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Incidence of Pfas in soil following long-term application of class B biosolids

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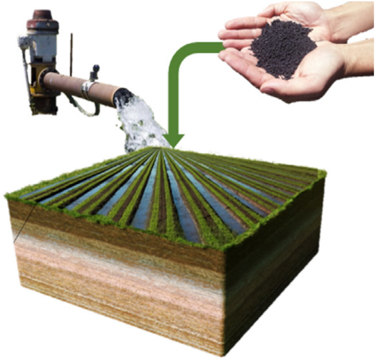
HIGHLIGHTS

- Long-term land application of biosolids resulted in low incidence of soil PFAS analytes.
- PFAS soil concentrations in irrigated agricultural plots with or without land application of biosolids were similar.
- Biosolids and irrigation water were sources of PFAS.
- >70% attenuation of total PFAS occurred within the surface 180 cm of soil.

GRAPHICAL ABSTRACT



PFAS Accumulation and Leaching
in Agricultural Soils

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ABSTRACT

This field study investigated the impact of long-term land application of biosolids on PFAS presence in soils that received annual repetitive land application of Class B biosolids from 1984 to 2019. Soil samples were collected from three depths of 30.5, 91 and 183 cm below land surface. Biosolid and groundwater samples used for irrigation were also collected. Concentrations measured for 18 PFAS compounds were evaluated to assess incidence rates and potential impact on groundwater. No PFAS analytes were detected at the three sampling depths for soil samples collected from undisturbed sites with no history of agriculture, irrigation, or biosolids application (background control sites). Relatively low mean concentrations of PFAS ranging from non-detect to 1.9 μg/kg were measured in soil samples collected from sites that were used for agriculture and that received irrigation with groundwater, but never received biosolids. PFAS concentrations in soils amended with biosolids were similarly low, ranging from non-detect to a mean concentration of 4.1 μg/kg. PFOS was observed at the highest concentrations, followed by PFOA for all locations. PFAS detected in the irrigation water were also present in the soil. These results indicate that biosolids and irrigation water are both important sources of PFAS present in the soils for all of the study sites. Not all PFAS detected in the biosolids were detected in the soil. Very long chain PFAS present in the biosolids were not detected or were detected at very low levels for soil, suggesting potential preferential retention within the biosolids. The precursor NMeFOSAA was present at the second highest concentrations in the biosolids but not detected in soil, indicating possible occurrence of transformation reactions. The total PFAS soil concentrations exhibited significant attenuation with depth, with a mean attenuation of 73% at the 183 cm depth. Monotonically decreasing concentrations with depth were observed for the longer-chain PFAS.

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1. Introduction

Per and polyfluoroalkyl substances (PFAS) are fluorinated compounds that comprise a family of anthropogenic chemicals that have been used for decades to make products resistant to heat, oil stains, grease, and water (e.g., Buck et al., 2011; Kotthoff et al., 2015). PFAS are emerging contaminants of concern due to their persistence, widespread distribution in the environment, and potential for adverse human-health effects (e.g., Ahrens, 2011; Washington et al., 2019; Brusseau et al., 2020). Studies have found associations between PFAS exposure and a range of health outcomes including immunotoxicity in children, dyslipidemia, and possible carcinogenic effects (Sunderland et al., 2019).

Exposure to PFAS can result from a variety of anthropogenic uses and products including aqueous-film forming foams (AFFFs) for firefighting, textiles, carpets, paper products, and food packaging (e.g., Bečanovā et al., 2016; Schaider et al., 2017). Household dust has also been shown to be a significant source of exposure to PFAS (Fraser et al., 2013). Due to their ubiquitous usage, PFAS are also found in wastewater, biosolids, and soil.

Perfluorooctanoate (PFOA) and perfluorosulfonate (PFOS) are two PFAS that have raised particular concern, and as a result have been a focus of mitigation efforts. PFOS was phased out of production in the early 2000s in the U.S., and PFOA by 2015. This has resulted in biosolids concentrations of PFOS and PFOA decreasing over time (CDC, 2019). In addition, blood levels of PFAS in the U.S. have also declined significantly (ATSDR, 2017). However, products containing PFAS can still be imported into the U.S., and legacy effects also warrant attention. More recently, attention has switched to shorter-chain PFAS and precursor PFAS that can break down into more recalcitrant PFAS, including perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs) (Buck et al., 2011). Such shorter-chain and other replacements for PFOA and PFOS include hexafluoropropylene oxide-dimer acid (GenX) and other perfluoroalkyl ether acids (PFEAs) (Brandsma et al., 2019; Munoz et al., 2019).

It has become clear that PFAS are ubiquitous in the environment, in both the U.S. and globally (e.g., Ahrens, 2011; Kraft and Riess, 2015; Washington et al., 2019; Brusseau et al., 2020). In particular, several studies have now documented the global importance of soil as a long-term reservoir of PFAS that can potentially adversely impact surface water, groundwater, and even the atmosphere (Brusseau et al., 2020; Washington et al., 2019; Rankin et al., 2016; Strynar et al., 2012). In most instances, industrial sites and military bases are where the highest levels of contamination have been reported, but even remote areas with no obvious source of PFAS have been documented as having low levels of PFAS (Rankin et al., 2016; Brusseau et al., 2020).

Given the widespread consumer use of products that contain PFAS, it is not surprising that PFAS can be found in wastewater and sewage sludges within wastewater treatment plants, and ultimately in biosolids and effluent that result from wastewater treatment (e.g., Gallen et al., 2018; Chen et al., 2012; Loganathan et al., 2007). Studies also show that treatment plants receiving sewage from PFAS industrial dischargers have higher concentrations of PFAS in their sludge than plants not receiving industrial inputs (Clarke and Smith, 2011; Lindstrom et al., 2011). However, the fact that PFAS have been found in sludge from municipal facilities without industrial inputs puts into perspective the importance of domestic sources of PFAS (Venkatesan and Halden, 2013).

Due to the multiple routes of exposure to PFAS, PFOA and PFOS have been reported in the blood serum and breast milk of almost all humans throughout the world (Poothong et al., 2020; Jian et al., 2018). This in turn has led to increased concern regarding exposure to PFAS via potable water (Boone et al., 2018). In response to this, EPA adopted a drinking water health advisory of 70 ng/L (ppt) for the combined concentrations of PFOS and PFOA in May 2016 (EPA, 2016). Standards set by several U.S. states are more stringent. Massachusetts and Vermont have adopted drinking water standards of 20 ng/L for the sum of the concentrations of six and five individual PFAS compounds, respectively, while California has set drinking water notification levels at 5.1 and 6.5 ng/L for PFOA and PFOS.

The presence of PFAS in biosolids has generated concern over the environmental impacts and potential human-health risks associated with land application of biosolids. One particular concern is transfer of PFAS from biosolids to soil, and subsequent leaching to groundwater. These concerns have led to various restrictions placed on land application across the U.S. For example, a moratorium was imposed on land application of biosolids in Pima County, Arizona on January 1, 2020 (Pima County, 2020) due to concerns over PFAS. This action, enacted by the Pima County Board of Supervisors, doubled management costs for biosolids.

The goal of this study was to evaluate the potential impact of land application of biosolids on PFAS incidence in soil, and the potential for groundwater contamination by PFAS. A field study was implemented in the Arizona agricultural communities of Pima and Pinal County, involving multiple agricultural plots receiving repetitive annual land application of Class B biosolids from 1984 to 2019. Depth-discrete soil samples were collected from the plots. Biosolids samples and samples of groundwater used for irrigation were also collected. PFAS concentrations measured for the samples were evaluated to assess incidence rates and potential impact on groundwater.

2. Materials and methods

2.1. Approach

This study was conducted at long-term biosolids land application sites in Pima and Pinal County, Arizona. Annual land application of Class B biosolids was initiated in 1984, and continued through 2019. Land application in Arizona is allowed on permitted lands registered with the Arizona Department of Environmental Quality, and requires annual documentation of loading rates and biosolids quality. Since biosolids are known to contain PFAS, loading rates allowed for the incidence of accumulated PFAS in soil to be determined following long-term application of known amounts of biosolids. Until 2014, thickened biosolids contained 3 to 7% solids and the material was applied via surface spraying or soil injection to a depth of 30 cm. From 2014 through 2019, cake biosolids with 14% solids were applied and disked into the soil to a depth of 1 f. (30 cm). Sample site selection was carefully considered to reflect biosolids application rates, crop diversity, seasonal crop rotations, groundwater hydrology, and possible sources of PFAS influence. For example, agricultural sites located near a small regional airport were excluded from this study as soil and irrigation water sources could potentially contain PFAS originating from fire training exercises at the airport.

The agricultural sites are comprised of approximately 809 ha spread out over a 277 km area including northern Pima County and Southern Pinal County, AZ. Two primary known sources of PFAS in the Tucson area are represented by the Davis Monthan Air Force Base and Tucson International Airport, which are located approximately 34 km south of agricultural application sites selected for this study. While both of these entities discharge domestic sewage to metropolitan wastewater treatment facilities, it is not believed that prior usage of aqueous film forming foams (AFFF) were discharged to sewers. Because the Santa Cruz River receives effluent from both the Tres Rios and Agua Nueva wastewater treatment facilities, samples sites were distributed throughout the valley in order to minimize the impacts of the Santa Cruz River as a potential source of contamination.

2.2. Soil samples

A total of 72 soil samples were collected at depths of 30.5, 91 and 183 cm below the surface using hand operated soil augers. Soil was collected from five field types with different management histories:

i) undisturbed desert soil (no agriculture); ii) irrigated agricultural soils that have never received biosolids; and iii) irrigated agricultural soils receiving biosolids at three different cumulative loading rate ranges per hectare: ≤44,834 (20 tons); 47,075–67,251 kg (21–30 tons); and >67,251 kg (30 tons) (Table 1). The Tres Rios WRF was the source of biosolids for all application sites. The primary crop for this area is cotton, with occasional double-cropping with barley or wheat. Four soil-boring locations were chosen for each field type. Additional surface soil samples were collected at a site located 0.8 km from agricultural parcels receiving the highest loading of biosolids to assess possible airborne dust deposition of PFAS generated during farming operations on nearby properties.

