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Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils

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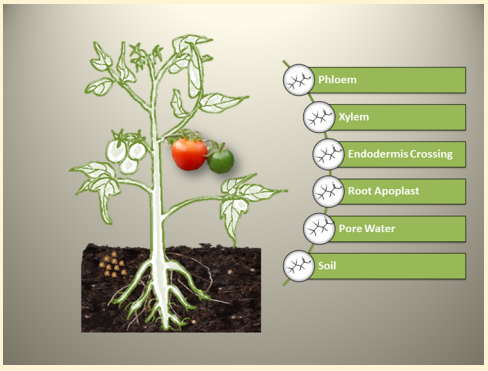
Supporting Information

ABSTRACT: Crop uptake of perfluoroalkyl acids (PFAAs) from biosolids-amended soil has been identified as a potential pathway for PFAA entry into the terrestrial food chain. This study compared the uptake of PFAAs in greenhouse-grown radish (*Raphanus sativus*), celery (*Apium graveolens* var. *dulce*), tomato (*Lycopersicon lycopersicum*), and sugar snap pea (*Pisum sativum* var. *macrocarpon*) from an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil. Individual concentrations of PFAAs, on a dry weight basis, in mature, edible portions of crops grown in soil amended with PFAA industrially impacted biosolids were highest for perfluorooctanoate (PFOA; 67 ng/g) in radish root, perfluorobutanoate (PFBA; 232 ng/g) in celery shoot, and PFBA (150 ng/g) in pea fruit. Comparatively, PFAA concentrations in edible compartments of crops grown in the municipal biosolids-amended soil and in the control soil were less than 25 ng/g. Bioaccumulation factors (BAFs) were calculated for the root, shoot, and fruit compartments (as applicable) of all crops grown in the industrially impacted soil. BAFs were highest for PFBA in the shoots of all crops, as well as in the fruit compartment of pea. Root-soil concentration factors (RCFs) for tomato and pea were independent of PFAA chain length, while radish and celery RCFs showed a slight decrease with increasing chain length. Shoot-soil concentration factors (SCFs) for all crops showed a decrease with increasing chain length (0.11 to 0.36 log decrease per CF_2 group). The biggest decrease (0.54−0.58 log decrease per CF_2 group) was seen in fruit-soil concentration factors (FCFs). Crop anatomy and PFAA properties were utilized to explain data trends. In general, fruit crops were found to accumulate fewer long-chain PFAAs than shoot or root crops presumably due to an increasing number of biological barriers as the contaminant is transported throughout the plant (roots to shoots to fruits). These data were incorporated into a preliminary conceptual framework for PFAA accumulation in edible crops. In addition, these data suggest that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAA industries) are unlikely a significant source of long-chain PFAA exposure to humans.



INTRODUCTION

Perfluoroalkyl acids (PFAAs) are used extensively both in industrial and consumer products,[1] but resist degradation by conventional wastewater treatment plants (WWTPs) and persist in both aqueous effluent and treated biosolids.[2,3] Land-application of biosolids on crops can therefore facilitate the entry of PFAAs into the terrestrial food web. Although PFAAs are regulated in biosolids used as fertilizer for agriculture in some parts of Europe (e.g., Bavaria),[4] currently, there are no federal regulations in the U.S. that govern the use and application of biosolids based on PFAA concentrations.[5] Land-application of biosolids primarily occurs on grain crops; however, sustainability movements are encouraging more liberal use of biosolids on home gardens by consumers.

While several studies have demonstrated uptake of PFAAs into plants, the majority of these studies used either spiked systems or hydroponics which both differ from aged field soils.[4,6−8] Blaine et al.[9] have shown that edible crops can uptake PFAAs from authentic biosolids-amended soils. Both lettuce

