Interaction of Perfluorooctanoic Acid with terrestrial plants: Uptake, transfer and phytotoxicity aspects

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1. Introduction

PFOA is concerned because of its widespread use and frequently detected in most regions of the world. Due to its low vapor volatility and extreme difficulty in degradation, PFOA can stay in soil for long period and cause lasting disadvantages to agricultural production [1,2]. PFOA in soil can be absorbed and enriched to plants. Among the perfluorinated compounds (PFCAs) detected in crops, PFOA was detected with high frequency in plant samples around the world [3–6]. Meanwhile, the bioaccumulation factors of PFOA in plants were also higher than other long-chain perfluoroalkyl carboxylic acids (PFCAs) [5,7]. Studies stated that PFOA was toxic to various plant species, mainly at physiological and biochemical levels. However, there is too little summary and discussion about the interaction of PFOA with terrestrial plants to clarify the internal mechanism and the deficiencies of existing research. Besides, screening plant varieties that suitable for planting in PFOA contaminated soil or plant species with high accumulation is also important for the safe utilization and remediation of contaminated soil. Here, we review the current most relevant studies to summarize the uptake and transport of PFOA in diverse plant species and provide implications for future research.

2. Uptake and translocation of PFOA in plants

PFOA can enter the plants through root absorption in the soil or leaf deposition from the atmosphere, and then effectively transfer to other organs [8,9]. Due to its strong C-F bond energy, it is difficult to decompose in plants and stays as a complete PFOA molecule when uptake and transfer [9]. Uptake of PFOA varied with plant species and exposure conditions, as summarized in Table 1. Among the existing studies, there are still few studies in field and woody plant experiments [10,11]. Besides, there are also limited phytotoxicity tests exposed to PFOA alone. Although mixed exposure is closer to the actual situation, individual exposure is essential to understanding the toxicological mechanism.

Studies have been carried out on the accumulation and distribution mechanism of PFOA in plant roots, including the distribution characteristics of PFOA from the root surface to the vascular column at tissue and cell level, the accumulation characteristics in subcellular, and the accumulation pathways of apoplasm and symplast [12–14]. However, currently, there is no conclusion on the way for plant utilization of PFOA. To summarize, there are two ways: PFOA was found mostly distributed in water-soluble fraction and cell wall, and transported from cortex to vascular bundle via symbiotic pathway [13]; PFOA was also found in the radial movement from epidermal cells to cortex through extracellular and symbiotic pathways [14]. In addition to being directly absorbed by roots, there is another way, metabolic transformation from other perfluorinated compounds [15]. Studies found that precursors such as fluorotelomer-based acrylate polymers (FTACPs) and fluorotelomer alcohols (FTOHs) can be
Table 1. The summary of existing PFOA uptake in terrestrial plants.

| Plant types | Plant species | Growth condition | Growth media | Pollutants | PFOA concentration | Time | PFOA in plants (ng/g) | BCF value | Uptake part |
|-------------|---------------|------------------|--------------|------------|--------------------|------|----------------------|-----------|-------------|
| Crop        | Triticum aestivum L. | chamber | soil | mixed | 200 ng/g, 500 ng/g, 1000 ng/g | 285 ng/g | 30d | 461 ± 86.8, 901 ± 158, 1417 ± 65.4 | 0.11 ± 0.02, 0.09 ± 0.01, 0.07 ± 0.03 | Root, shoot |
| Vegetable   | Lactuca sativa | greenhouse | soil | mixed | 3 μg/week | maturity | 298 ± 45.6, 95.7 ± 9.89, 38.0 ± 10.8 | 34.9 ± 5.34 (0.4%OC), 4.30 ± 0.44 (2%OC), 1.18 ± 0.34 (6%OC) | Leaf |
| Herb        | Brassica juncea | greenhouse | soil | mixed | 94,000 ng/week | 98–126d | 1814 ± 435 | 0.11 ± 0.02, 0.09 ± 0.01, 0.07 ± 0.03 | Root, shoot |

