SUPPORTING INFORMATION

Title: Effect of geochemical conditions on PFAS release from AFFF-impacted saturated soil columns

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S1. Chemicals and Materials

Soil characterization. Soil used in the columns was characterized for particle size distribution by hydrometer, cation exchange capacity by NH_4 displacement, anion exchange capacity at pH 7.0, soil pH, and carbon speciation (Table S1, Agvise Laboratories, Northwood, ND).

Table S1. Physical/chemical soil properties analyzed by Agvise Laboratories (Northwood, ND).

% sand	79
% silt	6
% clay	15
CEC	9.5
AEC	-0.04
%OC	1.1
pH	6.7

Chemicals. Natural abundance and enriched stable isotope PFAS standards were obtained from Wellington Laboratories (Ontario, Canada; Table S2). Salts used included: ammonium acetate (Thermo Fisher Scientific, Optima grade), manganese sulfate monohydrate (Sigma-Aldrich, ReagentPlus, ≥99% grade), sodium sulfate (Thermo Fisher Scientific, Certified ACS grade), calcium chloride (Thermo Fisher Scientific, Certified ACS grade), sodium tetraborate (Thermo Fisher Scientific, Certified ACS grade), sodium hydroxide (Thermo Fisher Scientific, Certified ACS grade), sodium chloride (Thermo Fisher Scientific, Certified ACS grade), sodium bicarbonate (Mallinckrodt Chemicals, ACS grade), sodium bromide (Mallinkrodt, ACS 99%+ grade), and hydrochloric acid (Thermo Fisher Scientific, TraceMetal grade). Liquids used in this study included: ammonium hydroxide (Thermo Fisher Scientific, Optima grade), methanol (Thermo Fisher Scientific, Optima LC/MS grade), isopropanol (Thermo Fisher Scientific, Optima LC/MS grade), and water (Thermo Fisher Scientific, Optima LC/MS grade), Artificial groundwaters were prepared every 3-4 days using deionized water (Millipore system, ASTM Type I).

Table S2. Natural abundance and associated enriched stable isotope (internal standard) reference materials used in targeted PFAS analysis.

Chemical Name	Acronym	Neutral Molecular Formula	Internal Standard
Perfluoroalkyl carboxylic acids			
Perfluoro-n-butanoic acid	PFBA	C4HO2F7	13C4-PFBA
Perfluoro-n-pentanoic acid	PFPeA	C5HO2F9	13C5-PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	13C2-PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	13C4-PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	13C4-PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	13C5-PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	13C2-PFDA
Perfluoro-n-undecanoic acid	PFUdA	C11HO2F21	13C2-PFUdA
Perfluoro-n-dodecanoic acid	PFDoA	C12HO2F23	13C2-PFDoA
Perfluoro-n-tridecanoic acid	PFTrDA	C13HO2F25	13C2-PFTeDA
Perfluoro-n-tetradecanoic acid	PFTeDA	C14HO2F27	13C2-PFTeDA
Perfluoro-n-hexadecanoic acid[ii]	PFHxDA	C16HO2F31	13C2-PFHxDA
Perfluoro-n-octadecanoic acid[ii]	PFODA	C18HO2F35	13C2-PFHxDA
Perfluoroalkane sulfonates			
Perfluoropropane sulfonate	PFPrS	C3HO3SF7	13C3-PFBS
Perfluorobutane sulfonate	PFBS	C4HO3SF9	13C3-PFBS
Perfluoropentane sulfonate	PFPeS	C5HO3SF11	18O2-PFHxS
Perfluorohexane sulfonate[i]	PFHxS	C6HO3SF13	18O2-PFHxS
Perfluoroheptane sulfonate	PFHpS	C7HO3SF15	18O2-PFHxS
Perfluorooctane sulfonate[i]	PFOS	C8HO3SF17	13C4-PFOS
Perfluorononane sulfonate	PFNS	C9HO3SF19	13C4-PFOS
Perfluorodecane sulfonate	PFDS	C10HO3SF21	13C4-PFOS
Perfluoroundecane sulfonate	PFUdS	C11HO3SF23	13C4-PFOS
Perfluorododecane sulfonate	PFDoS	C12HO3SF25	13C4-PFOS
Chlorinated perfluoroalkane sulfonates, ether sulfonates, cyclic sulfonates			
8-chloro-perfluorooctane sulfonate	Cl-PFOS	C8HO3SClF16	13C4-PFOS
9-chloro-3-oxa-perfluorononane sulfonate	Cl-O-PFNS	C8HO4SClF16	13C4-PFOS
11-chloro-3-oxa-perfluoroundecane sulfonate	Cl-O-PFUdS	C10HO4SClF20	13C4-PFOS
Perfluoro ethyl cyclohexane sulfonate	PFEtCHxS	C8HO3SF15	13C4-PFOS
Perfluoroalkane sulfonamides			
Perfluorooctane sulfonamide	FOSA	C8H2O2SNF17	13C8-FOSA
N-methylperfluoro-1-octane sulfonamide	MeFOSA	C9H4O2SNF17	d3-MeFOSA
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	C10H6O2SNF17	d5-EtFOSA
Perfluoroalkane sulfonamido acetic acids			
Perfluorooctane sulfonamido acetic acid[ii]	FOSAA	C10H4O4SNF17	d3-MeFOSAA
N-methylperfluorooctane sulfonamido acetic acid[i, ii]	MeFOSAA	C11H6O4SNF17	d3-MeFOSAA
N-ethylperfluorooctane sulfonamido acetic acid[i, ii]	EtFOSAA	C12H8O4SNF17	d5-EtFOSAA
Fluorotelomer sulfonates			
4:2 fluorotelomer sulfonate	4:2 FtS	C6H5O3SF9	13C2-4:2 FTS
6:2 fluorotelomer sulfonate	6:2 FtS	C8H5O3SF13	13C2-6:2 FTS
8:2 fluorotelomer sulfonate	8:2 FtS	C10H5O3SF17	13C2-8:2 FTS
10:2 fluorotelomer sulfonate	10:2 FtS	C12H5O3SF21	13C2-8:2 FTS
Fluorotelomer alkanoic acids			
6:2 fluorotelomer carboxylic acid[iii]	6:2 FTCA	C8H3O2F13	13C2-6:2 FTCA

8:2 fluorotelomer carboxylic acid[iii]	8:2 FTCA	C10H3O2F17	13C2-8:2 FTCA
10:2 fluorotelomer carboxylic acid[iii]	10:2 FTCA	C12H3O2F21	13C2-10:2 FTCA
2H-perfluoro-2-octenoic acid (6:2)[iii]	6:2 UFTCA	C8H2O2F12	13C2-6:2 UFTCA
2H-perfluoro-2-decenoic acid (8:2)[iii]	8:2 UFTCA	C10H2O2F16	13C2-8:2 UFTCA
2H-perfluoro-2-dodecenoic acid (10:2)[iii]	10:2 UFTCA	C12H2O2F20	13C2-10:2 UFTCA

i. Present in linear and branched isomers.
ii. PFHxDA, PFODA, FOSAA, MeFOSAA, and EtFOSAA excluded from high-level (>0.37 ng/mL) calibration standards to prevent instrument carryover.
iii. Stored in 100% Optima HPLC-grade isopropanol (IPA) to limit potential degradation. (All other compounds stored in 100% Optima HPLC-grade methanol.)

