

Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids

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S Supporting Information

ABSTRACT: The recent implementation of soil and drinking water screening guidance values for two perfluorochemicals (PFCs), perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) by the U.S. Environmental Protection Agency (EPA), reflects the growing concerns regarding the presence of these persistent and bioaccumulative chemicals in the natural environment. Previous work has established the potential risk to the environment from the land application of industrially contaminated biosolids, but studies focusing on environmental risk from land application of typical municipal biosolids are lacking. Thus, the present study investigated the occurrence and fate of PFCs from land-applied municipal biosolids by evaluating the levels, mass balance, desorption, and transport of PFCs in soils receiving application of municipal biosolids at various loading rates. This study is the first to report levels of PFCs in agricultural soils amended with typical municipal biosolids. PFOS was the dominant PFC in both biosolids (80–219 ng/g) and biosolids-amended soil (2–483 ng/g). Concentrations of all PFCs in soil increased linearly with increasing biosolids loading rate. These data were used to develop a model for predicting PFC soil concentrations in soils amended with typical municipal biosolids using cumulative biosolids loading rates. Mass balance calculations comparing PFCs applied vs those recovered in the surface soil interval indicated the potential transformation of PFC precursors. Laboratory desorption experiments indicated that the leaching potential of PFCs decreases with increasing chain length and that previously derived organic-carbon normalized partition coefficients may not be accurate predictors of the desorption of long-chain PFCs from biosolids-amended soils. Trace levels of PFCs were also detected in soil cores from biosolids-amended soils to depths of 120 cm, suggesting potential movement of these compounds within the soil profile over time and confirming the higher transport potential for short-chain PFCs in soils amended with municipal biosolids.



INTRODUCTION

Perfluorochemicals (PFCs) are environmentally persistent, bioaccumulative, toxic, and widely distributed in the environment.¹ PFC-based products have a wide variety of uses including nonstick coatings, stain-repellant fabrics, paper packaging products, and firefighting foams.² Two specific subclasses of PFCs, perfluorocarboxylates (PFCAs) and perfluoroalkylsulfonates (PFASs), have received particular attention in recent years. Because of their widespread use, PFCs have been detected in the influent, effluent, and sludge (biosolids) at municipal wastewater treatment plants (WWTPs).^{3–5} Municipal biosolids may not only contain PFCs but also a variety of chemical precursors that could be transformed to PFCs over time.^{4,6} Some of these precursors, such as 2-(N-ethylperfluorooctane sulfonamido) acetic acid (EtFOSAA), may be transformed to PFASs,⁷ while

others, such as the fluorotelomer alcohols (FTOHs), may be transformed to PFCAs.⁸

As of 2004, 7.2 million dry tons of biosolids were generated in the U.S. each year, and approximately 49% were applied to agricultural lands as fertilizer.⁹ Though the land application of biosolids in the U.S. is regulated, no regulations are currently in place with respect to PFCs in biosolids. This issue is coming under increased scrutiny, mainly after a recent event in Decatur,

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Table 1. Biosolids-Amended Soil Characteristics

soil	soil type	f_{oc}^a	loading rates ^b	years of application	last application
short-term W	silty clay loam	0.041	0–178	3	2006
short-term K	fine sand	0.011	0–133	3	2007
long-term plots	silt loam	NM	0–2218	32	2010
general fields	silt loam	0.047	47–1654	1–20	1983–2002

^a f_{oc} was analyzed for the following loading rates: short-term W at 178 Mg/ha, short-term K at 133 Mg/ha, and general field 2 at 1654 Mg/ha. ^b Loading rates are provided in Mg/ha on a dry weight basis. NM = not measured.

