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Review

Phytotechnology for Per- and Polyfluoroalkyl Substances (PFAS) Treatment: Mechanistic Insights into Environmental Behavior, Plant Uptake, and Phytomanagement Opportunities

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are ultra-persistent contaminants characterized by exceptional chemical stability, high mobility, and widespread environmental occurrence, posing significant challenges for remediation. Phytotechnology has emerged as a promising nature-based approach, yet its effectiveness is strongly governed by PFAS physicochemical properties and plant–soil interactions. This review provides a mechanistic synthesis linking PFAS environmental behavior with phytotechnology performance by examining PFAS sources, transport pathways, and structure-dependent properties that control persistence, partitioning, and mobility, with an emphasis on differences between short- and long-chain compounds. These characteristics determine bioavailability and influence treatment outcomes. Plant uptake mechanisms, including root absorption, xylem translocation, and tissue accumulation, are discussed alongside rhizosphere processes such as sorption, microbial interactions, and hydrological dynamics that regulate PFAS retention and redistribution. Current evidence indicates that phytotechnology functions primarily as a form of phytomanagement rather than a destructive solution, as mineralization is limited and field-scale treatment remains low. Instead, plant–soil–microbe systems reduce PFAS mobility and exposure through stabilization and sequestration. Future research should prioritize strategies for short-chain PFAS, integration with sorptive amendments, and data-driven approaches to optimize phytomanagement performance.

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Keywords: biochar-assisted remediation; constructed wetlands; environmental pollution; phytotechnology; phytoremediation; phytomanagement; plant uptake; rhizosphere

1. Introduction

The rapid expansion of industrialization and chemical manufacturing has led to the widespread release of synthetic compounds that exhibit exceptional resistance to environmental degradation [1,2]. Among these, a growing class of contaminants, often referred to as ultra-persistent pollutants, has attracted increasing scientific and regulatory attention due to their long environmental lifetimes, global distribution, and potential for bioaccumulation [3,4]. Unlike conventional organic pollutants, which may undergo biodegradation or chemical transformation over time, ultra-persistent compounds are characterized by strong molecular bonds, structural stability, and resistance to thermal, chemical, and biological breakdown processes [5,6].

Ultra-persistent pollutants are now routinely detected across environmental compartments, including surface waters [7], groundwater [8], soils [9], sediments [10], and even remote regions such as polar ecosystems [11]. Their persistence enables long-range transport through atmospheric and hydrological pathways [7], while continuous emissions from industrial activities, consumer products, and waste streams sustain their environmental presence. As a result, ultra-persistent pollutants represent a paradigm shift in environmental contamination, where long-term management and risk mitigation become more relevant than complete removal. This challenge necessitates the development of remediation strategies that are not only effective but also sustainable and adaptable to complex environmental systems.

Per- and polyfluoroalkyl substances (PFAS) are among the most prominent and extensively studied ultra-persistent pollutants [12]. Their unique physicochemical properties, arising primarily from the strength of the carbon–fluorine (C–F) bond, confer remarkable chemical stability, thermal resistance, and surface activity [13]. These characteristics have supported their widespread application in industrial processes and consumer products, including firefighting foams [14], non-stick coatings [15], water-repellent materials [16], and surfactants [17]. However, these same properties also underpin their environmental persistence and mobility. PFAS have been detected globally in aquatic systems [18], soils [19], biota [20], and atmospheric compartments [21,22], reflecting both localized emissions and long-range transport. Short-chain PFAS tend to be more mobile and water-soluble, facilitating transport through aquatic systems and groundwater [23], whereas long-chain PFAS exhibit stronger sorption to soils and sediments and greater potential for bioaccumulation [24].

Phytotechnology has emerged as a promising nature-based approach for managing PFAS-contaminated environments [25]. By integrating plant uptake, rhizosphere processes, and plant–microbe interactions, phytotechnology offers a low-energy, environmentally compatible strategy applicable across large, heterogeneous sites [26]. Recent research indicates that PFAS phytotechnology is more accurately described as phytomanagement rather than complete remediation [27]. Due to the recalcitrant nature of PFAS, plants and associated rhizosphere systems rarely achieve full mineralization. Instead, they influence contaminant fate by reducing mobility, limiting leaching, and controlling transfer into biota [28].

Table 1 presents a critical comparison of existing review studies on PFAS occurrence, environmental behavior, and treatment strategies, revealing a clear evolution in the literature from predominantly physicochemical and treatment-oriented perspectives toward

more integrative and system-based approaches. Most studies focus on the characterization, sources, and uptake of PFAS using conventional technologies such as adsorption, membrane filtration, and advanced oxidation processes, with a strong emphasis on water treatment efficiency and contaminant chemistry (e.g., adsorption- and treatment-focused studies) [5,13]. While these studies provide essential insights into PFAS structure–property relationships and transformation mechanisms, they largely overlook interactions across environmental compartments and fail to address biological pathways of contaminant fate.

Table 1. Critical comparison of prior literature reviews on PFAS pollution, identifying thematic focus, key findings, limitations, and the specific gaps addressed by the present study.

Reference (Year)	Focus Area	Key Contribution	Limitation	Gap Addressed in This Study
Evangelou and Robinson (2022) [28]	Phytomanagement of PFAS-contaminated soils; risk-based land management	• Introduces phytomanagement as a risk-based alternative to conventional remediation • Demonstrates that phytoextraction is largely infeasible for PFAS due to low bioaccumulation and long remediation times • Highlights importance of controlling PFAS mobility • Identifies role of soil amendments in enhancing PFAS immobilization • Emphasizes avoidance of food crops due to food-chain transfer risks	• Primarily conceptual and feasibility-focused • Limited mechanistic insight into plant–PFAS interactions • Lacks detailed differentiation between PFAS behavior in plants • Limited discussion on rhizosphere processes and plant–microbe interactions • Does not integrate hybrid or engineered phytotechnology systems • Limited consideration of uptake mechanisms and translocation pathways at physiological level	Advances beyond risk-based phytomanagement by providing a mechanistic understanding of PFAS behavior in plant–soil systems, including uptake pathways, rhizosphere interactions, and compound-specific dynamics, while integrating hybrid and enhanced phytotechnology strategies for improved remediation performance
Rekik et al. (2024) [13]	PFAS sources, environmental impacts, regulation, and treatment technologies	• Provides a comprehensive overview of PFAS chemistry, classification, and global occurrence • Explains environmental distribution across water, soil, plants, wildlife, and humans • Highlights ecotoxicological impacts, including effects on aquatic organisms, wildlife, and terrestrial plants • Reviews global regulatory frameworks and drinking water limits • Classifies treatment technologies into separation and degradation • Includes mechanistic insights into PFAS removal efficiency depending on chain length, functional groups, and system conditions	• Limited discussion on soil–plant remediation systems • Limited depth on plant uptake mechanisms and rhizosphere interactions despite acknowledging plant exposure pathways • Focuses primarily on physicochemical treatments • Lacks integration of multi-compartment transfer • Does not provide a unified framework linking environmental fate with remediation strategies	Integrating plant–soil interactions, phytoremediation mechanisms, and ecosystem-based solutions, while connecting environmental transport pathways to biological uptake and mitigation strategies
Hamza et al. (2025) [5]	PFAS adsorption mechanisms and structure–property relationships in water treatment	• Provides comprehensive classification of PFAS • Demonstrates that adsorption efficiency is strongly governed by molecular structure • Identifies dominant mechanisms • Highlights higher adsorption affinity of long-chain PFAS and sulfonates (PFSAs) compared to short-chain and carboxylates (PFCAs) • Reviews wide range of sustainable and advanced adsorbents (biopolymers, MOFs, COFs, MIPs)	• Integration with soil–plant or environmental biological systems • Limited discussion on rhizosphere processes and plant-mediated uptake or transformation • Does not address field-scale complexity or multi-compartment transport • Limited emphasis on hybrid or nature-based remediation strategies	Extends beyond adsorption-focused understanding by integrating PFAS behavior across soil–plant–water systems, incorporating rhizosphere interactions, plant uptake mechanisms, and hybrid phytotechnology approaches to address PFAS mobility and remediation in complex environmental settings

Table 1. *Cont.*

Reference (Year)	Focus Area	Key Contribution	Limitation	Gap Addressed in This Study
Al-Maqtari et al. (2025) [6]	PFAS in drinking water: physicochemical properties, sources, health impacts, and regulatory frameworks	• Provides a holistic review covering PFAS definition, classification, physicochemical properties, and environmental behavior • Identifies major sources and pathways • Summarizes human health impacts • Reviews ecological impacts and bioaccumulation across trophic levels • Offers detailed comparison of global regulations • Highlights limitations of current treatment technologies	• Strong emphasis on drinking water systems • Lacks mechanistic discussion on plant uptake, phytoremediation, or nature-based solutions • Does not explore coupled environmental compartments • Limited focus on sustainable remediation strategies beyond conventional treatment	Integrating soil–plant–rhizosphere dynamics, advancing knowledge on PFAS uptake, translocation, and phytoremediation potential, and proposing nature-based or hybrid remediation strategies for sustainable PFAS management beyond conventional water treatment
Vieira et al. (2025) [12]	Atmospheric PFAS: sources, transport, fate, analytical methods, and research priorities	• Provides a comprehensive synthesis of PFAS in the atmosphere • Identifies primary and secondary emission sources • Explains gas–particle partitioning and long-range atmospheric transport mechanisms • Distinguishes neutral vs. ionizable PFAS behavior in atmospheric systems • Reviews advanced analytical and sampling methods	• Strongly focused on atmospheric compartment • Lacks discussion on biological uptake pathways • Does not explore phytoremediation or nature-based mitigation strategies • Limited linkage between atmospheric deposition and terrestrial/ecosystem accumulation dynamics	Extends atmospheric understanding by linking air–soil–plant transfer pathways, particularly how atmospheric deposition contributes to plant uptake and food chain contamination, and evaluates phytoremediation and nature-based solutions to mitigate PFAS across environmental compartments
Marzi et al. (2025) [25]	Phytoremediation of PFAS: plant uptake, omics response, detection, and biomass management	• Provides a comprehensive, end-to-end framework of PFAS phytoremediation • Demonstrates plant uptake mechanisms • Introduces key phytoremediation metrics • Integrates omics approaches • Reviews advanced detection methods • Addresses critical issue of contaminated biomass disposal	• Primarily frame phytoremediation as a plant-based remediation technique, focusing on uptake, accumulation, and associated molecular responses, rather than positioning it within a broader phytomanagement framework that emphasizes long-term risk control and system-level processes. • Limited emphasis on hybrid remediation strategies	Addresses these limitations by repositioning phytoremediation within a phytomanagement framework. This study also advances the field by integrating hybrid phytotechnology strategies to enhance overall remediation performance and enable more scalable and effective management of PFAS-contaminated environments.
This study	Phytotechnology for PFAS remediation: environmental behavior, plant uptake mechanisms, rhizosphere interactions, and hybrid phytomanagement strategies	• Develops a mechanistically integrated framework • Synthesizes PFAS behavior across multiple environmental compartments • Differentiates short-chain vs. long-chain PFAS dynamics in plant systems • Integrates rhizosphere interactions and plant–microbe processes • Advances hybrid and enhanced phytotechnology approaches • Introduces phytomanagement as a realistic framework for PFAS mitigation, emphasizing risk reduction over complete removal	-	-

Recent research expands the scope by incorporating environmental distribution, regulatory frameworks, and health risk assessments, highlighting the global persistence, mobility, and potential for bioaccumulation of PFAS across water, soil, air, and biota [6,12]. However, these studies remain predominantly descriptive and compartmentalized, with limited integration of soil–plant systems, rhizosphere processes, and ecological feedback mechanisms. More recent literature demonstrates a growing interest in nature-based treatment approaches, including phytoremediation, as well as emerging tools such as omics technologies and machine learning for understanding plant–PFAS interactions [25]. Despite these advancements, current studies often address isolated components, such as plant uptake, microbial activity, or biomass disposal, without providing a unified framework that links environmental behavior, mechanistic processes, and phytomanagement strategies.

Across the reviewed literature, a consistent and critical gap emerges: the absence of a comprehensive, mechanistically grounded framework that integrates PFAS environmental behavior with plant uptake dynamics, rhizosphere interactions, and scalable phytotechnology solutions. This fragmentation limits the ability to fully evaluate the role of phytotechnology not only as a treatment tool but also as a long-term phytomanagement strategy for ultra-persistent contaminants.

Unlike previous reviews that primarily focus on individual aspects of PFAS phytotechnology, such as plant uptake, molecular responses, biomass management, or phytoremediation performance, this review proposes a system-level framework that integrates PFAS environmental behavior, plant physiological processes, rhizosphere interactions, and hybrid phytotechnology strategies within a single conceptual model. The novelty of this review lies in four key contributions. First, it explicitly links PFAS physicochemical properties and environmental transport pathways to bioavailability and plant uptake behavior, thereby connecting contaminant fate with phytotechnology performance. Second, it differentiates the treatment implications of short-chain and long-chain PFAS across uptake, translocation, stabilization, and management pathways. Third, it integrates rhizosphere-mediated processes, including microbial interactions, sorptive amendments, and hydrological controls, as central determinants of PFAS retention and mobility. Finally, it reframes PFAS phytotechnology from a conventional remediation perspective toward a phytomanagement paradigm that emphasizes long-term risk reduction, exposure control, biomass management, and integration with circular remediation approaches. Collectively, these elements provide a mechanistic and operational framework for evaluating PFAS phytotechnology beyond plant uptake alone and support the development of scalable field-oriented management strategies.

2. Review Methodology

2.1. Literature Search Strategy

A systematic literature search strategy was conducted to synthesize current knowledge on phytotechnology for PFAS treatment, with particular emphasis on environmental behavior, plant uptake mechanisms, phytomanagement approaches, rhizosphere interactions, biomass management, and hybrid remediation strategies. The review methodology was designed to ensure transparency, reproducibility, and comprehensive coverage of the rapidly expanding PFAS literature.

The literature search was performed using the SCOPUS database. The search strategy was developed using four thematic groups combined with Boolean operators. The first group focused on PFAS-related terminology, including “PFAS”, “perfluoroalkyl substances”, “polyfluoroalkyl substances”, “perfluoroalkyl acids”, “PFAA”, “PFOS”, and “PFOA”. The second group captured phytotechnology concepts, including “phytoremediation”, “phytotechnology”, “phytoextraction”, “phytostabilization”, “rhizofiltration”, and “phytomanagement”. The third group addressed biological and mechanistic processes, including “plant uptake”, “bioaccumulation”, “translocation”, “rhizosphere”, “plant–microbe interaction”, and “microbial transformation”. The fourth group focused on integrated and advanced treatment approaches, including “constructed wetlands”, “biochar”, “hybrid remediation”, “biomass management”, “biomass valorization”, and “resource recovery”. The original search was performed on 1 April 2026.

The SCOPUS search query was structured as follows:

(i) TITLE-ABS-KEY (“PFAS” OR “perfluoroalkyl substances” OR “polyfluoroalkyl substances” OR “perfluoroalkyl acids” OR “PFAA” OR “PFOS” OR “PFOA”) (20,228 documents)

(ii) TITLE-ABS-KEY ("phytoremediation" OR "phytotechnology" OR "phytoextraction" OR "phytostabilization" OR "rhizofiltration" OR "phytomanagement") (8289 documents)
(iii) TITLE-ABS-KEY ("plant uptake" OR "bioaccumulation" OR "translocation" OR "rhizosphere" OR "plant-microbe interaction" OR "microbial transformation") (70,112 documents)
(iv) TITLE-ABS-KEY ("constructed wetland*" OR "biochar" OR "hybrid remediation" OR "biomass management" OR "biomass valorization" OR "resource recovery") (3222 documents).

2.2. Screening and Selection of Studies

The initial database search returned a broad collection of publications covering PFAS occurrence, environmental fate, plant uptake, phytotechnology applications, and remediation technologies. All retrieved records were exported and compiled, where duplicate entries were identified and removed prior to screening.

The inclusion criteria applied during the title and abstract screening stage were:

(i) Publications written in English.
(ii) Studies containing keywords from at least two thematic groups connected using Boolean operators (AND).
(iii) Research directly addressing PFAS behavior, plant uptake, phytotechnology, phytomanagement, or hybrid remediation approaches.
(iv) Peer-reviewed journal articles, review papers, and relevant conference papers with clear scientific relevance.

This first screening resulted in 1157 documents. Following the initial screening, eligible studies underwent full-text assessment using the following exclusion criteria:

(i) Publications outside the timeframe of 2016–2026.
(ii) Studies focusing exclusively on PFAS occurrence, monitoring, or analytical detection without discussing remediation implications.
(iii) Research not related to plant-based remediation, phytomanagement, rhizosphere processes, biomass management, or integrated treatment systems.
(iv) Studies lacking sufficient methodological detail or quantitative data on PFAS uptake, translocation, accumulation, or treatment performance.
(v) Publications not originating from peer-reviewed scientific sources.

After the full-text assessment, 233 studies were selected for inclusion in this review. An additional 8 titles outside the 2016–2026 timeframe were added as fundamental references.

3. Environmental Occurrence and Behavior of PFAS

PFAS have been detected worldwide, reflecting the combination of widespread emissions and their remarkable persistence in the environment; hence, they are frequently designated as forever chemicals [12,29]. Their distinctive chemical stability and strong surface activity have supported broad industrial and consumer use, but these same traits also promote long environmental residence times and increase human exposure [12]. At the molecular level, this persistence is closely tied to the carbon–fluorine bond, one of the strongest bonds in organic chemistry, with a high bond dissociation energy (about 485 kJ/mol). The high electronegativity of fluorine further limits susceptibility to transformation by heat, light, or common chemical reactions. These properties impart hydrophobic character alongside exceptional thermal and chemical stability, explaining why PFAS have been widely adopted as water- and oil-repellent agents and incorporated into durable polymeric materials. However, PFAS behavior is shaped not only by the fluorinated backbone;

differences in functional groups (such as carboxyl, sulfonates, and hydroxyl groups) can substantially shift physicochemical properties, making environmental distribution and transport difficult to generalize across matrices [22].