S2. Column Parameters

Porosity. Soil columns were weighed before packing, after packing, and after saturation to calculate total porosity: total water content divided by the column nominal volume ({(soil weight x gravimetric water content) + (column saturated weight – packed column weight)}/ 0.271 L)

Dispersivity and effective media porosity. Conservative tracer experiments using NaBr were conducted simultaneously with monitoring the release of PFAS. After approximately 60 days of flow, NaCl in the artificial groundwater was replaced with an equimolar concentration of NaBr for one to two days while column effluents were sampled at intervals of 210-240 minutes. Effluent samples were refrigerated prior to analysis. Samples were filtered (0.45 μm, nylon) and analyzed for Br- with ion chromatography. HYDRUS 1- D (Version 4.17.0140) was used to model the desired parameters with the Isotopes HYDRUS 1-D module using the inverse solution capability. Effective media porosity was determined as the measured total porosity – modeled immobile water content. Column pH 7_b was assumed to have the same ratio of effective media porosity to total porosity as column pH 7_a.

Table S3. Column hydrologic properties

Column	flow rate (mL/hr)	pore volume (L)	bulk density (g/cm^3)	porosity	soil mass (g)
pH 7_a	8.85	0.091	1.582	0.334	429
pH 7_b	7.30	0.098	1.574	0.362	427
pH 3_a	6.56	0.098	1.624	0.363	440
pH 3_b	7.70	0.066	1.580	0.242	428
pH 10 NaCl_a	7.53	0.084	1.602	0.310	434
pH 10 NaCl_b	7.08	0.079	1.595	0.290	432

Table S4. Calculated dispersivity, immobile water contents, mobile-immobile phase exchange rates, and effective media porosity from HYDRUS 1-D

Column	**Dispersivity (cm)**	**Immobile Water Content (-)**	**Mobile-Immobile Phase Exchange Rate (day^{-1})**	**Effective Media Porosity (-)**
pH 7_a	0.53	0.042	0.00015	0.33
pH 3_a	0.54	0.027	0.00014	0.36
pH 3_b	4.8	0.18	0.091	0.24

pH 10 NaCl_a	0.69	0.098	0.00031	0.31
pH 10 NaCl_b	0.25	0.13	0.000091	0.29

S3. Instrumental Analysis

Column Effluent Sample Preparation. After collection, column effluent samples were stored in a dark refrigerator at 3 °C. Prior to analysis, the samples were removed from the fridge, vortexed to re-suspend any particulate matter, and immediately diluted into a 15 mL centrifuge tubing that contained previously prepared solvent and internal standard mixture to give the desired final solvent composition and internal standard concentration upon addition of the sample. Samples were diluted 1x to 400x in water such that the highest concentration PFAS (PFOS) was present at a concentration below 10,000 pg / 1350 µL. The combined solvents, sample, and internal standards were then mixed with a vortex mixer and centrifuged at 3,500 rpm for 15 minutes. Finally, 1350 µL of the supernatant was poured off into an HPLC vial and capped.

Calibrant and Quality Control Sample Preparation. Intermediate dilutions of PFAS reference standards were made in isopropanol (6:2 FTCA, 8:2 FTCA, 10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA and associated enriched stable isotope PFASs) or in methanol (all others). Column effluent samples, calibration standards, and quality control standards were prepared such that the final solution contained, by volume: 64% water, 23% methanol, 3% of 0.01% ammonium hydroxide in water, and 10% isopropanol, with 100 pg of enriched stable isotope (internal standard) PFASs per 1350 µL final volume. 15 calibration standards were prepared with each analytical sequence that contained between 0.1 and 10,000 pg / 1350 µL of each target PFAS with 100 pg / 1350 µL of each internal standard. To reduce instrument carryover, PFHxDA, PFODA, FOSAA, MeFOSAA, and EtFOSAA were not present in calibration standards that contained over 500 pg / 1350 µL. Analyzed every ten injections with each sequence were QC samples that contained 300 pg / 1350 µL of each target PFAS and internal standards, blanks with only internal standards, and double blanks with neither target nor internal standard PFASs. All solutions were analyzed in 2mL amber glass HPLC vials (2 mL, Agilent) with polyethylene, pre-slit caps (Verex Cert+, Phenomenex, Torrance, CA).

Liquid Chromatography. The same instrumentation, materials, analytical standards, and analytical methods were used as in Maizel et al. (2021). All PFAS analysis used a ExionLC (SCIEX, Framingham, MA) high-pressure liquid chromatography system (HPLC) with 1000 µL injection volumes and Gemini C18 analytical columns (3 mm x 100 mm x 5 µm; Phenomenex, Torrance, CA) preceded by SecurityGuard™ C18 Guard Cartridge (4 mm x 2 mm I.D.; Phenomenex) guard columns. Between the guard and analytical columns were two Zorbax DIOL guard columns (ESI- analysis, 4.6 mm x 12.5 mm x 6 µm; Agilent, Santa Clara, CA). All columns were kept within a column oven at 40 °C. A gradient elution was used with two mobile phases: (A) 20 mM ammonium acetate in water and (B) methanol. The gradient profile is shown in Table S5. Flow leaving the analytical column was diverted to waste for the first four minutes of each run.

Table S5. LC gradient profile for all PFAS analysis

Time (min)	**A** (%)	**B** (%)	**Flow Rate** (µL / min)
0	90	10	600
0.5	50	50	600
8	1	99	600
13	1	99	600
13.5	90	10	600
20 (end)	90	10	600

Mass Spectrometry. All PFAS analysis was collected with a X500R QTOF-MS (SCIEX) with SWATH Data-Independent Acquisition. Briefly, data-independent acquisition is an analytical technique in which ions within specified *m/z* ranges that enter the mass spectrometer simultaneously are fragmented together and the resulting fragment ions are associated with precursor ions by retention time and peak shape matching. Each run, TOFMS precursor ion data was collected over the *m/z* range 100-1200 for 1283 cycles with 20 ms accumulation time out of a total scan time of 842 ms. For the collection of TOFMS precursor ion data, the collision energy was -5 V with no spread and the declustering potential was -20 V with no spread. Product ion data (MS/MS) was collected over the *m/z* range 50-1200, across precursor ion *m/z* ranges 100-150, 150-200, 200-250, 250-300, 300-350, 350-400, 400-500, 500-600, 600-700, 700-800, 800-1200. MS/MS data for each precursor m/z range was collected with 50 ms accumulation times and collision energies of -35 V with 30 V spread. Electrospray voltage was -4500 V. The ion source temperature was 550 °C. The ion source, curtain, and collision gas pressures were set to 60, 35, and 10 psi, respectively. Mass calibrations were automatically performed every five injections.

S4. Data Analysis

Target Data Analysis. Calibration curves were fit with $1/x^2$-weighted linear regressions of the ratio of target PFAS peak area to internal standard peak area against the ratio of target PFAS injected mass to internal standard injected mass. Calibrations were only considered valid when each standard had recovery between 70 – 130% and the Pearson coefficient of fit was over 0.97. If calibrations failed to meet those criteria, the calibration range was narrowed until a valid calibration was obtained. The lowest valid calibration point was used to determine the batch specific quantification limit. Measured results were only considered when they were within the valid calibration range. Confirmation of targeted analytes was based on retention time matching with reference standards and mass error < 10 ppm.

