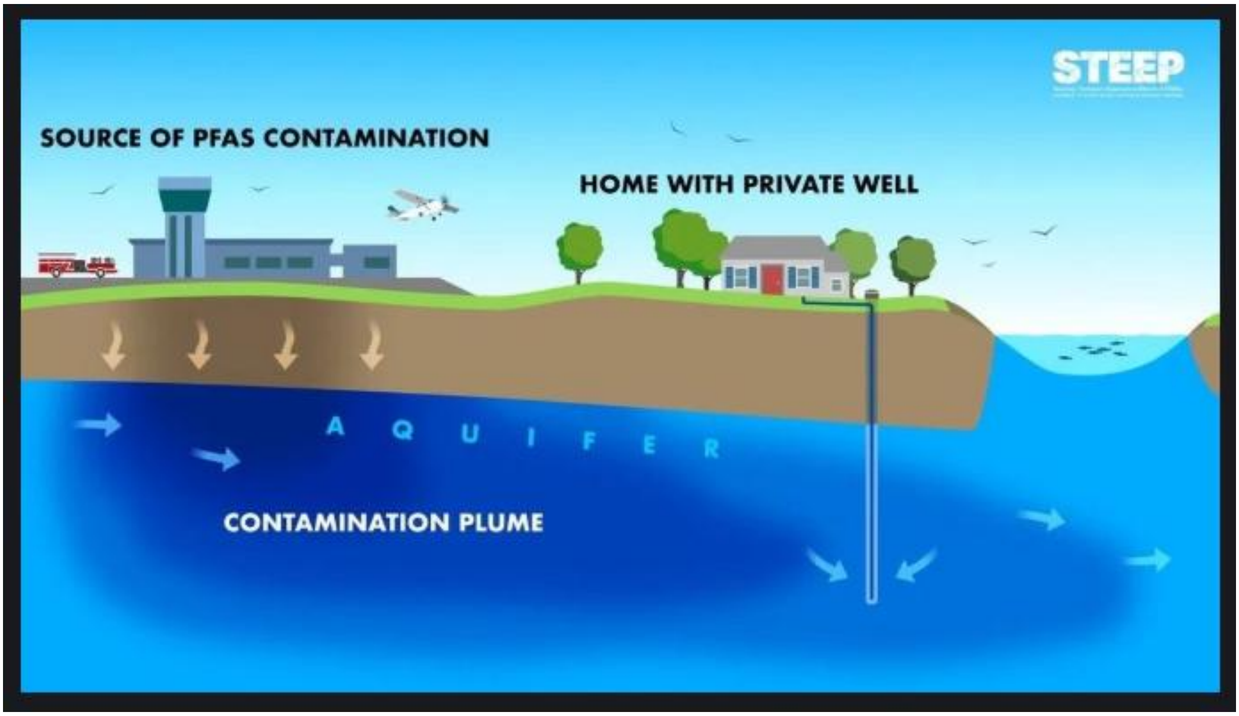

Figure 1: An example of a contamination plume that shows how PFAS expanded over groundwater over the areas of its source to the household wells (After Shea, 2023).

1.1 Defining "Forever Chemicals": Chemistry, Classification, and Sources

Part of what makes PFAS such an extraordinary useful, and eventually, notorious substance, is the fact that carbon-fluorine (C"F) bond is among the most stable chemical bonds in nature. This pairing has the electronegativity and short bond length, making PFAS compounds extraordinarily stable at thermal in both chemical and biological respects, significantly losing the personification merits an ominous title ofibernal altreatment forever chemicals (NIEHS, 2024). Figure 2 is used to visually describe this structural stability.

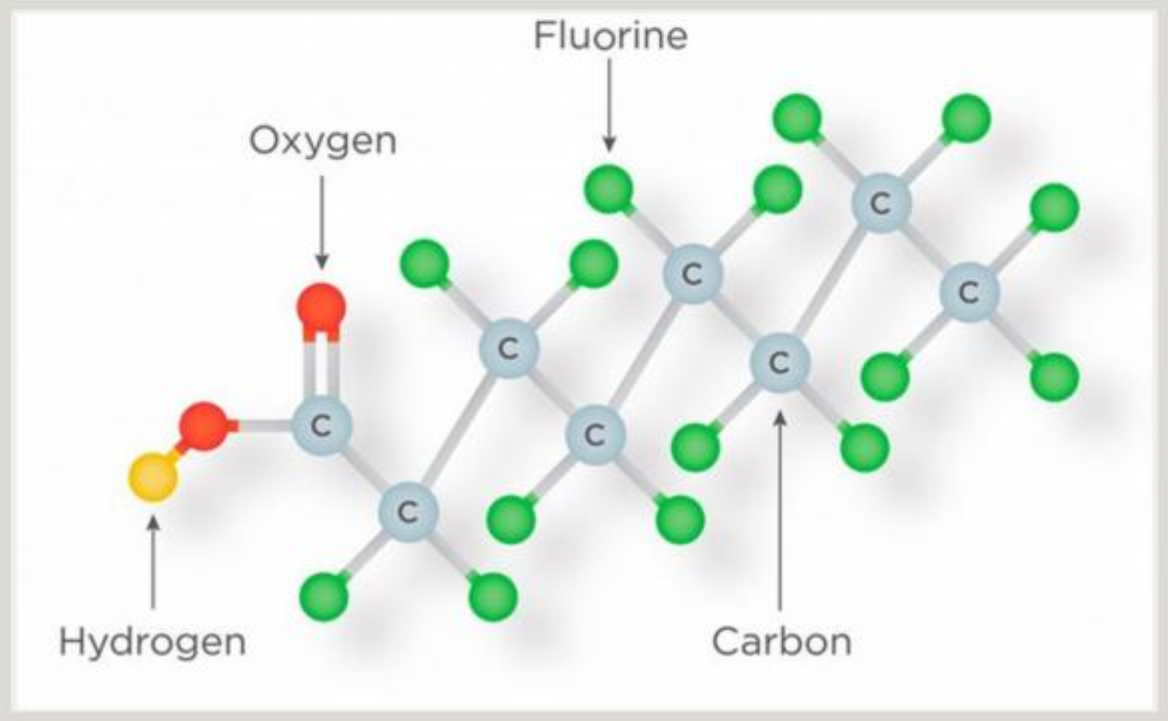

Figure 2: Informative diagram of the chemical structure of PFAS and its strong carbon-fluorine framework as the core of their high stability (After Satelytics, 2020).

The very size of this issue is emphasized in the thousands of different PFAS compounds as a result of which early regulation and scientific solutions were limited to the legendary, long-chain compounds, including Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) (EPA, 2024). Table 1 gives a summary of these major classifications.

Table1: Primary per- and polyfluoroalkyl substances Chemical classification and structure.

Molecular Group	Example Compound	Chemical Formula (Simplified)	Functional Group
Perfluoroalkyl Sulfonic Acids (PFSAs)	PFOS (C8)	$C_8F_{17}SO_3H$	Sulfonate (SO_3)
Perfluoroalkyl Carboxylic Acids (PFCAs)	PFOA (C8)	$C_7F_{15}COOH$	Carboxylate (COO)

With voluntary phase-outs of these legacy chemicals by large manufacturers the environmental situation was greatly more complicated. This move necessitated the use of newer and shorter chain alternatives, also known as GenX or short-chain PFAS (NIEHS, 2024). These substitution compounds, such as Perfluorobutane Sulfonate (PFBS) are typically more intrinsically mobile, and a difficult, dynamically challenging risk profile to groundwater monitors and remediation practitioners (ITRC, 2024).

