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UPTAKE OF PERFLUOROALKYL ACIDS INTO EDIBLE CROPS GROWN IN BIOSOLIDS-AMENDED SOIL

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UPTAKE OF PERFLUOROALKYL ACIDS INTO EDIBLE CROPS GROWN IN BIOSOLIDS-AMENDED SOIL

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LIST OF ACRONYMS

Abbreviation/Acronym	Definition
CTRL	control
DCM	dichloromethane
District	Metropolitan Water Reclamation District of Greater Chicago
HPLC	High Performance Liquid Chromatography
K_{ow}	octane-water partition coefficients
LC-MS/MS	liquid chromatography tandem mass spectrometry
LOQ	limits of quantitation
MeOH	methanol
MRM	multiple reaction monitoring
MSPS	Main Street Pumping Station
N	nitrogen
PFAA	perfluoroalkyl acids
PFAS	perfluoroalkyl substance
PFBA	perfluorobutanoate
PFBS	perfluorobutane sulfonate
PFCA	perfluorocrboxylates
PFDA	perfluorodecanoate
PFDS	perfluorodecane sulfonate
PFHpA	perfluoroheptanoate
PFHpS	perfluoroheptane sulfonate
PFHxA	perfluorohexanoate
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoate
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPeA	perfluoropentanoate
RCF	relative centrifugal force
RPM	resolutions per minute
TSCF	Transpiration Stream Concentration Factor
U.S.	United States
USEPA	United States Environmental Protection Agency
WWTP	wastewater treatment plant

BACKGROUND

Perfluoroalkyl acids (PFAAs), which have been used in a myriad of consumer and industrial products (e.g., stain repellents, non-stick food packaging, and fire-fighting foams), are ubiquitous and persistent in the environment (Buck et al., 2011). These compounds have been detected in air, house dust, water, sediment, soil, wildlife, and humans (Lau et al., 2007; Kovarova et al., 2008; Haug et al., 2011). In addition, longer chain PFAAs are poorly eliminated by many higher trophic level organisms, with elimination half-lives of more than five years in humans for some PFAAs (Lau, 2012). Toxicity to wildlife and laboratory animals is well established for perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), including adverse effects such as reduced survival rates, fertility, and abnormal maturation (Lau et al., 2007). The toxicity of shorter-chain PFAAs is less documented. The persistence, bioaccumulation, and potential toxicity of PFAAs make them high priority contaminants of emerging concern.

Perfluoroalkyl acids entering conventional wastewater treatment plants (WWTPs) or produced from precursors during treatment can exit the plant in either the aqueous or the sludge phase (Schultz et al., 2006). The presence of PFAAs in municipal biosolids is well documented (Higgins et al., 2005; Guo et al., 2010; Kunacheva et al., 2011). The land application of biosolids has been practiced for decades; in the United States (U.S.), approximately 60 percent of biosolids are land applied (Lu et al., 2012). Nutrient-rich biosolids are particularly attractive as a fertilizer for crop production. Currently, the United States Environmental Protection Agency (USEPA) regulates the land application of biosolids based on pathogen, metal, and nutrient content under the 40 Code of Federal Regulations Part 503 (USEPA, 1994). However, PFAAs in biosolids are not currently regulated in the U.S. (Lu et al., 2012). In Decatur, Alabama, industrially contaminated biosolids were applied to land used for grazing cattle and growing crops, resulting in perfluoroalkyl substances (PFAS) detections in soil, beef, grass, and groundwater from the biosolids-amended fields (USEPA, 2010; Yoo et al., 2011). While PFASs are known to be present in municipal biosolids (Higgins et al., 2005), it remains unclear whether the application of typical municipal biosolids to agricultural soil could pose any potential PFAS-related risks for human and ecological health.

Previous studies have documented the potential for PFAA bioaccumulation into crops, particularly for PFOS and PFOA (Stahl et al., 2009; Lechner and Knapp, 2011). When growing corn, wheat, potato, and oats in PFAA-spiked soils, Stahl et al. found PFOA and PFOS in the vegetative plant portions (Stahl et al., 2009), a finding that was confirmed in follow-up studies (Stahl et al., 2013). In a similar study using PFAA-spiked soils, Lechner and Knapp (2011) found carryover of PFOA and PFOS in carrots, cucumbers, and potatoes, with the highest transfer factors for the vegetative portions. Both studies found higher PFOA than PFOS levels; however, spiked soil systems are known to be problematic with respect to contaminant bioavailability (Loibner et al., 1998; Wu et al., 2011), and thus these studies may not adequately describe PFAA uptake from non-spiked, biosolids-amended soils. In a more relevant study, the transfer of PFAAs from industrially contaminated biosolids-amended soils into grass was observed (Yoo et al., 2011), with PFOA again bioaccumulating more than PFOS. Although grass may be consumed by animals, thereby enabling PFAA entry into the terrestrial food chain, it does not represent a direct human exposure scenario. PFAAs uptake in hydroponically grown lettuce has

also been observed (Felizeter et al., 2012), though again, this does not likely describe the bioavailability of PFAAs to plants grown in biosolids-amended soils (Trapp, 2007; Zabludowska et al., 2007).

Concerns about the potential bioaccumulation of PFAAs into crops grown in biosolids-amended soils are also supported by limited data on their plant uptake and transport behavior (Stahl et al., 2009; Yoo et al., 2011; Felizeter et al., 2012). While some predictions about plant uptake and transfer potential can be made based on plant physiology models (Trapp et al., 1994; Collins et al., 2006; Dettenmaier et al., 2009) and contaminant parameters, such as octanol-water partition coefficients (K_{ow}) (Michel and Buszewski, 2008), a very limited number of plant uptake studies have focused specifically on PFAAs. Initial models correlating the Transpiration Stream Concentration Factor (TSCF), or the concentration ratio of the compound in the xylem to the solution around the roots, to K_{ow} suggested maximal TSCFs for compounds with log K_{ow} values of 1.8 (Trapp et al., 1994). However, more recent models (Dettenmaier et al., 2009) suggest hydrophilic compounds (e.g., sulfolane) may actually be preferentially accumulated. Moreover, ionized contaminants are very soluble and non-volatile and thus have the potential to accumulate in plants (Swartjes, 2011).

