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# Linking drivers of plant per- and polyfluoroalkyl substance (PFAS) uptake to agricultural land management decisions

Special Collection: Special Topic Collection: Per- and Polyfluoroalkyl Substances (PFAS) at the Interface of Biological and Environmental Systems

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## Linking drivers of plant per- and polyfluoroalkyl substance (PFAS) uptake to agricultural land management decisions

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#### ABSTRACT

Widespread contamination of the per- and polyfluoroalkyl substance (PFAS) in agricultural areas is largely attributed to the application of  $\frac{1}{20}$  sewage sludge in which the PFAS can be concentrated. This creates a pathway for these contaminants to enter the food chain and by extensewage sludge in which the PFAS can be concentrated. This creates a pathway for these contaminants to enter the food chain and, by extension, causes human health and economic concerns. One barrier to managing land with PFAS contamination is the variation in reported ig plant uptake levels across studies. A review of the literature suggests that the variation in plant uptake is influenced by a host of factors 🔅 including the composition of PFAS chemicals, soil conditions, and plant physiology. Factors include (1) the chemical components of the PFAS such as the end group and chain length; (2) drivers of soil sorption such as the presence of soil organic matter (SOM), multivalent cation concentration, pH, soil type, and micropore volume; and (3) crop physiological features such as fine root area, percentage of mature roots, and leaf blade area. The wide range of driving factors highlights a need for research to elucidate these mechanisms through additional experiments as well as collect more data to support refined models capable of predicting PFAS uptake in a range of cropping systems. A conceptual framework presented here links drivers of plant PFAS uptake found in the literature to phytomanagement approaches such as modified agriculture or phytoremediation to provide decision support to land managers.

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#### I. INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) have yielded novel dangers to human and ecosystem health since they were first introduced to the environment in the 1940s.<sup>1</sup> The stable carbonfluorine bond, hydrophobic and lipophobic properties of PFAS make these compounds useful in consumer products such as food packaging, dental floss, textiles, paper products, nonstick pans, and aqueous film forming foams (AFFFs).<sup>2-6</sup> The chemical qualities of PFAS that make them water-resistant and durable are the same qualities that make them highly persistent and capable of bioaccumulating in the biotic environment.

PFAS contamination of agroecosystems is attributed to the use of aqueous film forming foam (AFFFs), industrial waste streams, and the application of sludge from wastewater treatment plants (WWTPs).<sup>7</sup> Historically, sludge (biosolids) from WWTPs has served as a financially attractive alternative to manufactured fertilizer and has been subsequently licensed for spreading on agricultural land. Some biosolids used for this purpose contained high concentrations of PFAS. The use of WWTP sludge containing PFAS has elevated contaminant concentrations in many agricultural soils, creating potential pathways for these contaminants to enter the food system.<sup>8</sup>

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The presence of PFAS in the food system is of great concern, as there is substantial evidence connecting PFAS to adverse health impacts among human, aquatic, and other terrestrial populations.<sup>1,9–11</sup> Human impacts of PFAS exposure, primarily via ingestion, include the depression of immune functioning in children, chronic autoimmune issues, increased thyroid disease, increased liver disease and liver cancer, increased lipid and insulin dysregulation, increased kidney disease, kidney cancer, and adverse reproductive and development outcomes.<sup>1,12,13</sup>

Soil remediation technologies have been used in agricultural fields with PFAS contamination to mitigate human exposure to PFAS through the food system. However, there are limitations in effectiveness, price, and practical applicability of these technologies. Current soil remediation technologies are limited to the soil immobilization/stabilization approach, which utilizes adsorbent materials such as activated carbon, resins, minerals, or biochar to limit PFAS availability in soils.<sup>14–16</sup> PFAS destruction technologies also exist, which include thermal treatment, chemical oxidation, and electron beam treatment; however, these techniques must be used *ex situ*. These approaches are often costly and few have been implemented beyond a laboratory scale.<sup>14</sup> Finally, there are soil separation technologies such as soil washing and foam fractionation with soil slurries, which are in emerging stages of testing.<sup>14</sup>

While remediation, destruction, and separation technologies may be necessary for high-value, highly contaminated soils, the cost and risk of exposure to PFAS from lightly contaminated soils, meaning soils with measurable contamination barely exceeding screening levels, could be mitigated by pursuing other, less costly, management options. To make these decisions, it is necessary to look at agroecosystems holistically to understand how the uptake of PFAS into the edible portions of plants can be minimized through modified agricultural approaches *or* methods for facilitating plant uptake by the phytoremediation of the soil to ensure future safe food production and farm viability.