The most significant source types affect aquifer systems, and most of these sources usually emit a large amount of contaminant mass (EPA, 2024):

1. **Aqueous Film-Forming Foams (AFFF):** AFFF, which is used regularly in the suppression of fires on military bases, at commercial airports and in industrial schools, presents the greatest point source of

concentrated PFAS contamination. The discharge events cause the source zones to go high-concentration in the subsurface, resulting in the development of far-reaching and continuous and large groundwater plumes (EPA, 2024). The immediacy of control over this source has prompted regulative activity, and states such as Washington State have required ban on the use of AFFF and have instated disposal programs on stocked materials (Washington State Department of ecology, 2023).

2. **Waste Management Sites:** Contemporary landfills and other waste disposal sites, such as the named Superfund and Resource Conservation and Recovery Act (RCRA) sites, are chronic, diffuse-based (Tolaymat et al., 202; EPA, 2024). The extensive distribution of PFAS across almost all landfill leachates confirms these locations are a high, long-term direction through which repeated leaching and erosions will be directed to the surrounding or adjacent soil and groundwater systems (Tolaymat et al., 202).
3. **Industrial Discharges:** It is released in the environment by wastewater discharges of definite manufacturing industries, such as chrome plating, electronics, and specialized textile production (EPA, 2023; EPA, 2024). In the chrome plating sector, as a case in point, decades were spent on the utilization of PFAS containing fume suppressants. The mitigation involves a total change of both protocols and equipment, including switching to such a substitution as trivalent chromium, to stop the source vegetable (EPA, 2023).

1.2 Public Health and Ecological Risk Rationale for Groundwater Focus

The concerns behind the aggressive treatment of PFAS in groundwater lie in the fact that the effects of negative health outcomes are manifested, with the half-lives of the compounds being extremely long in humans (NASEM, 2022). Biological persistence widely depends on the chemical structure. In the case of the long-chain Perfluoroalkyl Acids (PFAAs) that include PFOA and PFOS that are being studied, the estimates of the biological half-life vary between 2.7 years and an impressive 8 years, depending on the research (Li et al., 2018; NASEM, 2022). It serves as an extended biological retention most likely because of the effective reabsorption processes in the renal forum and enterohepatic recirculation cycle (EFSA, 2020; NASEM, 2022). On the other hand, shorter-chain, such as PFBA, are washed away much faster, so in general, within several days or a few months (EFSA, 2020; ITRC, 2024).

The result of this physiological permanence is severe: although the pathways of external exposure can be stopped within a short period, the existing body burden of the long-chain compounds will take years to completely discharge (NASEM, 2022). This explains why primary prevention is of critical critical vitality in terms of environmental cleanup and immediate phase-outs of the sources. The environmental analogy of what has been found to be a biological hurdle is the hydrogeological tenacity of PFAS in aquifers that can take decades to manifest itself, and therefore, the most serious entry point to ensure that the population remains safe is at the ground level. The mobility and non-degraduate nature of the compounds makes plumes infamously hard to contain and can readily threaten sensitive downgradient drinking water supplies (Wang et al., 2025).

1.3 Identification of the Research Gap and Review Focus

Even though PFAS has been in the environment decades and the broad range of toxicological and remediation literature has been established in recent decades, it remains a knowledge gap whether to model predictively through hydrogeology and implement sustainable, scaleable destruction technologies.

The two interacting failures in the existing scientific and engineering paradigm can be declared as the primary

Research Gap:

1. **Failure of Predictive Modeling:** Statistically integrated technological models of conventional groundwater transport are unable to predict the mass discharge and stability of intricate PFAS plumes over time. This failure is due to the lack of a sufficient quantitative incorporation of unconventional, non-linear retention processes, namely, competitive, chain-length-dependent matrix diffusion into low cells of permeability and air-water interface (AWI) separation into the unsaturated zone, which are what are involved in the massive majority of mass storage and then sequential, long-standing back-diffusion (Silva et al., 2019; ITRC, 2024).
2. **Absence of Sustainable Destruction:** There is an acute deficit of tested, scalable and economically feasible destructive technology that could mineralize PFAS in dilute groups of ground water streams (low 0.000:000 mcg/L to ng/L concentrations) without also forming acutely toxic, managed and costly second outputs (e.g. chlorate, hydrogen fluoride). This technological obstacle implies that modern-day destruction is more of a conversion of one environmental liability to the other (Meegoda et al., 2022).

The current critical review directly fills this gap by conducting a stringent synthesis of the newest data on hydrogeological fate and a needed performance and byproduct risk evaluation of the most popular remediation technologies. The framework that results thus offers a well-founded, scientific rationale of implementing a mandatory source control and combined hybrid treatment systems as the only possible long-term management instrument.

2. Hydrogeological Fate and Transport Mechanisms in Aquifer Systems

In order to be able to model and control PFAS plumes, the practitioners have to take a leaping step beyond classical contaminant transport models. The persistence nature of these plumes is a purely hydrogeological issue that is pushed by the special physico-chemical characteristics of the compounds that allow their complex retention processes (Newell et al., 2020). These processes make mass storage significantly more efficient, in agreement with the previous yet still disputed wisdom which deals with pump-and-treat remediation (ITRC, 2024).

2.1 Unique Chemical Properties Governing Subsurface Mobility

The prevailing aspect of the PFAS molecule affecting its behavior in the subsurface is the fact that it is an amphiphilic fusion of a hydrophobic fluorocarbon chain and a hydrophilic functional head group (Silva et al., 2019). This framework gives PFAS an excellent and complicated affinity to a variety of solid-fluid and fluid-fluid interfaces, differentiating their adsorbing profiles to conventional, solely hydrophobic organic pollutants (Brusseau et al., 2019). The orientation of these molecules (the one that causes them to behave the way they do) is shown in Figure 3.

