

Perspective

Sustainable Management of Poly- and Perfluoroalkyl Substances (PFASs)-Contaminated Areas: Tackling a Wicked Environmental Problem

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Abstract: This study evaluates the reasons and factors making soil pollution by poly- and perfluoroalkyl substances (PFASs) a wicked problem, reflecting upon the nature, persistence, mobility, and bioaccumulative properties of these compounds. The current regulation trends in the production and use of such substances are also explored. This study highlights the conflict between the need for phasing out the use of PFASs and their indispensable role in many strategic applications. We summarize the knowledge on the complex chemical properties and to the highly variable properties of the soils, mechanisms of partitioning and transport of PFASs in soil, and the exposure pathways to humans. In particular, we focus on the mechanisms that lead to PFAS accumulation in the edible parts of cultivated plants and present some potential sustainable management practices that could result in risk mitigation and environmental remediation actions. We present potential management practices stemming from the merging of theoretical considerations and pragmatic approaches for mitigating the problems related to the PFAS pollution of agricultural soils. We also highlight the importance of co-creation processes for the adoption of solutions for vast polluted areas that make the impacted populations discouraged, like being in front of an ‘untameable beast’, leading to protests and irrational behavior. In our opinion, this might engage the impacted population in more optimistic strategies to tackle this problem, soliciting authorities and stakeholders to implement strategies beyond the actual management practice and also supporting new policy development.



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1. PFAS: Sources and Human Exposure Pathways

Poly- and perfluoroalkyl substances (PFASs) are a group of thousands of synthetic molecules, in which C is partially or fully saturated with fluorine (F), except for the C of the functional groups [1]. Mass-produced since the 1940s, PFASs have been increasingly used for industrial applications owing to their hydrophobic and lipophobic behavior, low mechanical friction, and resistance to high temperatures [2], useful for a large variety of industrial high tech as well as everyday products [3]. Depending on the functional group present in their molecules, PFASs are classified as perfluorinated perfluoro carboxylic acids (PFCAs), perfluorosulfonates (PFSAs), sulfonamides (PFASAs), fluorotelomer alcohols (FTOHs), saturated and unsaturated fluorotelomer carboxylates (FTCAs), fluorotelomer sulfonates (FTSs), and perfluorophosphonic acids (PFPAs). The common feature of PFASs is the strength of the C–F bonds that confer them high thermal and chemical stability

and low or no biodegradability. For example, in CH_3F , the bond dissociation energy is $115 \text{ kcal mol}^{-1}$, higher than that of the C–H bond (104.9), and the energy increases upon increasing PFAS molecular complexity. Of the ca. 12,000 synthesized PFASs, only about two hundred have been used at broad industrial scale; nevertheless, it is estimated that more than 14,000 materials contain PFASs [4].

These PFASs are essential components of civil and military aerospace, automotive industry, chemicals, food and drugs industry, medical drugs and healthcare devices, semiconductor, electronics and energy storage apparatus, Heating, Ventilation and Air Conditioning-Refrigeration (HVAC-R) apparatus, emulsion agents for agrochemicals, and for personal and professional products, such as textiles, paper and cookware, emulsion agents of cosmetics, and adjuvants of pharmaceuticals. Their increased use since the 1950s, along with a lack of clear documentation, especially before the 2000s, on PFASs manufacturing and productive uses makes it impossible to account for all PFASs inputs into the environment [5]. Such uncertainties have also hindered their discovery in the environment and the understanding of their environmental diffusion and dynamics.

In the agricultural environment, the movement of PFASs is mainly mediated by water and, to a lesser extent, by food and fodder production, with plant uptake mainly occurring via contaminated water and soil. In humans, the main sources of PFASs are through the ingestion of contaminated drinking water and food. National Environmental Protection and Health Agencies adopt precautionary limits for PFASs concentrations in drinking water and guidance values for safe amounts of PFASs that a person can ingest regularly over a lifetime without any significant risk to health. For example, in the European Union, the European Food Safety Agency (EFSA) [6] has adopted a Tolerable Weekly Intake (TWI) based on epidemiological evidence of $4.4 \text{ ng/kg body weight per week}$, equivalent to 0.63 ng/kg b.w. if expressed as Tolerable Daily Intake (TDI), for the sum of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS). This is based on the serum level of these PFASs that leads to a 10% reduction in vaccination response in one-year-old children [7]. These four PFASs were regulated because they contributed a median of 46% to the total dietary exposures to PFASs according to the EFSA [6] report. However, PFBA and PFHxA also made significant contributions (16% and 15%, respectively), but they were not included in the evaluation due to a lack of epidemiological data [7].

In Australia and New Zealand, guidelines indicate TDI values of $0.16 \text{ } \mu\text{g/kg body weight/day}$ for PFOA and $0.02 \text{ } \mu\text{g/kg body weight/day}$ for the sum of PFOS and PFHxS. Human exposure to PFASs has been positively correlated with cancer, blood cholesterol levels, obesity, immune suppression, and endocrine disruption [8]. However, due to uncertainties related to non-standardized analytical methods and the lack of representative food consumption data in previous risk assessments, the European Commission (EC) in 2023 advised Member States to conduct new nationwide surveys, including fresh plant food, for a re-evaluation of the health risks associated with exceeding the TWIs for the four regulated PFASs. This is especially important given that exposure via vegetable products was identified as an area of uncertainty in EFSA's previous survey. Additionally, on 28 April 2023, the EC [9] amended the EU Regulation 2019/1021 on Persistent Organic Pollutants (POPs) to further limit PFOA and related compounds, reducing the maximum content of polytetrafluoroethylene (PTFE) to 1 mg/kg during the manufacturing stage of various products. This is because the PTFE, used in many industrial sectors, may contain PFOA as a contaminant or as a degradation product formed when PTFE is exposed to temperatures higher than $250 \text{ }^\circ\text{C}$. Similar limitations have been introduced for other fluorinated organics, such as the polyvinylidene fluoride (PVDF), which is used in the production of corrosion-resistant gas filters, heat exchange equipment, water filter membranes, medical tissue membranes,

containers for industrial waste materials, and food contact materials and articles (MOCAs). Advances in analytical methodologies now allow for the detection of not only target PFASs but also precursors that release shorter PFASs upon chemical oxidation [10,11].

Considering that the tolerability criteria cannot account for all potential sources of PFAS intake, even PFAS levels in food that do not exceed suggested values may pose a risk if other pathways are not effectively controlled in a cumulative risk assessment. In our opinion, the current recommendations, which regulate only a few PFASs, represent a significant limitation in risk assessments, especially for farmers and residents who primarily consume food produced on contaminated soils. Although risk assessments have historically been conducted for individual chemicals, the environmental persistence, mobility, and bioaccumulation and biohazard common to all known PFASs suggest that they should be managed as a class of substances for which effective strategies to reduce mobility and impact on humans and ecosystems are needed [12].

2. PFAS Environmental Pollution: Major Clusters in the European Union

The European Chemical Agency estimated that 4.4 million tons of PFASs could be released in the environment over the next 30 years unless restrictions are implemented [13]. Several accessible maps illustrating the distribution of PFAS-contaminated areas have been published by public authorities, such as the European Environmental Agency (EEA, <https://www.eea.europa.eu/publications/zero-pollution/cross-cutting-stories/pfas>, accessed on 7 August 2024), United States Geological Survey (USGS, <https://www.usgs.gov/tools/pfas-us-tapwater-interactive-dashboard>, accessed on 12 August 2024), and even by popular press (e.g., Le Monde, https://www.lemonde.fr/en/les-decodeurs/article/2023/02/23/forever-pollution-explore-the-map-of-europe-s-pfas-contamination_6016905_8.html#, the Forever Chemicals project, <https://foreverpollution.eu/> accessed on 12 August 2024). These maps show that most contaminated areas are where PFAS manufacturers and users are located, illustrating how these persistent pollutants move in the watershed according to the dominant hydrological processes [14]. Among the most well-documented cases in Europe are the areas of Antwerp (Belgium), Dordrecht (The Netherlands), Baden-Württemberg (Germany), and Vicenza Province (Italy). These cases provide compelling evidence of the link between the PFAS production, environmental pollution, food contamination, and bioaccumulation in humans [15–18].

For example, the PFAS contamination of surface water, groundwater, and drinking water in the Vicenza Province (N-E Italy, Figure 1), discovered in 2013, affected an area of 180 km² and impacted ca. 300,000 inhabitants. The PFOA concentration in the blood serum of these residents was up to ten-times higher than people living in unpolluted areas. In 2017, the National Public Health Institute (ISS), together with the Animal Protection Institute of Venezia (IZSVE) and the Veneto Region Environmental Protection Agency (ARPAV), concluded a monitoring survey of animal food produced in the most affected area (Figure 1). The focus was primarily on PFOA and PFOS, which are classified as environmentally persistent and bioaccumulative under the POPs Regulation of the Stockholm Convention. The survey reported that PFOA and PFOS concentrations in animal food exceeded background levels, prompting further controls on potential exposure within the livestock sector. Since then, the most polluted areas have been regularly monitored for a large range of PFASs [19], showing that despite the primary source being closed and currently under remediation, PFAS concentrations continue to fluctuate, establishing a new baseline, and the contamination plume is still expanding due to watershed hydrology.

