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Evaluation of Per- and Polyfluoroalkyl Substances Leaching from Biosolids and Mitigation Potential of Biochar through Undisturbed Soil Columns

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ABSTRACT: Land application of biosolids recycles nutrients and reduces the need for commercial fertilizers. However, per- and polyfluoroalkyl substances (PFAS) may leach from biosolids, resulting in groundwater contamination. We measured PFAS leaching from land-applied biosolids through undisturbed soil column trials and evaluated the treatment potential of amending biosolids with biochar. Synthetic rainfall was applied weekly to undisturbed soil columns from four regions in Wisconsin, including two fields with a history of biosolid application, simulating annual precipitation. The treatments consisted of a control (soil only), soil amended with biosolids, and soil receiving a mixture of biosolids and biochar. Concentrations of total PFAS in leachate were significantly affected by soil location and site history One-time application of biosolids may result in groundwater contamination, as PFAS concentrations in leachate exceeded the local groundwater standard (a combined perfluorooctanoic acid and perfluorooctanesulfonic acid groundwater concentration of 20 ng L^{-1}) at three locations. Legacy PFAS may pose a risk to human health years after biosolid application, as a control column from a site with an intensive history of biosolid application exceeded PFAS groundwater standards. Incorporation of biochar with biosolids during application mitigated PFAS (specifically from soils with elevated leaching potential) through significant reductions of C_7-C_{10} perfluoroalkyl carboxylic acids and C_4 and C_6-C_8 perfluorosulfonic acids (40% to 64% reduction in measured Σ^{28} PFAS). Biochar may facilitate sustainable use of biosolids through mitigation of long-chain PFAS leaching, pending a long-term field evaluation.

KEYWORDS: PFAS, biosolids, biochar, leaching, land application
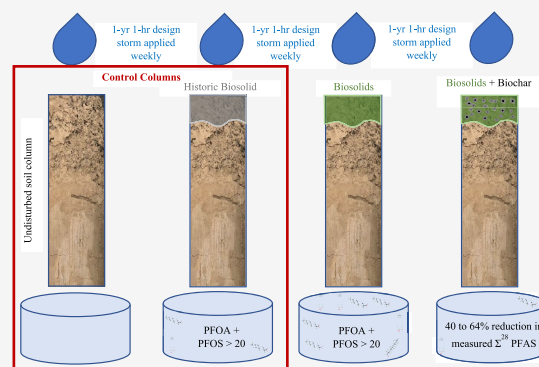
INTRODUCTION

In the United States, approximately 130 million m^3 of wastewater is treated daily at wastewater treatment facilities.[1] While treatment processes vary, most facilities produce two streams: a treated effluent that is discharged to the environment and the solid component commonly termed biosolids or sewage sludge. In the U.S., approximately 13.8 million tons of sludge is generated annually.[1] Biosolid land application is typically a less costly management practice than landfilling and incineration,[2] and roughly 28% of biosolids, or 3.95 million tons yr^{-1}, are land applied to agricultural fields as a beneficial reuse of nutrients.[1] Environmental benefits of land application include improvements to soil health and supplementation or replacement of synthetic fertilizers with a low-cost organic material that slowly releases nutrients over multiple growing seasons.[3]

Although biosolids are treated to reduce vector attraction and pathogens prior to land application, they can still contain hazardous chemicals from industrial wastewater and household

products.[4] U.S. federal regulations for land application of sewage sludge (40 C.F.R. §503) address only a fraction of the hazardous or priority pollutants monitored in other programs.[5] Existing controls based on the Clean Water Act require testing and application limits for only nine heavy metals and nitrogen. Current U.S. regulation excludes many pollutants on other hazardous lists (i.e., Resource Conservation and Recovery Act's hazardous waste listings, U.S. EPA priority pollutant list, and the National Institute for Occupational Safety and Health's list of hazardous drugs),[6] and no controls exist for PFAS. PFAS are a large group (>4,500) of persistent and stable chemicals

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Table 1. Land Application of Biosolids for Selected Counties[40]

Geographical region	County	Area of biosolid application (ha)	Annual biosolids application (dry ton yr^{-1})
Northern Highland	Marathon	786	2700
Eastern Ridges and Lowlands	Outagamie	474	7853
Western Upland	Grant	302	629
Eastern Ridges and Lowlands	Columbia	103	1162

on the EPA priority pollutant list with evidence of adverse human health implications. Biosolids may be the most diffuse source of soil PFAS contamination in the United States with a significant PFAS loading to U.S. soils as estimated by Venkatesan et al.[7] [1,375 to 2,070 kg of PFAS ($\sum$13 PFAS analytes), annually]. Furthermore, biosolids were found to function as significant sources of PFAS in surface soils across the world, with loadings up to 2,351 and 5,500 μg kg^{-1} for PFOA and PFOS, respectively.[8] Once biosolids containing PFAS are applied to soil, PFAS could be transported to groundwater[9−12] and could be a potential threat to human health.

Knowledge of the temporal leaching potential of PFAS is critical to understanding the risk to groundwater and drinking water sources. To date, local and regional knowledge stand limited on PFAS leaching from fields applied with biosolids,[10−12] and this knowledge along with driving parameters would be beneficial to groundwater protection. Field practices may be warranted to protect groundwater from PFAS contamination. Incorporation of high-surface-area carbon-based amendments into agricultural fields could reduce leaching of PFAS released from biosolids. Activated carbon has been used for sorption of PFAS from aqueous solutions with removal efficiencies greater than 90% for PFAS.[13] Potential alternative adsorptive media are biochar and ash. Biochar has potential to bind PFAS[14] and reduce loading to groundwater sources. Sørmo et al.[15] amended 1% biochar to a PFAS-contaminated soil and observed 31% to 96% reduction in PFAS leaching, with activated biochar resulting in the highest reduction.

Soil column experiments are commonly used to provide the benefits of swiftly and easily simulating field conditions at low cost in a controlled boundary environment, with the added advantage of replicability and reproducibility.[16] Few studies have successfully used soil columns as experimental units to research the behavior of PFAS in soils of various characteristics across the world.[17−19] For example, Lyu et al.[17] employed quartz sand packed columns to investigate the retardation mechanisms affecting PFOA transport in unsaturated porous media. Høisæter et al.[20] used unsaturated packed columns to evaluate the transport of aqueous film-forming foam PFAS in a soil media of a Norwegian firefighting training facility. Existing studies on the leaching potential of PFAS from agricultural fields receiving biosolids include two packed column studies[10,12] (30 and 10 cm in length); however, the use of undistorted soil columns in researching the transport of PFAS from agricultural fields has not been explored and furthermore has not been used to measure mitigation potential of biochar. Packed columns typically underestimate contaminate mobility measured in the field[21] due to the alteration of soil structure, decrease in micro- and macropores, and subsequent reduction in soil hydraulic conductivity.[22] Therefore, undisturbed column studies are critical to determine the leaching potential of PFAS and the human health risk from biosolid application.

