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PFAS in soil and groundwater following historical land application of biosolids

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ABSTRACT

The land application of digested sewage sludge (biosolids) is widely employed across the globe. Studies show that biosolids contain significant amounts of inorganic and organic materials, as well as emerging pollutants, including per- and polyfluorinated alkyl substances (PFAS). With the wide range of pollutants commonly reported in biosolids, the potential risks associated with long-term land application operations are concerning. In this study, PFAS in surface soils, deeper soils into the vadose zone, and immediately-underlying groundwater was measured at an agricultural station with a long record of biosolids applications plus irrigation using treated wastewater. Twelve PFAS homologues were detected in every near surface soil sampled 0–30 cm depth below ground surface with multiple PFAS (especially short-chain) distributed through the soil profile. Average measured concentrations of PFAS in these soils suggest the soil burden PFOS>PFDA>PFOA for all substations sampled, independent of the historical loading rates and patterns of agricultural operations on those substations. Measured concentrations of PFOA and PFOS in the soil profile (0–90 cm) suggest these compounds have migrated to deeper soil depths (up to 9 m below the surface) with quantifiable concentrations in the soil and the immediate underlying groundwater located approximately 17 m below. Estimates of the total mass of PFAS in surface soils were effectively made using PFAS levels reported in sludges from the USEPA NSSS combined with long-term loading rates on record at the substations. With the land application of biosolids in the USA regulated by the USEPA, additional and updated risk assessments and surveys to include emerging pollutants such as PFAS are needed to protect public health and the environment.

1. Introduction

Land application of sewage sludge (referred to as biosolids when treated to designated levels) is a common method employed around the world either as a disposal method or as a means to provide nutrients and organic amendments to agricultural soils (NEBRA, 2007). As a soil amendment, biosolids contain significant amounts of organic matter plus inorganic materials such as heavy metals and metal oxides (NRC, 2002). With the ever-increasing global production and consumption of organic chemicals, it is not surprising that there is concern over emerging pollutants in treated sewage sludge (Clarke and Smith, 2011; Venkatesan and Halden, 2013). Analysis of soil amendment products (Lazcano et al., 2020) and sludges from wastewater treatment facilities around the globe including Canada, China, Czech Republic, Denmark, Europe, Germany, Greece, Korea, Singapore, Spain, and USA consistently report levels of unregulated emerging pollutants such as per- and polyfluorinated alkyl substances (Loganathan et al., 2007; Clarke and Smith, 2011; Gómez-Canela et al., 2012; Kim et al., 2012; Venkatesan and Halden, 2013; Zareitalabad et al., 2013; Zhang et al., 2013; Arvaniti et al., 2014; Armstrong et al., 2016; Abril et al., 2020; Semerád et al., 2020; Lakshminarasimman et al., 2021).

Per- and polyfluorinated alkyl substances (PFAS), produced since the mid-20th century, are a family of compounds including thousands of substances (OECD, 2006) with PFAS detected in environmental media across the globe (ITRC 2020). From life-cycle analyses of commercial PFAS manufacturing from 1951 to 2002, researchers have estimated that 2600–5000 tonnes of $C_4 - C_{14}$ PFAS have been released (OECD, 2015). Furthermore, it is estimated that between 2015 and 2030, up to 5510 tonnes of $C_4 - C_{14}$ PFAS could be released into the environment (OECD, 2015). Global levels of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) detected in sewage sludge average 421 μg/kg (ranging from 1 to 5383 μg/kg) and 403 μg/kg (ranging from 0.5 to 4780 μg/kg), respectively (Zareitalabad et al., 2013). From an inventory of sewage sludges collected in from 94 wastewater treatment plants located throughout the US, Venkatesan and Halden (2013) report the average concentration of PFOS equal to 403 μg/kg (ranging from