Each soil sample was collected from a single 8 cm borehole at the designated soil depths. Field blanks and equipment blanks were collected. Strict precautions were taken to avoid extraneous PFAS contamination during sampling. Specifically, protocols from the Michigan Department of Environmental Quality Soil PFAS Sampling Guidance (11/2018) were followed. PFAS-free sampling equipment, field clothing, hygiene, personal protective equipment (PPE), and equipment decontamination procedures were critical to the collection of representative samples. Sampling equipment was constructed primarily of stainless steel and sample containers were high-density polyethylene (HDPE). Samplers did not use equipment containing Teflon materials or low-density polyethylene (LDPE). Clothing consisted of cotton uniforms, well laundered without fabric softener, and polyvinyl chloride waders in lieu of water repellent boots. Samplers did not shower on the morning of sampling events and avoided the use of cosmetics, perfumes, deodorants, and skin crèmes. Sampling equipment was decontaminated in the field between sample depths and at the laboratory after each sample event. PFAS free deionized water and pesticide grade methanol were used to rinse the equipment after each decontamination.

All soil samples were immediately transported to the University of Arizona Water and Energy Sustainable Technology Center (WEST), where they were air-dried prior to sieving (2 mm). The processed samples were then packaged for shipment to the commercial lab for analysis.

2.3. Biosolid samples

The Tres Rios Wastewater Reclamation Facility (WRF) is one of two large municipal sewage treatment facilities located in Tucson, AZ and provides 121,133 $m^3$of sewage treatment daily serving a population of approximately 367,000 people. The sewage is predominantly domestic in composition with very few industrial sources. Class B biosolids samples were taken from the Pima County Tres Rios WRF. Dewatered biosolids samples were collected four times in July of 2020 representative of four different digester contents at the Tres Rios WRF. No additional sampling equipment was necessary for sample collection. All samples were transported to the Pima County CRAO Laboratory and stored at 4 °C prior to shipment to Eurofins for subsequent PFAS.

2.4. Groundwater samples

Groundwater samples were collected from nine irrigation wells associated with the sampled agricultural sites. Water samples were collected from the discharge pipes immediately prior to entering the irrigation canals. HDPE sample bottles were provided by the contract lab. No additional sampling equipment was necessary for sample collection. All samples were transported to the Pima County CRAO Laboratory and stored at 4 °C prior to shipment to Eurofins for subsequent PFAS analysis.

2.5. Analytical methods

Samples of soil, groundwater, and biosolids were analyzed for a suite of PFAS compounds. The analyses were conducted by an international certified analytical laboratory, Eurofins TestAmerica, specializing in PFAS analyses of soil and water. Eurofins TA Sacramento analyzed all project samples using their SOP for *Method 537 (Modified), Method PFAS by LCMSMS Compliant with QSM Table B-15, Revision 5.1 and higher*. This is in line with Department of Defense (DoD) minimum QC requirements. Although some information in the SOP is confidential and proprietary, the following is a summary of the extraction procedure for soils and waters. 250 mL water samples were extracted using a solid phase extraction (SPE) cartridge. PFAS were eluted from the cartridge. For soils and biosolids, 5 g of well homogenized samples were extracted with a KOH/methanol solution using an orbital shaker for 3 h followed by sonication for 12 h. The mixture was centrifuged and the solvent filtered.

The final 80:20 methanol/water extracts were analyzed by LC/MS/MS. PFAS were separated from other components on a C18 column with a solvent gradient program. The mass spectrometer detector was operated in the electrospray (ESI) negative ion mode for the analysis of PFAS.

An isotope dilution technique was employed for the compounds of interest. The isotope dilution analytes (IDA) consisted of carbon-13 labeled analogs, oxygen-18 labeled analytes, or deuterated analogs of the compounds of interest, and were spiked into the samples at the time of extraction with every analyte having its own labeled isotope analogue, otherwise it was calculated with a closely related compound (1 carbon chain difference, etc.) This technique allowed for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. Quantitation by the internal standard method is employed for the IDA analytes/recoveries. IDA recoveries were to meet 25–150% recovery, however for any outside recoveries, it was assured that the data quality was not affected as long as the IDA signal-to-noise ratio was greater than 10:1, which was achieved in all samples reported.

Each sampling batch included a field sample duplicate, field blank, and equipment blanks were first submitted with three initial sampling events to ensure that the sampling procedures were being performed to eliminate cross contamination to the greatest extent possible. During analyses, Eurofins included a Laboratory Control Sample (LCS), and a Matrix Spike/Matrix Spike duplicate per preparatory batch. Matrix Spike and Matrix Spike Duplicates were included with each analytical batch. Although there were a few instances where the Matrix Spike was unacceptably higher than the laboratory specified limits, the associated Laboratory control Sample (LCS) recovery was acceptable and the

Table 1
Project sample plan criteria.

Field type	Agriculture	Irrigated[a]	Cumulative biosolids applied	Duration of application (years)
Undisturbed	No	No	–	–
Agricultural	Yes	Yes	–	–
Group 1	Yes	Yes	≤20 (tons/acre) (44,834 kg/ha)	4–9
Group 2	Yes	Yes	21–30 (tons/acre) (47075–67,251 kg/ha)	12–20
Group 3	Yes	Yes	>30 (tons/acre) (67,251 kg/ha)	6–9

[a] Irrigation with groundwater.

data result, if detected would have been slightly biased high and therefore remained included in the study. On two occasions the Matrix Spike was unacceptably lower than the laboratory specified limits, however the LCS recovery was acceptable and all samples reported for the affected PFA, which was PFTriA, was ND (below the method detection limit) for all samples analyzed in the study. All % RPDs were within the SOP's criteria of <30% RPD between spike duplicates. Data for field blanks, equipment blanks and % recoveries for matrix spikes are presented in Supplemental Information.

3. Results

3.1. PFAS concentrations in biosolids

When land application of biosolids began in Pima County in 1984, PFAS had not been identified as an emerging contaminant. Consequently, Pima County biosolids samples were not analyzed for PFAS during most of the early land application period. PFAS analyte data for biosolids analyzed in this current (2020) study are shown in Table 2. Data show that current concentrations of PFAS in the biosolids are in the low ppb range, with PFOS concentrations ranging from 14 to 36 μg/kg and <1.2 μg/kg for PFOA. This contrasts with data from the 2001 National Sewage Sludge Survey, where mean values of PFOS and PFOA in biosolids were reported to be 403 and 34 μg/kg respectively.

3.2. PFAS concentrations in irrigation water

Concentrations of PFAS in groundwater samples collected from the irrigation sources are presented in Table 3. Overall, 8 out of 18 PFAS compounds were detected in one or more irrigation sources with concentrations exhibiting considerable variation amongst the irrigation sources. The two irrigation sources containing the highest concentrations of PFOS and PFOA also had elevated concentrations of PFHxS and PFHxA. The source of these PFAS is unclear as irrigation sources at this location were also the furthest removed from any potential sources of PFAS such as an airport, fire-fighting activities, or the Santa Cruz River.

The amount of irrigation water applied to individual sites varies widely depending on the selected crops being grown. For example, a typical cotton crop receives approximately 4934 m^3 per ha of water each season whereas a seasonal rotation with cotton and wheat may receive >8364 m^3 per ha annually. While pasture crops such as alfalfa receive up to 7400 m^3 per ha of water annually, these are typically year-round crops and therefor receive less frequent biosolids applications.

3.3. Individual PFAS concentrations in soil

The incidence of PFAS in the five different field types comprising over 809 ha are shown in Tables 4–8. Data on individual soil borings are presented in Supplemental Information. The analysis of soil samples collected from undisturbed plots with no history of agriculture, irrigation, or land application of biosolids showed that no PFAS analytes were detected at any of the three sampling depths. In contrast, soil samples collected from locations with a history of irrigated agriculture but no land application of biosolids showed detectable amounts of eight PFAS, including PFOS and PFOA (Table 4). Tables 5, 6, and 7 provide PFAS data for soil samples from locations with a history of irrigated agriculture with land application of biosolids at different cumulative loading rates. The same PFAS analytes were detected in the soil samples receiving any of the three different biosolid-loading rates.

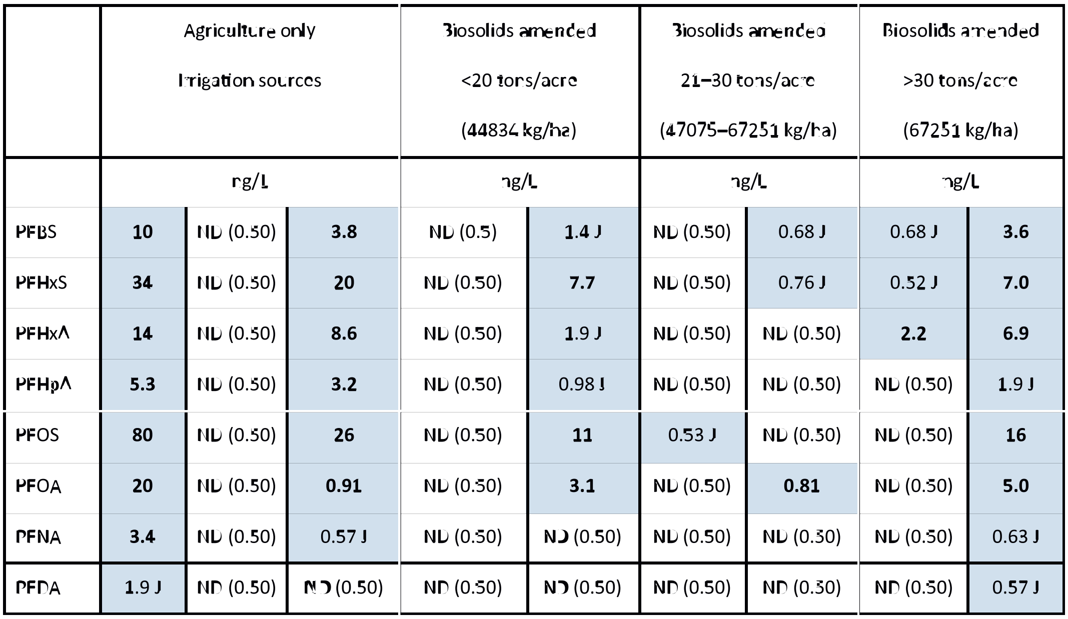
Overall, PFAS soil concentrations are relatively low for the biosolids-amended fields, with mean values ranging from non-detect to 4 μg/kg. PFOS and PFOA were detected at the highest concentrations for all plots. The maximum mean concentrations for PFOS are: 1.6 (±1.7) μg/kg (≤44,813 kg biosolids/ha); 3.1 (±2.0) μg/kg (44,813–110,688 kg biosolids/ha); and 4.1 (±1.9) μg/kg (>110,688 kg/ha). The mean PFOS soil concentrations increase with increasing cumulative loading rate of biosolids. However, the concentrations for PFOS and other PFAS vary across each plot type and, as a result, the standard-deviation ranges of the concentrations overlap for all three loading rates. For comparison, the maximum mean PFOS concentration is 1.9 (±1.2) μg/kg for the soil samples collected from the plots that received irrigation but no biosolids applications. The PFAS concentrations in irrigated agricultural soils

Table 2
PFAS analyte data for dewatered biosolids samples collected on 4 occasions at Tres Rios WRF (Pima County Arizona).