Suspect Data Analysis. Mass spectral features were integrated with SCIEX OS. Mass spectral features were compared against an extracted ion chromatogram (XIC) list that contained 1432 PFAS from 136 homologous series classes that were either previously reported or speculated to exist based on previously reported classes (e.g., n:3 fluorotelomer sulfonates based on the previous observation of n:3 fluorotelomer carboxylic acids in Weiner et al 2013). Additionally, mass spectral features were compared against a mass spectral library with MS/MS spectra for over 300 PFAS. Features were considered "XIC Hits" and associated with PFAS on the XIC list when precursor ion *m/z* was within 5 ppm of the nominal *m/z* ($[M-H]^-$) the isotope ratio difference was < 10%, the library spectral match score was < 70%, and the retention time was consistent across multiple runs and was plausible in relation to other observed PFAS. Features were considered "Library Hits" and associated with PFAS on the XIC list when the precursor ion *m/z* was within 10 ppm of the nominal *m/z*, the isotope ratio difference was < 20%, the library spectral match score > 70%, and the retention time was consistent across multiple runs and was plausible in relation to other observed PFAS. Additionally, in order to ensure the most representative effluent concentration profiles were available, features were marked as "Included" if the precursor ion */z* was within 10 ppm of the nominal *m/z*, the isotope ratio difference was < 20%, the library spectral match score < 70%, as well as having a retention time that had consistently been observed in other XIC or Library hits. Suspect PFAS were semi-quantitated by a previously reported procedure in which the concentrations of suspect compounds were estimated by association with a target PFAS, and assuming an identical molar response factor. Suspect data, including semi-quantitation associations, is available in the supplemental data sheet.

In this experiment, data were only collected with negative electrospray ionization (ESI-). In previous analyses, no cations were found in this soil.[1] However, due to many zwitterions ionizing less efficiently in ESI- than ESI+, some zwitterions previously reported in this soil were not detected here (e.g. TAmPr-FASA, TAmPr-FASA-PrA). Soil concentrations for zwitterions were also used from ESI- analysis for consistency (Table S11).

Semi-quantitation. PFAS without analytical standards were semi-quantified using a previously published method.> Different calibrants were used for pH 3 and pH 10 data compared to pH 7 data due to low recoveries of particular internal standards (Tables S6, S7). Standards with retention times greater than 9 minutes had low recoveries (<30%); therefore semi-quantitative analytes that eluted before 9 minutes were not paired with calibrants eluting after 9 minutes, as this would produce an artificially high semi-quantitative value. The difference in calibrants can cause up to a ~4x difference in semi-quantitative concentrations: pH 7 results calculated with the same calibrants as the pH 3/pH 10 data produced a range of 19%-417% of the original concentrations, with 39% of data points being <70% of the original concentration and 30% of data points being >130% of the original concentration.

Table S6. calibrants for pH3/10 and pH 7

Analyte	calibrant for pH 7 data	calibrant for pH 3/pH 10 data	same?
Am-CPr-FBSA	EtFOSA	PFOA	no
AmPr-FEtSA	EtFOSA	PFOA	no
AmPr-FPrSA	EtFOSA	PFOA	no
AmPr-FBSA	EtFOSA	PFOA	no
AmPr-FPeSA	EtFOSA	PFOA	no
AmPr-FHxSA	EtFOSA	PFOA	no
AmPr-FPrSA-PrA	EtFOSAA	4:2 FTS	no
AmPr-FBSA-PrA	EtFOSAA	4:2 FTS	no
AmPr-FPeSA-PrA	EtFOSAA	4:2 FTS	no
AmPr-FHxSA-PrA	EtFOSAA	4:2 FTS	no
Cl-PFPrS	PFPrS	PFPrS	yes
Cl-PFBS	PFBS	PFBS	yes
Cl-PFPeS	PFPeS	PFPeS	yes
Cl-PFHxS	PFHxS	PFHxS	yes
Cl-PFHpS	PFHpS	PFHpS	yes
CMeAmPr-FPrSA	EtFOSA	PFOA	no
CMeAmPr-FBSA	EtFOSA	PFOA	no
CMeAmPr-FPeSA	EtFOSA	PFOA	no
CMeAmPr-FHxSA	EtFOSA	PFOA	no
CMeAmPr-FBSAPrA	EtFOSAA	4:2 FTS	no
CMeAmPr-FHxSAPrA	EtFOSAA	4:2 FTS	no
FEtSA	FOSA	PFOA	no
FPrSA	FOSA	PFOA	no
FBSA	FOSA	PFOA	no
FPeSA	FOSA	PFOA	no
FHxSA	FOSA	PFOA	no
FHpSA	FOSA	PFOA	no
FEtSAA	FOSAA	4:2 FTS	no
FPrSAA	FOSAA	4:2 FTS	no
FBSAA	FOSAA	4:2 FTS	no
FPeSAA	FOSAA	4:2 FTS	no
FHxSAA	FOSAA	4:2 FTS	no
H-PFPeA	PFPeA	PFPeA	yes

H-PFHxA	PFHxA	PFHxA	yes
H-PFPrS	PFPrS	PFPrS	yes
H-PFBS	PFBS	PFBS	yes
H-PFPeS	PFPeS	PFPeS	yes
H-PFHxS	PFHxS	PFHxS	yes
H-PFOS	PFOS	PFHxS	no
H-PFDS	PFDS	PFDS	yes
H-UPFOS	PFHpS	PFHpS	yes
K-PFBS	PFPrS	PFPrS	yes
K-PFPeS	PFBS	PFBS	yes
K-PFHxS	PFPeS	PFPeS	yes
K-PFHpS	PFHxS	PFHxS	yes
K-PFOS	PFHpS	PFHpS	yes
K-PFNS	PFOS	PFOS	yes
MeFPrSA	MeFOSA	PFOA	no
MeFBSA	MeFOSA	PFOA	no
MeFPeSA	MeFOSA	MeFOSA	yes
MeFHxSA	MeFOSA	MeFOSA	yes
MeFEtSAA	MeFOSAA	4:2 FTS	no
MeFPrAA	MeFOSAA	4:2 FTS	no
MeFBSAA	MeFOSAA	4:2 FTS	no
MeFPeSAA	MeFOSAA	4:2 FTS	no
MeFHxSAA	MeFOSAA	4:2 FTS	no
O-PFBS	PFPrS	PFPrS	yes
O-PFPeS	PFBS	PFBS	yes
O-PFHxS	PFPeS	PFPeS	yes
O-PFHpS	PFHxS	PFHxS	yes
O-PFOS	PFHpS	PFHpS	yes
PFEtS	PFPrS	PFPrS	yes
PFPrSi	PFPrS	PFPrS	yes
PFBSi	PFBS	PFBS	yes
PFPeSi	PFPeS	PFPeS	yes
PFHxSi	PFHxS	PFHxS	yes
SPrAmPr-FPeSA	EtFOSA	PFOA	no
SPrAmPr-FHxSA	EtFOSA	PFOA	no
UPFHxS	PFPeS	PFPeS	yes
UPFHpS	PFHxS	PFHxS	yes
UPFOS	PFHpS	PFHpS	yes
UPFNS	PFOS	PFOS	yes
UPFDS	PFNS	PFNS	yes
7:1 PFOS	PFHpS	PFHpS	yes