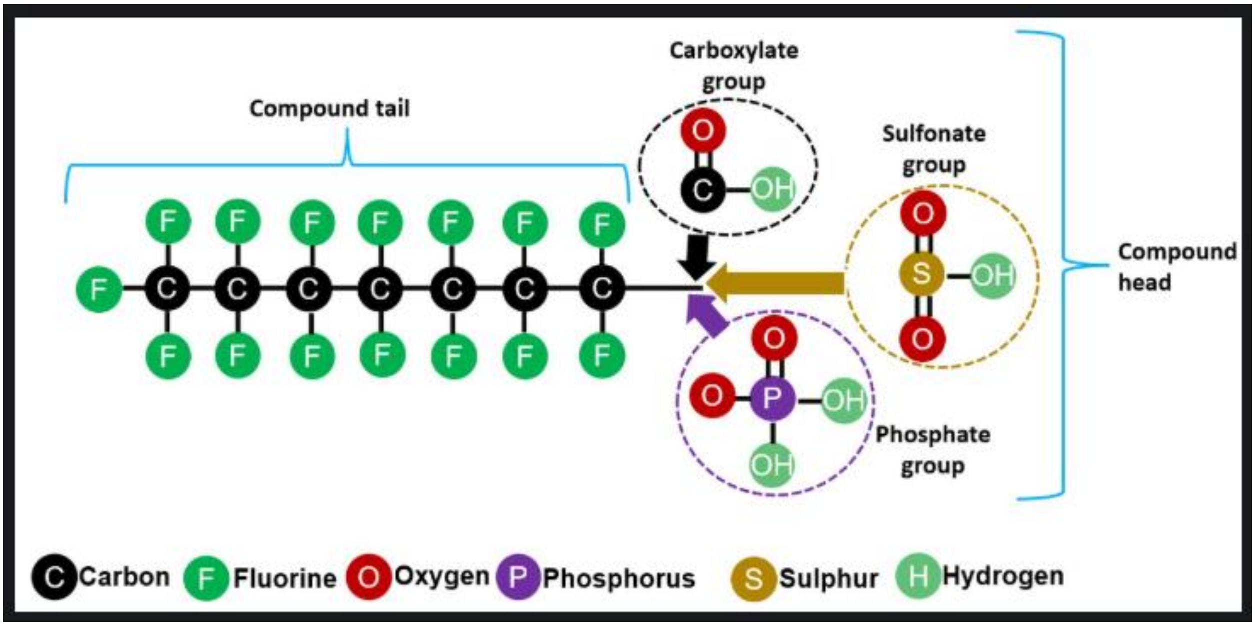

Figure 3: The conceptual figure of the amphiphilic PFAS molecule framework, that is, the fluorinated tail and the hydrophilic head group (After Penn State Extension, 2024).

It is important to mention that mobility and retention properties highly depend on the length of the carbon chain:

- **Long-Chain PFAAs (e.g., PFOS, PFOA):** Carbon-based compounds that have longer chains make them more hydrophobic and thus they tend to adsorb on soil organic carbon via conventional solid-phase adsorption. This increased retention retards their movement in the underground. (Deng et al., 2023; Brusseau et al., 2019)
- **Short-Chain PFAAs (e.g., PFBA, PFBS):** The decrease in carbon length leads to reduced hydrophobicity with the consequence that the solid phase adsorption will be weak, and its mobility will increase. These chemicals form the lead and the plume of the contaminants in both underground and groundwater as they move over long distances faster, and they are the first chemicals to reach downgradient receptors. (Li et al., 2023)

2.2 Advanced Retention and Retardation Processes in Heterogeneous Media

The correct hydrogeological characterization also involves the quantification of retention mechanisms that go beyond the notion of simple solidphase partitioning (Kd), which usually significantly underestimates real retardation, in particular with the short-chain compounds (Brusseau et al., 2019). Heterogeneity instills in the subsurface of the major interfacial processes, which are now understood to be principles in mass storage (ITRC, 2024).

2.2.1 Interfacial Adsorption in the Vadose Zone

The unsaturated (vadose) zone is one of the primary water mass reservoirs, in particular at those locations where there are surface sources, like the AFFF spillage (Silva et al., 2019). Fluid-fluid interfacial adsorption is one of the main mechanisms that delays the behavior of PFAS in this zone and retains it (Silva et al., 2019).

This is a complicated transport that includes various compartments in the environment, as illustrated by Figure 4.

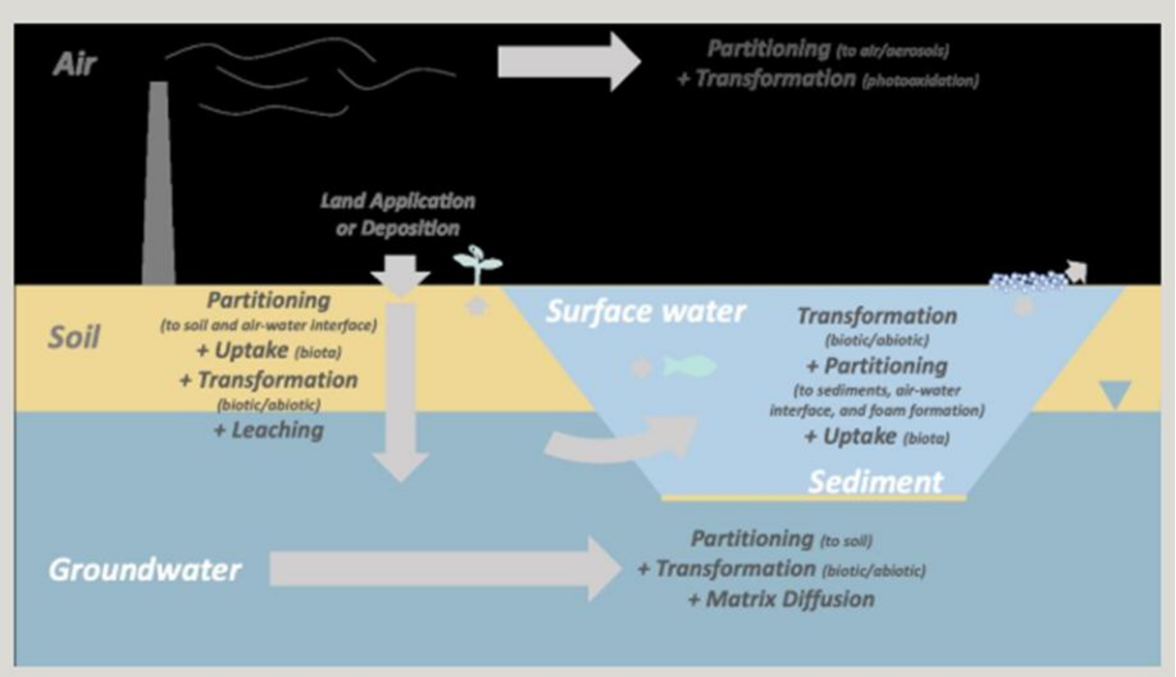

Figure 4: PFAS transportation describing matrices diffusion into areas of reduced permeability and parting in the vadose zone (After Clegg, 2013).

- **Air-Water Interface (AWI) Partitioning:** The amphiphilic properties of PFAS molecules cause them to cluster together at the interface between air and water in unsaturated porous medium (Silva et al., 2019; Brusasso et al., 2019). The hydrophobic fluorocarbon tail is separated by the bulk water, whereas the hydrophilic head remains in the aqueous phase (Silva et al., 2019). It is indicated that AWI partitioning makes about 50 to 75 percent of the total retents of PFAS among the variant field-relevant levels of water-saturation conditions (Silva et al., 2019). This huge bulk that is accumulated in the vadose zone forms a sustained secondary source and pours into the saturated zone, particularly when the water table varies. Thus, the predictive models need to include quantitative characterizations of interfacial area and surface-tension effects (Silva et al., 2019).
- **Non-Aqueous Phase Liquid (NAPL) Interaction:** The NAPLs of hydrocarbons may remain at the concentrated source areas, particularly in those where AFFF has been used (Brusseau et al., 2019). These residual NAPLs provide an additional route of retention by adsorbing at the interface of NAPL and water. Field and column experiments demonstrate that NAPL presence contributes greatly to the retardation of PFOS movement, and this interfacial adsorption has a significant bearing on the total group of storage of contaminants in the source zone (Brusseau et al., 2019).

2.2.2 Adsorption to Solids and Electrostatic Effects

PFAS can be sorbed as well as by hydrophobic interactions, longer chains, in particular, and also by sorbing on negatively charged mediums, e.g. the mineral surfaces having organic coatings. It is contrary to the mere assumption that sorption should have been inhibited by electrostatic repulsion (Brusseau, 2018). At normal groundwater pH, terminal PFAAs are anions and they should not tend to sorb onto negatively charged solids.

However, repulsion may also be minimized by mechanisms such as charge assisted hydrogen bonding, exchange of anions with metal oxides, and the occurrence of cationic co-contaminants to achieve retention (Brusseau, 2018).