The Colorado School of Mines, in collaboration with the USEPA Region 5, conducted greenhouse studies to study uptake of PFAAs in vegetable crops and also analyzed soil, corn stover and corn grain from farmers' fields receiving biosolids. The results from the greenhouse studies showed that uptake of PFAAs in lettuce and tomatoes was much lower from municipal biosolids treatments as compared to industrially impacted soil which had high concentrations of these compounds (Blaine et al., 2013). However, in the case of corn grown on farmers' fields receiving biosolids, only trace amounts of perfluorobutanoate (PFBA) and perfluoropentanoate (PFPeA) were detected in corn stover, and all PFAAs were below the LOQ in corn grain (Blaine et al., 2014).

The objective of this study was to examine PFAA bioaccumulation in lettuce (*Lactuca sativa*), radishes (*Raphanus sativus*), tomatoes (*Lycopersicon lycopersicum*), and sweet corn (*Zea mays*) grown in biosolids-amended soils in field conditions. Plant bioaccumulation was studied with unspiked, anaerobically digested, lagoon-aged, and air-dried biosolids from the Stickney Water Reclamation Plant operated by the Metropolitan Water Reclamation District of Greater Chicago (District). The above-mentioned crops were chosen because they represent common edible crops eaten fresh. This scenario represents the most direct route of human exposure from plants, thus avoiding complicating factors from processing and packaging. Although these fruits and vegetables are not commonly grown in biosolids-amended soils, they represent crops from the scenario of a home gardener using commercial biosolids as fertilizer.

PROJECT OVERVIEW

This study involved collaboration of the Colorado School of Mines, the USEPA Region 5, and the District.

Multi-year, field-scale trials (2011 to 2013), using six different crops (zucchini, tomatoes, sweet corn, lettuce, carrots, and radishes) and a control plus four biosolids application rates, were conducted at a site close to the District's Main Stream Pumping Station (MSPS) and maintained by District staff. The USEPA Region 5 supplied partial funding for the study. Lettuce and tomato tissues from the first-year crop (2011) and sweet corn and lettuce from the third-year crop (2013) and radish from the second (highest loading rate only) and third year crops (2012 and 2013) were analyzed. All crops from all four treatments for each year were not analyzed due to budgetary constraints. Samples were shipped to the Colorado School of Mines for analysis. Treatment details and resulting soil organic carbon concentration in surface soil are presented in Table 1.

MATERIALS AND METHODS

Chemicals

Perfluorinated standards, as well as stable-isotope labeled standards (Table 2), were obtained from Wellington Laboratories (Guelph, ON, Canada). Analytes in this study include PFBA, PFPeA, perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), PFOS, and perfluorodecane sulfonate (PFDS). All standards were prepared in a 70/30 (v/v) methanol/water with 0.01 percent ammonium hydroxide solution. High Performance Liquid Chromatography (HPLC)-grade methanol and high purity Chromasolv® dichloromethane from Sigma Aldrich (St. Louis, MO) were used for extractions. All other solvents were reagent grade from Sigma Aldrich. Water used in extractions was obtained from a MilliQ™ system (Millipore, Billerica, MA), and HPLC-grade water was used for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. For extraction clean up, Chromabond® diamino from Macherey-Nagel Inc. (Bethlehem, PA) and Supelclean™ ENVI-Carb™ from Sigma-Aldrich were used.

Field Study

A field study was conducted at the MSPS District site where eighteen plots (3.0 m x 4.6 m) were established, and each was planted with lettuce (*Lactuca sativa* "Black-Seeded Simpson"), tomatoes (*Lycopersicon lycopersicum* "Burpee Big Boy Hybrid"), corn (*Zea mays*), radishes (*Rapha nus sativus*), and zucchini (*Cucurbita pepo*). Fertilization via biosolids occurred at

TABLE 1: BIOSOLIDS APPLICATION TREATMENTS IN FIELD STUDY AND RESULTING SOIL CARBON MATTER CONTENT

Soils and Amendment Rates	% Organic Carbon
Control (unamended)	1.45
0.5X agronomic rate for N (5 Mg/ha)	1.84
1X agronomic rate for N (10 Mg/ha)	2.11
2X agronomic rate for N (20 Mg/ha)	2.34
4X agronomic rate for N (40 Mg/ha)	3.51

TABLE 2: PERFLUOROALKYL ACIDS AND SURROGATE STANDARDS USED IN THIS STUDY

Analyte	Surrogate Standard	
PFBA	[$^{13}C_4$]	PFBA
PFPeA	[$^{13}C_3$]	PFPeA
PFHxA	[$^{13}C_2$]	PFHxA
PFHpA	[$^{13}C_4$]	PFHpA
PFOA	[$^{13}C_4$]	PFOA
PFNA	[$^{13}C_5$]	PFNA
PFDA	[$^{13}C_2$]	PFDA
PFBS	[$^{18}O_2$]	PFHxS
PFHxS	[$^{18}O_2$]	PFHxS
PFHpS	[$^{18}O_2$]	PFHxS
PFOS	[$^{13}C_4$]	PFOS
PFDS	[$^{13}C_4$]	PFOS

five application rates (including control), with three replicate plots per application rate. The soil treatments included an unamended control (CTRL), one-half of the agronomic rate of biosolids application to meet nitrogen (N) requirements of the crop (0.5X), agronomic rate (1X), two times the agronomic rate (2X), and four times the agronomic rate (4X). Treatment details and soil organic carbon content of 0 – 15 cm layer are provided in Table 1. Crops were grown and harvested following normal agricultural practices. Lettuce, radishes, corn, and tomatoes were harvested at maturity (radishes ~ 45 days; lettuce ~ 45 days; tomatoes ~ 100 days; and corn ~ 120 days).