3.1. Sources and Pathways into Soil and Water

PFAS reach soils and aquatic systems through a connected set of pathways that link human activities, engineered infrastructure, and natural transport processes. In the literature, PFAS sources are commonly discussed through three parallel framings: direct versus indirect emissions, primary versus secondary sources, and indoor versus outdoor environments. The direct/indirect distinction emphasizes how PFAS enter the environment (release mechanism), the primary/secondary distinction captures where PFAS originate within the network (origin nodes versus reservoirs that store and re-emit mass), and the indoor/outdoor framing clarifies the dominant settings in which PFAS are generated, stored, exchanged, and mobilized. Figure 1 describes the conceptual framework linking PFAS emission mechanisms, source status, and environmental settings [30–32].

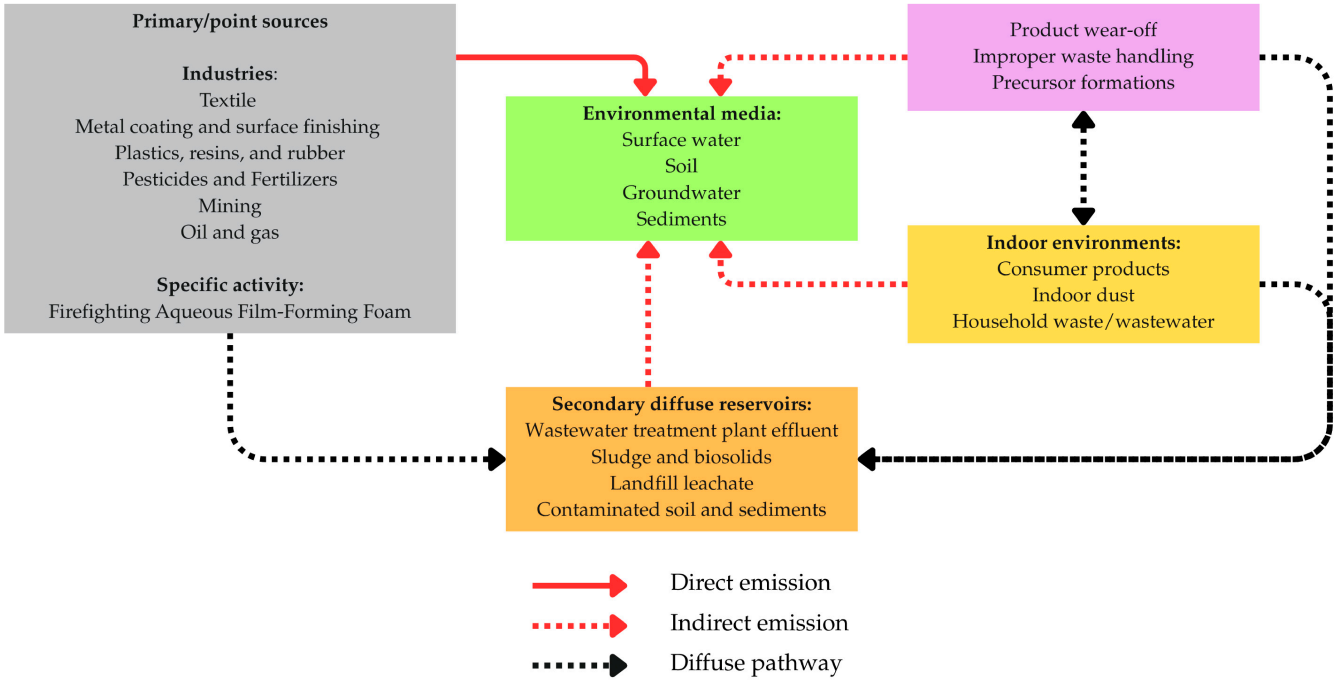


Figure 1. Conceptual framework linking PFAS emission mechanisms, source status, and environmental settings.

PFAS reach soils and aquatic environments through interconnected emission pathways that reflect both the modes of release and the dynamic behavior of these compounds in engineered and natural systems. Direct emissions refer to PFAS releases associated with manufacturing, product use, and transport activities in both industrial and domestic settings [31,32]. These emissions typically originate from localized point sources, including fluorochemical production and formulation facilities, metal-plating operations, and fire-fighting aqueous film-forming foam (AFFF)-impacted sites, where PFAS are discharged directly into soils, surface waters, or wastewater streams [31]. Following release, PFAS transport is largely governed by advective flow and infiltration processes, while subsequent partitioning is controlled by molecular structure, solution chemistry, and the characteristics of the receiving media.

Indirect emissions occur through mediated pathways involving consumer products and waste-management systems. These include the gradual release of PFAS from treated

materials, losses during waste handling, and the formation of terminal PFAS through photolytic, chemical, or biological transformation of precursor compounds [33]. Such pathways redistribute PFAS into secondary reservoirs, including wastewater treatment plant (WWTP) effluent, sludge and biosolids, landfill leachate, and contaminated soils or sediments, which function as long-term storage compartments capable of sustaining chronic environmental loading [33,34]. Field observations support the significance of these combined pathways. For example, PFAS concentrations of up to 40.8 ng/L have been reported in the Black Warrior River basin in Alabama, largely attributed to municipal WWTP discharges in the Birmingham area [35]. Similarly, major European rivers such as the Rhine and the Oder show elevated concentrations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) linked to the textile and metal-plating industries [36,37], while the Yangtze River in China exhibits cumulative PFAS burdens associated with multiple industrial inputs [18]. Additional point-source contributions may also arise from specialized applications; firefighting AFFF has been shown to release more than ten types of PFAS, including PFOS, when discharged into aquatic environments [38]. Extensive production and global distribution have resulted in PFAS contamination in soils across many regions. For example, soil samples collected at Stockholm Arlanda Airport in Sweden contained a wide range of PFAS; analysis identified 26 different substances at concentrations between 20 and 160 ng/g dry weight [14]. Similarly, Hale et al. [39] investigated soils from a Norwegian airport used as a firefighting training site and reported substantial PFAS contamination. Total and leachable concentrations were dominated by PFOS, with soil levels ranging from 9000 to 2,600,000 ng/kg, while associated leachate waters contained PFAS at concentrations between 1200 and 212,000 ng/L [39].

Although most PFAS are detected in ionic form within water, soil, and sediments, certain PFAS and their precursors are also present in the atmosphere, where they undergo long-range transport driven by air currents. PFAS may enter the atmosphere through volatilization, droplet formation, or association with particulate matter originating from PFAS-containing products and industrial activities [12]. Atmospheric detection can therefore reflect either local emissions or long-range transport, although current estimates vary by compound class and inventory boundary; while the fraction may be small in mass terms, atmospheric transport can disproportionately influence remote regions [21,40]. Once in the atmosphere, PFAS can be transferred to aquatic systems via wet deposition during precipitation or dry particle deposition, eventually accumulating in soils and sediments. A portion of PFAS stored in these media may subsequently volatilize and re-enter the atmosphere, forming a dynamic environmental cycle that enhances persistence, long-range distribution, and bioaccumulation potential. Through multiple exposure routes, including transfer into the food chain, PFAS may accumulate in organisms and exert toxic effects on biological systems [41]. Airborne PFAS emissions have also been associated with contamination of well water in regions located downwind of major sources, highlighting the capacity of atmospheric transport to affect local water supplies [30,42]. Several precursor compounds illustrate the importance of atmospheric transformation pathways. Fluoropolyalcohols, used in water-repellent coatings in the construction industry, may volatilize due to their high vapor pressure and react with water vapor and nitrogen oxides (NOx) to form perfluorocarboxylic acids (PFCAs) [31,43]. Other atmospheric precursors, such as perfluoroaldehydes and fluoropolyaldehydes, phototransform into PFCAs, contributing to their environmental persistence [44]. Volatile compounds like hydrochlorofluorocarbons (HCFCs) undergo atmospheric oxidation to yield perfluorobutanesulfonate (PFBS) and PFCAs. Similarly, N-methyl perfluorobutane sulfonamidoethanol (NMeFBSE) oxidizes primarily via OH radicals, producing PFBS (about 1% yield) and short-chain PFCAs (around 10% yield), with an atmospheric lifetime of roughly 2 days [44,45]. These transformations explain the

detection of PFCAs and PFBS in remote areas despite the short lifetimes of their precursors, because oxidation products bioaccumulate [45].

Within this integrated source–pathway framework, emissions can also be interpreted in terms of the environmental setting in which they occur, namely, indoor and outdoor compartments. Outdoor environments are open-air systems with continuous air circulation, whereas indoor environments are enclosed spaces with limited air exchange, such as homes, schools, restaurants, and vehicle cabins [12]. Exchange of air and particles between these compartments enables cross-contamination, linking indoor sources to outdoor environmental loads. Indoor environments often act as upstream micro-reservoirs, where PFAS from treated materials accumulate in indoor dust and household wastewater, which are subsequently transferred to outdoor systems through sewer networks and waste disposal pathways. This indoor-to-outdoor transfer reinforces the combined influence of primary point sources and secondary reservoirs on PFAS occurrence in soils and waters. PFAS distribution in environmental systems is best interpreted as the integrated outcome of emission mode, reservoir accumulation, and intercompartmental exchange processes, rather than as the result of isolated or mutually exclusive source categories.

3.2. Physicochemical Properties Governing Persistence

PFAS persistence is fundamentally governed by the combined effects of strong C–F bonding, high fluorination, and amphiphilic molecular structure, which together confer exceptional chemical, thermal, and interfacial stability (Table 2). These intrinsic properties control phase partitioning, sorption, and long-range transport, enabling PFAS to persist across air, water, soil, and sediment compartments. As a result, environmental behavior and treatment performance are strongly dictated by structure-dependent physicochemical characteristics rather than by a single dominant transformation pathway. The extraordinary persistence of PFAS in the environment is primarily controlled by the strength and stability of the carbon–fluorine (C–F) bond. This bond is widely regarded as the strongest single bond in organic chemistry, a property arising from the high electronegativity of fluorine (3.98 on the Pauling scale) and its strong attraction to the partially positive carbon center [46]. As a result, the C–F bond exhibits a high dissociation energy of approximately 485 kJ/mol, which is further reinforced by its short bond length of about 1.35 Å [47]. Increasing the degree of fluorination strengthens the overall molecular framework, as surrounding fluorine atoms form steric and electrostatic barriers that protect the carbon backbone from nucleophilic attack [30]. The strong electronegativity of fluorine also increases molecular polarization, imparting a more ionic character, stronger bonding, and greater acidity relative to hydrocarbon analogs [30]. Fluorine substitution reduces susceptibility to common transformation pathways such as hydrolysis, oxidation, and photolysis by forming a protective sheath around the carbon chain [46]. In highly fluorinated structures, the arrangement of multiple fluorine atoms can produce a helical-like shield that protects the carbon skeleton from nucleophilic, oxidative, and reductive reactions, while inductive effects simultaneously strengthen adjacent C–C bonds [48,49]. These structural features collectively underpin the exceptional chemical and thermal resistance that defines PFAS persistence.

Beyond bond strength, PFAS environmental behavior is strongly influenced by physicochemical properties that control phase partitioning, such as solubility, volatility, and ionization state. The air–water partitioning of PFAS is commonly described by Henry's law constant (*Kaw*), which governs their tendency to transfer between aqueous and atmospheric compartments [30,50]. Neutral PFAS generally exhibit higher Kaw values and therefore greater volatility than their ionized counterparts, while shorter-chain compounds such as Perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS) display higher

water solubility, promoting mobility in aquatic systems [30]. Neutral species, including fluorotelomer alcohols (FTOHs), exhibit elevated K_{aw} values due to their lower polarity, thereby enabling long-range atmospheric transport prior to their transformation into persistent perfluorinated products [41]. In contrast, ionized species such as PFOA anions show negligible volatility in aqueous systems. Still, they may protonate in organic matrices or under acidic conditions, increasing their effective K_{aw} and facilitating losses from surfaces such as asphalt [51]. These phase-partitioning behaviors directly influence environmental distribution and persistence across compartments.

Table 2. Key physicochemical properties governing PFAS environmental persistence and behavior.

Physicochemical Property	Governing Mechanism	Persistence Implication in the Environment	References
Strong C–F bond	High bond dissociation energy (about 485 kJ/mol) due to strong electronegativity of fluorine and short bond length	Extremely resistant to hydrolysis, oxidation, photolysis, and biodegradation, leading to long environmental lifetimes	[46,47]
High degree of fluorination	Multiple fluorine atoms create steric and electrostatic shielding around the carbon backbone	Reduces susceptibility to nucleophilic, oxidative, and reductive attacks, increasing chemical and thermal stability	[30,48,49]
Molecular polarization and acidity	Strong electronegativity of fluorine increases bond polarity and ionic character	Promotes stability of anionic forms in water and reduces reactivity compared with hydrocarbon analogs	[30]
Solubility and chain length	Short-chain PFAS exhibit higher water solubility, while long-chain PFAS show stronger hydrophobic interactions with organic matter	Short-chain PFAS are more mobile in aquatic systems; long-chain PFAS accumulate in soils, sediments, and biota, increasing long-term environmental reservoirs	[30,49]
Air–water partitioning (Henry's law constant, Kaw)	Determines tendency of PFAS to transfer between aqueous and atmospheric phases	Neutral PFAS and precursors can volatilize and undergo long-range atmospheric transport before transformation into persistent products	[30,41,50]
Ionization state	Neutral species have higher volatility; ionized species are more water-bound but can protonate under certain conditions	Controls phase distribution, surface losses, and transport between air, water, and solid matrices	[51]
Thermal stability	Strong C–F bonds resist cleavage at elevated temperatures (PFCAs about 200–400 °C; PFSAs > 450 °C)	Enables persistence during incineration, industrial processes, and natural fires; mineralization requires extreme conditions	[52,53]
Amphiphilic structure	Hydrophobic fluorinated tail and hydrophilic headgroup promote surface activity	Drives accumulation at air–water and NAPL–water interfaces, reducing bulk degradation and enhancing long-range transport	[48]
Low C–F polarizability	Dense molecular packing at interfaces reduces surface tension more than hydrocarbon surfactants	Facilitates formation of surface films and interfacial accumulation, affecting transport and persistence in multiphase systems	[54]

Thermal stability represents another key physicochemical factor contributing to PFAS persistence. Many PFAS can withstand elevated temperatures without decomposition, allowing them to persist across a wide range of environmental and industrial conditions. Long-chain PFAS, such as PFOA (≥7 carbons), tend to sorb strongly to soils through organic

carbon partitioning, whereas shorter-chain analogs are more water-soluble and mobile in aquatic environments [49]. In terms of thermal resistance, perfluoroalkyl carboxylic acids (PFCAs) can remain stable at temperatures of approximately 200–400 °C, while perfluoroalkyl sulfonic acids (PFSAs) may resist transformation at temperatures exceeding 450 °C. This resilience is largely attributed to the strong C–F bond (about 485 kJ/mol), enabling PFAS to persist during incineration, industrial processes, and even natural fires [52,53]. Effective mineralization often requires extreme conditions, such as temperatures above 700 °C in the presence of catalysts like granular activated carbon, underscoring the chemical recalcitrance of these compounds.

Another defining physicochemical feature is the amphiphilic structure of PFAS, consisting of fluorinated tails that are both hydrophobic and lipophobic/oleophobic, and hydrophilic functional headgroups. This molecular architecture imparts exceptional surface activity, enabling PFAS to reduce surface tension more effectively than conventional hydrocarbon surfactants due to the low polarizability of the C–F bond. As a result, PFAS preferentially accumulate at interfaces such as air–water or non-aqueous phase liquid (NAPL)–water boundaries, where concentrations may reach several times those in the bulk solution. At these interfaces, PFAS can form surface films or hemi-micellar structures even below critical micelle concentrations, altering interfacial transport processes. For example, up to 87% of the PFOS mass has been reported at air–water interfaces in unsaturated soils, thereby limiting bulk-phase transformation while enhancing long-range transport potential [48]. The low polarizability of the C–F bond enables dense molecular packing at interfaces, reducing water surface tension from approximately 72 mN/m to as low as 10–16 mN/m, substantially lower than the 30 mN/m typically achieved by hydrocarbon surfactants. Sulfonate headgroups often outperform carboxylates in reducing surface tension, likely due to tighter interfacial packing driven by headgroup geometry and charge density [54].

3.3. Mobility, Bioavailability, and Sorption Behavior

The mobility, sorption, and bioavailability of PFAS in environmental systems are primarily governed by molecular structure, especially chain length and functional group chemistry, together with soil characteristics and aqueous geochemistry. In general, long-chain PFAS display stronger sorption to solid phases, whereas short-chain analogs remain more soluble and mobile in aquatic environments. Because solubility is a key driver of transport, shorter-chain compounds such as C4 PFBAs and C4 PFSAs exhibit higher aqueous solubility than their longer-chain counterparts, which promotes their migration across environmental compartments [30,41]. Both laboratory and field studies consistently demonstrate that short-chain PFAS (typically <C8) exhibit greater aqueous solubility and mobility than long-chain compounds (≥C8), leading to their more frequent detection in groundwater and surface water systems [55,56]. For example, PFH_xA and PFBS are predominantly found in the dissolved phase in aquatic environments, enabling downstream transport and groundwater infiltration more readily than long-chain PFAS, which tend to associate with suspended particles or sediment surfaces [55].