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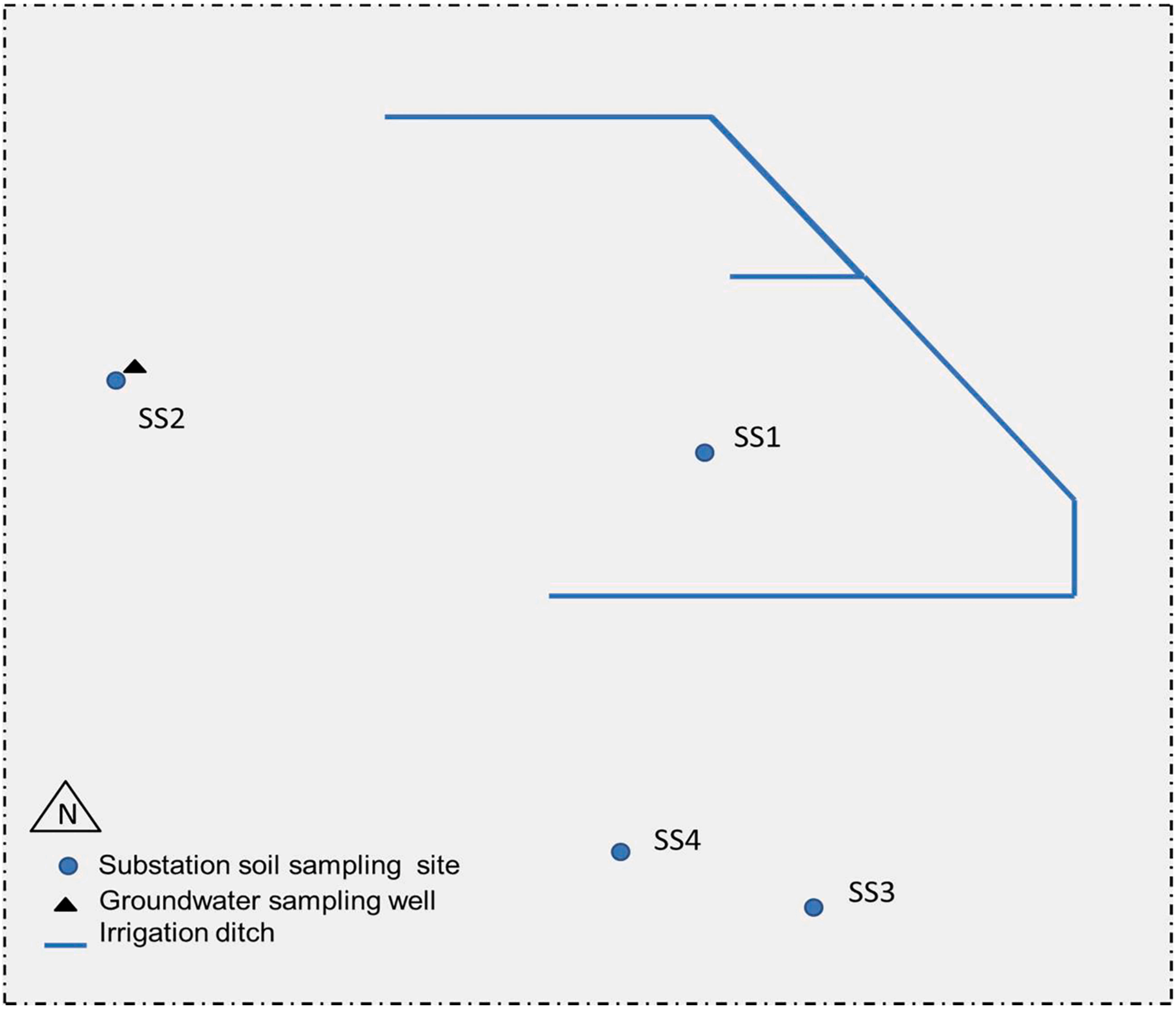

Fig. 1. Map (not to scale) illustrating the general location of substation soil sampling sites, the groundwater well, and the station's irrigation ditch.

308 to 618 μg/kg) and PFOA equal to 34 μg/kg (ranging from 11.8 to 70.3 μg/kg). Furthermore, several researchers have characterized the concentrations of PFAS in sewage sludges collected from publicly owned treatment works with results showing both regional and seasonal variability in PFAS concentrations (Higgins et al., 2005; Schultz et al., 2006; Sinclair and Kannan 2006; Loganathan et al., 2007; Kim et al., 2012). For example, Loganathan et al. (2007) report PFOA concentrations in sludge samples collected across four seasons (winter, spring, summer, and fall) at a wastewater treatment plant in Kentucky (USA) ranged from 8.3 to 219 μg/kg (fall and winter, respectively). In those same sludge samples, PFOS concentrations ranged from 8.2 to 110 μg/kg (fall and spring, respectively). Sinclair and Kannan (2006) report the average concentrations of PFOA and PFOS measured in sludge from a wastewater treatment plant in New York State (USA) equal to 144 and 25 μg/kg, respectively, while those average concentrations equaled 10 and 170 μg/kg for sludge collected from wastewater treatment plants in the western USA (Higgins et al., 2005).

PFAS are known to be environmentally persistent, bioaccumulative (especially long-chain homologues), synthetic, and ubiquitous in soils (Buck et al., 2011; Rankin et al., 2016; Brusseau et al., 2020). In a study by Rankin et al. (2016), global background soil concentrations of PFAS were quantified from soils collected from 62 remote locations including North America ($n = 33$), Europe ($n = 10$), Asia ($n = 6$), Africa ($n = 5$), Australia ($n = 4$), South America ($n = 3$), and Antarctica ($n = 1$). Total perfluoroalkyl carboxylic acids ($\sum_9$PFCAs) and sulfonic acids ($\sum_3$PFSAs) ranged 0.029–14.3 μg/kg and <LOQ – 3.270 μg/kg, respectively, with max concentrations of PFOA and PFOS equal to 3.4 and 3.1 μg/kg, respectively. Similarly, PFAS concentrations reported from soil survey studies representing >1400 sampling locations including from residential yards, agricultural fields, and commercial sites with background soil concentrations of PFOA and PFOS ranging from 0.01 to 123.6 μg/kg and 0.003 to 162 μg/kg, respectively, with median max concentrations equaling 2.7 μg/kg for both compounds (Brusseau et al., 2020).

