A Green and Practical Approach for Removing PFAS from Contaminated Environments

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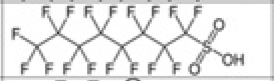
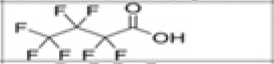
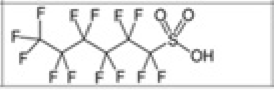
What are PFAS?

~ 3000-5000 PFAS

- Polymer PFAS
- Non-polymer PFAS
  - Perfluoroalkyl and Polyfluoroalkyl Substances
    - Perfluoroalkyl acids (PFAAs)
      - Perfluoroalkyl carboxylic acids (PFCAs)and Perfluoroalkyl sulfonic acids (PFSAs)
        - Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

PFASs name	Abbreviation	Chemical formula	Chemical structure	Molecular weight (g/mol)	Water solubility (g/L)	pK_a	Log K_{ow}
Perfluorooctanoic acid	PFOA	$CF_3(CF_2)_6COOH$		436	3.4	-0.2	4.59
Perfluorooctane sulfonic acid	PFOS	$CF_3(CF_2)_7SO_3H$		538	0.57	-3.27	5.26
Perfluorobutyric acid	PFBA	$CF_3(CF_2)_2COOH$		214	Na	0.4	2.32
Perfluorobutane sulfonic acid	PFBS	$CF_3(CF_2)_3SO_3H$		338	46.2	0.14	2.73
Perfluorohexanoic acid	PFHxA	$CF_3(CF_2)_4COOH$		314	15.7	-0.16	3.12
Perfluorohexane sulfonic acid	PFHxS	$CF_3(CF_2)_5SO_3H$		438	1.4	0.14	4.34

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Barlett and Davis, Remediation, 2018, 28:53–57.

History and use of PFAS

Table 2-1. Discovery and manufacturing history of select PFAS

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

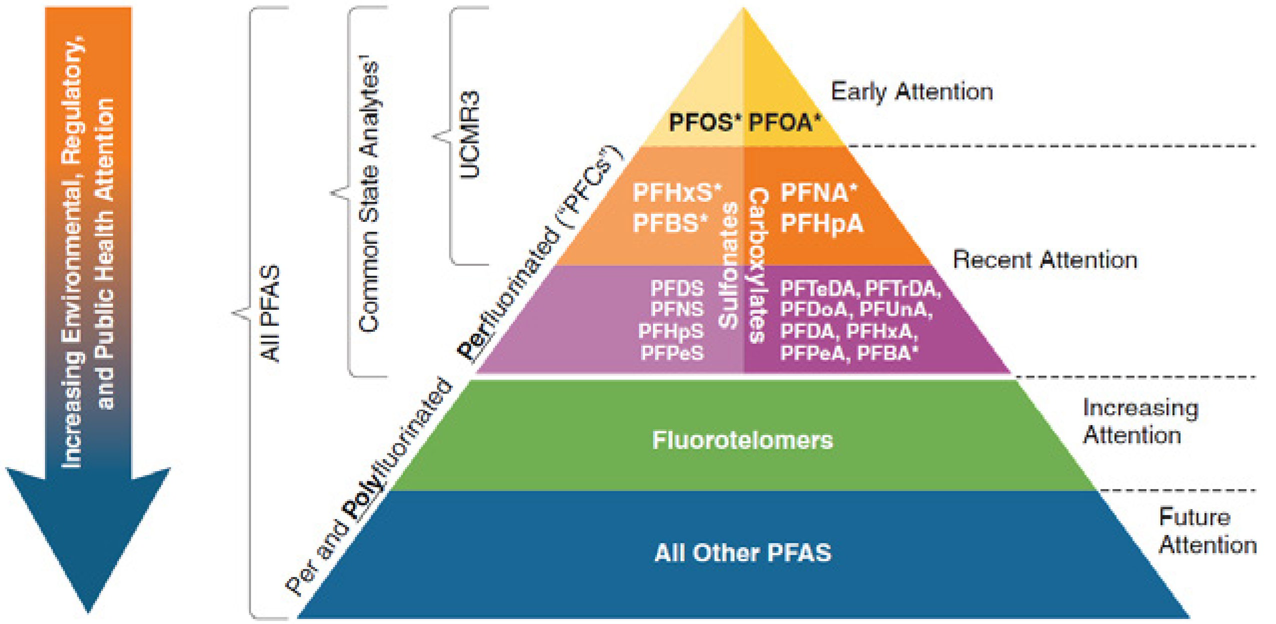
Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

Interstate Technology Regulatory Council (ITRC): History and Use of Per- and Polyfluoroalkyl Substances (PFAS), 2017.