Transport of PFAS from unsaturated soil is intricate, and previous mathematical modeling and field experimentation illustrated the impact of solid phase sorption, air water interfaces (AWI), and precursor transformation.[17,20,23−31] Sorption is dependent on the physical and chemical properties of PFAS (density, solubility, alkyl chain length, characteristic functional group and their ionic state, PFAS concentration of the soil pore solution), the physical, chemical, and hydraulic properties of the soil (i.e., texture, structure, moisture content, seepage rate, organic and carbon contents), and the chemistry of the soil pore solution (i.e., ionic strength, pH, presence of other chemical compounds).[9,11,32−36] Given their surfactant nature, as a result of their hydrophobic tail and polar functional groups, several PFAS will adsorb to the AWI within the nonsaturated soil pores. AWI particularly reduces the transport of PFAS with larger alkyl chain PFAS molecules ($\geq$7 carbon atoms), whereas shorter chain PFAS (<7 carbon atoms) tend to be less impacted resulting in relatively faster leaching down the soil profile.[37] The retardation effect of the AWI on PFAS leaching is dependent on soil moisture content. As soil moisture content increases, the size of AWI decreases resulting in subsequent decrease in surface activity, as demonstrated by Silva et al.,[9] creating ideal conditions for faster transport of PFAS. For saturated soils, molecular hydrophobicity has been previously measured as the main factor for the retention of anionic PFAS, and soil physiochemical properties have no impact to transport.[33] The impact of solid phase sorption on PFAS leaching has been previously characterized by the soil−water distribution coefficient (k_d) and its organic carbon content-normalized counterpart (K_{oc}). Values of K_{oc} have been published for several PFAS for various soil conditions,[32] yet most of these values were estimated in laboratory batch experiments and do not account for various field conditions. Silva et al.[9,31,35] determined that sorption of PFAS to AWI is an important factor contributing to retardation; therefore, partitioning between pore solution and air at the AWI of unsaturated soils should be accounted for in the investigation of PFAS leaching potentials, necessitating undisturbed soil column trials.

Previous modeling efforts by Silva et al.[9] to estimate leaching of PFAS from land-applied municipal biosolids simulated the release of PFAS from the biosolid amended surface soil through a two-site kinetic/desorption model. The two-site kinetic model assumes sorption sites in a dual porosity system, where water and solute can move between mobile and immobile domains, can be divided into two fractions: (1) a fraction with instantaneous sorption for the immobile domain and (2) a fraction with kinetic sorption for the mobile domain with relatively faster water movement.[38] Previous simulations modeled the source as diminishing over time, and precursor transformations were not included as the PFAS interaction with solid phases will govern the rate of PFAS leaching.[38] Currently, previous measurements of desorption kinetics included a field trial[11] and batch trial;[39] undisturbed columns

Table 2. Physical and Chemical Properties of Soil Used for Soil Columns

| Location	Soil depth (cm)	Sand %	Silt %	Clay %	USDA texture	Organic matter %	Soil pH	CEC (meq 100g^{-1})	Total N (%)	TOC (%)	Bulk density (g cm^{-3})	Water holding capacity (%)
Columbia	0−15	15	59	26	Silt loam	3.5	6.6	12	0.25	2.30	1.10	12.7
Columbia	15−30	13	59	28	Silt clay loam	2.6	6.7	11	0.20	1.60	1.25	13.4
Columbia	30−45	11	59	30	Silt clay loam	2.1	6.5	10	0.14	1.19	1.10	11.5
Grant	0−15	7	77	16	Silt loam	3.6	7.2	49	0.24	2.41	1.00	22.2
Grant	15−30	10	70	20	Silt loam	2.6	7.2	44	0.20	1.59	1.13	24.6
Grant	30−45	4	76	20	Silt loam	1.3	7.1	45	0.13	0.91	1.30	26.5
Marathon	0−15	21	67	12	Silt loam	4.5	6.1	42	0.30	2.87	1.20	13.9
Marathon	15−30	19	67	14	Silt loam	2.8	6.2	35	0.15	1.56	1.50	7.7
Marathon	30−45	23	61	16	Silt loam	1.6	5.9	27	0.03	0.40	1.61	6.2
Outagamie	0−15	58	24	18	Sandy loam	1.7	6.2	34	0.09	1.05	1.78	16.1
Outagamie	15−30	52	21	27	Sandy clay loam	1.1	6.9	38	0.07	0.87	1.83	14.7
Outagamie	30−45	48	24	29	Sandy clay loam	1.0	7.1	26	0.05	0.96	1.63	15.4
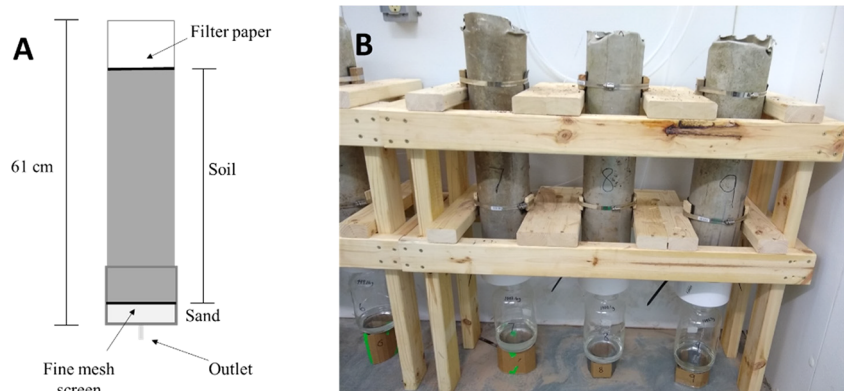
Figure 1. Undisturbed soil column for leaching experiments. (A) Soil column diagram. (B) Laboratory soil column arrangement.

have yet to be used to quantify desorption kinetics necessary for simulating the source zone.

The objectives of this study were to (i) quantify the leaching potential of PFAS from undisturbed vadose zone soil columns sampled from the main geographical regions of Wisconsin and amended with PFAS spiked biosolids to create a surficial source zone and (ii) evaluate the capability of biochar to mitigate leaching of PFAS when incorporated during land application. The study also explored how soil characteristic differences between geographical locations influence the PFAS transport and biochar effectiveness.

■ MATERIALS AND METHODS

Undisturbed soil columns were taken from four locations in Wisconsin in three different geographical regions, including the northern highland, eastern ridges and lowlands, and western upland (Table 1). The eastern ridges and lowland regions included two locations, a southeastern location (silty soils) and a northern location (loamy or clay soils) (Table 2).

■ SITE HISTORIES

Soil columns for the northern location of the eastern ridges and lowland region (Outagamie) were collected from a field in Outagamie County, mapped as the Onaway−Ossineke fine sandy loam soil series, receiving biosolids from a local wastewater treatment plant. The field was conventionally tilled, planted with corn, and injected with biosolids on five occasions over the previous 10 years (2011, 2013, 2015, 2017, and 2020) at a rate from 100 to 123 kg N ha^{-1}. Chemical

additions of nitrogen were also made to meet the nitrogen requirements of the crops.

Soil column sampling for the southern location of the eastern ridges and lowland region (Columbia) was completed from a field mapped as the Plano silt loam soil series in Columbia County. The field received biosolids from 1971 to 1973 and from 2005 to 2008 and was planted during this time with corn. Only animal manure and conventional fertilizer were applied after 2008. During the most recent rotations in 2018, 2019, and 2020, the field was planted with no-till corn silage and rye cover crops. Liquid manure had been fall-applied using direct injection in 2018 (39.4 m^3 ha^{-1}), 2019 (45.4 m^3 ha^{-1}), and 2020 (37.9 m^3 ha^{-1}). Additionally, the field received spring applications of 32% urea ammonium nitrate as needed to supplement nitrogen needs and 36.7 kg ha^{-1} of starter fertilizer with seeding. In 2021, soybeans were planted with no fertilizer application, and soil cores were taken in the summer prior to harvest.