The potential impact of PFAS present in soil amendments including biosolids on overall soil and groundwater quality is of concern. Researchers across the globe have reported PFAS and related compounds in groundwater and soils following the application of PFAS-containing soil amendments including biosolids and compost (Washington et al., 2010; Yoo et al., 2010; Gottschall et al., 2010; Lindstrom et al., 2011; Sepulvado et al., 2011; García-Valcárcel et al., 2012; Gottschall et al., 2017; Pepper et al., 2021; Röhler et al., 2021). The first published study, conducted in 2009, aimed to qualify the accumulation and vertical distribution of PFAS in near surface soils following the long-term application of soil amendments included soils collected by the USEPA from fields in Decatur, AL, where operations included more than a decade of land applying fluorochemical industry impacted biosolids (reported to have 10- to 100-fold greater concentrations of PFOA than biosolids from municipal wastewater treatment plants) (Washington et al., 2010; Lindstrom et al., 2011). Overall, the results and analysis suggest PFAS vertical migration beyond the zone of biosolids incorporation with increasing PFAS surface-soil concentrations directly proportional to the cumulative biosolids loading rates (Washington et al., 2010). Similar results showing PFAS leaching through the soil profile as a function of short-term and long-term land application of municipal biosolids have been reported (Sepulvado et al., 2011). Additionally, Pepper et al. (2021) reports PFAS soil concentrations following 35 years of land application of biosolids in Arizona with larger soil concentrations measured in soils receiving larger biosolids loading rates. An extensive search of the literature indicates that the characterization of PFAS following the long-term land application of dewatered municipal biosolids including the vertical distribution in near surface soils to the deeper soil profile of the vadose zone and the immediate underlying groundwater has not been reported.

In this study, the impact of land applying biosolids on the occurrence, concentration, and distribution of PFAS in soils, the vadose zone, and the immediately underlying groundwater at an agricultural station with a long history of land applying biosolids plus irrigation using treated wastewater effluent for planted feedstock crops was investigated. This is the first study to include the characterization of PFAS following the land application of biosolids in near surface soils to deeper soils and to underlying groundwater. Surface soil samples were collected along a nearly 4600 m transect of an agricultural station with characterization of the soil concentrations and vertical distribution of twelve PFAS homologues. The differential behavior of short-chain and long-chain PFAS is described. Additionally, depth profiles for PFOA and PFOS, combining those measured surface soil concentrations in this study with soil and groundwater concentrations is also presented.

2. Materials and methods

2.1. Study site

The field site is an agricultural feedstock station located in the western US. According to soil surveys by the natural resources conservation service (USDA), the region is mostly flat with ground slope <1%. Approximately 40% of the station's surface soil is composed of Garces loam. Tennco and Kimberlina fine sandy loams make up nearly 45% of the region with Calflax loams covering approximately 5% of the area and Calfax fine sandy loams making up close to 5% of the remaining soils (USDA WSS, 2020).

The land application of dewatered biosolids from multiple publicly owned treatment works (POTW) operating in a neighboring, highly populated city began at the station mid-1990s loading Class B product (USEPA, 1994) with operations switching to Class A product early 2000 to today. Biosolids incorporation at the site is typically conducted via cross discing, ripping, followed by cross discing again prior to seeding of feedstock crops on the farm. Irrigation operations at the station include flood irrigation of locally-sourced reclaimed water from a nearby POTW. It may be of interest to note that the treated sewage sludge and the treated wastewater effluent, both used to enhance farming operations at the station, are generated at different POTWs in the region. The agricultural station is surrounded by drainage ditches plus berms aimed to ensure containment of excess/overflow of irrigation water (see Fig. 1).

2.2. Sample collection

Near surface soil cores ($n = 52$) were collected from hand augered boreholes to 90 cm below ground surface (bgs). Soil boring samples ($n = 50$) were collected through the vadose zone to approximately 18 m bgs during well installation at the site. Moisture content through the vadose

Table 1

Measured and reported concentrations of PFAS in surface soils, biosolids, and wastewater.

	Soil Concentration (μg/kg) This Study[a, b] $n = 34$	Biosolids Concentration (μg/kg)			Wastewater Concentration (μg/L)
		This Study[c] $n = 2$	EPA 2001 NSSS[d] Average (Min, Max)	Literature Average (Min, Max), Schultz et al. (2006)[e] Higgins et al. (2005)[f]	This Study[c], $n = 2$
Perflourinated sulfonic acids					
PFBS	1.3	(0.20)	3.4 (2.5, 4.8)	—	(0.0041)
PFHxS	(0.42)	(0.23)	5.9 (5.3, 6.6)	ND[g] NM[g]	(0.0019)
PFOS	55	12	403 (308, 618)	100 (81, 160) 170 (22.6, 444)	0.065
PFDS	7.4	<0.05	NM	91 (90, 93) 50 (29.4, 91.0)	<0.0048
Perfluorinated carboxylic acids					
PFPeA	1.4	<0.20	3.5 (1.8, 6.7)	—	0.030
PFHxA	1.8	(0.53)	6.2 (2.5, 11.7)	—	0.040
PFHpA	(0.98)	<0.05	3.4 (1.2, 5.4)	—	(0.0026)
PFOA	11	(0.44)	34 (11.8, 70.3)	<3 10 (<6, 13.3)	0.016
PFNA	5.1	(0.24)	9.2 (3.2, 21.1)	9.9 4.4 (ND, 6.94)	(0.0024)
PFDA	26	1.4	26.1 (6.9, 59.1)	5.9 (5.4, 6.4) 6.3 (4.33, 10.5)	(0.0043)
PFUnDA	3.0	(0.60)	11.7 (2.8, 38.7)	6.8 (5.9, 8.4) 6.42 (ND, 7.87)	<0.0050
PFDoDA	6.2	1.1	10.9 (4.5, 26)	3.8 (3.6, 4.2) 4.78 (ND, 6.51)	<0.0050

[a] Average surface soil (0–30 cm) concentrations listed after scaling for biosolids loading rates.

[b] (denotes estimated magnitude, results below method reporting limit).

[c] Sampled 2015, collected from one contributing municipal WWTP; < denotes below listed detection limit.

[d] 94 WWTPs located in 32 states (Venkatesan and Halden, 2013).