Soil and Produce Sampling. Soil and plant tissue samples were collected using a sample collection protocol developed to minimize cross-contamination. Duplicate soil samples, as well as lettuce, corn, radishes, and tomato samples from each plot, were collected. Clean nitrile gloves were worn during each sampling event. Prior to use, the equipment (e.g., a stainless steel shovel) was decontaminated by physically wiping with a clean paper towel to remove any attached soil/debris, rinsed twice with methanol, and then rinsed once with de-ionized water. PFAA contamination was minimized before and during sampling events by avoiding potential consumer product sources (e.g., clothing with stain- or water-repellents, self-sticky memos). All soil and plant samples were stored in polypropylene or polyethylene containers to avoid PFAA contamination. All samples were placed on ice and shipped to the laboratory where they were frozen at -20°C until extraction. Soil samples for all three years and from all treatments were analyzed.

Extraction and Perfluoroalkyl Acids Analysis

Plant Tissue Extraction Procedure. Plant material was homogenized prior to extraction using a food processor. An aliquot of the homogenized plant tissue (0.5 – 2 g) was transferred to a 50 mL polypropylene vial to which a surrogate spiking solution, containing 2 ng of each isotopically labeled surrogate standard, was added. A solvent mixture of 50/50 dichloromethane (DCM) and 99:1 (v/v) methanol (MeOH) and ammonium hydroxide was chosen based on the exhaustive extraction results of Yoo et al. (2011). The solvent mixture (7 mL) was added to the sample and heated (30°C) in a sonication bath (Fisher Scientific FS110H, Pittsburg, PA) for 30 minutes followed by shaking (VWR 5000 STD 120V, West Chester, PA) for one hour. The sample was centrifuged (Eppendorf 5810, Hamburg, Germany) at 2700 resolutions per minute (RPM) (1467 relative centrifugal force [RCF]) for 20 minutes, and the extract was decanted into a separate 50 mL tube. This procedure was repeated twice for a total of three extraction cycles. The combined extract was evaporated at 50°C under N (Organomation Associates Inc. N-EVAP 112, Berlin, MA) to dryness. To minimize matrix effects, the extract was cleaned up via oxidation with 1 mL of a basic hydrogen peroxide solution (20 µL ammonium hydroxide and 980 µL 30 percent hydrogen peroxide), vortexed, and sonicated in a heated (30°C) bath for two hours. An additional aliquot (7 mL) of the basic DCM/MeOH mixture was added to each oxidized extract, vortexed, and heated in a sonication bath for 30 minutes. The extract was centrifuged at 2700 rpm (1467 RCF) for 20 minutes and decanted into a glass 20 mL scintillation vial. This re-extraction procedure was repeated twice for a total of three cycles. The combined extract was evaporated at 50°C under N to dryness and reconstituted with 1 mL of 99:1 (v/v) MeOH and acetic acid. The extract was run through a clean-up column packed with 100 mg of diamino and 100 mg ENVI-Carb™. To analyze, 105 µL of the cleaned extract was transferred to an autosampler

vial, along with 1350 µL of water and 45 µL of dilution water, consisting of 0.01 percent ammonium hydroxide. All results are reported on a dry-weight basis, which was determined by drying separate aliquots of plant tissue at 70°C overnight (at which time no additional change in mass was observed).

Soil Extraction Procedure. Soil samples were extracted, as per established protocols (Sepulvado et al., 2011). Soil samples were extracted by placing a 1 g aliquot into a 50 mL polypropylene vial to which a solution containing isotopically labeled surrogate standard was added prior to sequential extraction via sonication with basic methanol, as per established protocols.[1] All extracts were combined, evaporated to dryness, reconstituted in acidic methanol, subjected to a dispersed ENVI-Carb™ clean up, and analyzed by LC-MS/MS. Further details for the soil extraction method are available in Blaine et al. (2013). All results are reported on a dry-weight basis, which was determined by drying separate aliquots of soil overnight at 105°C.

Perfluoroalkyl Acids Analysis. All PFAAs were analyzed using isotope dilution LC-MS/MS under conditions similar to those previously described (Sepulvado et al., 2011). Briefly, chromatography was performed using an aqueous ammonium acetate (10 mM) and MeOH (10 mM) gradient delivered at a flow rate of 800 µL/min by a Shimadzu LC-20AD unit (Kyoto, Japan). Samples and standards were injected (1 mL) by a Shimadzu SIL-5000 Auto Injector onto a 50 mm x 4.6 mm Gemini C18 column with a 3-micron particle size (Phenomenex, Torrance, CA) also equipped with a C18 Guard Column and Cartridge. Initial eluent conditions were 50 percent MeOH and 50 percent water. The percent MeOH was ramped to 95 percent over four minutes, held at 95 percent over four minutes, ramped back down to 50 percent over 1.5 minutes, and re-equilibrated at 50 percent until 13 minutes. An MDS Sciex Applied Biosystems API 3200 (MDS Sciex, Ontario), operating in negative electrospray ionization scheduled multiple reaction monitoring (MRM) mode, was used to monitor two MRM transitions for all analytes.