Table S7. Average internal standard recoveries

Internal Standard	average recovery across all pH 3/pH 10 samples	average recovery across pH 7 samples
13C2-6:2 FTCA	33%	65%
13C2-8:2 FTCA	21%	64%
13C2-10:2 FTCA	12%	75%
13C3-PFBS	47%	124%
18O2-PFHxS	41%	92%
13C4-PFOS	18%	59%
13C4-PFBA	106%	111%
13C5-PFPeA	45%	98%
13C2-PFHxA	42%	81%
13C4-PFHpA	39%	88%
13C4-PFOA	32%	79%
13C5-PFNA	19%	55%
13C2-PFDA	18%	87%
13C2-PFUdA	13%	85%
13C2-PFDoA	9%	82%
13C2-PFTeDA	4%	39%
13C2-PFHxDA	6%	11%
13C2-4:2 FTS	35%	70%
13C2-6:2 FTS	30%	67%
13C2-8:2 FTS	18%	85%
13C8-FOSA	24%	96%
d3-MeFOSA	26%	81%
d5-EtFOSA	26%	70%
d3-MeFOSAA	17%	73%
d5-EtFOSAA	15%	85%
13C2-6:2 UFTCA	37%	N/A
13C2-8:2 UFTCA	23%	68%
13C2-10:2 UFTCA	11%	70%

S5. Elemental analysis

Elemental analyses (Al, B, Ba, Ca, Fe, Mg, Mn, Na, P, S, Sr; Figure S1) were performed with inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 8300 (PerkinElmer, Waltham, MA)). Other elements (e.g. Cu, K, Zn) were also included in analysis but were mostly <LOQ. Prior to analysis, column effluent samples were filtered (0.45 μm, nylon), diluted 1:1 in water, and preserved with 2% HNO_3.

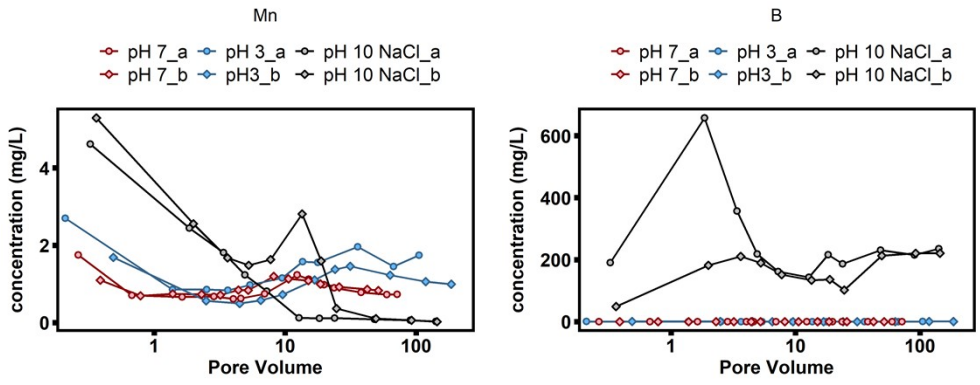
Table S8. Concentrations of individual ions in AGW.

Ion	pH 3	pH 7	pH 10, high NaCl	pH 10, high $CaCl_2$
Mn	0.325 mg/L	0.325 mg/L	0.325 mg/L	0.325 mg/L
Na	114 mg/L	114 mg/L	872 mg/L	298 mg/L
Ca	-	-	-	1004 mg/L
B	-	-	215 mg/L	215 mg/L
S	40.8 mg/L	40.8 mg/L	40.8 mg/L	40.8 mg/L

Table S9. 2022-02-21 ICP-OES cumulative masses eluted for SI.xlsx

Table S10. ANOVA with posthoc bonferroni correction results for ICP-OES data (only elements with $p<0.05$ shown).

compound	p value pH3-pH10	p value pH7-pH10	p value pH3-pH7
Al	0.0000179	0.0000183	1
B	0.00208	0.00207	1
Ba	0.2	0.0114	0.038
Ca	0.647	0.0222	0.012
Fe	0.0971	0.0554	0.0104
Mn	0.0158	1	0.0242
Na	0.000843	0.00069	0.79
P	0.000808	0.000472	0.0865
S	0.282	0.0494	0.0159
Sr	1	0.0131	0.0118



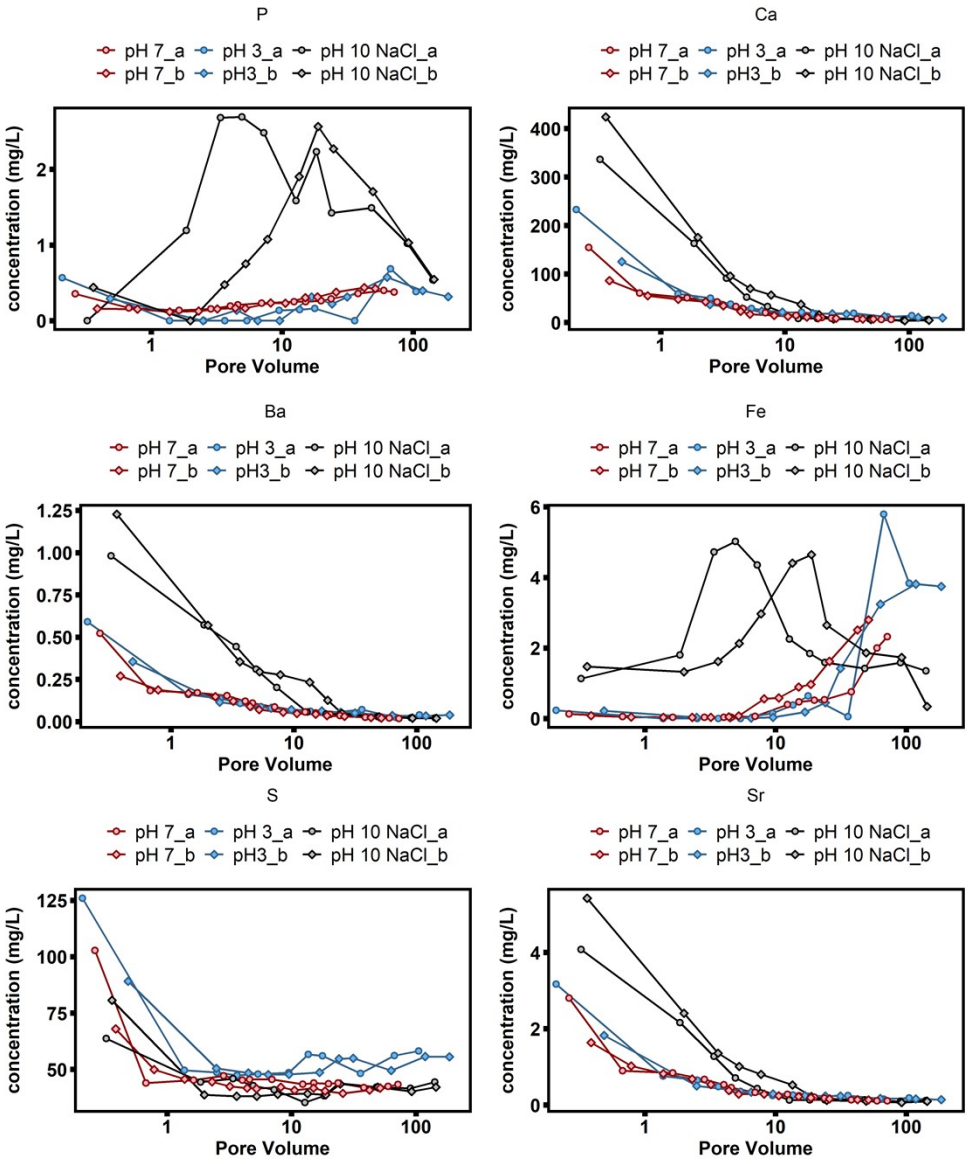


Figure S1. Elemental concentrations vs pore volume (log-scale) analyzed by ICP-OES for the three treatments.