Phytomanagement is the use of plants to minimize environmental and health risks while also providing an economic return for the agricultural management of PFAS-contaminated land, which can include modified agricultural practices and phytoremediation.<sup>17</sup> In this context, modified agricultural practices could include the practice of using soil amendments, vegetation management, or crop choices that respond to the initial concentration, anticipated mobility, and uptake potential of PFAS in edible crop portions, in order to allow growers to maintain production and consumer safety.<sup>16</sup> For example, growing a low-accumulating crop in lightly contaminated soil has the potential to provide growers with a source of income without posing a risk to human health. Meanwhile, phytoremediation is the more specific use of plants to extract contaminants from the soil.<sup>17</sup> An example of this might be the repeated cultivation, harvest, and removal of a hyperaccumulating nonedible crop to extract PFAS from the soil.

The objective of this review is to (1) highlight the PFAS chemical structure, behavior in soil, and crop physiology driving plant uptake, and bioaccumulation of PFAS and (2) contextualize these factors in a framework that is useful for evaluating management strategies for the continued agricultural productivity of lightly contaminated land.

#### **II. PFAS CHEMICAL STRUCTURE**

PFAS are defined as chemicals with at least one fully fluorinesaturated methyl or methylene group, although most are highly fluorinated aliphatic compounds.<sup>18</sup> The chemical structures of PFAS compounds define their unprecedented ability to persist in the environment. A variation in their chemical structures, however, produces disparities between the fate and transport of different PFAS compounds across soil and plant interfaces as well as within plant compartments.<sup>19,20</sup> Therefore, the transport and subsequent fate of the suite of PFAS compounds present within an agricultural setting determine the level of risk associated with farming on a particular site and by extension potential management approaches. Here, we discuss the chemical properties (e.g., end group and carbon chain length) of commonly occurring PFAS compounds.

The scope of this review extends to the most studied and commonly detected types of PFAS congeners in biosolid-amended soils: perfluoroalkyl carboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs).<sup>21</sup> These are of great importance as they represent the compounds present in agricultural systems from the legacy contamination of biosolids. Additionally, more recent PFAS compounds, described as "precursors," have been shown to be susceptible to biotransformation into PFCAs and PFSAs.<sup>22</sup>

Long-chain PFASs are commonly studied due to the known adverse human health impacts associated with these compounds, potential for bioaccumulation, and their elevated concentrations in biosolid-amended soils. Long-chain PFASs exhibit longer half-lives in paired human urine and serum samples, with PFOS taking 2.6 years to be reduced by half, compared to the short-chained PFBS half-life of 44 days.<sup>23</sup> While there are concerns that restrictions on the manufacturing and use of long-chain PFCAs and PFSAs will result in increased concentrations of shorter-chain compounds in the environment, it also appears likely that the breakdown of novel precursor compounds will result in more PFCAs and PFSAs exhibiting long-chainlike behaviors.<sup>21,22,24</sup>

#### A. End group

PFCAs and PFSAs are distinguishable by the carboxylic acid versus sulfonate end group attached to the carbon chain.<sup>18</sup> Both have negatively charged hydrophilic end groups, which influence the electrostatic and hydrophobic interactions between these PFAS and the surrounding soil/water/plant environment, dictating their partitioning behavior. This influences the degree to which the compounds accumulate within the abiotic and biotic environment.<sup>25–28</sup> A variety of field and greenhouse studies have shown PFCAs to be more readily bioavailable to plants than PFSAs of similar molecular size, although there is uncertainty as to what causes this effect.<sup>29</sup>

#### **B.** Chain length

The PFSA and PFCA end groups are connected to a fully fluorinated carbon tail with variation in the length, referred to as chain length. Chain length is designated based on the number of carbon atoms in the chain, typically ranging from two to fourteen, where compounds containing two to three carbons are defined as ultra-short-chain, four to five (PFSAs), or four to seven (PFCAs) are short-chain, and compounds above those thresholds are considered long-chain.<sup>30,31</sup> Based on these definitions, it is clear that the chain length is not only associated with the absolute number of carbons in the chains but also a way to communicate the partitioning behavior of a compound. This is important when considering how these designators affect PFAS mobility and uptake in crops.<sup>18,32,33</sup> Furthermore, these distinctions and the chemical characteristics associated with them have different implications for the fate and transport of PFASs in the plant-soil interface, as well as relative risks to human health.

