Water Research 288 (2026) 124674

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Per- and polyfluoroalkyl substances (PFAS) transport from biosolids-amended soils: An experimental and numerical approach

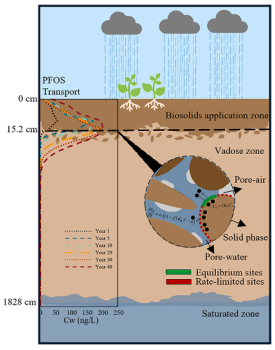
Alonso Doria-Manzur [a], Evan P. Gray [a], Summer S. Streets [b], Jennifer L. Guelfo [a,*]

[a] Civil Environmental and Construction Engineering, Texas Tech University, USA
[b] Minnesota Pollution Control Agency (MPCA), USA

HIGHLIGHTS

- Two biosolids-amended soils were studied in saturated flow-through columns.
- Up to 98 % of total PFAS remained in post-leaching soils.
- PFAS release from soil was rate-limited in saturated flow.
- Modeling showed <1 ng/L PFAS in groundwater after 40 years.
- Biosolids management should focus on shallow soils and runoff control.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
2-site transport model
Biosolids
HYDRUS
Leaching
PFAS
Rate-limited desorption

ABSTRACT

Per- and polyfluoroalkyl substance (PFAS) do not mineralize in conventional wastewater treatment processes and accumulate in effluents and biosolids. Land-application of biosolids improves soil health; however, PFAS may leach from applied biosolids posing a threat to underlying groundwater systems. In general, transport mechanisms controlling PFAS leaching from biosolids are not fully understood. In this study, two municipal biosolids were mixed with soil at agricultural loading rates and packed in saturated flow-through columns. Biosolids, biosolids-amended soils (pre- and post-leaching) and column eluants were analyzed via targeted analysis, total oxidizable precursor assay (TOP), and suspect screening. Saturated column results were modeled using HYDRUS 1-D to obtain transport parameters. Resulting parameters were used to simulate long-term leaching of two PFAS under field-relevant conditions. Mass balances in column systems show that the majority of precursors (>65 %) in biosolid-amended soils remained sorbed after flow-through experiments. TOP assay results for column eluants suggested that the small fraction of unknown precursors mobilized in column experiments were short-chain precursors (≤C7). Transport modeling in HYDRUS 1-D demonstrated that PFAS desorption from biosolid-amended soils was rate-limited under saturated conditions. Long-term modeling of perfluorooctanoic acid and perfluorooctane sulfonate transport using conditions representative of the upper midwestern United States found aqueous concentrations of 107 and <1 ng/L, respectively, reaching the saturated zone after 40 yrs of annual biosolids applications. This suggests that at some land application sites, best management practices focused on PFAS in municipal biosolids should include multi-pathway exposure analysis, considering the soil to

* Corresponding author.
E-mail address: jennifer.guelfo@ttu.edu (J.L. Guelfo).

https://doi.org/10.1016/j.watres.2025.124674
Received 3 May 2025; Received in revised form 20 August 2025; Accepted 24 September 2025
Available online 24 September 2025

groundwater pathway for more mobile PFAS and shallow soils and porewater, along with processes such as plant uptake, runoff, and tile drainage for less mobile PFAS.

1. Introduction

Biosolids are nutrient-rich residuals from wastewater treatment plants (WWTPs), that undergo physical and chemical treatments prior to reuse (e.g. agricultural land application) or disposal (e.g. landfill, incineration) (Beecher et al., 2022). United States (US) federal biosolids regulations include limits on ten metals, but a recent study identified >90 additional, unregulated compounds in biosolids (e.g., flame retardants, pharmaceuticals) (Kumar et al., 2022; Newmeyer et al., 2024). In 2022, 3.76 million dry metric tons of biosolids were managed in the US, of which 56 % were land applied and 27 % were landfilled (USEPA, 2025a). Land application in agricultural settings improves both nutrient (N, P) and micronutrient (e.g. B, Cl, Fe, Mn, Mo and Zn) content of soils (Lu et al., 2012; USEPA, 2025a). However, there are increasing concerns regarding unregulated contaminants in land-applied biosolids including per- and polyfluoroalkyl substances (PFAS) (Hall et al., 2021; Izuegbunam, 2025; Kim Lazcano et al., 2019; MPCA, 2025; Pepper et al., 2023; Popoola et al., 2023; Sepulvado et al., 2011; Tansel et al., 2024; USEPA, 2025b).

PFAS are persistent organic pollutants that do not mineralize during conventional wastewater treatment, accumulate in wastewater treatment residuals (e.g., biosolids), and may undergo transformation from precursor to terminal PFAS after release in the environment. Classes of PFAS identified in US biosolids include perfluoroalkyl carboxylic acids (PFCAs; 22–177 ng/g), perfluoroalkyl sulfonic acids (PFSAs; 21–412 ng/g), methyl- and ethyl- sulfonamide acetic acids (MeFASAAs; 5–154 ng/g, EtFASAAs; 10–582 ng/g), n:2 fluorotelomer sulfonates (FTSs; 1–30 ng/g), n:3 fluorotelomer carboxylic acids (FTCAs; 64–89 ng/g) and disubstituted polyfluoroalkyl phosphates (diPAPs; 8–142 ng/g) (Higgins et al., 2005; Lee et al., 2014; Link et al., 2024; Munoz et al., 2022; Schaefer et al., 2023; Thoma et al., 2022; Thompson et al., 2023; Venkatesan and Halden, 2013). MeFASAAs, EtFASAAs, n:2 FTSs, n:3 FTCAs, and diPAPs are perfluoroalkyl acid (PFAA) precursors that can transform into terminal PFCAs and PFSAs in the environment (Hamid et al., 2020; LaFond et al., 2023; Weidemann et al., 2022; Weidemann and Gassmann, 2023; Wu et al., 2024).

PFAS and other micropollutants in biosolids pose concerns for the practice of biosolids land application, which otherwise is an important beneficial use of wastewater residuals. As a result, regulatory agencies in the US and internationally are restricting or banning land application of biosolids in favor of other methods of disposal (e.g., landfills, incineration) due to concerns about PFAS (Colorado Department of Public Health and Environment, 2024; Department of Environment, Great Lakes, and Energy, 2024; Hall et al., 2021; Maine Department of Agriculture, Conservation and Forestry, 2022; Maryland department of environment, 2024; Missouri Department of Natural Resources, 2023; MPCA, 2025a; New Hampshire Department of Environmental services, 2022; Saliu and Sauvé, 2024; State of Maine, 2022; USEPA, 2025c). However, alternatives such as landfill disposal and incineration are also concerning. Landfill disposal of biosolids uses sometimes scarce landfill capacity with organic material and will be a source of PFAS in leachate, and fate of PFAS during incineration is still poorly understood (Garg et al., 2023; Helmer et al., 2022; Liu et al., 2022; Tolaymat et al., 2023). Studies are needed to better elucidate fate and transport of PFAS in land-applied biosolids, support biosolids risk assessments, and support assessments of the feasibility of continued beneficial reuse of biosolids through land application.

Following land application of biosolids to agricultural soils, PFAS may undergo multiple transport processes including leaching through the vadose zone into the saturated zone (Johnson, 2022; Pepper et al., 2021; Peter and Lee, 2025; Röhler et al., 2021). Numerous prior studies have investigated PFAS leaching in batch, column, and modeling studies (Bierbaum et al., 2023b; Guelfo et al., 2020; Holly et al., 2024; Johnson, 2022; Openiyi et al., 2025; Pepper et al., 2021; Schaefer et al., 2022a; Silva et al., 2019; Stults et al., 2024). PFAS sorption is impacted by multiple soil (e.g. organic carbon content, pH) and PFAS properties (e.g. carbon chain-length, functional groups) (Barzen-Hanson et al., 2017; Campos-Pereira et al., 2023; Guelfo and Higgins, 2013; Li et al., 2018; Nguyen et al., 2020; Nickerson et al., 2023). For example, sorption increases with increasing organic carbon content and chain length (i.e., hydrophobicity), and decreases with increasing pH for anionic PFAS as a result of electrostatic repulsion (Gagliano et al., 2020; Nguyen et al., 2020; Zhang and Yazaydin, 2024). Further, studies have found sorption-desorption of PFAS is sometimes rate-limited, which can lead to plume tailing during long-term leaching scenarios (Arshadi et al., 2024; Brusseau, 2020; Brusseau et al., 2019; Guelfo et al., 2020; Guo et al., 2022, 2020; Nguyen et al., 2022; Stults et al., 2024; Zeng et al., 2021; Zeng and Guo, 2021; Zhao et al., 2014). Similarly, air-water interfacial partitioning can increase PFAS retention in soils (Brusseau, 2020; Brusseau et al., 2019; Guelfo et al., 2020; Schaefer et al., 2019; Silva et al., 2021, 2019; Stults et al., 2024). Despite growing knowledge of PFAS leaching, relatively few studies have focused on PFAS leaching in biosolids land application scenarios, as further described below.

Prior PFAS fate and transport studies focused on biosolids-amended soils have focused primarily on field-collected, biosolids-amended soils (Bierbaum et al., 2023a; Holly et al., 2024; Röhler et al., 2021). In some cases these field soils received multiple biosolids applications and were exposed to environmental conditions prior to experimental evaluation (Bierbaum et al., 2023a; Röhler et al., 2021). Another study used PFAS-spiked biosolids at concentrations above normal occurrence (Holly et al., 2024). Studies are lacking that use column experiments to evaluate PFAS leaching and rate-limited desorption immediately following a single application of municipal biosolids containing representative PFAS concentrations to an agricultural soil. Such studies are critical for establishing baseline transport parameters from which long-term models of PFAS fate at land application sites can be developed.

Additionally, although other studies have recognized the potential impacts of PFAA precursor leaching from biosolids-amended soils (Bierbaum et al., 2023b; Holly et al., 2024; Openiyi et al., 2025; Pepper et al., 2021; Röhler et al., 2021; Schaefer et al., 2022a; Sepulvado et al., 2011), few have quantified it (Bierbaum et al., 2023a; Schaefer et al., 2021). Of these, one column study quantified total fluorine at limited time points, while the second study quantified unknown PFAS leaching from weathered field soils and not immediately following application (Bierbaum et al., 2023b). Although studies investigating precursor fate in biosolids have found that transformation of many precursors occurs rapidly (~1 yr) following biosolids application (Lee et al., 2014; Liu and Liu, 2016; Schaefer et al., 2022a), an improved understanding of parent precursor mobility prior to transformation is important for understanding overall PFAS fate immediately following land application.

This study addressed key knowledge gaps regarding PFAS leaching and mobility at biosolids land application sites through three objectives. First, we used column studies to evaluate leaching of PFAS (including precursors) from two biosolids-amended soils immediately following a single biosolids application. Second, numerical modeling was coupled with column data to estimate PFAS transport parameters relevant to biosolids-amended soils. Lastly, transport parameters obtained during Objective 2 and representative of a single biosolids application were used to evaluate leaching long-term leaching of PFAS from biosolids-amended soils under field-relevant conditions.

2. Materials and methods

2.1. Materials and reagents

Two municipal Biosolids (labeled C and E) were obtained from anonymized locations within the state of Minnesota. Both biosolids are from a suite (A-H) collected for a larger research effort, so we are using designations of Biosolids C and E in order to maintain continuity with other studies that may be published using these biosolids. Biosolids were amended into a background agricultural soil sampled from a site in Rosemount Minnesota. Properties of the biosolids and background agricultural soils can be found in the Supporting Information (**Table S1-S2**). Remaining materials are in the Supporting Information (**Section S1, Table S3**).

2.2. Column experiments

Columns experiments were conducted using the background agricultural soil amended with either Biosolid C or E at agronomic rates based on biosolid nitrogen content (**Table S4**). Background soils, biosolids, and biosolids-amended soils were characterized for PFAS and fraction of organic carbon (f_{oc}) prior to column experiments as described below. Each amended soil was air-dried in a fume hood for 2 days and packed in 1 cm increments into duplicate 2.5 × 15 cm glass chromatography columns (Kimble Chase, Vineland, NJ). Clean sand (1 cm) and glass wool were used for bed support and flow distribution of the influent end of the column. Stainless steel mesh, a 1 cm increment of clean sand, and a 2 cm increment of 5 mm glass beads were used as bed support in the effluent end cap. Details of column operation and sampling intervals are provided in the Supporting Information (**Section S2, Table S5**).

2.3. Sample preparation

Aqueous samples were prepared in autosampler vials containing 50 % aqueous sample and 50 % LC-MS grade methanol containing 200 ng/L (targeted analysis) or 667 ng/L (suspect screening) mass-labelled internal standard (IS) mixture (**Table S3**) and analyzed directly via high pressure liquid chromatography quadrupole time of flight-mass spectrometer (HPLC-QTOF-MS). Soils and biosolids were extracted using previously published methodology (Guelfo and Higgins, 2013; Shojaei et al., 2022b; Yang et al., 2023) based on basic methanol extraction (**Section S3.1**). Similarly, the TOP assay (**Section S3.2**) was performed on a subset of aqueous samples and solid extracts prior to targeted analysis to evaluate occurrence of PFAS in samples beyond those that are captured in routine targeted analysis (Houtz et al., 2013; Houtz and Sedlak, 2012; Shojaei et al., 2022b). After oxidation, samples were prepared with 50 % LC-MS grade methanol with 200 ng/L of IS for analysis as described below.