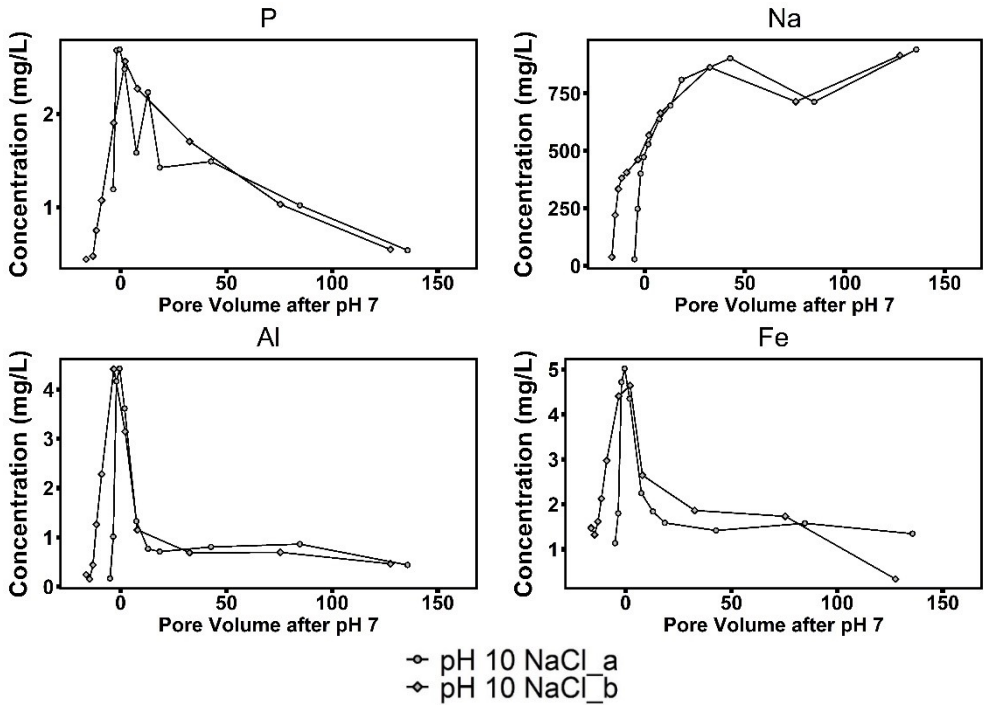


Figure S2. Elemental concentrations vs pore volumes after reaching pH 7 for pH 10 NaCl data analyzed by ICP-OES. Column A effluents reached pH 7 at 5 pore volumes and column B effluents reached pH 7 at 17 pore volumes. Adjusting the x axis in this manner aligns the two columns' profiles for these elements.

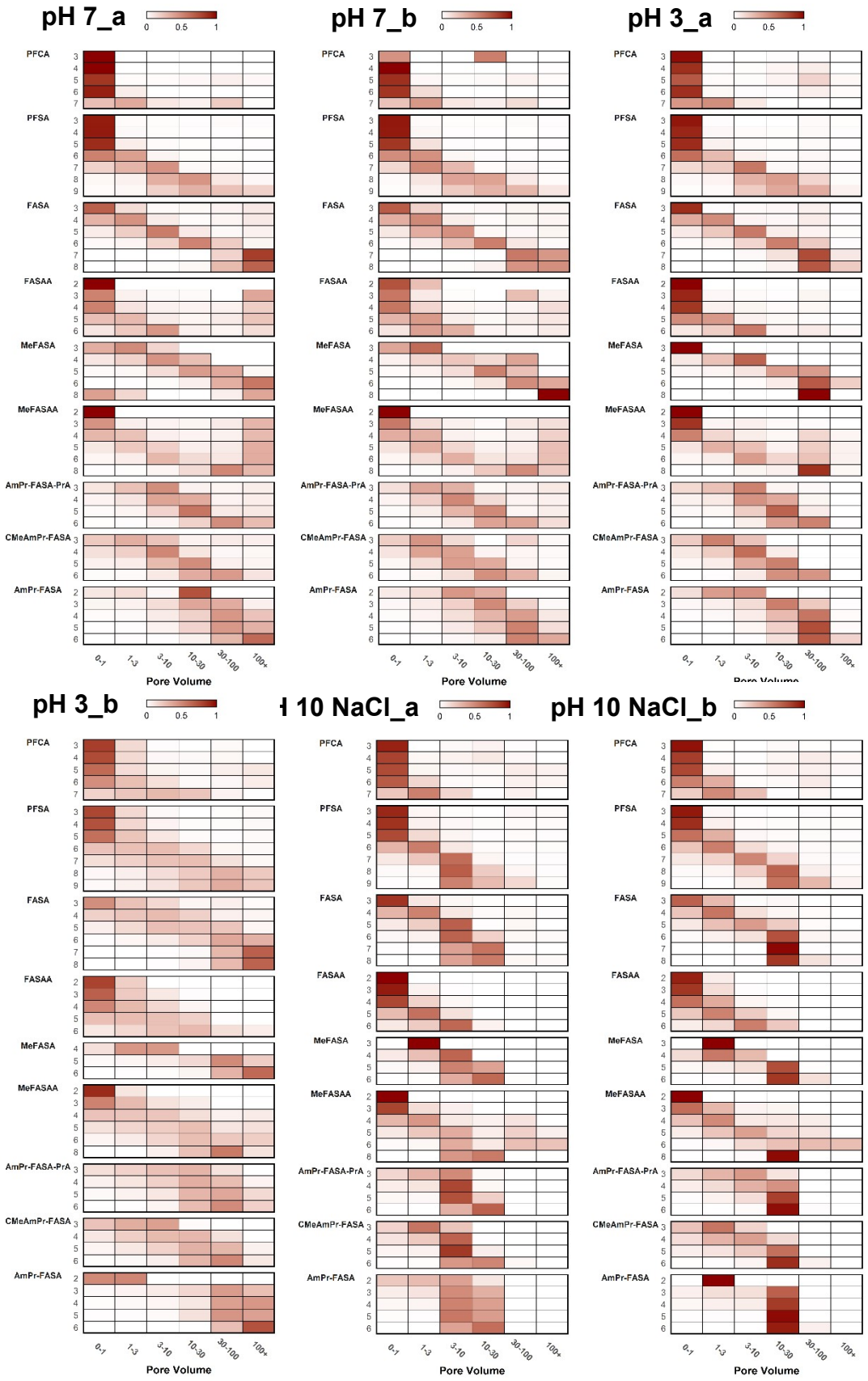


Figure S3. The fraction of the total eluted mass within 0− 1, 1−3, 3−10, 10−30, 30−100, and >100 pore volumes calculated for select PFAS classes in each column, organized by perfluorinated chain length.