Location	**TRES RIOS WRF**			
Sample date	**7/16/2020**	**7/16/2020**	**7/27/2020**	**7/27/2020**
PFAS	**Units = μg/kg (ppb)**			
PFBS	**1.9**	**1.4**	**6.5**	ND (0.13)
PFHxS	**3.7**	**3.5**	**15**	ND (0.16)
PFHxA	**4.2**	**4**	**4.1**	**2**
PFHpA	ND (1.4)	ND (1.4)	ND (0.15)	0.15 J
NEtFOSAA	ND (19)	ND (19)	ND (1.9)	**11**
NMeFOSAA	**21**	**22**	**23**	**18**
PFOS	**34**	**36**	**27**	**14**
PFOA	ND (4.3)	ND (4.3)	ND (0.44)	**1.2**
PFNA	ND (1.8)	**2**	**2**	**1.1**
PFDA	**12**	**13**	**12**	**12**
PFUnA	**2.3**	**2.1**	**2.4**	**1.8**
PFDoA	**8**	**7.3**	**7.4**	**6.5**
PFTriA	ND (2.5)	ND (2.5)	ND (0.26)	ND (2.5)
PFTeA	**3.2**	**3.3**	ND (1.0)	ND (1.0)

Notes: μg/kg = micrograms of contaminant per kilogram of dry weight of biosolids, equivalent to parts per billion (ppb).
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects on all dates: DONA; F-53B (Major); F-53B (Minor); GenX.

Table 3
PFAS in groundwater used for irrigation.



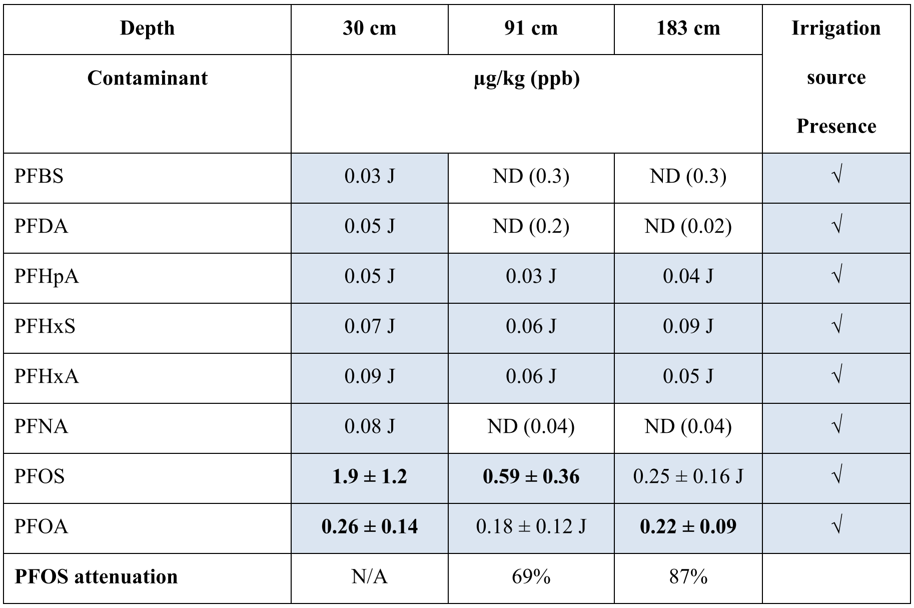
	Agriculture only Irrigation sources			Biosolids amended <20 tons/acre (44834 kg/ha)		Biosolids amended 21–30 tons/acre (47075–67251 kg/ha)		Biosolids amended >30 tons/acre (67251 kg/ha)	
	ng/L			ng/L		ng/L		ng/L	
PFBS	**10**	ND (0.50)	**3.8**	ND (0.5)	**1.4 J**	ND (0.50)	0.68 J	0.68 J	**3.6**
PFHxS	**34**	ND (0.50)	**20**	ND (0.50)	**7.7**	ND (0.50)	0.76 J	0.52 J	**7.0**
PFHxA	**14**	ND (0.50)	**8.6**	ND (0.50)	**1.9 J**	ND (0.50)	ND (0.50)	**2.2**	**6.9**
PFHpA	**5.3**	ND (0.50)	**3.2**	ND (0.50)	0.98 J	ND (0.50)	ND (0.50)	ND (0.50)	**1.9 J**
PFOS	**80**	ND (0.50)	**26**	ND (0.50)	**11**	0.53 J	ND (0.50)	ND (0.50)	**16**
PFOA	**20**	ND (0.50)	**0.91**	ND (0.50)	**3.1**	ND (0.50)	**0.81**	ND (0.50)	**5.0**
PFNA	**3.4**	ND (0.50)	0.57 J	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	0.63 J
PFDA	1.9 J	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	ND (0.50)	0.57 J

Multiple irrigation sources are depicted for each soil group.
ND indicates not-detected.
ng/L = ppt.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects for all irrigation waters: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA, PFUnA.

without any history of biosolids application are in the similar low-ppb range as those measured for the soils with land application of biosolids.

The highest soil concentrations for some of the PFAS are associated with the shallowest sampling interval. Additionally, the concentrations decline monotonically with depth for these PFAS. This is illustrated in Fig. 1, which presents the concentration distribution of PFOS. The concentration distributions for PFBS, PFHxS, PFHpA, and PFOA deviate from this trend. For these four PFAS, the highest measured soil concentrations are associated with the intermediate or deepest sampling intervals. Hence, the concentrations do not decline monotonically with

Table 4
PFAS soil concentrations in agricultural soils without land application of biosolids. Agricultural parcels represent historically farmed locations receiving groundwater irrigation, but without land applied biosolids.



Depth	**30 cm**	**91 cm**	**183 cm**	**Irrigation source Presence**
Contaminant	**µg/kg (ppb)**			
PFBS	0.03 J	ND (0.3)	ND (0.3)	√
PFDA	0.05 J	ND (0.2)	ND (0.02)	√
PFHpA	0.05 J	0.03 J	0.04 J	√
PFHxS	0.07 J	0.06 J	0.09 J	√
PFHxA	0.09 J	0.06 J	0.05 J	√
PFNA	0.08 J	ND (0.04)	ND (0.04)	√
PFOS	**1.9 ± 1.2**	**0.59 ± 0.36**	0.25 ± 0.16 J	√
PFOA	**0.26 ± 0.14**	0.18 ± 0.12 J	**0.22 ± 0.09**	√
PFOS attenuation	N/A	69%	87%	

N/A: not applicable.
ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).

Table 5
PFAS soil concentrations in agricultural soils that received <20 tons of biosolids/acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation, and received biosolid applications of <20 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation source**
PFBS	ND (0.03)	0.08 J	0.04 J	√	√
PFDA	0.10 J	ND (0.03)	ND (0.03)	√	
PFHpA	0.08 J	0.06 J	ND (0.03)	√	√
PFHxS	0.10 J	0.17 J	0.04 J	√	√
PFHxA	0.14 J	0.11 J	ND (0.05)	√	√
PFNA	0.06 J	ND (0.04)	ND (0.04)	√	√
PFOS	**1.6 ± 1.7**	0.29 ± 0.20 J	ND (0.22)	√	√
PFOA	**0.32 ± 0.33**	**0.26 ± 0.25**	ND (0.1)	√	√
PFOS attenuation	**N/A**	**82%**	**93%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA, PFUnA.

Table 6
PFAS soil concentrations in agricultural soils that received 21–30 tons of biosolids per acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation, and received biosolid applications of 21–30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation source**
PFBS	0.17 J	0.10 J	0.12 J	√	√
PFDA	**0.56 ± 0.42**	0.06 J	0.05 J	√	
PFDoA	0.04 J	ND (0.08)	ND (0.08)	√	
PFHpA	0.09 J	0.09 J	0.06 J	√	√
PFHxS	ND (0.04)	0.04 J	0.05 J	√	√
PFHxA	0.13 J	0.09 J	0.09 J	√	
PFNA	**0.43 ± 0.09**	0.12 J	ND (0.04)	√	
PFOS	**3.1 ± 2.0**	**0.64 ± 0.30**	0.22 ± 0.09 J	√	√
PFOA	**0.47 ± 0.28**	**0.49 ± 0.18**	**1.7 ± 2.3**	√	√
PFOS attenuation	**N/A**	**79%**	**93%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFUnA.

Table 7
PFAS soil concentrations in agricultural soils that received >30 tons of biosolids per acre. Data represent the mean of four soil-boring locations at the three depths. These land parcels have been farmed, received irrigation and have received biosolid applications of greater than 30 tons/acre. The table also indicates which PFAS compounds were detected in the irrigation wells and biosolids used for these land parcels.