Alabama, where industrially-contaminated biosolids were applied to land used for grazing cattle and growing crops, resulting in PFC detections in soil, beef, grass, and groundwater from the biosolids-amended fields.^{10,11} Indeed, it was out of growing concern about the potential exposure to PFCs in soil and groundwater that provisional health advisories and residential soil screening guidance values were developed.^{12,13} For example, the U.S. Environmental Protection Agency (EPA) recently issued drinking water provisional health advisories (PHA) for perfluorooctanoate (PFOA, a PFCA) and perfluorooctane sulfonate (PFOS, a PFAS), of 0.4 $\mu\text{g}/\text{L}$ and 0.2 $\mu\text{g}/\text{L}$, respectively.¹⁴ In addition, EPA's residential soil screening guidance values for PFOA and PFOS are 16,000 $\mu\text{g}/\text{kg}$ and 6000 $\mu\text{g}/\text{kg}$, respectively.¹² While PFCs are known to be present in municipal biosolids,⁴ it remains unclear whether the application of typical municipal biosolids to agricultural soil could pose any potential PFC-related risks for human and ecological health.

If PFCs and PFC precursors in typical municipal biosolids are transferred to biosolids-amended soils, their environmental fate will depend on several processes. PFC precursors may be transformed to PFCs over time, while the PFCs themselves may either accumulate in the surface soil and/or leach into the subsurface. To the best of our knowledge, the potential accumulation and/or leaching of PFCs in soils amended with typical municipal biosolids has not been documented. Additionally, there is no prior work documenting transformation of PFC precursors in soils amended with typical municipal biosolids, though transformation of FTOHs in soils receiving industrially contaminated biosolids has been documented.⁸ Furthermore, there are no studies investigating leaching of PFCs or PFC precursors in soils amended with typical municipal biosolids. Previous work with industrially contaminated biosolids has suggested the potential for PFC leaching, particularly for shorter chained PFCs.¹⁵ Finally, equilibrium partitioning can provide an indication as to the leaching potential of organic contaminants, and relevant work has been done investigating equilibrium partitioning of PFCs in spiked sediment-water systems.¹⁶ These data suggest a greater leaching potential for short-chain PFCs under equilibrium conditions. However, previous work with other organic chemicals in biosolids¹⁷ suggests soil–water partitioning coefficients derived from adsorption experiments do not accurately predict desorption behavior from biosolids, particularly under field conditions. For example, the desorptive release of biosolids-borne chemicals such as triclosan and triclocarban is often incomplete.¹⁷ To this end, desorption data from laboratory batch experiments using field samples of biosolids-amended soils are needed to evaluate the fate and transport of PFCs applied to soils via municipal biosolids, and these data should be compared to observations of leaching in intact soil cores.

The objective of this study was to examine the occurrence and fate of select PFCA, PFAS, and PFC precursors in biosolids-

amended soils through a combination of field and laboratory studies. Specifically, we tested whether the repeated application of typical municipal biosolids results in predictable accumulation of PFCs in the biosolids-amended surface soils over time. In addition, concentrations of PFCs and PFC precursors applied to soil via municipal biosolids over a three-year period were compared to concentrations measured in the amended soils. The resulting mass balance calculations enabled a first evaluation of the potential formation of PFCs from PFC precursors in biosolids-amended soils. Laboratory desorption experiments were completed with field samples of biosolids-amended soils to verify previous observations of higher leaching potential for short-chain PFCs and to enable evaluation of previously measured adsorption-derived partition coefficients vs desorption-derived partition coefficients. Lastly, analysis of PFCs in soil cores from fields receiving biosolids was completed to determine if chain-length dependent leaching is also observed in the field.

MATERIALS AND METHODS

Materials. Standards of perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluoroheptanesulfonate (PFHpS), PFOS, perfluorodecanesulfonate (PFDS), 2-(N-methylperfluorooctane sulfonamido) acetic acid (MeFOSAA), and EtFOSAA as well as stable-isotope surrogate standards (Table S1) were purchased from Wellington Laboratories. Stock solution of these analytes and the surrogate standards were prepared in a 70/30 (v/v) methanol/aqueous ammonium hydroxide (0.01%) solution. Unless otherwise specified, all other chemicals and solvents were of reagent grade and were purchased from Fisher Scientific, Mallinckrodt Chemicals, or Sigma Aldrich.