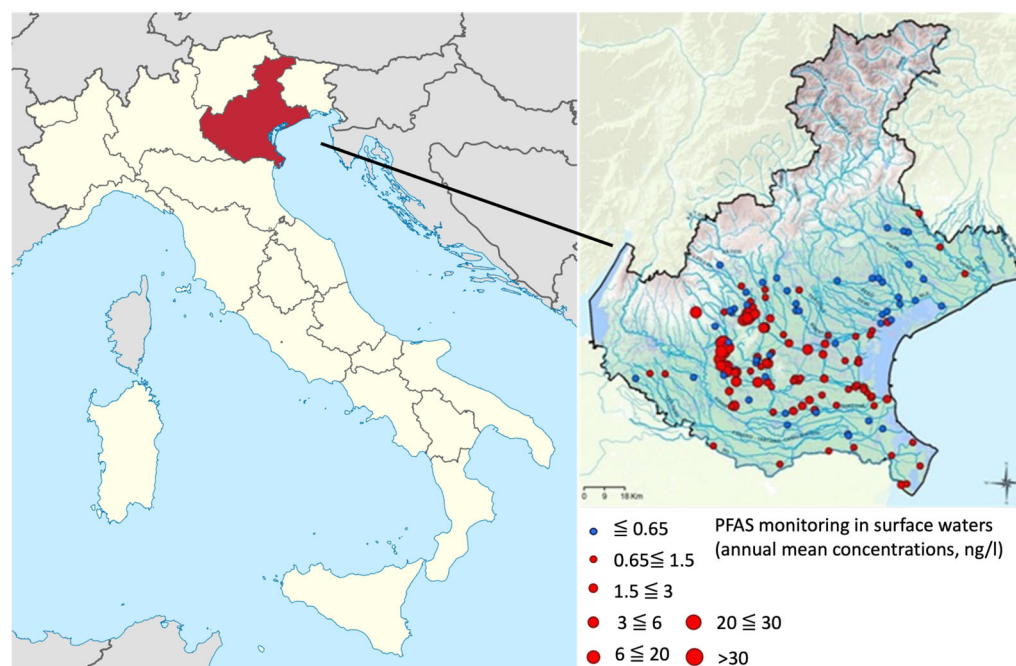


Figure 1. Map of the PFAS-polluted area of the Veneto Region. The red-colored area indicates the municipalities served by contaminated water installations. The red area is divided into Red Area A (dark red) for the municipalities located directly on the contaminated water table and Red Area B (light red) for municipalities outside the contamination zone. The white stranded area indicates the contaminated aquifer; the pink dot marks the location of the chemical plant suspected of being the primary source of pollution. The blue lines indicate the major rivers; the thick black line marks the boundaries of new areas added to the Red Area in 2018, with nine municipalities included [20]. Modified from [19].

Although long-chain PFASs are thought to be the most harmful to living organisms due to their bioaccumulative properties, this study primarily discusses the effects of short-chain PFASs and their precursors, as robust scientific evidence exists for these compounds.

It is important to note that the listing of substances in the Stockholm Convention limits the disposal of waste containing more than 50 mg/kg of these substances, requiring their destruction or irreversible modifications before disposal. Such wastes are prohibited from recovery, recycling, reclamation, or direct reuse. Further restrictions are imposed by the Basel Convention on the Transboundary Movements of Hazardous Waste and their Disposal.

Compared to industrial and agricultural environments, fewer studies have focused on the exposure of forest ecosystems to PFASs. The limited available data show variable levels of different PFASs in forest environments [21,22], primarily attributed to the wet and dry atmospheric deposition of gas-phase or particulate-bound PFASs [23,24]. This atmospheric deposition can also include degraded precursors, which are subject to long-range transport [25]. In general, the impact of POPs in forest environments has been attributed to their deposition onto foliage and subsequent uptake [26]. Forest leaves can absorb atmospheric POPs through stomata, cuticles, and particle-bound deposition [27]. Although PFASs have lower volatility than their corresponding alkanes, particularly sulfonated and aminated PFAS, the ionic forms can bind to particulate matter in the air and follow the transportation and deposition dynamics [28]. While atmospheric transport might be a significant exposure pathway for humans indoors, its contribution to PFAS mobility in the open environment is particularly relevant around production or usage sites with uncontrolled emissions. Forests accumulate nonpolar POPs, such as organochlorine pesticides [29], polycyclic aromatic hydrocarbons (PAHs) [29], and polychlorinated biphenyls (PCBs) [30]. However, there are no

consistent data on PFASs in forest soils. As forest foliage falls, PFASs are transferred to the forest floor, serving as a 'conveyor' that enhances their transmission from the atmosphere to the soil and biota [30,31].

3. Elements of Global and Local Regulatory Trends

Global restrictions on the use and management of POPs apply to those listed under the Stockholm Convention of the United Nations Environment Programme, UNEP [31]. Currently, over 800 precursor substances of PFOA and PFOS are listed. The Stockholm Convention's criteria for restricting PFOS, PFOA, and their precursors have been progressively integrated into national environmental legislation. As of June 2022, PFHxS and its salts were also included in the Stockholm list [32], and as of May 2023, long-chain (C_{9–23}) carboxylic PFASs are under consideration for a global ban.

In the European Union (EU), Regulation EU 2019/1021 on POPs (<https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02019R1021-20230828>, accessed on 12 August 2024) aims to protect human health and the environment from POPs by minimizing, prohibiting, or substituting PFASs where feasible. This regulation establishes specific provisions regarding PFAS-containing waste, based on the precautionary principle. Additionally, the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (EC 1907/2006) includes several PFASs on the list of candidate Substances of Very High Concern (SVHC), although various exceptions exist. However, this regulatory approach has led to the replacement of regulated PFASs with non-regulated alternatives, with no significant reduction in the associated risk.

Parallel to the U.S. Food and Drug Administration (FDA), the European Chemical Agency (ECHA) is conducting further studies to promote the substitution of PFASs focusing on restricting the use of C₉–C₁₄ PFAS as of February 2023 (EU Regulation 2021/1297). In the EU, substances that are subject to derogation can still be used up to 18 months after the ban publication, with certain exceptions allowing usage for 6.5 or 13 years. Important derogations exist for plant protection and veterinary products, whereas temporary exemptions cover polymeric fluorinated compounds and food contact materials.

Polymeric fluorinated compounds, as well as aromatic per- and polyfluorinated compounds, constitute other large groups of PFASs, including polymers with fluorinated side chains such as FMA and fluoropolymers with a fluorinated backbone such as PTFE, PVDF, FED, and PFA, but a detailed treatment of their environmental dynamics and impacts is out of the scope of this study.

As the total ban and progressive restrictions on specific PFASs have driven industries to adopt alternative PFASs, in January 2023, Norway, Sweden, Denmark, Germany, and The Netherlands submitted a proposal to the ECHA for a universal PFAS ban. This proposal targets any substance containing at least one fully fluorinated C atom, aiming to limit non-essential uses of PFASs, which would affect not only EU domestic goods but also imported goods. The evaluation of this proposal began in April 2023, and it is still ongoing and was corroborated by in-depth analyses of PFAS diffusion, which have overcome the planetary boundaries and reached unsafe levels in most of the anthropized environment [33]. In the Regulation (EC No 1272/2008) on the Classification Labelling and Packaging of substances and Mixtures (CLP Regulation), the following PFASs are covered: perfluorooctane sulphonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and ammonium perfluorooctanoate (APFO). Perfluoroheptanoic acid (PFHpA) and perfluorooctanol 6:2 FTOH are currently candidate substances for regulation.

In line with the EU Chemicals Strategy and the Zero Pollution Action Plan, in 2023, the European Chemicals Agency (ECHA) initiated discussions on a potential restriction of

approximately 10,000 PFASs based on their risks to human health, the environment, and the socio-economic impacts. A harmonized decision on the restriction is expected in 2025 from the European Commission and the EU Member States. In the meantime, major PFAS producers, such as 3M, have announced they will cease PFAS manufacturing by 2025 [34] and anticipated that Solvay may also discontinue PFAS production soon. However, there are currently no viable alternatives, particularly for medical technology.