Quality Control

Quantitation was performed using the software Analyst®. A minimum of twenty percent of all samples in each matrix was extracted and analyzed in triplicate. In general, the relative standard deviation for analytical replicates was less than 25 percent. Values presented in this study are averages of experimental (greenhouse) or field (outdoor) replicates (n = 3 to 18). Limits of quantitation were derived from the lowest calibration standard calculated to be within 30 percent of its actual value and were analyte, matrix, and run-dependent. The LOQs, in general, ranged from 0.01 to 1.5 ng/g_{dw}. Field, experimental, and analytical blanks were employed to monitor contamination. Sample values that were not at least twice the level of the highest concentration in a blank were reported as < LOQ. Internal surrogate standards were used for each analyte to correct for any losses during extraction. Plant surrogate recovery varied with matrix and analyte, but typically ranged from 10 percent to 60 percent, and samples with less than eight percent were excluded from any calculations. These recoveries are low in comparison to soil recoveries, however (Sepulvado et al., 2011), and are somewhat typical in plant matrices (Yoo et al., 2011; Felizeter et al., 2012) due to matrix ion suppression. The results of additional spike-recovery experiments (accounting for surrogate losses) showed that there were no clear chain-length dependent trends among analytes.

RESULTS AND DISCUSSION

Concentrations of Perfluoroalkyl Acids in Control and Biosolids-Amended Soil

The five biosolids treatments used in the pilot-scale field trial plots were selected to represent increasing application rates; however, PFAA soil concentrations above background (i.e., >1.5 ng/g) were only observed for PFOA, PFNA, PFDA, PFOS, and PFDS (Table 3). The two highest concentrations were for PFOS (13.9 ng/g) and PFOA (5.2 ng/g) in the 4X amended soil. Soil concentrations of shorter chain PFAAs did not significantly increase with an increased biosolids amendment rate (Table 3). These field soil values of PFAAs were significantly lower (3 - 20 times) than the levels found in the soils used in the greenhouse study. The concentrations of PFAAs in biosolids-amended soils increased with increasing cumulative biosolids loading, as shown in Figure 1. The concentrations of PFAAs in the soil ranged from <0.5 ng/g dry weight for most of the perfluorocarboxylates to > 3.0 ng/g dry weight for PFOS. Consistent with earlier work (Sepulvado et al., 2011), PFAA levels in the soils generally increased with increasing cumulative biosolids loading.

Levels of Perfluoroalkyl Acids in Lettuce Grown in Biosolids-Amended Soils in 2011 and 2013

As a result of low initial soil concentrations, limited plant uptake data from the field trials were obtained, restricting the comparisons that could be made. PFAA concentrations in test crops were averaged for the three replicate soil plots only if all three replicate values were above the LOQ (Table 3). In general, none of the PFAA was taken up by lettuce when biosolids were applied at an agronomic rate (1X, 10 Mg/ha) and only two compounds were detected at low concentrations at twice that rate (2X, 20 Mg/ha) (Table 3). The highest concentrations found were for PFBA (27.5 ng/g) and PFPeA (16.4 ng/g) in the 4X amended soil treatment. The lettuce exhibited uptake of >10 ng/g dw of PFPeA in plants grown in 4X amended soils from 2011, 2012, and 2013 and in 2X amended soils from 2013 as shown in Figure 2. Only two other PFAAs were present in lettuce samples at concentrations above the quantitation limits, which are PFBS (~3 ng/g dw) and PFBA (>120 ng/g dw). The presence of predominantly short-chain acids (i.e., PFBA, PFPeA) in the lettuce is consistent with our previous studies examining PFAA accumulation in lettuce from biosolids-amended soils (Blaine et al., 2013). However, the significantly elevated levels of PFBA from the 2013 4X samples suggests a much higher extent of bioaccumulation of PFBA than would be expected based on earlier work (Blaine et al., 2013). While one might initially point to analytical and/or blank issues, the reproducibility for this sample was fairly good (~9 percent relative standard deviation), and no other samples appeared to have such high levels. One potential explanation is the presence of significant quantities of PFBA precursors in the biosolids-amended soil, which also accumulated and were converted (either by the plant or during the extraction process) to PFBA, though additional measurements would be needed to ascertain if indeed this can explain the anomalously high levels of PFBA in this lettuce sample.