[e] Municipal WWTP, Pacific NW, U.S.

[f] Average of five municipal WWTPs, Western U.S.

[g] Not Measured (NM).

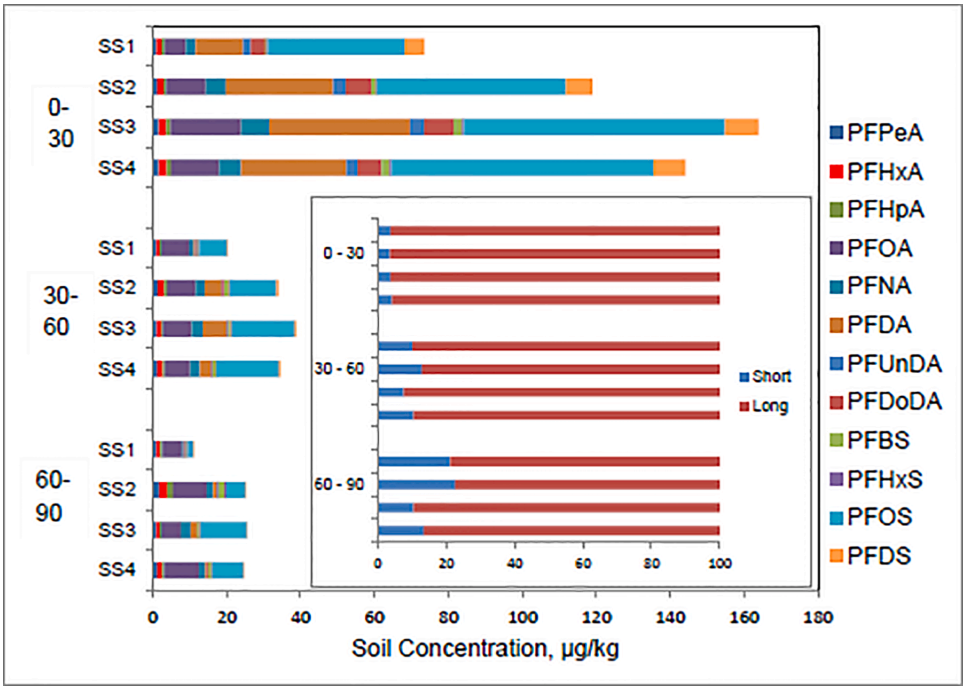

Fig. 2. Measured PFAS soil concentrations and percent contribution of short- versus longchain PFAS (inset) in the near-surface soil profile (0–30, 30–60, 60–90 cm bgs).

zone ranged approximately 2–18%. Groundwater samples ($n = 2$) were collected from the perched aquifer located approximately 17 m bgs. Near surface soil sampling included composite samples collected along a ~4600 m transect at the station. Sampling locations included four substations (SS) with cumulative biosolids loading rates ranging from 341 to 770 MTD/ha and annual loading rates ranging from 50 to 60 MTD/ha/yr (Table 2).

From hand augered boreholes, near surface soil samples ($n = 110$) were collected using pre-cleaned/decontaminated standard 3¼-in hand augers. Three discrete-level composite samples of approximately 80 g of soil each were collected in triplicate from each layer (representing the 0–30 cm, 30–60 cm, and 60–90 cm soil layers). Upon collection, each composite sample was transferred to dedicated, pre-cleaned/decontaminated stainless steel pans and mixed using a pre-cleaned/decontaminated stainless steel spoon. Soils collected from each interval were homogenized using the cone and quarter technique (USEPA 600) and subsampled into pre-labeled, clean 250 mL, discrete widemouth HDPE sampling bottles (ALS Environmental, Kelso, WA). Upon collection, samples were immediately placed on ice in dedicated coolers and shipped overnight for immediate analysis (ALS Environmental, Kelso, WA). Additionally, soil samples ($n = 2$) were similarly collected from an irrigation ditch running across the station (Fig. 1). These farm ditches serve to contain overflow during flood irrigation with treated wastewater effluent and represent station soils historically void of land applied biosolids.

Soil boring samples were collected during well drilling through the vadose zone ($n = 50$) at the site. Sampling included discrete soil collection at depth into pre-labeled, wide-mouth HDPE sampling bottles provided by ALS Environmental, Kelso, WA. Samples were placed on ice and shipped overnight for immediate analysis (ALS Environmental, Kelso, WA). Well construction, including a well screen and sand pack, yielded a monitoring well drilled through the sandy subsurface system. The well screen (approximately 1.5 m length) was installed upon detection of perched groundwater ranging at approximately 17 m bgs. Groundwater samples ($n = 2$) were collected into pre-labeled HDPE bottles provided by ALS Environmental, Kelso, WA. Samples were immediately placed on ice and shipped for immediate analysis (ALS Environmental, Kelso, WA).

One grab sample of municipal sewage sludge (26.5% total solids; collected in duplicate) was collected from the currently contributing municipal wastewater treatment plant and characterized for PFAS concentrations (Table 1). Similarly, one grab sample of treated wastewater was collected (in duplicate) from the respective wastewater treatment plant and characterized for PFAS (Table 1).