PFAS is highly intrinsically mobile, which leads to low retardation factors in porous media. Indicatively, Brusseau et al. (2019) set the retardation factor of PFOS transport to have a 3.6 in saturated soil. Such high mobility combined with almost zero attenuation rate makes long, lingering plumes (Newell et al., 2020). In spite of the rapid movement of terminal PFAAs, zwitterionic or cationic polyfluorinated precursors tend to diffuse further into low-permeable areas. This is encouraged by positive electronegative interactions and the increased content of organic carbon that occur in such layer (ITRC, 2024).

2.3 The Critical Challenge of Plume Persistence: Matrix Diffusion and Back-Diffusion

The longest plume that the groundwater can have is the most notable hydrogeological characteristic of PFAS. It is due to the fact that the chemicals are not affected in the least by the tendency to break down, which increases the level of matrix diffusion and the resultant back-diffusion tenfold (ITRC, 2024). The conceptualization of figure 5 illustrates the process of diffusion that finds the low permeability areas.

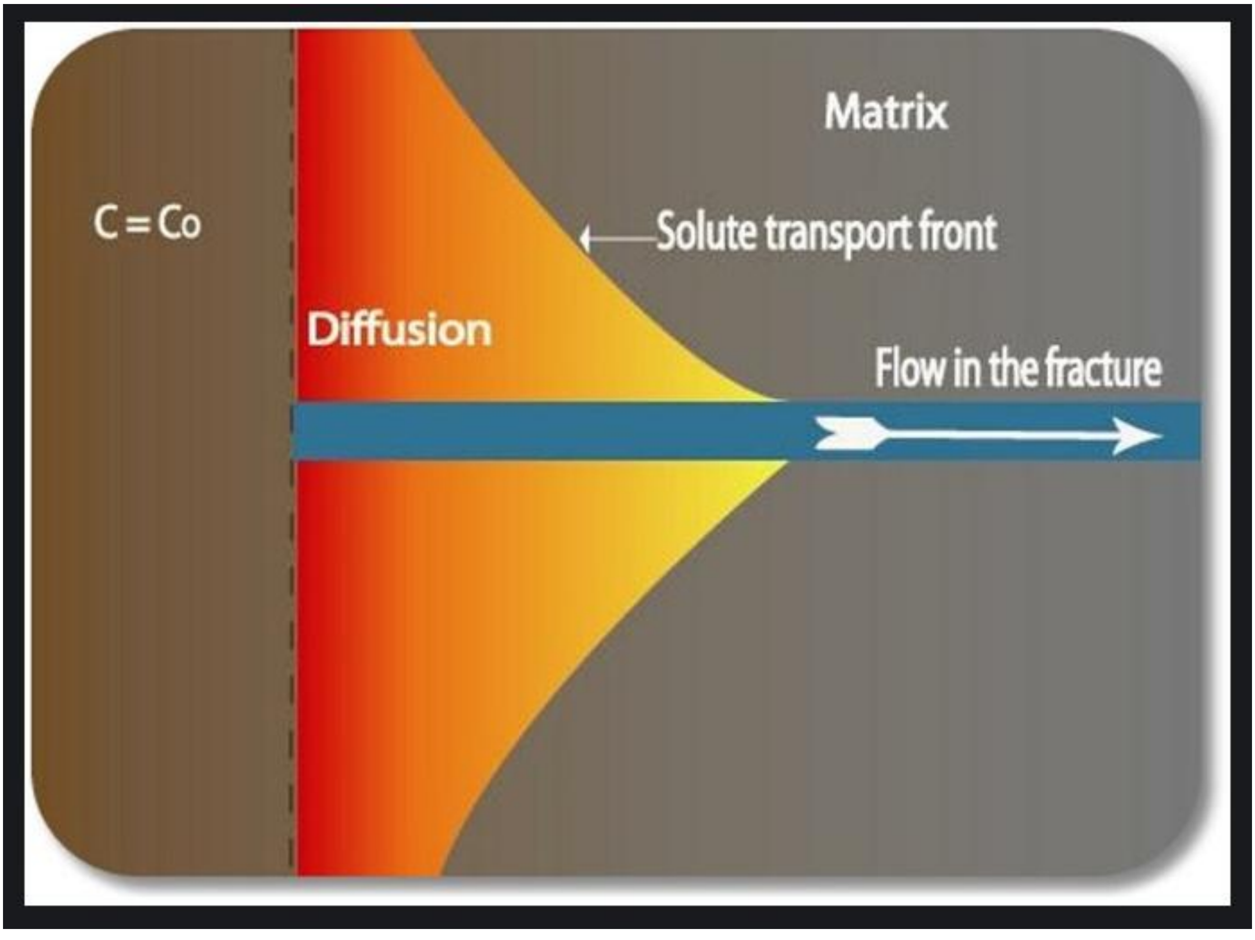

Figure 5: Conceptual diagram illustrating the process of matrix diffusion in heterogeneous subsurface environments (After Department: Water and Sanitation, 2011).

Matrix Diffusion and Mass Storage

Matrix diffusion is the rate-limited movement of dissolved contaminant mass from the high-permeability, flowing zones of an aquifer into the micro-pore spaces of adjacent, lower-permeability materials, such as clay lenses or aquitards (ITRC, 2024). The process is very efficient on PFAS since: 1) compounds are relatively small and therefore, they diffuse across the molecular level; and 2) fine-grained, low-permeability materials typically have more portions of organic carbon, which enhances the partitioning coefficient (Kd) of most PFAS (ITRC, 2024).

The importance of this mechanism can hardly be overestimated. On-site research at AFFF- presence location has revealed the extent of the storage, as it was determined that an approximation of 82% of the overall total mass of PFAS was holding in the lower-permeability soil and sediment matrices (ITRC, 2024). This gigantic, buried bulk determines the final time required to clean up.

Back-Diffusion and Plume Rebound: The Non-Degradable DNAPL

This understanding of the notion of back-diffusion implies that once the primary source control has been successful or a pump-and-treat system has been switched off, the intensive load of the high-level of PFAS mass located in the inactive pores will subsequently start to actively pass through the flowing groundwater (ITRC, 2024).

In Figure 6, the data are presented that shows this phenomenon. The first one is the forward diffusion of contaminants into the aquitard followed by the back-diffusion of contaminants into the aquitard, thus making the plume live longer.