The chain length of PFAS compounds has been directly linked to compound persistence in agroecosystems. Compounds with longer chain length, and concomitantly a greater number of carbon-fluorine bonds, possess a greater hydrophobic surface area, strengthening the hydrophobic interactions underlying soil sorption.<sup>32</sup> Partially for this reason, long-chain PFASs are less concentrated in aboveground plant compartments, despite being more persistent in soil, and more consistently bound to the upper layers of the soil.<sup>20,33–36</sup> Another important feature is whether PFAS fluorocarbon chains are branching or linear. While branched isomers have received less attention in the literature, the degree of branching has been shown to affect sorption and biotransformation in soils.<sup>37,38</sup>

Overall, considering PFAS end group and chain length is vital in evaluating farm risk, but it is important to recognize that PFAS fate and transport are also highly impacted by soil properties and the physiology of the crop being grown.

#### III. PFAS IN SOIL

Soil sorption is the association of contaminants with soil particles, primarily through binding to soil surfaces, and it greatly influences the persistence and mobility of contaminants within agroecosystems.<sup>39–41</sup> The sorption of trace organic contaminants is inversely related to bioavailability in soil. Therefore, it is essential that management approaches respond to the potential for soil sorption and bioavailability within a given soil.<sup>42–44</sup> For example, phytoremediation efforts should target soils with low PFAS sorption potential and high PFAS bioavailability, while modified agriculture and immobilization strategies are best suited to agricultural soils with high sorption capacity and low bioavailability. In this section, we discuss soil conditions that influence PFCA and PFSA soil sorption.

There are two primary mechanisms driving the soil sorption of PFASs: hydrophobic interactions and electrostatic interactions.<sup>39</sup> These are modulated by PFAS chemical and soil biogeochemical characteristics including soil organic carbon content, pH, micropore volume, cation exchange capacity, soil texture, aluminum and iron oxides, cation content, and the interactions of these characteristics.<sup>39,45,46</sup>

#### A. Hydrophobic interactions

Hydrophobic interactions between the fluorocarbon tails of PFAS and soil particles are regarded as the strongest drivers of long-chain PFCA and PFSA sorption.<sup>46,47</sup> Soil organic matter (SOM) contains hydrophobic moieties that can interact with the tails of PFCAs and PFSAs as both seek exclusion from water.<sup>40,42</sup>

As a result, increased amounts of SOM have been linked to the increased sorption of the PFAS.  $^{46,48}$ 

The impacts of soil organic matter are compounded by the chain length, with long-chain PFASs having greater hydrophobicity, and by extension more potential to sorb to SOM.<sup>39,42,46</sup> In fact, sorption (Kd) values of C4–C14 PFCAs increased 0.39 to 0.48 log units with each addition of a fluorinated-carbon atom.<sup>49</sup> Similar results were observed by Nguyen *et al.*<sup>32</sup> Biosolids used as fertilizers are enriched in long-chain PFAS compounds, which increases the likelihood of PFAS sorption to soils through hydrophobic interactions.<sup>48</sup>

The interaction of PFAS chain length and soil sorption is supported by findings that show hydroponically grown plants to have increased root uptake of long-chain PFASs relative to plants grown in soil or potting media where no chain length dependency or a decrease in the uptake with increasing chain length has been found, suggesting that long-chain PFASs were sorbed to soil in these experiments.<sup>20,34,50</sup> High amounts of long-chain PFASs found in agricultural soils are of concern, and their greater reported abundance, relative to shorter-chained compounds, may be explained by a combination of their enrichment in the contaminant source and the increased propensity of long-chain compounds to remain in upper soil horizons, while shorter-chained compounds are more readily mobilized within the environment and may leach deeper into the soil or even to the groundwater prior to testing.