2.3. Analytical methods

Soil samples, reagent blanks, trip blanks, and field blanks were analyzed under a NELAP-approved quality assurance program at a NELAC-accredited laboratory in Kelso, WA (ALS Environmental). Analytical quality assurance and quality control methods included internal standards using N-methyl-d3-perfluoro-1-octanesulfonamide, method blanks, lab control samples (spike with recovery), matrix spike-and-recovery experiments, and replicate samples. Surrogate standards including sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate, perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid, perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid, sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate, perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid, perfluoro-n-[1,2-$^{13}C_2$] decanoic acid, perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid, and perfluro-n-[1,2-$^{13}C_2$] dodecanoic acid were added to soil and lab control samples prior to extraction with recovery evaluated for all surrogates (including select internal standard) against acceptance limits/criteria (50–150%) as defined by the lab's standard operating procedures. Batch quality control methods included matrix spike samples conducted in duplicate. Field Ottawa sand blanks ($n = 4$) aimed to qualify accidental or incidental cross-contamination during soil sampling yielded nondetectable concentrations of PFOS and PFOA (respective detection limit 0.20 μg/kg).

Perfluorinated sulfonic acids and perfluorinated carboxylic acids were analyzed in each soil sample by selected ion monitoring HPLC/MS with an average method detection limit equal to 0.1 (± 0.002) μg/kg and method reporting limit equal to 1.0 (±0.005) μg/kg. Analysis for twelve PFAS homologues included perfluorobutane sulfonic acid (PFBS), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA),

Table 2
Soil properties and biosolids loading records at target substations (SS).

	Soil Type[Γ]	Soil pH (0–30 cm) (30–60 cm) (60–90 cm)	Organic Matter%	Total Years of Biosolids Application	Years Since Last Application	Cumulative Biosolids Loading, MTD ha^{-1}	Average Annual Biosolids Loading, MTD ha^{-1}
SS1	Garces loam	7.66 ($n = 2$) 8.91 ($n = 2$) 9.21 ($n = 2$)	3.3 ± 0.21 ($n = 21$)	6	10	341	57
SS2	Garces loam; Calflax loam	7.14 ± 0.31 ($n = 6$) 8.83 ± 0.18 ($n = 5$) 9.13 ± 0.30 ($n = 5$)		10	2	502	50
SS3	Kimberlina fine sandy loam; Calflax loam	6.12 ± 0.29 ($n = 5$) 7.61 ± 0.22 ($n = 5$) 7.88 ± 0.12 ($n = 5$)		12	5	722	60
SS4	Tennco fine sandy loam; Garces loam; Kimberlina fine sandy loam	7.09 ± 0.30 ($n = 5$) 7.87 ± 0.09 ($n = 7$) 8.12 ± 0.18 ($n = 5$)		15	1	770	51

[Γ] USDA WSS 2020.

perfluorohexane sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorodecane sulfonic acid (PFDS), perfluorododecanoic acid (PFDoDA), and perfluoroundecanoic acid (PFUnDA). Soil and lab control samples were serially extracted in triplicate using ultrasonic extraction (EPA 3550B preparation method). Matrix spike-and-recovery experiments performed in duplicate resulted in surrogate recoveries ranging 94–113%. For example, recovery of perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid averaged 104% (86–122%), sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octane sulfonate averaged 113% (94–125%), and perfluoro-n-[1,2-$^{13}C_2$] decanoic acid averaged 111% (96–127%).

2.4. Quality control measures

Sample equipment decontamination and subsequent soil sampling was conducted using standard operation procedures as described by the U.S. EPA Environmental Response Team (USEPA, 2006, 2012). Quality control procedures included field blanks (analyzed to detect accidental or incidental contamination), field rinsate blanks (deionized water passed over sampling equipment to detect residual contamination), and trip blanks (analyzed to detect cross contamination on shipping). All QA/QC water samples analyzed resulted in nondetectable concentrations (ng/L) for PFPeA, PFBS, PFHpA, PFOA, PFNA, PFDA. Concentrations of PFHxA, PFHxS, PFOS, PFUnDA, PFDoDA were either nondetectable or reported below method reporting limits equal to 0.2 (±0.02) ng/L. Quality control procedures for soil sampling included sampling in triplicate plus blind duplicates to detect discrepancies in laboratory reporting procedures.

All sampling equipment including stainless steel hand augers, stainless steel pans, and stainless steel sampling spoons were pre-cleaned and decontaminated prior to the collection of each soil sample. Pre- and on-site decontamination procedures included the physical removal of surface debris using dedicated nylon brushes followed by a complete surface cleaning with an anionic non-phosphate detergent (Liquinox Liquid Detergent; Alconox). Detergent-washed equipment was then double rinsed using laboratory grade deionized (DI) water followed by a methanol rinse (pesticide grade; Fisher Chemical), and a final DI rinse. Finally, air-dried equipment was double wrapped in heavy duty aluminum foil for transport to discrete sampling locations at the agricultural station.

3. Results and discussion

3.1. PFAS in surface soil

All targeted PFAS homologues ($n = 12$) were detected at quantifiable concentrations (100% detection frequency) in every near surface soil sample collected (0–30 cm bgs; $n = 34$) with total PFAS ($\sum_{12}$PFAS) concentrations ranging from 73 to 196 µg/kg, $\sum_8$PFCA 30–98 µg/kg, and $\sum_4$PFSA 43–100 µg/kg. The majority of targeted PFAS (excluding PFHpA and PFHxS) were measured in substation surface soils at concentrations greater than respective method reporting limits (Fig. 2 and Table 1). In contrast, those twelve homologues were nondetectable in soils collected from the irrigation ditch at the station. Note that in this study, a maximum likelihood estimator (MLE) of ½ the respective method detection limit (0.1 ± 0.002 µg/kg) is employed to provide numerical values for nondetectable concentrations such as those measured from soils collected in the irrigation ditch.