Detection and regulation

- Organic fluorine compounds were first detected in human serum in 1960s.
- In 2006, EPA invited eight major leading companies in the PFAS industry to join in a 2010/2015 PFOA global stewardship program.
- In 2009, US EPA: 400 parts per trillion (ppt) and 200 ppt for PFOA and PFOS, respectively
- In May 2016, US EPA updated drinking water guideline for PFOS and PFOA: lifetime health advisory, a max. 70 ng/L, separately or combined .
- New Jersey: Sept 4, 2018, MCL for PFNA of 13 ng/L;
  March 13, 2019, an interim specific GW quality standard for PFOA and PFOS, each at 10 ng/L.
-

Emerging awareness



*Common regulatory criteria or health advisories
¹Sum of informal poll (NJ, NH, MN)

Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

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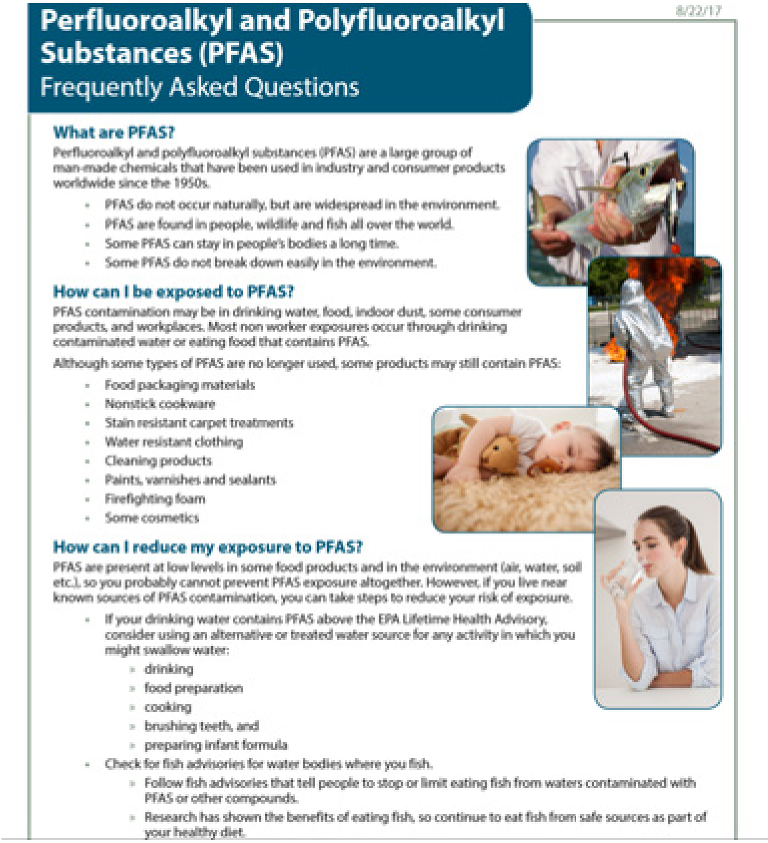
Interstate Technology Regulatory Council (ITRC): History and Use of Per- and Polyfluoroalkyl Substances (PFAS), 2017.

Exposure to PFAS



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Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
Frequently Asked Questions

What are PFAS?

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of man-made chemicals that have been used in industry and consumer products worldwide since the 1950s.

- PFAS do not occur naturally, but are widespread in the environment.
- PFAS are found in people, wildlife and fish all over the world.
- Some PFAS can stay in people's bodies a long time.
- Some PFAS do not break down easily in the environment.

How can I be exposed to PFAS?

PFAS contamination may be in drinking water, food, indoor dust, some consumer products, and workplaces. Most non worker exposures occur through drinking contaminated water or eating food that contains PFAS.

Although some types of PFAS are no longer used, some products may still contain PFAS:

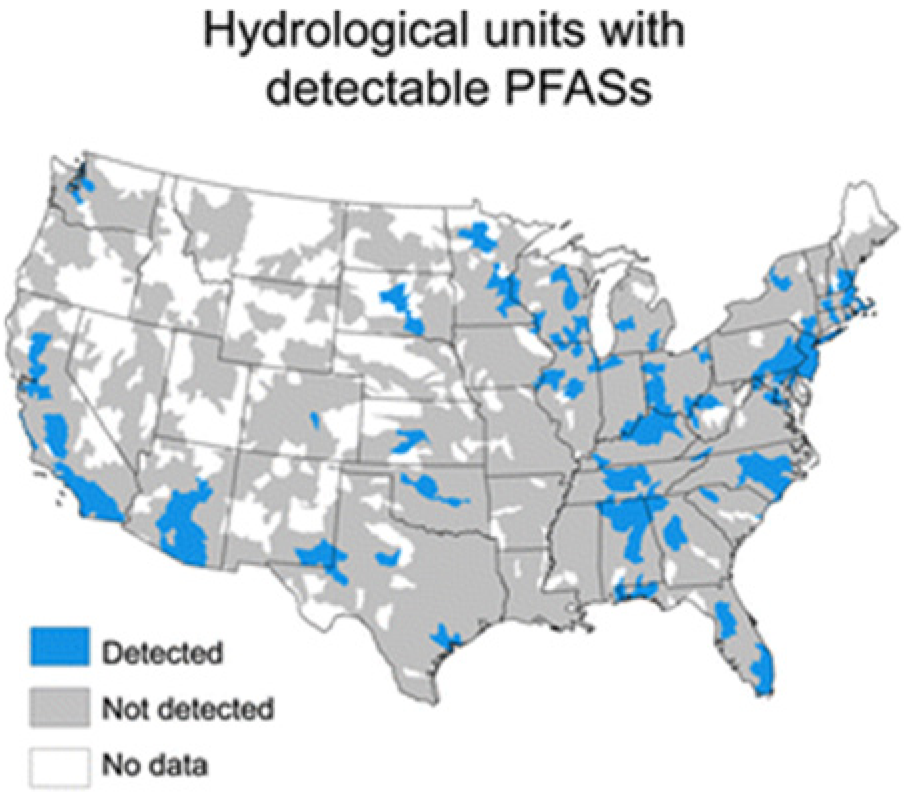
- Food packaging materials
- Nonstick cookware
- Stain resistant carpet treatments
- Water resistant clothing
- Cleaning products
- Paints, varnishes and sealants
- Firefighting foam
- Some cosmetics

How can I reduce my exposure to PFAS?

PFAS are present at low levels in some food products and in the environment (air, water, soil etc.), so you probably cannot prevent PFAS exposure altogether. However, if you live near known sources of PFAS contamination, you can take steps to reduce your risk of exposure.

- If your drinking water contains PFAS above the EPA Lifetime Health Advisory, consider using an alternative or treated water source for any activity in which you might swallow water:
  - drinking
  - food preparation
  - cooking
  - brushing teeth, and
  - preparing infant formula
- Check for fish advisories for water bodies where you fish.
  - Follow fish advisories that tell people to stop or limit eating fish from waters contaminated with PFAS or other compounds.
  - Research has shown the benefits of eating fish, so continue to eat fish from safe sources as part of your healthy diet.

https://www.atsdr.cdc.gov/pfas/docs/pfas_fact_sheet.pdf



Hu et al., Env. Sci. Technol. Letter. 2016

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PFAS contaminated sites close to Albany, NY

Specific industries:

- St Gobain Performance Plastics, Honeywell at Hoosick Falls: PFOA, PFBA, PFHxA, PFHpA, PFPeA, PFNA, PFOS
- Taconic Plastics at Town of Petersburgh, PFOA dominant

Use of Aqueous Film Forming Foam (AFFF)

- Stewart Air National Guard Base, DOD, City of Newburgh, PFOS and many other PFAS

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http://www.dec.ny.gov/chemical/108831.html