(Continued)
| Plant types | Plant species | Growth condition | Growth media | Pollutants | PFOA concentration | Time (week) | PFOA in plants (ng/g) | BCF value | Uptake part | R |
|-------------|---------------|-----------------|--------------|------------|--------------------|-------------|----------------------|-----------|-------------|---|
| Arbor | Populus canescens | field sediment | PFOA | 95.0 ± 3.71 ng/g | - | 13.3 ± 1.44 | 0.14 | Root | (11) |
| | Fraxinus pennsylvanica | greenhouse soil | PFOA | 94,000 ng/week | 98 | 1 ± 0 (foliage), 23 ± 12 (woody); 105 ± 49 (foliage), 3 ± 2 (woody); 1123 ± 396 (foliage), 64 ± 14 (woody); 3442 ± 241 (foliage), 241 ± 52 (woody) | 0.00; 0.90; 45.80; 10.90; 9.70; 28.90 | | (10) |
| | Picea ponderosa | greenhouse mixed | PFOA | | 126 | | | | | |
| | Pinus taeda | greenhouse mixed | PFOA | | | | | | | |
| | Betula nigra | greenhouse soil | PFOA | | | | | | | |
| | Liquidambar styraciflua | greenhouse soil | PFOA | | | | | | | |
| | Platanus occidentalis | greenhouse soil | PFOA | | | | | | | |
| | Salix nigra | greenhouse soil | PFOA | | | | | | | |