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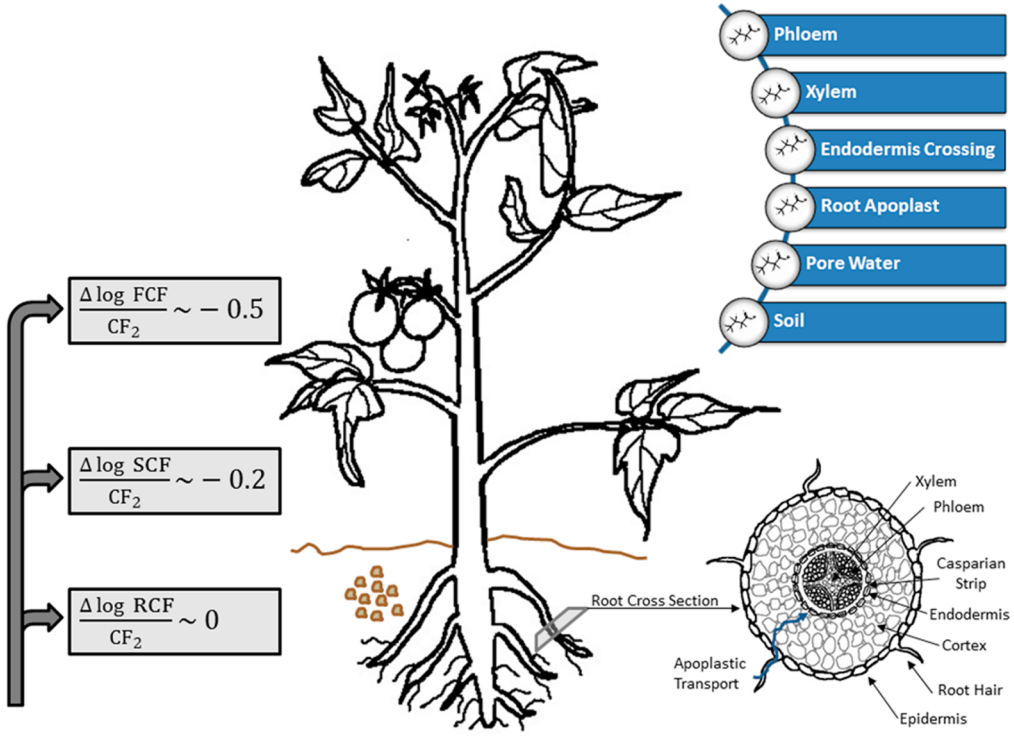

Figure 1. Conceptual model of perfluorocarboxylate uptake as exhibited in a tomato plant. Approximate values are shown for change in log bioaccumulation factor per CF_2 group. Root, shoot, and fruit concentration factors are RCF, SCF, and FCF, respectively. Uptake pathway is shown in the top right corner. Root cross-section modified from Taiz and Zeiger.[16]

leaves and tomato fruit had bioaccumulation factors (BAFs) greater than one for short-chain perfluorocarboxylates (PFCAs).[9] In addition, carbon chain length dependent trends were seen in lettuce leaves, resulting in an approximately 0.3 log decrease for each CF_2 group.[9] However, as only the edible portions were analyzed, more general correlations between plant compartment and PFAA accumulation were not made. In another recent greenhouse study, an inverse relationship between BAF and carbon chain length was also seen for PFCAs in alfalfa plants.[10] Felizeter et al.[8] studied accumulation of PFAAs in hydroponic lettuce and found that long-chain PFAAs accumulated more in the roots than in the foliage, whereas for short-chain compounds, there was more translocation from the roots to the foliage.[8] A more mechanistic study by Wen et al.[11] determined that PFOA and PFOS may have different uptake mechanisms in maize; potential active uptake and entry by anion channels were suggested for PFOA, while entry by aquaporins (water channels) or anion channels (different than the ones used by PFOA) were suggested for PFOS.

The translocation and partitioning behavior of a chemical in a plant is highly varied and complex. Various plant uptake models have been explored over the years with the majority focusing on uptake of neutral hydrophobic chemicals based on the octanol–water partition coefficient (K_{ow}).[12−14] In these models, chemical uptake from soil is usually driven by passive diffusion, as only natural or structurally similar chemicals are actively transported,[13] and small, neutral substances are most easily carried into the roots.[15] Although early models indicated that plant uptake of hydrophilic (low log K_{ow}) chemicals was limited, a more recent empirical model indicates that hydrophilic chemicals are extensively taken up by plants.[14] Although there are some discrepancies among the various plant uptake models, the basic pathway of chemicals within a plant is fairly well-defined. Chemicals can travel across the root cortex through the apoplast (extracellular space) or symplast (intracellular space) until they reach the Casparian strip at the endodermis.[16] At this point, they must cross through a cell membrane (Figure 1). While neutral, hydrophobic chemicals may easily pass through a membrane, hydrophilic and/or ionized chemicals may have to pass through as neutral salts, through anion channels, or through water pores in the membrane.[11,17] The Casparian strip acts as an ion trap, allowing for higher concentrations of solutes in the xylem than in the pore water.[16]

While nonpolar chemicals are mostly confined to the surface of root membranes due to lipid partitioning, polar chemicals can enter the transpiration stream and migrate throughout the plant.[18,19] Once within the transpiration stream, a chemical can be transported throughout the plant, first to the shoot (i.e., stem and leaves) via the xylem and then to storage organs (e.g., fruit) via the phloem. The xylem and phloem are separated by the vascular cambium, a single row of cells. Accumulation of solutes in plant cells near the leaves helps drive translocation from source (e.g., leaf) to sink (e.g., fruit) via a pressure-flow[16] model. As the concentration in a cell escalates, water is absorbed osmotically thus building up hydrostatic pressure. The subsequent movement of the water and solutes through the system of phloem sieve tubes equalizes the pressure. The sieve tubes are separated by sieve plates which allow flow through transport pores (plasmodesmata). Eventually, chemicals may be stored in cell vacuoles or in intercellular spaces. Neutral and ionized polar chemicals with low lipophilicity, low volatility, and high persistence are particularly prone to accumulation in the leaves and other sinks by phloem transport.[20] PFAAs generally meet these criteria. In particular,

PFAAs, being anionic at environmental pH values,[21] are generally nonvolatile, thereby eliminating potential release into the air from the leaf stomata.