Characterization of Study Sites. All biosolids and biosolids-amended soils analyzed in this study were provided by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). Samples from four series of biosolids-amended soils were examined. General soil types and characteristics are summarized in Table 1. Soils were selected to represent a variety of soil types, biosolids loading rates, duration of biosolids application, and time since last biosolids application. First, short-term plots of Soil W (loam) and Soil K (sand) received biosolids applications over three consecutive years at various biosolids loading rates as part of a previously described, field-scale experiment at two farms in Illinois.¹⁸ Samples of the six source biosolids applied to these soils were also analyzed for PFC content. Second, archived soil cores from a previously characterized¹⁹ site (long-term plots) were selected for plots that have received various cumulative biosolids loading rates. Finally, soil samples were collected from three general fields

(Fields 2, 40, and 51) that have received multiple applications of biosolids in varying years.²⁰ All sites included control plots to which no biosolids were applied, and corn was grown in all fields. The biosolids loading rates used for both the short-term W and K plots encompassed the typical agronomic rates for biosolids applications for these soils, whereas the biosolids loading rates for the long-term application plots represent various worst-case scenarios¹⁹ in which more than 100 years of agronomic biosolids applications were applied within a 33 year window.

Sample Collection. Composite samples of the biosolids applied to the short-term plots (Soils W and K) were collected at the time of biosolids application and stored at $-20\text{ }^{\circ}\text{C}$ until analysis. Composite soil samples were collected from the long-term plots in fall 2005, short-term W plots in fall 2007, and short-term K plots in spring 2008. All soil samples were sieved through a 2-mm sieve and stored at $-20\text{ }^{\circ}\text{C}$ until analysis. Further details about sample processing are given elsewhere.^{18,19} Samples collected from the general application fields were collected from 0 to 15 cm in summer 2010 and shipped to the laboratory on ice. Soil samples used in batch desorption experiments were analyzed by a commercial laboratory for f_{oc} by the Walkley Black method. Organic carbon content within each soil varied with the biosolids loading rate, and thus only the f_{oc} values relevant to desorption experiments are reported in Table 1.

Batch Desorption Experiments. After confirming the presence of PFCs, batch desorption experiments were conducted with soil from a short-term W plot (cumulative biosolids loading rate 178 Mg/ha), a short-term K plot (133 Mg/ha), and Field 2 (1654 Mg/ha). Equilibrium desorption experiments were conducted over 14 days to determine the time necessary for the soil–water mixtures to reach equilibrium, with the resultant data enabling the calculation of desorption-based organic carbon–water partitioning coefficients (K_{oc} values). Results of the equilibrium desorption experiments were used to calculate soil–water distribution coefficients (K_{des}) as follows

$$K_{des} = \frac{C_s}{C_w} = \frac{m_s^0 - m_v - m_w *}{m_w} \frac{V_w}{M_{soil}} \quad (1)$$

where C_s is the concentration of the analyte in the solid phase, C_w is the concentration of analyte in the aqueous phase, m_s^0 is the mass of analyte in the solid phase before desorption, m_v is the mass of analyte lost to the desorption reactor vial, m_w is the mass of PFC in the aqueous phase at equilibrium, V_w is the volume of the aqueous phase, and M_{soil} is the mass of soil in the reactor. Resulting K_{des} values were then organic carbon normalized to calculate K_{oc}

$$K_{oc} = \frac{K_{des}}{f_{oc}} \quad (2)$$

Sample Extraction and Analysis. All solid samples were extracted as received, though all concentrations are reported on an oven-dry weight basis. Soils (50–1000 mg) and biosolids (100 mg) were spiked with surrogate standards and extracted using a procedure modified from a previous study.¹⁶ Cleaned-up extracts were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS). All biosolids and biosolids-amended soil samples were extracted and analyzed in triplicate. Aqueous sample preparation and analysis protocols were also modified from a previous study.¹⁶ All biosolids extracts, soil extracts, and aqueous samples were quantified by LC-MS/MS using protocols similar to those previously described.⁴ A MDS

Sciex Applied Biosystems 3200 Q trap mass spectrometer (MDS Sciex, Ontario) was used to monitor two MRM transitions for each analyte. Quantitation was performed using Analyst software. The limits of quantitation (LOQs) were analyte, matrix, and run-dependent but were approximately 0.02–0.5 ng/g in soil and 0.9–9 ng/L in aqueous samples. All values reported are corrected for recovery of the surrogate standards, as appropriate, which were generally greater than 60% for all samples in all matrices. Additional details on sample analysis including eluents, eluent conditions, transitions, and quantitation are provided in the Supporting Information.