Table 1. (Continued).
| Plant type | Plant species | Exposure concentration | Growth Media | Exposure time | RCFs<sup>a</sup> | TFs<sup>b</sup> | R          |
|-----------|-------------|------------------------|---------------|--------------|----------------|----------------|------------|
| Vegetable | Carrots;    | 681 ± 160, 676 ± 88;   | soil          | 63d;         | -              | C<sub>plant</sub> / C<sub>soil</sub> 0.53; | [30]       |
|           | Potatoes;   | 276 ± 22, 796 ± 10;    | soil          | 71d;         | -              | 0.40 ± 0.02;   | [31]       |
|           | Cucumbers;  | 0.86 ± 36, 805 ± 63 μg/kg | soil          | 69d;         | -              | 0.88 ± 0.12;   | [32]       |
|           | Radish;     | 0.05 ± 0.04, 78.52 ± 10.65; | biosolid-amended soil | 67d;         | 0.85 ± 0.17;   | 9.68 ± 3.72;   | [33]       |
|           | Celery;     | 1491 ± 0.29 ng/g       | biosolid-amended soil | 224d;        | 1.42 ± 0.37;   | 0.58 ± 0.30;   | [34]       |
|           | Tomato;     | 162d;                  | biosolid-amended soil | 129d;        | 0.96 ± 0.10;   | 2.60 ± 0.80;   | [35]       |
|           | Sugar snap pea; | 416.8 ± 29.5 ng/g | biosolid-amended soil | 45d;         | 0.79 ± 0.22;   | 0.72 ± 0.25;   | [36]       |
|           | Radish;     | 500 ng/g               | sludge-amended soil | 98d;         | 0.497          | 6.46           | [37]       |
|           | Lettuce;    | 0.1, 1, 5, 10 mg/kg    | soil          | 72d;         | 0.08;          | 0.00;          | [38]       |
|           | Alfalfa;    | 4.30                    | soil          | 10.30        | 10.30          | 0.30           | [39]       |
|           | Radish;     | 4 mg/kg                | soils         | 30d;         | 0.47 ± 0.79;   | 2.22 ± 0.62;   | [40]       |
|           | Lettuce (Italian mottle-leaf variety); | 0.1, 0.5 mg/L | nutrient solution | 3d;  | 25.30 ± 1.10; | 0.04 ± 0.01;   | [41]       |
|           | Lettuce (QK Italian variety); | 0.1, 0.5 mg/L | nutrient solution | 3d;  | 30.90 ± 2.20; | 0.05 ± 0.00;   | [42]       |
|           | Wheat;      | 0.3, 5, 10, 25, 50 mg/kg | soil          | 110d;        | -              | 0.09 ± 0.02;   | [43]       |
| Crop      | Spring wheat; | 0.25, 1.0, 10, 25, 50 mg/kg | soil          | 97d;         | -              | 0.03 ± 0.05;   | [44]       |
|           | Oat;        | 144-146d; 139d         | soil          | 110d;        | -              | 0.08 ± 0.06;   | [45]       |
|           | Maize;      | 0.01, 0.5 mg/L         | nutrient solution | 100h;       | 23.94;         | 0.24;          | [46]       |
|           | Wheat;      | 0.1 mg/L               | nutrient solution | 2d;      | 40.00;         | 0.13;          | [47]       |
|           | Wheat;      | 0.1, 0.5 mg/L          | nutrient solution | 3d;      | 23.94;         | 0.24;          | [48]       |
|           | Wheat;      | 0.01, 0.5 mg/L         | nutrient solution | 3d;      | 30.90 ± 2.20; | 0.05 ± 0.00;   | [49]       |
|           | Wheat;      | 300, 50, 1000 ng/g     | soil          | 30d;         | 0.09 ± 0.02;   | 0.09 ± 0.02;   | [50]       |
| Herb      | Maize;      | 416.8 ± 29.5 ng/g      | biosolid-amended soil | 45d;       | 1.69;          | 1.22 ± 0.07;   | [51]       |
|           | Soybean;    | 1.0 mg/L               | nutrient solution | 100h;     | 23.94;         | 0.24;          | [52]       |
|           | Italian ryegrass; | -          | nutrient solution | 97d;      | 32.1;          | 0.09;          | [53]       |
|           | Yam;        | - field                | -             | 2.30;        | 2.30;          | 0.56;          | [54]       |
|           | Peenianal grasses; | -            | nutrient solution | 80h;      | 108.00;        | 0.02;          | [55]       |
|           | Wheat;      | 0.1 mg/L               | nutrient solution | 70d;      | 0.03 ± 0.006;  | 0.29;          | [56]       |
|           | Wheat;      | 285 ng/g               | soil          | 70d;         | 0.09 ± 0.005;  | 0.58;          | [57]       |
|           | Wheat;      | 285 ng/g               | soil          | 70d;         | 0.09 ± 0.005;  | 0.58;          | [58]       |
|           | C. sarophorus; | 410 μg/kg           | soil          | 190d;        | 1.00 ± 0.34;   | 1.19 ± 0.18;   | [59]       |
|           | Canna indica; | 50 μg/L            | nutrient solution | 30d;      | 35.40 ± 0.69;  | 0.25 ± 0.01;   | [60]       |
|           | Cyperus alternifolius; | 50 μg/L            | nutrient solution | 30d;      | 35.40 ± 0.69;  | 0.25 ± 0.01;   | [61]       |
|           | Arundo donax; | 50 μg/L              | nutrient solution | 30d;      | 16.10 ± 0.73;  | 0.27 ± 0.02;   | [62]       |
|           | Cichorium intybus L.; | 100, 200 ng/g     | soil          | 87d;         | 8.40 ± 1.20;   | 0.14 ± 0.04;   | [63]       |
|           | Cichorium intybus L.; | 125, 250 μg/L     | nutrient solution | 38d;      | 6.92 ± 1.21;   | 0.53 ± 0.22;   | [64]       |
|           | Arisbepis thaliana; | 5, 20 mg/L       | nutrient solution | 21d;      | 37.02 ± 27.40; | 2.81 ± 2.73;   | [65]       |

<sup>a</sup> RCFs = C<sub>plant</sub> / C<sub>soil</sub> / C<sub>微生物</sub> / C<sub>植物</sub> / C<sub>土壤</sub>.

<sup>b</sup> TF = C<sub>plant</sub> / C<sub>soil</sub> (If no special explanation, TF = C<sub>微生物</sub> / C<sub>植物</sub>);

DW, dry weight; data are mean values in the cited literature.
Table 3. Phytoxic effects of plants under exposure of PFOA.