The highest concentration of PFAS was measured for PFOS with surface-soil concentrations ranging from 36 to 100 µg/kg. PFOS was also the most abundantly detected PFAS in the previously described short- and long-term field experiments conducted by Sepulvado et al. (2011) and PFOS is commonly reported as the measured PFAS burden in municipal biosolids such as those characterized as part of this study (e.g., see Table 2). The soil burden PFOS>PFDA>PFOA was measured at all substation sampling locations independent of the varying annual average loading rates at the respective substations (Fig. 2). Those same three compounds were indicated as the dominant PFASs analyzed and detected at a field site in Decatur, AL following >10 years of PFAS industrial waste-impacted biosolids application (Washington et al., 2010).

In this study, total perfluoroalkyl carboxylic acids ($\sum_8$PFCAs) and sulfonic acids ($\sum_4$PFSAs) averaged 58 µg/kg and 67 µg/kg, respectively in the surface soils. These total concentrations of PFCAs are >1 order of magnitude higher than those reported as global background soil levels (Rankin et al., 2016) and total PFSAs are >2 orders of magnitude higher. Note that this comparison was made only for those homologues tested across both studies thereby including only PFHxA, PFHpA PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, PFOS, and PFDS. The average surface soil concentrations for PFOA ranged from 3.7 to 32 µg/kg and measured

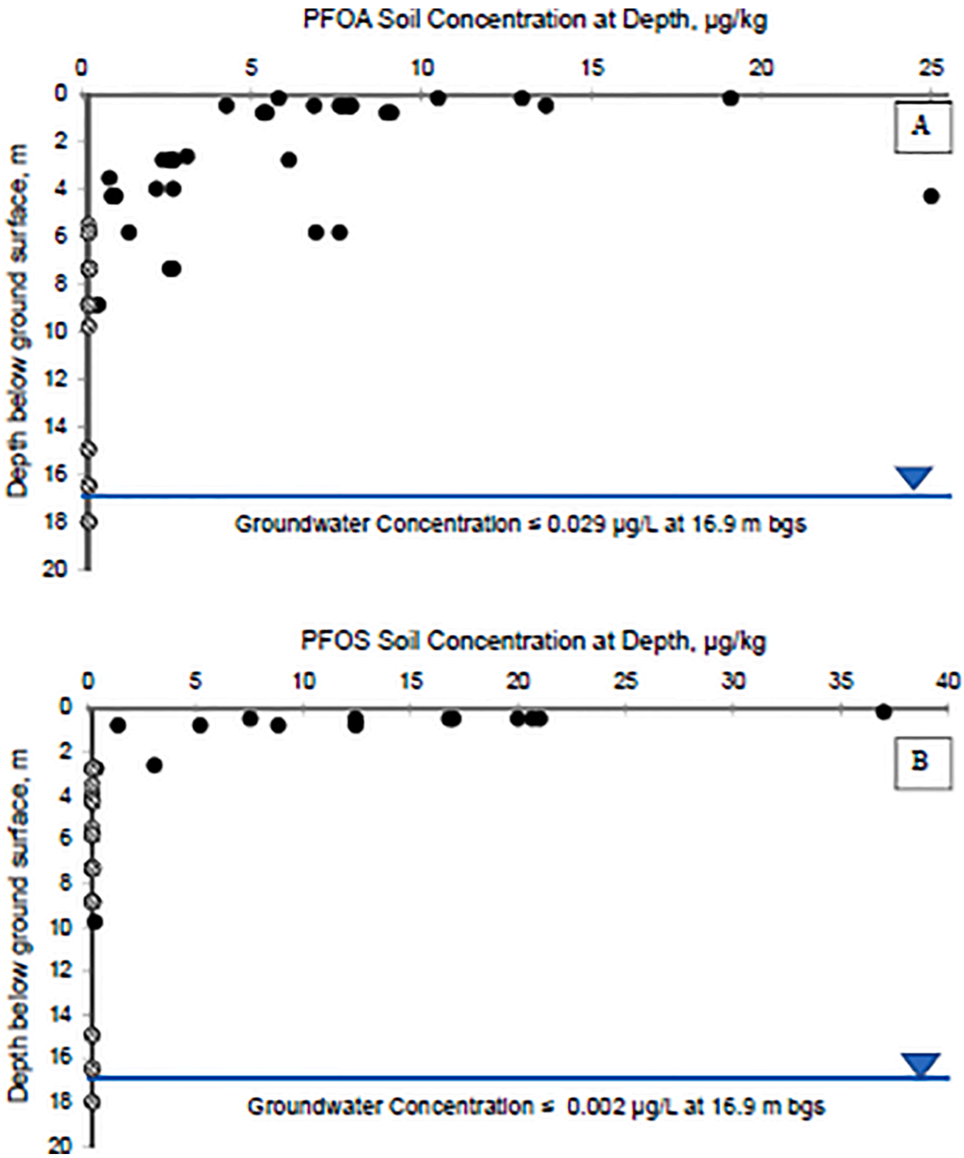

Fig. 3. PFOA and PFOS concentrations measured in surface soils, deep soils, and groundwater. Hatched markers indicate concentrations detected at or below method detection limit equal to 0.21 µg/kg. (A) PFOA; (B) PFOS.

median max concentrations for PFOA and PFOS equaled 16 and 69 µg/kg, respectively. These max soil concentrations are >5x higher than those reported in background soils from soil surveys (Brusseau et al., 2020). Finally, considering nondetectable PFAS homologues ($n = 12$) in soils collected from the station's irrigation ditch, representing soils with no historic application of biosolids, these findings suggest the presence of PFAS in surface soils on the farm (0–30 cm bgs) are associated with the historical land application of biosolids.