This study evaluated the PFAA distribution in various plant structural compartments by examining both the edible and nonedible portions of radish (*Raphanus sativus*), celery (*Apium graveolens* var. *dulce*), tomato (*Lycopersicon lycopersicum*), and sugar snap pea (*Pisum sativum* var. *macrocarpon*) grown in biosolids-amended soils. Radish represents an edible root crop (i.e., below ground crop), although radish tops are also edible. Celery represents an edible shoot crop (i.e., stem and leaf crop) although certain varieties of celery are also harvested for the bulb and seeds. Tomato represents an edible fruit crop. Sugar snap pea, a legume, also represents a fruit and edible seed crop. Bioaccumulation factors for the root, shoot, and fruit portions were calculated. To our knowledge, this is the first study to examine PFAA uptake in celery, snap pea, and radish; in addition, it is one of the most detailed studies addressing intercompartmental translocation of PFAAs in edible crops to date.

MATERIALS AND METHODS

Chemicals. Native perfluorinated standards and stable isotopes were obtained from Wellington Laboratories (Guelph, ON, Canada) and prepared as per established methods.[9] Analytes studied include perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and perfluorooctanesulfonate (PFOS; Supporting Information (SI) Table S1). HPLC-grade methanol (MeOH), high purity Chromasolv dichloromethane (DCM), and all other reagent grade solvents were obtained from Sigma-Aldrich (St. Louis, MO). A Milli-Q system (Millipore, Billerica, MA) was used to provide water for extractions, and HPLC-grade water was used for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. Chromabond diamino from Macherey-Nagel Inc. (Bethlehem, PA) and Supelclean ENVI-Carb from Sigma-Aldrich were used in extract cleanup.

Greenhouse Study. Two biosolids-amended soils as well as an unamended control soil were used in this study: a soil amended with industrially impacted biosolids (industrially impacted soil), a soil receiving multiple applications of municipal biosolids over a span of 20 years (municipal soil), and an unamended control soil. Although the control soil was obtained from an unamended field, its proximity to biosolids-amended fields likely led to minor cross-contamination resulting in the detection of trace levels of PFAAs. Details on all three soils can be found in Blaine et al.;[9] PFAA concentrations in the soils are reported in the SI Table S2. In general, soils were sieved (6.3 mm) for homogeneity and pots were filled on a dry weight basis. Four edible crops including radish, celery, tomato, and pea were grown from seed. Five pot replicates were grown for each crop in each soil. Pots were randomly arranged to account for any spatial variations in light and temperature within the greenhouse. Additional information about propagation and greenhouse environmental conditions are given in the SI. Both edible and nonedible parts of all crops were harvested (SI Table S3) at maturity and frozen at −20 °C in sealed plastic bags until extraction.

Extraction and Analysis. *Sample Extraction.* Prior to sample preparation, plant material was homogenized using a food processor. Aliquots (0.5−2 g) of soil or plant material were transferred to 50 mL polypropylene vials. To each vial, 2 ng of isotopically labeled surrogate standard was added. Plant samples were then extracted with a 50/50 (v/v) solution of DCM and 99:1 (v/v) MeOH with ammonium hydroxide as detailed elsewhere;[9] soil samples obtained prior to planting were extracted based on the protocol from Sepulvado et al.[3] Results for both plants and soils are presented on a dry weight basis.

PFAA Analysis. All PFAAs were analyzed with isotope dilution using LC-MS/MS under conditions outlined in previous work,[9] though the method was validated for the wide variety of plant matrices included in the present study (SI Figure S1). Chromatography was performed using a Shimadzu LC-20AD unit (Kyoto, Japan). Samples were injected onto a Gemini C18 Column with a 3-μm particle size (Phenomenex, Torrance, CA). Two transitions for each analyte were observed using an MDS Sciex Applied Biosystems API 3200 (MDS Sciex, Ontario) with negative electrospray ionization operating in scheduled multiple reaction mode. No attempt to analytically differentiate between branched and unbranched isomers was made.