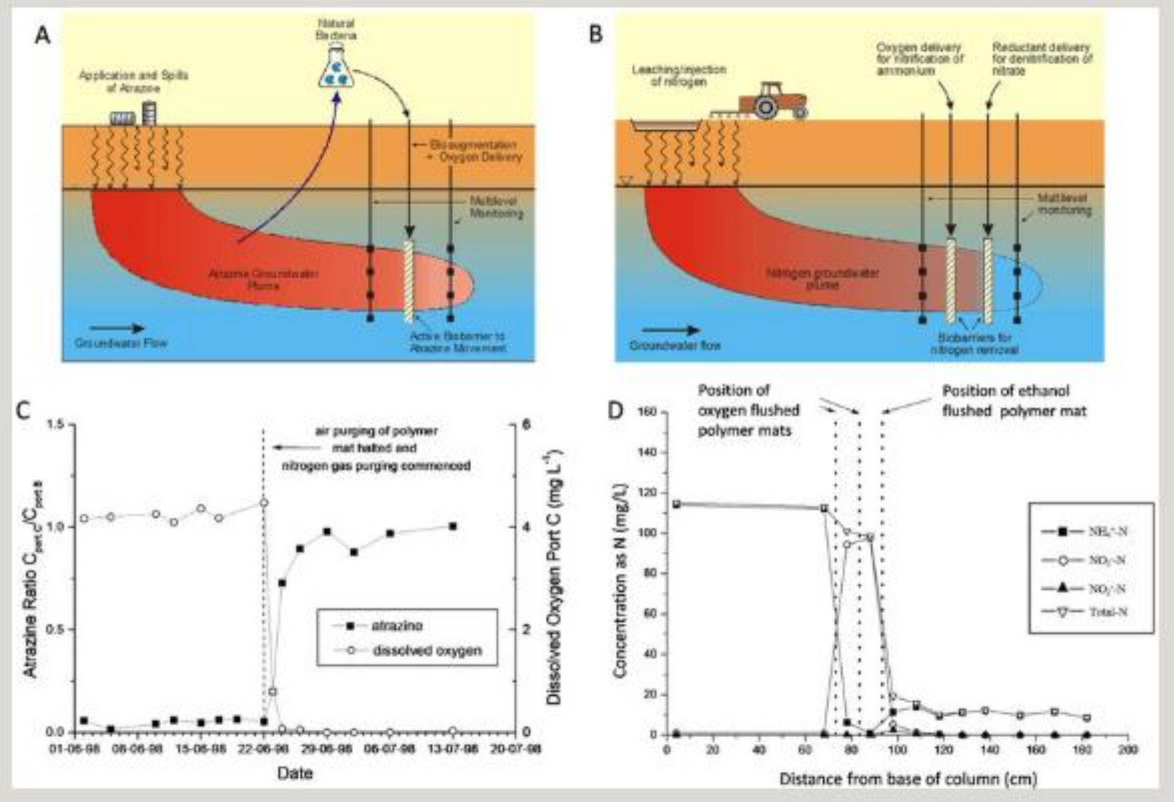

Figure 6: A conceptual diagram and a data show how the contaminants diffuse to an aquitard during forward diffusion and subsequently, back to the aquifer hence extending the plume (Patterson et al., 2002a & b).

Since the terminal PFAS compounds are not biodegraded under any natural conditions, this back-diffusion circulation is significantly more chronic and widespread than the properties of traditional biodegradable contaminants, including chlorinated solvents (Newell et al., 2020; ITRC, 2024). Consequently, dissolved-phase concentrations within the aquifer may revert to close to pre-remediation levels within a finite timeframe - in most cases, decades (Newell et al., 2020). This long-term process resembles the persistence issue observed in the case of Dense Non-Aqueous Phase Liquid (DNAPL) locations where an inactive source constantly releases mass (Newell et al., 2020). Hence, remediation plan needs to be directed less on the temporary concentration abatement but on the long-term consistent reduction in the mass discharge rates to control a total contaminant variability exiting the source location (Newell et al., 2020).

Stable predictive hydrogeology models should also have non-linear and decreasing diffusion coefficients with an increase of PFAS molar volume, to as precisely model this chronic mass release (ITRC, 2024).

3. State-of-the-Art Groundwater Remediation Technologies

PFAS plumes cannot be properly managed unless a multi-dimensional technological method is applied. The combination of technologies requires a strategic approach: to capture the mobile mass and concentrate it (sequestration) first and permanently eliminate it (destruction) second (Meegoda et al., 2022).

3.1 Physical Mass Transfer (Sequestration) Techniques

These interim technologies are effective to capture and sequester PFAS mass, though it does not break the C-F bond. Consequently, they generate a concentrated end waste stream, spent media or brine, which provides residual long-term environmental risk and corresponds to the further management (Meegoda et al., 2022).

- **Granular Activated Carbon (GAC) Adsorption:** GAC is an established technology, which mainly eliminates impurities using a hydrophobic contact (Li et al., 2023). It is an excellent solver of the remnants, the long-chain PFAS like PFOS. Nevertheless, GAC does not withstand the replacement chemicals that are short chains in PFAS. The HPLC medium–scaled adsorption capacities (Q8) in comparison with long-chain PFAS are notably smaller because such compounds as PFBA and PFBS are less hydrophobic (Li et al., 2023). This capacity difference results in too early breakthrough of short have chains of PFAS, preceding prior to full saturation of the media, necessitating expensive and frequent media replacement cycles (Li et al., 2023; Concawe, 2020).
- **Ion Exchange Resins (IXR):** IXR systems tend to be more efficient than GAC in the treatment of PFAS, due to their relying on the intensive interaction on the basis of strong electrostatics specific anion exchange (Deng et al., 2023). Figure 7 shows the conventional industrial arrangement of an IXR system.