2.4. Analysis

PFAS analysis (targeted and suspect screening) was performed using a HPLC-QTOF-MS (X500R, SCIEX, Framingham, MA, USA). Samples were injected (500 μL) onto a C18 analytical column (Gemini®, 3 μM, 100×3 mm ID, Phenomenex, CA, USA) coupled with a guard column (Gemini®, C18 4 × 2.0 mm ID, Phenomenex, CA, USA) and eluted in 2 mM ammonium acetate solution in ultrapure water and 100 % LC-MS grade methanol. For targeted analysis, multiple reaction monitoring high resolution (MRMHR) acquisition mode was used for sample data acquisition. Two transitions (quantifier and qualifier) were monitored for each compound where possible (**Section S3.3, Table S6**). Target PFAS and their acronyms are in **Table S3**. Suspect screening data was acquired using a data-independent acquisition mode. Additional information regarding chromatographic and mass spectrometer conditions and target and suspect screening data acquisition are available in the supporting information (**Section S3.3**).

Sciex OS (V2.2) was used for data acquisition and processing for both targeted analysis and suspect screening. Target analytes were quantified using isotope dilution over a calibration range of 1–5000 ng/L (R^2>0.99). Suspect screening data was screened using a extracted ion chromatogram (XIC) library containing molecular formulas for 1400+ PFAS (Place, 2021). Of the PFAS in the library, ~320 compounds had MS/MS spectra, which were used in library matching. As in prior work, confidence levels were assigned to PFAS identification using criteria for retention time, isotope radio difference, match to library MS/MS spectra, and Kendrick mass defect (KMD) (Schymanski et al., 2014). Additional information on data processing is provided in the supporting information (**Section S3.4**). Soil and biosolid f_{oc} was determined using a total organic carbon analyzer (Elementar, vario TOC select). Further details of the method for f_{oc} analysis are described in supporting information (**Section S3.5**).

2.5. Targeted analysis quality assurance/quality control (QA/QC)

Soil and biosolid extracts for targeted analysis were prepared and analyzed in triplicates. Concentrations are reported as the average of triplicate analysis. Quality control samples included method blanks, solvent blanks, instrument sensitivity checks, and calibration verification. IS recoveries were used to calculate matrix effects and target analyte losses during extraction. The vial composition of all quality control samples was the same as unknown samples (50/50 water/methanol v/v) Additional information on QA/QC for targeted analysis can be found in the supporting information (**Section S3.6**).

2.6. Suspect screening QA/QC

Quality control measures for initial peak selection and subsequent identification using suspect screening analysis followed methods similar to previous studies (LaFond et al., 2024; Schaefer et al., 2023; Shojaei et al., 2022a,2021). Each analytical batch included at least two solvent blanks (50 % ultrapure water and 50 % methanol). Peaks were only considered for identification if they were present in a minimum of 2 replicates and the response was 10 times higher than the response of the instrument blanks.

2.7. Numerical modeling

HYDRUS 1-D was used to model the column data and obtain rate-limited desorption parameters. Specifically, a 2-site sorption model was selected that assumes a fraction of sorption sites are represented by equilibrium PFAS desorption while another fraction undergoes rate-limited (i.e., non-equilibrium) desorption (**Section S4, Eq. S9–S11**). Sorption distribution coefficients (K_d) were estimated for each PFAS in each soil (**Tables S7**) based on previously reported organic-carbon-water coefficients (K_{oc}) (Campos Pereira et al., 2018; Guelfo et al., 2020) and the f_{oc} of each biosolid-amended soil. Hydrodynamic properties were determined as described above (**Table S5**). Model inversion was used to determine the fraction of sites at equilibrium (f) and rate-limited coefficients (α; h^{-1}). A more detailed description of column modeling methods is in the supporting information (**Section S4**).

2.8. Field-relevant models

Transport simulations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from land-applied biosolids under more field-relevant conditions were set up using HYDRUS 1-D, transport parameters (f, α) obtained from column studies, and variably saturated flow conditions. PFOA and PFOS were selected among studied PFAS based on recent regulatory focus (e.g., maximum contaminant levels, MCLs) (USEPA, 2022) and consideration of these PFAS in the recently published United States Environmental Protection Agency (USEPA)

Draft Sewage Sludge Risk Assessment (USEPA, 2025b). Two scenarios were considered. The first scenario considered a single biosolid application and subsequent PFOA and PFOS leaching over 40 yrs. The second scenario considered PFOA and PFOS transport at a site where biosolids were applied annually for 40 yrs. HYDRUS was used for preliminary simulations to evaluate whether inclusion of air-water interfacial partitioning was critical for understanding porewater concentrations reaching the saturated zone under the conditions modeled. Site characteristics were based on agricultural and soil properties of Renville County, Minnesota (MN), which was selected because in 2023, this county had the biggest production of corn in the state of MN (USDA, 2023). So, these characteristics were considered agriculturally representative for the region where the biosolids were collected. Although all biosolids and agricultural soils used were from MN, it is important to underscore that the location of biosolids collection and sites where Biosolids C and E have been land applied (if any) are unknown. Agricultural vadose zone properties (e.g. soil type, bulk density, depth to groundwater), evapotranspiration, and precipitation for this area were obtained from both USGS and soil survey dataset soil survey dataset (**Table S8, Figure S1)** (Minnesota State Climatology Office, 2025; Soil Survey Staff et al., 2024; USGS, 2025). Additional details of the long-term modeling approach (including K_d, hydraulic conditions, and air-water interfacial parameters) are provided in the Supporting Information (**Section S5, Table S9**).

3. Results

3.1. PFAS in biosolids C and E

The total PFAS composition of Biosolids C and E was established using targeted analysis and the TOP assay. Across both biosolids, 24 PFAS were identified (**Figures S2A-S2B; Table S10**) including C2-C12 PFCAs (2.05×10^{-3} - 9.43×10^{-2} nmol/g), C4-C6, C8, and C10 PFSAs (6.19×10^{-3} - 0.278 nmol/g), C4 and C8 perfluoroalkyl sulfonamides (FASAs, 8.46×10^{-3} - 2.96×10^{-2} nmol/g), 6:2 and 8:2 FTSs (7.77×10^{-4} - 2.36×10^{-3} nmol/g), 5:3 and 7:3 FTCAs (4.16×10^{-3} - 2.99×10^{-2} nmol/g), and Et- and Me-FASAAs (7.77×10^{-4} - 3.84×10^{-2} nmol/g). Importantly, bis-perfluoromethyl sulfonimide (bis-FMeSI) was detected in both biosolids (6.73×10^{-4} - 6.63×10^{-3} nmol/g). This compound is receiving increasing attention for use in lithium ion batteries and international occurrence in water, soil, and sediment (Guelfo et al., 2024). To our knowledge, this is the first published detection in biosolids.

TOP analysis showed that unknown oxidizable precursors (i.e., PFAS not captured during routine, targeted analysis) accounted for 14 and 21 % of total PFAS found in Biosolids C and E ($8.01\times10^{-1} \pm 1.73\times10^{-2}$ and $4.72\times10^{-1} \pm 1.25\times10^{-2}$ nmol/g), respectively (**Table S11, Figure S3A and S3B**). The primary products of the TOP assay were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), and perfluoroheptanoic acid (PFHpA) (**Figure S3C and S3D**). This suggests the unknown precursor fraction is comprised of PFAS that have 1 or 2 alkyl tails (e.g., diPAPs) with 7 fluoroalkyl carbons or less (Houtz and Sedlak, 2012). Notably, a single diPAP, which studies have shown to be prevalent in some biosolids (Kim Lazcano et al., 2019; Lee et al., 2014; Munoz et al., 2022; Schaefer et al., 2023), generates two PFCAs during oxidation. Target PFAS in both biosolids were within the range reported in prior studies (**Section S6, Figure S4**). For example, ∑PFCAs and ∑PFSAs ranges in the US reported in the literature range between 4.98×10^{-2}–4.65×10^{-1} (Schaefer et al., 2023; Thoma et al., 2022) and 3.50×10^{-2}–9.18×10^{-1} nmol/g (Thompson et al., 2023; Venkatesan and Halden, 2013), respectively. Meanwhile, ∑PFCAs and ∑PFSAs concentrations from municipal biosolids from this study ranged 1.39×10^{-1}–2.73×10^{-1} and 1.29×10^{-1}–3.25×10^{-1} nmol/g. This demonstrates applicability of ∑PFAS of biosolids used in this study to other regions and demonstrates the broader applicability of biosolids fate and transport studies presented here.

3.2. PFAS in biosolids-amended soils

Concentrations of PFAS in background agricultural soil and soils amended with Biosolids C and E were evaluated using targeted analysis, TOP assay, and suspect screening. Although PFCAs (C3–C5, C7, C9) and PFSAs (C8) were detected in agricultural soils, concentrations were below quantitation limits and detected in blanks (Flags J and B, **Table S10**) so biosolids were the primary source of PFAS in amended soils. Some PFAS detected in biosolids were not detected in amended soils (e.g., FBSA, FOSA, 6:2 FTS, 8:2 FTS, 5:3 FTCA, and 7:3 FTCA; **Figures S5A and S5B**) because levels were below the limit of detection after dilution of biosolids in amended soils. Except as noted, PFAS were detected in amended soils at levels lower than concentrations in the source biosolids (**Figures S6A and S6B**), as expected based on addition into unimpacted background soils. TOP assay results demonstrated that unknown precursors accounted for 21 and 17 % of total PFAS in soils amended with Biosolid C and E, respectively (Fig. 1**A; Figure S7A**). Although application rates will vary based on nutrient levels (USEPA, 1994), concentrations observed here in amended soils provide insights into PFAS levels, including concentrations of unknown, oxidizable precursors, that can be anticipated following a single biosolids application into unimpacted soils. These concentrations are compared to prior assessments of biosolids amended soils in the Supporting Information (**Section S6.2**).

3.3. Suspect PFAS occurrence

Suspect screening was performed on biosolids and biosolid-amended soils to elucidate the composition of the unknown PFAS concentration measured by TOP assay. Based on peak-screening criteria (**Section S3.4**), 7 suspect PFAS were annotated in Biosolid C and Biosolid C-amended soil and 5 were annotated in Biosolid E and Biosolid E-amended soil (**Table S12-S13**). 6:2 diPAP, 8:2 diPAP, 8:2/6:2 diPAP, 6:6 perfluorophosphinic acid (PFPiA), and perfluoroethanoic acid (PFEtA) were detected in both biosolids and/or their amended soils. 6:8 PFPiA and oxa-perfluorohexanane sulfonate (O-PFHxS) were detected only in Biosolid C or E, respectively. In Biosolid E, more suspect PFAS were detected in biosolids vs. amended soils, which is consistent with lower concentrations following addition of biosolids into unimpacted soils. Conversely, Biosolid C-amended soil had detection of suspect PFAS not originally detected in the biosolid (e.g. 8:2-, and 6:2/8:2 diPAP, PFeTA, 6:6 PFPiA), which may be attributable to a matrix effect (i.e., signal suppression) in Biosolid C extracts or instrumental variability. TOP assay data did not suggest significant presence of unknown precursors in the background agricultural soil, so these PFAS were introduced through the source biosolids. Uses and prior occurrence of these PFAS is discussed in the Supporting Information (**Section S6.4**), and occurrence of suspect PFAS in post leaching soils is further discussed below (**Column mass balances, Section S6.5**).

3.4. Column mass balances

Column mass balances were calculated by comparing pre-leaching PFAS masses in biosolids-amended soil to the sum of PFAS recovered in column eluates and post-leaching biosolids-amended soils (Figs. 1A, **S7A and Tables S14, S15**). Compared to pre-leaching soil, total PFAS recovery in column eluates plus post-leaching soils amended with Biosolid C was 111 % (Fig. 1A, **Table S14**). This included recoveries of 98 % for PFCAs, 72 % for unknown precursors, and 133 % for PFSAs. Similarly, recovery of total PFAS in Biosolid E-amended soil was 99.6 % (**Figure S7A, Table S15**) including recovery of 119 %, 88 %, and 62 % for PFCAs, unknown precursors, and PFSAs, respectively. Pre-leaching PFSA concentrations exhibited a high standard deviation (**Table S15**), which likely explains the apparent under recovery in Biosolid E column mass balances. Within individual PFAS, there were some mass balance over recoveries (**Section S6.7**), but overall, column mass balances were

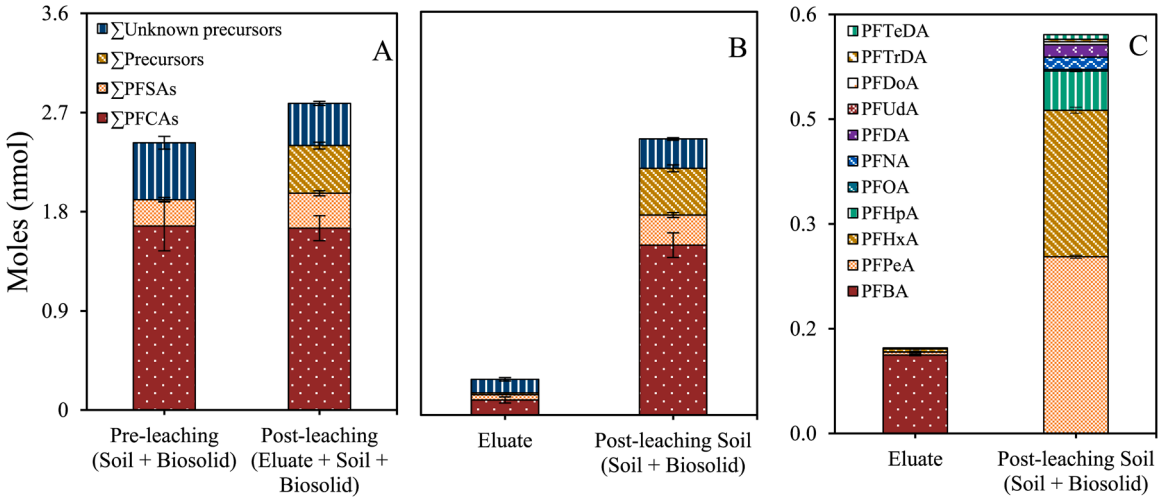


Fig. 1. Mass balance results for columns with Biosolid C-amended soil. Total PFAS mass in soil amended with Biosolid C (i.e., pre-leaching soil) and total PFAS mass recovered in eluates plus post-leaching soils (A). Total PFAS recovered in column eluates and post leaching soils (B). Total molar increases in PFCAs in eluates and post-leaching soils (C).

excellent and validated column experimental methods and results.