Figure S4. UV-vis absorbance at 254 nm vs pore volume; only limited samples analyzed.

S6. PFAS in Soils and Column Effluents

Table S11. 2022-05-03 soil concentrations for SI.xls

Table S12. 2022-02-03 summary max cum mass eluted for SI.xls

Table S13. 2022-05-23 summary max cum mass eluted C15and16 for SI.xls

Table S14. ANOVA with pairwise t test (Bonferroni correction) results for cumulative mass eluted. Only significant ($p<0.05$) results are shown.

compound	p.value pH3-pH10	p.value pH7-pH10	p.value pH3-pH7
PFHpA	1.0000	0.0547	**0.0395**
PFOA	1.0000	**0.0379**	0.0563
FOSA	**0.0106**	**0.0108**	1.0000
FOSAA	1.0000	**0.0031**	**0.0031**
PFHxS	1.0000	**0.0133**	**0.0148**
PFEtCHxS	0.9365	**0.0219**	**0.0391**
MeFBSAA	0.1139	**0.0235**	**0.0065**
FBSA	**0.0291**	**0.0008**	**0.0023**
FHxSA	0.9046	**0.0408**	**0.0224**
K-PFHxS	0.3234	**0.0380**	0.1605
FBSAA	0.3311	**0.0102**	**0.0052**
FPeSAA	**0.0089**	**0.0023**	**0.0005**
FHxSAA	**0.0379**	**0.0030**	**0.0011**
MeFHxSAA	**0.0088**	**0.0015**	**0.0146**
AmPr-FBSA	1.0000	**0.0319**	**0.0393**
AmPr-FBSA-PrA	0.6797	0.0867	**0.0361**
AmPr-FPrSA	0.5657	**0.0131**	**0.0263**

PFPeSi	0.4420	**0.0049**	**0.0030**
PFHxSi	0.7461	**0.0203**	**0.0116**
FPrSA	0.3490	**0.0230**	0.0725
MeFHxSA	1.0000	0.0695	**0.0381**
AmPr-FPrSA-PrA	1.0000	**0.0062**	**0.0046**
FPeSA	0.4042	**0.0063**	**0.0123**

Table S15. Pore volumes at which the normalized cumulative mass eluted is 90% (or closest value available). Only analytes with ANOVA p value <0.05 are shown. After posthoc analysis with bonferroni correction, only five compounds had significant differences (p<0.05).

Column	Analyte	Normalized cumulative mass eluted	Pore volume	ANOVA p value	posthoc p value pH 3-pH 10	posthoc p value pH 7-pH 10	posthoc p value pH 3-pH 7
pH 7_a	4:2 FTS	0.906	65.01	0.0161	1.000	**0.031**	**0.031**
pH 7_b	4:2 FTS	0.903	42.41	0.0161	1.000	**0.031**	**0.031**
pH 3_a	4:2 FTS	1.000	0.44	0.0161	1.000	**0.031**	**0.031**
pH 3_b	4:2 FTS	1.000	0.89	0.0161	1.000	**0.031**	**0.031**
pH 10 NaCl_a	4:2 FTS	1.000	0.63	0.0161	1.000	**0.031**	**0.031**
pH 10 NaCl_b	4:2 FTS	0.858	0.69	0.0161	1.000	**0.031**	**0.031**
pH 7_a	CMeAmPr-FPrSA	0.936	95.61	0.0081	1.000	**0.015**	**0.016**
pH 7_b	CMeAmPr-FPrSA	0.961	69.69	0.0081	1.000	**0.015**	**0.016**
pH 3_a	CMeAmPr-FPrSA	0.895	3.88	0.0081	1.000	**0.015**	**0.016**
pH 3_b	CMeAmPr-FPrSA	0.902	7.31	0.0081	1.000	**0.015**	**0.016**
pH 10 NaCl_a	CMeAmPr-FPrSA	0.918	3.70	0.0081	1.000	**0.015**	**0.016**
pH 10 NaCl_b	CMeAmPr-FPrSA	0.879	3.30	0.0081	1.000	**0.015**	**0.016**
pH 7_a	FBSAA	0.922	162.42	0.0171	1.000	**0.032**	**0.034**
pH 7_b	FBSAA	0.903	105.37	0.0171	1.000	**0.032**	**0.034**
pH 3_a	FBSAA	0.900	2.29	0.0171	1.000	**0.032**	**0.034**
pH 3_b	FBSAA	0.899	5.30	0.0171	1.000	**0.032**	**0.034**
pH 10 NaCl_a	FBSAA	0.902	1.24	0.0171	1.000	**0.032**	**0.034**
pH 10 NaCl_b	FBSAA	0.927	1.67	0.0171	1.000	**0.032**	**0.034**
pH 7_a	MeFOSAA	0.916	162.42	0.0169	0.119	**0.022**	0.170
pH 7_b	MeFOSAA	0.892	120.41	0.0169	0.119	**0.022**	0.170
pH 3_a	MeFOSAA	0.906	77.25	0.0169	0.119	**0.022**	0.170
pH 3_b	MeFOSAA	0.884	92.33	0.0169	0.119	**0.022**	0.170
pH 10 NaCl_a	MeFOSAA	0.886	13.89	0.0169	0.119	**0.022**	0.170
pH 10 NaCl_b	MeFOSAA	0.916	24.66	0.0169	0.119	**0.022**	0.170