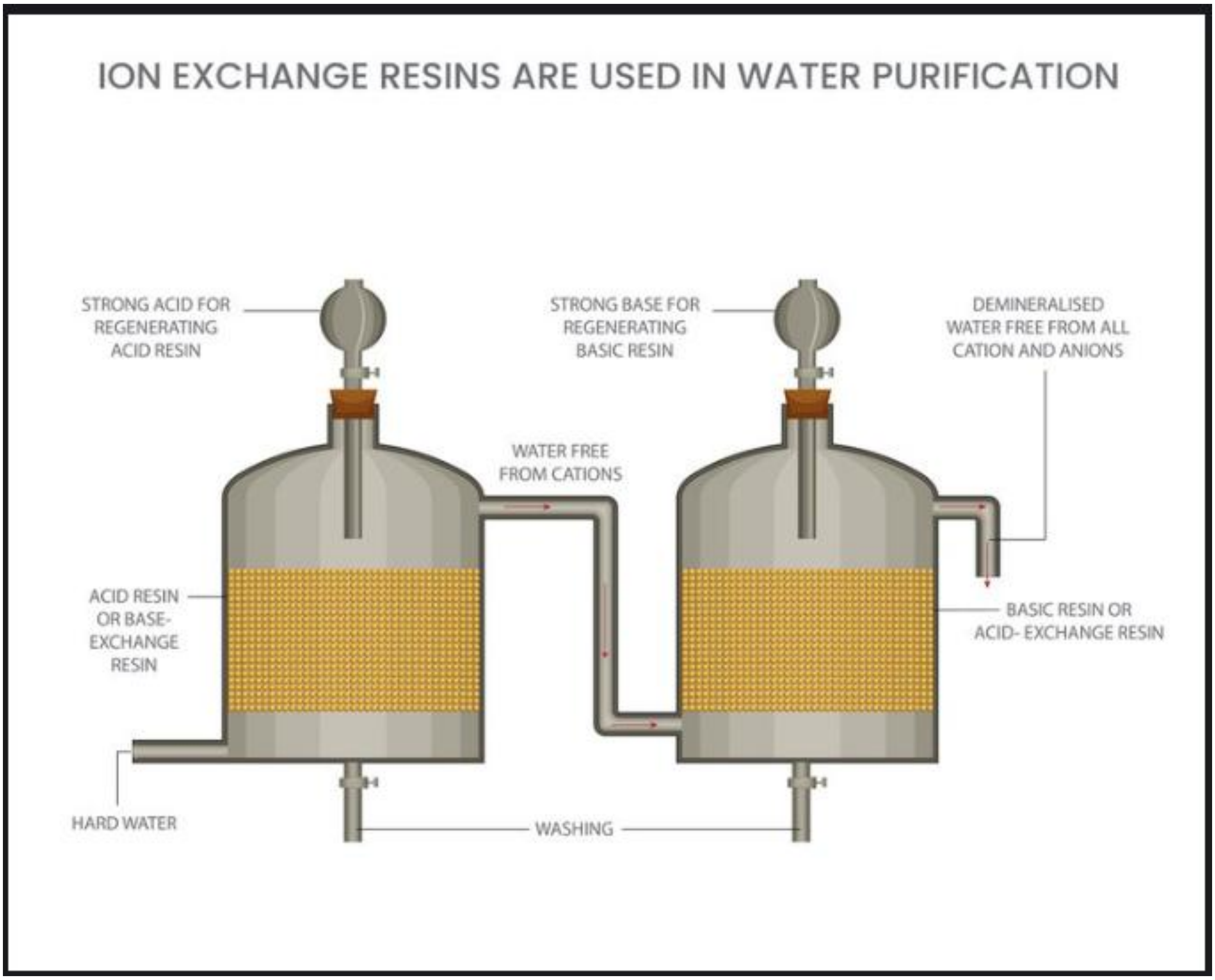

Figure 7: How ion-exchange resin beads look and how to set these beads and the vessel as part of the water treatment (After Sarkar, 2024).

The very functional beads of resin are stable concerning the different lengths and various functional groups of chains the beads are very efficient with the intricate mixes in the field (Li et al., 2023). As an example, when working with a cationic nanocellulose adsorbent, the greatest adsorption capacity (Qm) profile was: PFOS (559 -1g) > PFOA (405 -1g) > PFBS (319 -1g) > PFBA (121 -1g). This indicates a good performance of both long- and short-chain species which is facilitated by the interactions between ions, which is a strength compared to pure hydrophobic GAC (Li et al., 2023).

  - **The Competitive Desorption Challenge:** Although IXR systems have a high capacity, these systems are susceptible to competitive desorption. Research indicates that long-chain strongly adsorbing PFAS have the capacity to push out and bump-off other weakly adsorbed short-chain PFAS (Li et al., 2023; Concawe, 2020). Figure 8 demonstrates this difference in the breakthrough behavior.

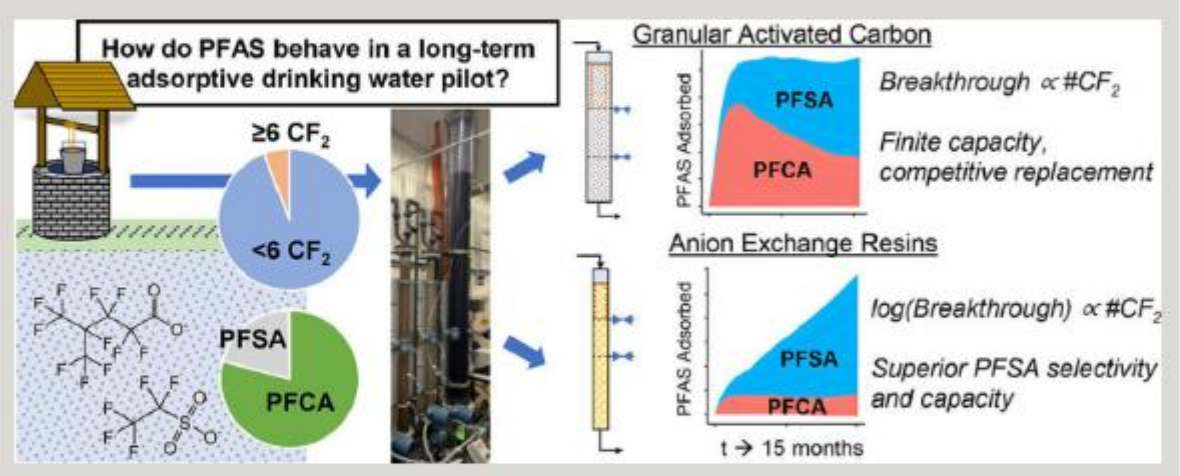

Figure 8: Graphical depiction and diagram of filtration processes (GAC vs. IXR), with enhanced breakthrough rates of short-chain (PFBA) as compared to long-chain (PFCA) compounds (Graphical Abstract After Chow et al., 2022).

Such interactions of complex field mixes demand advanced staging and monitoring to ensure the more mobile compounds break through unexpectedly and unauthorised (Concawe, 2020).

- **Membrane Filtration (Nanofiltration and Reverse Osmosis):** Physical separation of PFAS can be done through nanofiltration (NF) and reverse osmosis (RO). The rejection of PFAS molecules occurs regarding their size and charge (Concawe, 2020). These processes are however subject to intensive pre-treatment to avoid fouling. More importantly, they generate a highly concentrated waste flow, or brine (Concawe, 2020). The control of this brine is a complicated, expensive and ecologically dangerous procedure. Discovery is usually followed by the destruction of high costs or a much lower but still highly concentrated amount of waste (Concawe, 2020).

Table 2 provides a comparative study of adsorption capacities of GAC versus IXR.

Table 2: Comparative Adsorption Capacity (*Qm*) of GAC vs. IXR for Select Long- and Short-Chain PFAS

PFAS Compound	**Chain Length**	**GAC Max Capacity (Q_m) (mg g⁻¹)**	**IXR Max Capacity (Q_m) (mg g⁻¹)**	**Efficacy Profile**	**Primary Mechanism**
PFOS	Long (C8 Sulfonate)	High (e.g., 400–600)	Very High (559)	Excellent for both. IXR is slightly superior.	Hydrophobic (GAC) / Electrostatic (IXR)
PFOA	Long (C8 Carboxylate)	High (e.g., 300–500)	High (405)	Excellent for both.	Hydrophobic (GAC) / Electrostatic (IXR)
PFBS	Short (C4 Sulfonate)	Low (Early Breakthrough)	Moderate-High (319)	IXR vastly superior to GAC.	Hydrophobic (GAC) / Electrostatic (IXR)
PFBA	Short (C4 Carboxylate)	Very Low (Rapid Breakthrough)	Low (121)	Only IXR offers viable capacity; highly mobile.	Hydrophobic (GAC) / Electrostatic (IXR)

3.2 Destructive Technologies for Permanent Elimination

Destructive technologies have the objective of breaking the CF bond conclusively. The best candidates to this effect are Supercritical Water Oxidation (SCWO) and Electrochemical Oxidation (EO). Figure 9 gives an example of the elaborate infrastructure needed in these advanced treatment trains.

Figure 9: Drawing of different PFAS treatment and destruction technologies, which are a sign of sophistication of advanced destruction skids (After Maratek, 2024).

- **Supercritical Water Oxidation (SCWO):** SCWO is a sophisticated thermal treatment technology, involving the use of water that is pressurized and heated above its critical temperature so as to allow full oxidation-or mineralization- of organic pollutants (Meegoda et al., 2022). The technology has demonstrated itself to be effective in the industry, particularly when it comes to verified elimination of high concentrations of waste streams, like spent AFFF and contaminated media (Revive Environmental, 2024). Another advantage of SCWO has to do with environmental protection since it avoids the generation of typical combustion by-products such as NOx and SOx (Meegoda et al., 2022). Its economic feasibility is, however, constrained by the high cost of heating and pressurising large volumes of liquid and, therefore, is not feasible in the treatment of dilute ground water with a volume bigger than about 50,000 gallons per day (Meegoda et al., 2022). Furthermore, the inevitable generation of highly corrosive acidic species (H_2SO_4, HCl, HF) necessitates specialized, expensive, and corrosion-resistant reactor materials, escalating capital and maintenance costs significantly (Meegoda et al., 2022).