Data Analysis. *Quality Control.* The software Analyst was used for quantitation in this study. For each matrix, a minimum of 20 percent of the samples were extracted and analyzed in triplicate. The relative standard deviation for analytical replicates was less than 18%. Sample values are presented as the mean experimental replicate value (n = 3 to 5). One extraction blank with surrogate standard and one double blank without surrogate standard were prepared with each batch of samples. Limits of quantitation (LOQ) ranged from 0.03 to 0.71 ng/g; they were determined by the lowest calibration standard calculated to be within 30% of its actual value and were analyte, matrix, and run-dependent. LOQs were also required to be at least twice as high as the highest concentration in the corresponding blanks and have signal-to-noise ratios greater than 30. To account for any loss during the extraction process, each sample was fortified with isotopically labeled surrogate standards. PFBS was the only analyte that did not have a corresponding surrogate; therefore, PFHxS was used (SI Table S1). Surrogate recoveries for the samples averaged 35% for root tissues, 36% for shoot tissues, and 40% for fruit tissues across all analytes. While lower than typical soil surrogate recoveries,[3] this range is typical in plant matrices[8,22] due to matrix ion suppression. Native spike-recovery experiments (which account for surrogate losses) showed an average native recovery of 73% in root tissues, 80% in shoot tissues and 71% in fruit tissues for all analytes (SI Figure S1). PFBS showed lower native recovery than PFHxS despite the use of the same surrogate; this indicates that PFHxS may not have corrected for additional matrix suppression of PFBS and thus PFBS values in this study may be slightly underestimated. All data presented in this study are reported in terms of surrogate-corrected concentrations.

Statistical Analysis. Data are shown as means with standard errors. Statistical analyses and regression lines were calculated using OriginPro 9.0. Statistical difference of means was established by an analysis of variance (ANOVA) with Tukey's Test (α = 0.05); homogeneity of variance was assessed by Levene's Test (α = 0.05).

Bioaccumulation Metrics. Bioaccumulation factors (BAFs), ratios between the chemical determined on a dry weight basis in the respective plant tissue and soil, were