In addition to chain length, PFAS mobility is further influenced by structural characteristics and environmental conditions that regulate phase partitioning. Variations in pH, salinity, and organic matter content can alter ionization, solubility, and sorption behavior, thereby affecting persistence across air–water–soil systems [30,41]. Increased pH promotes ionization and enhances aqueous-phase stability, while elevated salinity may reduce solubility through salting-out effects. Dissolved organic matter can also facilitate colloidal transport by providing additional partitioning phases. Functional group chemistry introduces further variability. Sulfonate PFAS, such as PFOS and PFH_xS, typically

exhibit lower pK_a values (approximately −1 to −3), greater hydrophobicity, and higher polarizability than their carboxylate analogs, resulting in stronger interactions with soil organic matter and mineral surfaces [57,58]. Sulfonates sorb more strongly (higher log K_d/K_{oc}) to soils/sediments than equivalent carboxylates (PFOS > PFOA; PFH_xS > PFH_xA), due to stronger electrostatic binding to minerals (via charge density) and hydrophobic chain enhancement from the sulfonate's electron withdrawal, which increases tail perfluoroalkyl polarity [59]. Solution ionic strength plays an important role in controlling PFAS sorption by altering electrostatic interactions at solid–water interfaces [60]. As ionic strength increases, the electrical double layer surrounding charged surfaces becomes compressed, which reduces repulsive forces between negatively charged PFAS headgroups (such as $–COO^-$ and $–SO_3^-$) and soil particles. This screening effect allows PFAS molecules to approach surfaces more closely, enhancing sorption and leading to higher distribution coefficients (K_d), particularly for short-chain PFAS where electrostatic interactions are more influential. The effect becomes more pronounced in the presence of multivalent cations; for example, Ca^{2+} exerts a stronger influence than Na^+ by more effectively neutralizing surface charges and promoting reorientation of the fluorinated tail toward the solid surface, thereby increasing van der Waals interactions [60]. These structure-dependent sorption mechanisms directly influence PFAS mobility and bioavailability. Compounds that remain predominantly in the dissolved phase exhibit greater transport potential and exposure risk, whereas those with stronger sorption affinities tend to accumulate in soils and sediments, forming long-term environmental reservoirs. PFAS bioavailability reflects a balance between aqueous mobility and solid-phase retention, both of which are governed by molecular structure and surrounding geochemical conditions.

3.4. Challenges in Treating Short-Chain vs. Long-Chain PFAS

Based on their chain length, PFAS are categorized as either short-chain or long-chain compounds (Table 3). Short-chain PFAS include perfluoroalkyl carboxylic acids (PFCAs) with seven or fewer carbons, such as perfluorohexanoic acid (PFH_xA) [61]. Long-chain PFAS consist of PFCAs with eight or more carbons, such as perfluorooctanoic acid (PFOA), and PFSAs with six or more carbons, including perfluorooctane sulfonic acid (PFOS) [61]. Short-chain PFAS are generally more challenging to treat than long-chain analogs because their physicochemical properties favor aqueous mobility over solid-phase retention. Their low sorption coefficients (log *Koc* < 3) and predominantly electrostatic interactions keep them largely in the dissolved phase. Short-chain PFAS generally exhibit substantially lower adsorption affinity and earlier breakthrough than long-chain PFAS under comparable operational conditions [62].

Table 3. Comparative characteristics of short-chain and long-chain PFAS [31,63–65].

Aspect	Short-Chain PFAS (<C8)	Long-Chain PFAS (≥C8)	Environmental Implication
Typical examples	PFBA, PFBS, PFH_xA	PFOA, PFOS, PFH_xS, PFNA	Short-chain increasingly used as substitutes for legacy long-chain PFAS
Molecular size	Shorter perfluorinated carbon chain	Longer perfluorinated carbon chain	Chain length controls hydrophobicity and sorption behavior
Water solubility	Higher aqueous solubility	Lower solubility; more hydrophobic	Short-chain PFAS remain predominantly in dissolved phase
Sorption to soil/sediment	Weak sorption; low *Kd* to organic/mineral surfaces	Stronger sorption to organic matter and mineral surfaces	Long-chain PFAS accumulate in soils and sediments

Table 3. *Cont.*

Aspect	Short-Chain PFAS (<C8)	Long-Chain PFAS (≥C8)	Environmental Implication
Mobility in groundwater	High mobility; easily transported through porous media	Limited mobility due to stronger sorption	Short-chain PFAS more frequently detected in groundwater
Volatility (for precursors)	Some short-chain precursors show high volatility	Lower volatility for long-chain acids	Enhances atmospheric transport of short-chain precursors
Bioaccumulation potential	Lower bioaccumulation factors	Higher bioaccumulation in biota and food webs	Long-chain PFAS pose greater biomagnification risks
Environmental persistence	Highly persistent, but more mobile	Highly persistent and more strongly retained in solids	Both remain long-term environmental contaminants via different pathways
Dominant environmental phase	Dissolved phase in water bodies	Sorbed phase in soils, sediments, and biota	Leads to different exposure pathways
Treatment by adsorption	Lower adsorption efficiency	Higher adsorption efficiency	Short-chain PFAS more difficult to remove by conventional adsorption

Under the conditions summarized by Zhang et al. [66], the reaction kinetics and pathways differ markedly between long- and short-chain PFAS. In particular, photocatalysis exhibited the fastest apparent reaction rates, with values of 63.0/h for long-chain PFAS and 19.7/h for short-chain PFAS, suggesting more efficient treatment of long-chain compounds under comparable conditions [66]. Short-chain PFAS are more challenging to treat than long-chain PFAS due to their low adsorption potential, high polarity, solubility, and mobility, which make them less effectively removed by conventional methods such as activated carbon filters. While long-chain PFAS can be removed from water using these filters, short-chain PFAS persist in the environment due to their high mobility and extreme chemical stability. These properties favor persistence in the aqueous phase, facilitating transport through the hydrological cycle and leading to detections in surface waters and drinking water sources at concentrations exceeding health-based thresholds [56]. Although adsorption remains the most widely implemented approach because of its low energy demand and broad applicability across concentration ranges, its effectiveness for short-chain PFAS is largely governed by electrostatic interactions rather than hydrophobic partitioning, which dominates long-chain PFAS uptake [67].

Destructive treatment approaches are often considered as alternatives to separation-based methods; however, their practical application is frequently limited by high energy requirements and incomplete mineralization. Electrochemical oxidation and photocatalysis offer promising approaches for PFAS transformation via direct electron transfer or radical attacks (such as –OH, SO_4^{-}–), but transformation products and cost barriers limit scalability [66]. Electrochemical systems employing boron-doped diamond (BDD) or SnO_2-based anodes have demonstrated transformation efficiencies of approximately 80–99% for long-chain PFAS, such as PFOA ($k = 10^{-3}$–10^{-2} $M^{-1}{\cdot}s^{-1}$), primarily via anodic oxidation and indirect radical-mediated mechanisms [68]. However, these processes frequently result in stepwise shortening of the perfluorinated chain (PFOA → PFPeA → PFBA), indicating incomplete mineralization, with total organic carbon (TOC) reductions typically remaining below 60%. In addition, the substantial energy requirements (20–100 kWh/m^3) and the high cost of electrode materials, including Ir/Ru-coated titanium, significantly limit large-scale implementation [68].

High-energy treatment approaches, such as plasma discharge, thermolytic, and sonochemical processes, are technically capable of achieving near-complete mineralization.

However, short-chain PFAS display greater resistance to defluorination than their long-chain counterparts, thereby requiring substantially higher energy inputs and tighter operational control to achieve meaningful degradation [67]. Recent advances in adsorptive materials illustrate efforts to overcome these limitations. In response to these limitations, recent research has focused on improving sorptive materials to enhance capture efficiency. For example, a polyethylenimine–polyvinyl chloride electrospun nanofiber (PEI–PVC NF) adsorbent demonstrated considerable adsorption capacities at neutral pH for both short- and long-chain PFAS, including 84.26 mg/g for PFBA, 214.37 mg/g for PFBS, 213.76 mg/g for PFOA, and 326.39 mg/g for PFOS, indicating substantially improved affinity relative to conventional adsorbents [69]. These findings suggest that surface functionalization and tailored polymer architectures can partially overcome the weak retention typically associated with short-chain PFAS [69]. However, competitive interactions remain a critical challenge in multicomponent systems. In bisolute conditions, the presence of long-chain PFAS reduced the adsorption capacity of short-chain PFAS on granular activated carbon (GAC) by approximately 30–50% relative to single-solute systems, highlighting competitive sorption dynamics that complicate treatment performance in real waters [70]. Considering the widespread detection of PFAS in the environmental media worldwide, the development of effective and scalable mitigation strategies is increasingly urgent. Current evidence points to four key research priorities: advancing technologies specifically tailored to short-chain PFAS, designing multi-barrier treatment systems that integrate capture and destruction processes, managing PFAS-containing residuals to prevent secondary pollution, and developing cost-effective solutions for small community water systems [71]. Addressing these priorities will be essential for sustainable PFAS treatment.

4. Fundamentals of Phytotechnology for PFAS Contaminant

4.1. Overview of Phytotreatment Mechanisms of PFAS in Soil–Plant Systems

In soil–plant systems, PFAS phytotreatment involves a series of interconnected processes: contaminant partitioning in soil and pore water, root uptake, internal translocation, compartment-specific accumulation, and eventual retention in root tissues or partial concentration via harvestable biomass. Brusseau et al. [72] noted that PFAS retardation in the subsurface is influenced not only by solid-phase sorption but also by air–water interfacial adsorption and, in some cases, nonaqueous phase partitioning. This comprehensive retention framework is significant because plant uptake is primarily determined by the mobile, bioavailable fraction of pore water, rather than by total soil concentration. Supporting this, Felizeter et al. [73] demonstrated that pore-water concentrations more accurately predicted plant uptake in field crops than bulk-soil concentrations. Wang et al. [74] further observed that PFAS sorption–multiple interacting factors govern desorption behavior at the soil-water interface.

Root uptake is the primary route of PFAS entry into plants, and current evidence suggests that this process involves both passive and transporter-mediated mechanisms [75]. Wang et al. [76] demonstrated that uptake of PFOA and PFOS by *Alisma orientale* is facilitated by active transport through water transporters and anion channels, involving both symplastic and apoplastic movement. More generally, Fawad et al. [77] and Yates et al. [78] observed that PFAS may adsorb to tissues between the root surface and the *Casparian strip* before xylem entry, indicating that a balance among membrane crossing, root-surface retention, and vascular transport governs uptake. This mechanistic understanding accounts for the greater bioavailability and root-to-shoot translocation observed for short-chain PFAS, ether-PFAS, and certain H/F-substituted alternatives, while longer-chain or Cl/F-substituted compounds are more strongly retained in roots [78].

Once PFAS enter the transpiration stream, PFAS distribution among roots, shoots, leaves, and edible organs is strongly influenced by molecular structure and plant species. Reviews by Ghisi et al. [79], Kavusi et al. [80], and Fawad et al. [77] consistently indicate that short-chain PFAS exhibit greater mobility and are more readily translocated to aboveground tissues, whereas long-chain PFAS predominantly accumulate in roots. Sharma et al. [81] found that shorter-chain PFAAs were more concentrated in willow leaves, while long-chain PFAAs accumulated in roots. Similarly, Zhang et al. [82] observed that PFAS uptake by *Juncus effusus* varied with chain length, with limited upward transport for more strongly retained compounds. Wang et al. [76] reported contrasting intracellular partitioning between PFOA and PFOS. At the crop scale, Felizeter et al. [73] confirmed that root retention increased with chain length, while concentration factors for fruit and leaves decreased as chain length increased.

Research in wetland and aquatic plant systems demonstrates that PFAS attenuation involves both plant accumulation and non-plant sinks. Zhang et al. [83] reported that PFAS distribution in aquatic plant-based systems is jointly influenced by soil adsorption, plant uptake, and changes in microbial community structure. Li et al. [84] quantified this interaction, finding that 33.59–88.99% of PFAAs in constructed wetlands could be treated through a combination of sediment sorption, macrophyte uptake, and microbial bioaccumulation, with significant contributions from planktonic microbes, biofilms, and extracellular polymeric substances. Wang et al. [85] observed that industrial and domestic wastewater treatment plants only partially treated PFAAs, and that adjacent aquatic plants in rivers and artificial wetlands accumulated these compounds, particularly the more mobile short-chain homologs. Qian et al. [86] further demonstrated that PFAS exposure can alter microbial function in constructed wetlands, suggesting that both plant uptake and PFAS-induced changes in wetland biogeochemistry influence treatment performance. Collectively, these findings indicate that PFAS phytotreatment should not be conceptualized solely as phytoextraction. In many soils, extraction rates are relatively low [87]. For example, Gobelius et al. [88] estimated plant-mediated treatment at a contaminated fire-training site to be only about 1.4 g Σ26 PFAS/ha·yr under optimal conditions.

Recent reviews increasingly characterize PFAS plant-based treatment as phytomanagement rather than rapid cleanup. In this context, phytomanagement refers to the strategic use of plants and associated rhizosphere processes to control the mobility, bioavailability, and exposure risks of PFAS, rather than achieving complete removal or mineralization. Due to the extreme persistence of PFAS, driven by the strength of the carbon–fluorine bond, plant-based systems are generally unable to fully degrade these compounds. Instead, phytomanagement focuses on stabilizing PFAS within the soil–plant system, reducing leaching to groundwater, limiting off-site transport, and regulating their transfer into biota. This is achieved through a combination of mechanisms, including root uptake and partial accumulation, rhizosphere sorption, microbial sequestration, and vegetation cover to control hydrological fluxes and erosion. In this framework, plants function not only as uptake agents but also as regulators of contaminant fate and exposure pathways. Consequently, phytomanagement represents a long-term, risk-based approach that integrates plant selection, soil amendments, and rhizosphere engineering to mitigate PFAS impacts while maintaining ecosystem functionality. Evangelou and Robinson [28] suggested that low-accumulating timber or non-food vegetation may be preferable to edible crops for limiting exposure on PFAS-contaminated land. Renella et al. [89] emphasized that risk mitigation in agricultural areas may require integrating plant cover, rhizosphere filtering, and amendments such as PFAS-free biochar. Similarly, Zhang and Liang [90] demonstrated that adding sorbents to biosolids-amended soils can substantially reduce PFAS bioavailability to plants, while surfactant-induced mobilization may enhance uptake and facilitate

assisted phytoextraction. Thus, the most accurate mechanistic perspective is that PFAS phytotreatment in soil–plant systems encompasses a continuum from phytoextraction and phytoaccumulation to phytostabilization and amendment-assisted phytomanagement. The main mechanisms involved in PFAS phytotreatment are summarized in Table 4.

Table 4. Overview of PFAS phytotreatment mechanisms, influencing factors, and effectiveness across plant-based systems.

Mechanism	Process Description	Influencing Factors	Example Species	Effectiveness for PFAS	Key References
Phytoextraction	PFAS are taken up by plant roots from soil pore water and translocated to aboveground tissues through the transpiration stream, allowing partial contaminant removal through biomass harvesting.	PFAS chain length, functional group, pore-water bioavailability, transpiration rate, plant species, soil properties, soil–water sorption behavior	*Salix* spp., *Juncus effusus*, *Alisma orientale*, field crops	Low to moderate; generally, more effective for short-chain and more mobile PFAS, but overall field-scale treatment remains limited	[73,81,88]
Phytoaccumulation	PFAS accumulate within plant tissues after uptake, either in roots or shoots, depending on compound properties and plant species. This mechanism emphasizes contaminant storage in biomass rather than rapid site cleanup.	Molecular structure, carbon-chain length, xylem mobility, root tissue affinity, interspecific variation	*Salix* spp., *Alisma orientale*, wetland plants, agricultural crops	Moderate for biological retention and monitoring purposes; accumulation can be substantial for certain PFAS, but does not necessarily indicate efficient treatment	[77,79,80]
Phytostabilization	Plants reduce PFAS mobility by retaining contaminants in the root zone or soil matrix, thereby limiting leaching, off-site migration, or transfer into edible plant parts while maintaining vegetative cover on contaminated land.	Soil sorption capacity, organic matter, soil texture, PFAS type, root architecture, vegetation type, hydrological conditions	Non-food vegetation, woody species, permanent cover plants	Moderate to high for risk reduction and mobility control, especially for long-chain PFAS that are more strongly retained in roots and soil; low for total mass removal	[28,78,89]
Rhizofiltration/ Rhizosphere retention	PFAS are retained around roots through adsorption to root surfaces, biofilms, root exudates, and rhizosphere compartments. This mechanism is especially relevant in wetland, saturated, or soil–water interface systems.	PFAS concentration in pore water, root exudates, microbial biofilms, pH, ionic strength, redox conditions, flooding regime	*Alisma orientale*, submerged macrophytes, constructed wetland plants	Moderate for reducing the mobile and bioavailable PFAS fraction, particularly in aquatic or wetland systems; not a destructive mechanism	[76,84,91]
Phyto-microbial sequestration	PFAS are retained within plant–microbe systems through accumulation in microbial biomass, biofilms, and extracellular polymeric substances (EPS), shifting contaminant distribution into rhizosphere-associated compartments.	Microbial community structure, EPS production, plant species, oxygen conditions, hydrology, PFAS exposure level	Constructed wetlands, aquatic macrophytes, contaminated rhizosphere systems	Moderate for local immobilization and attenuation; useful for reducing mobility and exposure, but not for complete mineralization	[83,84,86,92]

4.2. Rhizosphere Processes and Plant–Microbe Interactions

The rhizosphere serves as a critical control zone for PFAS behavior by mediating interactions among roots, soil solution, sorption surfaces, and microbial communities. Fawad et al. [77] emphasized that PFAS uptake and bioaccumulation are intrinsically linked to rhizosphere sorption dynamics, plant physiological barriers, and microbial processes. Liu et al. [92] demonstrated that PFAS contamination directly affects both plant roots and rhizosphere bacteria, with toxicity influenced by carbon chain length, contamination level, and exposure duration. Their experiments revealed that PFAS bioaccumulation in roots increased with higher contamination intensity and longer exposure, while both short-term and long-term exposures altered root antioxidant systems and physiological metabolism. These results suggest that PFAS effects in the rhizosphere originate with root-level stress responses and subsequently lead to microbial community restructuring.

Rhizosphere microbial responses under PFAS stress are not static. Liu et al. [92] found that single- and mixed-PFAS contamination altered microbial diversity, community composition, and interspecies interactions, and identified *Sphingomonadaceae* and *Rhizobiaceae*

as groups with potential relevance to phyto-microbial treatment. In aquatic macrophyte systems, Li et al. [84] similarly reported that PFAS exposure reduced microbial richness while increasing the relative abundance of certain strains, including *Betaproteobacteriales*, *Sphingomonadales*, and *Cytophagales*. Zhang et al. [83] also showed that PFAS contamination in aquatic plant-based systems altered microbial community structure while PFAS mass remained distributed across sediment, plants, and microbial fractions. Together, these studies support the view that PFAS-contaminated rhizospheres undergo ecological filtering, in which tolerant taxa are enriched while more sensitive members decline.