- **Electrochemical Oxidation (EO):** EO systems mineralize PFAAs by generating powerful, highly reactive radical species (e.g., hydroxyl, $SO_4^{\cdot -}$) through the electrolysis of water and salts at the surface of specialized electrodes, often expensive Boron-Doped Diamond (BDD) (Meegoda et al., 2022). EO is highly effective, achieving >99% removal for both long- and short-chain PFAAs within a few hours (Meegoda et al., 2022). Scaling EO for full-scale, dilute groundwater remediation is currently hampered by the high initial capital investment for the BDD electrodes (e.g., USD$7125/m2) and significant energy consumption (Meegoda et al., 2022).
    - **The Critical Synergy:** A breakthrough finding demonstrates that coupling EO with the concentrated brine or eluent from an Ion Exchange Resin (IXR) system significantly improves the economics (Meegoda et al., 2022). The IXR effluent is naturally rich in dissolved salts, providing the high ionic strength (conductivity) necessary for efficient EO operation, thereby eliminating the need for expensive chemical dosing to enhance the efficiency of the electrochemical process (Meegoda et al., 2022).

The Unacceptable Risk of Secondary Byproducts

A critical, often overlooked, and potentially catastrophic risk in the deployment of EO is the documented formation of highly regulated and acutely toxic secondary byproducts. The EO process can produce highly corrosive hydrogen fluoride (HF) vapor and various oxidation byproducts derived from the salts present in the water, most notably **perchlorate** and **chlorate** (Meegoda et al., 2022).

In a single overall review, post treatment chlorate levels were reported to vary over an absurdly wide range between 6mM and 720mM(Meegoda et al., 2022). In its perspective, they are as much as 3.4 million times higher than the 210microg/L Health Reference Level of the US EPA in drinking water (Meegoda et al., 2022). The that mind-blowing discovery indicates that, practically, the destruction process is frequently followed by the simple transformation of one controlled toxic chemical into another (PFAS, a thyroid disturber). This requires multi-phase, multi-phase byproducts management system only, which has a drastic effect on total cost, complexity, and predisposed risk to human health of the remediation process (Meegoda et al., 2022).

3.3 Strategy: The Inescapable Necessity of Hybrid Treatment Trains

The natural constraints of the above sequestration (liability of waste) and destruction (risk of cost and byproduct in dilute streams) are resoundingly decisive in concluding that the sole responsible and effective management strategy of the long term would be the implementation of hybrid trains of treatments. Table 3 provides a summary of the trade-offs, which require this hybrid approach.

The Mandated Hybrid Model: In the upstream direction, diffuse PFAS mass must be effectively concentrated and gathered by high-throughput technologies, such as Ion Exchange Resins (IXR) or membrane filtration of the enormous quantity of the dilute groundwater. The resulting concentrated secondary waste stream (spent resin or brine) is thereafter channeled as the feedstock of energy intensive destruction technologies. This concentration-based, Concentrate-and-Destroy (IXR →EO or SCWO) method that regulates the complicated competitive adsorption kinetics of a mixed plume can promise the long-term environmental responsibility of sequestered waste at the same time (Meegoda et al., 2022). The IXR waste stream has a high ionic strength, which offers the optimal, low-resistance input to operate an EO with the required efficiency creating an essential, cost-effective synergy.

Table 2: Comparative Performance, Costs, and Critical Byproduct Risks of Key PFAS Remediation Technologies

Technology	Primary Mechanism	Short-Chain Efficacy	Scalability Challenge	Energy/Cost Factor	Critical Byproduct Risk
GAC	Hydrophobic Adsorption	Low (Rapid Breakthrough)	High throughput for large volumes; generates waste.	Moderate operational cost (media replacement).	**Spent Media Disposal Liability.**
IXR	Anion Exchange/Electrostatic	High (Superior to GAC)	High throughput; generates concentrated waste.	Moderate operational cost (regeneration/dispo.	**Spent Resin Destruction Liability.**
SCWO	Thermal Oxidation (Mineralization)	High (Comple)	Costly for large, dilute volumes (~50,000GPD) due to heating demands.	**Very High** (Heating/Pressurization).	**Corrosive Acids** (H_2SO_4, HF, HCl) that require specialized reactors.
EO	Electrochemical Oxidation (Mineralization)	High (Comple)	High upfront capital cost for electrodes. Energy cost is reduced significantly by IXR coupling.	**Very High** (Can be mitigated by IXR coupling).	**High Concentration Chlorate** (6–7206–720mM) and HF vapor, necessitating intensive post-treatment.

4. Global Regulatory Landscape and Strategic Management Frameworks

More importantly, the world reaction to PFAS contamination is characterized by a high level of divergence in the regulation, which is indicative of radically dissimilar views on toxicology, risk assessment, and practicality of implementation (SGS, 2024). These models are supported with conflicting scientific suppositions on the accumulation risk of PFAS mixtures.

4.1 Disparity in International Drinking Water Standards and Toxicological Rationale

The mechanisms of how the drinking water standards of PFAS are established by the major global jurisdictions vary in a dramatic way, and the differences are directly bonded to the toxicological approaches applied in developing the Maximum Contaminant Levels (MCLs) (EPA, 2024; EFSA, 2024).

US EPA Proposed Limits and Dose Additivity

The Environmental Protection Agency (EPA) has also suggested very strict and enforceable MCLs of either single PFOA and PFOS of 4 parts per trillion (ppt) in the United States (EPA, 2024; SGS, 2024). The regulation also introduces a Hazard Index process of a mixture of four other PFAS substances (PFNA, PFHxS, PFBS and GenX), the determination of cumulative risk of a co-exposure (EPA, 2024).

The scientific tenet that enables one to reach these minimal limits that are as low as possible is the conservative assumption of combining doses on mixtures of PFAS (EPA, 2024). The standpoint of EPA is that several PFAS compounds exhibiting similar adverse actions were observed to occur in major biological pathways (e.g., immune system reaction, lipid metabolism) but where particular evidence shows distinct effects, then those analogs are assumed to act jointly and mutually (EPA, 2024). It means that being exposed to a mixture, in spite of the fact that each separate compound is located lower than its theoretical normal, still could child a societal substantial level of aggregate health danger (EPA, 2024). It is an extreme line of defense supported by more than twenty organizations including the National Academies of Sciences, Engineering, and Medicine (NASEM), which inevitably shifts regulatory thresholds down to the analytical bottom (NASEM, 2022; EPA, 2024).

EU DWD Standards and the Critical Endpoint Approach

The Drinking Water Directive (DWD) of the European Union, in turn, follows a numerically higher and more general standard 0.1 micrograms per liter (100ppt) of the aggregate of 20 selected PFAS (∑PFAS20) (SGS, 2024).

PFOA, PFOS, PFNA, PFHxS: The four most toxic common PFAS determine an amount of scientific basis of the EU standard which is called a group Tolerable Weekly Intake (TWI). The TWI in this assessment is based on a one, specific critical endpoint, i.e. the response of an immune system to vaccination, as the most sensitive and most relevant health impact (EFSA, 2024). The EU system has standard techniques of assessment of combined exposure and determines one level of group intake which is a level of protection considered valid at the population level (EFSA, 2024). The 100ppt level of ∑PFAS20, is a practical, achievable, technologically valid criterion of large water treatment plants (SGS, 2024).