3.2. PFAS in soil profile

Results of PFAS concentrations measured in soils representing the 30 – 60 cm bgs profile yielded 96 to 100% detection frequency. Detection frequencies in the 60 – 90 cm soil profile equal 83 – 94% with non-detectable (ND) concentrations of PFDS and PFDoDA found in the 60 – 90 cm profile for several soil samples at all substations. Additionally, four out of 20 soil samples collected at SS3 had ND concentrations of PFBS. These results suggest multiple PFAS have vertically migrated through the soil profile at the station (Figure 2). Overall, the results show preferential leaching of short-chain PFAS compounds through the soil profile as can be seen in Figure 2 (inset) and as has been previously reported in the literature (e.g., Washington et al., 2010; Baduel et al.. 2017).

As discussed by the National Research Council (NRC 2002), long-term land application of biosolids may cause soil pH changes. In this study, soil pH ranged from 5.2 to 7.6 in the 0–30 cm soil layer and increased with depth (see Table 2), ranging from 6.9 to 9.6 in the 60–90 cm profile. The suspected migration of PFAS through the soil profile is possibly related to the measured increasing soil pH through that profile as sorption of PFAS compounds have been shown to decrease with increasing pH (Arvaniti et al., 2014; Du et al., 2014). Specifically, PFAS variable sorption behavior with soil pH, especially in the presence of Ca^{+2} or Mg^{+2} in water (Du et al., 2014), may be associated with electrostatic interactions between PFAS anions and positively charged surfaces of natural geomaterials, such as, metal-oxide surfaces found in soils (Zareitalabad et al., 2013). Additionally, while the overall sorption behavior of PFAS is commonly reported to be dominantly associated with hydrophobic interactions onto organic matter of adsorbents (Higgins and Luthy, 2006; Jeon et al., 2013), the electrostatic surface potential of organic matter is a function of soil pH (Higgins and Luthy 2007; Jeon et al., 2013; Du et al., 2014).

PFAS soil concentrations measured in core samples collected during

Table 3
Regression results and associated statistics for short versus long-chain PFAS in soil as a function of biosolids loading rate (MTD/ha).

	Carbon Chain	Regression Results[a]			
		Slope	+/-	R^2	P-value
Short-chain PFAS compounds[b]					
PFBS	4	0.003	7e-4	0.994	0.003
PFPeA	5	0.002	5e-4	0.989	0.0005
PFHxA	6	0.003	7e-4	0.984	0.0008
Long-chain PFAS compounds					
PFOA	8	0.02	8e-3	0.959	0.004
PFOS	8	0.1	1e-2	0.997	0.00007
PFNA	9	0.01	3e-3	0.978	0.001
PFDA	10	0.05	2e-2	0.963	0.003
PFDS	10	0.01	3e-2	0.985	0.0008
PFDoDA	12	0.01	4e-3	0.959	0.004
Totals					
	∑PFAS	0.2	0.04	0.990	0.0004
	∑PFCA	0.1	0.03	0.973	0.002
	∑PFSA	0.1	0.01	0.997	0.00006

[a] Linear regression: measured soil concentrations vs. historical biosolids loading rate.

[b] Short and long-chain as defined by Buck et al. (2011).

well installation at the station suggest that PFOA and PFOS have migrated through the surface soil profile to deeper soils of the vadose zone (Fig. 3). Quantifiable soil concentrations of PFOA were detected up to approximately 9 m bgs (and up to ~3 m bgs for PFOS) at the station with both PFOA and PFOS detected in deeper soils (up to 18 m bgs). Measured concentrations of PFOA in groundwater located approximately 17 m bgs were reported ≤ 0.029 μg/L (PFOS in groundwater ≤ 0.002 μg/L). Researchers have shown soil concentrations of PFAS compounds are commonly detected at higher concentrations than corresponding soil pore waters with soil serving as a significant long-term reservoir for PFAS in the environment (e.g., Rankin et al., 2016). Brusseau (2018) has qualified multiple mechanisms potentially impacting the overall transport and fate behavior of PFOA and PFOS through natural geomedia including air-water partitioning and air-water interfacial adsorption. These phenomena, commonly associated with PFAS in the vadose zone, contribute to long-term sources of PFAS to groundwater (Weber et al., 2017; Brusseau 2018; 2019).

3.3. PFAS and biosolids loadings

The highest total PFAS soil concentrations (including $\sum_{12}$PFAS, $\sum_{8}$PFCA, and $\sum_{4}$PFSA) were measured in surface soils collected from substations having the largest long-term average biosolids loading rates. As shown in Table 3, linear regression results ($R^2 \geq 0.97$) indicate statistically significant linear correlations (p-value <0.005) between measured $\sum_{12}$PFAS, $\sum_{8}$PFCA, and $\sum_{4}$PFSA and the respective long-term historical (cumulative) biosolids loading rates. Similarly, statistically significant linear correlations between max soil concentrations of all twelve PFAS ($R^2 \geq 0.96$) were also found. Similar linear relationships have been reported linking PFAS soil concentrations to biosolids loadings (Washington et al., 2010; Sepulvado et al., 2011). A comparison of the slopes describing this linear relationship for long-chain (≥C7) versus short-chain compounds shows an order of magnitude increase in the slope for long-chain (average slope 0.02) versus short-chain (average slope 0.003) homologues. These results suggest that long-chain PFAS compounds tend to be more bioaccumulative and environmentally persistent than short as previously reported in the literature (Washington et al., 2010; Buck et al., 2011; Sepulvado et al., 2011).