TABLE 3: AVERAGE CONCENTRATION OF PERFLUOROALKYL ACIDS IN SOIL AND LETTUCE AS AFFECTED BY BIOSOLIDS LOADING

Analyte	Control Treatment		Biosolids Rate 0.5X		Biosolids Rate 1X		Biosolids Rate 2X		Biosolids Rate 4X	
	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce
	2011									
	ng/g									
PFBA	0.72 ± 0.11	LOQ	0.42 ± 0.07	LOQ	0.48 ± 0.05	LOQ	0.43 ± 0.03	LOQ	0.69 ± 0.04	27.50 ± 1.66
PFPeA	0.39 ± 0.10	LOQ	0.24 ± 0.02	LOQ	0.32 ± 0.02	LOQ	0.58 ± 0.06	8.52 ± 5.84	1.01 ± 0.08	16.42 ± 2.37
PFHxA	0.34 ± 0.09	LOQ	0.22 ± 0.02	LOQ	0.36 ± 0.04	LOQ	0.76 ± 0.08	LOQ	1.49 ± 0.12	LOQ
PFHpA	0.19 ± 0.04	LOQ	0.21 ± 0.02	LOQ	0.35 ± 0.02	LOQ	0.51 ± 0.04	LOQ	1.03 ± 0.09	LOQ
PFOA	0.42 ± 0.07	LOQ	0.74 ± 0.08	LOQ	1.48 ± 0.09	LOQ	2.11 ± 0.07	LOQ	5.17 ± 0.28	LOQ
PFNA	0.14 ± 0.01	LOQ	0.32 ± 0.02	LOQ	0.73 ± 0.05	LOQ	1.12 ± 0.04	LOQ	3.01 ± 0.18	LOQ
PFDA	LOQ	LOQ	0.51 ± 0.07	LOQ	0.13 ± 0.08	LOQ	1.75 ± 0.05	LOQ	4.00 ± 0.20	LOQ
PFBS	0.20 ± 0.02	LOQ	0.20 ± 0.01	LOQ	0.30 ± 0.04	LOQ	0.31 ± 0.04	LOQ	0.80 ± 0.09	1.62 ± 0.26
PFHxS	0.07 ± 0.01	LOQ	0.08 ± 0.01	LOQ	0.14 ± 0.02	LOQ	0.13 ± 0.01	LOQ	0.33 ± 0.03	0.50 ± 0.04
PFHpS	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	0.16 ± 0.02	LOQ
PFOS	1.22 ± 0.16	LOQ	2.20 ± 0.23	LOQ	4.31 ± 0.34	LOQ	6.12 ± 0.25	2.14 ± 1.27	13.91 ± 0.91	1.39 ± 0.17
PFDS	LOQ	LOQ	0.17 ± 0.02	LOQ	0.61 ± 0.07	LOQ	1.19 ± 0.11	LOQ	3.17 ± 0.21	LOQ
	2013									
PFBA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	128.2 ± 11.3
PFPeA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	15.6 ± 4.9	LOQ	14.7 ± 2.9
PFHxA	LOQ	LOQ	N/A	N/A	0.07 ± 0.04	LOQ	0.15 ± 0.01	LOQ	0.43 ± 0.17	LOQ
PFHpA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
PFOA	0.03 ± 0.01	LOQ	N/A	N/A	0.26 ± 0.11	LOQ	0.74 ± 0.14	LOQ	1.81 ± 0.44	LOQ
PFNA	0.01 ± 0.00	LOQ	N/A	N/A	0.17 ± 0.06	LOQ	0.44 ± 0.05	LOQ	1.22 ± 0.19	LOQ
PFDA	0.02 ± 0.00	LOQ	N/A	N/A	0.31 ± 0.21	LOQ	0.73 ± 0.02	LOQ	1.67 ± 0.12	LOQ
PFBS	LOQ	LOQ	N/A	N/A	0.11 ± 0.08	LOQ	0.37 ± 0.05	LOQ	0.86 ± 0.06	LOQ
PFHxS	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	2.12 ± 0.23	LOQ	3.37 ± 0.68
PFHpS	0.003 ± 0.0	LOQ	N/A	N/A	0.02 ± 0.01	LOQ	0.04 ± 0.02	LOQ	0.09 ± 0.05	LOQ
PFOS	0.08 ± 0.02	LOQ	N/A	N/A	0.65 ± 0.45	LOQ	1.54 ± 0.09	LOQ	3.57 ± 0.64	LOQ
PFDS	LOQ	LOQ	N/A	N/A	LOQ	LOQ	0.35 ± 0.02	LOQ	0.83 ± 0.22	LOQ

FIGURE 1: LEVELS OF PERFLUOROALKYL ACIDS IN BIOSOLIDS-AMENDED SOILS. VALUES SHOWN REPRESENT THE MEAN OF EXPERIMENTAL REPLICATES

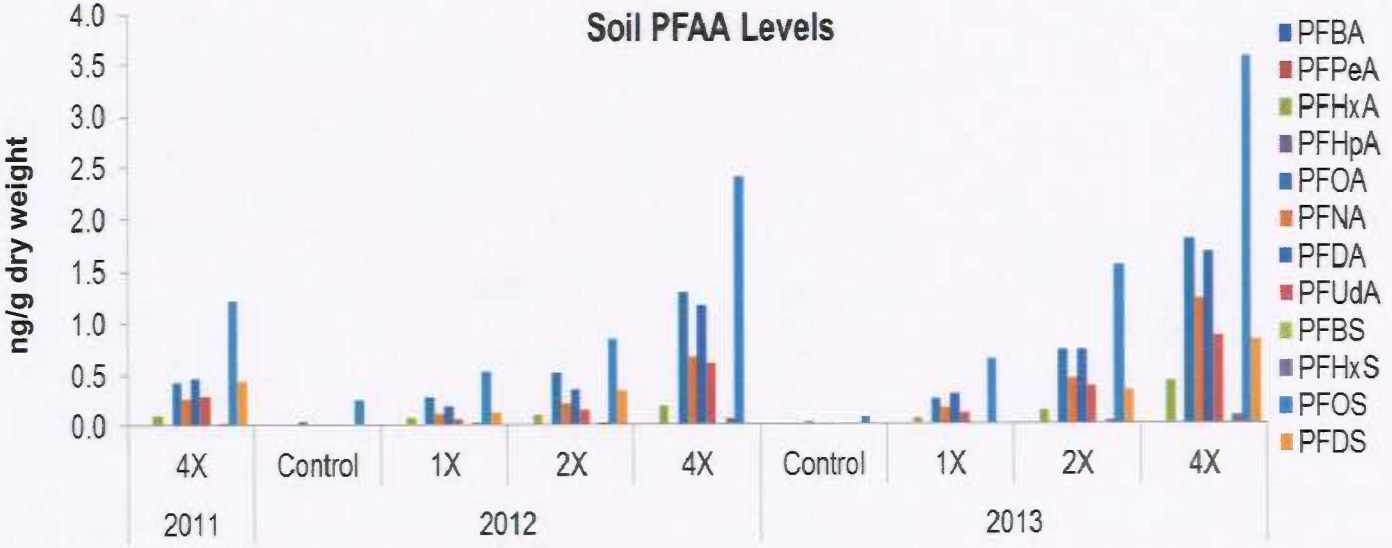
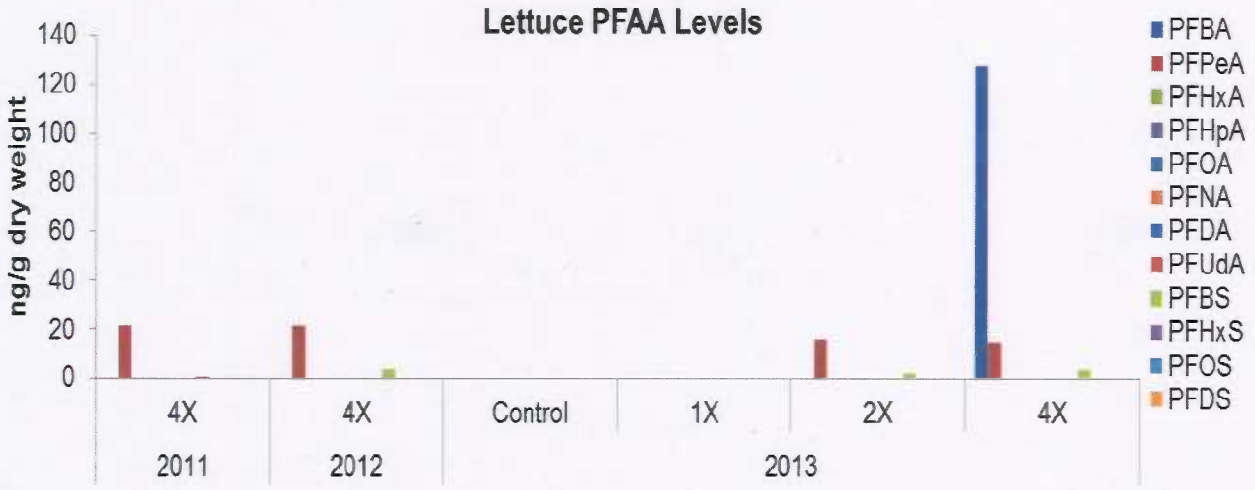