PFAS mass recovered in column eluates vs. post elution soils provides qualitative insights into PFAS fate in biosolids-amended soils (Fig. 1**B, Tables S14-S15)**. In both biosolids-amended soils, the majority of total PFAS (98 % in Biosolid C-amended soil and 81 % in Biosolid E-amended soil) remained in post-leaching soils. This included 86 % (Biosolid E-amended soil) to 92 % (Biosolid C-amended soil) of total PFCAs, 71 % (Biosolid E-amended soil) to 85 % (Biosolid C-amended soil) of total PFSAs, and 59 % (Biosolid E-amended soil) to 71 % (Biosolid C-amended soil) of total unknown precursors (Figs. 1B and **S7B, Tables S14-S15**). Although the majority of PFCAs were retained in both biosolids-amended soils, they were still the most mobile fraction of PFAS comprising 44 % (Biosolid C-amended soil) to 86 % (Biosolid E-amended soil) of the total PFAS mass eluted. PFSAs were the least mobile fraction in each amended soil. Only 16 % leached from soils amended with both Biosolid C and E. This is consistent with higher overall mobility of PFCAs relative to other homologous series of PFAS (e.g., PFSAs) noted in prior studies (Fabregat-Palau et al., 2021; Guelfo and Higgins, 2013; Hunter Anderson et al., 2019; Shojaei et al., 2021).

Precursor mass balances were calculated ate the sum of target precursors, unknown precursors by TOP assay in eluates, and unknown by TOP assay in post-leaching soils, and they demonstrated that 83 % (Biosolid C-amended soil) and 69 % (Biosolid E-amended soil) were retained in post-leaching soils. Importantly, of these fractions, 43 % and 50 % of retained precursors were unknown precursors in soils amended with Biosolids C and E, respectively. Following the TOP assay, PFBA was the dominant product (>90 % of oxidizable precursors) generated by TOP assay in eluants from both biosolids-amended soils (Figs. 1C and **S7C**). In contrast, increases in C5-C11 carboxylates were observed post-leaching soil, implying oxidation of precursors with higher chain length. These patterns are consistent with higher mobility of short-chain precursors and retention of longer-chain precursors during leaching of PFAS from biosolids-amended (Tsou et al., 2023). Suspect screening analysis of post-leaching soils yielded varied results, which is further discussed in the Supporting Information (**Section S6.5**). Regardless, TOP assay and limited suspect screening results highlight high retention of biosolids-relevant precursors, although as noted transformation products may be more mobile.

3.5. PFAS column breakthrough curves (BTCs) and modeling

Consistent with prior studies of PFAS transport, eluant breakthrough curves exhibited chain-length dependent transport in soils amended with Biosolids C and E (Fig. 2, **Tables S16 and S17**) (Gellrich et al., 2012; Guelfo et al., 2020; Sepulvado et al., 2011; Stahl et al., 2013; Vierke et al., 2014; Weidemann et al., 2022). Specifically, lower sorbing, short-chain PFAS (e.g., PFBA) eluted earlier than stronger sorbing, long-chain PFAS (e.g., PFOA; Fig. 2). Similarly, PFCAs exhibited earlier breakthrough than PFSAs of the same chain length (**Figure S8A**). As mentioned, bis-FMeSI was detected in Biosolids C and E. Bis-FMeSI breakthrough curves and modeling demonstrated that this compound has similar mobility as PFBS (**Figure S8B**). This is notable because prior work suggested that bis-FMeSI has characteristics similar to PFBS, which has been designated as very persistent and very mobile (vPvM) in the European Union (Guelfo et al., 2024). However, this is the first study to confirm bis-FMeSI transport properties in laboratory studies.

As noted above (see **Column Mass Balances**), TOP assay results for column eluants confirmed mobilization of unknown precursors in column leachate (**Figure S9**). Unknown precursor elution fluctuated over time, which may result from elution of different-sized precursors (**Figure S9**). As noted**,** studies have found that precursors may undergo rapid transformation (~1 yr) following land application, and our results demonstrate that a large fraction of this mass will be retained in biosolids-amended soils. However, these results confirm that, as observed in prior work (e.g., Schaefer et al., 2022a), some mobilization of precursors can occur prior to transformation.

HYDRUS 1-D was used to fit measured column data and determine rate-limited transport parameters (f, α) that describe PFAS breakthrough in soils amended with Biosolids C and E (Figs. 3 and **S10, Table S18**). Based on preliminary modeling, fitted models used values of K_d calculated from literature-determined K_{oc} values and the f_{oc} of the biosolids-amended soils (2.8 % and 2.6 % for soils amended with Biosolids C and E, respectively) and not the f_{oc} of the biosolids in which the PFAS originated (**Figure S11**). Model performance was evaluated based on R^2 values calculated by HYDRUS 1-D (**Table S19-S20**). Values of R^2 were $\geq$ 0.80 for all PFAS except PFNA (0.08) and FOSA (0.19) in soils amended with Biosolid C and PFNA (0.06), PFOS (0.67), and FOSA (0.23) in soils amended with Biosolid E. Poorer fits for PFNA and FOSA in both amended soils are likely attributable to analytical variability since measured concentrations were near the LOQ (1–10 ng/L) (**Figures S10G-H** and **M-N, Tables S16-S17**). Concentrations near the LOQ are related to both the initial concentrations in biosolids-amended soil and to factors controlling desorption, which are further discussed below.

Similar to prior work with PFAS-impacted soils, column elution of PFAS from biosolids-amended soils was best described using rate-limited

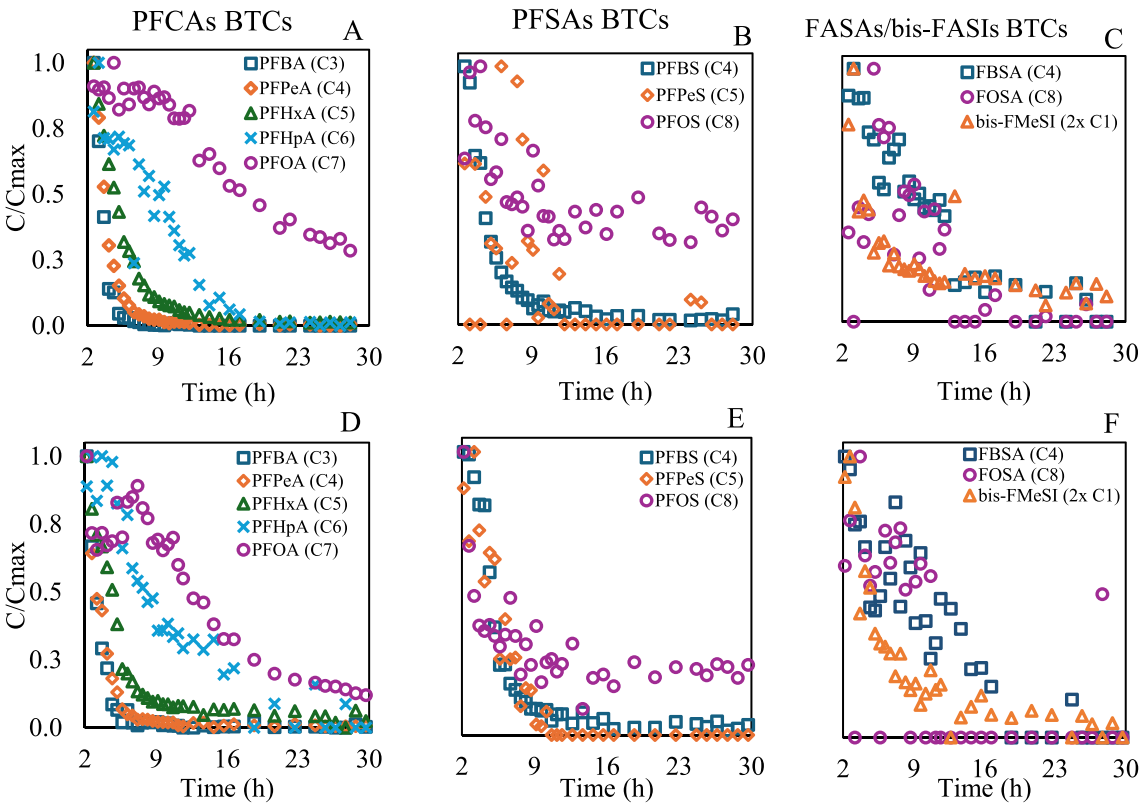


Fig. 2. BTCs for representative PFAS eluted in columns with Biosolid E-amended soils (A to C) and Biosolid C-amended soil (D to F) including PFCAs (A and D), PFSAs (B and E), and FASAs/bis-FASIs BTCs (C and F). Individual concentrations are summarized in Tables S16 and S17.

desorption models (Bierbaum et al., 2023a; Guelfo et al., 2020; Stults et al., 2025, 2024). Two transport parameters describing rate-limited desorption (f, α) were obtained from model fits for most PFAS. A third parameter (K_d) was obtained for a limited number of PFAS where literature K_{oc} results in biosolids-amended soils were limited or not available for calculating K_d (bis-FMeSI, FBSA, FOSA) (**Table S18**). To our knowledge these are the first reported rate-limited parameters for PFBA, FBSA, FOSA, and bis-FMeSI (**Table S18**). For remaining PFAS modeled, f values obtained from model fits were within those previously reported in the literature, with the exception of PFHxA (**Table S18**) (Bierbaum et al., 2023a; Guelfo et al., 2020; Schaefer et al., 2022b,2021; Stults et al., 2024). Values for PFHxA (0.20–0.35) were slightly lower than previously reported (0.53–0.83). Regardless, results here and in the literature highlight variability in this parameter across studies. For example, values reported from PFOS vary from essentially zero (as observed here) to 0.93 (Bierbaum et al., 2023a). In prior studies, variations of f for a single compound were attributed to differences in organic matter content (Brusseau et al., 2019; Schaefer et al., 2022b). Similarly, previous studies discussed the relationship between sorbate hydrophobicity and rate-limitations, where a higher degree of hydrophobicity leads to higher level of rate-limitation (Bierbaum et al., 2023a; Guelfo et al., 2020; Schaefer et al., 2021).

Based on trends in hydrophobicity with f, we might anticipate a decrease in f with increasing compound chain length within homologous series. There were no clear trends in f with chain length in soils amended with either biosolid (**Table S18**); however, there is still evidence for the influence of hydrophobicity. Overall, the lowest values of *f* were observed for PFOS, which was one of the most hydrophobic PFAS measured in column eluants. Key exceptions in values of *f* were observed for PFBA (f of 0.007 and 0.04 in soils amended with Biosolids C and E, respectively). This may be attributable to multiple factors. First, values of K_d used here were calculated based on K_{oc} values from the literature. If these values are different from the "real" K_d values that describe desorption of PFAS from study soils, this would influence fitted values of *f*. Second, trends in *f* may be convoluted by the number and/or type of sorption sites available to each PFAS. For example, if PFBA can access an increased fraction of smaller pore space in soils, then it may have more overall sites available for sorption and a high fraction that are described by rate-limited desorption based on mass transfer limitations from smaller, deeper pore sizes. These results demonstrate that while there is an increased conceptual understanding of factors that impact f, more studies are needed to develop predictive tools that will facilitate estimation of f based on compound and soil properties. As discussed in the Supporting Information (**Section S6.12**), transport models are sensitive to this parameter, so currently, site-specific values may be needed for the most representative estimates of leaching, particularly where short-term mobility is of concern.

Prior studies have found that α is influenced by multiple factors including sorbate and sorbent hydrophobicity, molecule structure, shape, and size, and pore-water velocity (Brusseau et al., 1991a; Brusseau, 1992; Piatt and Brusseau, 1998). As with f, trends in α with chain length were unclear. However, for each PFAS, values of α were within an order of magnitude for Biosolid C- and Biosolid E- amended soils with the exception of PFNA (**Table S18**). Similarities in transport across both biosolids-amended soils is further discussed below.