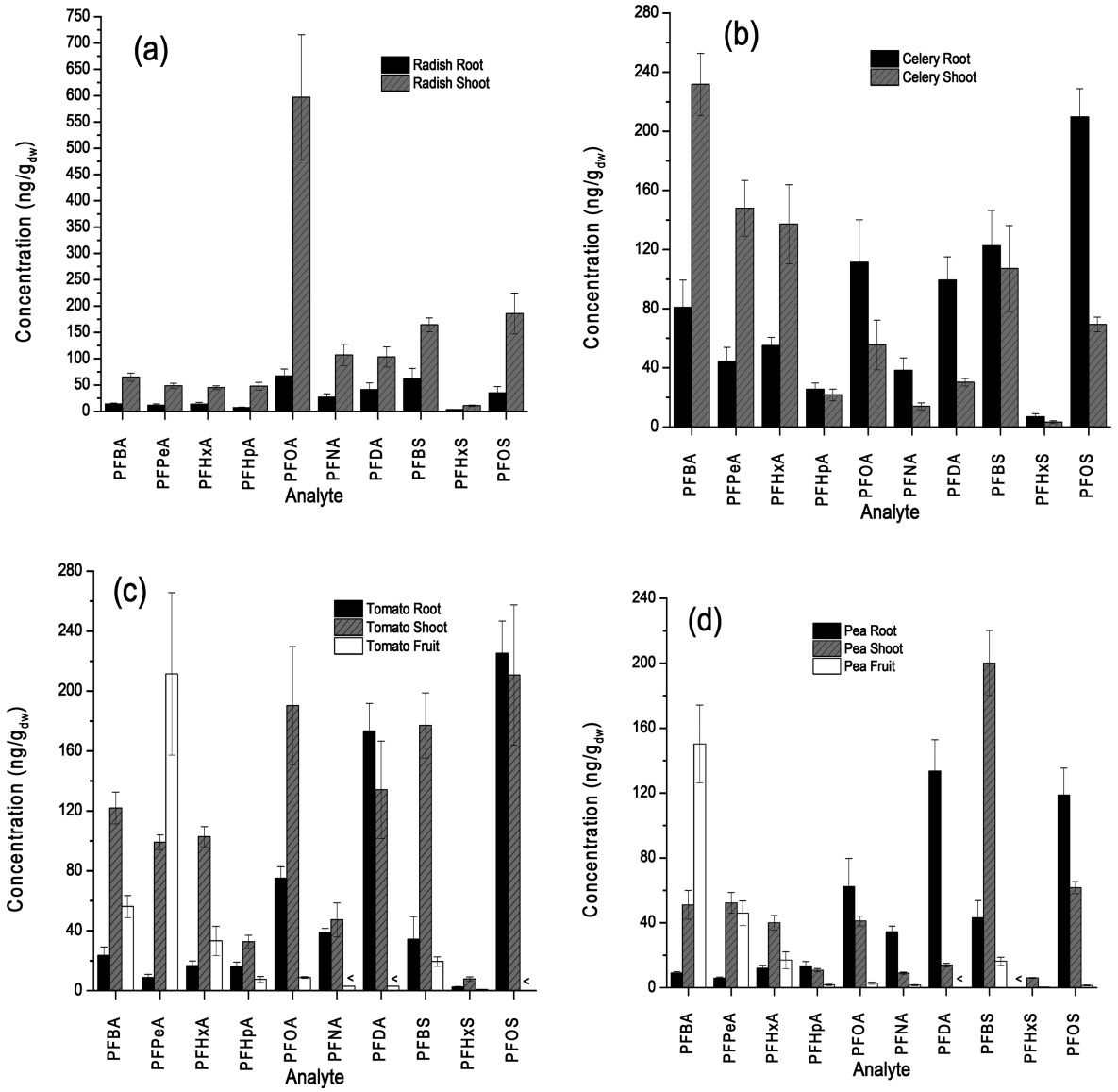

Figure 2. Concentrations of PFAAs in greenhouse radish (a), celery (b), tomato (c), and pea (d) grown in industrially impacted soil. Values for tomato fruit are from a previous study.[9] Bars represent means and standard errors of five determinations. Values less than the LOQ are denoted by <; LOQs for respective matrix and analyte are listed in SI Table S4 and Table S5.

calculated (eq 1) leading to estimations of root concentration factors (RCFs; SI eq S1), shoot concentration factors (SCFs; SI eq S2), and fruit concentration factors (FCFs; SI eq S3).

$$\text{BAF} = \frac{\text{PFAA concentration in plant tissue}(\text{ngg}^{-1})}{\text{PFAA concentration in soil}(\text{ngg}^{-1})} \quad (1)$$

Due to the ionized nature of PFAAs at environmental pH values (i.e., ∼ 4 to 9), plant entry into the stomata from the air was assumed to be insignificant compared with uptake through the roots. BAFs were calculated using crops grown in the industrially impacted soil for each PFAA that had concentrations in the plant tissues above the LOQ.

Root-pore water concentrations (RCF_{pw}) were calculated (SI eq S4) by dividing the concentrations in the roots (ng/g) by the pore water concentrations (ng/mL) derived in previous work.[9] Briefly, pore water concentrations were obtained by dividing soil concentrations by the fraction of organic carbon in the soil and soil-water equilibrium partitioning coefficients obtained from Guelfo and Higgins.[23]

In addition, intercompartmental concentration factors (ratio of concentrations on a dry weight basis) were calculated for shoot to root (SRCFs; SI eq S5) and fruit to shoot (FSCFs; SI eq S6).

RESULTS AND DISCUSSION

Edible Portions. In the radish root grown in the industrially impacted soil, PFAA concentrations were highest for PFOA (67 ng/g), PFBS (62 ng/g), PFDA (41 ng/g), and PFOS (35 ng/g) (Figure 2a); these four analytes also had the highest concentrations in the soil. In the municipal and control soils, PFBS concentrations in the radish root were the highest at 24 ng/g and 22 ng/g, respectively (SI Table S4). For celery grown in the industrially impacted soil (Figure 2b), concentrations of PFAAs in the shoot were greatest for the short-chain (i.e., C6 and below) compounds, PFBA (232 ng/g), PFPeA (148 ng/g), PFHxA (137 ng/g), and PFBS (107 ng/g). Comparatively,

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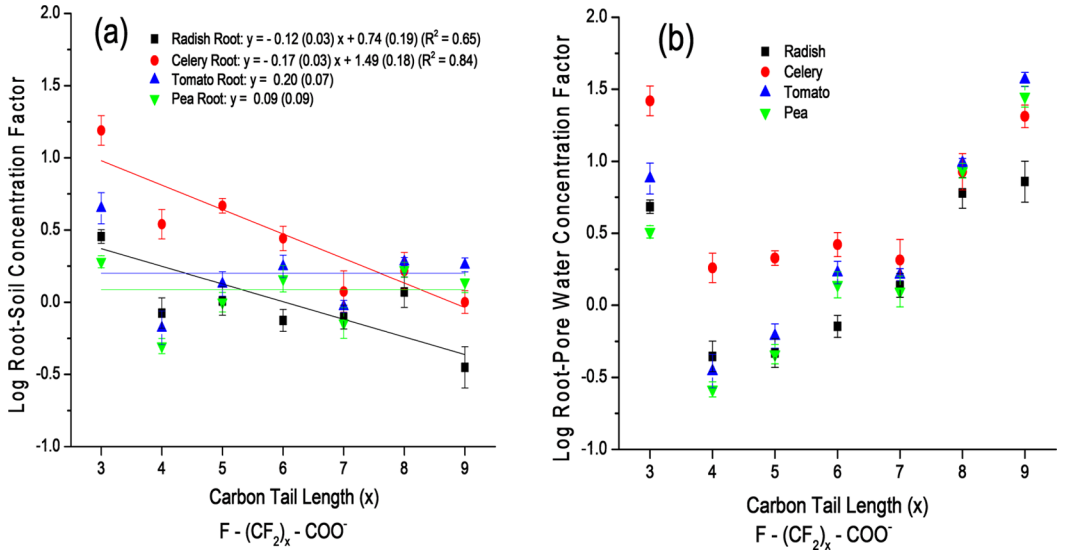