| Plant                        | Exposure concentration | Phytoxic response                  | R |
|------------------------------|------------------------|------------------------------------|---|
| **Toxic effects on growth and development** |                        |                                    |   |
| Lettuce sativa               | 62.5, 125, 250, 500, 1000, 2000 mg/L | Root growth i (>1000 mg/L), germination rate i (>62.5 mg/L); Root growth j (>1000 mg/L), germination rate j (>125 mg/L);   | (59) |
| Brassica rapa chinensis      |                        | Root growth i (>250 mg/L)           |   |
| Cucumis sativus              |                        | No adverse effect on seed germination, root growth i (>62.5 mg/L) | (45) |
| Brassica chinensis           | 0.1, 1, 10,100, 200, 300, 400 mg/kg | Root growth i (>100 mg/kg)          |   |
| Zea mays L cv. TY2           | 0, 1.0, 10, 50, 100, 200 mg/L | Root growth i (>10 mg/L); decreased biomass: (root>shoot) | (21) |
| Arabidopsis thaliana         | 0 to 181 mmol F L⁻¹    | Root growth i (>1193 ± 29.5 μmol F L⁻¹); shoot growth i (>73.7 ± 20.2 μmol F L⁻¹) | (9)  |
| *Triticum aestivum*          | 0, 0.02, 0.2, 2, 20, 200 μg/kg, 2, 20, 100, 800, 1600 mg/kg | Seedling growth root length i (<0.2 mg/kg) root and shoot growth, germination rate i (>800 mg/kg) | (46) |
| Arabidopsis thaliana; Nicotiana benthamiana | 0,15,50,150, 350 mg/kg | Root growth i (≤15 mg/kg); Root growth j (≥50 mg/kg); | (52) |
| Arabidopsis thaliana         | 20, 50, 100, 200 μmol/L | Chlorophyll content ↓; shoot growth ↓ (20, 50, and 100 μmol/L); root growth ↓ (20, 50, and 100 μmol/L); | (61) |
| **Toxic effects on the molecular scale** |                        |                                    |   |
| Arabidopsis thaliana         | 0 to 181 mmol F L⁻¹    | Shoot H₂O₂ ↑ (362, 725 μmol F L⁻¹); MDA (362 μmol F L⁻¹ ↓ 725 μmol F L⁻¹ ↓) | (9)  |
| *Triticum aestivum*          | 0, 0.02, 0.2, 2, 20, 200 μg/kg, 2, 20, 100, 800, 1600 mg/kg | Proline content ↑ (>2 mg/kg); POD activity ↑ (2, 200, 800 mg/kg); CAT activity ↓ (>2 mg/kg) | (61) |
| *Cucumis sativus*            | 0, 0.2, 5 mg/kg in soil | 1,2,4-benzenetrol ↓, 1-hydroxyanthraquione ↓, glutamic acid ↓, glutamine ↓, palmitic acid, phenylalanine ↓, and proline ↓ (amino acid) | (38) |
| *Lactuca sativa*             | 0, 5, 50 μg/L          | Amino acids: Phenylalanine↓, lysine, tryptophan↓; TCA cycle: proline↓, arginine↓, tyrosine↓; soluble proteins(312%)↓; 50 μg/L citric acid↑, cis-aconitic acid↑, malic acid↑, glucose↓, sucrose↓, trehalose↓ (5 μg/L); Polyphenols: phenylalanine↓, cinnamic acid↓, p-coumaric acid↓, 5-O-cafferoylquinic acid↓, coumarin↓, isoflavonoid↓, flavonoid↓, quercetin↓, flavonol↓; Alkaloids: terpenoid↓, benzylisoquinoline↓, ornithine↓; RO5H₂O₂↓, -OH↓ and O₂•↓↑ GSH↓; POD↑ and GPX↑; APX↑ (50 μg/L) | (60) |
| *Arabidopsis thaliana;*      | 0, 15, 50, 150 mg/kg;  | Metabolisms of carbon and nitrogen: sucrose↓, glucose↓, fructose-6-phosphate↓, trehalose↓; valine↓, tryptophan↓; glutamate↓, γ-aminobutyric acid (GABA)↓, threonine↓, lysine↓, methionine↓, mevalonate↓, isoleucine↓; TCA cycle: citric acid↓ and cis-aconitic acid↓; isocitric acid↓, succinic acid↓, fumaric acid↓, malic acid↓; Polyphenols: phenylalanine↓, p-coumaric acid↓, naringenin chalcone↓, naringenin↓, 3-O-p-coumaroylquinic acid↓ (50 μg/L); shikimate↓; Alkaloid biosynthesis: geranyl diphasophate↓, astaxanthin↓, betulinic acid↓, limonene↓, nootkatone↓, α-farnesene↓, phenylalanine↓ | (52) |
| *Nicotiana benthamiana*      | 0, 15, 50, 150 mg/kg;  | POD↑, SOD↑, CAT↑ (≤50 mg/kg) | (52) |
| *Arabidopsis thaliana*       | 0, 20, 50, 100 μmol/L | Shoot: Zn↑, Cu↑, Mn↑, Mg↑ (100 μM↓), K↓, Ca↓; root: Zn↓ (20,50 μM), K↓ (20,50 μM), Fe↓ (50,100 μM); SOD↓, APX↓, CAT↓; GSSG↑, total glutathione↑ | (63) |
| **Toxic effects on DNA**      |                        |                                    |   |
| *Lactuca sativa*             | 500, 5000 ng/g         | 8-Hydroxy-deoxyguanosine (8-OHdG)↑ | (40) |
| *Arabidopsis thaliana*       | 0, 100 μmol/L          | RNA-seq: 443 DEGs↑ and 146 DEGs↓ in shoot; 323 DEGs↑ and 327 DEGs↓ in root; Genes in shoot: CAT2↓, APX1↓, sAPX↓, Fe-SOD↓ | (43) |