FIGURE 2: CONCENTRATIONS OF PERFLUOROALKYL ACIDS IN LETTUCE GROWN IN BIOSOLIDS-AMENDED SOILS. VALUES SHOWN REPRESENT THE MEAN OF TWO TO THREE EXPERIMENTAL REPLICATES



Levels of Perfluoroalkyl Acids in Tomatoes Grown in Biosolids-Amended Soils in 2011

In general, no accumulation was found in tomatoes grown in the 1X and 2X biosolids treatments (Table 4). For tomatoes, the highest concentrations were for PFBA (17.0 ng/g) in the 0.5X treatment and PFPeA (15.0 ng/g) in the 4X treatment.

Levels of Perfluoroalkyl Acids in Sweet Corn Grain Grown in Biosolids-Amended Soils in 2013

The concentrations of PFAAs in corn grain samples were below the LOQs in all of the samples obtained from 2013 (Table 5), and only PFBA was detected in the 4X biosolids treatment from 2011 (6.4 ng/g dw). The apparent lack of PFAA uptake by corn under normal field conditions is consistent with the findings of Blaine et al. (2013) in a full-scale study of corn grown in biosolids-amended farmers' fields.

Levels of Perfluoroalkyl Acids in Radishes Grown in Biosolids-Amended Soils in 2013

The radish data suggest that a larger variety of PFAAs accumulated in the radishes than in the other plants, with concentrations exceeding 50 ng/g dw for PFBA as shown in Figure 3. The concentrations of PFAAs in the radish samples were much higher than the concentrations in corresponding soil samples, which, in some cases, were below the LOQ. However, the radishes grown in the control soil exhibited particularly high levels of PFHpA, PFOA, and PFDA (Table 6). The presence of these compounds, which are some of the least bioaccumulative of the perfluorocarboxylates, suggests that some degree of sample contamination may have occurred for the radish samples (which did not occur for the other samples, suggesting this was not a result of laboratory contamination). Though precautions were taken during sample collection, it is possible that precursors to these compounds (or these compounds themselves) were introduced during sample collection and/or initial processing. Additional follow-up work would be needed to assess if this was, indeed, the case. Incomplete washing of soil from the radishes is unlikely, as more strongly sorbing (and generally higher concentration PFAAs), such as PFOS, were not detected in these controls.

TABLE 4: AVERAGE CONCENTRATION OF PERFLUOROALKYL ACIDS IN SOIL AND TOMATO AS AFFECTED BY BIOSOLIDS LOADING IN 2011

Analyte	Control Treatment		Biosolids Rate 0.5X		Biosolids Rate 1X		Biosolids Rate 2X		Biosolids Rate 4X	
	Soil	Tomato	Soil	Tomato	Soil	Tomato	Soil	Tomato	Soil	Tomato
	ng/g									
PFBA	0.72 ± 0.11[1]	LOQ[2]	0.42 ± 0.07	17.04 ± 4.41	0.48 ± 0.05	LOQ	0.43 ± 0.03	LOQ	0.69 ± 0.04	12.56 ± 3.68
PFPeA	0.39 ± 0.10	LOQ	0.24 ± 0.02	LOQ	0.32 ± 0.02	6.44 ± 0.49	0.58 ± 0.06	LOQ	1.01 ± 0.08	14.97 ± 1.98
PFHxA	0.34 ± 0.09	LOQ	0.22 ± 0.02	LOQ	0.36 ± 0.04	LOQ	0.76 ± 0.08	LOQ	1.49 ± 0.12	10.17 ± 1.20
PFHpA	0.19 ± 0.04	LOQ	0.21 ± 0.02	LOQ	0.35 ± 0.02	LOQ	0.51 ± 0.04	LOQ	1.03 ± 0.09	LOQ
PFOA	0.42 ± 0.07	LOQ	0.74 ± 0.08	LOQ	1.48 ± 0.09	LOQ	2.11 ± 0.07	LOQ	5.17 ± 0.28	LOQ
PFNA	0.14 ± 0.01	LOQ	0.32 ± 0.02	LOQ	0.73 ± 0.05	LOQ	1.12 ± 0.04	LOQ	3.01 ± 0.18	LOQ
PFDA	LOQ	LOQ	0.51 ± 0.07	LOQ	0.13 ± 0.08	LOQ	1.75 ± 0.05	LOQ	4.00 ± 0.20	LOQ
PFBS	0.20 ± 0.02	LOQ	0.20 ± 0.01	LOQ	0.30 ± 0.04	LOQ	0.31 ± 0.04	LOQ	0.80 ± 0.09	LOQ
PFHxS	0.07 ± 0.01	LOQ	0.08 ± 0.01	LOQ	0.14 ± 0.02	LOQ	0.13 ± 0.01	LOQ	0.33 ± 0.03	LOQ
PFHpS	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	0.16 ± 0.02	LOQ
PFOS	1.22 ± 0.16	LOQ	2.20 ± 0.23	LOQ	4.31 ± 0.34	LOQ	6.12 ± 0.25	LOQ	13.91 ± 0.91	LOQ
PFDS	LOQ	LOQ	0.17 ± 0.02	LOQ	0.61 ± 0.07	LOQ	1.19 ± 0.11	LOQ	3.17 ± 0.21	LOQ