Figure 3. Correlations between log RCF for PFCAs based on soil (a) and calculated pore water (b) concentrations and carbon tail length in greenhouse radish, celery, tomato, and pea grown in industrially impacted soil. Means and standard errors are shown (n = 3 to 5). Linear regressions with slopes (if significantly different than zero at α = 0.05) and intercepts are shown; associated error values are shown parenthetically after each coefficient.

lettuce grown in the same soil had similar concentrations of the short-chain compounds: PFBA (266 ng/g), PFPeA (236 ng/g).[9] In the municipal soil, PFAA celery concentrations were all less than 8 ng/g with the exception of PFOS (17 ng/g), which is most likely due to the relatively high concentration of PFOS and low concentrations of short-chain PFAAs in the soil (SI Table S4). All PFAA concentrations in the celery grown in control soil were less than 6 ng/g (SI Table S4). Concentrations of PFAAs in the pea fruit grown in industrially impacted soil were highest for PFBA (150 ng/g) and PFPeA (46 ng/g); all PFAAs were below LOQ (0.03−0.71 ng/g) for pea fruit grown in municipal and control soils (SI Table S4). Although no quantifiable data was collected to measure overall plant health in each of the three soils, qualitatively, more robust growth was observed for the plants grown in biosolids-amended soils versus the control soil. This increased vigor, in turn, likely led to increased transpiration, which may have promoted additional uptake of PFAAs. PFAA concentrations in the crops grown in the industrially impacted and municipal soils were compared to the control (unamended) treatments by an ANOVA test; statistical differences are shown in SI Figure S2. Low PFAA concentrations in the municipal and control soils limited the ability to determine accumulation trends, and thus the remainder of the results and discussion focuses on the crops grown in the industrially impacted soil.

Plant Compartments. PFAA concentrations in nonedible plant compartments grown in the industrially impacted soil were also analyzed and plotted alongside edible compartment concentrations in Figure 2. The concentrations of PFAAs in the radish shoot follow the same trends as in the radish root (and the soil), but are approximately 5−10 times higher. Physiologically, radishes lack the typical barrier (Casparian strip) between the edible bulb and the above ground shoot.[24] The swollen edible portion of the radish is actually formed at the intersection of the hypocotyl (embryonic stem) and the fine roots below; as the fine roots below the bulb are not generally eaten, they were not analyzed as part of the edible root portion. Therefore, although the analytes accumulate in the same proportions, more accumulation is seen in the shoot, perhaps due to the unrestricted upward flow of PFAAs. For celery, the shoot and root portions do not have parallel concentration trends. The celery shoot has higher concentrations of short-chain PFCAs while the celery root has higher concentrations of long-chain PFCAs and perfluoroalkyl sulfonates (PFSAs). The tomato plant has three compartments: root, shoot, and fruit. Within the tomato plant, the root has the highest concentrations of PFDA and PFOS, the longest chain compounds analyzed, whereas the tomato shoot has the highest concentrations of all the other PFAAs except PFPeA. The majority of PFAAs in the tomato fruit, as reported in Blaine et al.,[9] are short-chain compounds. Pea roots and shoots exhibit similar results to the celery and tomato in that long-chain compounds are highest in the roots while short-chain compounds are highest in the shoots. Pea fruit is similar to tomato fruit in that it accumulates primarily the short-chain compounds.

Bioaccumulation. *PFCAs.* Root to soil concentration factors plotted versus carbon chain length of PFCAs for the four crops grown in the industrially impacted soil are shown in Figure 3a; linear trend lines with equations and associated errors are also shown. In general, the RCF values of celery are greater than the other three crops, indicating more overall accumulation in celery root. This could be due to the greater surface area of celery roots or could be correlated to the total water transpired during the duration of the crop. Tomato and pea have very similar RCF values, most likely resulting from similar root physiology and crop duration times. The slopes of the trend lines for tomato and pea root are not statistically different from zero (α = 0.05), indicating no preferential accumulation of short- or long-chain PFCAs in the root tissues as compared to soil. Both of these crops have thicker tap root systems which may allow larger contaminants to cross the epidermis into the apoplast and yet be retained in the root tissue.[17] The trend line for radish shows a slope of −0.12, indicating a slight preference for uptake of the short-chain compounds. Taking into consideration that the edible portion of the radish root exhibits characteristics of both root and stem as a hypocotyl, this difference could reflect the prior impeded