Quality Assurance/Quality Control Measures. Soils and biosolids were extracted in triplicate, desorption reactors were prepared in sets of three, and all analytical results are reported as the average of the three values. Solid and aqueous spike-recovery experiments and sequential extraction experiments were conducted to ensure the validity of the data (Table S2, Figure S1). As a result of poor recovery (either under or over recovery) during aqueous spike-recovery experiments, aqueous-phase data for PFBA, PFPeA, PFUdA, PFDoA, MeFOSAA, and EtFOSAA were removed from additional analysis. Finally, control reactors were prepared for desorption experiments to account for losses in the reactors. If losses for an analyte were greater than 10%, then these results were used to calculate m_v for the analyte (see eq 1) to account for losses to the vial when determining K_{des} values. Additional details regarding materials, batch desorption experimental setup, sample extraction and analysis, and quality assurance/quality control measures are provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence in Biosolids and Biosolids-Amended Soils. Six composite samples of biosolids applied to the short-term plots were collected from 2004 to 2007 and analyzed for the full suite of PFCs. The most abundant PFCs or PFC precursors in all six biosolids were PFOS (80–219 ng/g), followed by MeFOSAA (63–143 ng/g), EtFOSAA (42–72 ng/g), and PFOA (8–68 ng/g) (Figure S2). To facilitate comparison to previously reported concentrations, mean total PFCs (sum of PFOA, PFNA, PFDA, PFUdA, PFDoA, MeFOSAA, EtFOSAA, PFHxS, PFOS, and PFDS) and mean PFOS concentrations were calculated and were 433 ± 121 ng/g and 144 ± 57 ng/g, respectively. Data from this study were compared to data from a previous study that was collected post 2002 when the use of certain PFCs was phased out.⁴ Mean, total PFCs and mean PFOS concentrations are not statistically different from the values of 436 ng/g and 124 ng/g, respectively, that were reported in a previous study,⁴ confirming that the biosolids applied to these soils were representative of typical municipal biosolids.

Soil analysis showed PFCs do occur in soils amended with typical municipal biosolids. As in biosolids, PFOS was the most abundant PFC detected in the short-term plots (Soils W and K). PFOS concentrations ranged from 2 to 11 ng/g over the various biosolids loading rates in these soils. Though MeFOSAA was abundant in the applied biosolids, concentrations in the biosolids-amended soils were less than 4 ng/g, suggesting transformation of this PFC precursor. PFOS was also the most abundant PFC in the soil samples from the long-term plots and the general application fields. In these soils, PFOS was detected at 5.5–483 ng/g over various biosolids loading rates, with the 5.5 ± 0.4 ng/g PFOS levels from Field 51 (single biosolids application in 1988). Control soils with no biosolids application were also analyzed for

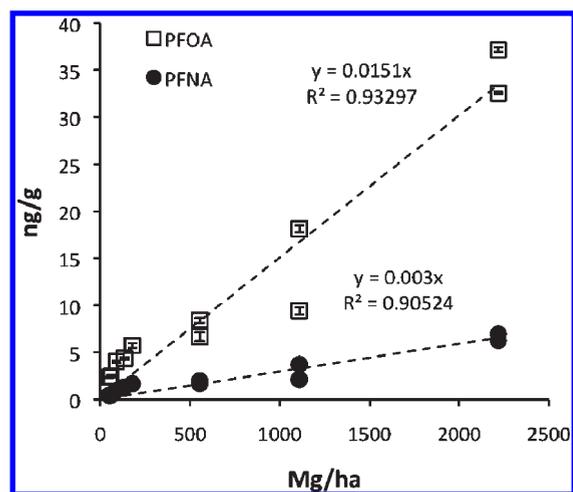


Figure 1. Example regressions of measured soil concentration vs cumulative loading rate for PFOA and PFNA in the short-term W and long-term plots. Regressions and associated statistics for all PFCs are available in the Supporting Information (Table S4).