#### **B. Hydrophobic interactions**

Electrostatic interactions between charged PFCA or PFSA end groups and charged functional groups in the soil are the primary mechanisms driving short-chain PFAS sorption.<sup>51</sup> Electrostatic interactions include direct interaction between the negatively charged PFCA/PFSA end group and positively charged mineral or amine groups.<sup>42</sup> Alternatively, ligand bridging occurs, which is the result of a positively charged ion connecting the negative charges of PFCAs/PFSAs and SOM.<sup>42</sup> At lower multivalent cation concentrations, PFCA/PFSA ligand bridging potentials are reduced.<sup>42,50</sup> In these conditions, negatively charged SOM functional groups repel the negatively charged end groups of PFCAs/PFSAs, resulting in their greater partitioning to the soil–water solution. For this reason, soil cation exchange capacity, the ability of soil or sediment to exchange cations, has been linked to soil sorption.<sup>42</sup> Cation concentrations vary as a result of pH and the soil mineral content, which is a potential reason for conflicting results relating to the role of SOM in PFAS sorption across the experiments.<sup>46,50</sup>

Soil p*H* greatly influences functional group charge and, therefore, electrostatic interactions with anionic materials.<sup>52,53</sup> PFCAs and PFSAs become more anionic (deprotonated) with increasing p*H*, heightening the repelling forces between PFASs and SOM. This effect is compounded when reduced ligand bridging is occurring due to low concentrations of multivalent cations. As a result, several researchers have observed an inverse relationship between the soil p*H* and sorption of PFCAs/PFSAs, especially under conditions with low cation concentrations in pore water.<sup>29,46,54</sup>

#### C. Additional drivers

Soil is complex, and it is recognized that a variety of soil properties interact with PFCA and PFSA chemistry to influence their soil sorption. For example, in a multiple linear regression model, sorption was described well when the model included combinations of soil organic carbon, silt-plus-clay content, and soil micropore volume.<sup>32</sup>

The availability of the soil surface area indicated by the size distribution and presence of micropores influences PFAS sorption. Soils with smaller particle size offer a greater surface area available for the PFAS to bind.<sup>39</sup> Clay particles are the smallest ( $\leq 0.002 \text{ mm}$ ) followed by silt (0.002-0.05 mm) and then sand (0.05-02.0 mm).<sup>52</sup> Clay particles can also add to the available pool of positively charged mineral binding sites. As a result, clay has been linked to the highest levels of absorption, with some clay amendments even being suggested for immobilization strategies.<sup>15,39</sup>

Interactions between the soil microbiome and PFAS contamination can further influence plant uptake. While rare, there are microorganisms with the capacity to biotransform PFAS.<sup>55</sup> In most cases, the reactions do not yield energy for the microorganism but are the result of cometabolism.<sup>22</sup> A few instances do exist of transformations that can support microbial growth, but they generally do not result in mineralization, and PFCAs are often end points of the transformation of precursor compounds. Metabolites may have increased or decreased bioavailability as a result.<sup>22</sup>

In addition to the microbial effects on the PFAS mixture in soil, the presence of PFAS in the soil can affect the soil microbial community structure and function, including shifts in soil bacterial and fungal abundance, decreased soil respiration, and increased soil pH.<sup>56–58</sup> As stated, soil properties such as pH affect PFAS sorption to soil; therefore, shifts in the soil structure and function in response to PFAS contamination could impact sorption indirectly. This highlights the need for more research on how plant–soil–microbiome feedbacks affect the uptake of PFAS by plants, particularly in the rhizosphere where microbial abundance is high and root exudates may also influence PFAS uptake.

Additional properties linked to greater sorption include higher noncrystalline forms of Fe and Al such as oxyhydroxides or organometal complexes in addition to the location of PFCA and PFSA compounds in the surface rather than subsurface soil horizons.<sup>46</sup>

#### IV. UPTAKE IN PLANTS

The soil environment and chemical structure of the PFAS are found to have a significant influence on the availability of the PFAS to crops, but once bioavailable, there are a variety of possible outcomes driven by variations in plant species physiology and plant compartment. Therefore, it is imperative that management options consider PFAS concentrations in edible plant portion concentrations for modified agriculture approaches and total crop uptake for phytoremediation approaches.