The Marathon and Grant fields have no documented record of biosolid applications. Northern highland soil columns (Marathon) were collected from a field in Marathon County, mapped as a Fenwood−Rozellville silt loam soil series. In the six growing seasons preceding soil collection, the field was planted in a legume-rich rotational-grazing pasture mix for three years, followed by corn silage for one year and two years with an alfalfa brome mixture. The field was tilled in spring 2019 and spring 2020 using a chisel plow, followed by a field cultivator. In 2019, a 20−10−20 corn starter commercial fertilizer was applied at 168 kg ha^{-1}. Otherwise, nutrient amendment on the field has been managed with dairy manure,

Table 3. Biosolid PFAS Concentrations of Biosolids and Soil[a]

Compound	Abbreviation	CAS #	Alkyl chain length	Method detection limit water (ng L⁻¹)	Method detection limit soil (ng kg⁻¹)	Max U.S. biosolid conc. (ng g⁻¹)	Current study biosolid conc. (ng g⁻¹)	Columbia soil PFAS (ng g⁻¹)	Grant soil PFAS (ng g⁻¹)	Marathon soil PFAS (ng g⁻¹)	Outagamie soil PFAS (ng g⁻¹)
Perfluorobutanoate	C4 PFBA	375-22-4	4	2.6	0.27	3.2	27	0.2	0.3	ND	0.11
Perfluoropentanoate	C5 PFPeA	2706-90-3	5	1.28	0.12	6.7	45	0.15	ND	ND	0.08
Perfluorohexanoate	C6 PFHxA	307-24-4	6	1.2	0.15	11.7	92	0.14	0.26	0.43	0.11
Perfluoroheptanoate	C7 PFHpA	375-85-9	7	1.73	0.23	5.4	24	0.11	ND	ND	0.14
Perfluorooctanoate	C8 PFOA	335-67-1	8	0.63	0.17	70.3	290	0.27	ND	ND	76
Perfluorononanoate	C9 PFNA	375-95-1	9	0.87	0.15	21.1	80	0.91	ND	ND	0.17
Perfluorodecanoate	C10 PFDA	335-76-2	10	1.24	0.16	59.1	190	0.1	ND	ND	2
Perfluoroundecanoate	C11 PFUnA	2058-94-8	11	0.97	0.3	38.7	89	0.16	ND	ND	ND
Perfluorododecanoate	C12 PFDoA	307-55-1	12	0.69	0.21	26	5.9	ND	ND	ND	ND
Perfluorobutanesulfonate	C4 PFBS	45187-15-3	4	0.35	0.12	4.8	16	0.53	ND	ND	0.05
Perfluoropentanesulfonic acid	C5 PFPeS	2706-91-4	5	0.57	0.41	NM*	ND	ND	ND	ND	ND
Perfluorohexanesulfonate	C6 PFHxS	108427-53-8	6	0.9	0.21	6.6	19	0.35	ND	ND	ND
Perfluoroheptanesulfonate	C7 PFHpS	757124-72-4	7	0.57	0.53	NM	12	ND	ND	ND	ND
Perfluorooctanesulfonate	C8 PFOS	45298-90-6	8	0.89	0.19	618	1300	0.31	ND	ND	0.02
Perfluorooctane sulfonamide	C8 PFOSA	754-91-6	8	0.71	0.17	68.1	180	ND	ND	ND	ND
Fluorotelomer sulfonate 6:2	FtS 6:2	425670-75-3	8	1.9	0.28	NM	1	ND	ND	ND	ND
Fluorotelomer sulfonate 8:2	FtS 8:2	39108-34-4	10	1.1	0.52	NM	81	ND	ND	ND	ND
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	6	1.17	0.35	NM	ND	ND	ND	ND	ND
N-Ethylperfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	12	1.17	0.64	NM	5.1	ND	ND	ND	ND
N-Methylperfluorooctanesulfonamidoacetic Acid	N-MeFOSAA	2355-31-9	11	0.64	0.65	NM	11	ND	ND	ND	ND
11Cl-PF3OUdS	11CL-PF3OUdS	83329-89-9	9	0.47	0.24	NM	0.55	ND	ND	ND	ND

[a]NM = not measured. ND = nondetectable.

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applied passively by grazing livestock at a rate of 14.5 thousand kg ha^{-1} in 2016−2017 and actively applied in 2019 and 2020 at rates of 78.5 thousand kg manure per hectare and 112 m^3 slurry manure per hectare, respectively.

The western upland region soil columns (Grant) were taken from a field in Grant County. The field sampled is classified as a Tama silt loam in a crop rotation of oats with alfalfa seeding, three years of alfalfa, and three years of continuous corn. The soil columns were taken from the field following the third year of corn in the rotation. Conventional tillage management was used during corn production. Liquid manure had been fall-applied using direct injection in 2018 (270 m^3 ha^{-1}), 2019 (74 m^3 ha^{-1}), and 2020 (282 m^3 ha^{-1}). Solid pack manure had been applied in the fall of 2019 (31 tons ha^{-1}) and spring of 2021 (16 tons ha^{-1}). The field received spring applications of 28% urea ammonium nitrate as needed to supplement nitrogen needs.

UNDISTURBED SOIL COLUMN COLLECTION

Soil columns were obtained by pressing aluminum irrigation pipe (15 cm in diameter and 61 cm in length) into the soil profile and digging a trench next to the column for extraction, similarly to Fermanich et al.[41] (methods for soil column sampling are shown in SI Figure S1). Columns were then capped with a mesh screen and quartz sand (<2 cm) to provide drainage (Figure 1A). Filter paper was added above the soil to provide an even distribution of artificial precipitation. Columns were then secured in a wooden structure in a climate-controlled room for leaching experiments (Figure 1B). Soil samples were collected directly near the soil column extraction locations from a depth of 0−15, 15−30, and 30−45 cm and characterized at the UW Soil and Forage Analysis Laboratory (Madison, WI) for texture (percent sand, silt, and clay), organic matter content, soil pH, cation exchange capacity (CEC), total nitrogen (TN), and total organic carbon (TOC) (Table 2).

BIOSOLIDS AND BIOCHAR

Biosolids were obtained from a municipal wastewater treatment plant employing activated sludge treatment with enhanced biological phosphorus removal. Biosolids were a mixture of primary and thickened secondary solids that were subjected to mesophilic anaerobic digestion. Digested biosolids were collected as a liquid slurry with 4.7% solids content and total nitrogen content of 93 g kg^{-1} dry weight. Upon collection, biosolids were stored for less than 72 h at 4°C prior to spiking with representative concentrations of a mixture of PFAS molecules. Biosolids were spiked with PFAS compounds to an elevated level of PFAS (Table 3) to ensure the presence of common analytes, to increase leaching resolution, and to analyze potential treatment differences. Spiking of biosolids was completed stepwise similarly to Karnjanapiboonwong et al.[42] using dry biosolids spiked with PFAS in methanol. After PFAS were incorporated into biosolids, they were then held at room temperature to allow the methanol to evaporate. Biosolids were then hydrated with Milli-Q water to hydrate them to their original moisture content. Maximum PFAS concentrations previously measured in the U.S. biosolids[7] (Table 3) were used as target spike concentrations for individual PFAS analytes. Individual PFAS concentrations measured in the spiked biosolids were 2- to 8-fold higher than maximum PFAS concentrations measured

from the U.S. national biosolid inventory,[7] likely as a result of PFAS present in the initial biosolids. Biosolids (35 g) and biochar (70 g) were hand-incorporated to a depth of 15 cm to simulate injection/incorporation at rates of 415 kg N ha^{-1} and 38 tons ha^{-1}, respectively. Biochar was purchased from Carbon Tera (Wallerstein, Germany) and was produced from a mixture of 80% coniferous and 20% deciduous woods at a temperature of 700 °C for 36 h holding time (elemental analysis by % weight 85.7 C, 7.6 H, 0.2 N, 5.3 O).