[1]Standard error, n = 3 to 7.
[2]Less than limit of quantitation.

TABLE 5: AVERAGE CONCENTRATION OF PERFLUOROALKYL ACIDS IN SOIL AND SWEET CORN AS AFFECTED BY BIOSOLIDS LOADING IN 2013

Analyte	Control Treatment		Biosolids Rate 0.5X		Biosolids Rate 1X		Biosolids Rate 2X		Biosolids Rate 4X	
	Soil	Corn	Soil	Corn	Soil	Corn	Soil	Corn	Soil	Corn
	ng/g									
PFBA	LOQ[1]	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	6.4 ± 0.8[2]
PFPeA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
PFHxA	LOQ	LOQ	N/A	N/A	0.07 ± 0.04	LOQ	0.15 ± 0.01	LOQ	0.43 ± 0.17	LOQ
PFHpA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
PFOA	0.03 ± 0.01	LOQ	N/A	N/A	0.26 ± 0.11	LOQ	0.74 ± 0.14	LOQ	1.81 ± 0.44	LOQ
PFNA	0.01 ± 0.00	LOQ	N/A	N/A	0.17 ± 0.06	LOQ	0.44 ± 0.05	LOQ	1.22 ± 0.19	LOQ
PFDA	0.02 ± 0.00	LOQ	N/A	N/A	0.31 ± 0.21	LOQ	0.73 ± 0.02	LOQ	1.67 ± 0.12	LOQ
PFUdA	LOQ	LOQ	N/A	N/A	0.11 ± 0.08	LOQ	0.37 ± 0.05	LOQ	0.86 ± 0.06	LOQ
PFBS	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
PFHxS	0.003 ± 0.0	LOQ	N/A	N/A	0.02 ± 0.01	LOQ	0.04 ± 0.02	LOQ	0.09 ± 0.05	LOQ
PFOS	0.08 ± 0.02	LOQ	N/A	N/A	0.65 ± 0.45	LOQ	1.54 ± 0.09	LOQ	3.57 ± 0.64	LOQ
PFDA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	0.35 ± 0.02	LOQ	0.83 ± 0.22	LOQ

[1]Less than limit of quantitation.
[2]Standard error, n = 3 to 7.

FIGURE 3: CONCENTRATIONS OF PERFLUOROALKYL ACIDS IN RADISH GROWN IN BIOSOLIDS-AMENDED SOILS. VALUES SHOWN REPRESENT THE MEAN OF TWO TO THREE EXPERIMENTAL REPLICATES