Hydrological fluctuations introduce additional complexity to PFAS dynamics. Shi et al. [91] showed that alternating submergence and emergence significantly increased PFAS transport and root bioaccumulation compared to continuously submerged or emerged conditions. The study also found that such hydrological alteration altered PFAS partitioning by increasing organic acids and carbohydrates in root exudates while decreasing lipids, and shifted rhizosphere microbial communities toward *Patescibacteria*, *Thermodesulfobacteriota*, and *Sphingomonas*. It was also revealed that hydrological alternation strengthened interactions between root exudates and rhizosphere microbes, suggesting that PFAS stress under fluctuating water regimes can reorganize the rhizosphere into a more integrated plant–microbe response system. This phenomenon is particularly relevant for wetlands, riverbanks, and intermittently flooded soils, where redox oscillations and water-level changes may enhance PFAS mobility.

Mechanistically, rhizosphere microorganisms can influence PFAS fate even when complete degradation of terminal PFAS is limited. Li et al. [84] emphasized the roles of microbiota, biofilms, and extracellular polymeric substances in PFAS retention within constructed wetlands, while Zhang et al. [83] observed PFAS redistribution in conjunction with microbial community changes in aquatic plant systems. These results align with Kavusi et al. [80], who argued that PFAS phytotreatment primarily involves bioaccumulation and redistribution rather than full mineralization. Additionally, Zhang et al. [93] reviewed precursor biotransformation, suggesting that microbial and plant-associated systems may contribute to the transformation of certain PFAS precursors, even though cleavage of terminal perfluoroalkyl acids remains challenging.

Consequently, recent management-oriented literature increasingly prioritizes rhizosphere engineering over plant uptake alone. Evangelou and Robinson [28] proposed phytomanagement strategies that integrate vegetation selection with soil conditioners to limit PFAS mobility and exposure. Renella et al. [89] argued that rhizosphere amendments can function as in situ filters, while Yates et al. [78] emphasized that effective risk mitigation requires understanding how PFAS molecular structure influences soil bioavailability, root retention, and translocation to edible tissues. Thus, plant–microbe interactions in PFAS-contaminated soils are valuable not only for contaminant uptake, but also for buffering stress, modifying PFAS bioavailability, supporting sequestration, and reducing transfer into the food web.

Overall, plant–microbe interactions in PFAS-contaminated systems should be interpreted as a coupled adaptive response. Roots alter PFAS availability through uptake, exudation, and rhizosphere chemistry, while microbes alter PFAS behavior through sorption, ecological selection, and possible precursor transformation [25]. Therefore, the most promising future direction is not stand-alone phytoextraction, but integrated phyto-microbial management that combines plant selection, rhizosphere microbiome support, sorptive amendments, and safe biomass handling.

4.3. Phytoextraction vs. Phytostabilization for Recalcitrant Compounds

Phytoextraction and phytostabilization are two distinct phytotreatment strategies used to manage soils contaminated with recalcitrant compounds, including heavy metals and persistent organic pollutants such as pesticides, dyes, and pharmaceuticals. These contaminants resist transformation due to their low solubility, low volatility, and complex chemical structures. The key difference between the two approaches lies in their objective: phytoextraction aims to remove contaminants from the site through plant uptake and harvesting, whereas phytostabilization focuses on immobilizing contaminants within the soil–plant system to prevent their spread.

Phytoextraction, also referred to as phytoaccumulation, involves the uptake of contaminants by plant roots followed by their translocation and accumulation in aboveground tissues such as stems and leaves. Contaminants are removed from the site when the biomass is harvested. This method is particularly effective for metals and provides an additional opportunity for resource recovery through phytomining, in which harvested biomass is processed (e.g., by incineration) to recover valuable elements. However, its effectiveness depends on plant uptake capacity, contaminant bioavailability, and biomass production.

In contrast, phytostabilization, also known as phytosequestration, does not aim to remove contaminants but to reduce their mobility and bioavailability. This process involves root uptake, adsorption onto root surfaces, and the release of plant-derived compounds that promote contaminant precipitation, complexation, or immobilization in the rhizosphere. Phytostabilization is particularly effective for controlling contaminant migration, reducing leaching into groundwater, and preventing off-site transport. In addition, vegetation cover stabilizes soil structure, reduces erosion, and limits contaminant dispersion through enhanced transpiration [94].

The two strategies differ significantly in terms of performance and application. Phytoextraction enables gradual contaminant uptake but requires long timeframes and careful biomass management. In contrast, phytostabilization provides faster risk reduction by limiting contaminant mobility, but it does not reduce the total contaminant mass. Enhancing phytoextraction often involves increasing contaminant bioavailability with chelating agents such as EDTA; however, EDTA is poorly biodegradable and poses risks of phytotoxicity and groundwater contamination. As a result, biodegradable alternatives such as citric acid are preferred due to their lower environmental risk [95,96].

For PFAS-contaminated systems, these differences become more pronounced. PFAS are relatively soluble and mobile, particularly short-chain compounds, making them more amenable to phytoextraction [97,98]. Once taken up, PFAS are transported via the transpiration stream and distributed across plant tissues depending on molecular structure and plant species [98]. Short-chain PFAS exhibit higher mobility and are more readily translocated to shoots, whereas long-chain PFAS are more hydrophobic and tend to remain associated with root tissues or soil particles [99,100]. Consequently, phytoextraction is generally more effective for short-chain PFAS, while phytostabilization is more relevant for long-chain PFAS that are strongly retained in soils.

PFAS uptake by plants occurs through both passive and active mechanisms. Passive uptake is driven by transpiration and favors smaller, more mobile compounds, whereas active uptake involves membrane transporters, such as ion channels, that facilitate the movement of ionized species. In addition, aerial uptake through leaves and bark has been reported. Plant species with high biomass and extensive root systems, such as trees and wetland plants, generally exhibit greater uptake capacity, although performance varies by PFAS type [101,102]. Experimental studies further illustrate these dynamics. Zhang et al. [82] reported that *Juncus effusus* showed increased uptake of perfluoroalkyl acids (PFAAs) with increasing exposure concentrations, with short-chain compounds more readily translocated

to shoots. Tang et al. [103] identified species such as red fescue, black willow, and Japanese oak as effective accumulators. Field-scale observations by Yin et al. [104] demonstrated PFAS uptake efficiencies of up to 96% in a tropical wetland system, largely driven by plant uptake and sorption processes. However, practical implementation requires safe handling and treatment of contaminated biomass.

Mechanistic studies also highlight the importance of molecular structure. Zhang et al. [99] showed that PFAAs transport in wheat is an active, energy-dependent process influenced by carbon chain length, with short-chain compounds preferentially accumulating in shoots. Studies on aquatic plants such as *Potamogeton crispus* and *Nelumbo nucifera* indicate a high capacity for bioaccumulation [85]. In agricultural systems, PFAS uptake by crops such as corn and wheat is typically concentrated in non-edible tissues, such as straw and husks, rather than in grains. Nevertheless, the use of food crops for treatment is generally discouraged due to the risk of PFAS transfer into the food chain [103].

A critical limitation of the current PFAS phytotechnology literature is the lack of comprehensive quantitative mass-balance assessments under field conditions. Most studies focus on PFAS concentrations in soils or plant tissues and report uptake factors, translocation factors, or treatment efficiencies, while comparatively few quantify the complete distribution of PFAS among soil, pore water, groundwater, vegetation, leachate, and other environmental compartments over time [82,101,102]. Consequently, the long-term fate of PFAS retained within vegetated systems remains poorly resolved. Although plant uptake and rhizosphere processes can reduce contaminant mobility and lower groundwater exposure risks [104], it is often unclear whether PFAS are permanently sequestered within biomass and soil matrices or merely experience delayed transport through hydrological systems. In many cases, vegetation may function primarily as a hydrologic retardant, slowing contaminant migration by intercepting water fluxes, promoting rhizosphere retention, and reducing leaching rates [105]. Furthermore, harvested biomass represents a secondary PFAS reservoir [77] that requires appropriate management to prevent re-release into the environment (Discussed in Section 8.3).

Overall, phytoextraction and phytostabilization should be viewed as complementary strategies rather than competing approaches. Phytoextraction is more suitable for removing mobile contaminants, particularly short-chain PFAS, while phytostabilization is more effective for controlling the spread of strongly sorbed compounds. Given the persistence of PFAS, phytotreatment is best applied as a long-term management strategy. Future research should focus on identifying high-biomass, non-food plant species with enhanced uptake capacity and integrating these strategies into optimized phytomanagement systems [98].

4.4. Role of Plant Enzymes in Pollutant Transformation

Plant-derived enzymes play a central role in phytotreatment by driving the transformation of environmental contaminants through a range of biochemical processes. In the context of PFAS, enzymatic activity is primarily associated with oxidative transformation pathways, where enzymes produced by plants and their associated microorganisms facilitate the partial breakdown of these highly persistent compounds [106]. Key enzymatic groups involved include oxidoreductases such as laccases [107], peroxidases [108], and cytochrome P450 enzymes [109], which contribute to the transformation of PFAS precursors and, to a limited extent, PFAAs. However, despite these capabilities, the complete degradation of highly stable PFAS compounds such as PFOA and PFOS remains a significant challenge due to the strength of the carbon–fluorine bond [110].

Oxidative enzymes, particularly peroxidases and laccases, are among the most extensively studied in PFAS transformation. These enzymes function by generating reactive radical species through redox reactions, often mediated by co-substrates or electron

donors [107]. For example, horseradish peroxidase (HRP) catalyzes reactions in the presence of hydrogen peroxide and organic mediators such as 4-methoxyphenol, producing highly reactive radicals that initiate the decarboxylation of PFOA [111]. This process leads to the formation of shorter-chain intermediates and partial degradation of the parent compound. Experimental studies have demonstrated that HRP-mediated systems can achieve up to 68% PFOA transformation within a short time frame [112]. However, this transformation is typically accompanied by very low defluorination efficiency (<1%), indicating that the fluorinated backbone largely remains intact and may result in the formation of equally persistent or more mobile by-products.

Laccases, which are multi-copper oxidases widely distributed in plants, fungi, and bacteria, have also shown potential for PFAS transformation. Unlike peroxidases, laccases use molecular oxygen as the electron acceptor, producing water as the only by-product, making them more suitable for environmentally relevant applications [107]. In laccase-mediated systems, transformation typically occurs via indirect oxidation, in which reactive radicals generated by mediators such as 1-hydroxybenzotriazole (HBT) attack PFAS molecules [111]. Studies have reported transformation efficiencies of up to 59% for PFOS and partial defluorination under optimized conditions [107]. The presence of metal ions such as Fe^{3+} and Cu^{2+} can further enhance transformation by acting as ionic bridges that reduce electrostatic repulsion between negatively charged PFAS molecules and enzyme active sites, thereby improving reaction efficiency.

In addition to oxidative enzymes, other enzymatic systems contribute to PFAS transformation, particularly in the metabolism of precursor compounds. Cytochrome P450 enzymes are involved in Phase I metabolic reactions, facilitating the oxidation of fluorotelomer alcohols (FTOHs) to intermediates. Similarly, dehydrogenases such as alcohol dehydrogenase (ADH) and aldehyde dehydrogenase (ALDH) catalyze the oxidation of PFAS precursors into more stable forms. Phase II detoxification processes are mediated by enzymes such as glutathione-S-transferase (GST), which conjugates PFAS metabolites with glutathione, thereby enhancing their detoxification and cellular tolerance [111,113].

Rhizosphere processes further enhance enzymatic transformation through interactions among plant roots, microorganisms, and soil chemistry. Root exudates, including low-molecular-weight organic acids such as citric and malic acids, stimulate microbial activity and enzyme expression in the rhizosphere, thereby increasing the potential for PFAS transformation. This plant–microbe synergy creates a reactive microenvironment that facilitates contaminant transformation, although the extent of PFAS degradation remains limited [111].

Despite growing interest in enzymatic and rhizosphere-mediated PFAS transformation pathways, current evidence suggests that biologically driven transformation of terminal perfluoroalkyl acids (PFAAs), including PFOS, PFOA, PFHxA, and PFBS, remains extremely limited [114,115]. Although oxidative enzymes such as laccases, peroxidases, and other redox-active biocatalysts may facilitate the transformation of certain PFAS precursors or influence contaminant speciation indirectly, their capacity to cleave carbon–fluorine bonds within terminal PFAAs is severely constrained by the exceptionally high C–F bond dissociation energy [106]. Consequently, reported biological defluorination rates for terminal PFAAs are typically negligible, often below 1% under environmentally relevant conditions [116]. Most observed reductions in PFAS concentrations within plant-based systems are therefore attributed to uptake, sequestration, sorption, dilution, or redistribution rather than true mineralization.

4.5. Selection Criteria for PFAS Phytotreatment Plants

Environmental contamination by PFAS often involves the simultaneous presence of multiple compounds, which is why most phytotreatment investigations are designed to address multiple PFAS simultaneously. A common unit used to assess the effectiveness of plants in binding contaminants is the treatment efficiency, defined as the ratio of the mass of PFAS bound in plant tissue to the initial mass of PFAS present in the soil [25,117]. Certain specific factors measure the capacity of plants to absorb, transport, and store PFAS. These factors, such as the bioaccumulation factor (BAF) or bioconcentration factor (BCF), are calculated by comparing the amount of a contaminant in plant tissues with that in the surrounding environment, such as soil or water. Another important measure is the translocation factor (TF), which is determined by comparing the concentration of a contaminant in the plant's above-ground parts to its concentration in the roots. A TF value higher than 1 indicates that the plant can not only withstand PFAS exposure but also transport the compounds to its above-ground parts, a characteristic often seen in hyperaccumulator plants [118–120].

Successful treatment of PFAS using plants depends on identifying species that can take up large amounts of these chemicals and store them in easily harvested plant parts. Screening has been conducted on various plant types, including farm crops, trees, and plants found in wetlands and other water areas. The main factors considered for selection are bioaccumulation potential [118,119], biomass production [121,122], resistance to PFAS [120,123], ease of harvest [28], and the structure and depth of its root system [124] (Table 5).

Table 5. Key criteria for selecting plants for PFAS Phytotreatment.

Selection Criteria	Brief Explanation	Example Species	References
Bioaccumulation potential (BCF, RCF, SCF, TF) *	Ability of plants to absorb and translocate PFAS into root, stem, and leaf tissues.	Wheat (*Triticum aestivum*), Alfalfa (*Medicago sativa*)	[118,119]
Biomass production	High-biomass plants can uptake greater total PFAS mass.	*Phragmites australis*, *Typha latifolia*	[121,122]
Tolerance to PFAS	Ability to grow in contaminated environments without significant phytotoxicity.	Poplar (*Populus* spp.), Willow (*Salix* spp.)	[120,123]
Harvestability	Ease of harvesting and managing PFAS-contaminated biomass.	Food crops (maize, wheat)	[28]
Root architecture and depth	Root depth and architecture determine access to PFAS in different soil layers.	*Oenothera rosea*, Wetland grasses (*Carex* spp.)	[124]

* BCF = bioconcentration factor, RCF = root concentration factor, SCF = shoot concentration factor, TF = translocation factor.

Despite growing attention to PFAS-related environmental pollution, evidence of PFAS accumulation in hyperaccumulator plants has not yet been established, unlike for metal contamination [87]. Since PFAS differ markedly from organic contaminants [125], the accumulation of PFAS in plants depends mainly on their physical and chemical properties and on water transport through plants rather than on active cellular processes [126,127]. The bioaccumulation factors of PFAS by different plant species vary significantly, according to a recent review paper by Xu et al. [127], ranging from 0.002 in maize grain to 488.67 in lettuce.

The selection process for PFAS-accumulating plants must focus on criteria based not only on PFAS properties but also on plant species. The fact that short-chain PFAS can reach aboveground plant tissues, while long-chain compounds remain in roots due to their

strong chemical bonds with cell walls and organic matter, shows that accumulation levels depend heavily on PFAS properties. However, recent studies suggest that species with high transpiration rates, dense root systems, and chemical resistance will uptake more PFAS over time, regardless of carbon chain length [75,119,128]. The extensive surface area of plants with fine, fibrous root systems enables greater PFAS absorption and improved contact between roots and rhizosphere microorganisms, while their xylem system efficiently transports mobile compounds to the upper parts of the plant [75,129]. Furthermore, fast-growing grasses and herbaceous species exhibit better mass-balance performance than woody plants because they produce biomass at a faster rate, enabling more effective contaminant treatment through rapid regeneration [130]. Nevertheless, high-level PFAS exposure causes stress responses that reduce photosynthetic output and alter nutrient absorption patterns in vulnerable species [131,132].

5. Mechanistic Insights into Plant–PFAS Interactions

5.1. Phytofiltration in Water Systems

Phytofiltration uses plant roots and whole plants to trap and hold pollutants. Recently, its application in the treatment of PFAS-contaminated surface water, groundwater, and industrial effluents has attracted increasing attention [87]. Unlike soil phytotreatment, phytofiltration systems are commonly hydroponic or semi-hydroponic, in which plant roots remain consistently exposed to contaminated water [102]. This technique increases mass transfer toward the rhizosphere and allows better operational control over hydraulic residence time (HRT), thereby enhancing contaminant–root contact efficiency and improving overall pollutant treatment performance [133].

The available evidence indicates that PFAS reduction in phytofiltration systems depends on PFAS physical and chemical characteristics, which influence plant root absorption and root surface adsorption [127]. The short-chain perfluoroalkyl acids, perfluorobutanoic acid (PFBA) and perfluorohexanoic acid (PFHA), are relatively mobile because they can freely pass through water. They lack a strong affinity for mineral surfaces; in contrast, long-chain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorodecanoic acid (PFDA), exhibit strong binding properties that enable them to interact strongly with organic matter and root-associated microbial communities [119,126,134].

In addition to PFAS characteristics, rhizosphere activities, including root exudation, biofilm formation, and plant-microbial associations, have been reported to influence PFAS availability and uptake, thereby affecting phytofiltration performance [87,102,127]. Research on hydroponics demonstrates that PFAS can accumulate in plant roots during brief periods, ranging from several days to multiple weeks, depending on the plant type and test environment [100,135,136]. A study by Wu et al. [137] shows that the release of root exudates may stimulate microbial growth and biofilm development, thereby increasing the surface area available for PFAS absorption via hydrophobic and electrostatic interactions [138]. The phytofiltration mechanisms of PFAS are illustrated in Figure 2.