One consistent finding across all plant groups is that the chain length is the most prominent influencer of transfer factors (TFs), the ratio of PFAS analyte concentration in plant tissue relative to its concentration in colocated soil samples both on a dry weight basis.<sup>29</sup> Researchers have found TFs among different crop groups to rank from the highest to lowest as follows: leaf vegetables>root vegetables>flower vegetables>shoot vegetables.<sup>33,56</sup> This is in tension with a previous study completed outside a fluorochemical industrial park, which showed (highest to lowest) bioaccumulation rankings as shoot vegetables>fruit vegetables>flower vegetables>root vegetables.<sup>59</sup> This discrepancy is likely due, at least in part, to airborne transmission and the different classifications of crops—for example, lettuce fell into the "shoot" category in Liu *et al.*<sup>59</sup>, but in the leaf category in Xu *et al.*<sup>23</sup> However, this inconsistency also highlights the potential variation in uptake within crop groups as a result of soil properties and the profile of PFAS chemical contamination at a site.

Trends within plant compartments have been consistent with respect to the PFAS chain length, which is useful for considering human health risk and farm viability.<sup>60</sup> Overall, roots hold larger concentrations of the long-chain PFAS, while aboveground plant parts have higher concentrations of short-chain compounds.<sup>25,26,33,34</sup> Within aboveground compartments, transfer factors for short-chain PFAS rank from the highest to lowest as follows: leaf blade>fruit>stem.<sup>20,33,34</sup>

#### A. Roots

Roots are the primary pathway of PFAS uptake from biosolid-amended soils into plants.<sup>61</sup> Root macrostructure can play an important role in facilitating uptake.<sup>33</sup> In a study of four urban weeds (*Phyllanthus urinaria, Justicia procumbens, Eleusine indica,* and *Aster indicus*), the root area and leaf area were highly correlated with PFAS TFs.<sup>62</sup> A larger root surface area relative to root volume is associated with finer roots, implying that plant species with fibrous, highly branching root systems have a higher potential for PFAS uptake in contrast to species with taproots, or those with lesser root surface area relative to root volume. This may be the result of greater surface soil volume available for root interception by fibrous rooted species, a greater number of unmatured root tips (potentially exacerbated by root sloughing and regrowth cycles of some agricultural cropping, e.g., forage grasses), or the interaction of the two.

Root exudates are substances secreted by plants into the rhizosphere and have been linked to the intraspecies variation in the PFOA uptake, impacting its bioaccumulation in lettuce.<sup>63,</sup> <sup>54</sup> This effect was attributed to oxalic acid, a common root exudate, which was shown to decrease the sorption of PFOA to soil, increasing its bioavailability. Lettuce varieties have varying concentrations of oxalic acid and even show varying concentrations of oxalic acid levels at different points of the growth cycle. Lettuce varieties in this study were characterized as "low accumulating" or "high accumulating," specifically in reference to their oxalic production and subsequent PFOA accumulation.63 Root exudates, including but potentially not limited to oxalic acid, could be influential in explaining the variation in the bioaccumulation factors of PFOA, and potentially other analytes, across plant species and between cultivars of the same species.

Water, and molecules dissolved within it, enter crop plant roots by traveling through the root cortex via symplastic (through cells via plasmodesmata), apoplastic (between and through cell walls), and transmembrane pathways.<sup>42,65</sup> In the root cortex, the symplastic and transmembrane pathways are selective against the transport of some PFASs (particularly long-chain compounds), while the apoplastic pathway is not. The Casparian strip is a lignin suberin-rich layer in the root endodermis that prevents the

apoplastic passage of water and associated solutes beyond the root cortex.<sup>66</sup> As a result, the passage of PFCAs and PFSAs into aboveground plant compartments is limited to compounds, which can travel through the selective symplastic and transmembrane pathways, where long-chain compounds are filtered out to a greater extent due to the larger molecular size and greater hydrophobicity.42 This results in greater relative transport of the shorter chain length PFASs into aboveground plant parts.<sup>20,33,34,67</sup> In addition, the Casparian strip is normally absent in immature root tips, but there are no data to our knowledge highlighting the concentrations of PFASs across root growth and development. The total PFAS content of root vegetables may, therefore, be influenced by the ratio of cortex tissue relative to tissue within the vascular cylinder, and the presence, quantity, and location of secondary growth characteristics (e.g., cambial layers). Modified stem vegetables such as potatoes should probably be considered more akin to fruit tissue, drawing on the transport model described by Lesmeister et al., as they are located further along the transpirational water transport pathway than roots (i.e., postfiltration of the Casparian barrier) and, however, are not exposed to the same potential for the evaporational deposition of PFCAs/PFSAs in xylem water that leafy tissues maybe, and instead likely have a ratio of xylem flow relative to phloem transport that more closely resembles that of fruit tissue.