pH 7_a	FPrSAA	0.919	142.63	0.0124	1.000	**0.024**	**0.024**
pH 7_b	FPrSAA	0.947	96.76	0.0124	1.000	**0.024**	**0.024**
pH 3_a	FPrSAA	0.913	0.93	0.0124	1.000	**0.024**	**0.024**
pH 3_b	FPrSAA	0.899	2.89	0.0124	1.000	**0.024**	**0.024**
pH 10 NaCl_a	FPrSAA	0.875	0.63	0.0124	1.000	**0.024**	**0.024**
pH 10 NaCl_b	FPrSAA	0.934	1.01	0.0124	1.000	**0.024**	**0.024**
pH 7_a	FOSA	0.874	174.46	0.0459	0.098	0.082	1.000
pH 7_b	FOSA	0.852	129.57	0.0459	0.098	0.082	1.000
pH 3_a	FOSA	0.921	113.35	0.0459	0.098	0.082	1.000
pH 3_b	FOSA	0.892	173.55	0.0459	0.098	0.082	1.000
pH 10 NaCl_a	FOSA	0.897	16.10	0.0459	0.098	0.082	1.000
pH 10 NaCl_b	FOSA	0.894	33.52	0.0459	0.098	0.082	1.000
pH 7_a	MeFBSAA	0.888	162.42	0.0442	0.653	0.061	0.179
pH 7_b	MeFBSAA	0.900	120.41	0.0442	0.653	0.061	0.179
pH 3_a	MeFBSAA	0.901	67.07	0.0442	0.653	0.061	0.179
pH 3_b	MeFBSAA	0.889	77.93	0.0442	0.653	0.061	0.179
pH 10 NaCl_a	MeFBSAA	0.908	54.81	0.0442	0.653	0.061	0.179
pH 10 NaCl_b	MeFBSAA	0.899	17.69	0.0442	0.653	0.061	0.179
pH 7_a	MeFHxSA	0.892	174.46	0.0421	0.090	0.075	1.000
pH 7_b	MeFHxSA	0.887	129.57	0.0421	0.090	0.075	1.000
pH 3_a	MeFHxSA	0.923	113.35	0.0421	0.090	0.075	1.000
pH 3_b	MeFHxSA	0.891	173.55	0.0421	0.090	0.075	1.000
pH 10 NaCl_a	MeFHxSA	0.898	13.89	0.0421	0.090	0.075	1.000
pH 10 NaCl_b	MeFHxSA	0.870	29.10	0.0421	0.090	0.075	1.000
pH 7_a	PFOA	0.896	59.79	0.0384	1.000	0.062	0.098
pH 7_b	PFOA	0.900	42.41	0.0384	1.000	0.062	0.098
pH 3_a	PFOA	0.891	2.74	0.0384	1.000	0.062	0.098
pH 3_b	PFOA	0.896	21.18	0.0384	1.000	0.062	0.098
pH 10 NaCl_a	PFOA	0.903	3.70	0.0384	1.000	0.062	0.098
pH 10 NaCl_b	PFOA	0.905	5.27	0.0384	1.000	0.062	0.098
pH 7_a	UPFDS	0.915	131.28	0.0169	1.000	1.000	0.932
pH 7_b	UPFDS	0.892	96.76	0.0169	1.000	1.000	0.932
pH 3_a	UPFDS	0.941	67.07	0.0169	1.000	1.000	0.932
pH 3_b	UPFDS	0.935	72.03	0.0169	1.000	1.000	0.932
pH 10 NaCl_a	UPFDS	0.898	11.68	0.0169	1.000	1.000	0.932
pH 10 NaCl_b	UPFDS	0.913	22.33	0.0169	1.000	1.000	0.932
pH 7_a	AmPr-FEtSA	1.000	17.07	0.0361	1.000	0.101	0.055
pH 7_b	AmPr-FEtSA	0.916	15.94	0.0361	1.000	0.101	0.055
pH 3_a	AmPr-FEtSA	0.850	4.33	0.0361	1.000	0.101	0.055
pH 3_b	AmPr-FEtSA	1.000	2.89	0.0361	1.000	0.101	0.055
pH 10 NaCl_a	AmPr-	0.903	9.47	0.0361	1.000	0.101	0.055

	FEtSA						
pH 10 NaCl_b	AmPr-FEtSA	1.000	2.98	0.0361	1.000	0.101	0.055
pH 7_a	AmPr-FHxSA	0.908	174.46	0.0404	0.100	0.065	1.000
pH 7_b	AmPr-FHxSA	0.910	129.57	0.0404	0.100	0.065	1.000
pH 3_a	AmPr-FHxSA	0.881	105.03	0.0404	0.100	0.065	1.000
pH 3_b	AmPr-FHxSA	1.000	159.92	0.0404	0.100	0.065	1.000
pH 10 NaCl_a	AmPr-FHxSA	0.896	16.10	0.0404	0.100	0.065	1.000
pH 10 NaCl_b	AmPr-FHxSA	0.936	29.10	0.0404	0.100	0.065	1.000
pH 7_a	CMeAmPr-FHxSA	0.886	95.61	0.0457	0.095	0.083	1.000
pH 7_b	CMeAmPr-FHxSA	0.892	69.69	0.0457	0.095	0.083	1.000
pH 3_a	CMeAmPr-FHxSA	0.911	67.07	0.0457	0.095	0.083	1.000
pH 3_b	CMeAmPr-FHxSA	0.909	92.33	0.0457	0.095	0.083	1.000
pH 10 NaCl_a	CMeAmPr-FHxSA	0.898	21.63	0.0457	0.095	0.083	1.000
pH 10 NaCl_b	CMeAmPr-FHxSA	0.884	24.66	0.0457	0.095	0.083	1.000

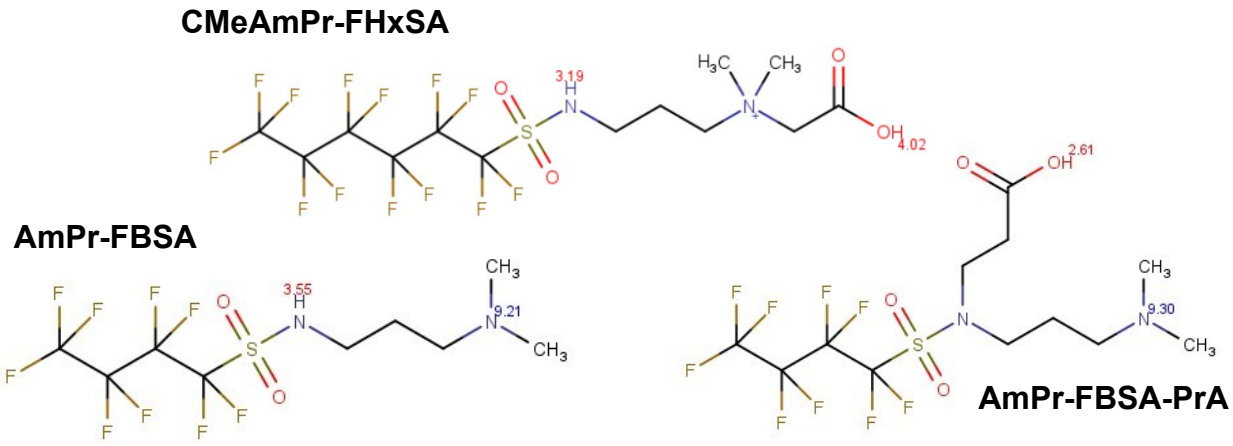


Figure S5. Estimated pKa values of detected zwitterions (one per class – pKa values of different chain lengths did not vary more than ~0.5) calculated with MarvinSketch (Chemaxon). Mejia-Avendaño et al. 2020 calculated pKas for CMeAmPr-FOSA using SPARC and the results differed significantly (2.26, 6.78).

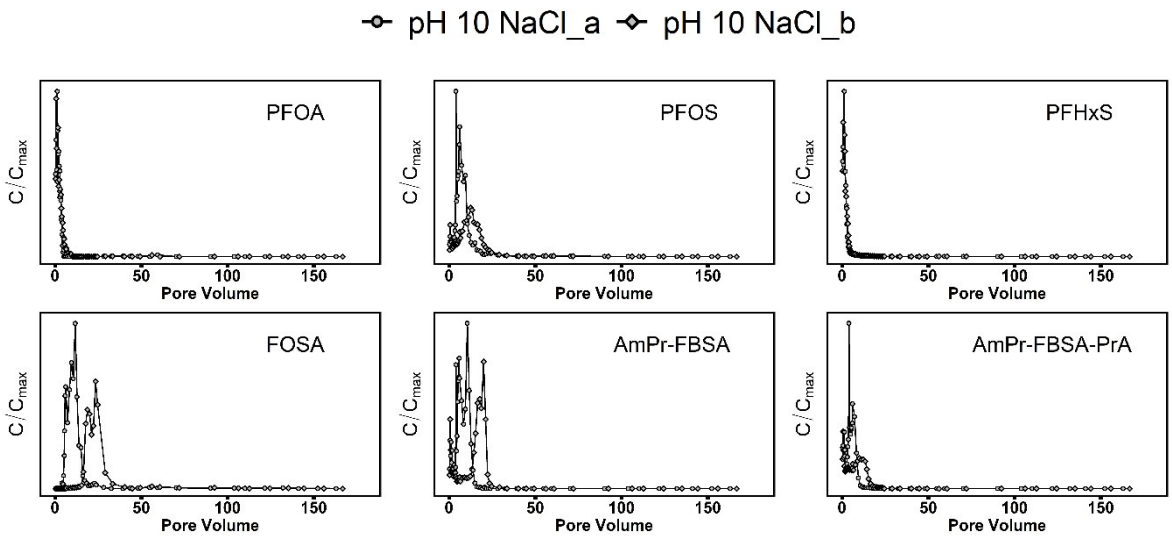


Figure S6. Normalized concentration (C/C_{max}) vs pore volumes for pH 10 NaCl data.