Depth	**30 cm**	**91 cm**	**183 cm**	**PFAS present**	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation wells**
PFBS	**0.37 ± 0.47**	0.20 J	0.14 J	√	√
PFDA	**0.98 ± 0.41**	0.11 J	0.15 J	√	√
PFDoA	**0.24 ± 0.17**	ND (0.08)	0.08 J	√	
PFHpA	0.19 J	0.16 J	**0.24 ± 0.29**	√	√
PFHxS	0.12 J	0.15 J	0.16 J	√	√
PFHxA	**0.51 ± 0.51**	**0.22 ± 0.21**	0.13 J	√	√
PFNA	**0.43 ± 0.17**	0.15 J	0.05 J	√	√
PFOS	**4.1 ± 1.9**	**1.2 ± 1.4**	0.46 ± 0.46 J	√	√
PFOA	**0.84 ± 0.48**	**1.3 ± 1.4**	**0.51 ± 0.61**	√	√
PFTeA	0.09 J	ND (0.06)	ND (0.06)	√	
PFUnA	0.10 (0.04)	ND (0.04)	ND (0.04)	√	
PFOS attenuation	**N/A**	**71%**	**89%**		

ND indicates not detected at the MDL.
Shaded values indicate values above the method detection limit (MDL).
Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTriA.

depth. This behavior is illustrated in Fig. 2 for PFOA. This non-monotonic distribution generally results from higher concentrations reported for just one or two of the plots rather than all plots. An extreme example of this variability is reflected in the observation that the standard deviation for PFOA concentrations at the deepest interval is larger than the mean value for the Group 2 fields (Table 6).

3.4. Total PFAS concentrations in soil

Total mean concentrations of PFAS in soil samples for the different field types are presented in Table 8. The concentrations for the sites receiving the lowest biosolids application are very similar to those receiving no biosolids. The total concentrations are approximately twice and three-times as large for the field receiving the intermediate and highest biosolids application, respectively. However, as noted previously, the concentrations of individual PFAS range greatly across the plots for each field type, and the concentration ranges overlap between field types.

The mean concentrations of short-chain versus long-chain PFAS are also presented in Table 8. The magnitudes of the concentrations are similar for the no-biosolids and lowest-application fields, and higher for the intermediate and highest biosolids application fields, similar to the total PFAS concentrations. Overall, the short-chain PFAS comprise a small fraction of the total.

The total PFAS concentrations are highest in the shallowest sampling interval for all four field types. In addition, the highest concentrations of the total short-chain and long-chain PFAS are also highest in the shallowest intervals. Monotonic declines in total concentrations with depth are observed for all field types except for Group 2 biosolids-amended fields. For example, the values decrease from 2.5 to 0.9 to 0.6 µg/kg with depth for the sites that received irrigation but no biosolids. The mass-fraction of short-chain PFAS is observed to increase with depth. These results are consistent with prior field-sampling studies examining PFAS concentration distributions in soil cores (e.g., Washington et al., 2010; Sepulvado et al., 2011; Brusseau et al., 2020).

4. Discussion

The goal of this study was to evaluate the potential impact of land application of biosolids on PFAS incidence in soil, and the subsequent potential for impacts to groundwater. Soils were sampled from five types of sites, which varied with respect to history of irrigated agricultural activity, and extent of land application of biosolids. Soils that received land applied biosolids were typical of arid land soils with respect to pH, which were routinely around pH 8, and soil organic matter levels, which were low and routinely less than 1%. The textures of the land applied soils varied widely from sandy loams to loams to clay loams and even a clay. This variability in soil texture was present in each of the five types of sites.

4.1. Biosolids PFAS concentrations

Current biosolids PFAS concentrations from Tres Rios WRF were at a low ppb level, with several of the PFAS not detected (Table 2). PFOS is present at the highest concentrations, up to 36 ppb. This finding is consistent with other reports where PFOS is the dominant PFAS found in biosolids (Gallen et al., 2018; Clarke and Smith, 2011). In addition, the

Table 8
Mean total PFAS concentrations in biosolids, soil, and groundwater.

Biosolids		Undisturbed soil (no agriculture)	
	Concentration (μg/kg)		Concentration (μg/kg)
Total PFAS	87.6	Total PFAS	ND[b]
Total short-chain[a]	6.3	Total short-chain[a]	ND
Fraction SC	0.07	Fraction SC	–
Total long-chain	81.3	Total long-chain	ND
Fraction LC	0.93	Fraction LC	–

Soil: agricultural sites (irrigation, no biosolids)				
Concentration (μg/kg)	30 cm	91 cm	183 cm	Groundwater (μg/L)
Total PFAS	2.5	0.9	0.6	0.081
Total short-chain[a]	0.2	0.1	0.1	0.015
Fraction SC	0.07	0.10	0.14	0.19
Total long-chain	2.3	0.8	0.6	0.066
Fraction LC	0.93	0.90	0.86	0.81
Soil: Group 1 (biosolids amended, <20 tons/acre) (44,834 kg/ha)				
Total PFAS	2.5	1.0	0.08	0.015
Total short-chain[a]	0.3	0.2	0.04	0.003
Fraction SC	0.10	0.26	0.47	0.18
Total long-chain	2.2	0.7	0.04	0.012
Fraction LC	0.90	0.74	0.53	0.82
Soil: Group 2 (biosolids amended, 21–30 tons/acre) (47075–67,251 kg/ha)				
Total PFAS	5.0	1.6	2.2	0.004
Total short-chain[a]	0.4	0.3	0.3	0.001
Fraction SC	0.08	0.17	0.12	0.35
Total long-chain	4.6	1.3	2.0	0.002
Fraction LC	0.92	0.83	0.88	0.65
Soil: Group 3 (biosolids amended, >30 tons/acre) (>67,251 kg/ha)				
Total PFAS	8.6	4.0	1.9	0.024
Total short-chain[a]	1.1	0.6	0.5	0.008
Fraction SC	0.12	0.15	0.26	0.33
Total long-chain	7.6	3.4	1.4	0.016
Fraction LC	0.88	0.85	0.74	0.67

[a] Short-chain is defined by convention as those perfluoroalkyl carboxylic acids and others with <7 perfluorinated carbons and perfluoroalkane sulfonates with <6 perfluorinated carbons (Buck et al., 2011).

[b] ND = non-detect.

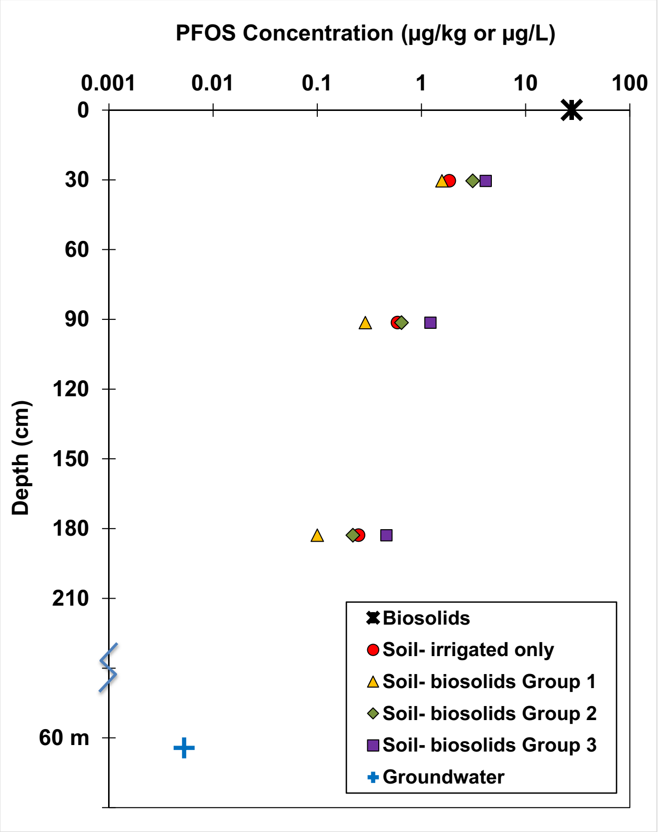


Fig. 1. Mean concentrations of PFOS in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.

concentrations of PFHpA, PFOA, PFNA, PFDA, PFUnA, and PFDoA in the Tres Rios biosolids are very similar to those reported by Gallen et al. (2018). A primary observed difference is the presence of PFHxA and PFHxS at single-digit ppb concentrations in the Tres Rios biosolids versus <1 ppb levels for the Gallen et al. study.

The Pima County biosolids PFAS concentrations are lower than values reported in earlier studies (Venkatesan and Halden, 2013). For example, concentrations of PFOS and PFOA in biosolids samples collected in a 2001 National Sewage Sludge survey averaged 403 and 34 ppb respectively (Venkatesan and Halden, 2013). Lower concentrations of PFAS from more recent studies most likely reflects the fact that PFOS and PFOA were phased out of production in the early 2000s, such that the current source of these compounds are from legacy products. Note also that the levels of PFAS in the Pima County biosolids are much lower than those reported for biosolids receiving industrial inputs of PFAS (Sepulvado et al., 2011).

4.2. PFAS concentrations in soils

Field and equipment blanks were all negative for PFAS analytes except PFHxS blanks taken during sampling of undisturbed soil samples. However, the actual undisturbed soil samples were found to be negative for PFHxS.

No PFAS analytes were detected at any of the three sampling depths for the soil samples collected from undisturbed sites with no history of agriculture, irrigation, or biosolids application. This is in contrast to prior studies wherein PFAS have been detected in soils at the great majority of locations tested, including agricultural fields (Brusseau et al., 2020; Rankin et al., 2016). The Method Detection Limits (MDL) for PFOS and PFOA were 0.2 and 0.085 μg/kg respectively. This provides some indication that ambient levels of PFAS in soils in the study area are very low. An additional surface soil sample was collected approximately 0.8 km from agricultural soils receiving the highest loads of biosolids, and analyzed for PFAS. However, no PFAS analytes were detected (data not shown), illustrating that airborne dust deposition of PFAS generated during farming operations had not occurred at measurable levels. The observation of non-detectable PFAS concentrations in the undisturbed soils is likely due at least in part to the absence of industrial sources of PFAS in the region.

Analysis of soils from locations with a history of irrigated agriculture but no land application of biosolids revealed low-ppb levels of PFOS and PFOA, and multiple detectable amounts of other PFAS analytes (Table 4). The likely source of the PFAS is the groundwater used for irrigation that has been applied over the years. First, no biosolids have ever been applied to these sites. Second, PFAS are present at moderately high concentrations in the groundwater used at the sites for irrigation (Table 3). Third, the PFAS present in the soils are the same compounds detected in the irrigation water (Tables 3 and 4). The possible source of PFAS in groundwater is unclear.