COLUMN LEACHING TESTS

Column treatments included a control consisting of soil only (C), soil receiving biosolids (B), and soil receiving biosolids amended with biochar (BC). B columns included soil fertilized with spiked biosolids (3.2 to 70.3 ng g^{-1} for C$_4$−C$_{12}$ perfluoroxcarboxylates (PFCAs) and C$_4$−C$_{10}$ perfluorosulfonates, Table 3) at a rate of 68 kg N ha^{-1} biosolids. BC columns received an application of previously prepared biosolids (68 kg N ha^{-1}) amended with biochar (38 t ha^{-1}). Initially, all of the treatments were replicated in triplicate for each sampling location. Due to the nature of taking intact soil cores, some columns resulted in ponding due to compaction. As a result, Grant County columns ended with only duplicates due to soil column clogging, and Columbia County ended with duplicates for BC treatment. Leaching experiments were initiated with saturation of the columns using simulated precipitation (0.01 M CaCl$_2$ in DI) followed by 72 h of free drainage. The soil columns received a weekly simulated precipitation of a 1-yr 1-hr design storm (2.5 cm, 7.7 mL min^{-1}, resulting in 60 cm total precipitation for the study) for Wisconsin. Columns received rainfall weekly over six months with a total volume representative of average precipitation during a Wisconsin growing season (April through September, 60 cm of total precipitation). PFAS were measured on composite samples of leachate (weeks 1 to 9, 10 to 16, and 17 to 24). PFAS analysis was completed by ALS Environmental (Holland, MI) following a modified EPA 537 method using LC/MS/MS including the following 22 analytes: C$_4$−C$_{13}$ perfluoroxcarboxylates (PFCAs) and C$_4$−C$_{10}$ perfluorosulfonates (PFSAs), N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA), N-methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA), hexafluoropropylene oxide-dimer acid (HFPO-DA), 4,8-dioxa-3H-perfluorononanoic acid (DONA), 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-Pf3OUdS), 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS), 4:2 fluorotelomer sulfonic acid (FtS) 4:2, FtS 6:2, and FtS 8:2. Initial leachate from the Outagamie columns (weeks 1−4) was sampled and analyzed to determine PFAS in initial leachate due to intensive applications of biosolids. The method detection limits for all PFAS for water and soil measurements are provided in Table 3.

DATA ANALYSIS

Weekly leachate volume, PFAS loads, and flow weighted PFAS concentrations were used to evaluate the leaching potential of PFAS from undisturbed soil columns, determine significant differences between treatments, and evaluate the effect of soil characteristic differences between locations on PFAS leachability. Loading was calculated as a product of flow volume, concentration, and time; flow-weighted concentration was normalized by dividing the load by the cumulative leachate volume using methods similar to Holly et al.[43]
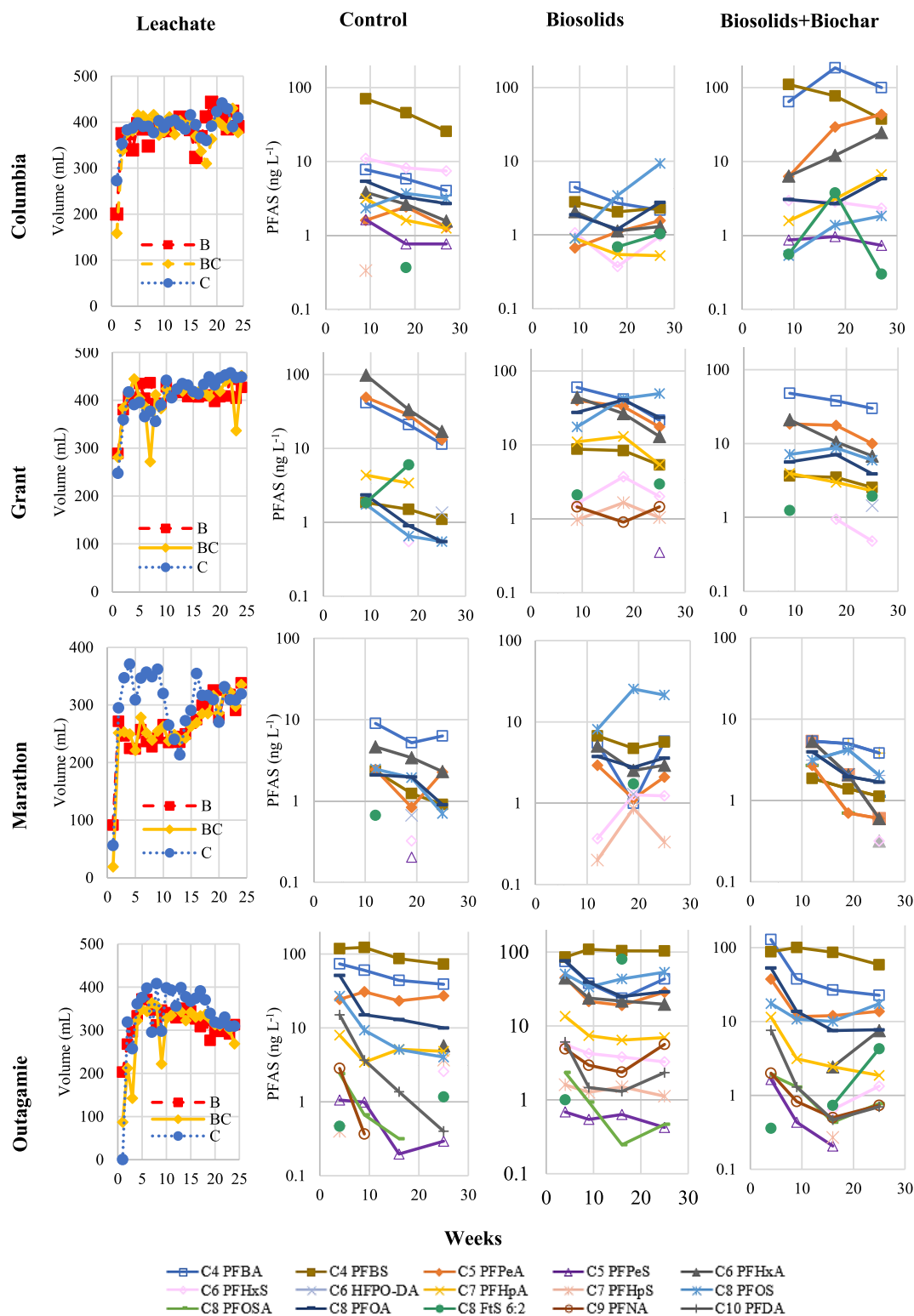
Figure 2. Mean leachate volume and PFAS concentrations in leachate.

Disappearance rate was calculated as the initial concentration of PFAS in columns (soil PFAS and biosolid PFAS) less the cumulative loading at each sample time step. Zero-, first-, and second-order kinetic models were used to fit the measured data through eqs 1, 2, and 3:

$$D_t = D_o - k_1 t \tag{1}$$

$$D_t = D_o e^{-k_2 t} \tag{2}$$

$$\frac{1}{D_t} = \frac{1}{D_o} + k_3 t \tag{3}$$

where D_o and D_t are the mass of a specific PFAS (ng) in soil columns at initial time and sampling time t, respectively; k_1 (ng kg^{-1} day^{-1}), k_2 (day^{-1}), and k_3 (ng^{-1} kg day^{-1}) are the

Table 4. Flow Weighted PFAS Concentrations (ng L⁻¹) in Leachate[a]