Differences between α values observed here and those in prior studies (**Table S18**) suggest trends with pore-water velocity. For example, in this study α values at a pore-water velocity of ~0.09 cm/min for PFOA (9.37×10^{-3} - 1.18×10^{-2} hr^{-1}; **Table S18,** Fig. 3**C-D**) and PFOS (1.08×10^{-3} - 1.83×10^{-3} hr^{-1}; **Table S18,** Fig. 3**E-F**) were an order of magnitude higher than those previously reported (3.00×10^{-4} - 4.17×10^{-4} hr^{-1} for PFOA, 2.10×10^{-4} hr^{-1} for PFOS) in saturated columns at a lower pore-water velocity of ~0.001 cm/min (Bierbaum et al., 2023a; Guelfo et al., 2020). Additionally, values of α for PFOS were lower than those previously reported (7.70×10^{-1} - 9.00×10^{-1} hr^{-1} for PFOS) in saturated columns at a higher pore-water velocity of ~0.1

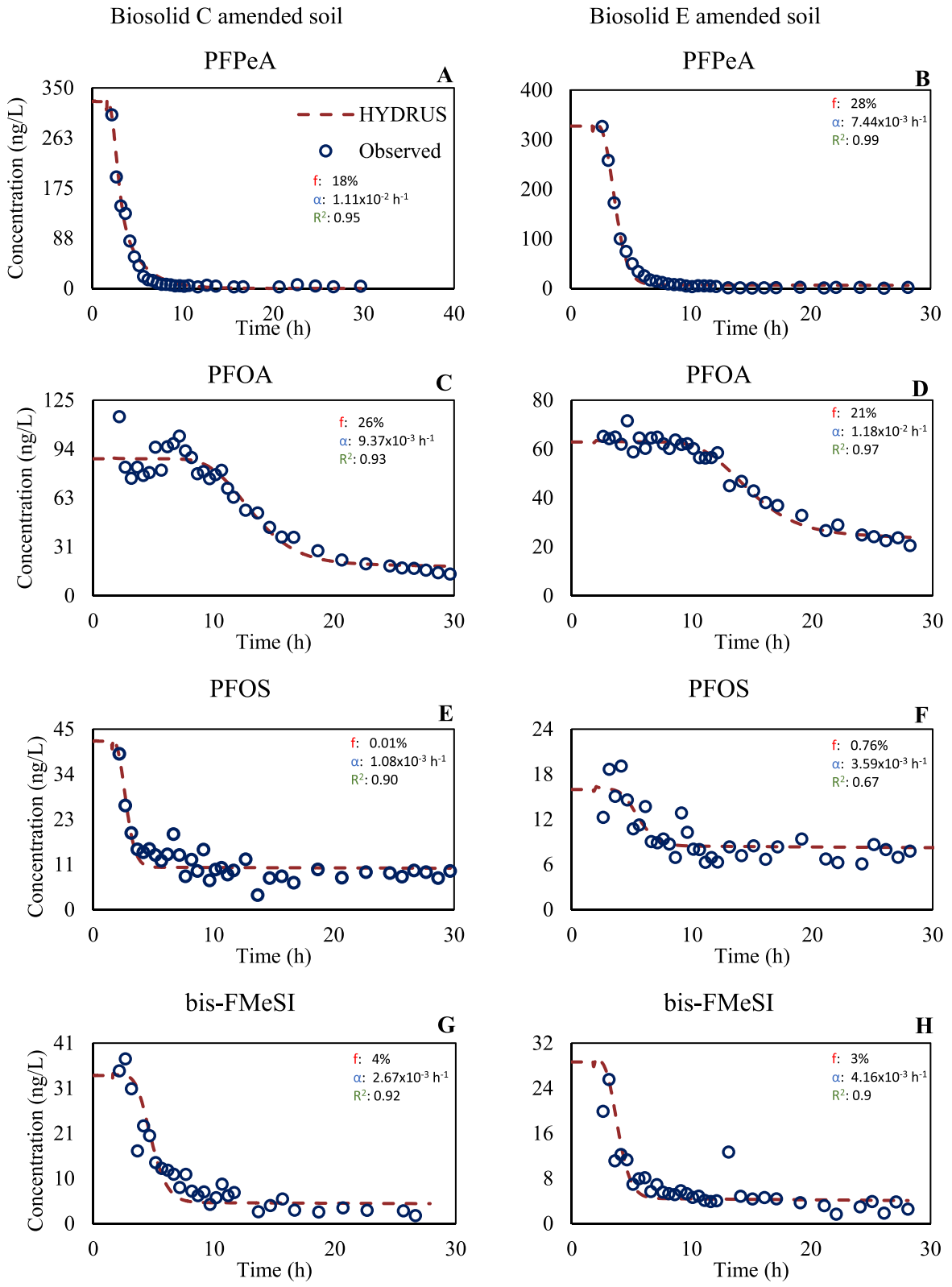


Fig. 3. Measured breakthrough for select PFAS vs. breakthrough modeled with rate-limited desorption parameters (f, α) obtained using HYDRUS 1-D. Data are shown for PFPeA, PFOA, PFOS, and bis-FMeSI in soils amended with Biosolid C in the left column (A, C, E, G) and in soils amended with Biosolid E in the right column (B, D, F, H).

cm/min (Brusseau et al., 2019; Nguyen et al., 2022). These data suggest that values of α increase, or are faster, with increasing porewater velocity, as has been seen for other classes of contaminants (e.g., 1, 4-dichlorobenzene, naphthalene) (Abgaze and Sharma, 2015; Brusseau, 1992; Maraqa et al., 2011; Zhang et al., 2021).

Fully elucidating the cause of trends in α with porewater velocity is beyond the scope of this study, but prior work offers insights. Observations have been attributed to a time scale effect (i.e., experimental duration) (Brusseau, 1992). Additionally, higher velocities, imply faster diffusion of chemicals out of the immobile domain (lower times), and increased magnitudes of α (Rao et al., 1980; Van Genuchten and Wierenga, 1977). Further, these trends have been attributed to velocity-dependence of solute diffusion through the organic carbon matrix (Brusseau, 1992; Brusseau et al., 1991a, 1991b, 1989; Brusseau and Rao, 2015; Nkedi-Kizza et al., 1989). Regardless of mechanism, it is clear that extrapolation of α from column experiments to transport in field scenarios is complicated by changes with porewater velocity. Here we have applied values of α to field transport scenarios that are based on variably saturated flow, which overall represents a slower range of porewater velocities than used in column experiments. While this may overestimate PFAS concentrations and mass transport, these values are considered the best available.

BTCs across both biosolid-amended soils followed similar trends and timing (**Figure S12 A-D**), implying similarities in transport mechanisms influencing PFAS transport in both soils. To further explore this, fitted parameters (f and α) from columns with Biosolid E-amended soil were used to predict (i.e., forward model) BTCs from columns with Biosolid C-amended soil (Fig. 4A-D). Results showed that transport parameters obtained from PFPeA and PFOA BTCs in soils amended with Biosolid E led to good predictions (R^2>0.9) of BTCs for the same PFAS in soils amended with Biosolid C. Prediction of PFBS and PFOS transport was not as good (R^2<0.7), but visual inspection shows that predicted transport is reasonable. Additionally, these parameters were only able to achieve an R^2 of 0.67 in columns with Biosolid E-amended soil (i.e., the soil from which they were obtained as fitted parameters). A key implication of these results is that PFAS transport in single-application scenarios may be understood based on PFAS concentrations in biosolids amended soil and hydrogeological characterization of the background soil. Though it merits evaluation in additional biosolids and background soils, the nature of the biosolid (e.g., organic carbon content, moisture content) appears to have minor impact on PFAS transport. Note that overall sensitivity of model fits to values of f and α as well as the literature K_{oc} values selected for use in this study are further assessed in the Supporting Information (**Section S6.12** and **Figures S13 A-I**).

3.6. Long-term modeling

Transport parameters obtained for PFOA and PFOS from column data were applied in forward simulations to understand mobility in agricultural settings under two biosolids application scenarios. The first scenario considered a one-time application of Biosolid E at a 1 % rate to elucidate transport of PFOA and PFOS for 40 yrs after a single application. Air-water interfacial partitioning was not considered in these simulations based on the outcomes of preliminary screening which demonstrated a negligible effect on porewater concentrations of PFOS reaching the top of the saturated zone under the conditions modeled (**Section S6.14, Table S22, Figures S14A-S14B**). After one year, the maximum groundwater concentrations of PFOA and PFOS were 106 and 48.9 ng/L at depths <15 cm (i.e., the tilling zone; Figs. 5**A-5B**). After 40 yrs, maximum concentrations were 7.37 and 6.32 ng/L at depths of 1509 and 266 cm for PFOA and PFOS, respectively. Greater depth of penetration of PFOA is consistent with lower K_{oc} and lower fraction of non-labile (i.e., 1-f) mass (**Table S18**). The concentration of PFOS at the top of the saturated zone (1525 cm) was < 1ng/L; however, concentrations of PFOA predicted to reach the top of the saturated zone exceeded the MCL (Figs. 5**A-5B**). Greater penetration of PFOA vs. PFOS was also observed in previous modeling of biosolids-amended soils (Silva et al., 2022), and overall these trends are consistent with prior

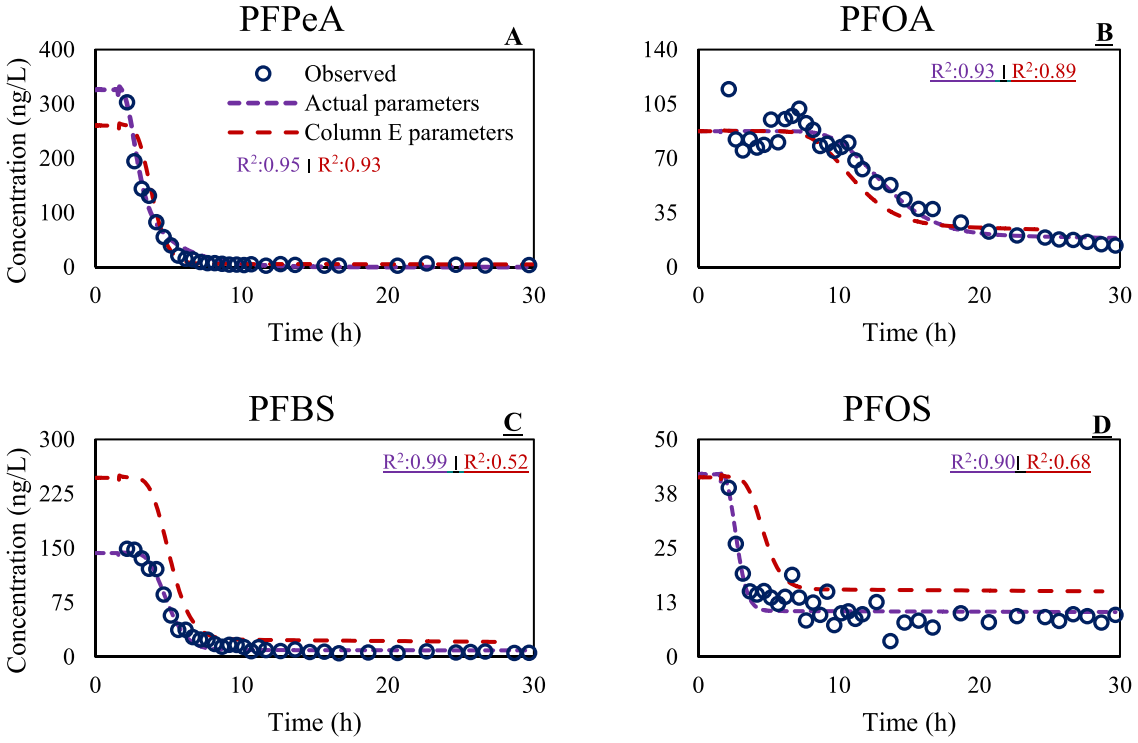


Fig. 4. Measured breakthrough for select PFAS from soils amended with Biosolid C vs. breakthrough modeled with rate-limited desorption parameters (f, α) based on fitting from soils amended with Biosolid C (purple) and Biosolid E (red) obtained using HYDRUS 1-D. Data are shown for PFPeA (A), PFOA (B), PFBS (C), and PFOS (D). Purple R^2 are fits achieved by model inversions to BTCs in Biosolid C-amended soil and red R^2 are fits achieved by predicting breakthrough in Biosolid C-amended soil with transport parameters from Biosolid E-amended soil. Transport parameters (f, α) for each biosolid-amended soil are in Figs. 3, S10, and Table S18.