The concentrations of PFAS in the irrigation water were significantly lower than the soil concentrations measured for the shallowest (30-cm) sampling interval. The soil:groundwater concentration ratios range from approximately 4 to 58, with a geometric mean of 20. These ratios are considerably larger than the magnitudes of sorption equilibrium coefficients expected for these PFAS. For example, the ratio for PFOS is roughly an order of magnitude larger than the sorption coefficients measured for PFOS sorption by soils similar to those present at the field sites (Brusseau et al., 2019). The large soil:groundwater

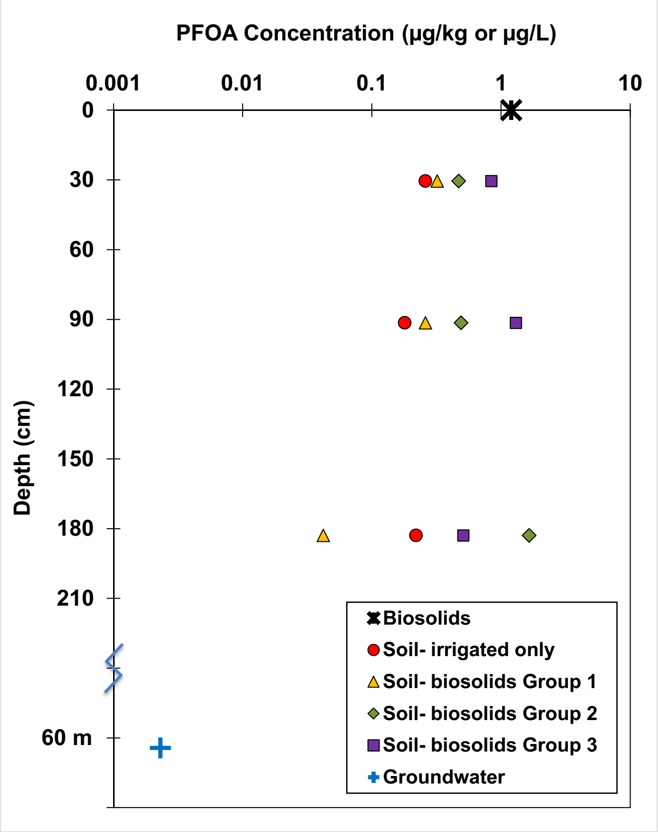


Fig. 2. Mean concentrations of PFOA in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.

concentration ratios are likely the result of the long-term application of irrigation water to the fields.

PFAS concentrations in soils sampled from locations with a history of irrigated agriculture plus land application of biosolids were also in the low-ppb range (Tables 5, 6, and 7). The mean soil concentrations of PFOS, PFOA, and some other PFAS were larger for the soils receiving higher biosolids application rates, but the values are within the range of variability exhibited for all field types. For the highest maximum cumulative biosolids loading rate, the mean concentrations of the two highest analytes detected were 4.1 and 0.84 μg/kg for PFOS and PFOA, respectively.

Thirteen out of the 18 PFAS analyzed were detected in the biosolids samples. Eight of these 13 were detected in all three of the biosolids-amended soil groups. In addition, low levels of PFDoA were present for Group 2 soils and low levels of PFDoA, PFUnA, and PFTeA were present for Group 3 soils. Notably, these longer-chain PFAS were not detected for the Group 1 soils, those with the lowest rate of biosolids amendment. In addition, PFNA and PFDA were detected at very low levels for only the shallowest sampling interval for these soils. These results suggest that the longer-chain PFAS may be retained within the biosolids to a greater degree than the shorter-chain PFAS.

Interestingly, the precursors NEtFOSAA and NMeFOSAA were present in the biosolids but were not detected in any of the soils. In fact, the concentrations of NMeFOSAA (~20 μg/kg) are the second highest of all PFAS in the biosolids, and are just slightly lower than those of PFOS (~27 μg/kg). The absence of detectable levels of NEtFOSAA and NMeFOSAA in the soils indicates that transformation processes likely occurred after application of the biosolids to the soil. Transformation of these precursors would contribute to the total mass of PFOS present in the soils. Given the relatively high concentrations of NMeFOSAA in the biosolids, precursor transformation may be one reason why the mean PFOS soil concentrations are larger in the higher-rate biosolids-amended fields than the non-amended fields.

One way in which to evaluate the relative significance of the measured concentrations in soil is to compare them to concentrations measured for other secondary-source sites reported in a recent meta-analysis of PFAS in soil (Brusseau et al., 2020). Secondary-source sites are those that represent for example locations at which biosolids and other amendments were applied to the ground surface, and/or sites at which surface water, groundwater, or treated wastewater was used for irrigation. The medians of the maximum PFOS and PFOA soil concentrations reported for these sites are 680 and 38 μg/kg, respectively. These levels are approximately two orders-of-magnitude higher than the concentrations measured in the present study. The soil concentrations observed in the present study can also be compared to values reported for prior specific studies of biosolids-amended field sites. Washington et al. (2010) and Sepulvado et al. (2011) both reported PFOS concentrations ranging up to >400 μg/kg in surface soil samples collected from fields that received biosolids applications. These concentrations are approximately two orders-of-magnitude greater than the PFOS soil concentrations reported in the present study.

Another way to evaluate the relative significance of the measured soil concentrations is to compare them to soil screening levels. For example, the US EPA provides risk-based soil screening levels (SSLs) for Superfund sites. It is important to note that these SSLs are not cleanup standards, and that they were developed specifically for use at Superfund sites. Specific SSLs are provided for PFBS in the EPA Regional Screening Levels tables (EPA, 2020). The resident soil value for noncancer direct child exposure is 1300 mg/kg, whereas the industrial soil value for noncancer direct exposure is 13,000 mg/kg. Values for other PFAS are not listed in the EPA tables. The Interstate Technology & Regulatory Council reported resident-soil SSLs generated using the EPA risk calculator for PFOS (1260 μg/kg) and PFOA (1260 μg/kg) (ITRC, 2020). The maximum PFOS, PFOA, and PFBS soil concentrations measured for the present study are orders of magnitude below these SSLs. These SSLs are for exposure via direct contact (ingestion, inhalation, dermal contact) with soil. Another set of SSLs are determined for protection of drinking-water sources (e.g., groundwater). These represent screening levels for soil that would be protective of groundwater that is used for drinking water (i.e., the exposure route is via ingestion of water). The EPA tables list a value of 130 μg/kg for PFBS, which is much higher than values observed in the present study. Again, no values are listed for PFOS or PFOA; however, the ITRC lists values of 0.378 and 0.172 μg/kg for PFOS and PFOA, respectively, based on application of the EPA risk calculator. These values are lower than the highest concentrations reported for the study. It is unclear if the assumptions and simplifications made in application of the risk calculator are applicable for the conditions present at the study site. For example, the groundwater-protection SSLs are determined based on the assumption of aqueous-phase leaching of contaminants from the ground surface to groundwater. Given the arid climate and the use of managed irrigation, the magnitude of leaching is likely to be small. A robust determination of leaching rates would require a full-scale mathematical modeling analysis, which is beyond the scope of this study.

It is important to note that PFAS concentrations in the soils that received biosolids were similar to the levels found in agricultural soils that received irrigation water but no biosolids. It should also be noted that the groundwater irrigation source containing the highest PFAS concentrations had no previous history of biosolids application. Comparison of the data sets is complicated by the variability in PFAS concentrations in the irrigation water observed across the sites. However, the similarity of soil concentrations for the sites with and without biosolids application indicates that both irrigation water and biosolids are important sources of the PFAS present in the soils. However, the relative inputs of PFAS from these two sources are unclear. A full-scale examination of the relative impact of irrigation water versus biosolids on PFAS concentrations in the soil profile would require detailed consideration of irrigation rates, annual crop conditions, biosolids loading rates, biosolids and irrigation-water PFAS concentrations, and other factors.

The total PFAS concentrations are highest in the shallowest sampling interval for all four field types. Individual PFAS concentrations in soil generally decreased monotonically with depth. Exceptions were observed for some plots for PFBS, PFHxS, PFHpA, and PFOA. In addition, with one exception (Group 2 fields), the total mean PFAS concentrations decreased monotonically with depth. The mean magnitude of attenuation was 73% at the 183 cm soil depth. This significant amount of apparent attenuation occurred despite the use of the flooded-furrow method of irrigation, which may maximize the potential for irrigation-induced leaching. The fraction of total PFAS comprised of short-chain compounds increased with depth. This may indicate preferential leaching of the short-chain versus the long-chain PFAS. This is consistent with the expected differential retention of PFAS as a function of chain length, or molecular size. The potential presence of PFAS at depths below the sampling domain was not investigated. Determining the potential for migration of PFAS beyond the sampling interval would require mathematical modeling analysis, which as noted previously is beyond the scope of this study.

It is possible that a fraction of PFAS present in the soil may have been removed via phytoaccumulation. Uptake of PFAS into crops was demonstrated for example by Blaine et al. (2013). Specifically shorter chain PFAS were preferentially taken up over longer chain PFAS. However, much remains to be learned about the effects of multiple variables on plant uptake including soil properties, crop type, and biosolids PFAS concentration and application rate.

5. Conclusion

The presence of PFAS in biosolids has generated concern over the environmental impacts and potential human-health risks associated with land application of biosolids. One particular concern is transfer of PFAS from biosolids to soil, and subsequent leaching to groundwater. A field study was implemented in Pima and Pinal County, AZ, involving multiple agricultural plots comprising 809 ha distributed over a 445 km^2 area that have received land application of Class B biosolids from 1984 to 2019. Depth-discrete soil samples were collected from the plots. Biosolids samples and samples of groundwater used for irrigation were also collected. PFAS concentrations measured for the samples were evaluated to assess incidence rates and potential risks to groundwater.

Even after decades of land application, the concentration and accumulation of PFAS in soils receiving the biosolids was comparatively low. In addition, it was observed that ~73% attenuation of PFAS occurred within 183 cm of the soil surface. These results suggest that the potential for groundwater contamination is relatively small, particularly considering the significant depth to groundwater (~61 m below ground surface), the low rates of precipitation, and the high rates of evapotranspiration in the region. The potential for leaching of PFAS is enhanced with irrigated agriculture in arid regions, where 3700–6167 m^3 of irrigation water are routinely applied during a crop growing season. Despite this, minimal apparent migration of the analytes was observed. Such magnitudes of attenuation and the associated retention processes have been discussed in other studies (Washington et al., 2010; Sepulvado et al., 2011; Brusseau, 2018, 2019, 2020; Guo et al., 2020).