	Site											
	Columbia			Grant			Marathon			Outagamie		
Treatment	Control	Biosolids	Biosolids + Biochar	Control	Biosolids	Biosolids + Biochar	Control	Biosolids	Biosolids + Biochar	Control	Biosolids	Biosolids + Biochar
C4 PFBS	45 ± 38 A	2.4 ± 1.3 A	64 ± 89 A	1.0 ± 0.5 C	7.3 ± 0.2 A	2.2 ± 0.2 B	1.7 ± 0.6 B	5.8 ± 1.8 A	1.5 ± 0.5 B	94 ± 48 A	102 ± 17 A	80 ± 52 A
C4 PFBA	5.7 ± 2.6 A	3.0 ± 1.1 A	4.5 ± 4.4 A	23 ± 5.6 A	40 ± 1.7 A	31 ± 12 A	7.3 ± 3.6 A	4.3 ± 2.6 A	4.8 ± 1.9 A	49 ± 28 A	40 ± 12 A	41 ± 10 A
C5 PFPeS	1.0 ± 0.9 A	0.0 ± 0.0 A	0.3 ± 0.4 A	0.0 ± 0.0 A	0.1 ± 0.2 A	0.0 ± 0.0 A	0.1 ± 0.1 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.5 ± 0.4 A	0.6 ± 0.4 A	0.4 ± 0.2 A
C5 PFPeA	1.7 ± 0.9 A	1.2 ± 1.6 A	0.9 ± 1.2 A	28 ± 26 A	29 ± 0.6 A	14 ± 4.3 A	2.0 ± 0.6 A	2.2 ± 0.5 A	1.5 ± 1.2 A	26 ± 24 A	26 ± 8 A	16 ± 6.4 A
C6 PFHxS	8.8 ± 7.1 A	0.8 ± 0.2 A	1.7 ± 1.5 A	0.0 ± 0.0 B	1.3 ± 0.0 A	0.4 ± 0.4 B	0.1 ± 0.2 B	0.9 ± 0.4 A	0.1 ± 0.2 B	1.9 ± 1.5 A	4.0 ± 1.1 A	1.4 ± 0.1 A
C6 PFHxA	2.6 ± 0.4 A	1.5 ± 1.4 A	1.3 ± 0.3 A	37 ± 44 A	20 ± 2.3 A	10 ± 2.6 A	0.0 ± 0.8 A	0.4 ± 0.7 A	0.0 ± 1.2 A	23 ± 12.3 A	25 ± 11.0 A	14 ± 5.7 A
C6 HFPO-DA	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.6 ± 0.0 A	0.0 ± 0.0 B	0.7 ± 0.2 A	0.0 ± 0.3 A	0.0 ± 0.4 A	0.0 ± 0.1 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A
C7 PFHpS	0.1 ± 0.2 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 B	0.7 ± 0.1 A	0.0 ± 0.0 B	0.2 ± 0.0 A	0.4 ± 0.4 A	0.6 ± 0.0 A	1.3 ± 2.1 A	1.3 ± 0.2 A	0.1 ± 0.2 A
C7 PFHpA	1.9 ± 0.8 A	0.6 ± 0.3 A	0.5 ± 0.2 A	1.3 ± 0.4 B	9.3 ± 0.4 A	2.9 ± 1.2 B	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	5.0 ± 4.2 A	7.9 ± 2.5 A	3.7 ± 0.7 A
C8 PFOS	3.1 ± 2.4 A	5.5 ± 5.1 A	1.2 ± 0.6 A	0.7 ± 0.6 B	37 ± 4.6 A	5.1 ± 4.1 B	1.9 ± 0.6 A	17 ± 12 A	3.1 ± 1.9 A	8.4 ± 4.0 B	45 ± 14 A	13 ± 8.5 B
C8 PFOSA	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.5 ± 0.7 A	0.8 ± 0.8 A	1.0 ± 0.8 A
C8 PFOA	3.7 ± 2.4 A	2.1 ± 1.6 A	1.8 ± 0.4 A	0.9 ± 0.6 B	30 ± 5.9 A	4.0 ± 4.3 B	1.8 ± 0.4 A	3.4 ± 0.9 A	2.7 ± 1.4 A	17 ± 5.3 B	37 ± 8.3 A	15 ± 2.6 B
C8 FtS 6:2	0.1 ± 0.2 A	0.7 ± 0.4 A	0.9 ± 0.0 A	2.2 ± 3.2 A	1.9 ± 0.7 A	1.5 ± 1.3 A	0.3 ± 0.6 A	0.5 ± 0.9 A	0.0 ± 0.0 A	0.5 ± 0.2 A	0.2 ± 0.0 A	1.9 ± 2.4 A
C9 PFNA	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.4 ± 0.5 B	3.7 ± 1.3 A	0.8 ± 0.8 B
C10 PFDA	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 B	1.1 ± 0.1 A	0.0 ± 0.0 B	0.0 ± 0.0 A	0.0 ± 0.0 A	0.0 ± 0.0 A	3.3 ± 3.6 A	2.3 ± 0.9 A	1.5 ± 0.8 A

[a]Treatments with the same letter for a location are not statistically different at α = 0.05.

disappearance reactions for zero-, first-, and second-order kinetics, respectively; t is time expressed in day (number of day after the initiation of the experiment).

Kruskal−Wallis tests with pairwise Wilcoxon rank sum multiple comparison testing were used to assess significant differences in leachate volume collected from soil columns. Analysis of variance (ANOVA) and Tukey post hoc tests were executed on the flow weighted PFAS concentrations to evaluate the statistical significance of differences between treatments within locations, and Games−Howell post hoc tests were completed to evaluate the statistical significance of differences between location within treatments. Levene's test for homogeneity of variance and the Shapiro−Wilk test for normality were used to verify underlying assumptions of the ANOVAs. Statistical analysis was completed using the *car* and *multcomp* packages in R 4.3.1[44] and IBM SPSS Statistics (Version 27).

RESULTS AND DISCUSSION

Initial Soil PFAS. Initial soil sampled from sites with past biosolids application, Outagamie and Columbia, had measurable concentrations of nine and ten PFAS analytes (primarily longer chain C_7−C_{11} PFCAs; C_4, C_6, and C_8 PFSAs), with total Σ^{28} PFAS concentrations of 78 and 2 ng g^{-1}, respectively (Table 3). Buildup of legacy PFAS in Outagamie and Columbia soils was likely a result of previous biosolid application, with elevated concentrations in Outagamie due to more recent and frequent applications (last applied in 2020 and 2008, respectively). Most PFAS detected in the Outagamie and Columbia soils were large alkyl chain molecules, which suggests the significant contribution of AWI and sorption in their retention, as compared to small alkyl chain PFAS that are theoretically less retained.[9] The majority of PFAS measured in the Outagamie soil was PFOA (76 ng g^{-1}) and could be attributed to food packaging. The major employer for the community that generated biosolids applied to the Outagamie site was a food packaging company. PFOA has been measured in leachate from both directly fluorinated and nonfluorinated food containers.[45] Although manufacturing and import of PFOA ceased through the U.S. EPA toxic substances control act, PFOA manufactured or imported before 2020 may still be in use.[46] Perfluorinated carboxylic acids may also be produced during direct fluorination of high density polyethylene material; however, mostly short-chain PFAS are produced.[47] The Outagamie soil had lower concentrations of PFAS (total Σ^{28} PFAS 78 ng g^{-1}) in comparison with a previous study measuring PFAS from sludge applied soils in Alabama[11] (4,000 to 6,000 total PFAS ng g^{-1}), likely attributed to an elevated concentration of PFAS in the biosolids applied to the Alabama soils[11] (PFOA 27 to 1,800 ng g^{-1} compared to the U.S. max of 20 ng g^{-1}). Grant soil also had detectable levels of PFAS, but at lower concentrations (0.56 ng g^{-1}), despite having no documented application of biosolids. Numerous sources of PFAS in the environment exist, but studies have suggested PFAS may be in pesticides either as an active ingredient or surfactant carrier and should be studied further.[48] The field in Grant County had received regular pesticide treatments, which could have been a potential source of initial PFAS in those soils.