Note: ↑ represents that the content of biomarkers increased under exposure of PFOA or the growth status of plants was stimulated; ↓ represents that the content of biomarkers decreased under exposure of PFOA or the growth status of plants was inhibited.
Figure1. Phytotoxicity of PFOA to plants in aspects.

biotransformed to PFOA in soil [15–18] and absorbed by plants. Furthermore, the presence of plants in soil can improve the degradation efficiency of precursors, because root exudates can promote the soil microbial abundance and facilitate the transformation of these precursors to PFOA [15,16,19]. Similar transformation from precursors in plants was also proved in soybean [20] and ryegrass [16].

Research has noticed the relationship between PFOA accumulation and the organic components in roots, but still very limited. Channel inhibitor experiments proved that the absorption of PFOA by maize was a passive absorption process mediated by water channel and anion channel protein carrier [21]. This indicated that proteins played an important role in root accumulation of PFOA, but the key proteins for PFOA transport have not been elucidated yet [21]. Lipid contents of plant roots also played a role. PFOA accumulation in plant roots was shown negatively correlated with root lipid contents (contrary to wetland plants) and positively with that of root protein [14,22]. More studies focusing relationship between plant biological components and PFOA accumulation are needed.

Various factors affect the BCF values, including plant species, exposure doses, exposure time, and culture conditions, as summarized in Table 1. BCF values of PFOA varied among 0.012–84, especially higher in solution medium [23–25], indicating that the hydroponic terrestrial plant tests cannot fully reflect the fate of PFOA in real soil. It is essential to have more soil experiments to evaluate the utilization of PFOA in terrestrial plants. Especially, plants with different genotypes showed different absorption and utilization capacity of PFOA [12], reminding people to carry out necessary variety screening when facing PFOA contaminated soil.

PFOA may be filtered out by the Casparian strip at the early entry point, resulting in a shorter translocation distance and faster equilibrium [26]. Table 2 summarized the root concentration factors (RCFs) and transfer factors (TFs) of PFOA in plants. The majority of PFOA was found in the plant roots, and different plants showed unlike PFOA root accumulation and translocation abilities. RCF values changed in a range of 6.92–108 for those exposed in nutrition solution, 0.03–11.8 for those in soil, and 0.005–0.33 in field, indicating that hydroponic experiments overestimated PFOA accumulation in plant roots. TF values changed in a range of 0–9.68, mostly <0.5, indicating high root accumulation by low transfer to shoot [52]. Although PFOA was more readily taken up in the translocation stream and its accumulation in plant roots was high, its transfer rate from root to stem was low [12,27]. Still, there is no relevant datum on woody plants, unfavorable to assessing their potential in phytoremediation.