Overall, the results of this study suggest that contamination of groundwater at the study sites by leaching of biosolids-associated PFAS is unlikely due to a number of factors. One is the relatively low levels of PFAS present in the Pima County biosolids, likely reflecting the absence of significant industrial inputs to the wastewater system. Another important factor is the climatic and associated conditions, including the great depth to groundwater and the high evapotranspiration rates. The significance of this study is shown by the fact that following publication of the data in a report (Pima County, 2020), the moratorium on land application of biosolids in Pima County was rescinded in November of 2020 with a resumption in land application of biosolids in February of 2021.

CRediT authorship contribution statement

Ian L. Pepper: Writing – review & editing. **Mark L. Brusseau:** Writing – review & editing. **Frank J. Prevatt:** Writing – review & editing, Supervision. **Barbara A. Escobar:** Writing – review & editing, Resources.

Declaration of competing interest

None of the authors have competing or conflict of interests in the subject material of this study, or the manuscript. Two of the authors are employees of Pima County Wastewater Reclamation Department.

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Supplementary data

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SUPPLEMENTAL INFORMATION

INCIDENCE OF PFAS IN SOIL FOLLOWING LONG-TERM APPLICATION OF CLASS B BIOSOLIDS

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Table S1. Matrix Spike Average Percent Recoveries & RPD for MS/MSD for Soils

Analyte	**Matrix Spike Avg % Recovery**	**Matrix Spike Dup Avg % Recovery**	**%RPD**
DONA	112	110	2
F-53B Major	114	113	1
F-53B Minor	110	112	2
HFPO-DA (GenX)	108	108	0
N-ethylperfluorooctanesulfonamidoacetic acid (NEtF	111	110	1
N-methylperfluorooctanesulfonamidoacetic acid (NMe	108	106	2
Perfluorobutanesulfonic acid (PFBS)	110	110	0
Perfluorodecanoic acid (PFDA)	107	107	0
Perfluorododecanoic acid (PFDoA)	101	104	3
Perfluoroheptanoic acid (PFHpA)	105	106	1
Perfluorohexanesulfonic acid (PFHxS)	97	95	2
Perfluorohexanoic acid (PFHxA)	106	103	3
Perfluorononanoic acid (PFNA)	106	105	1
Perfluorooctanesulfonic acid (PFOS)	118	116	2
Perfluorooctanoic acid (PFOA)	100	101	1
Perfluorotetradecanoic acid (PFTeA)	104	104	0
Perfluorotridecanoic acid (PFTriA)	93	94	1
Perfluoroundecanoic acid (PFUnA)	110	114	4

Table S2. PFAs and surrogate (IDA) standards used in this study for Soil Samples

Analyte	**Isotope Dilution Analyte (Surrogate)**	**Avg % Recoveries**
DONA	$^{13}C_4$ PFOS	74.2
F-53B Major	$^{13}C_4$ PFOS	74.2
F-53B Minor	^{13}C4 PFOS	74.2
HFPO-DA (GenX)	^{13}C3 HFPO-DA	78.9
N-ethylperfluorooctanesulfonamidoacetic acid (NEtF	d_5-NEtFOSAA	59.0
N-methylperfluorooctanesulfonamidoacetic acid (NMe	d_3-NMeFOSAA	53.9
Perfluorobutanesulfonic acid (PFBS)	$^{13}C_3$ PFBS	74.8
Perfluorodecanoic acid (PFDA)	$^{13}C_2$ PFDA	80.0
Perfluorododecanoic acid (PFDoA)	$^{13}C_2$ PFDoA	79.0
Perfluoroheptanoic acid (PFHpA)	$^{13}C_4$ PFHpA	83.3
Perfluorohexanesulfonic acid (PFHxS)	$^{18}O_2$ PFHxS	78.7
Perfluorohexanoic acid (PFHxA)	$^{13}C_2$ PFHxA	78.3
Perfluorononanoic acid (PFNA)	$^{13}C_5$ PFNA	82.6
Perfluorooctanesulfonic acid (PFOS)	$^{13}C_4$ PFOS	74.2
Perfluorooctanoic acid (PFOA)	$^{13}C_4$ PFOA	80.1
Perfluorotetradecanoic acid (PFTeA)	$^{13}C_2$ PFTeDA	76.8
Perfluorotridecanoic acid (PFTriA)	$^{13}C_2$ PFDoA	79.0
Perfluoroundecanoic acid (PFUnA)	$^{13}C_2$ PFUnA	79.3

Table S3. Field blank and equipment blank results.

Soil Descriptions	Sample Date	Units	PFBS	GenX	DONA	PFHxS	PFHxA	PFHpA	F-53B (Minor)	NEtFOSAA	NMeFOSAA	PFOS	PFOA	PFNA	F-53B (Major)	PFDA	PFUnA	PFDoA	PFTriA	PFTeA
Location A-2 (Field Blank)	6/9/20 7:40	ng/L	ND (0.21)	ND (1.6)	ND (0.19)	0.32 J	ND (0.62)	ND (0.27)	ND (0.34)	ND (2.0)	ND (3.3)	ND (0.57)	ND (0.90)	ND (0.29)	ND (0.25)	ND (0.33)	ND (1.2)	ND (0.58)	ND (1.4)	ND (0.31)
Location A-2 (Equipment Blank)	6/9/20 6:35	ng/L	ND (0.29)	ND (2.2)	ND (0.26)	0.53 J	ND (0.83)	ND (0.36)	ND (0.46)	ND (2.7)	ND (4.5)	**5.7**	ND (1.2)	ND (0.39)	ND (0.35)	ND (0.45)	ND (1.6)	ND (0.79)	ND (1.9)	ND (0.42)
Location B-1.1 (Equipment Blank)	6/16/2020 6:40	ng/L	**5.3**	ND (1.6)	ND (0.19)	0.34 J	ND (0.60)	ND (0.26)	ND (0.33)	ND (2.0)	ND (3.2)	1.3 J	ND (0.89)	ND (0.28)	ND (0.25)	ND (0.32)	ND (1.1)	ND (0.57)	ND (1.4)	0.67 J
Location B-2 (Field Blank)	6/17/2020 6:48	ng/L	ND (0.23)	ND (1.7)	ND (0.20)	0.37 J	ND (0.65)	ND (0.28)	ND (0.36)	ND (2.1)	ND (3.5)	ND (0.61)	ND (0.96)	0.30 J	ND (0.27)	ND (0.35)	ND (1.2)	ND (0.62)	ND (1.5)	ND (0.33)
Location B-3 (Equipment Blank)	6/18/2020 6:30	ng/L	ND (0.23)	ND (1.7)	ND (0.21)	0.40 J	ND (0.67)	ND (0.29)	ND (0.37)	ND (2.2)	ND (3.6)	0.96 J	ND (0.98)	ND (0.31)	ND (0.28)	ND (0.36)	ND (1.3)	ND (0.63)	ND (1.5)	ND (0.33)
Location C-3 (Field Blank)	7/9/2020 6:56	ng/L	ND (0.19)	ND (1.4)	ND (0.17)	0.33 J	ND (0.56)	ND (0.24)	ND (0.31)	ND (1.8)	ND (3.0)	ND (0.52)	ND (0.82)	ND (0.26)	ND (0.23)	ND (0.30)	ND (1.1)	ND (0.53)	ND (1.3)	ND (0.28)
Location E-2 (Field Blank)	8/4/2020 7:23	ng/L	ND (0.18)	ND (1.4)	ND (0.16)	0.26 J	ND (0.53)	ND (0.23)	ND (0.29)	ND (1.7)	ND (2.8)	ND (0.49)	ND (0.77)	ND (0.25)	ND (0.22)	ND (0.28)	ND (1.0)	ND (0.50)	ND (1.2)	ND (0.26)
Location D-2.2 (Field Blank)	7/15/2020 6:58	ng/L	ND (0.19)	ND (1.4)	ND (0.17)	0.27 J	ND (0.55)	ND (0.24)	ND (0.30)	ND (1.8)	ND (2.9)	ND (0.51)	ND (0.80)	ND (0.25)	ND (0.23)	ND (0.29)	ND (1.0)	ND (0.52)	ND (1.2)	ND (0.27)
Location F-2 (Field Blank)	7/28/2020 6:33	ng/L	ND (0.18)	ND (1.4)	ND (0.16)	0.27 J	ND (0.53)	ND (0.23)	ND (0.29)	ND (1.7)	ND (2.8)	ND (0.49)	ND (0.77)	ND (0.25)	ND (0.22)	ND (0.28)	ND (1.0)	ND (0.50)	ND (1.2)	ND (0.26)