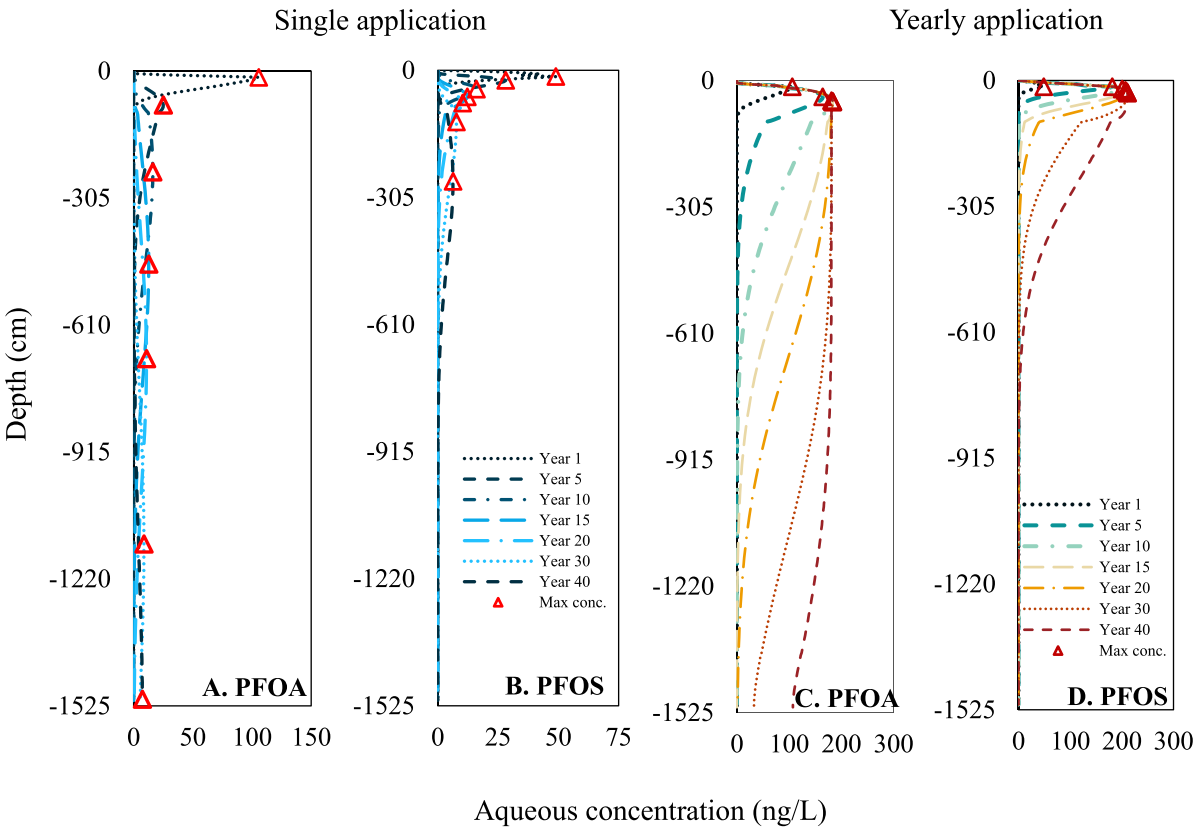


Fig. 5. Forward modeling results for PFOA (A, C) and PFOS (B, D) transport in the vadose zone following two biosolids application scenarios in the top 15.4 cm. Scenario 1 (A-B) shows aqueous PFAS concentrations in the unsaturated zone for 40 yrs following a single application of Biosolid E. Scenario 2 (C-D) shows PFAS concentrations in the unsaturated zone for 40 yrs of annual biosolids applications. Note that the full depth to groundwater (1525 cm) is not shown because concentrations are ~0 ng/L at these depths across all scenarios and that the y-axis scales of A-B differ from C-D.

modeling of PFAS transport in impacted soils (Guo et al., 2022). Lastly, these results are similar to a field study that indicated concentrations of PFOA and PFOS in shallow groundwater (2 m below ground surface) were in the low parts per trillion (e.g., <2.5 ng/L) ~1 yr after application (Gottschall et al., 2017).

In the second biosolids application scenario, land application occurred annually for 40 yrs at the same rate (i.e., a worst-case scenario) leading to higher predicted concentrations of PFAS penetrating to greater depths. For example, the maximum predicted concentration of PFOA (184 ng/L), which extended to depths of ~500 cm was 26x higher than the concentration at that same depth 40 yrs after a single application (Fig. 5**C**). Similarly, the maximum concentration of PFOS at 267 cm (105 ng/L) after 40 yrs of continuous application was 17x higher than the concentration observed at the same depth 40 yrs after a single application (Fig. 5D). At the top of the saturated zone (1525 cm below ground surface), the predicted concentration of PFOA was 107 ng/L after 40 annual biosolids applications; however, PFOS concentrations were <1 ng/L, implying little to no contamination of the saturated zone. Another recent study observed up to 73 % attenuation of total PFAS by a depth of 183 cm below ground surface in soils with a ~35 yr history of Class B biosolids application (Pepper et al., 2021). Although conditions of this prior study (semi-arid) are not equivalent to those used in our work, both studies demonstrate that groundwater impacts may not always be the primary concern for PFAS in biosolids. Whereas PFOA concentrations reaching the saturated zone are concerning, particularly for the worst-case scenario of annual application, predicted PFOS impacts to the saturated zone are minimal.

There are important limitations in applying modeling results shown here to other biosolids application sites. Many variables will change between sites including PFAS concentrations in biosolids, annual application rates, years of application, precipitation, evapotranspiration, use of irrigation, subsurface geochemistry, and depth to groundwater. Results discussed above did not consider evapotranspiration, so they may overestimate the depth of contaminant leaching, particularly for PFOA. Long-term modeling of the annual application scenario that included regional evapotranspiration data (**Table S8**) (Minnesota DNR, 2025), showed PFOA and PFOS retention at depths shallower than ~600 cm, and reduced predicted PFOA concentrations at the top of the saturated zone to < 1ng/L (**Figures S15A-B**).

Additionally, while model scenarios here used variably saturated water flow, based on initial screening they did not consider PFAS partitioning to the air-water interface, which in our screening models primarily impacted the shallow porewater concentrations (**Figures S14A-B**) and is most applicable to longer chain PFAS (e.g., PFOA, PFOS) (Stults et al., 2024). Notably, however, studies have also found that this mechanism is not critical for predicting long-term PFAS leaching (Stults et al., 2024), and that high levels of saturation applicable at many biosolids application sites (e.g., due to irrigation or high precipitation) may eliminate the need to consider it, particularly in screening-level evaluations (Silva et al., 2022). Models here also do not consider heterogenous subsurface geology, which can significantly increase or decrease contaminant migration towards the saturated zone (Brusseau, 1994; Jardine et al., 1993; Mousavi Nezhad et al., 2011; Silva et al., 2022). For example, prior studies have concluded that preferential flow pathways may accelerate PFAS migration through the vadose zone to the saturated zone by as much as 19 years (Zeng and Guo, 2021). Increased vadose zone mobility of PFOS resulted from greater advection, dispersion and lower retardation due to decreased access of PFAS to air-water interfaces as a result of increased water saturation within the vadose zone surrounding the preferential flow path. This implies that incorporation of

preferential flow into the modeling scenarios in this study could increase the PFAS concentrations in porewater at the top of the saturated zone.

Lastly, our long-term models do not consider precursor transformation. Precursor analysis of our column data indicated that only 17 - 28 % of precursors were mobilized with water infiltration, suggesting the potential for high retention in the shallow vadose zone in field scenarios. As noted above, precursor transformation to more mobile intermediate PFAS and terminal PFAAs may occur rapidly (~1 yr) following biosolids application (Lee et al., 2014; Liu and Liu, 2016; Schaefer et al., 2022a). Our long-term models do not consider generation of PFCAs or PFSAs as a result of precursor transformation in the shallow vadose zone.

4. Discussion

Occurrence results demonstrated that PFAS concentrations in Biosolids C and E are representative of those reported in prior studies (Link et al., 2024; Oviedo-Vargas et al., 2025; Schaefer et al., 2023; Sepulvado et al., 2011; Thoma et al., 2022), so results in this study have implications for the broader practice of land applying biosolids. At least 8 states in the US have established regulatory criteria for PFOA and PFOS in biosolids (Izuegbunam, 2025). For example, Minnesota is implementing an annual biosolid testing requirement and a tiered-based approach where required actions depend on concentrations of PFOA and PFOS in biosolids (**Section S6.13, Table S21**) (MPCA, 2025). Based on this guidance, Biosolid C would be a Tier 4 biosolid because the PFOS concentration (138.7 ± 5.0 ng/g) exceeds 125 ng/g, and further land application would not be allowed. Biosolid E would be a Tier 2 biosolid because PFOA (16.3 ± 1.4 ng/g) and PFOS (49.4 ± 3.8 ng/g) are within 21- 50 ng/g, and land application would be allowed. Long-term modeling scenarios support that continued application of Biosolid E poses low risk for impacts to the saturated zone.

In addition to state-level regulations, the USEPA recently issued a risk assessment for PFOA and PFOS in sewage sludge (USEPA, 2025b). Importantly, the USEPA document is not intended to establish regulatory criteria and focuses on risks to the farmer and those nearby (USEPA, 2025b). The assessment included estimated groundwater concentrations (1240 cm below surface) of PFOA and PFOS resulting from a 1 ng/g loading (2.42×10^{-3} and 2.00×10^{-3} nmol/g for PFOA and PFOS, respectively) using best-case (i.e., high) K_{oc} values of 1100 L/g for PFOA and 22,000 L/g for PFOS and worst case (i.e., low) K_{oc} values of 26 L/g for PFOA and 220 L/g for PFOS (K_d was estimated for both PFOA and PFOS based on a 1.5 % f_{oc}). The USEPA assessment considered solute transport from a finite source with equilibrium linear partitioning. These scenarios resulted in estimated groundwater concentrations of 0.12 ng/L - 4.5 ng/L for PFOA and 2×10^{-5} ng/L - 0.98 ng/L for PFOS after 40 annual applications of 0.10 g/cm^2, suggesting that these conditions could lead to groundwater concentrations in excess of MCLs.

Long-term modeling here used higher biosolid application (0.15 g/cm^2 of Biosolid E; **Table S4)**, higher PFOA and PFOS concentrations in biosolids (16.3 and 49.3 ng/g, respectively), and greater values of infiltration (2.77×10^{-3}–1.60×10^{-2} cm/hr vs. 2.29×10^{-4}– 1.75×10^{-3} cm/hr used by USEPA). K_{oc} values used here were between the USEPA worst- and best-case scenarios (200 L/g for PFOA and 631 L/kg for PFOS; **Table S7**,). Despite the relatively more aggressive (i.e., worst-case) conditions used here, the long-term modeling results for PFOS (<1 ng/L at depths below ~815 cm) were similar to USEPA best case scenario (2×10^{-5} ng/L). This may be due to USEPA's use of an equilibrium sorption assumption for a considerably rate-limited compound (i.e. PFOS), which can lead to higher predicted aqueous concentrations (**Figure S16A-B**). Rate-limitation implies a time dependent release that delays mass release relative to equilibrium transport. Additionally, it is important to note that an equilibrium assumption may underestimate the duration of exposure, since it will not capture the long-term leaching of low-level concentrations. If the latter occurs at concentrations above regulatory levels (e.g., MCLs), then use of an equilibrium scenario should not, by default, be considered the "worst-case" scenario. We also note that using conditions modeled here, the biggest impacts of rate-limited desorption on PFOS mobility were observed in porewater concentrations just below the bottom of the biosolids application layer (depth of ~15.24 cm; **Figure S16B),** and concentrations at depths below 300 cm were essentially the same under equilibrium and rate-limited conditions (**Figure S16B**). More details about the significance of rate-limited transport are in the Supporting Information (**Section S6.14, Table S23**).

Unlike PFOS, modeled PFOA porewater concentrations at the top of the saturated zone after 40 yrs of application (107 ng/L) were higher than those in the USEPA worst-case (i.e., low K_{oc}) assessment (4.5 ng/L). This is likely due to USEPA's use of a constant f_{oc} with depth. Studies have shown that soil f_{oc} rapidly decreases with depth, reaching minimum values (<1 %) in the first 100–200 cm below ground surface (Hobley and Wilson, 2016), and this is also consistent with soil survey data for our study region (**Figure S1**). Overestimation of f_{oc}, and thus K_d, would cause underestimation of porewater PFAS concentrations and depth of leaching, particularly for comparatively labile compounds, such as PFOA.

Regardless, both equilibrium and rate-limited modeling highlight occurrence of higher PFAS porewater concentrations in the shallow vadose zone. This increases the potential for uptake of porewater PFAS by plant roots, which might be reduced through use of stabilization techniques in biosolid-amended soils. Biochar (Barth et al., 2021; Garg et al., 2023; Sørmo et al., 2021; Zhang and Liang, 2022a, 2022b), activated carbon based materials (granulated, colloidal, powdered) (Barth et al., 2021; Navarro et al., 2023; Shin and An, 2025; Zhang and Liang, 2022a), clay based sorbents (Barth et al., 2021; Jiang et al., 2023) are among the PFAS stabilization agents currently being evaluated for use in biosolids-amended soils. As an added benefit, stabilization would also reduce PFAS mobilization towards the saturated zones, which could be critical for more mobile constituents such as PFOA.

In all, model results here highlight that it is difficult to make broad generalizations regarding the risk of PFAS in land-applied biosolids, and, as noted in prior studies, site-specific considerations are beneficial (Pepper et al., 2023). For example, arid and semi-arid climates might decrease the risk of PFAS mobility while humid conditions (as presented by this study) might promote it. Similar to our long-term modeling results, prior studies have found concentrations of PFOA in groundwater that exceed European regulatory limits after 40 yrs of application (Alvarez-Ruiz et al., 2024). However, results presented here also suggest that the soil to groundwater pathway will not be the only (or even primary) pathway of concern for all PFAS at all sites. Exposure via pathways that involve surficial soil or shallow porewater may be of greater overall concern at some land application sites. Critically, this may include exposure via plant uptake of porewater PFAS or, as noted in a recent study (Peter and Lee, 2025), exposure to PFAS inputs to surface water via tile drainage.

5. Conclusions

This study presents results of saturated column experiments using an agricultural soil amended with two biosolids. Column experiments were modeled using a 2-site, rate-limited model and resulting parameters were used to model two long-term (e.g., 40-year) field-scale scenarios. Results from this study add to the current understanding of PFAS fate and transport following land application of municipal, wastewater biosolids. The work presented here demonstrated the following key results:

- Following amendment of Biosolids C and E, PFAS concentrations of 1.83×10^{-2} - 2.37×10^{-2} nmol/g were observed in biosolids-amended soils, and this is representative of PFAS concentrations that may be observed immediately after a single application of a typical, municipal biosolid. Further, upon application, a significant fraction

of this mass (21 - 25 % in this study) was comprised of precursors with potential to transform into PFAAs.