Leachate Volume. The weekly average leachate volume produced from the soil columns (262 ± 62 to 413 ± 54 mL) ranged from 57% to 89% of the artificial precipitation applied (462 mL), with a significant difference between all locations

(p-value <0.001). Grant soil columns produced more weekly leachate volume (409 mL) than the other columns (Columbia, 375 mL; Outagamie, 320 mL; Marathon, 276 mL). Leaching from columns typically reached a steady state at 4 weeks (Figure 2). Control columns produced greater amounts of leachate than the other treatments ($p < 0.01$), particularly in the Marathon and Outagamie soils ($p < 0.0005$). All columns experienced some loss of irrigated water to evaporation, with the highest evaporative losses occurring in Marathon soils amended with biosolids or biosolids + biochar. Some of the differences in leachate volume among treatments in the Marathon columns during the first 9 weeks may have been an artifact of how the columns were irrigated. However, the overall higher evaporation rates from amended Marathon columns can primarily be explained by increased water retention near the surface of the columns by the added organic carbon and higher air−water interfacial area in these well-drained soils due to their lower water holding capacity (Table 2).

PFAS Concentrations in Leachate. Collected leachate across all soil columns had measurable concentrations of 23 PFAS analytes of the 28 measured (i.e., C_4−C_{13} PFCAs, C_4−C_8, and C_{10} PFSAs, FtS 6:2, FtS 8:2, N-EtFOSAA, N-MeFOSAA, DONA, and HFPO-DA). Recently developed PFAS replacements, FtS 6:2 (industrial replacements for PFOA and aqueous film forming foam[49]) and HFPO-DA (used as a polymerization aid in the manufacture of some types of fluorinated polymer[50]) were measured in the leachate samples but not detected in the initial soil samples or biosolids used in the current study (Table 3), which could suggest previous soil contamination below detection limits or precursor biotransformation. Total PFAS leaching from biosolids has been measured to exceed PFAS present in biosolids and soils in other PFAS leaching studies.[10,51,52] Differences in mass leached and mass initially present were previously attributed to the presence of precursors (>75% of PFAS fluorine mass leached was associated with precursors).[10]

Biosolid application could result in PFAS groundwater contamination above the recommended groundwater standards for PFAS. PFOA + PFOS flow weighted concentration (FWC) from Grant, Marathon, and Outagamie B columns were all at or above the current Wisconsin Department of Health Services[53] recommended groundwater standard for combined PFOA and PFOS of 20 ng L^{-1} (66 ± 7, 20.4 ± 12, and 82 ± 17 ng PFOA+PFOS L^{-1}, respectively) (Figure 4, Table 4). Notably, PFOA and PFOS concentrations were two times higher than the maximum biosolids concentrations measured in 2001;[7] therefore, PFOA and PFOS concentrations are representative of a worst-case scenario for a one-time application of biosolids. Grant and Outagamie PFOA and PFOS concentrations in leachate were also above the interim recommendations for addressing groundwater contaminated with PFOA and PFOS (screening level and preliminary reduction goals of 40 and 70 ng PFOA+PFOS L^{-1}).

PFAS measured in leachate from the current study was lower than that of PFAS leached from previous packed column trials. PFBS, PFHxS, and PFOA concentrations were lower (Figure 3, 4 and Table 4) than measured concentrations from a packed columns study receiving composted biosolids from two facilities by Levine et al.[54] (395, 163, and 88 ng L^{-1} of PFBS, PFHxS, and PFOA). In parallel, PFAS concentrations from the current study were also lower than packed columns receiving biosolids from seven wastewater treatment plants by

Table 5. Zero-Order PFAS Disappearance Constants and Half-Lives

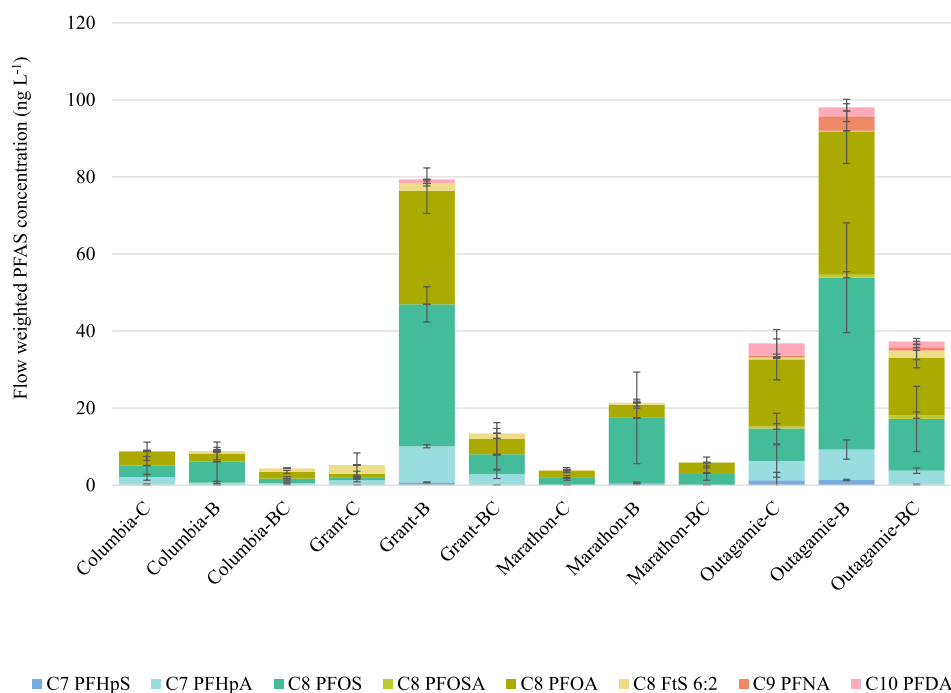|	Columbia		Grant		Marathon		Outagamie	
	k (pg kg^{-1} day^{-1}) (R^2)	$t_{1/2}$ (yr)	k (pg kg^{-1} day^{-1}) (R^2)	$t_{1/2}$ (yr)	k (pg kg^{-1} day^{-1}) (R^2)	$t_{1/2}$ (yr)	k (pg kg^{-1} day^{-1}) (R^2)	$t_{1/2}$ (yr)
C4 PFBS	−12.1 ± 1.3 (0.98)	6.3	−14.0 ± 3.8 (0.87)	0.9	−11.5 ± 0.9 (0.98)	0.8	−338.5 ± 20.5 (0.99)	0.2
C4 PFBA	−15.6 ± 2.7 (0.91)	16.7	−121.7 ± 9.3 (0.87)	3.1	−13.0 ± 2.0 (0.94)	1.2	−122.6 ± 14.2 (0.94)	1.2
C5 PFPeS							−1.8 ± 0.2 (0.80)	
C5 PFPeA	−9.3 ± 2.1 (0.78)	23.0	−58.4 ± 6.7 (0.87)	0.4	−5.1 ± 0.9 (0.89)	5.3	−80.5 ± 6.8 (0.97)	1.5
C6 PFHxS	−4.2 ± 1.2 (0.83)	14	−3.3 ± 1.9 (0.62)	4.3	−2.4 ± 1.0 (0.74)	4.7	−13.0 ± 0.8 (0.98)	0.8
C6 PFHxA	−11.0 ± 0.9 (0.99)	22	−57.1 ± 18.4 (0.80)	6.2	−9.8 ± 0.9 (0.98)	5.6	−78.7 ± 7.9 (0.96)	2.3
C6 HFPO−DA			−4.5 ± 2.5 (0.62)	0.1	−2.2 ± 0.9 (0.74)	0.0		
C7 PFHpS					−2.4 ± 0.9 (0.79)	3.0	−4.4 ± 0.6 (0.94)	1.4
C7 PFHpA	−3.3 ± 0.5 (0.94)	46	−13.6 ± 3.5 (0.89)	1.3			−24.6 ± 2.1 (0.98)	7.4
C8 PFOS	−40.8 ± 15.6 (0.76)	33	−19.6 ± 1.6 (0.93)	50	−37.6 ± 7.8 (0.94)	21	−142.1 ± 21.4 (0.93)	6.5
C8 PFOSA							−2.3 ± 0.5 (0.66)	40
C8 PFOA	−10.5 ± 2.7 (0.80)	52	−8.9 ± 2.3 (0.88)	24	−9.3 ± 0.8 (0.99)	19	−113.6 ± 19.1 (0.93)	808
C8 FtS 6:2	−3.4 ± 1.4 (0.73)	0.3	−13.1 ± 3.2 (0.90)	0.1			−0.3 ± 0.2 (0.40)	1.3
C9 PFNA							−11.3 ± 2.4 (0.88)	22
C10 PFDA							−6.8 ± 1.2 (0.86)	371

Figure 3. Flow weighted concentrations for long chain PFAS (≥7 carbon atoms) in leachate. B = biosolids, BC = biosolids and control, C = control.