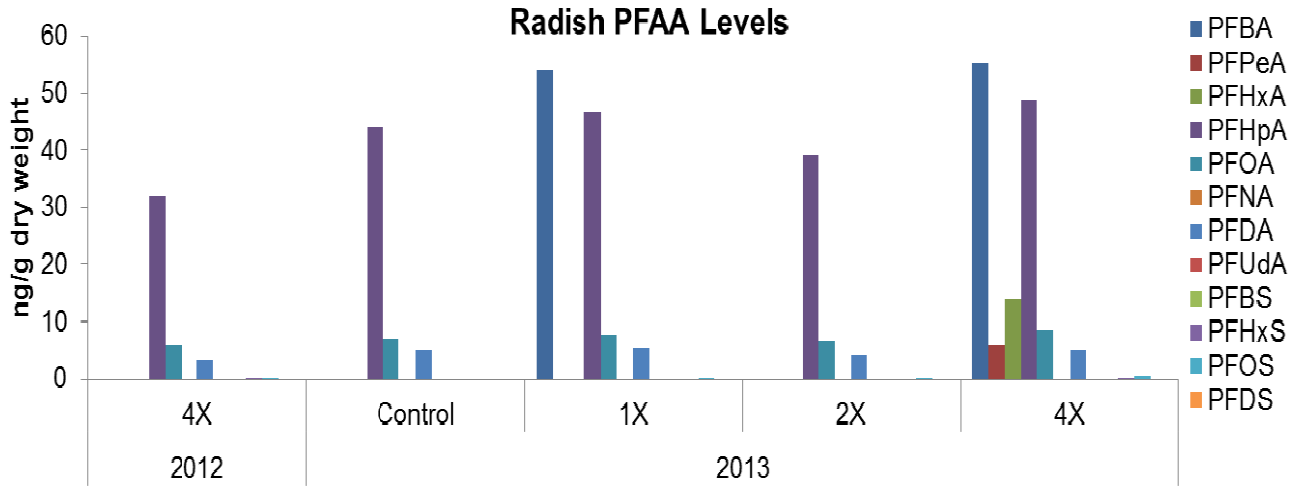


TABLE 6: AVERAGE CONCENTRATION OF PERFLUOROALKYL ACIDS IN SOIL AND RADISH AS AFFECTED BY BIOSOLIDS LOADING IN 2013

Analyte	Control Treatment		Biosolids Rate 0.5X		Biosolids Rate 1X		Biosolids Rate 2X		Biosolids Rate 4X	
	Soil	Radish	Soil	Radish	Soil	Radish	Soil	Radish	Soil	Radish
	ng/g									
PFBA	LOQ[1]	LOQ	N/A	N/A	LOQ	54.3 ± 2.6[2]	LOQ	LOQ	LOQ	55.2 ± 3.8
PFPeA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	5.8 ± 0.5
PFHxA	LOQ	LOQ	N/A	N/A	0.07 ± 0.04	LOQ	0.15 ± 0.01	LOQ	0.43 ± 0.17	13.92 ± 0.53
PFHpA	LOQ	44.2 ± 10.3	N/A	N/A	LOQ	46.6 ± 8.0	LOQ	39.4 ± 3.9	LOQ	48.7 ± 5.3
PFNA	0.01 ± 0.00	LOQ	N/A	N/A	0.17 ± 0.06	LOQ	0.44 ± 0.05	LOQ	1.22 ± 0.19	LOQ
PFDA	0.02 ± 0.00	5.19 ± 1.65	N/A	N/A	0.31 ± 0.21	5.30 ± 0.47	0.73 ± 0.02	3.99 ± 0.69	1.67 ± 0.12	5.10 ± 0.69
PFUdA	LOQ	LOQ	N/A	N/A	0.11 ± 0.08	LOQ	0.37 ± 0.05	LOQ	0.86 ± 0.06	LOQ
PFBS	LOQ	LOQ	N/A	N/A	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
PFHxS	0.003 ± 0.0	LOQ	N/A	N/A	0.02 ± 0.01	LOQ	0.04 ± 0.02	LOQ	0.09 ± 0.05	0.16 ± 0.06
PFOS	0.08 ± 0.02	LOQ	N/A	N/A	0.65 ± 0.45	0.35 ± 0.17	1.54 ± 0.09	0.27 ± 0.06	3.57 ± 0.64	0.39 ± 0.10
PFDA	LOQ	LOQ	N/A	N/A	LOQ	LOQ	0.35 ± 0.02	LOQ	0.83 ± 0.22	LOQ

[1]Less than level of quantitation.
[2]Standard error, n = 3 to 7.

CONCLUSIONS

The results of this study indicate that the chances of PFAAs bioaccumulating in vegetable crops grown in biosolids-amended soils under field conditions are low and very much dependent on the crop and the PFAA. The biosolids loading rate appears to be an important determinant, as the samples from the 4X treatment in year 2013 soil generally showed the broadest suite of compounds and/or the highest levels of PFAAs (both in the soils and the plants). However, it should be noted that by 2013, the 4X treatment received cumulative loading of biosolids 12 times higher than the recommended application rate. Unexpectedly, the radish samples (including controls) appeared to display elevated levels of three perflurocrboxylates (PFCAs), suggesting that accumulation patterns of these compounds in radishes from this set of samples should be viewed with caution. In row crops, for example, there was no uptake of these compounds in sweet corn. Also, little or no uptake was reported in tomatoes and lettuce crops from treatments receiving the agronomic rate of biosolids application.

Implications

While some PFAA crop accumulation data are available from literature, this is the first study examining PFAA accumulation in food crops grown in unspiked, biosolids-amended soils, though amendment rates were generally above typical agronomic application rates. In addition, uptake differences in crops suggest that the vegetative structure of the crop may affect the amount of bioaccumulation. In general, the data presented here suggest fruit crops accumulate fewer long-chain PFCAs than do 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 radishes 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.

With respect to overall exposure, it is highly 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. More work is needed to verify the trends observed in this study, as plant accumulation of PFAAs varies with soil properties, crop type, biosolids application rate, and analyte.

Based on these results, it is clear that farmland application of biosolids as a nutrient source to grow row crops like corn is a safe practice, as these compounds were not detected in grains. For vegetable garden use, the District's future plan of providing composted biosolids generated by composting with wood chips may be safe, as the composting process may reduce the concentrations of PFAAs further, and also, the dilution effect of wood chips may further reduce the concentrations of these compounds in the composted biosolids significantly. Conducting a small study on the concentrations of these compounds in composted biosolids and their uptake by vegetables grown in composted biosolids-amended soils is recommended.

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APPENDIX A

LIMITS OF QUANTITATION FOR EACH COMPOUND AND SAMPLE MATRIX

APPENDIX TABLE 1: LIMITS OF QUANTITATION FOR EACH COMPOUND AND SAMPLE MATRIX

Matrix	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFBS	PFHxS	PFOS	PFDS
	ng/g dry weight											
Soils	0.024	0.061	0.012	0.061	0.012	0.0012	0.012	0.012	0.12	0.001	0.012	0.024
Radish	0.28	2.8	0.057	0.28	0.11	0.06	0.28	0.28	0.057	0.057	0.057	0.057
Lettuce	1.3	6.3	3.1	1.3	0.06	0.63	1.3	0.13	0.13	0.13	0.63	0.31
Tomato	0.07	0.14	0.07	0.07	0.14	0.01	0.07	0.04	0.04	0.04	0.04	0.04
Corn stover	0.29	0.57	0.57	0.57	0.57	0.29	1.43	0.14	0.57	0.29	0.14	0.14
Corn grain	0.20	0.10	0.20	0.20	0.20	0.10	0.10	0.10	0.10	0.04	0.10	0.10