all sites. In these samples, any PFCs present were detected at concentrations of approximately 1 ng/g or less, with the exception of PFOS. In the long-term control plots, PFOS was measured to be 22 ± 2 ng/g and 96 ± 4 ng/g. The high background concentration of PFOS in the long-term control plots is likely due to cross-contamination from maintenance activities such as plowing and planting because of the close proximity of these control plots to the plots receiving the highest biosolids applications. There are no physical barriers to separate the control plots from the biosolids-amended plots, and all plots were plowed and planted as a single unit. Atmospheric deposition can be eliminated as a source of the elevated PFOS levels in the long-term control plots since elevated PFOS concentrations are not found in control plots from the short-term W and K sites and the general fields, which are from the same geographic region.

Occurrence with Biosolids Loading Rate. Once occurrence of PFCs in soils amended with municipal biosolids was established, trends of PFC concentrations in these soils with varying loading rates were examined. This was done using data from the short-term W plots and long-term plots as a cumulative data set, plotting individual PFC concentrations vs cumulative biosolids loading rate, and then performing regressions on the cumulative data set (Figure 1 and Table S3). These regressions took the form of

$$[\text{PFC}] = m \cdot \text{LR} \quad (3)$$

where [PFC] is the individual PFC concentration (i.e., [PFOS]; ng/g), m is the slope (ng/g per dry Mg/ha), and LR is the cumulative loading rate (dry Mg/ha). Some variability was observed, but the overall regressions of PFC concentrations in surface soil vs cumulative biosolids loading rates were statistically significant ($p < 0.05$) for all PFCs, with the exception of PFBS. Within each soil, PFBS showed increases with loading rate; however, when the data sets from the soil types were combined, there was not a consistent increase in soil concentrations with increased biosolids loading rate. As a result, PFBS could not be modeled. Regressions were performed with the y -intercept set to zero since some control plot PFC concentrations were falsely elevated due to cross contamination, and additional background PFC concentrations were not

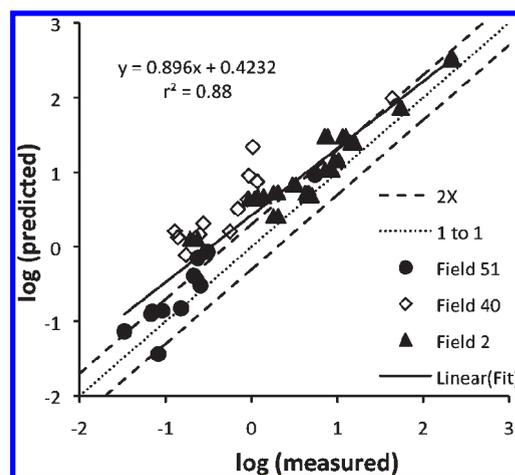


Figure 2. Measured concentrations for all PFCs detected in the general fields plotted vs predicted values for all modeled PFCs using linear regressions derived from the short-term W and long-term plots.

available. The results of these regressions confirm that the primary source of PFCs to these soils is the biosolids, as opposed to atmospheric deposition, and that levels of PFCs increase with increased biosolids loading rate.