5.2. Root Uptake Pathways of PFAS

The primary pathway of PFAS from soil into plants is via root uptake by passive diffusion and facilitated transport. Initially, dissolved PFAS in soil pores will move toward the rhizosphere via the PFAS concentration gradient and, to a significant extent, via the water potential gradient generated by transpiration [139]. This process is regulated by soil constituents, particularly soil organic matter (SOM) and mineral surfaces, which can sequester PFAS through hydrophobic interactions, electrostatic forces, hydrogen bonding, and cation bridges [140]. This statement is supported by Mei et al. [119], which highlights

the hypothesis that elevated SOM content typically leads to greater PFAS binding and reduced root uptake.

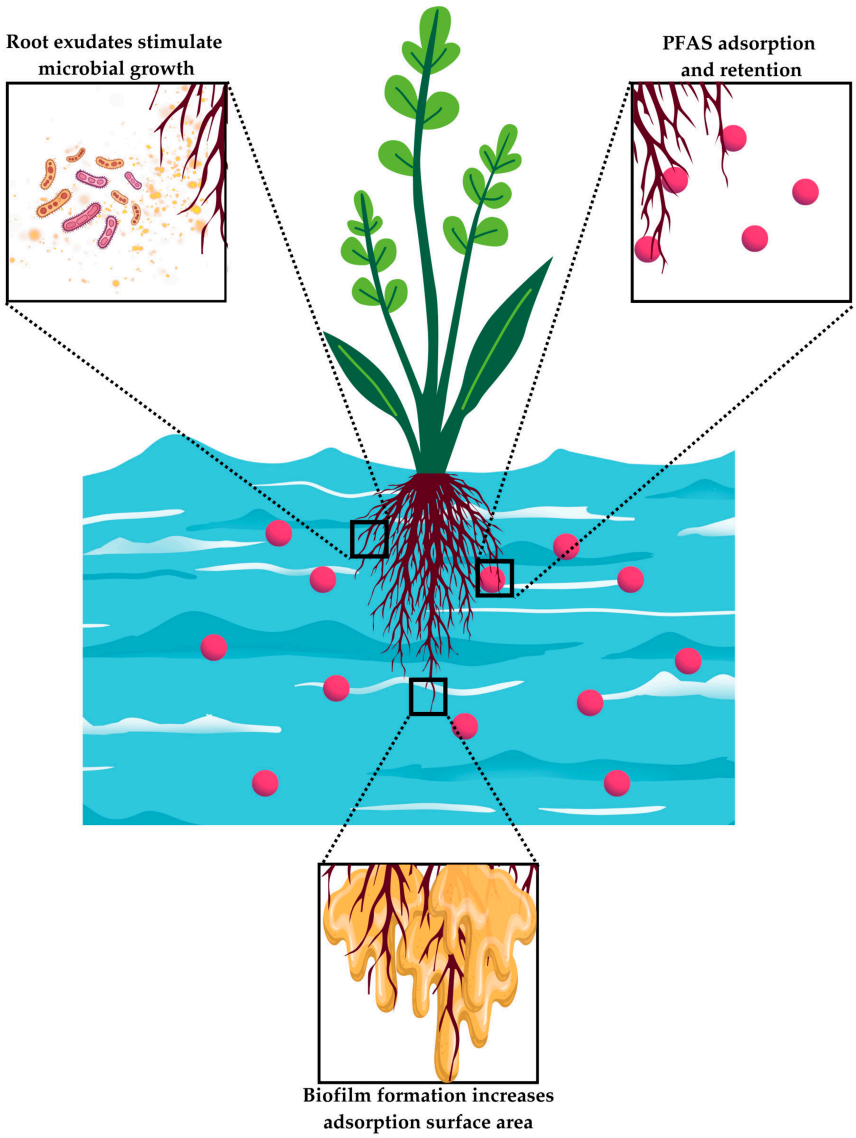


Figure 2. Phytofiltration mechanisms of PFAS by aquatic plants.

Once at the root surface, PFAS will be transported into vascular tissue via apoplastic, symplastic, or transmembrane pathways, involving passive diffusion and energy-dependent transport via carrier proteins, anion channels, or aquaporins. Apoplastic pathways enable the movement of PFAS through the cell wall matrix and intercellular spaces without crossing the plasma membrane [141]. However, these pathways are obstructed by a suberized barrier known as the Casparian strip, which forces solutes to cross the plasma membrane before entering the stele rather than entering directly. In contrast, the symplastic pathway facilitates the bypass of molecules across the barrier once the solute enters the cytoplasm [142]. The transmembrane pathway generally involves active transport, like in wheat and maize [139,143].

Within root tissues, significant retention of PFAS occurs in the cell wall, with pectin and hemicellulose via hydrogen bonding and electrostatic interactions. For example, as reported by [124], over 50% of PFAS accumulation occurs within the root tissue of *Oenothera rosea*, which highlights the role of cell wall binding in controlling the mobility of PFAS and root-to-shoot translocation. However, root lipids have a high potential to hinder translocation due

to their hydrophobic nature. Long-chain PFAS tend to accumulate in lipid-rich roots rather than entering the xylem stream. This accumulation will reduce root-to-shoot movement, thereby limiting PFAS translocation to aerial plant tissue [119,124].

5.3. Translocation from Root to Shoot

The transport of contaminants from root tissue to aerial plant compartments, including stems, leaves, and edible organs, is mediated through vascular systems, especially the xylem [127,144]. However, this process is strongly influenced by the physiological characteristics of plants and the properties of PFAS. After uptake by the root, PFAS are transported toward the stele and loaded into the xylem via transpiration-induced water flow. During transpiration, the continuous mass flow of water from the root to the shoot generates a negative pressure gradient that facilitates the movement of dissolved PFAS toward aerial tissue [145]. Dissolved PFAS in the xylem sap will be transported along with the transpiration stream towards aerial tissue, where a higher transpiration rate often results in greater contaminant accumulation in shoots [146].

However, root-to-shoot translocation depends on the balance between vascular transport and root sequestration processes [127]. Some compounds that remain mobile within xylem sap are more easily transported compared to compounds with a stronger affinity toward root binding. The extent of translocation is commonly determined using the translocation factor (TF), which represents the ratio of PFAS concentration in shoots to that in roots, where a higher TF value indicates efficient transfer to aerial tissue [139,147].

5.4. Influence of Chain Length and Functional Groups

The mechanism of PFAS absorption within a plant system is significantly influenced by PFAS properties, such as carbon chain length and functional group composition [145]. These properties influence the movement of PFAS from root to shoot through aqueous solubility, sorption affinity, and interactions with plants and soil. Generally, short-chain PFAS exhibit higher water solubility while having lower sorption toward SOM and root tissues [140]. This enhances the mobility of PFAS and efficient transport via xylem to aerial tissue. In contrast, long-chain PFAS exhibit higher hydrophobicity and stronger affinity for SOM, resulting in greater retention in soils and roots and limiting translocation to shoots [145]. In this phase, the TF value was close to zero, indicating limited translocation. This process is further limited by the Casparian strip that restricts the translocation of long-chain PFAS [146]. This relationship summarizes the impact of chain length on translocation and bioconcentration factors as stated by Xu et al. [127].

Functional group chemistry further modified PFAS behavior in the plant system. PFAS consist of three primary polar functional groups, including carboxylates and carboxylic acid, sulfonates and sulfonic acid, and phosphonate and phosphoric acid [148]. Generally, perfluoroalkyl sulfonic acids (PFSAs) exhibit stronger sorption towards soil and root tissue compared to perfluoroalkyl carboxylic acids (PFCAs). This difference is due to the presence of the sulfonate group, which exhibits strong electrostatic interactions and greater hydrophobicity [149]. Additionally, the branching effect in compound structures could enhance hydrophilicity, mobility, and translocation potential compared with linear isomers. Other than that, fully fluorinated compounds also exhibit stronger repulsion from water and a strong affinity towards hydrophobic domains [140]. Overall, short-chain and carboxylate PFAS are more mobile and readily translocated to aerial tissue, while long-chain and sulfonated PFAS are retained in root and soil matrices.

5.5. Accumulation Patterns Across Plant Species

The accumulation patterns of PFAS across plant species vary due to differences in morphology, physiology, and biomass allocation. This interspecies heterogeneity deter-

mines food safety and the possibility of phytotreatment. The accumulation profile of each plant species depends on the type of tissue and the growth characteristics. Generally, leafy vegetables tend to show the highest PFAS concentration in edible tissues compared to other plant species [77]. This elevated accumulation is linked to the characteristics of plants with rapid growth, large transpiring surface area, and extensive biomass allocation to leaves [150]. These characteristics lead to pollutant enrichment in foliar tissues. In addition, short-chain PFAS often dominate edible leaf tissue due to their higher bioaccumulation factors (BAFs) [77].

In contrast, root vegetables displayed a more heterogeneous pattern with significant PFAS storage in subterranean tissues [77,150]. Even though contaminant uptake is highest in root tissues, rapid root biomass growth can dilute PFAS concentrations in edible portions [127]. As a result, the accumulation in the root is governed not only by contaminant loading but also by growth-biomass partitioning. For example, carrots and radishes are representative of root vegetables that exhibit high uptake through their roots. In addition, cereal crops exhibit comparatively lower PFAS accumulation within the edible grains even though this plant species is exposed to PFAS longer through soil and irrigation [150]. This behavior exposed species-specific partitioning properties, whereby pollutants are preferentially retained in vegetative tissue rather than transmitted to reproductive organs [127]. This variability among cereal species suggests that the internal allocation system affects the distribution of contaminants within the plant, in addition to total intake.

Aside from crops, some woody and aquatic species showed a unique accumulation pattern suitable for treatment applications. Woody species such as willow and poplar exhibit high biomass productivity and PFAS storage capacity [151]. In these cases, PFAS accumulation occurs through biomass expansion despite the concentration alone. Similarly, aquatic macrophytes often accumulate PFAS readily due to direct contact with contaminated water, thereby supporting their role in phytostabilization systems [152].

5.6. Rhizosphere-Mediated PFAS Mobilization

The rhizosphere represents an efficient soil-to-plant interface that regulates contaminant bioavailability before root uptake. The rhizosphere is continuously modified by root activity, microbial interactions, and physicochemical gradients [153]. Beyond chemical effects, root exudates modulate the activity and composition of rhizosphere microbial communities. Microorganisms in this zone respond quickly to exudate-derived carbon sources, leading to changes in community structure, SOM turnover, and metabolic activity [154]. Even though PFAS are mostly resistant to biodegradation, microbial processes significantly influence their fate by altering the redox conditions of the soil, the composition of dissolved organic matter, and the partitioning of contaminants between solid and aqueous phases [155]. These changes can either increase PFAS mobility by increasing solubility or stabilize them by improving sorption.

The combination of root exudates and microbial communities can form an integrated rhizosphere system. Basically, exudates not only stimulate microbial activity but are also transformed by microbes into secondary metabolites [156]. This interaction resulted in spatially diverse microenvironments in which PFAS mobility is continuously regulated at the root-soil interface. As studied by Secomandi et al. [157], fluctuations in hydrological conditions amplified stress in the integrated system by altering exudate composition and microbial diversity.

5.7. Omics Analysis in PFAS Phytotreatment

Researchers have also developed omics analyses to understand the interactions between plants and PFAS (Table 6). This technique offers a comprehensive, holistic view

of the effects of contaminants on physiological, metabolic, and molecular processes [25]. PFAS affect gene expression related to water transport, metabolism, and oxidative stress in genomics and transcriptomics. Research has demonstrated that genes controlling stomatal conductance and xylem conductivity are differentially expressed [79,123,158]. Proteomics analysis reveals that metabolic pathways have been disrupted. Exposure to PFAS leads to modifications in proteins involved in defense mechanisms (such as antioxidant enzymes and stress proteins) [20,132,145]. In metabolomics and ionomics research, PFAS disrupts ion balance (Ca, Mg, and K) and energy metabolism. Analysis of metabolites reveals interference with photosynthesis and respiration pathways [159,160]. According to Marzi et al. [25], omics analysis is a powerful methodology for selecting appropriate species for phytotreatment of PFAS. Research combining AI and machine learning will ultimately be required to forecast PFAS-plant interactions, accelerate large-scale data analysis, and reduce the duration of time-consuming field experiments [161].

Table 6. Omics analysis in PFAS Phytotreatment.

Omics Approach	Key Findings	Implications for Phytotreatment	References
Genomics/Transcriptomics	PFAS exposure alters gene expression related to water transport, stomatal conductance, xylem hydraulic conductivity, and stress response.	Identifies genetic markers for PFAS tolerance and uptake efficiency; supports breeding/engineering of hyperaccumulator plants.	[25,79,139,158]
Proteomics	PFAS induces changes in antioxidant enzymes (SOD, CAT, POD) and stress-related proteins.	Reveals defense pathways activated by PFAS; helps design strategies to enhance plant resilience.	[20,25,145]
Metabolomics	PFAS disrupts energy metabolism, photosynthesis, and respiration pathways.	Highlights metabolic bottlenecks; guides interventions to improve contaminant assimilation.	[25,160,162]
Ionomics	PFAS exposure alters ion balance (Ca, Mg, K, Fe), affecting nutrient uptake and plant growth.	Suggests ionomic profiling as a diagnostic tool for PFAS stress; informs nutrient management in remediation sites.	[25,160,163]
Integrated Omics (Systems Biology)	Multi-omics reveals coordinated changes across genes, proteins, metabolites, and ions under PFAS stress.	Provides holistic understanding of PFAS–plant interactions, enables predictive modeling of uptake and translocation.	[25,161]

5.8. Potential Phytotransformation and Metabolic Limitations

Phytotreatment of PFAS is largely dependent on phytoaccumulation rather than on partial or complete degradation of contaminants. The limited capacity of plants to phytotransform PFAS is largely attributed to the exceptional stability of carbon-fluorine (C-F) bonds, which confer high chemical stability, resistance to enzymatic cleavage, and low reactivity toward the biological oxidation pathway [125]. There are a few studies reported, mainly on PFAS precursors rather than on terminal perfluoroalkyl acids. For example, in wheat, perfluorooctane sulfonamide (PFOSA) undergoes carbon-carbon bond cleavage and partial defluorination, producing shorter-chain transformation products [146]. In woody plants such as willow, changes in mass recovery patterns suggest possible transformation of the precursor into PFOS, with limited precursor conversion occurring during long-term exposure [151].

Other than that, enzymatic processes involved in oxidative stress response may also contribute to PFAS transformation by the production of oxidative enzymes such as laccases and peroxidases [111]. These enzymes often participate in oxidative coupling and decarboxylation, such as horseradish peroxidase (HRP), which has been shown to accelerate the transformation of PFOA into shorter-chain fluorinated chemicals via enzyme-mediated oxidative reactions [164]. However, this type of reaction does not result in complete PFAS degradation, highlighting the biochemical constraints of plant-based transformation systems. Despite this limitation, PFAS exposure causes significant metabolic and physiological disturbances in plants, even at allowable concentrations. This is due to PFAS behavior that disrupts gene expression, protein synthesis, and the plant's metabolic balance by inducing oxidative stress and reactive oxygen species [165]. The stress response will activate the defensive pathways that will further result in growth inhibition as an adaptive response.

In terms of metabolic pathways, PFAS exposure alters energy metabolism, amino acid synthesis, carbohydrate metabolism, and lipid regulation [145]. For example, exposure to PFOA and PFOS in lettuce roots affects multiple processes, such as the tricarboxylic acid cycle and the metabolism of glyoxylate, dicarboxylates, pyruvate, nitrogen, and fatty acids [127]. Furthermore, PFAS also interfere with mineral nutrient balance by altering the concentration of essential elements such as calcium, magnesium, iron, copper, sodium, and molybdenum. This action can impair enzymatic activity and overall physiological performance. Other than that, PFAS exposure can reduce stomatal conductance and increase the vulnerability of the xylem to hydraulic failure, thus affecting water transport efficiency and reducing plant productivity [145].

However, the extent of these impacts depends heavily on the plant species. For example, *Salix* spp. may withstand high concentrations of PFAS with little suppression of growth, whereas for species like *Nicotiana benthamiana*, high PFAS levels can significantly decrease plant biomass [145,166]. In contrast, some hyperaccumulator species, such as *Oenothera rosea,* exhibit adaptive mechanisms, including enhanced PFAS translocation and reduced cell wall remodeling, whereas non-hyperaccumulating populations increase deposition of pectin and hemicellulose in root cell walls to limit contaminant movement to aerial tissues [124].

6. Phytotechnology Applications for PFAS-Contaminated Environments

6.1. Plant Screening and Lab-Scale Treatment Studies

Phytotreatment studies have identified several plant species capable of absorbing PFAS under controlled conditions (Table 7). A study by Hilliard et al. [167] evaluated ten native Pacific Northwest plant species in greenhouse bioswales. Rushes (*Juncus patens*) and dicots (*Achillea millefolium*, *Mahonia repens*) achieved the highest PFAS uptake efficiencies (75–80%), outperforming uncultivated controls. Cultivars of *Salix* spp. (Loden, Wilhelm, Ester) demonstrated robust growth and PFAS absorption in contaminated firefighting soils. Loden showed the highest root accumulation (1500 µg/kg PFAS22), while Ester translocated more PFAS to shoots [168]. Phytoscreening of white willow (*Salix alba*), black poplar (*Populus nigra*), and black alder (*Alnus glutinosa*) revealed species-specific absorption, with white willow leaves containing up to 1800 µg/kg PFAS, dominated by short-chain PFCAs [169]. Research by Gobelius et al. [88] found that birch (*Betula pendula*) and spruce (*Picea abies*) accumulated PFAS in foliage (up to 97 µg/kg), while ground cover plants (*Aegopodium podagraria*, *Phegopteris connectilis*) also showed significant absorption. Greenhouse trials conducted by Huff et al. [117] with 15 species found hyperaccumulation in tall fescue (*Schedonorus arundinaceus*), recovering 42% of PFPeA in shoots. Woody plants such as black willow retained long-chain PFAS in their roots.

Table 7. Screening studies of several plant species for PFAS uptake.