It is important to note that, under national and local legislations, PFAS analysis is mandatory for discharge waters and in occupational settings within industrial plants that produce or utilize PFASs. It is also mandatory for drinking water and surface and groundwaters in areas where high levels of PFAS contamination have been detected. However, PFAS analysis in the atmosphere, soil, vegetation, biomass, compost, digestates, and biosolids is generally not required, as these matrices are not typically listed in environmental legislation. To our knowledge, only the State of Baden Württemberg in Germany mandates PFAS soil analysis of and the pre-harvest screening for crops grown on polluted soils before their use [35].

The Drinking Water Directive (2020/2184/EU) sets a limit of 100 ng/L for the sum of 20 PFAS compounds that can be accurately measured. Each EU Member State can set additional target values for individual or groups of PFASs, especially in areas where specific substances are found in drinking water or aquifers. Similarly, the United States Environmental Protection Agency (USEPA) has introduced federal-level PFAS regulations for drinking water (Table 1). However, individual states may enforce additional regulations, which can align or differ significantly from federal limits. Other major industrialized countries, such as the United Kingdom and China, are adopting more gradual approaches to PFAS regulation, focusing on drinking water standards and the disposal of PFAS-containing products. These regulations primarily address substances that pose clear health risks. In Australia and New Zealand, PFASs have been regulated under the National Environmental Management Plan since 2018 [4].

Remediation actions and risk management for PFASs rely on threshold concentration values, standard analytical procedures for detection, exposure modelling, and toxicity-based risk assessment. To date, PFAS concentration limits have been established for drinking water, and, in some cases, limits for surface and groundwater have also been adopted (Table 1). Despite these national limits, regional or local PFAS concentration limits often vary, based on site-specific risk assessment. For instance, Australia has established toxicological criteria for PFOA, PFOS, and PFHxS, adopting a threshold of 70 ng/L for PFOS+PFOA in drinking water and a screening level of 0.23 ng/L for PFOS in receiving waters [36]. These values are consistent with those established by the USEPA (Table 1). However, only a few countries have established PFAS limits for surface and groundwater, and no countries have set concentration limits for soil and biosolids (Table 1).

India and Japan were not included in this survey, as these countries, despite joining the Stockholm Convention in 2006, have not accepted the amendment list, and PFASs remain unregulated. A similar situation exists in Central and South America, Africa, and other developing countries, where no published PFAS regulations exist. However, Argentina and Brazil have joined the Stockholm Convention, including the amendments to Annex B, which restrict the use of PFOA and PFOS.

Table 1. Current limits for environmental natural and artificial matrices in some world areas.

Country	Matrix and Concentrations							References
	Surface and Groundwater	Discharge/Immission Water	Drinking Water	Soil	Biosolids	Food	Other Matrices	
USA	70 ng/L for PFOA and PFOS and their sum	TBD at Federal level Limits for different States (see references)	PFOA 4.0 ng/L, PFOS, 4.0 ng/L, PFHxS 10 ng/L, PFNA 10 ng/L, HFPO-DA [GenX] 10 ng/L, Mixtures containing two or more of PFHxS, PFNA, HFPO-DA, and PFBS Hazard Index = 1 (see references)	Non legally binding regional Guidance Screening Levels for PFAS	ME PFOS = 5.2[μg/g] PFOA = 2.5[μg/g] PFBS = 1900[μg/g] MI: PFOS = 125[μg/g]	TBD	None	[37–39]
Canada		TBD at National Limits for different States	Sum of 30 PFAS ≤ 30 ng/L Determined with the USEPA methods 533 and or 537.19	PFOS = 10 (μg/g)	TBD	TBD	None	[40–42]
European Union	PFOS = 0.65 ng/L annual average for sea water	TBD at Community level Limits for different States and Regions	Total PFAS 0.500 ng/L or 100 ng/L for the sum of 20 C ₄ –C ₁₃ carboxyl and sulfonic PFAS	DK: 400 ng/g sum of 12 PFAS; NL: 0.9 ng PFOS, 0.8 ng/g PFOA SE: 3–20 ng/g PFOA+PFOS DE: 100 ng PFAS/g < 100 μg/L total PFAS by leaching test for landfilling	100 μg/kg PFOA+PFOS *	4.4 ng/kg b.w./week	None For fertilizers (DE) 100 ng/g	[7,43–47]
China		TBD at National level	PFOA 80 ng/L, PFOS 40 ng/L for PFOS			None	None	[48]
Australia and New Zealand		TBD at Federal level Limits for different States (See references)	PFOA 560 ng/L, PFOS and PFHxS 70 ng/L	1 mg/kg PFOS 10 mg/kg PFOA	ng/g PFOS = 1 PFOS+PFHxS = 2 PFHxS = 3 PFOA = 4 PFBA, PFPeA, PFHxA = 1 Sum C ₉ –C ₁₄ PFCA = 10 PFSA = 1 n:2 FTS = 4	TDI = 160 ng/kg b.w./day for PFOA 20 ng/kg b.w./day for PFOS + PFHxS	None	[4,49–51]
World Health Organization		None	PFOS and PFOA 100 ng/L singly	None	None	None	None	[51]

* Limit value of PFAS for sewage sludge used as soil fertilizer in Germany introduced in 2008: 100 μg/kg total PFOS+PFOA. Whether the concentration of a single PFAS exceeds 50 μg/kg, this must be declared on the label.

4. Chemical Properties Controlling PFAS Environmental Persistence and Mobility in Soil

The persistence of PFASs in the environment stems from the exceptional strength of the carbon–fluorine (C–F) bond. The difference in electronegativity between carbon and fluorine creates a high electron density around the fluorine atoms, with the development of partial charges (C^{δ+}, F^{δ−}). This contributes to significant polarity and dipole moment for C–F bonds. The high strength of the C–F bond acts as an energy barrier to defluorination reactions in the environment and limits the potential biodegradation of PFASs. This chemical effect becomes more pronounced as the fluorine saturation in the carbon chain increases, resulting in reduced interactions of PFASs with hydrocarbons and water. The strength of the C–F bond is further enhanced by electron-attracting groups, such as sulfonic, amidic, and phosphonic functional groups.

When PFASs are released into the environment, they tend to form micelles in the aqueous media by excluding water molecules [52]. This micelle formation, along with the formation of orthogonal and reversible supramolecular associations, may explain the greater hydrophobicity of PFASs compared to hydrocarbon analogues, as well as the absence of intermolecular interferences. Carboxylic PFASs are more water soluble than the sulfonic ones with the same chain length. For example, PFOA and PFOS have solubilities in distilled water at 25 °C of 9.5×10^3 and 6.8×10^2 mg/L, respectively. Since PFASs are ionic molecules, they exhibit lower volatility than fluorotelomer alcohols and sulfonamides [53]. Recent studies have shown that newer PFASs, such as 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFESA or F53B) and hexafluoropropylene oxide dimer acid (HFPO-DA), used as substitutes of PFOS and PFOA, have been detected in environmental samples [54], indicating that these alternative substances are also mobile and persistent.

In complex and reactive systems like soil, PFAS concentrations in soil solution can be predicted by partition coefficients (K_d). Available data show higher sorption onto soil solid phases for long-chain PFASs compared to short-chain ones and for the sulfonic over carboxylic PFASs with the same chain length [55]. The influence of chain length, functional group, and molecular size on PFAS behavior in soils and sediments was well documented by Burkhardt et al. [56]. They estimated the sorption of 428 PFASs onto Granular Activated Carbon (GAC), by means of the Polanyi Potential Adsorption Theory, and reported that the Freundlich isotherm parameters depended on the PFAS length, conformation, and functional group. However, the complexity of soils, which contain particulate, dissolved organic matter, and reactive mineral solid phases, increases the uncertainty associated with PFAS detection and generally reduces the sensitivity and precision of the standard analytical methods.

Recently, it has been proposed that total organic fluorine could be used as an indicator of PFASs in polluted waters, offering a valuable method for identifying PFAS species, solving the lack of analytical methods for modified PFASs. However, methods for measuring total organic fluorine are not yet routine, and no standardized approaches exist.

In summary, the high molecular stability conferred by the strength of the C–F bond is responsible for the persistence of PFASs in soil, while chain length and functional groups control their mobility in soil, water, and plant compartments. Mobility decreases as chain length increases.

Persistence is the most relevant parameter applied to monomeric PFASs in risk assessments, while polymeric fluorinated substances (e.g., PTFE) are considered persistent but not toxic as they are insoluble in water, immobile, and non-bioaccumulative. However, the potential release of micro-, nano-, and sub-nanometric particles from polymeric PFASs during wear and tear or disposal should be investigated. If such nano-sized polymeric PFAS particles are indeed formed, they could be taken up by biota and humans.