Of public concern, corp grains, such as wheat and rice, were found to contain minimal or no PFOA [28,29], indicating a low risk of PFOA entering the human body through the grain crops. The risk of intergenerational transmission of PFOA in plants, influencing the growth and development of the next generation through seeds, might be low, but at present, there is little research in this area, and further research is needed. However, there are vegetables with higher TF values over 1, including cucumber [30], radish [22,31,32,53], tomato [31] and some lettuce varieties [25]. It seems that such vegetables could contribute most to human exposure, indicating a high risk for human exposure to PFOA through dietary intake by vegetables [3].
To develop remediation technologies for PFOA-contaminated farmland, it is important to research on the interaction between PFOA and soil composition, including soil physical and chemical properties, as well as coexisting pollutants. However, there is limited research on how such factors affect the PFOA fate in soil-plant system. Liu, et al. [33] found types of dissolved organic matter (DOM) in soil that inhibited the bioaccumulation and transport of PFOA in wheat due to their strong combination with PFOA. Plant root exudates and their low molecular weight organic acid (LMWOA) components also showed a great influence on the linear adsorption-desorption isotherms of PFOA in soil. Wherein, oxalic acid was considered to play a key role in activating PFOA uptake [34]. Exchangeable ions were also important factors. Knight, et al. [35] found that the exchangeable K⁺ content and cation exchange capacity (CEC) in soil were closely related to the plant accumulation of PFOA. In addition, studies showed that co-existing copper or CuO nanoparticles significantly affected PFOA translocation in plants [32,36]. These studies highlighted the potential to regulate PFOA risk in agricultural field and enhance phytoremediation for PFOA contaminated soil, but more studies are needed to explore feasible technology and the underlying mechanism [32].

3. Phytotoxicity of perfluorooctanoic acid

PFOA phototoxicity showing as agronomical parameters, antioxidative activities, photosynthetic indices, and DNA injuries was studied (Figure 1). Phytotoxicity of PFOA is related to many factors, including PFOA concentration range, soil properties, and plant species, as summarized in Table 3. Its disturbance to antioxidant defense system explained for some studies. Yang, et al. [9] compared the toxicity of sodium fluoride (NaF) and perfluorooctanoic acid to Arabidopsis thaliana and found that PFOA caused oxidative stress, affected cell metabolism and led to reduced biomass, showing higher toxicity than inorganic F. Zhang, et al. [37] found that PFOA inhibited the activities of superoxide dismutase (SOD) and catalase (CAT) and destroyed the antioxidant defense system in J. effusus roots. Studies have been carried out on the metabolic disorder caused by PFOA, and showed that the metabolic disorder of carbohydrates, phenols, amino acids and fatty acids played a central role in plant response to PFOA stress. PFOA inspired the antioxidant defense pathway, interfered the tricarboxylic acid (TCA) cycle, and led to the decline in photosynthesis and final biomass [38–42]. Transcriptome analysis further showed that PFOA could regulate the gene expression in a tissue-specific manner, and provide candidate genes for transporters that involved in PFOA uptake and translocation [43].

Similarly to plant uptake, the toxicity of PFOA is also related to the growth medium. Compared with the exposure levels in real field conditions, the pollution levels of plants cultured in hydroponics were amplified [24,25]. Soil properties, including organic matter (OM), CEC, pH value, and clay contents were proved to impact the phytotoxicity of PFOA [32,44]. Zhao, et al. [45] found that the toxicity threshold of PFOA to Brassica chinensis grown in soil with low OM or CEC was lower than that in soil with high OM or CEC. Zhou, et al. [46] also found that wheat root growth was more vulnerable to PFOA in soils with lower OM or CEC.

4. Conclusion

Based on previous research, this article describes the PFOA uptake, transport, phytotoxicity in terrestrial plants. Nowadays, there are limited studies carried out with plants exposed to PFOA alone, so it is hard to understand the underlying mechanism for plant utilization and toxicity action. Especially, the key proteins for PFOA transmembrane transport and influencing factors need to be further studied. Current hydroponic experiments overestimated the plant utilization and phytotoxicity of PFOA, so more experiments should be carried out to explore the PFOA risk in real soil conditions, especially field studies that comprehensively consider soil and climate factors. Besides, more attention should be paid to the potential of phytoremediation for PFOA contaminated soil, especially the possibility of the higher woody plants or nanotechnology in enhancing phytoremediation.

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