Next, PFC concentrations in the general fields were predicted by incorporating loading rates from the general fields into the linear equations (Table S3) obtained from the regressions of the short-term and long-term plots. These predicted concentrations were then compared to the PFC concentrations measured in surface soil samples taken from the general fields (Figure 2). The regressions slightly overpredicted concentrations of all PFCs, particularly for the plot amended at a rate of 497 Mg/ha (Field 40), suggesting that some losses of PFCs from the surface soils may have occurred since the last application in 1983. Nonetheless, relatively accurate predictions of soil PFC levels in the general fields can be made despite the highly variable biosolids applications. However, as all soils and biosolids included in this study are from the same region with presumably similar PFC levels in the source biosolids, the application of these regressions for predicting PFC levels in biosolids-amended soils must be done with caution: slight differences in PFC levels in source biosolids could translate to substantial differences in biosolids-amended soil concentrations, particularly when these differences are integrated over many years. Nevertheless, in the absence of PFC concentrations in typical municipal biosolids applied to a particular site, these regressions provide a first approximation of expected PFC levels in soil based on cumulative biosolids loading rates.

PFC Fate in Surface Soils. Comparison of PFC concentrations in source biosolids vs the amended soils suggested a potential loss of PFC precursors from the surface soil layer between biosolids application and the time of sample collection. To explore the potential for PFC precursors to contribute to PFC concentrations and to examine any increases or decreases in PFCs levels, mass balance calculations were performed to determine how much mass of each PFC applied in the biosolids was recovered in the short-term W and K plots. A range of expected soil concentrations for each PFC was determined for each biosolids loading rate using a mean (\pm the standard deviation) of the measured concentration of PFC in biosolids applied at each site over a three-year period, the incorporation

Table 2. K_{oc} Results vs Previous Studies

analyte	$\log K_{oc}$	StdDev	$\log K_{oc}$ prev. work ^a
PFHxA	1.91	0.39	N/A
PFHpA	2.19	0.65	N/A
PFOA	2.31	0.35	2.06
PFNA	2.33	0.31	2.39
PFDA	3.17	0.14	2.76
PFHxS	2.70	0.38	N/A
PFOS	3.34	0.27	2.57

^a $\log K_{oc}$ values determined in previous studies of PFC sorption in sediment.¹⁶

depth (0.15 m for short-term W plots, 0.2 m for short-term K plots), the measured loading rates,¹⁸ and the soil bulk density (1.3 g/cm³ short-term W, 1.6 g/cm³ short-term K). The range of calculated concentrations for each PFC was then compared to the measured range of concentrations in the short-term W and K plots. Though these calculated concentrations represent only an estimate of the expected soil concentrations, comparison to the measured values can provide an estimate of any significant increases or decreases in PFC levels relative to what was applied. Complete mass balance results are provided in the Supporting Information (Table S4). In both soils, the biggest increases in PFC concentrations were observed for PFBS, where, on average, PFBS was ~300% to ~2000% of what would be anticipated for the short-term W and K plots based on the applied biosolids. Because mass-labeled PFHxS is used as a surrogate standard for PFBS (Table S1), standard additions were performed to determine if matrix effects contributed to the significantly elevated PFBS measurements (see the Supporting Information). Though matrix effects did lead to artificially high soil measurements, they could not entirely account for the elevated levels of PFBS in the short-term W and K plots, strongly suggesting that significant quantities of PFBS were being formed from a PFC precursor over the short-term. The most notable losses in each soil were of the two PFC precursors, MeFOSAA and EtFOSAA, where, on average, concentrations were only 23–69% of what was expected. These results further indicate potential transformation of PFC precursors, though full conversion of these precursors to end product PFCs was not observed. For example, PFOS, a known transformation product of EtFOSAA⁷ was well within the expected range of concentrations, with average recoveries in Soil W and Soil K plots of 97% and 83%, respectively. Future efforts should focus on temporal monitoring of biosolids-borne PFCs and PFC precursors to better understand the transformation rate and formation of any potential intermediates.