PFOA in contaminated aquifer

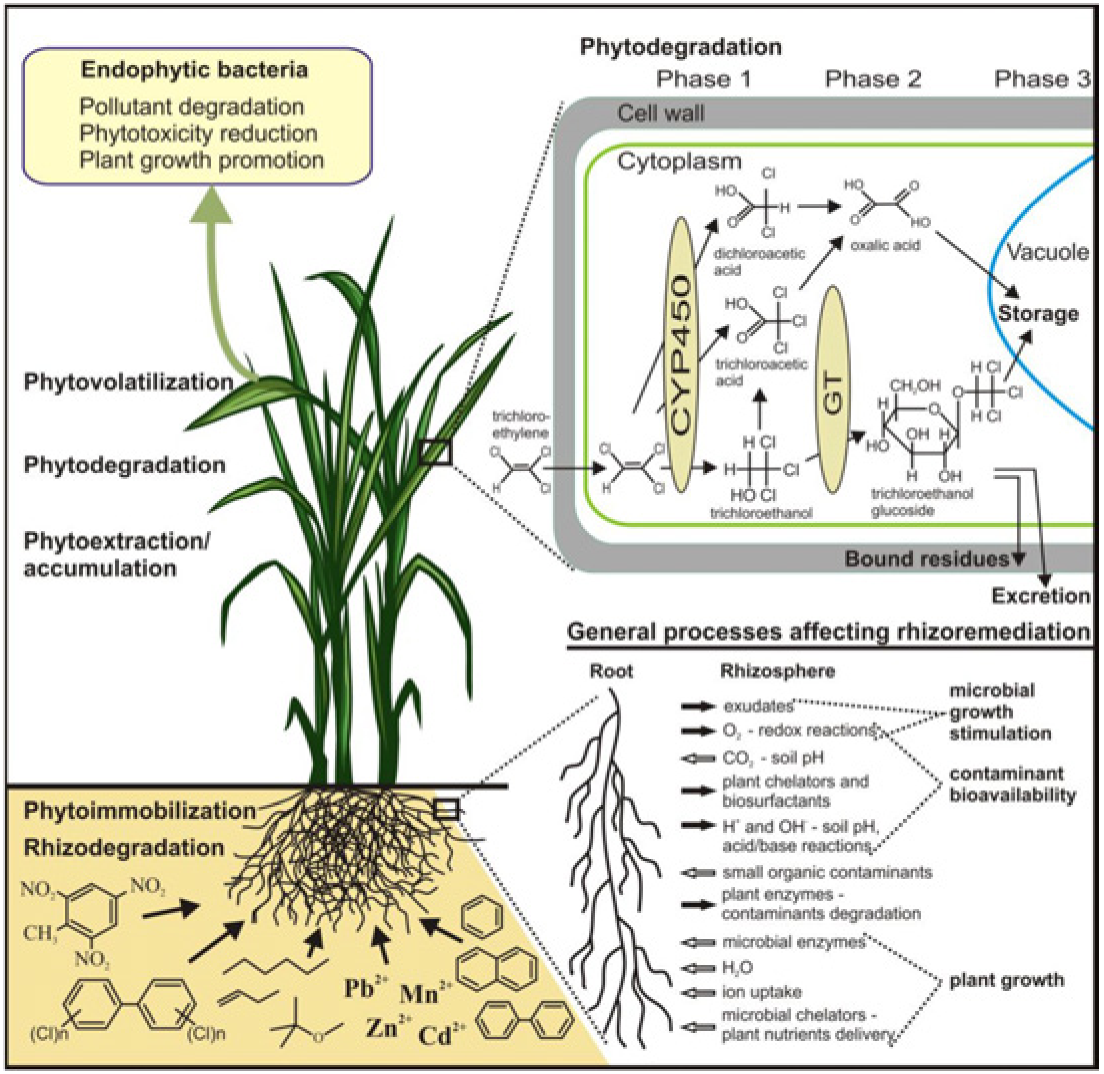
https://www.dec.ny.gov/docs/administration_pdf/mccdatasummary.pdf

How to remove PFAS?

PFAS remediation technologies

- **Non-destructive**
  - Sorption
    - Activated carbon, Resins, Polymers, Nanomaterials, Minerals, Biochar
  - Coagulation/ flocculation
    - Conventional coagulants, Specialty coagulants, Electrocoagulation
  - Membrane filtration
    - RO, Nanofiltration, Membrane filtration, Microfiltration, Electrodialysis
- **Destructive**
  - Chemical reaction
    - Ozone, Sonochemical, electrochemical, metal, thermochemical, plasma, photolysis
  - Biodegradation
    - Aerobic, Anaerobic, pure strains, mixed community

Phytoremediation – plant-microbe-soil interactions



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Truua et al., Phytoremediation And Plant-Assisted Bioremediation In Soil And Treatment Wetlands: A Review. The Open Biotechnology Journal, Volume 9, 2015

Juncus effusus – hydroponic experimental design

Plant	Conc. range (μg/L)	Harvest time (days)	Replicates	Note
Yes	0	21	3	No PFAS control
Yes	1x	7	3	
Yes	1x	14	6	
Yes	1x	21	6	
Yes	10x	7	3	
Yes	10x	14	3	
Yes	10x	21	6	
No	10x	21	6	No plant control
No	10x	21	3	With sodium azide (8 mM)

PFAS	Abbr.	Designed Conc.		Real Conc. in each bottle	
		1x (μg/L)	10x (μg/L)	1x (μg/L)	10x (μg/L)
Perfluoropentanoic acid	PFPA (C5)	66	660	76.44±6.30	604.46±62.83
Perfluorobutanesulfonic acid	PFBS (C4)	110	1100	115.00±7.61	1172.28±113.83
Perfluorohexanoic acid	PFHxA (C6)	120	1200	115.29±8.70	1183.03±96.59
Perfluoroheptanoic acid	PFHpA (C7)	75	750	80.40±7.25	810.31±73.16
Perfluorohexanesulfonic acid	PFHxS (C6)	290	2900	272.19±20.20	2876.20±267.57
Perfluorooctanoic acid	PFOA (C8)	250	2500	288.72±25.29	3065.86±144.08
Perfluorooctanesulfonic acid	PFOS (C8)	4300	43000	4104.59±466.43	44088.64±3822.62

Experimental procedure

- Mesocosms were established in a greenhouse.
- Plants were harvested on day 7, 14, and 21.
- For PFAS analysis, roots and shoots are separated, freeze-dried and subject to extraction and analysis by LC/MS/MS.
- For stress study, fresh roots and shoots were separated and homogenized on ice and subject to analysis of H_2O_2 content, activities of superoxide dismutase (SOD) and catalase (CAT).