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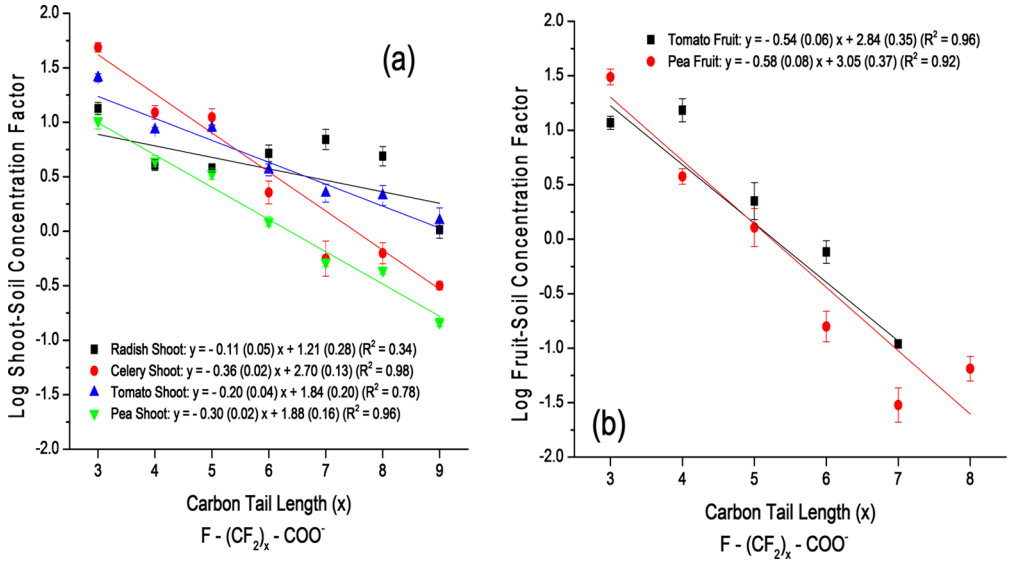

Figure 4. Correlations for PFCAs between log SCF (a) and log FCF (b) and carbon tail length in greenhouse radish, celery, tomato, and pea grown in industrially impacted soil. Means and standard errors are shown (n = 3−5). Linear regressions with slopes and intercepts; associated error values are shown parenthetically after each coefficient.

movement of long-chain compounds by the Casparian strip during translocation from the fine roots to the bulb. In this way, the radish data resemble more of a shoot trend than the expected root trend. However, other entryways into the hypocotyl may be possible (aquaporins or direct diffusion through hypocotyl endodermis) thus allowing more long-chain compounds than seen in the other crops.[24] The trend line for celery has a more obvious downward slope of −0.17, showing preferential entry for short-chain PFCAs. This could be due to the fact that celery has a very finely branched root system that is more likely to filter out larger contaminants by the Casparian strip at an early entry point. RCF_{pw} values were also calculated for PFCA accumulation in the four crops (Figure 3b). When plotted versus chain length, all four crops exhibit a U-shape that is consistent with the trend reported by Felizeter et al.[8] for hydroponically grown lettuce and by Krippner et al.[7] for maize. PFBA as well as the long-chain PFCAs have higher sorption tendencies to organic carbon,[23] thus reducing their concentrations in the pore water and driving up the RCF_{pw}.

Shoot to soil concentration factors plotted versus PFCA chain length are shown in Figure 4a with corresponding linear trend lines, equations and associated errors. Comparing among crops, celery shoots have higher accumulation of the short-chain PFCAs, likely due to exclusion of long chain PFCAs by the roots, while radish and tomato shoots have higher accumulation of the long-chain PFCAs. Pea shoots have the least amount of accumulation; perhaps the woody, dry characteristics of its stem and its minimal leaves reduce the available accumulation area in the shoots. Celery, tomato and pea SCFs show a decrease of 0.36, 0.20, and 0.30 log units, respectively, per CF_2 moiety. As these SCFs encompass the movement of PFCAs traveling from soil through the root to the shoots, the slightly larger value for celery (0.36) may reflect the fact that the preferential accumulation of short-chain length compounds in the celery root is compounded by additional increased selectivity from the root to shoots. When shoot-to-root (intercompartmental) factors are compared (SI Figure S3a), relative PFCA accumulation from roots to shoots are similar for celery and tomato; pea shows the greatest log decrease per CF_2 moiety. Overall, the preferential exclusion of long-chain PFCAs seen in celery, tomato, and pea shoots is consistent with the trend found for lettuce shoots (decrease of 0.3 log units) in Blaine et al.[9] and for maize shoots in Krippner et al.[7] Relative PFCA accumulation in radish shoots, however, is an exception: the trend of log SCF vs chain length is significantly flatter and the slope is statistically equivalent (α = 0.05) to the log RCF trend line (Figure 4a), resulting in no preferential accumulation of long- or short-chain PFCAs in the radish shoot as compared to the root (SI Figure S3a). Considering that once PFCAs are in the radish root (hypocotyl), no Casparian strip prevents upward translocation to the shoot; this lack of a trend is consistent with the Casparian strip serving as an important barrier to the interplant movement of long-chain PFCAs. Although, trend-wise, the radish root and shoot accumulation patterns correlate, more overall accumulation is seen in the shoot since after entry into the edible bulb, contaminants are subsequently transported upward with the flow of xylem and then accumulate in the leaves. There is potential for some of the smaller PFCAs to return to the bulb via the phloem as the plant stores nutrients for the winter in the bulb; however, this translocation is likely insignificant as radish is harvested before dormancy. In addition, small increases of PFAA concentration in the bulb may be obscured by growth dilution.