PFAS Biodegradation: Past and Recent Evidence

The degradation of PFASs in the natural environment can only occur after their biotic or abiotic defluorination, leading to the formation of the hydroxylated or hydrogenated homologous organic compounds, which can then enter cellular catabolic pathways. Abiotic defluorination of PFASs requires reaction conditions that are unlikely to be present in environment matrices, where the free energy is generally too low for the spontaneous dissociation of the C–F bond. The strength of the C–F bond also explains why the biological fluorination of organic molecules is not a common biological process and also highlights the rarity of functional genes coding for defluorinase enzymes in living organisms. The few known natural fluorinated organic compounds are monofluorinated low-molecular-weight organic acids, such as fluoroacetic acid, which is produced by some plant

species [57,58]. This so-called ‘fluorous effect’, which prevents biological degradation of PFASs, is well illustrated by the defluorination of fluoroacetic acid. Microorganisms expressing fluoroacetate defluorinase [59] can degrade fluoroacetate, whereas di- and trifluoroacetate are not biologically degraded [60]. The low F abstracting capacity of oxoreductive enzymes produced by living organisms is not fully explained by the high bond dissociation energy of the C–F bond. Theoretically, reductive defluorination could be energetically favorable for anaerobic microorganisms [61]. However, chemical orthogonality, steric effects for long-chain molecules, and high site selectivity of F transfer to other substances may also contribute to the low biodegradability of PFASs [12].

The key thermodynamic characteristics of C–F bond dissociation have been studied in laboratory reactors but remain poorly understood in the natural environment, where multiple factors influence the structure and stability of PFASs and the potential generation of PFAS-derived radicals. Although reductive defluorination has been shown to be energetically favorable [61], microbial degradation of PFAS is still a relatively unexplored process, primarily studied through single-strain in vitro cultures. Partial degradation of PFOS, PFOA, PFHxA and PFBA has been reported for quite some time [62]. Yi et al. [63] reported the degradation of PFOA by *Pseudomonas parafulva*, and *Pseudomonas aeruginosa* and *Pseudomonas plecoglossicida* were found to degrade PFOS [62,64]. Huang and Jaffé [57] reported that *Acidimicrobium* sp. strain A6A could degrade both PFOA and PFOS in vitro. This strain belongs to the Feammox physiological group, which oxidizes ammonium to nitrate while reducing Fe(III) to Fe(II). Genome sequencing revealed the presence of dehalogenase genes, potentially explaining the strain’s defluorination capacity and its release of inorganic F and acetate. These findings are similar to those reported by Chetverikov et al. [56], where the biodegradation of partially fluorinated PFASs, such as fluorotelomers, appeared more favorable as compared to fully fluorinated PFASs [65].

However, the chemical conditions created in vitro are difficult to replicate in soil environments, where temperature, nutrient availability, ionic strength, and microbial densities are far lower than in laboratory reactors. Recent studies suggest that microorganisms possess genes coding for a broad array of dehalogenases [66–68] and aromatic oxidative enzymes [69,70], which could lead, under specific conditions, to PFAS defluorination, even through non-specific enzymatic mechanisms [53,71,72]. An example is the degradation of the 6:2 fluorotelomer alcohol by *Phanerochaete chrysosporium*, *Gloeophyllum trabeum*, and *Trametes versicolor* and other fungal genera known for their wood decomposition activity, isolated from polluted sites, which have been associated with a partial degradation of PFASs [73]. Similarly, poorly characterized microbial biodegradation pathways of PFASs could be triggered in highly reactive environments, such as aerobic or anaerobic sludge treatment plants [74,75], where conditions for microbial activity are more favorable than in oligotrophic environments such as water bodies and soils.

The ionic strength of soil solution is reported to be around 0.005 M [76,77], but this value pertains to bulk soil. The rhizosphere, i.e., the soil volume adhering to plant roots, is expected to have a higher ionic strength due to the high concentration of low-molecular-weight organic molecules released by plant roots [78]. As discussed in Section 5.1, the higher density and activity of microorganisms in the rhizosphere may facilitate PFAS biodegradation in soils. Computational chemistry simulations have shown that PFAS degradation is more likely to release fragments of two or three carbon atoms rather than single fluorinated carbons atoms. This finding could explain the frequent detection of trifluoroacetic acid in waters of PFAS-polluted areas. Although trifluoroacetic acid can originate from various processes, it may be formed by the degradation of longer PFASs. It has been detected in 94% of drinking water samples in Europe analyzed by the Pesticide Action Network, with concentrations ranging from 20 to 4000 ng/L.

For the purposes of this study, it is important to highlight that ultrashort C₂ and C₃ PFASs are not routinely analyzed in monitoring campaigns. As a result, many surface and groundwater sources may be considered pollution-free when they are not. We, therefore, urge further studies to build a critical mass of information that will enable regulators to introduce threshold limits for drinking water, discharge waters from industry and agriculture, for surface and groundwater, food, and fodder, as C₂–C₃ PFASs are surely environmentally mobile and toxic for humans.

5. Management Options of PFAS-Polluted Areas

As outlined in Section 1, the diffusion of PFASs in the environment is primarily due to their transport by water flows, the reuse and recycling of contaminated inorganic and organic materials, or release from point (e.g., landfills) and non-point sources (e.g., household). Current environmental management options include the closure and remediation of primary sources, treatment of wastewaters of active industrial plants, granular activated carbon (GAC) treatment of drinking water with GAC filters, prohibiting the use of wells accessing polluted groundwater, and screening of animal and plant foodstuff. However, these controls vary globally, and considering the international movement of goods, discrepancies can result in the transfer of PFASs to non-polluted areas, increasing their potential to accumulate in plants and bioaccumulate in the global food web.

Both wild and cultivated plants have different accumulation potential and behavior towards various PFAS compounds [79–81]. The quantification of the plant bioaccumulation factor (BAF) can be used to predict PFAS transfer from soil to plants, inferring potential risks for human health. Due to the lack of significant biodegradation, intact PFASs can be transferred to humans, particularly through raw fresh food. There is consensus that diet is the major source of human exposure, with fish, meat, eggs, and dairy products being the main animal sources, and cereals and vegetables are the primary plant-based sources [82]. BAF values have been used seldom and sparingly in PFAS transfer studies; however, it is crucial to highlight that the analysis of bioaccumulation and biomagnification for PFASs is more complex than for other persistent organic pollutants (POPs). PFASs bioaccumulate in aquatic organisms, even at concentrations below the quantification limits, meaning that water concentrations alone are not predictive of bioaccumulation. Therefore, measuring PFAS content in specific organisms is essential for reliable risk assessments.

Biomagnification—the increase in pollutant concentration in an organism as compared to organisms lower in the food chain—has been poorly studied for PFASs, particularly in terrestrial ecosystems. We hypothesize that biomagnification, if present, could occur in specific ecological pipelines depending on the species' ecology and on the PFAS molecule involved, as these compounds exhibit widely varying residence times in biota. Aquatic organisms and plants at the base of the food web likely play a significant role in this process.

Another challenge in risk assessment is the limited number of PFAS compounds that can be routinely detected and quantified (approximately 30) compared to the total produced and used by industry (around 240). The analysis of oxidisable precursors, which can generate a wide array of PFASs [83], is crucial, as demonstrated by the monitoring of the polluted area of Brilon-Scharfenberg in North Rhine-Westphalia (Germany) by Röhler et al. [84]. Their findings showed seasonal patterns for short-chain PFASs, likely due to immobilization in the dry season and mobilization during the wet season, as well as the degradation of long-chain precursors. This hypothesis is supported by studies showing that the aerobic degradation of fluorotelomers, such as 6:2 FTSA and FTOH, and of polyfluoroalkyl phosphate esters can release PFPeA and PFHxA [85–87].

5.1. Current Approaches to Remediation and Management of PFAS-Polluted Soils

The remediation of polluted soils, like any other environmental matrix, requires treatments that reduce pollutant concentrations to background levels or below the legal threshold. Soil remediation technologies can be grouped into three main categories: removal, disposal, and destruction. The removal of pollutants from soil is typically carried out through soil washing in dedicated plants. Grimison et al. [88] reported on the performance of a soil-washing plant for PFAS-polluted soils. The plant was utilized for physical fractionation to disperse the clay minerals and partition of PFASs into the aqueous phase, which was then treated with GAC filters and ion-exchange resins, achieving up to 97% removal efficiency for carboxylic PFASs and 95% for sulfonic PFASs [88]. The overall efficiency from soil to the washing solution was 90%, with more than 99% of PFASs sorbed onto granular active carbon.

Soil washing, which has been used for a long time in soil remediation [89], can be combined with technologies, like active charcoal filters, ion-exchange resins, or high-pressure reverse osmosis and nanofiltration. These methods, which filter most PFASs based on porosity, represent a viable solution for industrial sites but may be inefficient for short-chain PFASs. Furthermore, they produce enriched solid and liquid wastes that require further treatment or safe disposal. Solid PFAS-enriched materials can be regenerated, incinerated, or landfilled, while concentrated liquids may undergo PFAS destruction or be stored in underground injection wells.