Zhang WL., Zhang DQ., Zagorevski DV., Liang YN. 2019. Exposure of Juncus effusus to seven perfluoroalkyl acids: uptake, accumulation and phytotoxicity. Chemosphere. In review.

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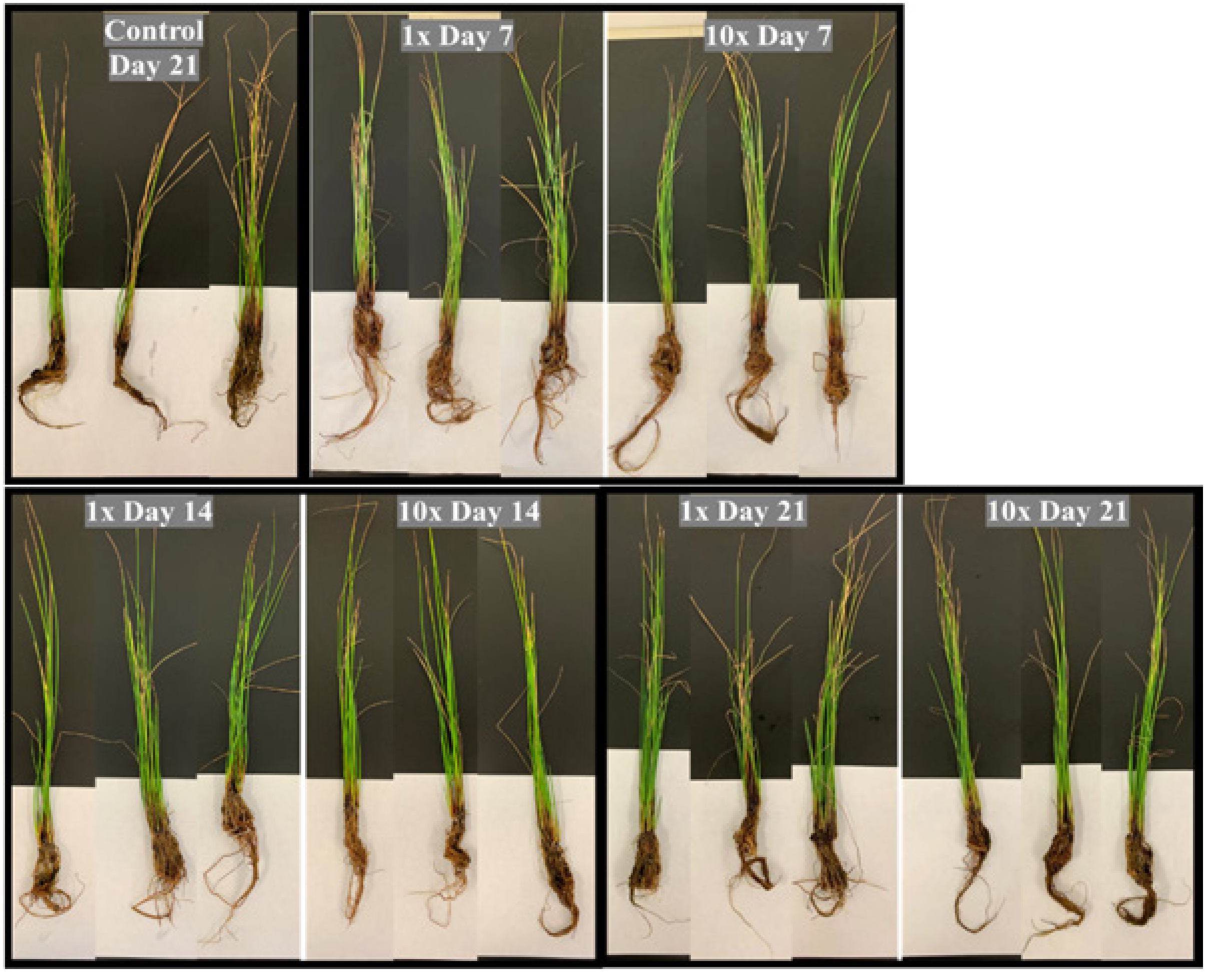
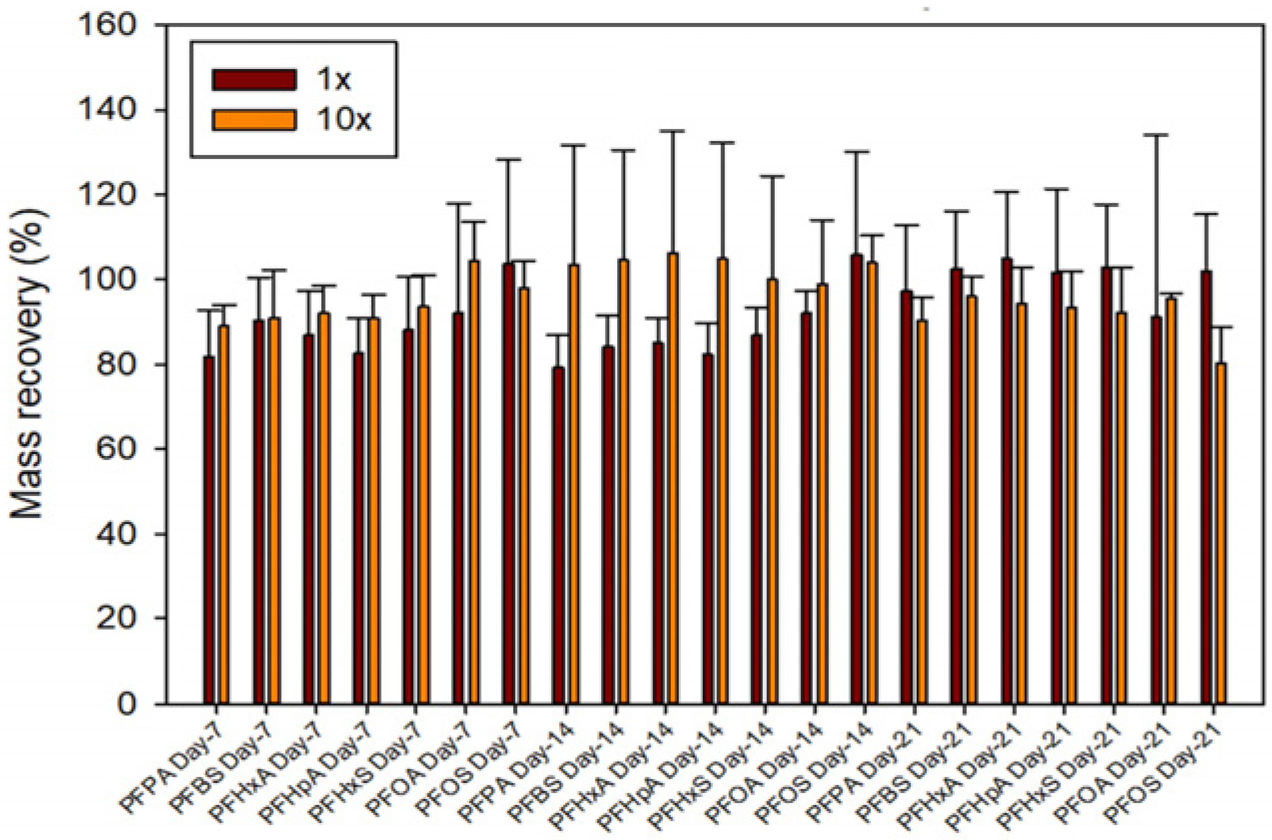
Optimized LC/MS/MS parameters for target PFAAs