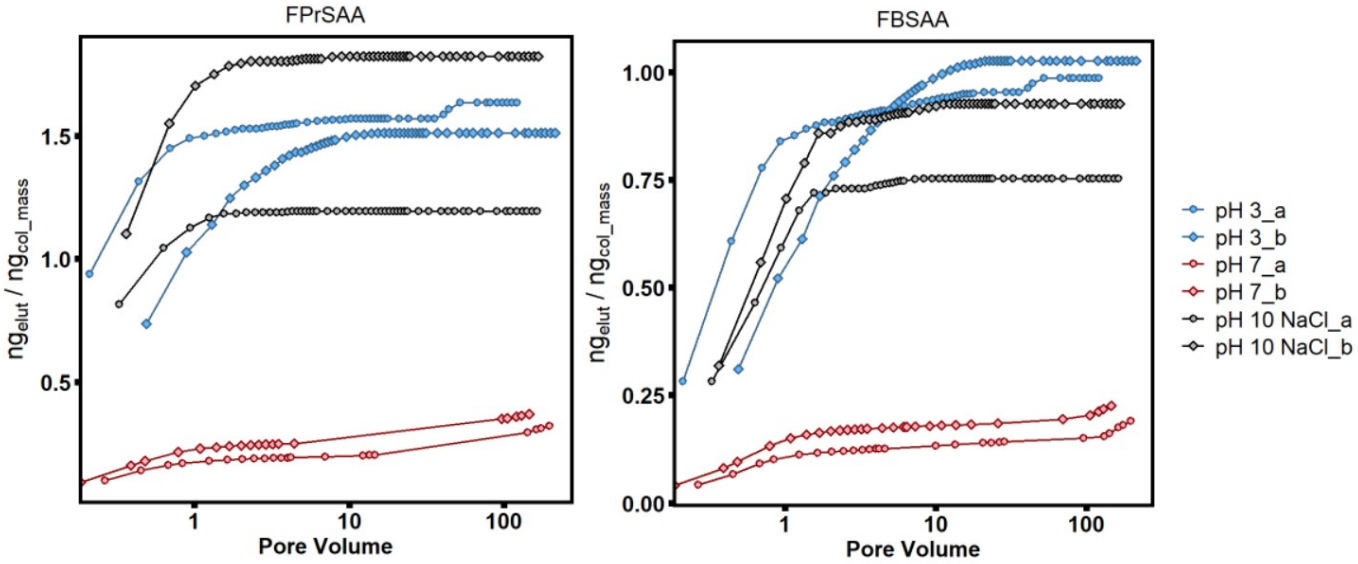


Figure S7. Cumulative mass eluted (normalized to mass on soil) vs pore volume (log scale) for the three treatment groups.

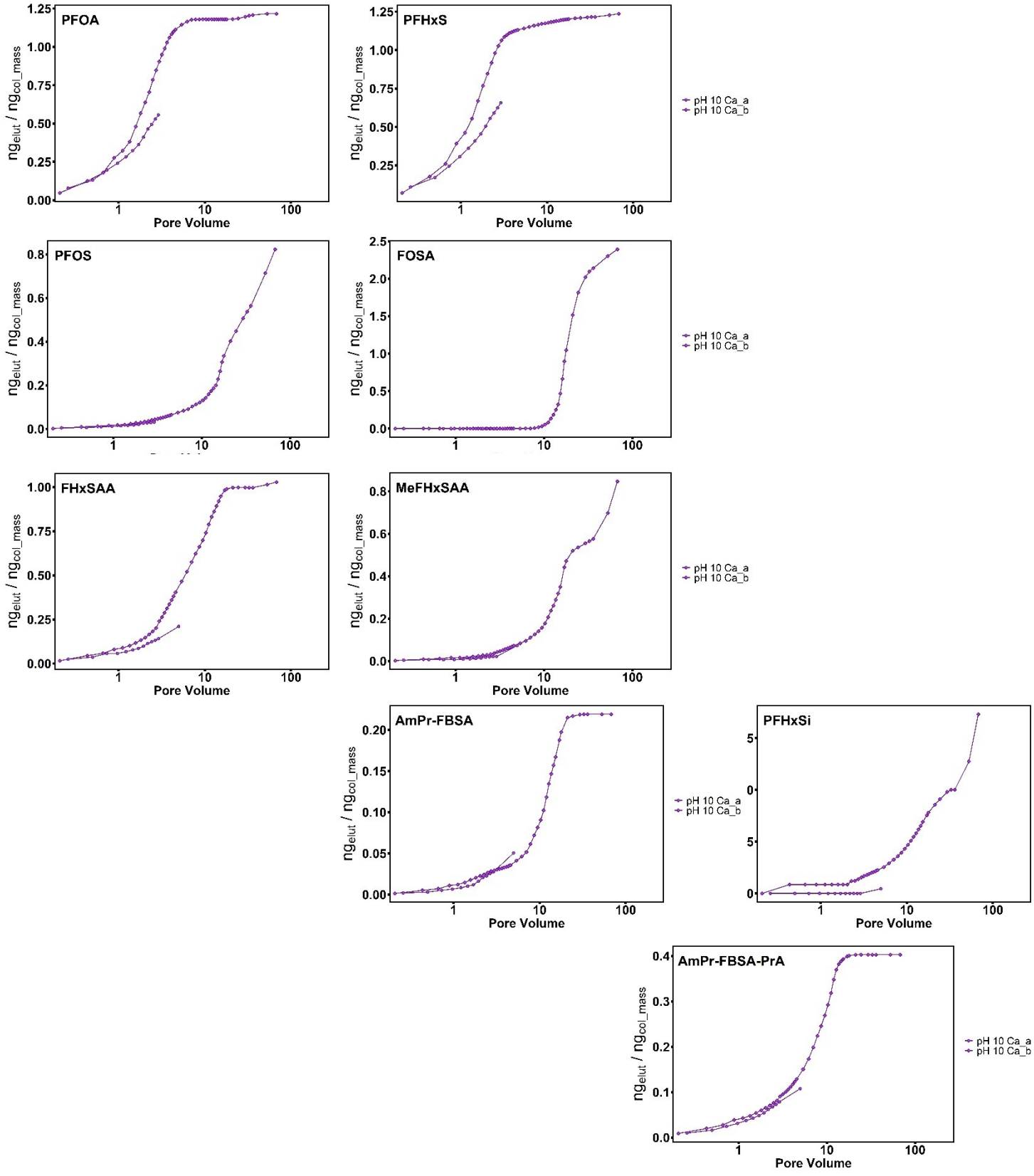


Figure S8. Cumulative mass eluted (no
in the pH 10 high Ca columns.