Plant Species	PFAS Type(s)	Initial Contamination	Uptake	Reference
10 native PNW plants (*Deschampsia cespitosa*, *Danthonia californica*, *Juncus patens*, *Scirpus acutus*, *Carex densa*, *Carex obnupta*, *Achillea millefolium*, *Sidalcea*, *Gaultheria shallon*, *Mahonia repens*)	C4–C10 PFCAs, C4–C8 PFSAs, C6–C8 FASAs	Stormwater 1000 ng/L each	Grasses and sedges uptake 72−74%. Rushes/dicots uptake 75–80%; smaller PFAS in shoots, larger PFAS in soil	[167]
Salix spp. (Loden, Wilhelm, Ester)	PFAS4, PFAS11, PFAS22	Soil 93–110 µg/kg; groundwater 350–500 ng/L	Loden roots 1500 and shoot 690 µg/kg PFAS22; Ester shoots 1100 and root 680 µg/kg PFAS22	[168]
White willow (*S. alba* L.), black poplar (*P. nigra* L.), black alder (*A. glutinosa* L.)	23 PFAS	Soil 66–420 µg/kg; eluate 0.18–26 µg/L	White willow leaves up to 1800 µg/kg PFAS; dominated by short-chain PFCAs	[169]
Silver birch (*Betula pendula*), Norway spruce (*Picea abies*), bird cherry (*Prunus padus*), mountain ash (*Sorbus aucuparia*), ground elder (*Aegopodium podagraria*), long beechfern (*Phegopteris connectilis*), and wild strawberry (*Fragaria vesca*).	26 PFAS	Soil 16–160 ng/g; groundwater 1200–34,000 ng/L	Birch leaves 97 ng/g wet weight; spruce needles 94 ng/g wet weight; foliage highest BCFs	[88]
15 plants species (Herbaceous: *Amaranthus tricolor*, *Brassica juncea*, *Cynodon dactylon*, *Esquisetum hyemale*, *Helianthus annus*, *Schedonorus arundinaceus*, *Festuca rubra*, *Trifolium incarnatum*; Woody: *Betula nigra River*, *Fraxinus pennsylvanica*, *Liquidambar styraciflua*, *Liriodendron tulipifera*, *Platanus occidentalis*, *Pinus taeda*, *Salix nigra*)	PFPeA, PFHxA, PFOA, PFBS, PFHxS, PFOS	Irrigation 1 mg/L each PFAS	Tall fescue (*Schedonorus arundinaceus*) recovered 42% PFPeA; woody plants retained long-chain PFAS in roots	[117]

Studies have shown that plant uptake of PFAS is dependent on multiple variables. These factors include PFAS type (long-chain or short-chain), plant biomass, root system, leaf morphology, plant type (herbaceous, woody, grassy, or aquatic), concentration, and exposure duration [25]. Short-chain PFAS, specifically PFBA and PFPeA, are more mobile and easily transported to leaves, whereas long-chain PFAS, such as PFOS and PFDoA, tend to remain in roots [81,117]. A greater biomass will lead to greater overall PFAS uptake, as seen in sunflower and hemp, which had higher total PFAS burdens than mustard due to their larger biomass [162]. Large root systems and wider vascular cylinders in the root system factor enhance PFAS uptake and translocation [170]. The morphology of leaves also affects PFAS uptake in plants. Research by He et al. [163] and Qian et al. [160] found that bigger leaf areas lowered translocation factors (TF), whereas smaller leaf areas raised TF. Factors influencing PFAS absorption also include PFAS concentration and exposure duration. Greater accumulation will result from higher concentrations and longer exposure periods [171].

PFAS uptake varies among plant species, although similar accumulation patterns are generally observed across woody, herbaceous, and wetland plants. PFAS are typically

found at higher concentrations in leaves than in stems or roots, although the extent of accumulation can vary with PFAS type and plant species [25]. Wooded plants have also been investigated for PFAS phytotreatment in polluted soil. Poplar and willow trees are frequently used in phytotreatment procedures because of their quick growth rates and extensive root systems. Greenhouse studies consistently show preferential translocation of short-chain PFAS (C4–C7) to shoots, whereas long-chain homologs (C8–C14) are largely retained in roots. Among investigated tree species, birch and willow exhibit the greatest PFAS accumulation [169]. Birch (*Betula* spp.) accumulates PFAS predominantly in leaves, with short-chain PFCAs dominating tissue profiles due to their greater mobility and bioavailability. The herbaceous species *Oenothera rosea* has been identified as a PFAS hyperaccumulator, exhibiting root-to-shoot translocation factors of 3.07–58.6 across 18 PFAS compounds [124].

Furthermore, studies have used crop growth models to assess PFAS uptake. Lettuce is widely used as a model crop for PFAS uptake studies because of its rapid growth and high water content. Lettuce preferentially accumulates short-chain PFCAs, particularly PFBA and PFPeA [172,173]. Hydroponic studies indicate that long-chain PFAS preferentially accumulate in roots, whereas translocation to shoots is limited. Short-chain PFAS showed higher TF values, indicating greater mobility to edible tissues [172,173]. Research has demonstrated distinct species-specific variations in PFAS uptake between *Solanum lycopersicum* (tomato) and *Phaseolus vulgaris* (French bean). High levels of short-chain PFAS (PFBA, PFBS, and PFPeA) were discovered in the fruits of French bean, whereas longer-chain PFAS (PFNA, PFDA) were retained in the roots. Research on radish, pea, maize, and wheat has shown that tomato plants have lower overall bioaccumulation, with significant uptake limited to PFCAs up to C6. These findings demonstrate that PFAS uptake is governed by both compound chemistry and plant physiology [170,174,175]. Short-chain PFAS are more easily transported to aerial parts, whereas long-chain PFAS tend to accumulate in roots. Carrots, because of their root structure, tend to accumulate greater PFAS concentrations than storage organs such as potatoes and cucumbers [73,129]. To maximize phytotreatment efficiency, Huff et al. [117] suggested that phytotreatment systems combining short-lived herbaceous plants with long-lived tree species could be developed and refined. Several studies of PFAS phytotreatment are summarized in Table 8.

Table 8. Phytotreatment Studies for PFAS.

Plant Species	PFAS Class/Compound	Medium/System	Exposure Concentration	Duration	BAF/BCF	TF	Treatment Efficiency (%)	Scale	Reference
Oenothera rosea	18 PFAS	Contaminated soil	21.1–32.4 ng/g	60 d	3.09–40.5	3.07–58.6	NA	Field	[124]
Hemp (*Cannabis sativa*)	Mixed PFAS	Contaminated soil	1.5 ± 0.9 mg/kg	90 d	1170	NA	0.2–24	Field	[162]
Willow (*Salix* spp.)	Mixed PFAS	Contaminated soil	66–420 µg/kg	1 year	NA	NA	NA	Field	[169]
Poplar (*Populus* spp.)	Mixed PFAS	Contaminated soil	66–420 µg/kg	1 year	NA	NA	NA	Field	[169]
Juncus effusus	PFPA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFOS	Constructed wetland	4.6 mg/L	21 d	NA	Decreased with chain length	11.4	Lab	[82]
Juncus sarophorus	PFHxS, PFOA, PFOS	Constructed wetland mesocosm	10–100 µg/L	180 d	NA	PFHxS > PFOA > PFOS	9–11	Lab	[20]
Phragmites australis	PFOA, PFOS	Floating wetland	10 µg/L	28 d	11.8 (PFOA) 14.8 (PFOS)	3.29 (PFOA) 0.26 (PFOS)	53 (PFOA) 42 (PFOS)	Lab	[176]
Lettuce (*Lactuca sativa*)	PFBA, PFPeA	Hydroponic	10 µg/L	144 h	NA	2.93	NA	Lab	[173]
Tomato (*Solanum lycopersicum*)	PFBA, PFPeA, PFNA, PFDA	Contaminated soil	0.59–30.6 mg/kg	52 d	NA	0.8–50.2	NA	Lab	[174]

Table 8. *Cont.*

Plant Species	PFAS Class/Compound	Medium/System	Exposure Concentration	Duration	BAF/BCF	TF	Treatment Efficiency (%)	Scale	Reference
Maize	PFBA, PFPeA, PFNA, PFDA	Contaminated soil	0.0192–30.8 mg/kg	28 d	NA	0.32	NA	Lab	[174]
Ryegrass (*Lolium perenne*)	Mixed PFAS (AFFF-derived)	Contaminated soil	1.07 mg/kg	45 d	0.2–20	NA	43–84	Lab	[177]
Carex comosa	Ether-PFAS (GenX, ADONA, PFMOBA, PFMOPrA, F-53B)	Contaminated soil	105 µg/kg	92 d	NA	NA	2.2–16	Lab	[178]
Juncus krausii	PFOA, PFOS	Floating wetland	10 µg/L	28 d	4.6 (PFOA) 5.2 (PFOS)	2.65 (PFOA) 0.84 (PFOS)	5 (PFOA) 5 (PFOS)	Lab	[176]
Baumea articulata	PFOA, PFOS	Floating wetland	10 µg/L	28 d	7.2 (PFOA) 8.5 (PFOS)	1.93 (PFOA) 0.63 (PFOS)	29 (PFOA) 24 (PFOS)	Lab	[176]
Phragmites australis	PFBA, PFBS, PFOA, PFOS	Constructed wetland	8.43–34.32 µg/L	5.1 d	NA	NA	61–83.7	Pilot	[179]

NA: Not available.

Among the species evaluated, *P. australis* emerged as one of the most promising candidates for practical applications. In floating wetlands, it achieved treatment efficiencies of 42–53% while maintaining relatively high BAF values and moderate translocation of PFOA. Furthermore, pilot-scale constructed wetlands planted with *P. australis* achieved PFAS reductions of 61–83.7%, substantially exceeding the performance reported for *J. effusus* (11.4%), *J. sarophorus* (9–11%), and *J. krausii* (5%). This superior performance likely reflects not only plant uptake but also the combined effects of extensive root systems, rhizosphere interactions, hydraulic retention, and substrate sorption. The results emphasize that treatment efficiency is influenced by the entire treatment system rather than plant uptake alone.

A comparison of BAF/BCF values and treatment efficiencies further demonstrates that high accumulation does not necessarily translate into high remediation performance. Hemp exhibited the highest reported BAF (1170), indicating strong PFAS accumulation potential, yet field-scale treatment efficiencies remained relatively modest (0.2–24%). Conversely, ryegrass achieved comparatively high treatment efficiencies (43–84%) despite lower BAF values (0.2–20). This discrepancy suggests that biomass productivity, growth rate, harvestability, and contaminant accessibility may be more important determinants of overall PFAS removal than accumulation factors alone. Therefore, relying solely on BAF or TF values may overestimate the practical effectiveness of certain species under field conditions.

Table 8 also highlights the substantial gap between laboratory and field-scale performance. Most studies reporting high TF, BAF, or treatment efficiencies were conducted under controlled hydroponic, greenhouse, or mesocosm conditions. In contrast, field studies involving hemp, willow, poplar, and *O. rosea* generally reported lower or less quantifiable treatment outcomes. This difference likely reflects the influence of soil heterogeneity, PFAS aging, hydrological variability, and reduced contaminant bioavailability under real-world conditions. Consequently, laboratory results should be interpreted as indicators of phytotechnology potential rather than direct predictors of field-scale performance.

6.2. Constructed Wetland for PFAS Phytotreatment

Constructed wetlands (CWs) are engineered ecosystems that mimic natural wetland processes to treat contaminated water. They combine substrate sorption, plant uptake, and microbial transformation to treat pollutants. For PFAS, CWs are considered a promising nature-based solution because they are cost-effective, sustainable, and adaptable for large-scale applications [176,179,180]. Savvidou et al. [180] evaluated the role of CWs as nature-based solutions for PFAS treatment. Key findings of the study showed that, among CW types, free water surface (FWS) wetlands had the highest median PFAS treatment

(64%). Horizontal subsurface flow (HF) wetlands achieved moderate treatment efficiency (46%). Vertical-flow (VF) wetlands showed negligible or inconsistent treatment efficiency (median: 0%). PFAS treatment is primarily driven by substrate adsorption and plant root/rhizosphere interactions. Microbial transformation contributes but remains poorly quantified. Large variability in treatment efficiency, with some systems showing negative removal due to PFAS desorption from sediments.

Table 8 also highlights the significant influence of both PFAS physicochemical properties and plant species on treatment performance in constructed wetland systems. Across all studies, short-chain PFAS exhibited greater mobility and were more readily translocated to aboveground tissues, whereas long-chain compounds, particularly PFOS, were preferentially retained within roots. Species such as *Phragmites australis* and *Juncus sarophorus demonstrated* relatively high uptake capacities, with *P. australis* achieving up to 50% reduction in PFAS mass flow and showing substantial accumulation in roots, stems, and leaves [179]. Similarly, *J. sarophorus* exhibited high tolerance to PFAS exposure and preferential uptake of PFHxS over PFOA and PFOS [20]. These findings indicate that plant selection is a critical design parameter in PFAS phytotechnology, as differences in root architecture, transpiration rates, and contaminant partitioning strongly influence PFAS uptake and distribution within plant tissues.

However, the data also reveal important limitations that constrain the role of constructed wetlands as a standalone PFAS remediation technology. Although moderate PFAS reductions were reported, treatment efficiencies were highly variable among systems and compounds, ranging from negligible removal in some vertical-flow wetlands to a median removal of 64% in free-water surface systems [180]. Furthermore, the dominant treatment mechanisms were substrate sorption and phytoaccumulation rather than contaminant destruction, indicating that PFAS are primarily redistributed within the wetland system rather than permanently eliminated. The accumulation of PFAS in plant biomass also creates secondary management challenges, as harvested biomass may require further treatment to prevent re-release into the environment.

Collectively, these studies demonstrate that constructed wetlands can reduce PFAS concentrations through a combination of substrate retention, plant uptake, and rhizosphere interactions. However, treatment performance is highly compound-specific, with short-chain PFAS exhibiting greater plant translocation and long-chain PFAS showing stronger retention within roots and wetland substrates. Current evidence suggests that CWs function primarily as phytomanagement systems that reduce PFAS mobility and exposure, rather than substantially destroying contaminants. Consequently, long-term performance depends on wetland design, plant selection, hydraulic conditions, and appropriate management of PFAS-containing biomass [176].

6.3. Field-Scale Case Studies

Field application of PFAS phytotechnology should prioritize native plant species because they are ecologically adapted, require minimal maintenance, and are generally compatible with local regulations. Equally important is implementing effective biomass treatment and disposal strategies to prevent the re-release of accumulated PFAS. Compared with laboratory and greenhouse studies, field-scale applications remain limited and are primarily deployed at sites affected by aqueous film-forming foams (AFFFs), landfill leachate, and wastewater discharges (Table 8). In most cases, phytotechnology functions as a risk-management tool rather than a stand-alone remediation technology, with treatment performance strongly influenced by site hydrology, PFAS composition, and system design [180–183]. Furthermore, the scarcity of comprehensive mass-balance studies limits direct comparison of treatment effectiveness across sites.

Constructed and natural wetlands represent the most common field-scale applications. For example, *P. australis* reduced PFAS mass flow by up to 50% in contaminated groundwater in Italy [179], while industrial hemp (*Cannabis sativa*) was used to intercept PFAS-contaminated soils at the former Loring Air Force Base through phytoextraction of short-chain PFAS into aboveground biomass [171]. Field studies also demonstrate that PFAS accumulation in crops is governed primarily by chain length, soil interactions, and plant species. Short-chain PFAS are generally more mobile and readily accumulated in edible tissues, whereas long-chain compounds are strongly retained in soils and roots [73,184]. Notably, greenhouse studies often report substantially higher accumulation than field trials, suggesting that controlled experiments may overestimate phytotechnology performance under realistic conditions.

6.4. Factors Governing the Success of PFAS Phytomanagement

Researchers have also examined the factors that contribute to the success of PFAS phytomanagement. PFAS properties are influenced by factors including chain length, functional groups, and ionic state. Other factors contributing to the issue included soil and environmental conditions (such as soil organic carbon (SOC), pH, moisture levels, and salinity, as well as the presence of contaminants), plant characteristics, and physiological traits (root structure, biomass yield, protein and lipid content, and transpiration rate) [56,79]. Short-chain PFAS, C3–C7, are more soluble in water, less likely to bind to soil, and more easily absorbed and transported by plants. Long-chain PFAS ($\geq$C8) are more hydrophobic, strongly sorbed to soil and root surfaces, and accumulate in roots [56,79]. Functional groups like PFCAs are typically more mobile and accessible to biological systems than PFSAs of the same length. PFSAs, which are larger and more strongly sorbed, limit plant uptake [178,185]. High levels of soil organic carbon increase PFAS sorption, thereby reducing their bioavailability and plant uptake, particularly for long-chain PFAS [185,186]. Soil pH below neutral increases PFAS uptake, especially for long-chain compounds, by reducing the negative charge on soil particles and increasing PFAS mobility [187–189]. High soil moisture and salinity conditions can increase PFAS mobility and plant uptake by influencing transpiration and ionic interactions [163,190]. Moreover, other contaminants, whether organic or inorganic, can compete for sorption sites or impact plant stress responses, thereby affecting PFAS uptake [88]. A study by Liu et al. [191] stated the importance of considering soil heterogeneity and co-contaminant interactions in risk assessment and treatment strategies for PFAS-contaminated sites. Phytotreatment success is also determined by PFAS accumulation and uptake, as previously described, as well as by species-specific traits. Root systems that are deep, fine, and highly branched improve access to PFAS in soil and boost uptake [160,170]. Species with high biomass can take up a larger total PFAS mass even if their tissue concentrations are moderate [162]. The content of root proteins is positively associated with PFAS accumulation, whereas high lipid content may reduce uptake due to hydrophobic partitioning [79,139]. Species that grow quickly and have high rates of water loss exhibit greater PFAS movement to shoots and leaves [163,171].

7. Hybrid and Enhanced Phytotechnology Approaches

Hybrid and enhanced phytotechnology approaches integrate conventional phytotreatment with emerging technologies to strengthen the efficiency and reliability of environmental restoration [192]. These innovative strategies leverage the natural abilities to remediate contaminated environments. In settings burdened by diverse and interacting pollutants, phytotreatment plants often exhibit a limited capacity to address the full spectrum of contaminants present, including a range of approaches to treat soil, wastewater, and air [192]. While certain compounds may be efficiently absorbed or transformed, others

remain largely unaffected, resulting in partial treatment and the continued presence of environmental risks.