- To our knowledge, this study is the first to demonstrate occurrence of bis-FMeSI in municipal biosolids (6.73×10^{-4}–6.63×10^{-3} nmol/g), which underscores the results of an increasing number of studies highlighting environmental concerns about this relatively unstudied, lithium-ion battery associated PFAS.
- Mobility of PFAS in column studies exhibited the same trends observed in column studies of other types of PFAS-impacted soil (e.g., manufacturing, firefighting foams). This includes chain-length dependent transport, and greater mobility of PFCAs relative to PFSAs of the same chain length. Studies suggest that transformation of a large fraction of unknown precursors in biosolids will occur within 1 yr of application, but only a few studies have investigated the potential for precursor transport before transformation (i.e., immediately following land application). This study supports limited prior work that demonstrates some unknown precursors are mobilized upon land application of biosolids, but the majority (58–68 %) are retained in shallow soil.
- As in other types of PFAS-impacted soils, consideration of rate-limited sorption/desorption processes was needed to model release and retention of PFAS in biosolids-amended soils. Specifically, PFAS mass was divided between a mobile (or labile) fraction controlled by equilibrium sorption-desorption and a non-labile fraction controlled by rate-limited sorption-desorption. Rate-limited transport parameters (f, and α) suggested that the fraction of sites represented by equilibrium sorption (f) was lowest for more hydrophobic PFAS (e.g., PFOS), and when compared to other studies, there is evidence to support an increase in α with decreasing porewater velocity. This highlights that these transport parameters will be specific to the individual PFAS, soil characteristics (e.g., f_{oc}), and infiltration rates relevant to specific land application sites.
- Mobility of PFAS in soil amended with two different biosolids could be described by the same transport parameters (K_{oc}, f, and α) despite the application of biosolids with different properties (e.g., organic carbon content, PFAS concentrations). Thus, single application scenarios, these results suggest the background soil and water flow properties, and not the properties of the biosolid, will govern PFAS transport. By extension, this suggests PFAS transport in single application scenarios may be understood based on PFAS concentrations in biosolids-amended soil and hydrogeological characterization of the background soil.
- When modeling parameters obtained from column studies were extended to long-term modeling of PFOS under field-relevant conditions, incorporation of air-water interfacial partitioning decreased contaminant downward migration, while increasing accumulation in shallow-soil. However, this did not meaningfully impact long-term predictions of PFOS porewater concentrations reaching the saturated zone.
- For PFOA, long-term modeling showed differences in porewater concentrations reaching the saturated zone 40 years after a single application (7.37 ng/L) and after 40 yrs of annual applications (107 ng/L), although in both cases predicted porewater concentrations of PFOA at the top of the saturated zone exceeded the USEPA MCL. However, these concentrations were reduced to <1 ng/L at the top of the saturated zone when evapotranspiration was considered. This highlights that leaching of more mobile PFAS will be highly dependent on infiltration rates. Further, while the soil to groundwater pathway may not be a concern at all sites, risk resulting from exposure to groundwater impacted by PFAS containing biosolids cannot universally be excluded.
- Unlike PFOA, PFOS porewater concentrations were <1 ng/L at the top of the saturated zone in both long-term modeling scenarios. This this further underscores that the soil-to-groundwater pathway will not be the primary exposure route of concern for all PFAS or at all sites. Instead, other routes involving shallow surficial soil and porewater including plant uptake, runoff, and tile drainage, should also be considered in field-based risk assessments.
- Differences between equilibrium transport and 2-site transport models demonstrated the impact of rate-limited sorption-desorption in PFOS leaching from biosolid-amended soils. Whereas equilibrium transport predicts faster mass depletion and higher porewater concentrations, which could increase the concentration of exposure, rate-limitation may cause slower mass depletion and thus long-term leaching of low-level concentrations, which could extend the duration of exposure. These results emphasize previous literature reports of the importance of rate-limited sorption-desorption in understanding PFAS transport in the vadose zone.
- Under conditions modeled here, rate-limited sorption-desorption had the greatest impact on porewater concentrations in shallow depths (< 100 cm). So, consideration of rate-limited solute transport may have the greatest impact on understanding the bioavailable fraction for processes such as plant uptake as opposed to understanding porewater concentrations at the top of the saturated zone.
- Depending on modeling approach (i.e., inclusion of evapotranspiration, inclusion of air-water interfacial partitioning, rate-limited sorption-desorption process, or use of an equilibrium assumption), long-term models showed a range of porewater concentrations (<1 to 100 s of ng/L) reaching the saturated zone. So, it is critical to note that the results of this study should *not* be universally applied to all land application sites. Instead, site-specific considerations could be applied using similar modeling approaches to evaluate the relative importance of exposure pathways such as soil to groundwater or plant uptake.

Land application of biosolids has key benefits including improvement of soil health and sustainable management of wastewater residuals, but increasing focus on PFAS in biosolids is leading to policies that go as far as to restrict or ban all biosolids applications. Importantly, other methods of biosolids disposal including landfilling and incineration may not fully address environmental concerns of PFAS in biosolids. The best line of defense against environmental impacts of PFAS in biosolids is source control (i.e., reduction or elimination of PFAS entering wastewater treatment facilities). Until this can be achieved, best management practices (e.g., stabilization approaches, management of application rates and frequency) are needed to mitigate risks associated with PFAS in biosolids.

CRediT authorship contribution statement

Alonso Doria-Manzur: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Evan P. Gray:** Writing – review & editing, Writing – original draft. **Summer S. Streets:** Writing – review & editing, Resources, Methodology, Conceptualization. **Jennifer L. Guelfo:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Jennifer L. Guelfo reports financial support was provided by Minnesota Environment and Natural Resources Trust Fund Project 0-98B. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding for this project was provided by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-

Citizen Commission on Minnesota Resources (LCCMR; Project 0-98B). Support for Alonso Doria Manzur was also provided by the Environmental Research & Education Foundation (EREF) scholarship and the Distinguished Graduate Student Assistantship (DGSA) from Texas Tech University. We would also like to extend our thanks to Dr. Carl Rosen and Dr. Matthew McNearney at the University of Minnesota Twin Cities for collection and nutrient characterization of samples used in this project.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2025.124674.

Data availability

All data included in manuscript or supplementary material

References

Abgaze, T.A., Sharma, P.K., 2015. Solute transport through porous media with scale-dependent dispersion and variable mass transfer coefficient. ISH J. Hydraul. Eng. 21, 298–311. https://doi.org/10.1080/09715010.2015.1021281.

Alvarez-Ruiz, R., Lee, L.S., Choi, Y., 2024. Fate of per- and polyfluoroalkyl substances at a 40-year dedicated municipal biosolids land disposal site. Sci. Total Environ. 954, 176540. https://doi.org/10.1016/j.scitotenv.2024.176540.

Arshadi, M., Garza-Rubalcava, U., Guedes, A., Cápiro, N.L., Pennell, K.D., Christ, J., Abriola, L.M., 2024. Modeling 1-D aqueous film forming foam transport through the vadose zone under realistic site and release conditions. Sci. Total Environ. 919, 170566. https://doi.org/10.1016/j.scitotenv.2024.170566.

Barth, E., McKernan, J., Bless, D., Dasu, K., 2021. Investigation of an immobilization process for PFAS contaminated soils. J. Environ. Manage. 296, 113069. https://doi.org/10.1016/j.jenvman.2021.113069.

Barzen-Hanson, K.A., Davis, S.E., Kleber, M., Field, J.A., 2017. Sorption of fluorotelomer sulfonates, fluorotelomer sulfonamido betaines, and a fluorotelomer sulfonamido amine in national foam aqueous film-forming foam to soil. Environ. Sci. Technol. 51, 12394–12404. https://doi.org/10.1021/acs.est.7b03452.

Beecher, N., Beecher, J., Burke-wells, J., Lono-Batura, M., Goldstein, N., Kester, G., Toffey, B., 2022. National Biosolids Data Project: Biosolids Management in the US. https://www.biosolidsdata.org (Accessed 31 January 2025).

Place, B., 2021. Suspect List of Possible Per- and Polyfluoroalkyl Substances (PFAS). https://doi.org/10.18434/MDS2-2387.

Bierbaum, T., Hansen, S.K., Poudel, B., Haslauer, C., 2023a. Investigating rate-limited sorption, sorption to air–water interfaces, and colloid-facilitated transport during PFAS leaching. Environ. Sci. Pollut. Res. 30, 121529–121547. https://doi.org/10.1007/s11356-023-30811-2.

Bierbaum, T., Klaas, N., Braun, J., Nürenberg, G., Lange, F.T., Haslauer, C., 2023b. Immobilization of per- and polyfluoroalkyl substances (PFAS): comparison of leaching behavior by three different leaching tests. Sci. Total Environ. 876, 162588. https://doi.org/10.1016/j.scitotenv.2023.162588.

Brusseau, M.L., 2020. Simulating PFAS transport influenced by rate-limited multi-process retention. Water Res. 168, 115179. https://doi.org/10.1016/j.watres.2019.115179.

Brusseau, M.L., 1994. Transport of reactive contaminants in heterogeneous porous Media. Rev. Geophys. 32, 285–313. https://doi.org/10.1029/94RG00624.

Brusseau, M.L., 1992. Nonequilibrium transport of organic chemicals: the impact of pore-water velocity. J. Contam. Hydrol. 9, 353–368. https://doi.org/10.1016/0169-7722(92)90003-W.

Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1991a. Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes. Environ. Sci. Technol. 25, 134–142. https://doi.org/10.1021/es00013a015.

Brusseau, M.L., Khan, N., Wang, Y., Yan, N., Van Glubt, S., Carroll, K.C., 2019. Nonideal transport and extended elution tailing of PFOS in soil. Environ. Sci. Technol. 53, 10654–10664. https://doi.org/10.1021/acs.est.9b02343.

Brusseau, M.L., Rao, P.S.C., 2015. Sorption kinetics of organic chemicals: methods, models and mechanisms. In: Sparks, D.L., Suarez, D.L. (Eds.), SSSA Special Publications. Soil Science Society of America, Madison, WI, USA, pp. 281–302. https://doi.org/10.2136/sssaspecpub27.c11.

Brusseau, M.L., Rao, P.S.C., Gillham, R.W., 1989. Sorption nonideality during organic contaminant transport in porous media. Crit. Rev. Environ. Control 19, 33–99. https://doi.org/10.1080/10643388909388358.

Brusseau, M.L., Wood, A.L., Rao, P.S.C., 1991b. Influence of organic cosolvents on the sorption kinetics of hydrophobic organic chemicals. Environ. Sci. Technol. 25, 903–910. https://doi.org/10.1021/es00017a011.

Campos Pereira, H., Ullberg, M., Kleja, D.B., Gustafsson, J.P., Ahrens, L., 2018. Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon – Effect of cation composition and pH. Chemosphere 207, 183–191. https://doi.org/10.1016/j.chemosphere.2018.05.012.

Campos-Pereira, H., Kleja, D.B., Ahrens, L., Enell, A., Kikuchi, J., Pettersson, M., Gustafsson, J.P., 2023. Effect of pH, surface charge and soil properties on the solid–solution partitioning of perfluoroalkyl substances (PFASs) in a wide range of temperate soils. Chemosphere 321, 138133. https://doi.org/10.1016/j.chemosphere.2023.138133.

Colorado Department of Public Health and Environment (CDPHE), 2024. Colorado Biosolids-PFAS Interim Strategy. https://cdphe.colorado.gov/water-Biosolids-PFAS (Accessed 14 April 2025).

Department of Environment, Great Lakes, and Energy (EGLE), 2024. Interim Strategy – Land Application of Biosolids Containing PFAS (2024). Department of Environment, Great Lakes, and Energy (EGLE). https://www.michigan.gov/egle/about/organization/water-resources/biosolids/pfas-related (Accessed 14 April 2025).

Fabregat-Palau, J., Vidal, M., Rigol, A., 2021. Modelling the sorption behaviour of perfluoroalkyl carboxylates and perfluoroalkane sulfonates in soils. Sci. Total Environ. 801, 149343. https://doi.org/10.1016/j.scitotenv.2021.149343.

Gagliano, E., Sgroi, M., Falciglia, P.P., Vagliasindi, F.G.A., Roccaro, P., 2020. Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. Water Res. 171, 115381. https://doi.org/10.1016/j.watres.2019.115381.

Garg, A., Shetti, N.P., Basu, S., Nadagouda, M.N., Aminabhavi, T.M., 2023. Treatment technologies for removal of per- and polyfluoroalkyl substances (PFAS) in biosolids. Chem. Eng. J. 453, 139964. https://doi.org/10.1016/j.cej.2022.139964.

Gellrich, V., Stahl, T., Knepper, T.P., 2012. Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere 87, 1052–1056. https://doi.org/10.1016/j.chemosphere.2012.02.011.

Gottschall, N., Topp, E., Edwards, M., Payne, M., Kleywegt, S., Lapen, D.R., 2017. Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field. Sci. Total Environ. 574, 1345–1359. https://doi.org/10.1016/j.scitotenv.2016.08.044.

Guelfo, J.L., Ferguson, P.L., Beck, J., Chernick, M., Doria-Manzur, A., Faught, P.W., Flug, T., Gray, E.P., Jayasundara, N., Knappe, D.R.U., Joyce, A.S., Meng, P., Shojaei, M., 2024. Lithium-ion battery components are at the nexus of sustainable energy and environmental release of per- and polyfluoroalkyl substances. Nat. Commun. 15, 5548. https://doi.org/10.1038/s41467-024-49753-5.

Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. Environ. Sci. Technol. 47, 4164–4171. https://doi.org/10.1021/es3048043.

Guelfo, J.L., Wunsch, A., McCray, J., Stults, J.F., Higgins, C.P., 2020. Subsurface transport potential of perfluoroalkyl acids (PFAAs): column experiments and modeling. J. Contam. Hydrol. 233, 103661. https://doi.org/10.1016/j.jconhyd.2020.103661.

Guo, B., Zeng, J., Brusseau, M.L., 2020. A mathematical model for the release, transport, and retention of per- and polyfluoroalkyl substances (PFAS) in the Vadose Zone. Water Resour. Res. 56. https://doi.org/10.1029/2019WR026667.

Guo, B., Zeng, J., Brusseau, M.L., Zhang, Y., 2022. A screening model for quantifying PFAS leaching in the vadose zone and mass discharge to groundwater. Adv. Water Resour. 160, 104102. https://doi.org/10.1016/j.advwatres.2021.104102.

Hall, H., Moodie, D., Vero, C., 2021. PFAS in biosolids: a review of international regulations. Water E-J 5, 1–11. https://doi.org/10.21139/wej.2020.026.

Hamid, H., Li, L.Y., Grace, J.R., 2020. Formation of perfluorocarboxylic acids from 6:2 fluorotelomer sulfonate (6:2 FTS) in landfill leachate: role of microbial communities. Environ. Pollut. 259, 113835. https://doi.org/10.1016/j.envpol.2019.113835.

Helmer, R.W., Reeves, D.M., Cassidy, D.P., 2022. Per- and polyfluorinated alkyl substances (PFAS) cycling within Michigan: contaminated sites, landfills and wastewater treatment plants. Water Res. 210, 117983. https://doi.org/10.1016/j.watres.2021.117983.

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environ. Sci. Technol. 39, 3946–3956. https://doi.org/10.1021/es048245p.

Holly, M.A., Gunn, K.M., Keymer, D., Sanford, J.R., 2024. Evaluation of per- and polyfluoroalkyl substances leaching from biosolids and mitigation potential of biochar through undisturbed soil columns. ACS EST Water 4, 413–426. https://doi.org/10.1021/acsestwater.3c00414.

Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environ. Sci. Technol. 47, 8187–8195. https://doi.org/10.1021/es4018877.

Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ. Sci. Technol. 46, 9342–9349. https://doi.org/10.1021/es302274g.

Hunter Anderson, R., Adamson, D.T., Stroo, H.F., 2019. Partitioning of poly- and perfluoroalkyl substances from soil to groundwater within aqueous film-forming foam source zones. J. Contam. Hydrol. 220, 59–65. https://doi.org/10.1016/j.jconhyd.2018.11.011.

Izuegbunam, C., 2025. PFAS Land Application Regulations. https://mostpolicyinitiative.org/wp-content/uploads/2025/01/PFAS-Land-APPLICATION.pdf (Accessed 20 February 2025).

Jardine, P.M., Jacobs, G.K., O'Dell, J.D., 1993. Unsaturated transport processes in undisturbed heterogeneous porous Media: II. Co-contaminants. Soil Sci. Soc. Am. J. 57, 954–962. https://doi.org/10.2136/sssaj1993.03615995005700040013x.

Jiang, T., Pervez, Md.N., Quianes, M.M., Zhang, W., Naddeo, V., Liang, Y., 2023. Effective stabilization of per- and polyfluoroalkyl substances (PFAS) precursors in wastewater treatment sludge by surfactant-modified clay. Chemosphere 341, 140081. https://doi.org/10.1016/j.chemosphere.2023.140081.

Johnson, G.R., 2022. PFAS in soil and groundwater following historical land application of biosolids. Water Res. 211, 118035. https://doi.org/10.1016/j.watres.2021.118035.

Kim Lazcano, R., Perre, C., Mashtare, M.L., Lee, L.S., 2019. Per- and polyfluoroalkyl substances in commercially available biosolid-based products: the effect of treatment processes. Water Environ. Res. 91, 1669–1677. https://doi.org/10.1002/wer.1174.
Kumar, R., Vuppaladadiyam, A.K., Antunes, E., Whelan, A., Fearon, R., Sheehan, M., Reeves, L., 2022. Emerging contaminants in biosolids: presence, fate and analytical techniques. Emerg. Contam. 8, 162–194. https://doi.org/10.1016/j.emcon.2022.03.004.
LaFond, J.A., Hatzinger, P.B., Guelfo, J.L., Millerick, K., Jackson, W.A., 2023. Bacterial transformation of per- and poly-fluoroalkyl substances: a review for the field of bioremediation. Environ. Sci. Adv. 2, 1019–1041. https://doi.org/10.1039/D3VA00031A.
LaFond, J.A., Rezes, R., Shojaei, M., Anderson, T., Jackson, W.A., Guelfo, J.L., Hatzinger, P.B., 2024. Biotransformation of PFAA precursors by oxygenase-expressing bacteria in AFFF-impacted groundwater and in pure-compound studies with 6:2 FTS and EtFOSE. Environ. Sci. Technol. 58, 13820–13832. https://doi.org/10.1021/acs.est.4c01931.
Lee, H., Tevlin, A.G., Mabury, S.A., Mabury, S.A., 2014. Fate of polyfluoroalkyl phosphate diesters and their metabolites in biosolids-applied soil: biodegradation and plant uptake in greenhouse and field experiments. Environ. Sci. Technol. 48, 340–349. https://doi.org/10.1021/es403949z.
Li, Y., Oliver, D.P., Kookana, R.S., 2018. A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). Sci. Total Environ. 628–629, 110–120. https://doi.org/10.1016/j.scitotenv.2018.01.167.
Link, G.W., Reeves, D.M., Cassidy, D.P., Coffin, E.S., 2024. Per- and polyfluoroalkyl substances (PFAS) in final treated solids (Biosolids) from 190 Michigan wastewater treatment plants. J. Hazard. Mater. 463, 132734. https://doi.org/10.1016/j.jhazmat.2023.132734.
Liu, C., Liu, J., 2016. Aerobic biotransformation of polyfluoroalkyl phosphate esters (PAPs) in soil. Environ. Pollut. 212, 230–237. https://doi.org/10.1016/j.envpol.2016.01.069.
Liu, Y., Mendoza-Perilla, P., Clavier, K.A., Tolaymat, T.M., Bowden, J.A., Solo-Gabriele, H.M., Townsend, T.G., 2022. Municipal solid waste incineration (MSWI) ash co-disposal: influence on per- and polyfluoroalkyl substances (PFAS) concentration in landfill leachate. Waste Manag. 144, 49–56. https://doi.org/10.1016/j.wasman.2022.03.009.
Lu, Q., He, Z.L., Stoffella, P.J., 2012. Land application of biosolids in the USA: a review. Appl. Environ. Soil Sci. 2012, 1–11. https://doi.org/10.1155/2012/201462.
Maine Department of Agriculture, Conservation and Forestry (MEDACF), 2022. Fund to Address PFAS Contamination. https://www.maine.gov/dacf/ag/pfas/pfas-fund.shtml (Accessed 14 April 2025).
Maraqa, M.A., Zhao, X., Lee, J., Allan, F., Voice, T.C., 2011. Comparison of nonideal sorption formulations in modeling the transport of phthalate esters through packed soil columns. J. Contam. Hydrol. 125, 57–69. https://doi.org/10.1016/j.jconhyd.2011.05.001.
Maryland department of environment (MDE), 2024. PFAS in Biosolids. What You Need to Know. https://mde.maryland.gov/programs/land/RMP/Pages/sewagesludge.aspx (Accessed 14 April 2025).
Missouri Department of Natural Resources (MODNR), 2023. Per- and Polyfluoroalkyl Substances (PFAS) Biosolids, RCRA and CERCLA Regulation Workgroup Report. https://dnr.mo.gov/document/polyfluoroalkyl-substances-pfas-biosolids-rcra-cercla-regulation-workgroup-report-0 (Accessed 14 April 2025).
Mousavi Nezhad, M., Javadi, A.A., Rezania, M., 2011. Modeling of contaminant transport in soils considering the effects of micro- and macro-heterogeneity. J. Hydrol. 404, 332–338. https://doi.org/10.1016/j.jhydrol.2011.05.004.
MPCA, 2025. Minnesota Biosolids PFAS Strategy. https://www.pca.state.mn.us/sites/default/files/wq-wwprm2-113a.pdf (Accessed 20 February 2025).
Munoz, G., Michaud, A.M., Liu, M., Vo Duy, S., Montenach, D., Resseguier, C., Watteau, F., Sappin-Didier, V., Feder, F., Morvan, T., Houot, S., Desrosiers, M., Liu, J., Sauvé, S., 2022. Target and nontarget screening of PFAS in biosolids, composts, and other organic waste products for land application in France. Environ. Sci. Technol. 56, 6056–6068. https://doi.org/10.1021/acs.est.1c03697.
Navarro, D.A., Kabiri, S., Ho, J., Bowles, K.C., Davis, G., McLaughlin, M.J., Kookana, R.S., 2023. Stabilisation of PFAS in soils: long-term effectiveness of carbon-based soil amendments. Environ. Pollut. 323, 121249. https://doi.org/10.1016/j.envpol.2023.121249.
New Hampshire Department of Environmental services (NHDES), 2022. Interim Best Management Practices for Emerging Contaminants in Certified Biosolids. https://www.des.nh.gov/sites/g/files/ehbemt341/files/documents/web-29.pdf (Accessed 14 April 2025).
Newmeyer, M.N., Lyu, Q., Sobus, J.R., Williams, A.J., Nachman, K.E., Prasse, C., 2024. Combining nontargeted analysis with computer-based hazard comparison approaches to support prioritization of unregulated organic contaminants in biosolids. Environ. Sci. Technol. 58, 12135–12146. https://doi.org/10.1021/acs.est.4c02934.
Nguyen, T.M.H., Bräunig, J., Kookana, R.S., Kaserzon, S.L., Knight, E.R., Vo, H.N.P., Kabiri, S., Navarro, D.A., Grimison, C., Riddell, N., Higgins, C.P., McLaughlin, M.J., Mueller, J.F., 2022. Assessment of mobilization potential of per- and polyfluoroalkyl substances for soil remediation. Environ. Sci. Technol. 56, 10030–10041. https://doi.org/10.1021/acs.est.2c00401.
Nguyen, T.M.H., Bräunig, J., Thompson, K., Thompson, J., Kabiri, S., Navarro, D.A., Kookana, R.S., Grimison, C., Barnes, C.M., Higgins, C.P., McLaughlin, M.J., Mueller, J.F., 2020. Influences of chemical properties, soil properties, and solution pH on soil–Water partitioning coefficients of per- and polyfluoroalkyl substances (PFASs). Environ. Sci. Technol. 54, 15883–15892. https://doi.org/10.1021/acs.est.0c05705.
Nickerson, A., Maizel, A.C., Schaefer, C.E., Ranville, J.F., Higgins, C.P., 2023. Effect of geochemical conditions on PFAS release from AFFF-impacted saturated soil columns. Environ. Sci. Process. Impacts 25, 405–414. https://doi.org/10.1039/D2EM00367H.
Nkedi-Kizza, P., Brusseau, M.L., Rao, P.S.C., Hornsby, A.G., 1989. Nonequilibrium sorption during displacement of hydrophobic organic chemicals and calcium-45 through soil columns with aqueous and mixed solvents. Environ. Sci. Technol. 23, 814–820. https://doi.org/10.1021/es00065a009.
Openiyi, E.O., Lee, L.S., Alukkal, C.R., 2025. Evaluating sorbents for reducing per- and polyfluoroalkyl substance mobility in biosolids-amended soil columns. J. Environ. Qual. 54, 118–131. https://doi.org/10.1002/jeq2.20658.
Oviedo-Vargas, D., Anton, J., Coleman-Kammula, S., Qin, X., 2025. Quantification of PFAS in soils treated with biosolids in ten northeastern US farms. Sci. Rep. 15, 5582. https://doi.org/10.1038/s41598-025-90184-z.
Pepper, I., Kelley, C., Brusseau, M., 2023. Is PFAS from land applied municipal biosolids a significant source of human exposure via groundwater? Sci. Total Environ. 864, 161154. https://doi.org/10.1016/j.scitotenv.2022.161154.
Pepper, I.L., Brusseau, M.L., Prevatt, F.J., Escobar, B.A., 2021. Incidence of Pfas in soil following long-term application of class B biosolids. Sci. Total Environ. 793, 148449. https://doi.org/10.1016/j.scitotenv.2021.148449.
Peter, L.G., Lee, L.S., 2025. Sources and pathways of PFAS occurrence in water Sources: relative contribution of land-applied biosolids in an agricultural dominated watershed. Environ. Sci. Technol. 59, 1344–1353. https://doi.org/10.1021/acs.est.4c09490.
Piatt, J.J., Brusseau, M.L., 1998. Rate-limited sorption of hydrophobic organic compounds by soils with well-characterized organic matter. Environ. Sci. Technol. 32, 1604–1608. https://doi.org/10.1021/es970461t.
Popoola, L.T., Olawale, T.O., Salami, L., 2023. A review on the fate and effects of contaminants in biosolids applied on land: hazards and government regulatory policies. Heliyon 9, e19788. https://doi.org/10.1016/j.heliyon.2023.e19788.
Rao, P.S.C., Jessup, R.E., Rolston, D.E., Davidson, J.M., Kilcrease, D.P., 1980. Experimental and mathematical description of nonadsorbed solute transfer by diffusion in spherical aggregates. Soil Sci. Soc. Am. J. 44, 684–688. https://doi.org/10.2136/sssaj1980.03615995004400040004x.
Röhler, K., Haluska, A.A., Susset, B., Liu, B., Grathwohl, P., 2021. Long-term behavior of PFAS in contaminated agricultural soils in Germany. J. Contam. Hydrol. 241, 103812. https://doi.org/10.1016/j.jconhyd.2021.103812.
Saliu, T.D., Sauvé, S., 2024. A review of per- and polyfluoroalkyl substances in biosolids: geographical distribution and regulations. Front. Environ. Chem. 5, 1383185. https://doi.org/10.3389/fenvc.2024.1383185.
Schaefer, C.E., Culina, V., Nguyen, D., Field, J., 2019. Uptake of poly- and perfluoroalkyl substances at the air–Water interface. Environ. Sci. Technol. 53, 12442–12448. https://doi.org/10.1021/acs.est.9b04008.
Schaefer, C.E., Hooper, J., Modiri-Gharehveran, M., Drennan, D.M., Beecher, N., Lee, L., 2022a. Release of poly- and perfluoroalkyl substances from finished biosolids in soil mesocosms. Water Res. 217, 118405. https://doi.org/10.1016/j.watres.2022.118405.
Schaefer, C.E., Hooper, J.L., Strom, L.E., Abusallout, I., Dickenson, E.R.V., Thompson, K.A., Mohan, G.R., Drennan, D., Wu, K., Guelfo, J.L., 2023. Occurrence of quantifiable and semi-quantifiable poly- and perfluoroalkyl substances in united states wastewater treatment plants. Water Res. 233, 119724. https://doi.org/10.1016/j.watres.2023.119724.
Schaefer, C.E., Nguyen, D., Christie, E., Shea, S., Higgins, C.P., Field, J., 2022b. Desorption isotherms for poly- and perfluoroalkyl substances in soil collected from an aqueous film-forming foam source area. J. Environ. Eng. 148, 04021074. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001952.
Schaefer, C.E., Nguyen, D., Christie, E., Shea, S., Higgins, C.P., Field, J.A., 2021. Desorption of poly- and perfluoroalkyl substances from soil historically impacted with aqueous film-forming foam. J. Environ. Eng. 147, 06020006. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001846.
Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., Hollender, J., 2014. Identifying small molecules via high resolution mass spectrometry: communicating confidence. Environ. Sci. Technol. 48, 2097–2098. https://doi.org/10.1021/es5002105.
Sepulvado, J.G., Blaine, A.C., Hundal, L.S., Higgins, C.P., 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ. Sci. Technol. 45, 8106–8112. https://doi.org/10.1021/es103903d.
Shin, J., An, B., 2025. Adsorption characteristics of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in granular activated carbon (GAC) and modified GAC. Water Air Soil Pollut. 236, 267. https://doi.org/10.1007/s11270-025-07908-0.
Shojaei, M., Joyce, A.S., Ferguson, P.L., Guelfo, J.L., 2022a. Novel per- and polyfluoroalkyl substances in an active-use C6-based aqueous film forming foam. J. Hazard. Mater. Lett. 3, 100061. https://doi.org/10.1016/j.hazl.2022.100061.
Shojaei, M., Kumar, N., Chaobol, S., Wu, K., Crimi, M., Guelfo, J., 2021. Enhanced recovery of per- and polyfluoroalkyl substances (PFASs) from impacted soils using heat activated persulfate. Environ. Sci. Technol. 55, 9805–9816. https://doi.org/10.1021/acs.est.0c08069.
Shojaei, M., Kumar, N., Guelfo, J.L., 2022b. An integrated approach for determination of total per- and polyfluoroalkyl substances (PFAS). Environ. Sci. Technol. 56, 14517–14527. https://doi.org/10.1021/acs.est.2c05143.
Silva, J.A.K., Guelfo, J.L., Šimůnek, J., McCray, J.E., 2022. Simulated leaching of PFAS from land-applied municipal biosolids at agricultural sites. J. Contam. Hydrol. 251, 104089. https://doi.org/10.1016/j.jconhyd.2022.104089.
Silva, J.A.K., Martin, W.A., Johnson, J.L., McCray, J.E., 2019. Evaluating air-water and NAPL-water interfacial adsorption and retention of perfluorocarboxylic acids within