Table S4. Matrix spike recoveries and matrix spike duplicates

QC Type	Analysis Date	Units	PFBS	GenX	DONA	PFHxS	PFHxA	PFHpA	F-53B (Minor)	NEtFOSAA	NMeFOSAA	PFOS	PFOA	PFNA	F-53B (Major)	PFDA	PFUnA	PFDoA	PFTriA	PFTeA
Matrix Spike (6244419S)	7/12/2020	% Rec	111	106	103	91	108	98	109	123	123	106	99	101	113	110	113	94	102	107
Matrix Spike Dup (6244419D)	7/12/2020	% Rec	106	107	106	91	108	100	107	117	119	107	102	100	108	106	108	89	90	105
Matrix Spike (6244432S)	7/17/2020	% Rec	114	105	94	88	105	99	99	125	118	112	102	98	106	108	109	102	90	98
Matrix Spike Dup (6244432D)	7/17/2020	% Rec	104	105	95	90	107	97	103	112	116	107	99	100	102	105	102	97	91	105
Matrix Spike (627037S)	7/22/2020	% Rec	113	104	114	96	109	104	113	101	101	107	104	104	102	105	99	109	105	106
Matrix Spike Dup (627037D)	7/22/2020	% Rec	106	101	113	99	99	106	109	107	100	104	104	106	107	105	104	110	104	111
Matrix Spike (628951S)	7/25/2020	% Rec	113	108	116	98	108	113	109	110	105	100	100	109	103	104	114	99	93	104
Matrix Spike Dup (628951D)	7/25/2020	% Rec	120	109	121	95	105	114	123	113	110	114	99	115	115	107	119	111	112	106
Matrix Spike (628851S)	7/29/2020	% Rec	106	117	98	103	103	103	87	130	110	142 (M1)	102	113	105	101	121 (M1)	104	40 (M2)	95
Matrix Spike Dup (628851D)	7/29/2020	% Rec	115	112	96	91	102	110	80	122	98	123	104	107	100	98	128 (M1)	114	43 (M2)	99
Matrix Spike (631391S)	8/1/2020	% Rec	114	114	123	100	113	107	114	101	98	102	96	113	115	116	100	106	122	114
Matrix Spike Dup (631391D)	8/1/2020	% Rec	115	113	113	95	109	100	119	109	97	107	106	109	108	116	111	114	136	113
Matrix Spike (633401S)	8/6/2020	% Rec	110	99	125	96	111	106	122	97	101	100	98	108	111	92	94	92	105	109
Matrix Spike Dup (633401D)	8/6/2020	% Rec	115	110	131	96	101	113	129	106	99	103	97	102	110	106	110	104	101	93
Matrix Spike (633411S)	8/11/2020	% Rec	118	117	121	103	101	109	122	114	109	183	99	107	161	112	131	100	57	112
Matrix Spike Dup (633411D)	8/11/2020	% Rec	118	114	121	100	100	109	128	119	113	183	99	102	164	122	138	98	61	104
Matrix Spike (635671S)	8/17/2020	% Rec	106	108	127	99	110	109	122	113	113	120	103	113	117	115	115	111	116	108
Matrix Spike Dup (635671D)	8/17/2020	% Rec	107	111	111	103	105	111	113	107	107	109	106	114	110	108	115	101	98	114
Matrix Spike (6417513S)	9/5/2020	% Rec	98	97	95	91	99	104	102	96	99	103	92	91	105	107	106	94	99	91
Matrix Spike Dup (6417513D)	9/5/2020	% Rec	98	99	95	93	94	102	104	92	98	104	94	95	103	100	104	98	108	93

Table S5. PFAS soil concentrations in both undisturbed soils and agricultural soils without land application of biosolids. Agricultural parcels represent historically farmed locations that received groundwater irrigation but did not receive biosolids via land application. Sample duplicates were obtained from a second bore hole location within a meter of the initial location identification bore hole.

Sample Site	**Depth**	**Units**	**PFBS**	**GenX**	**DONA**	**PFHxS**	**PFHxA**	**PFHpA**	**F-53B (Minor)**	**NEtFOSAA**	**NMeFOSAA**	**PFOS**	**PFOA**	**PFNA**	**F-53B (Major)**	**PFDA**	**PFUnA**	**PFDoA**	**PFTriA**	**PFTeA**
Undesturbed Soils																				
Location A-1	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-1 (duplicate)	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-1	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A -1 (duplicate)	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-1	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A -1 (duplicate)	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-2	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-2	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-2	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-3	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-3	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location A-3	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.41)	ND (0.41)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Agricultural Soils																				
Location B-1	30 cm	ug/Kg dry	0.037 J	ND (0.12)	ND (0.02)	0.086 J	0.12 J	0.056 J	ND (0.02)	ND (0.41)	ND (0.43)	**2.4**	**0.31**	0.065 J	ND (0.03)	0.026 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-1 (duplicate)	30 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	0.094 J	0.18 J	0.085 J	ND (0.02)	ND (0.37)	ND (0.39)	**2.8**	**0.37**	0.11 J	ND (0.03)	0.047 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-1	91 cm	ug/Kg dry	ND (0.03)	ND (0.13)	ND (0.02)	0.064 J	0.051 J	ND (0.03)	ND (0.03)	ND (0.43)	ND (0.45)	**0.72**	0.15 J	ND (0.04)	ND (0.03)	ND (0.015)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location B-1 (duplicate)	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	0.075 J	0.067 J	0.031 J	ND (0.02)	ND (0.39)	ND (0.41)	**1.0**	0.16 J	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-1	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	0.098 J	0.076 J	0.041 J	ND (0.02)	ND (0.41)	ND (0.43)	0.29 J	**0.23**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-1 (duplicate)	183 cm	ug/Kg dry	ND (0.03)	ND (0.13)	ND (0.02)	0.12 J	0.088 J	0.042 J	ND (0.03)	ND (0.42)	ND (0.44)	**0.50**	**0.23**	ND (0.04)	ND (0.03)	ND (0.03)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location B-2	30 cm	ug/Kg dry	0.054 J	ND (0.12)	ND (0.02)	ND (0.04)	ND (0.05)	ND (0.03)	ND (0.03)	ND (0.42)	ND (0.44)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.03)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location B-2	91 cm	ug/Kg dry	0.044 J	ND (0.13)	ND (0.02)	ND (0.04)	ND (0.05)	ND (0.03)	ND (0.03)	ND (0.43)	ND (0.45)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.03)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location B-2	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.04)	ND (0.05)	ND (0.03)	ND (0.03)	ND (0.41)	ND (0.44)	ND (0.20)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.03)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location B-3	30 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	0.071 J	0.049 J	0.038 J	ND (0.02)	ND (0.37)	ND (0.39)	**2.1**	**0.30**	0.13 J	ND (0.03)	0.12 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-3	91 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	0.099 J	0.11 J	0.06 J	ND (0.02)	ND (0.39)	ND (0.41)	**0.53**	**0.34**	ND (0.04)	ND (0.03)	0.02 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location B-3	183 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	0.14 J	0.099 J	0.054 J	ND (0.02)	ND (0.37)	ND (0.39)	ND (0.20)	**0.35**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Irirgation source presence			√			√	√	√				√	√	√		√				

Shaded values indicates values above the MDL and **bold** values are above the MRL.

Table S6. PFAS soil concentrations for agricultural parcels amended with <20 tons/acre (44834 kg/ha) of biosolids. Sample duplicates were obtained from a second bore hole location within a meter of the initial location identification bore hole.

Sample Site	Depth	Units	PFBS	GenX	DONA	PFHxS	PFHxA	PFHpA	F-53B (Minor)	NEtFOSAA	NMeFOSAA	PFOS	PFOA	PFNA	F-53B (Major)	PFDA	PFUnA	PFDoA	PFTriA	PFTeA
<20 tons/acre Biosolids Amended Soils																				
Location C-2	30 cm	ug/Kg dry	0.047 J	ND (0.12)	ND (0.02)	0.19 J	**0.29**	0.16 J	ND (0.02)	ND (0.39)	ND (0.41)	**2.5**	**0.72**	0.093 J	ND (0.03)	0.13 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location C-2	91 cm	ug/Kg dry	0.15 J	ND (0.12)	ND (0.02)	**0.28**	**0.27**	0.17 J	ND (0.02)	ND (0.41)	ND (0.43)	0.27 J	**0.55**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location C-2	183 cm	ug/Kg dry	0.053 J	ND (0.12)	ND (0.02)	ND (0.04)	ND (0.05)	ND (0.03)	ND (0.03)	ND (0.42)	ND (0.44)	ND (0.21)	ND (0.10)	ND (0.04)	ND (0.03)	ND (0.03)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location C-3	30 cm	ug/Kg dry	0.075 J	ND (0.12)	ND (0.02)	0.16 J	0.22	0.13 J	ND (0.02)	ND (0.39)	ND (0.42)	**3.6**	**0.46**	0.12 J	ND (0.03)	**0.24**	ND (0.04)	0.097 J	ND (0.05)	ND (0.06)
Location C-3	91 cm	ug/Kg dry	0.15 J	ND (0.11)	ND (0.02)	**0.36**	0.12 J	0.058 J	ND (0.02)	ND (0.37)	ND (0.39)	**0.57**	**0.40**	0.02 J	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location C-3	183 cm	ug/Kg dry	0.061 J	ND (0.11)	ND (0.02)	0.11 J	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.36)	ND (0.38)	ND (0.21)	0.12 J	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-2	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.39)	ND (0.41)	ND (0.21)	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-2	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.40)	ND (0.42)	ND (0.21)	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location E-2	183 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.38)	ND (0.40)	ND (0.21)	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-3	30 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.37)	ND (0.39)	ND (0.21)	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-3	91 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.36)	ND (0.38)	0.21 J	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-3	183 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.39)	ND (0.41)	ND (0.21)	ND (0.09)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Irrigation source presence			√			√	√	√				√	√	√						√

Shaded values indicates values above the MDL and **bold** values are above the MRL.

Table S7. PFAS soil concentrations for agricultural parcels amended with 21 – 30 tons/acre (47075-67251 kg/ha) of biosolids. Sample duplicates were obtained from a second bore hole location within a meter of the initial location identification bore hole.