Leaching Potential. To understand leaching potential under equilibrium conditions, desorption was examined in soil from the short-term W and K plots as well as from the general fields (Field 2). Aqueous equilibrium, defined as when no statistical differences were observed in aqueous concentrations measured in subsequent time points (up to 14 days), was achieved for all PFCs within the first 24 h of desorption from the biosolids amended soils (Figure S3). Losses in control (no solids) vials were used to calculate a fraction of the PFC associated with the surfaces of a vial when the fraction of the total PFC mass lost in the control blank was greater than 10%. The remaining PFCs were assumed to remain in the solid phase, and this was verified for a subset of samples by extracting solids at the completion of

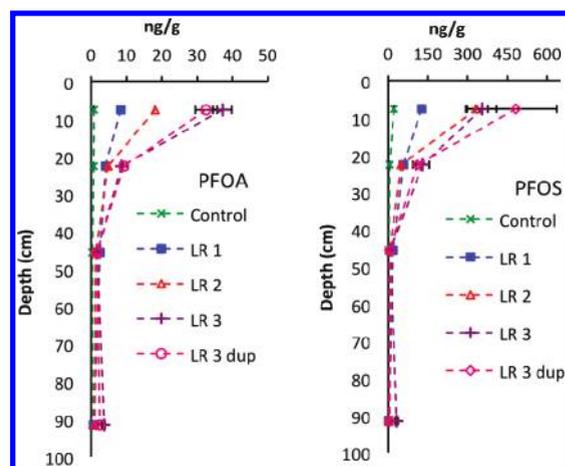


Figure 3. Concentrations of PFOA and PFOS with depth in the long-term plots at various loading rates. Control = 0 Mg/ha, LR 1 = 553 Mg/ha, LR 2 = 1109 Mg/ha, and LR 3 and LR 3 dup = 2218 Mg/ha (on dry weight basis).

the desorption experiments (Table S5). Using these data in conjunction with the measured PFC mass in the aqueous phase, equilibrium K_{des} values were calculated (eq 1) for all PFCs with detectable aqueous concentrations. The K_{des} values were normalized to f_{oc} for each biosolids-amended soil to calculate K_{oc} values (eq 2, Table S6). Desorption-derived K_{oc} values from the short-term W and K plots and the general fields were used to calculate an average $\log K_{oc}$ value for each PFC (Table 2). Similar to previous studies,¹⁶ $\log K_{oc}$ values showed a general increase with chain length, indicating greater leaching potential of short-chain PFCs under equilibrium conditions (Table 2 and Table S6). Values from this study are also similar to those reported previously¹⁶ (Table 2), with the exception of PFDA and PFOS, which were approximately one-half to one order of magnitude greater. The disagreement between previously measured K_{oc} values for PFOS and PFDA but not the shorter chain-length PFCs suggests that desorption of longer chain-length PFCs may be particularly slow. These data call into question the application of the previously determined adsorption K_{oc} values¹⁶ for predicting the transport of PFCs in biosolids-amended soils as adsorption-derived K_{oc} values may over predict the leaching potential of longer chain-length PFCs such as PFOS and PFDA in biosolids-amended soils.

Leaching Under Field Conditions. Laboratory batch desorption experiments with field samples demonstrated higher leaching potential for short-chain PFCs as compared to long-chain PFCs. This finding was confirmed in soil cores, which reflect the actual leaching of PFCs in the field. Analysis of soil cores from the long-term plots showed that levels of PFCs decreased with depth regardless of the biosolids loading rates (Figure 3 and Figure S4). However, PFCs were detected in the bottom depth interval at 120 cm. Data previously reported for these plots showed similar trends for triclocarban, triclosan, and PBDEs.¹⁹ This previous report concluded that detection of these relatively hydrophobic chemicals in the deeper layers of these soil cores suggests facilitated transport (e.g., via preferential flow paths) may have occurred.¹⁹ However, patterns of PFC concentrations in deeper layers suggest that leaching is likely responsible for the transport of PFCs in these cores. First, levels of PFCs in the core samples from the control plots (no biosolids amendment) were relatively