Regulatory Controversy and Policy Implications

The imposition of the strict limits by the US EPA has sparked a big debate that entails both scientific as well as economic factors. The EPA has been criticized as overestimating human health risk by its toxicology review, especially when it uses animal data and theorells of uncertainty because it is difficult to establish any clear adverse effects at blood levels in occupationally exposed populations that are many times greater than the ambient levels. Certain analyses have argued that the ultra-low limit quest could be the most expensive environmental regulation to have ever existed and therefore that the regulatory choice has been based not on technological viability and economic reality but on maximum theoretical protection.

This underlying policy split is therefore more of a philosophical decision: the US system has much to do with the highest possible theoretical defense against cumulative, additive influences, leading to very difficult and costly treatment objectives. The EU system is much more pragmatic, with its standard being a well-defined critical toxicological endpoint in order to be able to create a broad, manageable and immediately reproducible standard in a greater list of compounds (SGS, 2024).

4.2 Source Control and Pollution Prevention

With the unrefuted and irreversible nature of PFAS both in biological and hydro geological systems, the sole long term management approach that is sustainable and cost effective is a complete eradication of primary sources (NASEM, 2022). The concept of source control is not just a suggestion but it is an inevitable requirement.

- **Industrial Discharge Controls:** In the case of historical industrial sources, e.g. chrome plating works using PFOS as fume suppressants, regulatory policy is converting to more demanding pollution preventive practice and Best Management Practices (BMPs) (EPA, 2023). This involves requiring use of safer alternatives such as trivalent chromium which eliminates the need of suppressants or this can be strict limit of permits that would require end-of-pipe treatment (advanced end-of-pipe treatment, GAC, IXR, or RO) before discharge (EPA, 2023). This shifts the expensive and complicated cost of treatment to the generating point, the point at which the contaminant stream is the most concentrated.
- **AFFF Management:** The systematic decommissioning of AFFF will be essential in eliminating the single source of pollution on the groundwater of the most concentrated type (Washington State Department of Ecology, 2023). Globally, there is currently a requirement to collect and dispose of

stockpiled AFFF in a safe manner and include this as hazardous waste and dispose of it at an approved facility (safe level incineration or, more frequently, non-combustion thermal destruction) (Washington State Department of Ecology, 2023; Revive Environmental, 2024).

4.3 PFAS Waste Management Protocols

The very volume and ongoing presence of the PFAS-contaminated wastes is a significant challenge to infrastructure. In particular, landfills are known to be long-lasting sources, and PFAS was found in all leachates (Tolaymat et al., 202). Solid high concentrations of waste, including spent IXR media and concentrated RO brine, have to be handled in special places in authorized "hazardous waste sites (Washington State Department of Ecology, 2023). This concentrated waste should also be destroyed by following strict standards, either by high-temperature incineration or new, provable destruction methods (Meegoda et al., 2022). An effective regulatory system should put a full cradle-to-grave ban on all PFAS-containing products to avoid the establishment of a new set of environmental liabilities.

5. Conclusions and Future Research Directions

5.1 Synthesis of Hydrogeological Challenges and Remediation Limitations

The inert chemistry of the compounds which have been described by their ability to characterize the widespread contamination of vital aquifer systems is characterized by unparalleled persistence. The presence of PFAS in the amphiphilic structure ensures sustainability of the plumes since the landmark technology for efficient, massive storage in the ground: up to 82% of the total mass is stored in the low-permeability matrices (see Figure 5), and 50-75% of it is stored in the vadose zone through AWI adsorption (Silva et al., 2019; ITRC, 2024) (see Figure 4). The nature of this mass sequestration is the main cause of chronic decades-long true-back-diffusion-based plumebounce, eventually making it difficult to realize the traditional cleanup models (Newell et al., 2020).

The existing technological remediation toolkit is challenging and faulty. Physical sequestration (GAC) is not able to effectively trap highly mobile short-chain replacement chemicals, so better yet more complex Ion Exchange Resins have to be used (Li et al., 2023). True destructive technologies (EO, SCWO) have an insurmountable limit in the amount of groundwater that can be treated (vast volumes) because of economical barriers (Meegoda et al., 2022). Moreover, the application of EO poses the critical, documented risk of non-target generation of highly toxic secondary byproducts, e.g. chlorate, multiplied by millions of times exceeding drinking water criteria, proving that even an act of mere destruction can inadvertently initiate new and immediate public health disasters (Meegoda et al., 2022).

5.2 Policy Recommendations for Prevention and Cross-Jurisdictional Alignment

1. **Mandatory Upstream Source Elimination:** The basic analysis on costs-benefit heavily gives preference to prevention. Policy should focus on the immediate and compulsory stage of elimination and prohibition of all non-essential uses of PFAS. This implies that use of proven non-PFAS (for example, verified alternatives) would legally be required in all industrial and firefighting critical industries (NASEM, 2022; EPA, 2023). This is the best step that can ever be taken in order to reduce the future government spending on the prolonged management of the plume.
2. **Harmonization of Risk-Based Toxicological Standards:** The regulatory authorities across the world should sit down swiftly to come up with a coherent, scientifically sound approach of identifying

the actual combined risk of PFAS mixes. Such an undertaking needs to balance the extrem*\vingly protective US dosage-additive framework with the real-life and realistic EU TWI approach, to arrive at uniform economically viable, and transparent international norms (EPA, 2024; EFSA, 2024).

3. **Integrated Waste and Byproduct Regulation:** All future permitting of all remediation and waste destruction facilities should legally require the application of integrated trains of treatment (sequestration and destruction) and should set firm and binding regulatory limits of all toxic products of destruction (e.g., chlorate, perchlorate, hydrogen fluoride). Legally, remediation should be defined as not a mass removal, but as an authenticated final C−F bond mineralization in the absence of creating an additional regulated liability (Meegoda et al., 2022).

5.3 Knowledge Gaps and Future Research Priorities

1. **Quantitative, Time-Dependent Modeling of Mass Discharge:** Future work and initiatives should be associated with developing and ensuring the correct field certification of the advancement of hydrogeological models that can precisely and quantitatively assess the influence of the impact of matrix diffusion and AWI retention on the mass third rate of PFAS discharge over a long period of time under various field conditions (ITRC, 2024). A key research component involves determining precise, site-specific diffusion and partitioning coefficients for the full spectrum of legacy and replacement PFAS compounds and their precursors (ITRC, 2024).
2. **Sustainable, Non-Thermal Destruction Technologies:** The highest priority for applied research is the development of next-generation, energy-efficient destructive technologies capable of mineralizing PFAS from dilute groundwater streams *without* the use of high heat or the generation of regulated, hazardous secondary products (Meegoda et al., 2022). Research into low-power plasma reactors, advanced photocatalytic systems, and novel bio-electrochemical processes is essential to achieve a truly sustainable end-of-pipe solution.
3. **Environmental Fate of Novel PFAS and Precursors:** Extensive, multi-media field and laboratory studies are required to characterize the environmental fate, transport mechanisms, and potential for *incomplete* biotransformation of the thousands of currently unregulated, short-chain, and precursor PFAS replacement chemicals (NIEHS, 2024). The extensive mobility and precursors (such as fluorotelomer compounds) possible to decompose into tenacious terminal PFAS requires the monitoring and regulatory systems to improve and adapt quickly, to preclude the pervasive contamination by the next section of forever chemicals (ITRC, 2024).

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