Fruit to soil concentration factor values for tomato and pea fruits for each PFCA are generally similar (i.e., on the same order of magnitude); however, variations in the values still exist due to the myriad of differences in the physiology of the roots and shoots encountered during translocation. In both tomato and pea plants, contaminants encounter additional membrane barriers (e.g., the cambium) in order to be loaded into the phloem and transported to their final destination (i.e., the fruit compartment). Additional chain length exclusion is evidenced by the decrease of 0.2 to 0.3 log units per carbon chain length for fruit to shoot concentration factors (SI Figure S3b) resulting in cumulative decreases of 0.54 and 0.58 log units per carbon chain length for fruit to soil accumulation factors (Figure 4b).

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PFSAs. Bioaccumulation factors for PFSAs were also calculated (SI Table S6); however, as only three analytes were studied, chain length trends were not calculated with linear regressions. Differences between PFCAs and PFSAs seem to magnify from the roots upward. In the roots, all analyte RCFs are below 5, with the exception of PFBA. Values for SCFs for PFSAs are all below 8, compared to the SCFs for the short-chain PFCAs which reach up to 50. In tomato and pea, values of FCFs for PFSAs are all below 1, while values for short-chain PFCAs are primarily greater than 1. A more direct comparison can be made by comparing similar chain length analytes (e.g., PFPeA to PFBS or PFNA to PFOS). PFPeA has significantly higher values than PFBS for the celery and tomato SCFs as well as for both tomato and pea FCFs; PFNA compares fairly well to PFOS with the only significant difference being slightly higher SCF values in celery, tomato, and pea for PFOS. As the core structures of PFCAs and PFSAs are almost identical, the larger size of the sulfonate headgroup may be a contributing factor to the accumulation differences in the shoots and fruits for short-chain analytes. For larger analytes that are already restricted based on size, the larger headgroup may not matter as much. Other differences in accumulation patterns may be due to differing uptake mechanisms between PFCAs and PFSAs.[11]

Conceptual Model and Implications. Figure 1 shows a conceptual model of PFCA accumulation in tomato, a typical three compartment crop. The primary translocation pathway for PFCAs is illustrated via an enlarged root cross section and an outline showing movement of PFCAs from the soil all the way to the phloem. In addition, approximate bioaccumulation factors are shown for a tomato plant indicating increasing discrepancy in PFCA accumulation per CF_2 moiety with acropetal movement. Although the scope of this study was not fully mechanistic, uptake and distribution factors likely include specific plant physiology and transpiration rate parameters.

In general, chain length dependent accumulation is seen as PFCAs translocate upward from the roots. Each crop is anatomically different, presenting unique biological barriers in the translocation process; however, some common barriers do exist, namely the Casparian strip and in general, the permeation of membranes. To effectively model plant uptake of PFAAs, these various crop-specific factors as well as contaminant-specific factors must be considered. Plant factors examined in this paper were root structure and number of compartments, while the contaminant-specific factors examined included chain length and headgroup. Without plant-specific data, the best prediction that can be made consists of a generalization about plant compartment accumulation. In general, the data presented here suggest edible fruit crops accumulate fewer long-chain PFCAs than do edible shoot or root crops. For example, one would expect that 5 g of peas or tomatoes would contain roughly 5−25 times less PFOA than 5 g of celery or radish grown in the same soil. With a good understanding of plant physiology, it may be possible to extrapolate these generalizations to other crops; however, caution is warranted since visually similar crops can have anatomical or physiological differences that can significantly alter uptake potential. In terms of analytes, there is a much larger discrepancy; one could expect that shoot and fruit crops may have 1−3 orders of magnitude more PFBA than PFOA if these two analytes are present in equal concentrations in the soil. With industry trends shifting toward the use of short-chain PFAAs, it is important to recognize this increased potential of PFAA entry into the terrestrial food chain via plants.

With respect to overall exposure, it is unlikely that edible crops grown in soils conventionally amended for nutrients with biosolids (that are not impacted by PFAA industries) are a primary source of long-chain PFAA exposure to humans; this has also been suggested from recent food basket studies.[25] However, in the absence of comprehensive toxicological data on short-chain PFAAs, precaution may be warranted for production of fruit or shoot crops grown in PFAA contaminated soils. More work is needed to discern all applicable factors needed to comprehensively mechanistically model PFAA uptake in plants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional details are available regarding analytical methods, greenhouse experiment details, experimental design, PFAA concentrations in soils and crops, and plots of intercompartmental concentration factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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