In this study, PFAS concentrations in the station's historical land-applied biosolids (beginning in the mid-1990s) were not characterized as is commonly the case in these agricultural field studies. Without that historical record, the impact of the temporal and seasonal variation of PFAS expected in applied sewage sludge, albeit significant, cannot be qualified. Analysis of sludges collected in 2001 as part of the USEPA Targeted National Sewage Sludge Survey (NSSS, USEPA, 2009) reports select PFAS concentrations in US sludges (Venkatesan and Halden, 2013). Combining the reported biosolids loadings for substations in this study with those reported average (max and min) concentrations for PFAS tested across both studies ($n = 11$), ∑PFAS mass (kg) in surface soils (0–30 cm bgs) were predicted and compared to those measured. While the NSSS average ∑PFAS concentrations underpredict the total mass of PFAS measured in surface soils in this study by approximately 40%, the max ∑PFAS concentrations effectively predict the measured total mass (Fig. 4). It may be of interest to note that average ∑PFAS concentrations in sludges collected in the Pacific Northwest (Schultz et al. 2005) and sludges collected in the Western US (Higgins et al., 2005) underpredict ∑PFAS total mass measured in this study by >70%. While these results suggest that ∑PFAS concentrations characterized as

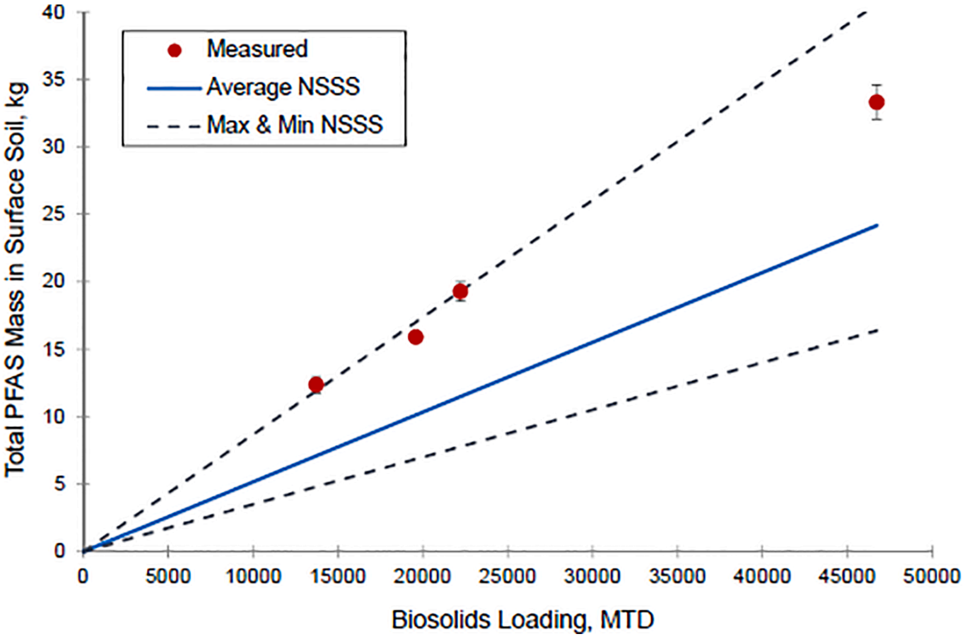

Fig. 4. Prediction of total PFAS mass in surface soils based on USEPA NSSS results combined with historical loading patterns on respective substations.

part of USEPA's NSSS may be a predictive tool to estimate ∑PFAS in surface soils, it is important to consider the significant impact of waste stream sources to PFAS concentrations in wastewater treatment plant sludges.

4. Conclusions

The concentrations of twelve PFAS homologues were measured in surface soils, deeper soils, and in groundwater from agricultural fields following many years of repeated biosolids loadings. Measured soil concentrations were 1 to 2 orders of magnitude higher than PFAS levels in global background soils. With nondetectable levels of all twelve PFAS homologues in soils collected from the station's irrigation ditch, to which no biosolids were historically applied, the contribution of PFAS from treated wastewater appears negligible. PFAS soil levels were significantly correlated with respective biosolids loading rates at sampled substations independent of the time since last application, of the planting and feedcrop harvesting, and of the overall pattern of historical biosolids application. These findings suggest a significant bioaccumulative and recalcitrant transport and fate behavior for PFAS in our environment. The observed distribution of multiple PFAS through the near surface soil profile indicates preferential leaching of short-chain PFAS. Both PFOS and PFOA were measured at quantifiable levels in the deeper soils of the vadose zone, and in the immediately underlying groundwater located 17 m below ground. With measured groundwater concentrations 1 to 2 orders of magnitude less than soil concentrations, the significant role of retention processes in soil systems contributing to PFAS overall transport and fate behavior in the subsurface is evident as well is the impact to overall soil quality. As the first known study to characterize PFAS in surface soils, to deeper soils of the vadose zone, and to immediately underlying groundwater following long-term application of biosolids, it is clear and prudent that additional efforts are needed to characterize the risk of land-applying biosolids with reported emerging pollutants as they impact our soil quality, groundwater, and drinking water supplies.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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