Schaefer et al.[10] (25 to 500 ng PFOA L^{-1} and 10 to 150 ng PFOS L^{-1}). PFOA and PFOS in biosolids for the study by Schaefer et al.[10] were notably lower (1 to 8 ng PFOA g^{-1} and 0.386 to 150 ng PFOS) than biosolids used in the current study. Packed columns have reduced micro- and macro-porosity (resulting in treatment differences between studies), and packed column trials will overestimate PFAS leached due to a reduction in AWI. In the current study, PFOA and PFOS concentrations from biosolid columns (0.3 to 47 ng L^{-1} and 0 to 61 ng L^{-1}) were within the range of previously measured PFOA and PFOS (0 to 1,500 ng PFOA L^{-1} and 0 to 98 ng PFOS L^{-1}) in U.S. groundwater wells (n = 254).[55] Although previous groundwater measurements indicated the significance of urban areas over agricultural fields in determining PFAS contamination,[55] future studies should evaluate the proximity

of contaminated wells to areas with a history of agricultural fields applying biosolids.

PFAS Disappearance Constants and Half-Lives. PFAS disappearance from biosolid columns was best fit by zero-order kinetics across all sites (Table 5). Therefore, PFAS disappearance was independent of soil PFAS concentration. Notably, PFAS precursor transformation was not analyzed in the current study, which could impact disappearance rates for individual PFAS. PFAS precursors (i.e., polyfluoroalkyl phosphoric acid diesters, or diPAPs, commonly used in food packaging) have been previously measured to make up on average 54% of total PFAS in biosolids.[56] Major transformation products of diPAPs include C$_8$ PFOA (2.1% of total transformation products), 5:3 fluorotelomer carboxylic acid (FTCAs) (9.3%), C$_6$ PFHxA (6%), and C$_5$ PFPeA (6.4%).[57]
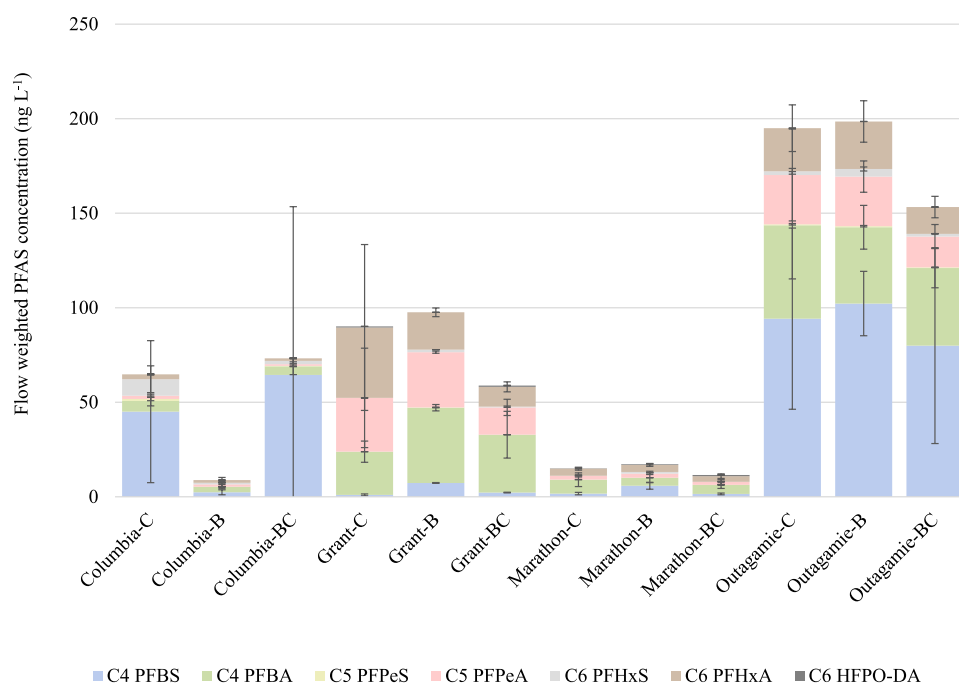
Figure 4. Flow weighted short-chain (<7 carbon atoms) PFAS concentrations in leachate. B = biosolids, BC = biosolids, and control, C = control.

Biosolids in the current study had elevated concentrations of PFAS (2−3 times the measured maximum PFAS concentrations of biosolids in the U.S.), and any biotransformation of PFAS would likely result in a small impact on measured kinetics (particularly long-chain PFAS).

PFAS transport in saturated soils was previously determined to be a nonideal transport, which can be interpreted as a nonequilibrium process dominated by multirate adsorption/desorption[58] modeled as a tempered one-sided stable density distribution.[59] Tempered one-sided stable density describes the disappearance rate in three regions: (1) The desorption/adsorption rate increases exponentially with the initial pore volumes. (2) The rate is independent of pore volume. (3) The disappearance rate decreases with pore volume in the extending tail region. A zero-order fit of disappearance in the current study is in parallel with segment (2) where the rate is independent of the pore volume. Therefore, calculated reaction rates are likely representative of segment (2) in the one-sided density distribution model. Notably, disappearance rate constants were specific to soil sites and are likely a function of the AWI and soil chemical composition. Future modeling efforts to predict PFAS leaching would benefit from additional undisturbed soil column trials with varying soil composition to facilitate quantifying the impact of soil type.

Half-lives were a function of chain length as previously found[11] with short-chain half-lives ranging from 0.2 to 23 years and long chain ranging from 0.1 to 808 years. Zero-order half-lives are dependent on initial PFAS concentrations and the rate of disappearance. Therefore, Outagamie and Grant columns had longer half-lives than Columbia and Marathon columns due to legacy PFAS. Measured half-lives were longer than previously modeled half-lives (1 to 3 years) for sludge applied soil in Alabama likely as a result of a first-order reaction model in the previous study.[11] Notably, calculated reaction rates in this study do not represent the decrease in rate upon breakthrough, and half-lives are expected to be longer.

Legacy PFAS and Leaching. Previous application of biosolids can result in legacy PFAS and sustained PFAS leaching after application. Leachate from the control Outagamie soil column had significantly greater flow weighted mean concentrations (FWC) of C_8 PFOA and C_8 PFOS than the FWC measured in leachate from the other control columns (Figure 3, Table 4). PFOA + PFOS leachate concentrations (26 ± 7 ng PFOA + PFOS L^{-1}) from the Outagamie control column were in exceedance of the recommended groundwater standard due to frequent application of biosolids (five occasions over the past 10 years). Despite no known history of biosolids application at the Grant and Marathon sites and the minimal PFAS detected in initial soil (only PFBA and PFHxA for Grant), measurable PFAS were detected in leachate from Grant and Marathon control columns (C_4−C8 PFCAs, C_4−C_6 and C_8 PFSAs, FtS 6:2, N-MeFOSAA, and HFPO-DA). Differences in PFAS detection in leachate and soil could have resulted from soil sampling or the transformation of precursors not measured in initial soil samples. Grant and Marathon soils may have been heterogeneous geospatially with preferential binding to layers with higher mineral content, resulting in no detection in initial composite soil samples. PFAS have been previously measured in insecticides[60] and are capable of long-range transport.[61] Therefore, multiple PFAS precursor sources for Grant and Marathon County soils could exist. Marathon control columns had relatively low leaching of PFAS from control columns (Figures 3 and 4) compared to Grant. Differences could be attributed to land use, as Marathon had been in pasture, while Grant has consistently been in grain or forage crop production with annual application of various pesticides.