Although effective, the cost of soil-washing treatments for PFAS-polluted soils, estimated at AUD 400–500 per cubic meter [88], makes it suitable for pollution hotspots, such as industrial sites, but not for large agricultural areas. Additionally, soil washing can degrade soil properties, making it unsuitable for agricultural soils. As noted by Bolan et al. [90], risk reductions in PFAS-polluted soils can be achieved through mobilization, immobilization, or degradation. However, with the exception of GAC filtration and a few other methods, most PFAS remediation approaches focus on coagulation, separation, chemical oxidation/reduction, thermal decomposition, and nanomaterial-assisted photocatalytic degradation [90,91]. Biodegradation remains at the laboratory or small pilot scale [92], with ongoing research exploring the biodegradation potential of microbial biofilms that may develop on granulated active particles in water filters.

The mobilization of PFASs can be a preliminary step for their transfer from contaminated matrices such as soils and sediments to liquid phases, as in in soil-washing treatments, or for biological uptake by PFAS (hyper)accumulator plants. Mobilization involves the transfer of PFASs from one environmental matrix to another, which must then be safely treated or stored. For instance, if PFASs were transferred to an aqueous phase, they could be concentrated and destroyed via incineration at temperatures above 1000 °C. Incineration trials on PFAS-contaminated waste have demonstrated that the strength of the C–F bond necessitates high temperatures (e.g., >600° to degrade PFOS) with emissions of fluorinated greenhouse gases (CF₄, C₂F₆) prevented only at temperatures in the order of 1000 °C [91] or in the presence of Ca(OH)₂ [93,94], which compromises the sustainability of this treatment.

Pyrolysis, an alternative thermal destruction method, has shown effectiveness at the pilot scale and is considered more sustainable than incineration because it requires less energy. However, the reported PFAS destruction efficiency varies from 50 to 98% depending on the molecule, and some by-products may re-release PFASs back into the environment. Pyrolysis poses challenges, such as the production of gaseous -CF₂- compounds and HF [92,95,96], which may necessitate post treatments of fumes and by-products [97].

Partial or complete PFAS mineralization to CO₂, F[−], and HSO₄[−] for sulfonic PFAS can be achieved using a range of physical and chemical technologies, such as sonochemistry and ultrasound degradation, microwave treatments, and subcritical or supercritical treat-

ments [98]. Supercritical water oxidation is an emerging technology that has demonstrated rapid efficient PFAS destruction at the pilot scale, achieving up to 99% destruction of selected PFASs in various media [95]. Some methods, like plasma technology, vapor energy generation, photochemical destruction, and thermal desorption, are still at a low readiness level, whereas thermal destruction by incineration and pyrolysis is more mature and has been tested at close-to-market scales. Verma et al. [98] provided a comprehensive review of PFAS destruction methods in various environmental matrices.

Other promising physic-chemical methods include electrochemical advanced oxidation generating radicals [99–101], as well as techniques combining PFAS degradation using UV light irradiation, sonochemistry (producing cavitation), and plasma [102]. Mineralization using strong alkali, such as NaOH, in polar, non-protic solvents such as dimethyl sulfoxide (DMSO) as conducted by Verma et al. [98] may offer effective treatments for small volumes of PFAS-contaminated phases. For soils, sediments, and other polluted matrices, proprietary adsorbents such as Rembind™, matCARE™, and similar sorbents [103] have demonstrated potential for PFAS immobilization [36]. Post treatments tested so far for PFAS degradation include photochemical, electrochemical, and thermal processes, with UV radiation (sufficiently powerful to generate hydrated electrons) or in electrochemical anodic oxidation potentially leading to complete PFAS mineralization [104–106].

Novel treatment technologies for PFAS compounds such as photo-induced reduction in the presence of Fe- and S- containing minerals can produce oxy- or hydroxyl radicals, fostering conditions for biodegradation in water bodies [107,108]. In reactor batch studies, the reductive defluorination of long-chain PFASs has been shown to fragment them into shorter-chain PFASs, with this potential for fragmentation increasing with the temperature and ionic strength of the solution [38]. Additionally, the defluorination of various chain-length PFASs has been reported for certain isolated microbial strains [109,110].

5.2. Circular Economy Can Recirculate PFASs in the Agricultural Environment: The Case of Biosolids

The persistence of PFASs in the environment and biomass can lead to their recirculation and spread, as regulations mandate that biomass shall be reused or recycled. For example, according to the European Environmental Agency [111], the EU has the ambition to recycle 65% of biowaste by 2030, increasing the production of renewable energy and soil improvers. Composting and anaerobic digestion are currently the most widely applied biowaste treatments together, accounting for approximately 17% of municipal waste; however, a large share of EU-generated biowaste is still landfilled or incinerated [111]. While more stringent limits are being applied to plastics and metals to meet the EU Green Deal objectives and ensure quality and safety of the recycled products, PFAS regulations are notably lacking.

Historically, the Directive has regulated the use of sewage sludge to maximize the nutrient recycling while protecting soil and surface and groundwater quality, primarily by setting maximum loads of specific heavy metals. However, only in 2018 (Decision EU 2018/853) and 2019 (Regulation EU 2019/1010) was the Directive amended to align it with updated environmental legislation and EU sustainability targets. Despite increased regulation and restriction, PFASs accumulated in biowastes produced in contaminated environments can still be concentrated, transferred, and released, increasing risks to the biota and humans as PFASs recirculate in agro-ecosystems. Landfilling, composting, and digestion of biowaste seldom reduce PFAS content in the residual mass; in some cases, the PFAS concentration may even increase in effluent sludge [112], leading to PFAS release into landfill leachates and in the biosolids used as soil amendments.

Common practices that may trigger circular PFAS dynamics include using contaminated biomass for aerobic and anaerobic digestion and applying sewage as a soil amendment. Although these practices are generally regulated to prevent the buildup of inorganic

and organic pollutants and to maximize nutrients and energy recycling, PFAS concentrations in organic amendments are not yet regulated, resulting in limited data on their concentrations in these matrices and their environmental transfer. Lazcano et al. [113] reported PFAS concentrations in compost at a level of 10–200 µg/kg, whereas concentrations in compost from food scraps are 1- to 2-times lower. Considering PFAS persistence and degradation modes (discussed in Sections 2 and 4), contaminated composts and biosolids may become secondary PFAS sources for soils, crops, and agrifood products, even in non-contaminated areas.

These risks are particularly relevant to the agricultural systems, where various biowastes are reused or recycled to soils, sometimes without adequate treatment (Figure 2). As noted, sewage sludge often contains PFASs [114], and current treatment technologies are not yet optimized to destroy PFASs, which can be concentrated in the final sludge. PFASs have also been detected in effluents of wastewater treatment plants [115], septic tanks [116], and in biosolids [117]. Some regulated PFASs may even form during wastewater treatment, likely due to the transformation of unknown precursors entering the plants [118]. For example, concentrations of PFOA and PFOS were higher in final stabilized biosolids than in raw sludge [116,119,120]. Risks of PFAS transfer to agricultural soils are potentially higher in regions where farmers are allowed to use untreated sludge injected or worked into the soil. Due to highly variable sludge management practices, which range from extensive agricultural recycling to high levels of landfilling and incineration across different countries and regions [115], the environmental fate of PFASs in sludge is difficult to predict, and establishing safe concentration limits for sludge-amended soils remains a challenge.