#### **B. Fruits**

PFAS uptake in fruit vegetables, such as tomatoes, has been studied by several groups, and the consensus is that a lower amount of uptake occurs in fruit compartments.<sup>19,20,26,34,68</sup> Other fruits such as peppers and pumpkins show this trend as well, but they are less studied.<sup>59</sup> Decreased PFAS concentration in these fruit vegetables has been proposed to be a result of the additional root uptake barrier provided by cambium, secondary growth in roots of eudicot plants, which also acts as a barrier to non-selective apoplastic transport.<sup>33</sup> However, the fruit of monocotyledonous grain crops also exhibits greatly reduced accumulation of the PFAS relative to other plant fractions.<sup>33,59</sup>

Generalized lower fruit uptake of the PFAS may be due, in part, to placental barriers or simply the lower contribution of the comparatively unfiltered xylem flow relative to more selective phloem transport, the ratio of which both progresses as the fruit develops, and is generally expected to be opposite to that of leafy tissue, which is typically expected to transpire vastly greater volumes of water.

#### C. Leaves

Aboveground compartments of leafy vegetables had the highest levels of PFCAs/PFSAs relative to storage structures such as fruits/grains and tubers.<sup>7,25,27,33,34,60</sup> As stated, the leaf area along with root structure was most correlated with TFs. This effect is attributed to greater volumes of transpirational flow, although in a study outside of a fluorochemical plant, Liu *et al.* noted that a larger leaf surface area provides a greater potential area for the atmospheric deposition of the airborne PFAS to collect posing an alternative hypothesis for high levels of accumulation in or on leafy vegetables.<sup>34,59</sup>

#### V. MANAGEMENT

The findings of this review are organized into a series of gradients to conceptualize the most important factors that may influence uptake. By extension, these gradients can help guide management decisions, through either modified agriculture or phytoremediation, in fields where concentrations are low but still pose a risk to food safety and farm viability (Fig. 1). Environmental conditions under which modified agriculture may be more desirable are when the predominant PFAS contaminating the site is longer-chain and, therefore, is less mobile; there are high levels of soil sorption due to soil type, texture, and other edaphic features; and crops can be grown, which accumulate relatively low levels of the PFAS in edible portions. In contrast, when PFASs are more mobile and bioavailable to chosen plant species, e.g., the site is contaminated with shorter-chain PFASs, and the soil is sandy with relatively low organic matter, phytoremediation options may be applicable to site cleanup with goals of bringing the land into production at a later time.

Specifically, less mobile PFASs are often long-chained compounds rather than short-chained and are more often PFSAs rather than PFCAs for chains of a given length. When considering soil conditions ideal for modified agriculture, soils with higher concentrations of clay and silt soils are expected to exhibit increased sorption of the PFAS than sandier soils due to having a greater surface area for electrostatic and hydrophobic interactions to take place. Finer textured soils also tend to have higher organic matter concentrations than coarser textured soils, as well as greater potential for increasing organic matter through amendments and other management practices. High amounts of organic matter and high multivalent cation concentrations that enable cation bridging can help immobilize the PFAS. Long-chain compounds are best immobilized in soils with high amounts of SOM where hydrophobic interactions take place. Bioavailability is further mediated by pH, where soils with lower pH are associated with an increased sorption potential.<sup>46</sup>

Physiology of the crop influences levels of bioaccumulation within edible portions. Crops suitable for modified agriculture are characterized by a less fine root area, a greater percentage of mature roots, low amounts of root exudates, and smaller aboveground vegetative compartments (i.e., leaf blade area). Crops with low potential for uptake are often fruits or grains where there is little uptake in the edible portion. Greens would represent a higher risk crop option in contaminated soil.