Influence of Soil Properties. Several soil properties (e.g., water holding capacity, organic carbon content, and pH) may have influenced PFAS leaching. Grant County soil had the greatest water holding capacity (Table 2), and the Grant biosolid columns leached significantly greater C_4−C_7 PFCAs and C_5, C_6, and C_8 PFSAs than PFAS from Columbia and

Marathon biosolid columns (Figure 3. and Figure 4). FWC treatment comparison across location is provided in the Supporting Information Tables S1 and S2). A greater water retention would correspond to a greater degree of saturated flow through pore spaces, decreasing AWI, which has been measured to decrease with increasing water contents.[62] Reduced AWI should also lower evaporation rates, explaining the highest leachate volumes collected for the Grant columns. Therefore, Grant County soil likely had a lower AWI, resulting in a decrease of PFAS surface activity (especially the long alkyl chain PFAS) and increased leaching. In contrast, the Marathon County soils had the lowest water holding capacity, resulting in the greatest evaporative losses and similar or lower disappearance rates for most PFAS, consistent with an increased AWI. PFAS leaching from batch leaching experiments found the PFAS leached was a function of the liquid to soil ratio[63] further supporting the importance of water holding capacity and leaching. Remarkably, the perceived impact of water holding capacity for the Grant soil resulted in more PFAS leaching than soils with a previous history of PFAS contamination (Columbia). Leachate from the Outagamie biosolids columns (second greatest water holding capacities) had significantly greater C_4 PFBS and C_8 PFOA than the Columbia and Marathon biosolid columns.

Studies using both meta-analysis of published values[64] and experimental measurement of PFAS soil sorption coefficients[65] have concluded that multiple soil properties predict PFAS sorption better than individual properties. Both of these studies found higher organic carbon content, lower pH, and higher clay or clay + silt content to be correlated with greater PFAS retention in soil, particularly for long-chain anionic PFAS. Our data are consistent with those findings. Although organic carbon contents in our soils were all low (<3%) and varied little, the soil columns with the lowest amount of leaching (Marathon) had the highest surface soil TOC and the lowest soil pH (5.9−6.2). Likewise, faster PFAS disappearance rates in Outagamie County soils correlate with lower silt + clay contents (≤52% compared to ≥77% for all other soils). Previous modeling efforts on field soils by Silva et al.[9] illustrated reduced AWI-mediated PFAS sorption for soil horizon textural heterogeneity. Previous AWI reductions were a result of restricting hydraulic conductivity and increasing saturated flow in the vadose zone. Outagamie columns had the greatest extent of textural heterogeneity (Table 2) (11% clay content variation with depth) compared to other locations (4% clay content variation with depth), which may have further increased the level of PFAS leaching. Conclusions regarding the impact of soil properties and PFAS leaching are cursory due to the limited number of replications evaluated in our study. Additional measurements with the support of tracer studies are warranted to provide reliable statistical analysis and modeling efforts.

Mitigation Potential of Biochar. For soil with elevated PFAS leaching potential (Outagamie and Grant in this study), amending biosolids with biochar during application resulted in the mitigation of PFAS in leachate (Figures 3 and 4). Biochar had the greatest reduction of PFAS analytes from the Grant columns with significant reductions of C_7, C_8, and C_{10} PFCAs and C_4 and C_6-C_8 PFSAs (40% reduction in measured Σ^{28} PFAS). Biochar also reduced PFAS in leachate produced from biosolids for Outagamie columns (significant reductions of C_8 and C_9 PFCAs; C_8 PFOS with a 64% reduction in Σ^{28} PFAS) and Marathon columns (C_4 PFBS and C_6 PFHxS with a 45% reduction in Σ^{28} PFAS). Individual PFAS were not significantly reduced by biochar for the Columbia columns, although reduction trends for C_8 PFOA and C_8 PFOS were measured. Sorption of PFAS is dependent on initial PFAS concentration, as sorption of PFAS in batch trials has been previously represented by pseudo-second-order model[66] and linear sorption.[67] Previously measured PFAS adsorption mechanisms include electrostatic interaction, hydrogen bonding, and hydrophobic interaction between long-chain hydrophobic PFAS and biochar.[68] At lower measured concentrations for Columbia and Marathon columns, PFAS adsorption to biochar may be driven by Henry's law, similar to other surfactants.[63,69] Electrostatic adsorption is dependent on the concentration, as surfactants are adsorbed by monomers. For higher PFAS concentrations, as measured for Grant and Outagamie columns, PFAS adsorption to biochar may be facilitated by lateral interactions between hydrocarbon chains, increasing the amount sorbed per concentration.

Biochar mitigated PFAS leaching to levels below the Wisconsin PFOA + PFOS groundwater standard for Grant and Marathon columns with no history of biosolid application (9 ± 6 and 6 ± 2 ng of PFOA+PFOS L^{-1}, respectively). Repeat application of biosolids resulted in PFOA + PFOS concentrations exceeding the groundwater standard for the biosolids and biochar Outagamie columns (28.4 ± 9 ng of PFOA+PFOS L^{-1}). Fields with an extended history of biosolid application may require additional biochar mass or deeper incorporation to reduce PFOA and PFOS below the groundwater recommendation.

Biochar had limited impact on leaching of short-chain PFAS (PFAS < C_7) (Figure 4, Table 4) (with an exception of reductions of C_4 PFBS, C_6 PFHxA, and C_6 PFHxS), as adsorption of PFAS to biochar increases with chain fluorocarbon chain length.[15] However, we cannot exclude the possibility that short-chain compounds (possibly as a result of transformation of precursors) leached from soil depths below the surface layer where the amendments were added, resulting in a reduction in the treatment potential. A best management practice of applying biochar to fields receiving biosolids could protect groundwater wells and resources from PFAS, necessitating a field evaluation. Additional long-term studies are needed to investigate the leaching potential of PFAS sorbed to biochar, which would be beneficial to biochar adoption.

■ CONCLUSIONS

Application of biosolids with elevated concentrations of PFAS raises potential risks to groundwater contamination, necessitating new regulations and technologies for mitigation. Water holding capacity of soils and organic carbon may drive PFAS leaching between locations. Biochar reduced long-chain PFAS losses from soils with an elevated potential for PFAS leaching, potentially lowering risks to human health. Long-term field assessment is needed to verify measured PFAS leaching and treatment potential of biochar, beneficial to the sustainable use of biosolids.

■ ASSOCIATED CONTENT

Data Availability Statement

Observed leaching volume and concentration data used in the analysis mentioned in the text are available at https://datadryad.org/stash/share/TZuSiRrafZnxyI8l4u_m9D-ycrhj8BFRA6kf0f-73U4.

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CRediT: **Michael Holly** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing-original draft, writing-review & editing; **Kpoti M. Gunn** data curation, formal analysis, validation, writing-original draft, writing-review & editing; **Daniel Keymer** investigation, methodology, supervision, writing-original draft, writing-review & editing; **Joseph R. Sanford** investigation, methodology, supervision, writing-review & editing.

Notes

The authors declare no competing financial interest.

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