the Vadose zone. J. Contam. Hydrol. 223, 103472. https://doi.org/10.1016/j.jconhyd.2019.03.004.
Silva, J.A.K., Martin, W.A., McCray, J.E., 2021. Air-water interfacial adsorption coefficients for PFAS when present as a multi-component mixture. J. Contam. Hydrol. 236, 103731. https://doi.org/10.1016/j.jconhyd.2020.103731.
Soil Survey Staff, Natural Resources Conservation Service (NRCS), United States Department (USDA)of Agriculture, 2024. Soil Series Classification Database. https://webharvest.gov/peth04/20041014220338/http://soils.usda.gov/survey (Accessed 5 January 2025).
Sørmo, E., Silvani, L., Bjerkli, N., Hagemann, N., Zimmerman, A.R., Hale, S.E., Hansen, C. B., Hartnik, T., Cornelissen, G., 2021. Stabilization of PFAS-contaminated soil with activated biochar. Sci. Total Environ. 763, 144034. https://doi.org/10.1016/j.scitotenv.2020.144034.
Stahl, T., Riebe, R.A., Falk, S., Failing, K., Brunn, H., 2013. Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: results of a pilot study. J. Agric. Food Chem. 61, 1784–1793. https://doi.org/10.1021/jf305003h.
State of Maine, 2022. An Act to Prevent the Further Contamination of the Soils and Waters of the State with So-Called Forever Chemicals. https://www.mainelegislature.org/legis/bills/getPDF.asp?paper=HP1417&item=8&snum=130 (Accessed 14 April 2025).
Stults, J.F., Schaefer, C.E., Fang, Y., Devon, J., Nguyen, D., Real, I., Hao, S., Guelfo, J.L., 2024. Air-water interfacial collapse and rate-limited solid desorption control perfluoroalkyl acid leaching from the vadose zone. J. Contam. Hydrol. 265, 104382. https://doi.org/10.1016/j.jconhyd.2024.104382.
Stults, J.F., Schaefer, C.E., MacBeth, T., Fang, Y., Devon, J., Real, I., Liu, F., Kosson, D., Guelfo, J.L., 2025. Laboratory validation of a simplified model for estimating equilibrium PFAS mass leaching from unsaturated soils. Sci. Total Environ. 970, 179036. https://doi.org/10.1016/j.scitotenv.2025.179036.
Tansel, B., Katsenovich, Y., Quinete, N.S., Ocheje, J., Nasir, Z., Manzano, M.M., 2024. PFAS in biosolids: accumulation characteristics and fate profiles after land application. J. Environ. Manage. 370, 122395. https://doi.org/10.1016/j.jenvman.2024.122395.
Thoma, E.D., Wright, R.S., George, I., Krause, M., Presezzi, D., Villa, V., Preston, W., Deshmukh, P., Kauppi, P., Zemek, P.G., 2022. Pyrolysis processing of PFAS-impacted biosolids, a pilot study. J. Air Waste Manag. Assoc. 72, 309–318. https://doi.org/10.1080/10962247.2021.2009935.
Thompson, J.T., Robey, N.M., Tolaymat, T.M., Bowden, J.A., Solo-Gabriele, H.M., Townsend, T.G., 2023. Underestimation of per- and polyfluoroalkyl substances in biosolids: precursor transformation during conventional treatment. Environ. Sci. Technol. 57, 3825–3832. https://doi.org/10.1021/acs.est.2c06189.
Tolaymat, T., Robey, N., Krause, M., Larson, J., Weitz, K., Parvathikar, S., Phelps, L., Linak, W., Burden, S., Speth, T., Krug, J., 2023. A critical review of perfluoroalkyl and polyfluoroalkyl substances (PFAS) landfill disposal in the United States. Sci. Total Environ. 905, 167185. https://doi.org/10.1016/j.scitotenv.2023.167185.
Tsou, K., Antell, E., Duan, Y., Olivares, C.I., Yi, S., Alvarez-Cohen, L., Sedlak, D.L., 2023. Improved total oxidizable precursor assay for quantifying polyfluorinated compounds amenable to oxidative conversion to perfluoroalkyl carboxylic acids. ACS EST Water 3, 2996–3003. https://doi.org/10.1021/acsestwater.3c00224.
USDA, 2023. Minnesota Ag News –2023 Corn County estimates. https://www.nass.usda.gov/Statistics_by_State/Minnesota/Publications/County_Estimates/2024/MN-CtyEst-Corn-02-24.pdf (Accessed 14 February 2025).
USEPA, 2025a. Basic Information About Biosolids. https://www.epa.gov/biosolids/basic-information-about-sewage-sludge-and-biosolids (Accessed 5 January 2025).
USEPA, 2025b. Draft Sewage Sludge Risk Assesment For Perfluorooctanoic Acid (PFOA) CASRN 335-67-1 and Perfluorooctane Sulfonic Acid (PFOS) CASRN 1763-23-1 (No. EPA-820P25001). Washington, DC.
USEPA, 2025c. Land Application of Biosolids. https://www.epa.gov/biosolids/land-application-biosolids (Accessed 14 April 2025).
USEPA, 2022. Drinking Water Health Advisories for PFAS Fact Sheet for Public Water Systems. https://www.epa.gov/sdwa/drinking-water-health-advisories-has (Accessed 23 February 2025).
USEPA, 1994. A Plain English Guide to the EPA Part 503 Biosolids Rule.
USGS, 2025. USGS Water Data for the Nation. https://nwis.waterdata.usgs.gov/nwis (Accessed 26 July 2025).
Van Genuchten, M.Th., Wierenga, P.J., 1977. Mass transfer studies in sorbing porous Media: II. Experimental evaluation with tritium (3H2O). Soil Sci. Soc. Am. J. 41, 272–278. https://doi.org/10.2136/sssaj1977.03615995004100020022x.
Venkatesan, A.K., Halden, R.U., 2013. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. J. Hazard. Mater. 252–253, 413–418. https://doi.org/10.1016/j.jhazmat.2013.03.016.
Vierke, L., Möller, A., Klitzke, S., 2014. Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions. Environ. Pollut. 186, 7–13. https://doi.org/10.1016/j.envpol.2013.11.011.
Weidemann, E., Gassmann, M., 2023. Transformation and leaching simulation of 6:2 and 8:2 diPAP and related metabolites in unsaturated soil column studies with MACRO. Environ. Model. Assess. https://doi.org/10.1007/s10666-023-09936-8.
Weidemann, E., Lämmer, R., Stahl, T., Göckener, B., Bücking, M., Breuer, J., Kowalczyk, J., Just, H., Boeddinghaus, R.S., Gassmann, M., 2022. Leaching and transformation of perfluoroalkyl acids and polyfluoroalkyl phosphate diesters in unsaturated soil column studies. Environ. Toxicol. Chem. 41, 2065–2077. https://doi.org/10.1002/etc.5417.
Wu, C., Goodrow, S., Chen, H., Li, M., 2024. Distinctive biotransformation and biodefluorination of 6:2 versus 5:3 fluorotelomer carboxylic acids by municipal activated sludge. Water Res.. 254, 121431. https://doi.org/10.1016/j.watres.2024.121431.
Yang, Z., Shojaei, M., Guelfo, J.L., 2023. Per- and polyfluoroalkyl substances (PFAS) in grocery store foods: method optimization, occurrence, and exposure assessment. Environ. Sci. Process. Impacts 25, 2015–2030. https://doi.org/10.1039/D3EM00268C.
Zeng, J., Brusseau, M.L., Guo, B., 2021. Model validation and analyses of parameter sensitivity and uncertainty for modeling long-term retention and leaching of PFAS in the vadose zone. J. Hydrol. 603, 127172. https://doi.org/10.1016/j.jhydrol.2021.127172.
Zeng, J., Guo, B., 2021. Multidimensional simulation of PFAS transport and leaching in the vadose zone: impact of surfactant-induced flow and subsurface heterogeneities. Adv. Water Resour. 155, 104015. https://doi.org/10.1016/j.advwatres.2021.104015.
Zhang, H., Jing, G., Luo, J., Tang, Y., Yu, Q.J., Zheng, C., Wang, M., 2021. Assessment of transportation processes of polyacrylamide in chernozem and saline soil by numerical model. Environ. Technol. 42, 2350–2360. https://doi.org/10.1080/09593330.2019.1701566.
Zhang, M., Yazaydin, A.O., 2024. The effect of perfluoroalkyl chain length and the type of acid group on PFAS adsorption from water. Chem. Eng. J. 499, 155851. https://doi.org/10.1016/j.cej.2024.155851.
Zhang, W., Liang, Y., 2022a. Changing bioavailability of per- and polyfluoroalkyl substances (PFAS) to plant in biosolids amended soil through stabilization or mobilization. Environ. Pollut. 308, 119724. https://doi.org/10.1016/j.envpol.2022.119724.
Zhang, W., Liang, Y., 2022b. Performance of different sorbents toward stabilizing per- and polyfluoroalkyl substances (PFAS) in soil. Environ. Adv. 8, 100217. https://doi.org/10.1016/j.envadv.2022.100217.
Zhao, L., Bian, J., Zhang, Y., Zhu, L., Liu, Z., 2014. Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. Chemosphere 114, 51–58. https://doi.org/10.1016/j.chemosphere.2014.03.098.