Sample Site	Depth	Units	PFBS	GenX	DONA	PFHxS	PFHxA	PFHpA	F-53B (Minor)	NEtFOSAA	NMeFOSAA	PFOS	PFOA	PFNA	F-53B (Major)	PFDA	PFUnA	PFDoA	PFTriA	PFTeA
21-30 tons/acre Biosolids Amended Soils																				
Location D-3	30 cm	ug/Kg dry	ND (0.03)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.38)	ND (0.40)	**0.73**	0.17 J	**0.34**	ND (0.03)	0.067 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location D-3	91 cm	ug/Kg dry	ND (0.02)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.36)	ND (0.38)	0.29 J	**0.32**	0.13 J	ND (0.03)	0.032 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location D-3	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	0.036 J	ND (0.02)	ND (0.41)	ND (0.43)	ND (0.22)	**0.41**	0.04 J	ND (0.03)	0.084 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location F-1	30 cm	ug/Kg dry	**0.25**	ND (0.11)	ND (0.02)	0.038 J	0.18 J	0.12 J	ND (0.02)	ND (0.37)	ND (0.39)	**4.2**	**0.49**	**0.45**	ND (0.03)	**0.79**	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location F-1 (duplicate)	30 cm	ug/Kg dry	**0.25**	ND (0.11)	ND (0.02)	0.040 J	0.20 J	0.12 J	ND (0.02)	ND (0.39)	ND (0.39)	**4.4**	**0.75**	**0.51**	ND (0.03)	**0.81**	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location F-1	91 cm	ug/Kg dry	0.11 J	ND (0.12)	ND (0.02)	0.047 J	0.074 J	0.09 J	ND (0.02)	ND (0.40)	ND (0.43)	**0.84**	**0.47**	0.12 J	ND (0.03)	0.025 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location F-1 (duplicate)	91 cm	ug/Kg dry	0.18 J	ND (0.12)	ND (0.02)	0.066 J	0.18 J	0.16 J	ND (0.02)	ND (0.40)	ND (0.42)	**0.80**	**0.68**	0.11 J	ND (0.03)	0.11 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location F-1	183 cm	ug/Kg dry	0.082 J	ND (0.11)	ND (0.02)	0.035 J	0.067 J	0.043 J	ND (0.02)	ND (0.39)	ND (0.41)	0.28 J	0.15 J	ND (0.04)	ND (0.03)	0.046 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location F-1 (duplicate)	183 cm	ug/Kg dry	**0.36**	ND (0.12)	ND (0.02)	0.150 J	**0.23**	0.13 J	ND (0.02)	ND (0.41)	ND (0.43)	0.26 J	**4.4**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location F-3	30 cm	ug/Kg dry	0.046 J	ND (0.11)	ND (0.02)	0.048 J	0.17 J	0.087 J	ND (0.02)	ND (0.38)	ND (0.40)	**2.4**	**0.34**	**0.26**	ND (0.03)	**4.1**	**0.41**	**0.35**	ND (0.05)	0.15 J
Location F-3	91 cm	ug/Kg dry	0.040 J	ND (0.12)	ND (0.02)	ND (0.03)	0.074 J	0.049 J	ND (0.02)	ND (0.39)	ND (0.41)	**4.2**	**0.31**	**0.31**	ND (0.03)	**1.5**	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location F-3	183 cm	ug/Kg dry	ND (0.02)	ND (0.11)	ND (0.02)	ND (0.03)	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.35)	ND (0.37)	**1.1**	**0.22**	0.13 J	ND (0.03)	0.14 J	ND (0.03)	ND (0.07)	ND (0.05)	ND (0.06)
Irrigation source presence			√			√		√				√	√							

Shaded values indicates values above the MDL and **bold** values are above the MRL.

Table S8. PFAS soil concentrations for agricultural parcels amended with > 30 tons/acre (67251 kg/ha) of biosolids. Sample duplicates were obtained from a second bore hole location within a meter of the initial location identification bore hole.

Sample Site	Depth	Units	PFBS	GenX	DONA	PFHxS	PFHxA	PFHpA	F-53B (Minor)	NEtFOSAA	NMeFOSAA	PFOS	PFOA	PFNA	F-53B (Major)	PFDA	PFUnA	PFDoA	PFTriA	PFTeA
>30 tons/acre Biosolids Amended Soils																				
Location E-1	30 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	0.071 J	0.060 J	ND (0.02)	ND (0.39)	ND (0.41)	**4.0**	**0.29**	**0.35**	ND (0.03)	**1.1**	0.05 J	0.072 J	ND (0.05)	ND (0.06)
Location E-1 (duplicate)	30 cm	ug/Kg dry	0.031 J	ND (0.12)	ND (0.02)	0.045 J	0.14 J	0.088 J	ND (0.02)	ND (0.40)	ND (0.40)	**3.5**	**0.30**	**0.30**	ND (0.03)	**1.8**	0.21 J	**0.47**	ND (0.06)	0.16 J
Location E-1	91 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	ND (0.03)	ND (0.02)	ND (0.40)	ND (0.42)	**1.8**	**0.39**	**0.24**	ND (0.03)	0.11 J	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location E-1 (duplicate)	91 cm	ug/Kg dry	0.032 J	ND (0.12)	ND (0.02)	0.033 J	0.068 J	0.069 J	ND (0.02)	ND (0.39)	ND (0.39)	**4.0**	**0.61**	**0.41**	ND (0.03)	**0.24**	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location E-1	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	ND (0.03)	ND (0.05)	0.043 J	ND (0.03)	ND (0.41)	ND (0.44)	0.55 J	**0.24**	0.058 J	ND (0.03)	0.084 J	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location E-1 (duplicate)	183 cm	ug/Kg dry	0.032 J	ND (0.12)	ND (0.02)	0.042 J	0.051 J	0.065 J	ND (0.03)	ND (0.41)	ND (0.41)	**0.58**	**0.39**	0.052 J	ND (0.03)	0.094 J	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location F-2	30 cm	ug/Kg dry	0.059 J	ND (0.12)	ND (0.02)	0.039 J	0.13 J	0.075 J	ND (0.02)	ND (0.41)	ND (0.43)	**6.6**	**0.28**	**0.52**	ND (0.03)	**0.79**	ND (0.04)	ND (0.07)	ND (0.06)	ND (0.06)
Location F-2	91 cm	ug/Kg dry	0.036 J	ND (0.12)	ND (0.02)	0.036 J	0.052 J	0.047 J	ND (0.02)	ND (0.39)	ND (0.41)	**2.2**	**0.61**	**0.26**	ND (0.03)	0.11 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location F-2	183 cm	ug/Kg dry	ND (0.03)	ND (0.12)	ND (0.02)	0.061 J	ND (0.05)	0.034 J	ND (0.02)	ND (0.41)	ND (0.43)	0.39 J	**1.9**	0.046 J	ND (0.03)	0.031 J	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location C-1	30 cm	ug/Kg dry	**1.3**	ND (0.10)	ND (0.02)	0.18 J	**1.4**	**0.34**	ND (0.02)	0.41 J	1.2 J	**2.4**	**1.2**	**0.28**	ND (0.03)	**1.3**	0.20 J	**0.48**	ND (0.05)	0.15 J
Location C-1 (duplicate)	30 cm	ug/Kg dry	**0.87**	ND (0.12)	ND (0.02)	0.16 J	**1.2**	**0.27**	ND (0.02)	ND (0.40)	0.81 J	**1.9**	**0.84**	0.18 J	ND (0.03)	**0.72**	0.11 J	**0.31**	ND (0.06)	0.11 J
Location C-1	91 cm	ug/Kg dry	0.17 J	ND (0.11)	ND (0.02)	0.052 J	**0.23**	0.059 J	ND (0.02)	ND (0.36)	ND (0.38)	0.39 J	0.21 J	**0.044**	ND (0.03)	0.17 J	ND (0.04)	0.072 J	ND (0.05)	ND (0.06)
Location C-1 (duplicate)	91 cm	ug/Kg dry	0.038 J	ND (0.11)	ND (0.02)	0.042 J	0.093 J	0.032 J	ND (0.02)	ND (0.38)	ND (0.40)	0.22 J	0.11 J	ND (0.04)	ND (0.03)	0.081 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location C-1	183 cm	ug/Kg dry	0.061 J	ND (0.11)	ND (0.02)	0.035 J	0.082 J	ND (0.03)	ND (0.02)	ND (0.37)	ND (0.39)	0.20 J	0.10 J	ND (0.04)	ND (0.03)	0.11 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location C-1 (duplicate)	183 cm	ug/Kg dry	0.029 J	ND (0.10)	ND (0.02)	ND (0.03)	0.064 J	0.017 J	ND (0.02)	ND (0.34)	ND (0.36)	ND (0.18)	ND (0.08)	ND (0.04)	ND (0.03)	0.057 J	ND (0.04)	ND (0.06)	ND (0.05)	ND (0.06)
Location D-1	30 cm	ug/Kg dry	**0.27**	ND (0.12)	ND (0.02)	0.18 J	**0.55**	**0.29**	ND (0.02)	ND (0.40)	ND (0.42)	**2.6**	**1.4**	**0.62**	ND (0.03)	**0.50**	0.05 J	0.13 J	ND (0.06)	0.06 J
Location D-1	91 cm	ug/Kg dry	**0.66**	ND (0.13)	ND (0.02)	**0.44**	**0.41**	**0.42**	ND (0.03)	ND (0.44)	ND (0.46)	0.34 J	**3.8**	ND (0.04)	ND (0.03)	0.096 J	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location D-1	183 cm	ug/Kg dry	**0.46**	ND (0.12)	ND (0.02)	**0.44**	**0.30**	**0.71**	ND (0.02)	ND (0.40)	ND (0.42)	**1.5**	**0.75**	0.11 J	ND (0.03)	**0.83**	0.17 J	**0.40**	ND (0.06)	0.15 J
Location D-2	30 cm	ug/Kg dry	0.18 J	ND (0.11)	ND (0.02)	0.17 J	0.24	0.18 J	ND (0.02)	ND (0.38)	ND (0.40)	**6.5**	**1.1**	**0.56**	ND (0.03)	**0.88**	0.10 J	**0.25**	ND (0.05)	0.11 J
Location D-2 (duplicate)	30 cm	ug/Kg dry	**0.22**	ND (0.11)	ND (0.02)	0.15 J	0.38	**0.20**	ND (0.02)	ND (0.39)	ND (0.41)	**5.5**	**1.3**	**0.61**	ND (0.03)	**0.72**	0.10 J	0.20 J	ND (0.05)	0.09 J
Location D-2	91 cm	ug/Kg dry	0.21 J	ND (0.11)	ND (0.02)	**0.26**	**0.29**	**0.31**	ND (0.02)	ND (0.38)	ND (0.40)	0.24 J	**1.6**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location D-2 (duplicate)	91 cm	ug/Kg dry	**0.46**	ND (0.11)	ND (0.02)	**0.30**	**0.62**	**0.32**	ND (0.02)	ND (0.39)	ND (0.41)	**0.56**	**3.2**	0.048 J	ND (0.03)	0.048 J	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Location D-2	183 cm	ug/Kg dry	**0.31**	ND (0.12)	ND (0.02)	**0.36**	**0.24**	**0.43**	ND (0.03)	ND (0.41)	ND (0.44)	ND (0.22)	**0.44**	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.08)	ND (0.06)	ND (0.06)
Location D-2 (duplicate)	183 cm	ug/Kg dry	0.20 J	ND (0.11)	ND (0.02)	**0.30**	**0.23**	**0.58**	ND (0.02)	ND (0.39)	ND (0.41)	0.28 J	0.20 J	ND (0.04)	ND (0.03)	ND (0.02)	ND (0.04)	ND (0.07)	ND (0.05)	ND (0.06)
Irrigation source presence			√			√	√	√				√	√	√		√				

Shaded values indicates values above the MDL and **bold** values are above the MRL.