Conversely, *in situ* phytoremediation will have a greater likelihood of success in soils with relatively low organic matter, coarse texture, low multivalent cations, and high pH. Based on our conceptual model of PFAS distribution in plants, the best candidate plant species for phytoremediation would be ones with a large fine root mass, high water uptake rate, and potential production of root exudates that facilitate PFAS transport into the roots. From a practical perspective, perennial plants that can be repeatedly harvested to remove the contaminated foliage would be ideal.

#### VI. RESEARCH NEEDS

The work of our review and those previously published have identified chemical, soil, and plant factors influencing PFAS



FIG. 1. Conceptual schematic featuring gradients of chemical, soil, and plant physiological drivers of uptake intended to support management decision-making on fields with light PFAS contamination. The arrow size corresponds to the PFAS uptake potential of the crop. When contaminated environments are not at one end of the gradient or the other, there is greater uncertainty surrounding transfer factors (TF) and, therefore, human health guidelines, and farmer decision-making. This creates a need for expanded datasets and predictive models. Created with BioRender.com.

uptake.<sup>3,29,33,46</sup> Future research needs surround the development of a deeper understanding of these separate factors through data sets and shared sampling protocols before models can be made to accurately predict PFAS fate and transport such as transfer factors and soil sorption. There is much to learn about the role of chemical characteristics such as initial concentration, chain length, and end group in PFAS mobility. Additionally, researchers are beginning to investigate the fate of branched versus linear compounds and precursors in plants and soil, with most of the literature focusing on linear compounds and legacy contaminants.<sup>37,38</sup> Most of the work on this has yet to incorporate recent findings of biotransformation among compounds in plant–soil environments across time, which will be central to future modeling endeavors.

The interaction between the PFAS and soil is muddled as a result of inconsistent soil conditions across studies.<sup>46,59,69</sup> This highlights the need for more paired field and greenhouse studies to elucidate the influence of soil factors on the sorption of the PFAS.<sup>26</sup> Additionally, the influence of soil microbial communities on the biotransformation of the PFAS and the response of these communities to PFAS contamination is an understudied area of research. Microbes have the potential to decrease or increase the bioavailability of the PFAS in soil; therefore, there is a need to better understand the role of the soil microbiome and root exudates of crops, specifically for making modified agriculture decisions that can inform phytomanagement plans.<sup>17,70</sup>

Finally, the diversity of crop species and cultivars poses challenges to creating models that apply to agriculture writ large. Further investigation of the plant physiological mechanisms that inhibit and enable transport of the PFAS, with attention to species-specific relationships with water transport pathways such as  $\frac{1}{2}$  transpiration and transfer between tissues, is needed. It is of an urgent need to obtain soil-to-plant TFs across a wider range of S crops, which will be useful for informing growers, health guidelines, and farmers. Once uptake mechanisms are better understood, research is needed to investigate the possibility of modified agriculture under conditions where PFASs are less mobile such as sites with a greater relative concentration of long-chain PFASs, specifically PFSAs, more soil organic matter, more multivalent cations, higher silt/clay contents, and higher micropore volumes. Evangelou and Robinson (2022) have pointed out that there is not sufficient information to make phytomanagement choices at this moment and, by no means, should crops with TFs that would lead to the contamination of food in excess of safety guidelines be farmed for human consumption.<sup>17</sup> This highlights a need for further research that can inform soil screening levels, the development of food safety guidelines for a wider range of PFAS compounds, the distributions of these compounds in edible portions, and the role of the soil microbiome and root exudates as they affect phytomanagement choices. With further research completed, there is a possibility for low TF crops, fodder, or nonfood crops to be used on lightly contaminated land, alleviating economic and environmental externalities associated with the PFAS contamination of agricultural lands.

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#### AUTHOR DECLARATIONS

#### Conflict of Interest

The authors have no conflicts to disclose.

#### Ethics Approval

Ethics approval is not required.

#### Author Contributions

Alex E. Scearce: Conceptualization (equal); Investigation (equal); Project administration (equal); Writing - original draft (equal); Writing - review & editing (equal). Caleb P. Goossen: Conceptualization (supporting); Writing - review & editing (equal). Rachel E. Schattman: Writing - review & editing (supporting). Ellen B. Mallory: Writing - review & editing (equal). Jean D. MaCrae: Conceptualization (equal); Project administration (equal); Supervision (equal); Writing - original draft (equal); Writing - review & editing (equal).

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