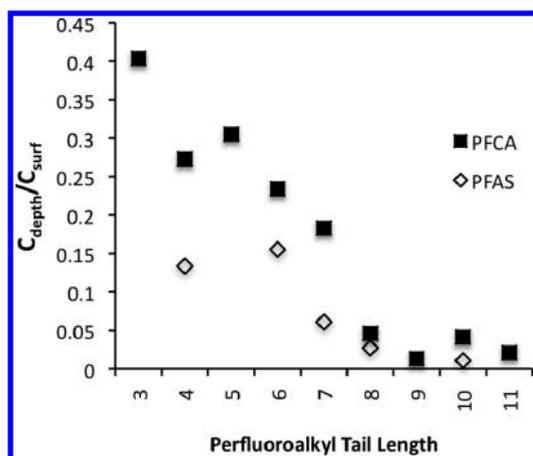


Figure 4. The ratios of surface concentration (C_{surf}) to concentration in the bottom soil core depth interval (60–120 cm, C_{depth}). Ratios represent an average of the ratios calculated for the long-term plots for each biosolids loading rate.

consistent with depth, with the exception of PFOS. As previously mentioned, PFOS was detected in high concentrations in the surface control samples, presumably due to cross contamination with plots receiving biosolids application. Second, statistically significant correlations of soil concentration vs loading rate were observed for some PFCs (including PFOA and PFOS) in the bottom layer of the soil cores. Finally, similar to the trends recently reported for soil cores from the Decatur site,¹⁵ the ratios of PFC concentration in the surface soil to PFC concentration in the lowest depth interval show an overall decrease with increasing chain length, indicating greater transport of the short-chain PFCs (Figure 4). These data strongly suggest leaching of PFCs from the biosolids application zone to a depth, in some cases, of 120 cm. However, as expected from the batch desorption studies, the longer chain-length PFCs appear to be much less mobile than the shorter chain-length PFCs.

Implications. To better understand the environmental significance of these data, it is useful to further examine the results in comparison to the recently outlined provisional health advisory values and residential soil screening guidance values. No soil concentrations measured in this study exceeded the residential soil screening guidance values, which were designed for protection against direct exposure to soil. However, soil screening standards for the protection of groundwater have not yet been developed; therefore, it is illustrative to calculate whether measured soil concentrations have the potential to lead to groundwater exceedances of the PHAs for PFOS and PFOA. These calculations represent a worst-case scenario, as there is likely substantial dilution of soil pore water in the subsurface. Equilibrium pore water concentrations for the short-term W and K plots at multiple biosolids loading rates were estimated using K_{oc} values from this study, f_{oc} values from this and previous work,¹⁸ and measured soil PFOA and PFOS concentrations. These calculations indicate the PHA for PFOA would be exceeded in the short-term W pore water at loading rates of 89 and 178 Mg/ha and in the short-term K pore water at 44 and 133 Mg/ha. Soil pore-water PFOS concentrations would also exceed the PHA in Soil K plots at 44 and 133 Mg/ha. The cumulative loading rates of 89 Mg/ha (Soil W) and 178 Mg/ha (Soil K) represent an agronomic rate of biosolids application over a five to ten year

period. Understanding that these estimates represent a worst-case scenario that does not account for dilution, these results indicate that the risk of groundwater impact from biosolids-borne PFCs is uncertain and will depend heavily on soil type and PFC concentrations in biosolids.

Once PFCs are introduced to the environment, two of the primary concerns for human health are the potential for contamination of water and food. This study focused on the potential for contamination of water from the application of typical municipal biosolids to agricultural fields. Collectively, the data in this study suggest that though the risk to groundwater is uncertain, transport of PFCs from soils amended with municipal biosolids is possible. However, there may be limitations to this transport, particularly for the long-chain PFCs. Further work is needed to determine the risk to food from land application of municipal biosolids, though plant uptake of PFCs from industrially contaminated biosolids has been documented.¹¹ Given the current movement toward increased regulation of PFCs, particularly PFOS and PFOA, this study emphasizes the importance of gaining an increased understanding of the fate and transport of PFCs in soils amended with typical municipal biosolids.

■ ASSOCIATED CONTENT

S Supporting Information. Additional details are available regarding the sample analysis, analytical methods, quality assurance/quality control measures occurrence of PFCs in biosolids, mass balance calculations, linear regressions, occurrence of PFCs with depth, desorption equilibrium, and desorption kinetics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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