7.1. Biochar-Assisted Plant Uptake

Biochar is widely used as an amendment in PFAS phytotechnology because it enhances contaminant retention, improves soil quality, and supports rhizosphere activity. Produced through the thermochemical conversion of biomass under limited-oxygen conditions, biochar possesses a high surface area, porous structure, and abundant functional groups that facilitate the adsorption of a wide range of contaminants [193]. In PFAS-contaminated systems, biochar can reduce contaminant mobility and plant uptake by increasing soil sorption capacity, particularly for short-chain PFAS, thereby functioning primarily as a risk-mitigation rather than a removal strategy [90,194–196].

Beyond contaminant retention, biochar improves soil structure, nutrient availability, and microbial habitat quality, promoting plant growth and rhizosphere activity [193,197,198]. Mechanistically, biochar contributes to treatment through multiple, interrelated pathways. Its porous structure provides abundant sorption sites for contaminants, enabling both immobilization and controlled release processes depending on environmental conditions. This dual role is particularly relevant for PFAS and other persistent contaminants, where strong adsorption can reduce leaching and off-site transport. At the same time, partial desorption may maintain a bioavailable fraction for plant uptake and microbial interaction. In addition, biochar can alter soil physicochemical conditions, such as pH, redox potential, and nutrient availability, thereby influencing contaminant speciation and mobility. The presence of functional groups on biochar surfaces further facilitates electrostatic interactions, hydrophobic partitioning, and π–π interactions with organic pollutants. Beyond sorption, biochar plays a significant role in shaping the rhizosphere environment. It provides a favorable habitat for microbial colonization, enhancing microbial biomass, diversity, and enzymatic activity. This supports the capacity of rhizosphere microorganisms to transform and promotes synergistic plant–microbe interactions. As a result, biochar-amended systems can improve both contaminant stabilization and transformation processes [193,197,198]. The benefits and mechanisms involved in biochar-assisted phytotreatment of PFAS are summarized in Figure 3.

7.2. Plant–Microbial Synergistic Transformation

Plant–microbe interactions, particularly those involving plant growth-promoting rhizobacteria (PGPR), play an important role in enhancing the performance of PFAS phytotechnology. Microorganisms can influence PFAS mobility and bioavailability through biosurfactant production, organic acid secretion, and rhizosphere modification, while simultaneously promoting plant growth and stress tolerance under contaminated conditions [199,200]. Although microbial communities may contribute to the transformation of certain PFAS precursors, evidence for substantial degradation of terminal PFAS compounds remains limited.

Effective phytotreatment relies on strategic management of the rhizosphere to optimize microbial activity and regulate pollutant bioavailability. This includes practices such as co-cropping, which can diversify root exudates and promote beneficial microbial consortia, as well as the application of targeted microbial inoculants to enhance specific functional processes. Manipulating rhizosphere conditions, such as nutrient availability, soil structure, and root exudation patterns, can further strengthen plant–microbe interactions and improve treatment efficiency. The integration of plants and microbes opens significant opportunities for sustainable treatment strategies [102,114,201]. Plant hormones, fertilizers, and the application of phytohormones or nutrients may increase plant biomass and, consequently, total PFAS treatment, though the effects on tissue concentrations are

variable [28,190,202]. The study by Nassazzi et al. [162] concluded that adding supplements, such as nutrients and soil amendments, can significantly improve the growth and PFAS uptake efficiency of short-rotation crops such as sunflower, hemp, and mustard, making them more effective candidates for phytotreatment. Intercropping or rotating with high-uptake species can enhance overall treatment efficiency and site sustainability [88,117]. It is implied that implementing effective management techniques can directly enhance phytotreatment, ultimately helping to reduce or eliminate PFAS pollution in the environment. These approaches contribute to a more dynamic and responsive treatment system in which biological processes are actively guided to enhance contaminant stabilization, transformation, and uptake [199,200].

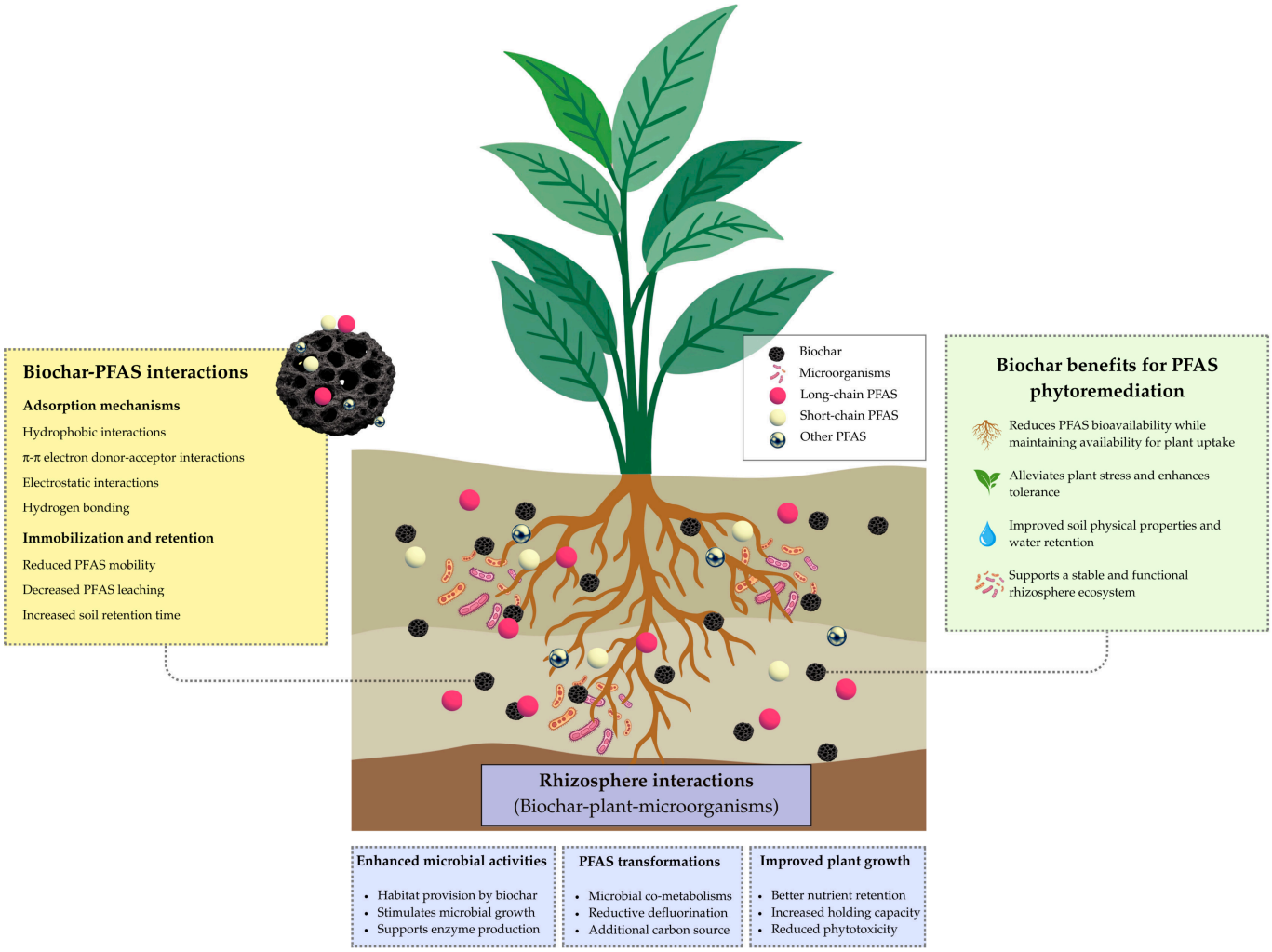


Figure 3. Benefits and mechanisms involved during biochar-assisted PFAS phytotreatment.

7.3. Integration with Engineered Treatment Systems

Combining phytotreatment with engineered systems, such as constructed wetlands, represents an advanced approach to enhancing overall pollutant treatment efficiency. By leveraging both biological and physicochemical processes, hybrid phytotechnology systems can achieve higher treatment performance compared to standalone approaches while maintaining sustainability and low energy requirements [203,204]. Several studies have demonstrated the effectiveness of hybrid phytotechnology systems in real-world applications. For instance, the use of *Eichhornia crassipes* in greywater treatment systems, combined with biochar-based filtration, has shown high treatment efficiencies for a range of contaminants. In such systems, biochar enhances adsorption and supports microbial activity, while

aquatic plants contribute to nutrient uptake and contaminant assimilation. This combined approach creates a synergistic treatment process in which physical filtration, chemical adsorption, and biological uptake operate concurrently [197,205].

8. Limitations and Environmental Risk

Although phytotechnology offers a sustainable, nature-based approach to managing PFAS-contaminated environments, its practical implementation is constrained by several technical, environmental, and ecological challenges. Unlike many conventional organic contaminants, PFAS exhibit exceptional persistence and resistance to biological degradation, limiting the effectiveness of plant-mediated destruction processes. Furthermore, the accumulation of PFAS in plant biomass raises concerns about trophic transfer, biomass disposal, and the potential redistribution of contaminants across environmental compartments. The long treatment timeframe, uncertainties surrounding field-scale performance, and the predominance of evidence from controlled laboratory and greenhouse studies further complicate the application of phytotechnology at contaminated sites. Therefore, a critical evaluation of these limitations is necessary to realistically assess the role of phytotechnology as a phytomanagement strategy for PFAS-contaminated systems. The major limitations and environmental risks discussed in this section, including low degradation efficiency, trophic transfer, biomass management challenges, and scalability constraints, are summarized in Figure 4.

8.1. Low Degradation of PFAS Within Plant Systems

Phytotreatment mechanisms depend heavily on the polluted matrix, the plant species, and the characteristics of the contaminants. PFAS have distinct amphiphilic properties and strong carbon-fluorine bonds. This group is widely known to be recalcitrant and resistant to degradation [206]. Plant systems are similarly constrained. PFAS transformation by plants is difficult and inefficient due to the carbon-fluorine bond, which forms three electron pairs around the fluorine atom, thereby shielding the carbon atom [77,123]. Nevertheless, plants can take up PFAS from contaminated sites and accumulate short-chain PFAS in their aboveground tissues, whereas long-chain compounds mainly persist in the rhizosphere [77].

Several studies have shown plants' ability to accumulate PFAS from soil and water [100,117,207]; however, information on PFAS transformation within plant systems remains limited [25,208]. Few phytotransformation studies have shown that enzymes such as peroxidase can catalyze the transformation of perfluorooctanoic acid (PFOA) [209], and that specific plants can enhance the transformation of perfluorosulfonamide (FOSA) to perfluorosulfonic acid (PFOS) in soil [210]. Moreover, Nason et al. [171] observed a decrease in PFAS in hemp plants associated with rhizosphere microbes. Nonetheless, the pathway and whether transformation occurs in plant systems remain indeterminable [208]. This accumulation of PFAS in plant systems seems like a double-edged sword. From an environmental restoration perspective, PFAS accumulation can facilitate the restoration of polluted sites. Still, plants containing PFAS can also be consumed by animals and humans, increasing the risk of transfer to other trophic levels [77].

8.2. Risk of Trophic Transfer

In general, plants used for phytotreatment should be inedible. Still, accumulation in crop plants can also occur due to factors including proximity of agricultural lands to fluorine industries, land application of PFAS-containing biosolids or other media, and irrigation with PFAS-contaminated groundwater [211]. Health and ecological risk assessments are multidisciplinary issues that require collaboration between laboratory data and field studies. Bioaccumulation results are not consistent across studies due to the complexity of factors

influenced by ecological conditions, PFAS biotransformation, and the physicochemical properties of PFAS and environmental matrices. Recommendations for improving trophic transfer studies include expanding the trophic levels examined, identifying precursors involved in biotransformation, and conducting detailed analyses of biotic and abiotic components [212].



Figure 4. Limitations and Environmental Risk of PFAS Phytomanagement.

Standardized methods to detect and quantify PFAS in plant systems are urgently needed, as methodological disparities are among the factors affecting estimates of PFAS bioaccumulation and biomagnification [25,213]. The global average trophic magnification factor (TMF) is 2, meaning that across ecosystems and compounds analyzed, PFAS concentrations are doubled when moving to higher trophic levels [213]. This finding calls for awareness of human health risks, as humans are apex predators in most ecosystems. Policy reforms are required, particularly stricter regulations on PFAS production, systematic testing and monitoring that include historical data on PFAS presence and leaks, and sustainable PFAS-containing waste management [213,214].

8.3. Disposal of PFAS-Loaded Biomass

Close attention needs to be given to the disposal of PFAS-containing materials to prevent further contamination of the environment and other organisms. Traditional waste management approaches include landfilling, wastewater treatment, and incineration. However, landfilling and wastewater treatment generally do not destroy PFAS; instead, they transfer contaminants to other environmental compartments, such as landfill leachate, wastewater effluent, or treatment residuals. Incineration has been proposed as a destruction technology; however, concerns remain regarding incomplete PFAS degradation, formation of fluorinated by-products, operational requirements, and potential emissions of volatile fluorinated compounds under suboptimal conditions [80,214]. Consequently, sustainable management strategies that combine contaminant destruction, waste reduction, and resource recovery are increasingly being explored [25].

In phytomanagement systems, handling PFAS-loaded biomass is a critical challenge because harvested biomass serves as a concentrated reservoir of contaminants. Thermochemical technologies, including pyrolysis and hydrothermal liquefaction (HTL), have been proposed as promising treatment options. Pyrolysis, typically conducted at temperatures between 500 and 700 °C, can convert biomass into biochar and other products while reducing biomass volume [77]. Similarly, HTL operates at temperatures of 250–350 °C and elevated pressures, converting wet biomass into biochar, aqueous products, and biocrude oil without requiring energy-intensive drying [25,215]. Despite these advantages, the effectiveness of both technologies for complete PFAS destruction remains variable and strongly dependent on operating conditions. Recent bench-scale research demonstrated that pyrolysis of PFAS-contaminated biosolids at 600 °C achieved an overall PFAS destruction efficiency of approximately 99.4%, with total PFAS concentrations decreasing from 409.9 ng/g in the feedstock to 0.31 ng/g in the resulting biochar and only trace concentrations detected in bio-oil and scrubber water [216]. This result was obtained under controlled conditions with relatively long gas residence times (10–12 s). HTL also offers a promising pathway for PFAS destruction while simultaneously converting contaminated biomass into valuable products. Under subcritical water conditions (250–300 °C, 2 h), complete degradation of the ether-PFAS compounds GenX and ADONA was achieved in both aqueous media and contaminated cattail biomass. However, degradation efficiency was strongly influenced by PFAS structure; the sulfonated compound F-53B was considerably more resistant, exhibiting only 12.9–33.8% removal in aqueous solution and up to 76.2–100% removal in biomass at 300 °C. The addition of $Ca(OH)_2$ further increased F-53B degradation to 100%, suggesting that alkaline conditions and catalytic constituents within biomass can substantially enhance HTL performance [217].

Incomplete degradation may result in the formation of shorter-chain PFAS, fluorinated intermediates, or volatile organofluorine compounds that require further treatment and emission control. In addition, the distribution of fluorine among gas, liquid, and solid fractions remains insufficiently characterized for many PFAS-contaminated biomass streams, creating uncertainty regarding long-term environmental performance and regulatory acceptance.

Biomass treatment through microbial transformation is also emerging as a greener alternative. Many microbes are adaptive to their environment. It is not surprising that PFAS persistence for decades could trigger surrounding microbes to adapt their metabolism to survive. Some microorganisms have demonstrated the ability to partially degrade PFAS or utilize transformation intermediates, but terminal mineralization of PFAS remains largely unresolved [25]. For example, Pseudomonas strains exhibit fluorine tolerance and produce enzymes to catalyze the transformation and defluorination of various PFAS [218]. Microbial processes often result in partial transformation rather than complete mineralization. Sig-

nificant uncertainties therefore remain regarding treatment times, degradation pathways, scalability, and the management of transformation products.

8.4. Timeframe and Scalability Issues

Evaluating treatment objectives is essential for determining whether phytomanagement for PFAS treatment is the most effective approach. In some cases, phytotreatment might be prohibitively expensive compared to other strategies, for instance, soil washing, due to the relatively long timescale and land value [28]. Extensive research has been conducted to select plants capable of undergoing phytotreatment in a shorter time. Studies have found that plants with higher biomass and growth rates are the most effective at accumulating PFAS due to their higher transpiration rates, which enhance passive translocation within the plant system [25,171,190].

Phytomanagement can be economically beneficial when applied to low-value lands, such as small urban lands and larger former agricultural lands, for which there is minimal economic incentive to develop them. Phytomanagement might also be suitable for areas contaminated by landfill leachate to prevent further spread of PFAS into groundwater [28]. Although the field study showed relatively low treatment efficiency, around 2%, phytotreatment of PFAS can still be optimized. Furthermore, phytotreatment is an effective strategy for the community, as people from diverse backgrounds can work together to address this environmental issue [28].

Despite promising results reported in laboratory and greenhouse studies, the scalability of PFAS phytotechnology remains uncertain because much of the existing evidence originates from simplified experimental systems. Hydroponic and pot-based studies typically employ homogeneous growth media, controlled environmental conditions, and freshly spiked PFAS, which may overestimate contaminant bioavailability and plant uptake compared with field conditions [25,171,190]. In contaminated sites, soil heterogeneity introduces substantial variability in organic matter content, mineral composition, pH, moisture distribution, and microbial activity, all of which influence PFAS sorption and transport [219,220]. Furthermore, PFAS residues at legacy-contaminated sites are often aged, resulting in stronger sequestration within soil matrices and reduced bioavailability compared with freshly introduced contaminants [221]. Another important limitation is preferential flow through soil macropores, root channels, and structural cracks, which can facilitate rapid PFAS migration beyond the active root zone, thereby reducing plant access to contaminants and limiting treatment efficiency [222]. These processes are rarely represented in controlled laboratory systems. Consequently, phytoextraction rates and translocation factors reported under bench-scale conditions may not accurately reflect field performance.