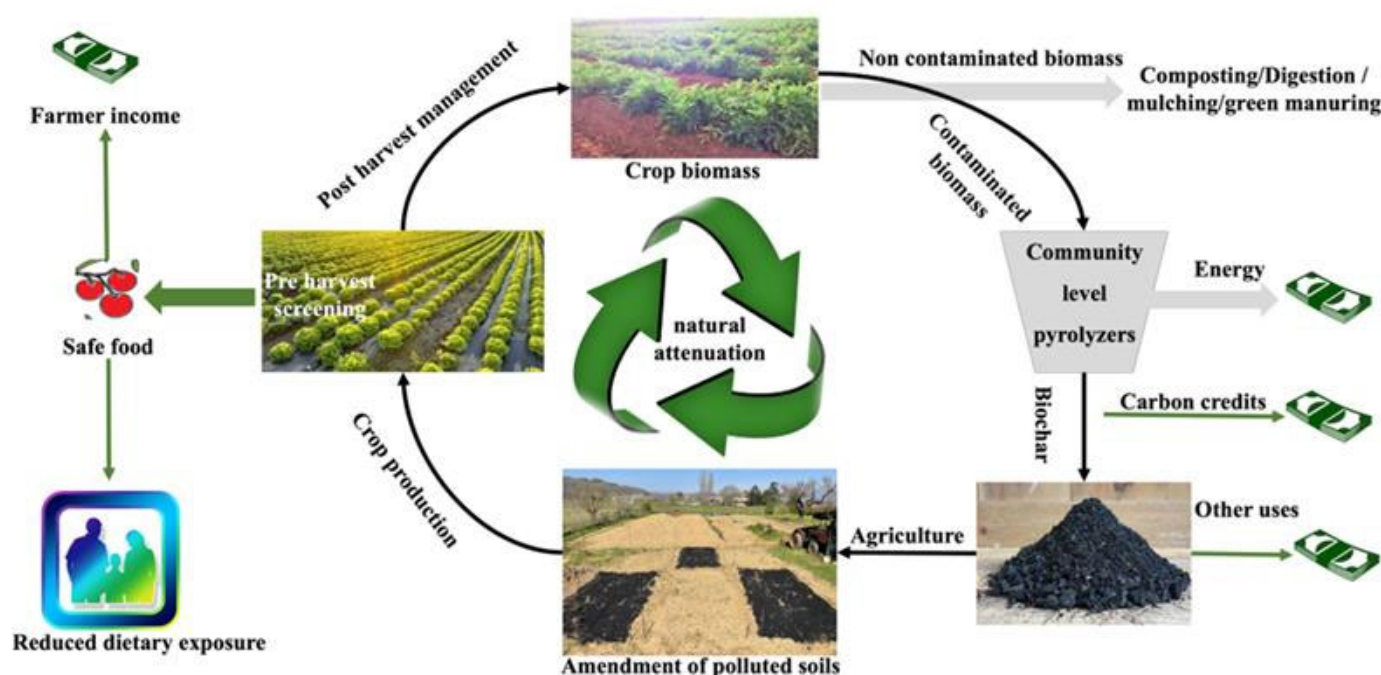


Figure 2. Pre-harvest screening pyrolysis-assisted management in PFAS-polluted areas. Hypothetical mechanisms that could induce PFAS biodegradation in the rhizosphere of plants cultivated on polluted soils.

For biomass undergoing composting and digestion, pre-treatment screening could be beneficial. While PFASs at concentrations of ng/kg in biomass may not inhibit the decomposition process, they could be concentrated in the final biofertilizers. The creation of a “PFAS safe” label for food and feed could significantly drive the implementation of

existing (bio)technologies that prevent secondary PFAS contamination in the environment. Such labels have already appeared for products like textiles, paper, and cookware.

6. Sustainable Management and Mitigation Strategies

Based on current theoretical knowledge and recent advancements in treatment, we propose three potentially sustainable and practical approaches to reduce human exposure to PFASs from contaminated agricultural land and achieve natural attenuation of the issue. The proposed mitigation strategies include community pyrolysis followed by soil amendment with biochar, phytoextraction coupled with tailored pyrolysis processes, and soil irrigation with rainwater. Effective and safe implementation of these strategies will require site-specific risk assessment, increased analytical capacity for PFASs (especially modified and ultrashort-chain PFAS), and strict prevention of fluorinated compound emissions into the atmosphere and hydrosphere during implementation.

6.1. Pyrolysis of Pre-Screened Harvests and Biochar-Assisted Mitigation

For plants cultivated in polluted areas, a mitigation strategy could involve pre-harvest screening coupled with community pyrolysis treatments. Pyrolysis has been shown to degrade PFASs, particularly transforming long-chain PFASs to short-chain PFASs at temperatures of 500–600 °C [121], making this process theoretically more sustainable than incineration. While the resulting biochar is typically PFAS-free, the emission of fluorinated volatile compounds remains a concern. During pyrolysis of contaminated biomass, most PFASs accumulate in the bio-oil, which could undergo further treatment, though the efficiency and overall sustainability of such post-treatments require thorough assessment. With recent advancements in PFAS detection and pyrolysis technologies, there is potential for increased PFAS degradation efficiency, reduced treatment times, and lower energy costs. This pre-harvest screening and pyrolysis approach is illustrated in Figure 2.

Pre-harvest screening of crops could be conducted similarly to practices adopted for crops grown on contaminated soils in Baden-Württemberg [35]. Pyrolysis could also be applied to animal biomass, reducing the spread of PFASs from this source.

Biochar can stabilize PFASs in soils through chemisorption, and its microporosity enables it to physically trap and immobilize PFASs from the soil solution. Recent advances in pyrolysis technology have enabled the use of humid biomass as feedstock in hydrocarbonization processes, producing hydrochar, which could have also PFAS-immobilizing properties. In the carbonization strategy we propose, pyrolysis could treat residual biomass of agri-food plants as well as biomass from PFAS-phytoextraction plants, with tailored thermal treatments to destroy PFASs and add energetic value to the biomass. Pyrolysis could also serve as a post-treatment for sewage sludge as this process can both degrade PFASs and form different PFAS solid sorbents, as demonstrated by Krahn et al. [122] and Kundu et al. [123]. These studies reported the quantitative destruction of PFOA and PFOS in biosolids at a temperature of 500–600 °C. However, the current understanding of PFASs' fate after pyrolysis remains limited. To avoid PFAS emissions during pyrolysis of contaminated biomass, further research is needed to establish a complete fluorine balance. Biochar, like other carbonaceous materials, has a high sorption capacity towards PFASs [83]. We propose that PFAS-free biochar, produced via efficient and environmentally safe biomass pyrolysis processes, could be used as a soil amendment to reduce PFAS uptake by crop plants. Biochar in the rhizosphere could act as an 'in situ' filter, limiting PFAS uptake by plants from soil, irrigation waters, or groundwater. However, biochar sorption sites can eventually saturate, potentially leading to PFAS release to plant or seepage water, creating the risk of a "chemical time bomb" that could release large PFAS quantities if soil properties drastically change due to agricultural practices or land-use changes. We suggest

that amending PFAS-contaminated soils with biochar could become a viable solution only if PFAS biodegradation is initiated by rhizosphere microorganisms.

Why should rhizosphere microorganisms initiate PFAS degradation? Compared to bulk soil, the rhizosphere is enriched with plant root exudates that consist of low-molecular-weight organic substances, which serve as energy sources for actively growing microbial communities [124]. Although the composition of rhizosphere microbial communities varies with plant species, growth, and environmental conditions, these microbes could potentially degrade PFASs by producing specific defluorinating enzyme activities or through unknown co-metabolism pathways. Laboratory studies have shown microbial defluorination of PFASs, and the evolution of biodegradation abilities towards synthetic organic pollutants, including dioxins, PET, antibiotics, and pesticides, has been observed in soil microorganisms [125]. The hypothesis of ‘metabolic infallibility’, introduced by Ernest Gale [126], suggests microorganisms can evolve degradation capabilities for virtually any organic compound. Co-metabolic PFAS defluorination by *Pseudomonas putida* has been linked to the toluene dioxygenase, a Rieske dioxygenase protein, expressed in various environmental bacteria during SOM decomposition [70]. Another potential degradation mechanism involves increased microbial oxidase activity in biochar-amended soils. Increased microbial oxidation potential has been associated with PFOA decomposition [127,128], particularly for fluorotelomers containing C-H bonds. It is also possible that S- or Fe-reducing bacteria with known dehalogenation activities could defluorinate PFASs in low-oxygen conditions. If activated, PFAS biodegradation in the rhizosphere could allow biochar to immobilize PFASs, preventing plant root uptake and enabling microbial proliferation in nutrient-rich hot spots within the rhizosphere (Figure 3). This hypothesis requires testing to assess factors, such as the higher C–F bond strength and tolerable PFAS concentrations for rhizosphere microbial communities.