Beyond the limitations associated with contaminant bioavailability and field heterogeneity, the practical feasibility of PFAS phytotechnology is strongly influenced by treatment duration, land availability, seasonal dynamics, and biomass management requirements. Compared with conventional treatment technologies, phytotechnology generally operates over timescales of years to decades rather than months, particularly at sites with high contaminant inventories or deep subsurface contamination [223]. Consequently, large land areas may be required to achieve meaningful reductions in PFAS mobility and exposure, limiting applicability in densely populated or high-value locations.

Seasonal variation further contributes to uncertainty in treatment performance. Plant growth rates, transpiration, root activity, and rhizosphere processes fluctuate throughout the year [224], resulting in temporal variability in PFAS uptake and retention. In temperate climates, periods of dormancy may substantially reduce treatment effectiveness, whereas extreme weather events can alter hydrological conditions and contaminant transport path-

ways. Biomass harvesting also presents operational challenges. Harvesting frequency must balance contaminant removal, plant regrowth, site management costs, and the risk of contaminant redistribution [225]. Excessively frequent harvesting may reduce overall biomass productivity, while insufficient harvesting may allow contaminants to remain within the system or become available to wildlife.

Another critical limitation is the lack of comprehensive field-scale mass-balance studies that can track PFAS fluxes among soils, pore water, groundwater, vegetation, and harvested biomass over multiple growing seasons. As a result, it remains difficult to determine whether observed reductions in contaminant concentrations represent permanent sequestration, temporary storage, or delayed transport. Therefore, realistic remediation endpoints should be framed in terms of risk reduction, contaminant containment, mobility control, and exposure mitigation rather than complete contaminant removal. From a practical perspective, the greatest value of PFAS phytotechnology may lie in long-term phytomanagement of low- to moderately contaminated sites, where reducing contaminant migration and ecological exposure is more achievable than attaining complete site restoration.

9. Future Perspectives and Research Needs

Although phytotechnology has shown considerable potential for managing PFAS-contaminated environments, its long-term effectiveness and practical implementation require further advances in plant science, rhizosphere engineering, biomass management, and regulatory frameworks. Future research should focus on developing innovative strategies to enhance PFAS uptake and containment, integrating circular treatment approaches, and addressing policy and field-scale implementation challenges. The key future research directions and opportunities discussed in this section are summarized in Figure 5.

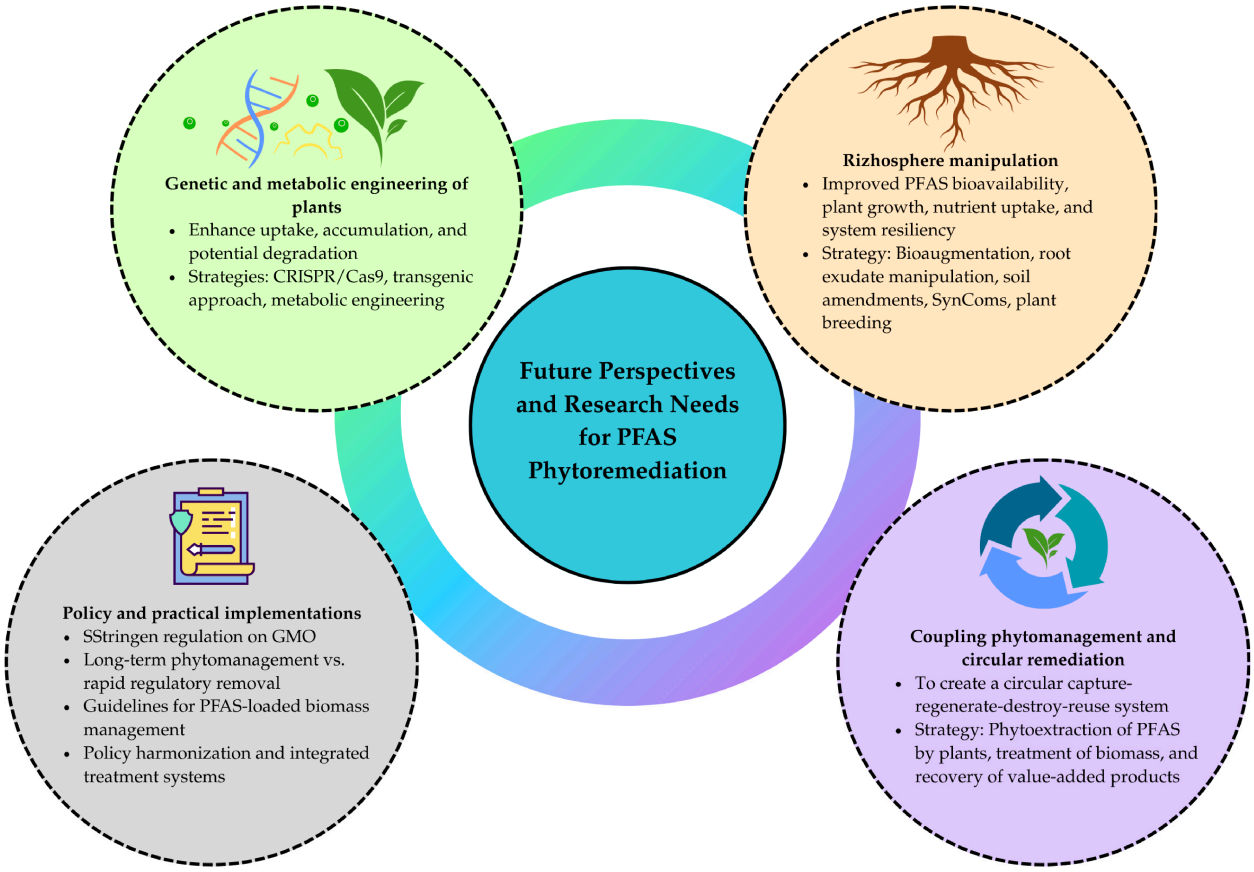


Figure 5. Future Perspectives and Research Needs for PFAS Phytomanagement.

9.1. Genetic and Metabolic Engineering of Plants

Genetic and metabolic engineering offer promising opportunities to enhance the effectiveness of PFAS phytotechnology by targeting traits directly related to contaminant uptake, sequestration, and transformation. Future research should prioritize identifying and modifying genes involved in PFAS transport, accumulation, and tolerance rather than general plant improvement [92]. Potential targets include membrane transporter proteins, such as ATP-binding cassette (ABC) transporters, which may facilitate PFAS uptake and translocation [226], as well as genes that regulate root architecture and exudate production, which influence contaminant bioavailability in the rhizosphere [223]. Engineering plants to produce biosurfactants or specific root exudates may further enhance the mobilization and capture of strongly sorbed PFAS, particularly long-chain compounds [227].

Metabolic engineering may also support the development of plant–microbe systems capable of transforming PFAS precursors. Candidate targets include dehalogenases, oxygenases, and other enzymes involved in the transformation of fluorinated compounds [228]. However, current evidence indicates that biological defluorination of terminal perfluoroalkyl acids (PFAAs) remains extremely limited because of the high carbon–fluorine bond dissociation energy [229]. Consequently, future engineering efforts should focus on improving PFAS uptake, sequestration, and precursor transformation rather than assuming complete mineralization of terminal PFAS compounds [230].

Modern genome-editing tools, particularly CRISPR/Cas systems, provide opportunities to precisely modify PFAS-relevant traits and investigate the genetic basis of PFAS uptake and tolerance. Nevertheless, significant challenges remain, including limited knowledge of PFAS transport pathways in plants, potential off-target effects, regulatory constraints associated with genetically modified organisms, and uncertainties regarding field-scale performance [124]. Therefore, future studies should integrate functional genomics, transcriptomics, metabolomics, and rhizosphere microbiome analyses to identify key genes and pathways to enhance PFAS phytomanagement under realistic environmental conditions.

9.2. Rhizosphere Manipulation Strategies

Rhizosphere manipulation strategies focus on optimizing the soil–root interface to enhance plant growth, nutrient uptake, and system resilience through coordinated microbial, chemical, and physical approaches. These strategies aim to regulate rhizosphere processes to improve contaminant bioavailability, plant uptake, and overall phytomanagement performance [231,232].

Core rhizosphere manipulation strategies include microbial inoculation (bioaugmentation), which involves introducing beneficial microorganisms, such as plant growth-promoting rhizobacteria (PGPR), fungi, and non-rhizobial endophytes, to enhance nutrient cycling and plant performance [233]. Synthetic microbial communities (SynComs) represent an emerging approach in which defined functional consortia are assembled to mimic beneficial natural microbiomes and improve plant resilience and system stability. Root exudate manipulation focuses on altering plant-derived chemical signals to selectively recruit beneficial microbes or regulate rhizosphere interactions; this can be achieved through plant selection or the addition of specific carbon substrates. Soil amendments, including organic matter and biochar, are used to improve soil structure and stimulate microbial activity, thereby supporting a favorable rhizosphere environment. Genetic manipulation and breeding approaches aim to develop plant varieties capable of producing targeted exudates that actively shape beneficial microbial communities without additional external inputs. Agronomic techniques, such as crop rotation, intercropping, and tailored soil management practices, further help regulate rhizosphere microbial dynamics. Microbiome engineering, supported by multi-omics tools, offers opportunities to design and optimize

root-associated microbial communities to improve tolerance to environmental stresses and enhance phytotechnology performance [231,234].

Future research should focus on integrating these strategies into coordinated rhizosphere engineering frameworks that link plant traits, microbial community design, and soil conditions to optimize PFAS phytomanagement. Particular emphasis is needed on developing tailored SynComs for PFAS-impacted environments, advancing root exudate engineering to control contaminant bioavailability, and applying multi-omics approaches to predict and regulate plant–microbe interactions. In addition, combining rhizosphere manipulation with sorptive amendments and system-level design is expected to enhance long-term stability and effectiveness of phytotechnology applications. Future work should further explore the targeted use of specific microbial groups, such as Actinobacteria, Proteobacteria, and Planctomycetes, as well as key rhizosphere metabolites (such as sucrose and phenylalanine), to selectively shape microbial communities and improve system performance under PFAS-contaminated conditions [235].

9.3. Coupling Phytotechnology with Circular Treatment

Coupling phytotechnology with circular treatment offers a sustainable, green approach to addressing PFAS in environmental media. This strategy uses plants, particularly through phytoextraction, to treat PFAS from contaminated soil and water, followed by treatment of harvested biomass via processes such as hydrothermal liquefaction (HTL) to destroy contaminants and potentially recover valuable resources [236].

Key aspects of this coupled approach include phytoextraction mechanisms, where plants take up PFAS, especially short-chain compounds and carboxylic acids, into their stems and leaves. Certain plant species, such as hemp, have demonstrated the capacity to accumulate PFAS from contaminated soils. The effectiveness of phytotechnology can be further enhanced through integrated treatment train systems, which combine rhizosphere optimization, plant selection, and controlled harvesting cycles to improve overall treatment performance. Managing plant regrowth through repeated harvesting can also contribute to sustained contaminant extraction.

A central component of this approach is the circular treatment of contaminated biomass. Instead of generating secondary waste, plant material containing PFAS can be processed using technologies such as HTL, which mimics natural geochemical processes to break down carbon–fluorine bonds while converting biomass into value-added products such as biofuels or chemical intermediates. This integration transforms phytotechnology from a passive treatment method into an active resource recovery system.

Although biomass valorization through pyrolysis, HTL, gasification, and related thermochemical technologies is increasingly proposed as a circular-economy solution for PFAS-contaminated biomass, these approaches present important challenges that remain insufficiently understood at the field scale. A key concern is the potential formation and release of volatile organofluorine compounds during thermal processing [237]. While high-temperature treatment may achieve substantial PFAS destruction, incomplete mineralization under suboptimal operating conditions can generate fluorinated intermediates and volatile fluorinated products that may require additional gas-phase treatment and emission controls [238]. In addition to biomass processing, ecological exposure pathways represent another important limitation of phytomanagement systems. Vegetation accumulating PFAS may act as a biological reservoir that remains accessible to herbivorous wildlife and livestock, particularly at unmanaged or unfenced sites [239]. Consumption of contaminated biomass can facilitate the transfer of contaminants into terrestrial food webs, potentially leading to secondary exposure in higher trophic levels. Recent meta-analyses have demonstrated trophic magnification factors (TMFs) exceeding unity for several PFAS,

with average values approaching 2 in some food webs [213], indicating the potential for biomagnification rather than dilution across trophic levels.

Future research should focus on optimizing integrated phytotechnology–circular treatment systems by improving plant selection strategies, enhancing PFAS uptake efficiency, advancing biomass conversion technologies, conducting comprehensive mass-balance assessments, evaluating fluorinated by-products, conducting life-cycle analyses, and conducting pilot-scale demonstrations to determine whether these technologies can provide sustainable and scalable solutions for PFAS-contaminated biomass management. Particular attention is needed to develop scalable treatment-train configurations that combine phytoextraction, rhizosphere engineering, and thermochemical processing. Future research should also prioritize long-term field-scale investigations that incorporate realistic soil heterogeneity, contaminant aging effects, seasonal variability, and hydrological processes to better evaluate the practical applicability of phytotechnology as a PFAS phytomanagement strategy. Furthermore, the deployment of PFAS phytotechnology should incorporate site-access controls, biomass harvesting strategies, and long-term ecological monitoring to minimize unintended trophic transfer. Finally, the design of closed-loop systems that enable simultaneous contaminant treatment and resource recovery represents a promising direction toward sustainable PFAS management. This coupled framework supports a transition from conventional treatment toward a circular capture–regenerate–destroy–reuse model [171,231,240].

9.4. Policy and Practical Implementation Challenges

Policy and regulatory considerations play a critical role in shaping future implementation pathways. The deployment of genetically modified organisms (GMOs) to enhance phytotreatment is currently limited by stringent environmental regulations, which restrict the use of engineered plant–microbe systems despite their potential for improved performance [232]. In addition, regulatory definitions of clean environments often prioritize rapid, complete contaminant removal, whereas phytotechnology is a gradual, long-term process [94]. The management of secondary waste, particularly PFAS-contaminated biomass, also requires alignment with hazardous waste regulations, emphasizing the need for integrated treatment and disposal strategies [80,214]. Furthermore, the lack of standardized, validated guidelines for the in situ treatment of emerging ultra-persistent contaminants, such as PFAS, continues to hinder regulatory acceptance. International frameworks, including the Stockholm Convention, further necessitate harmonization of national policies to address the full life cycle of persistent contaminants [236].

To advance phytotechnology for the treatment of ultra-persistent pollutants, several key research directions are proposed. A shift toward phytomanagement is essential, emphasizing the control of contaminant transport and exposure rather than complete removal [28]. From an economic perspective, phytomanagement offers several advantages over conventional PFAS treatment technologies, including lower energy requirements, reduced infrastructure demands, and suitability for large, low-value contaminated areas [25,27,87] where excavation, soil washing, or thermal treatment may be prohibitively expensive. However, its relatively slow treatment rate, long monitoring periods, land-use requirements, and the costs associated with biomass harvesting and management remain important limitations to consider when evaluating overall feasibility.

Enhancing plant–microbe symbiosis, including the use of plant growth-promoting bacteria (PGPB) and mycorrhizal systems, offers opportunities to improve contaminant stabilization and system performance while potentially reducing operational costs through improved plant productivity and resilience [235]. Biomass valorization strategies, such as converting PFAS-containing biomass into bioenergy, biochar, or other value-added

products, may help offset treatment costs and support circular treatment frameworks [216]. Nevertheless, the economic viability of these approaches depends on achieving effective contaminant destruction while minimizing secondary environmental risks and treatment costs associated with gaseous emissions, residual by-products, and process control.

In addition, hybrid systems that integrate phytotechnology with engineered approaches, such as electrokinetics [69], sorptive amendments [60,65], or targeted biomass treatment technologies [25,77,215], may enhance treatment efficiency and improve cost-effectiveness by reducing treatment timeframes and increasing contaminant capture. Future studies should incorporate techno-economic assessments, life-cycle analyses, and cost–benefit evaluations to compare phytotechnology with conventional treatment alternatives under realistic field conditions. Overall, phytotechnology represents a promising nature-based solution for managing ultra-persistent pollutants; however, its most realistic and economically sustainable application lies in long-term phytomanagement and risk reduction rather than rapid, complete [19,241].

10. Conclusions

This review synthesizes current understanding of per- and polyfluoroalkyl substances (PFAS) from the perspective of environmental behavior, plant–soil interactions, and the applicability of phytotechnology as a treatment strategy. The analysis highlights that PFAS persistence is fundamentally governed by their molecular structure, particularly the strength of the carbon–fluorine bond, degree of fluorination, and amphiphilic characteristics, which together control partitioning, mobility, and resistance to degradation across environmental compartments. Distinct differences between short-chain and long-chain PFAS further determine their environmental fate, bioavailability, and treatment challenges, with short-chain compounds exhibiting higher mobility and lower treatment efficiency in conventional systems.

Mechanistic insights into plant–PFAS interactions reveal that pore-water bioavailability, rhizosphere processes, and plant physiological traits primarily control phytotechnology performance. Root uptake, translocation, and tissue accumulation are strongly structure-dependent, with short-chain PFAS more readily transported to aboveground biomass, while long-chain compounds are predominantly retained in roots and soil matrices. In addition, rhizosphere processes, including sorption, microbial interactions, and hydrological dynamics, play a critical role in regulating PFAS retention, redistribution, and exposure pathways.

Collectively, the evidence indicates that phytotechnology should be conceptualized as a phytomanagement approach rather than a rapid or complete treatment solution. Due to the extreme recalcitrance of PFAS, plant-based systems generally do not achieve full mineralization but instead reduce risk through stabilization, sequestration, and controlled redistribution within soil–plant systems. This paradigm shift emphasizes the importance of managing contaminant mobility and exposure rather than solely targeting mass removal.

Despite its potential, several challenges remain for the practical implementation of phytotechnology for PFAS-contaminated sites. These include the limited efficiency for short-chain PFAS, uncertainties in long-term system performance, and the need for safe handling and disposal of PFAS-containing biomass. Future research should prioritize developing integrated strategies that combine phytotechnology with sorptive materials or engineered treatment processes and applying omics and data-driven approaches to improve plant selection and predict system performance. In addition, greater attention is required to field-scale validation, multi-contaminant scenarios, and the development of standardized assessment metrics.

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