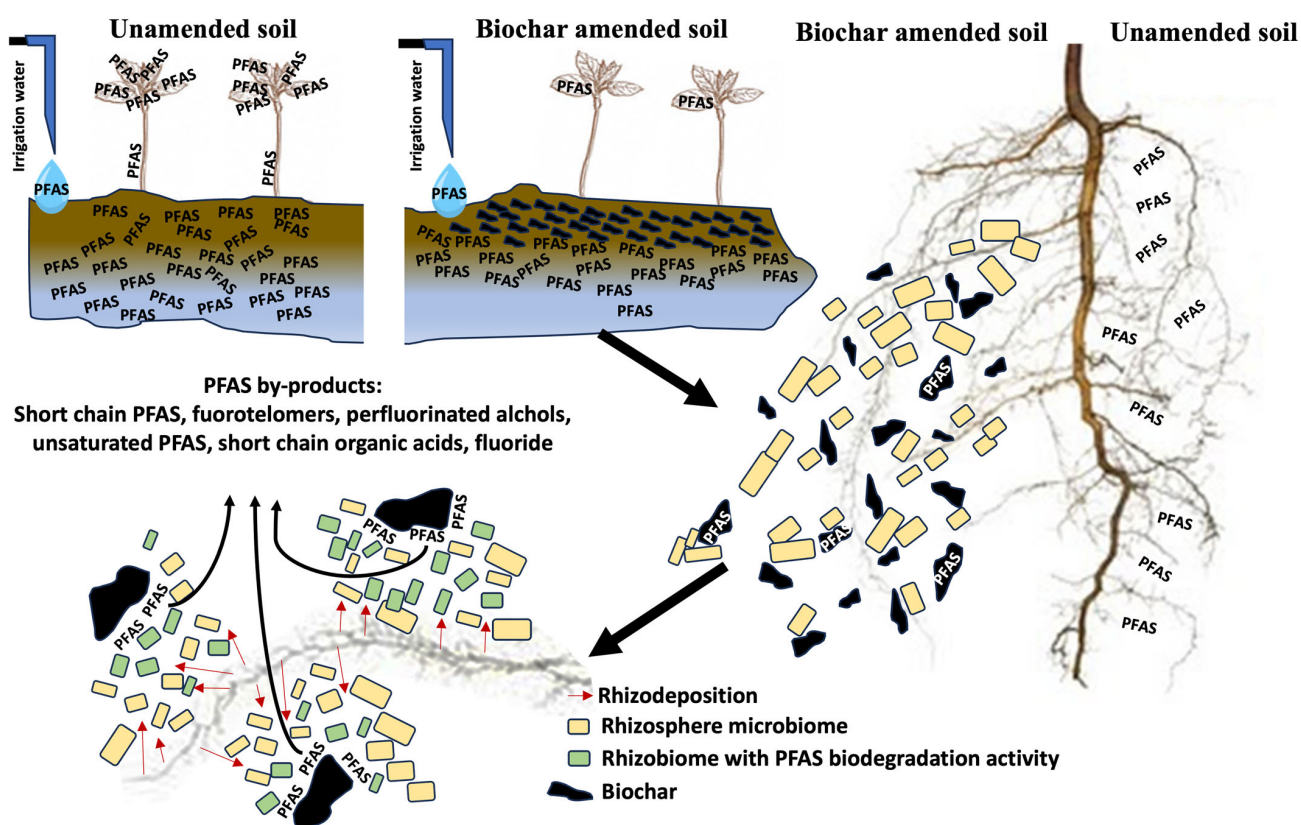


Figure 3. Hypothetical mechanisms that could induce PFAS biodegradation in the rhizosphere of plants cultivated on polluted soils.

6.2. Phytomanagement

Phytomanagement, the use of plants to remove or stabilize pollutants in soil and water, can be implemented using various approaches. Phytoextraction involves plants that can accumulate or hyperaccumulate pollutants from soils and water without significantly affecting growth or reproduction. Accumulator plants have high bioaccumulation factors (BAF) and high shoot/root translocation factors, meaning they store pollutants in the leaves, facilitating the management and valorization of non-contaminated plant biomass (Figure 4). This phytotechnology has been widely used in environmental management and remediation due to its environmental and economic sustainability [129] and its high social acceptance. However, current knowledge on PFAS phytoextraction for contaminated soils and waters remains limited. In a model experiment, Sharma et al. [130] showed that young-rooted cuttings of three willow species could accumulate a mixture of C₄–C₇ PFASs in leaves of high longer-chain (C > 7) PFASs in roots without impacting plant metabolism, demonstrating this woody plant's potential for PFAS phytoextraction. Nassazzi et al. [131] tested sunflower (*Helianthus annuus*), mustard (*Brassica juncea*), and industrial hemp (*Cannabis sativa*) for PFAS phytoextraction from substrates spiked with various C₃ to C₁₃ PFAS carboxylic and sulfonic acids, finding that all plants accumulated concentrations of PFASs up to approximately 40 mg/kg, with mustard and hemp showing higher root-to-shoot translocation for shorter-chain PFASs (C₃–C₆), confirming previous findings [130].

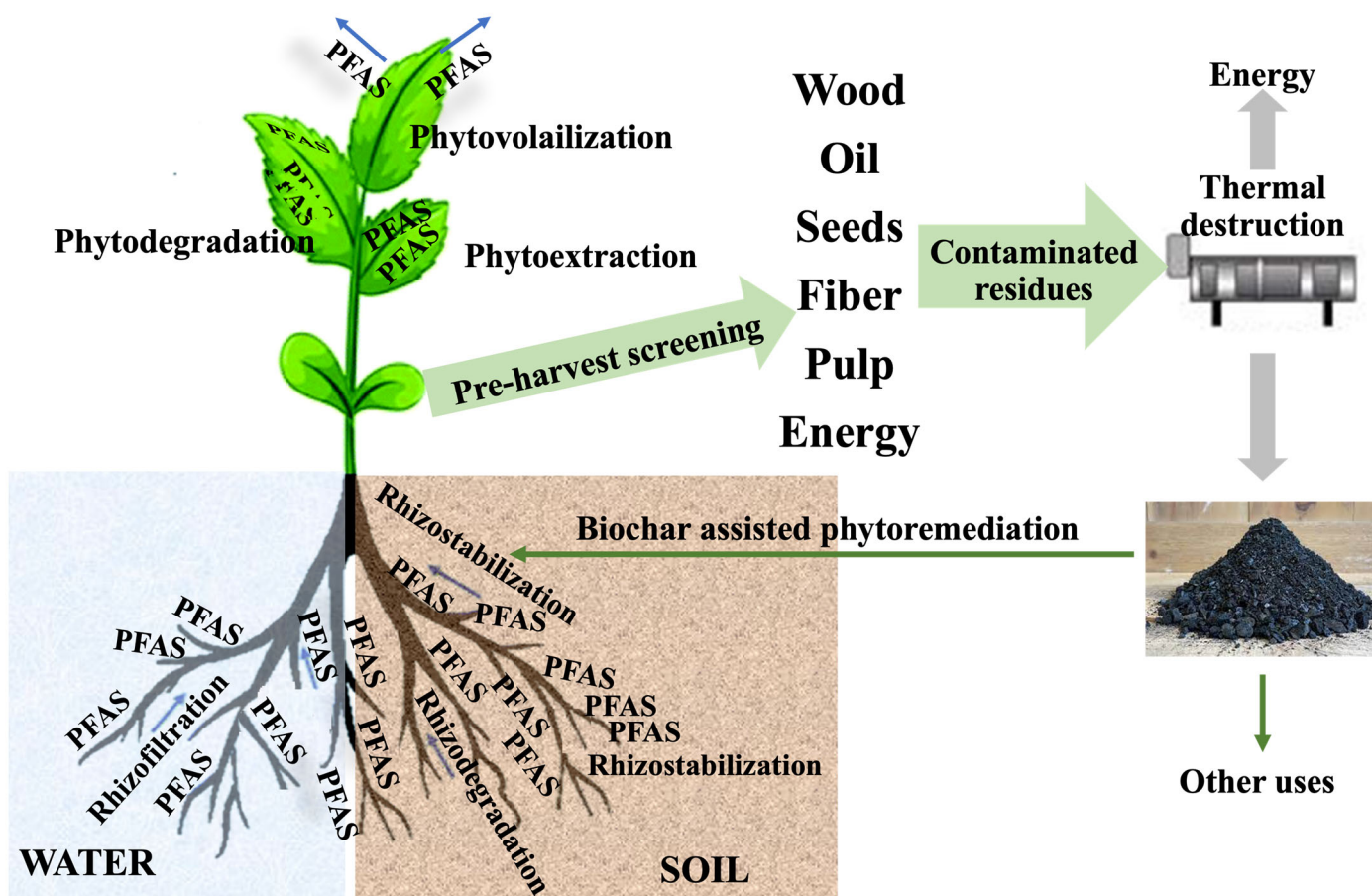


Figure 4. Phytoextraction–thermochemical PFAS destruction strategy for sustainable management of PFAS-polluted areas.

We hypothesize that phytoextraction with PFAS-tolerant plants, coupled with PFAS thermal destruction treatments, could serve as a sustainable management strategy for

contaminated areas (Figure 4). Some plant degradation pathways have been described, and endophytic bacteria have also demonstrated PFAS biodegradation in plants [132]. As with other organic and inorganic pollutants, PFAS phytomanagement could utilize either annual or perennial woody plants and shrubs. These plants can be analyzed, and their biomass can then be treated for PFAS destruction and valorization. However, in addition to the limitations of pyrolysis processes mentioned above in terms of PFAS destruction efficiency, this phytoextraction strategy must also prevent the potential transfer of PFASs to other environmental compartments due to herbivores and pollination activities by insects.

6.3. Irrigation with Rainwater

Scientific evidence strongly indicates that PFAS transport in the environment is mediated by water, the primary medium through which plants absorb PFASs from soil [79]. We hypothesize that, given a contamination level of water, PFAS uptake by plants depends on the quantity of water available for plant absorption. The amount of plant-available water depends on different fractions retained by gravimetric, osmotic, and matric forces [133] and can roughly be described as soil water content between field capacity and wilting point. This availability varies considerably by soil type, soil texture, soil organic matter (SOM) content, and climate [134].

Based on these assumptions about water availability and PFAS transfer from soil to plants, we hypothesize that irrigation with unpolluted water might reduce the PFAS uptake by cultivated plants. The mechanism behind this is that saturating, clean water may be more accessible to plants compared to PFAS-enriched soil matrix water, potentially displacing PFASs bound to soil particles into the soil solution. In practice, irrigation with PFAS-free water could counter the primary PFAS transfer mechanism into plants, creating a form of “in situ soil washing” over time (Figure 5).



Figure 5. Cont.

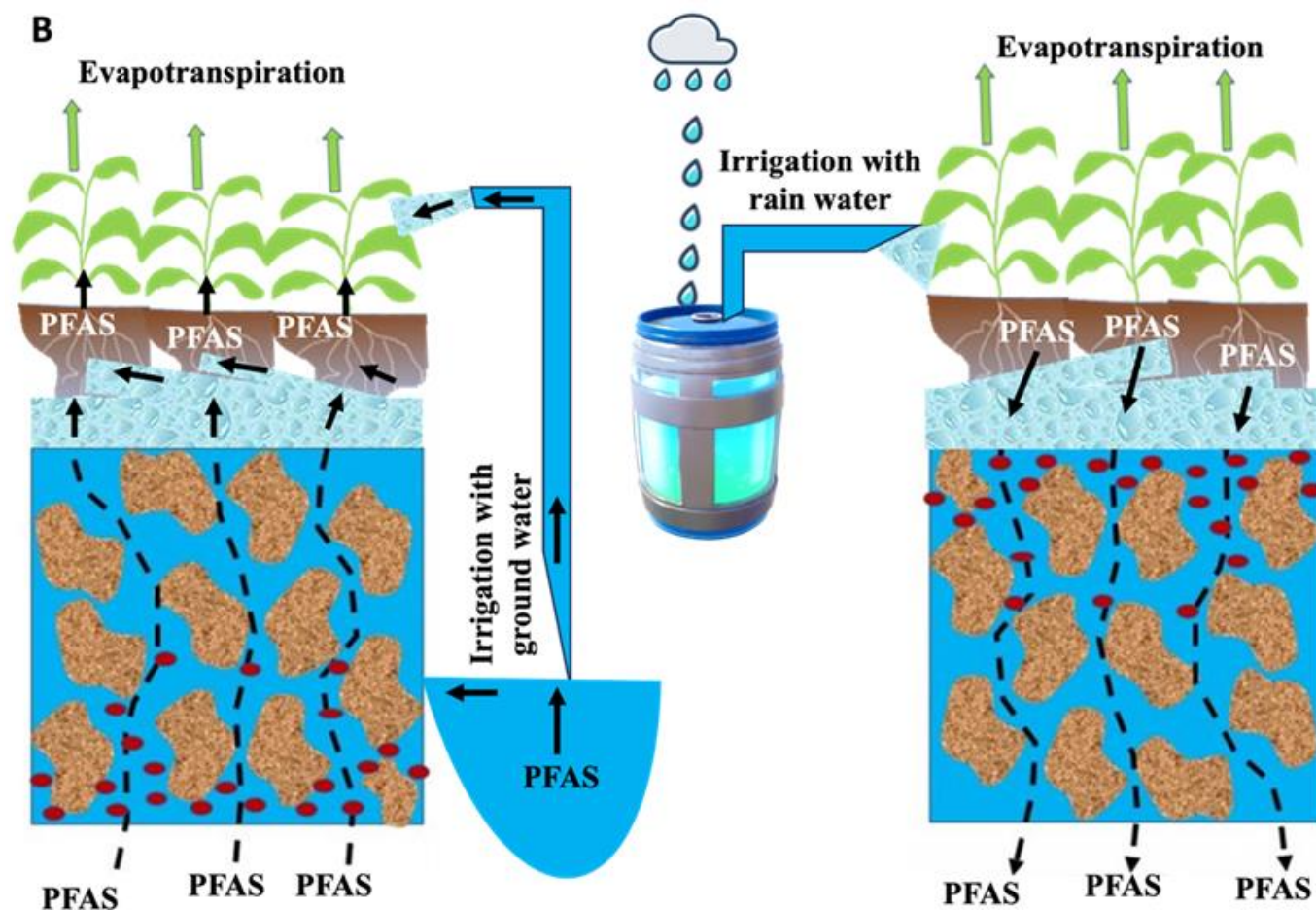


Figure 5. (A) Experimental plots of mitigation experiments of PFAS uptake by using biochar and rainwater irrigation conducted in the PFAS-polluted areas of Vicenza (Italy). (B) Representation of the hypothetical mechanisms preventing PFAS uptake by plants irrigated with rainwater due to the effective moisture plant uptake.

In polluted areas, groundwater used for irrigation may also contain PFASs. Therefore, we propose creating community-level rainwater to provide clean water for irrigation. While this approach may not be feasible for intensive agricultural systems due to water demands, it could be viable for smallholder farming. This strategy may be particularly effective in dry areas, where plants develop deeper branching roots to access scarce water resources [135,136].

7. Stakeholders' Engagement: From a Wicked Problem to Awareness and Consensus Solutions

In addition to scientific advancements and environmental technology development, sustainable management of a complex issue like PFAS pollution requires the coordination of diverse stakeholders with varying perspectives and priorities. Knowledge-based solutions do not always translate into policy updates, as top-down approaches can lead to conflicts between policy makers, businesses, citizens, and activists. Engaging multiple stakeholders to define and address the causes, consequences, and remediation of PFAS pollution goes beyond scientific knowledge alone; it involves encouraging active stakeholder participation in creating policies and actions that directly impact communities. The literature on PFASs highlights the need to transform theoretical knowledge into practical solutions and to spur policy responses through a range of strategies. Community or individual involvement can promote sustainable practices and effective PFAS management driven by health concerns,

regardless of age, gender, and socio-economic levels. For example, PFAS pollution raises gender-specific issues, as reports from the European Food Safety Authority (EFSA) and epidemiological studies suggest higher PFAS accumulation in men due to greater food intake and increased accumulation in male fat tissues. Additionally, PFASs have been shown to transfer to infants via breast milk, and there is concern over their ability to cross the placental barrier, potentially impacting fetuses during pregnancy. Public awareness efforts have brought these issues to light, influencing movements such as 'No PFAS mothers' or the 'Zero PFAS Mothers' mobilization in the Veneto Region, where PFAS levels in children's blood have been recorded up to 40-times above safe limits (8 ng/mL). This growing awareness has shifted public inquires to administrators from water contamination concerns to broader impacts on primary products and the entire food chain, calling not only for monitoring but also effective protection and remediation interventions.

One example of an inclusive process involving stakeholders is the use of "living labs" and "lighthouses", innovation hubs where research organizations, companies, citizens, and authorities collaboratively develop and validate solutions that can be applied in similar situations. However, to our knowledge, none of the current initiatives within the European Network of Living Labs [137] is focused on PFASs. In such settings, guidelines could be created for the safe composting of PFAS-polluted home biomass, reducing human exposure and preventing PFAS recirculation into the environment. Additionally, these initiatives can help minimize socio-economic impacts by reducing the need for waste transport and management costs.

8. Conclusions

The environmental persistence, mobility, and bioaccumulation of PFASs in humans and biota, coupled with their molecular diversity and analytical uncertainties, make PFAS pollution a challenging environmental problem. Although water has been identified as a primary source of human exposure, the contribution of food produced in contaminated areas has been sufficiently assessed and may be more significant than is currently understood. This could explain why, despite measures such as drinking water treatment and the prohibition of well use in polluted areas, high exposure remains among populations in rural environments, likely due to the consumption of self-produced or locally sourced food. Additional exposure pathways for farmers may include the use of PFAS-contaminated composts, biosolids, and soil amendments derived from the recycling of contaminated biowastes.

In this review, we propose potential mitigation strategies for managing PFAS contamination in affected areas: (i) community-based pre-harvest screening of crops combined with pyrolysis of contaminated biomass and biowastes; (ii) phytoextraction using PFAS hyperaccumulator plants, followed by thermal treatment for PFAS destruction and biomass valorization; and (iii) irrigation with rainwater coupled with pre-harvest screening. We emphasize that these strategies should only be implemented when accurate analytical methods can confirm PFAS destruction or safe post-treatment management.

Since a complete phase-out of PFAS production and use is not feasible in a short time, and large regions globally lack regulations or restrictions on PFASs, we argue that sustainable management strategies for PFAS-contaminated soils should be collaboratively developed and co-created by authorities, citizens, and stakeholders. This collaborative approach is essential given that PFAS pollution is widely perceived as an intractable problem, raising concerns about the future health and safety of populations. To address this complex socio-environmental issue, it is crucial to support new policy initiatives that leverage comprehensive, convergent knowledge bases. These policies should aim to prevent conflicts of interest and deliver sustainable, long-term benefits to affected communities.

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