Compound	Retention time	Quantitation transition	Collision energy
	(min)	(m/z)	(eV)
PFPA	7.60	263→219.0	12
PFBS	8.78	299.0→80.0	40
PFHxA	8.57	313.0→269.0	12
PFHpA	9.40	363.0→319.0	13
PFHxS	10.42	399.0→80.0	40
PFOA	10.18	413.0→369.0	13
PFOS	11.98	499.0→80.0	40
^{13}C-PFHxA	8.57	315.0→270.0	12
^{13}C-PFOA	10.18	415.0→370.0	13
^{13}C-PFOS	11.98	503.0→80	40

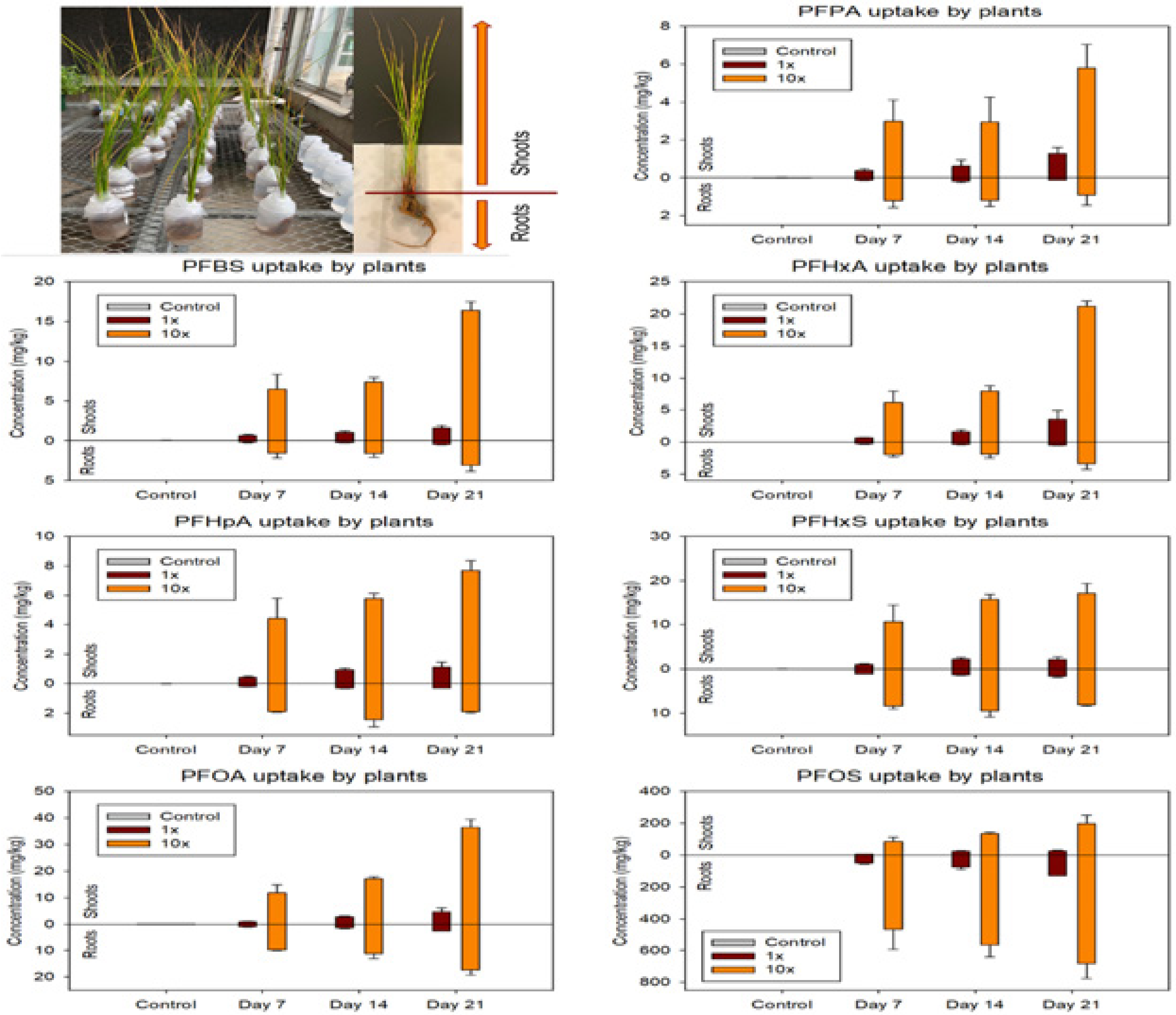
Plant growth



PFAS mass recovery

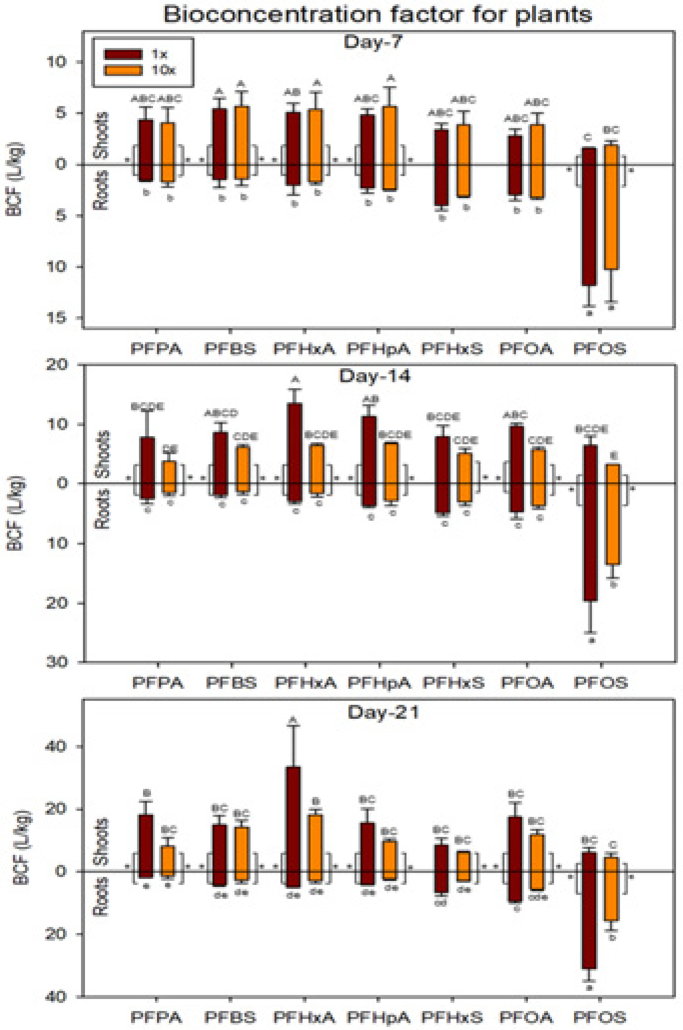


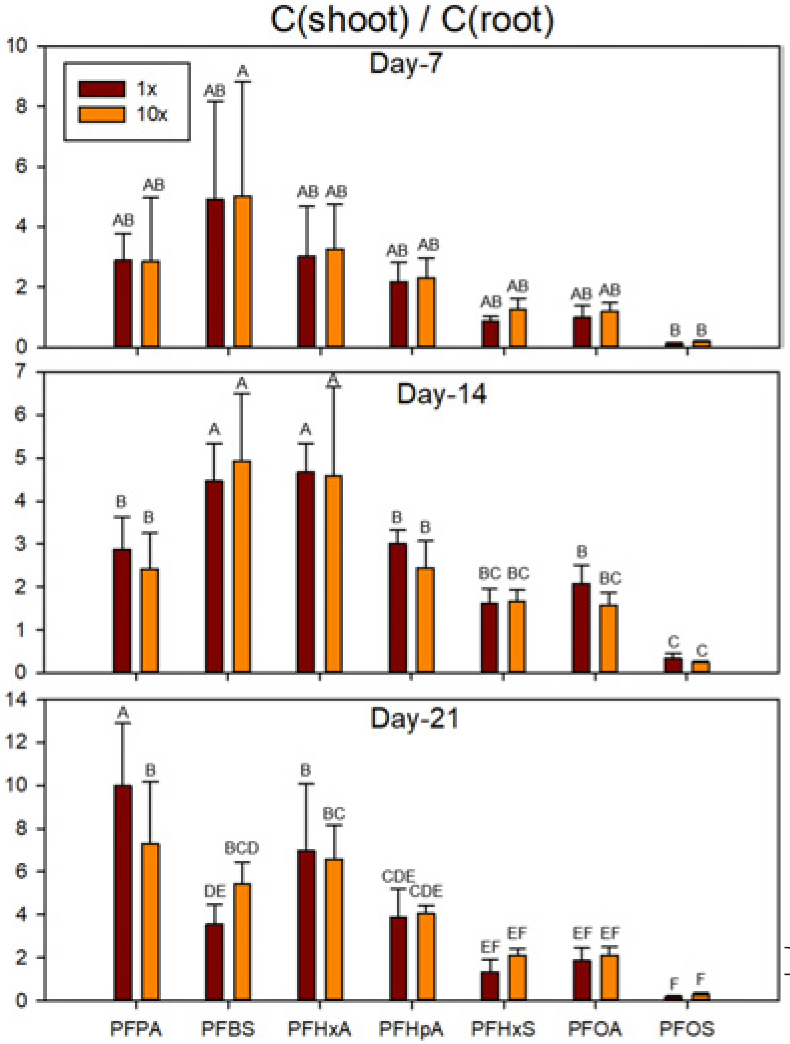
Results – Plant uptake



Variable	Factor	p value	Variable	Factor	p value
PFPA conc. in shoots	TimePoint	$<0.001^{***}$	PFPA conc. in roots	TimePoint	0.562
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	0.113		TimePoint × Conc.	0.666
PFBS conc. in shoots	TimePoint	$<0.001^{***}$	PFBS conc. in roots	TimePoint	0.006^{**}
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	$<0.001^{***}$		TimePoint × Conc.	0.045^{*}
PFHxA conc. in shoots	TimePoint	$<0.001^{***}$	PFHxA conc. in roots	TimePoint	0.013^{*}
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	$<0.001^{***}$		TimePoint × Conc.	0.066
PFHpA conc. in shoots	TimePoint	$<0.001^{***}$	PFHpA conc. in roots	TimePoint	0.036^{*}
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	0.016^{*}		TimePoint × Conc.	0.104
PFHxS conc. in shoots	TimePoint	0.009^{**}	PFHxS conc. in roots	TimePoint	0.191
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	0.074		TimePoint × Conc.	0.102
PFOA conc. in shoots	TimePoint	$<0.001^{***}$	PFOA conc. in roots	TimePoint	$<0.001^{***}$
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	$<0.001^{***}$		TimePoint × Conc.	0.001^{**}
PFOS conc. in shoots	TimePoint	0.002^{**}	PFOS conc. in roots	TimePoint	0.013^{*}
	Conc.	$<0.001^{***}$		Conc.	$<0.001^{***}$
	TimePoint × Conc.	0.016^{*}		TimePoint × Conc.	0.287

Bioconcentration factor (BCF) and translocation factor (TF)





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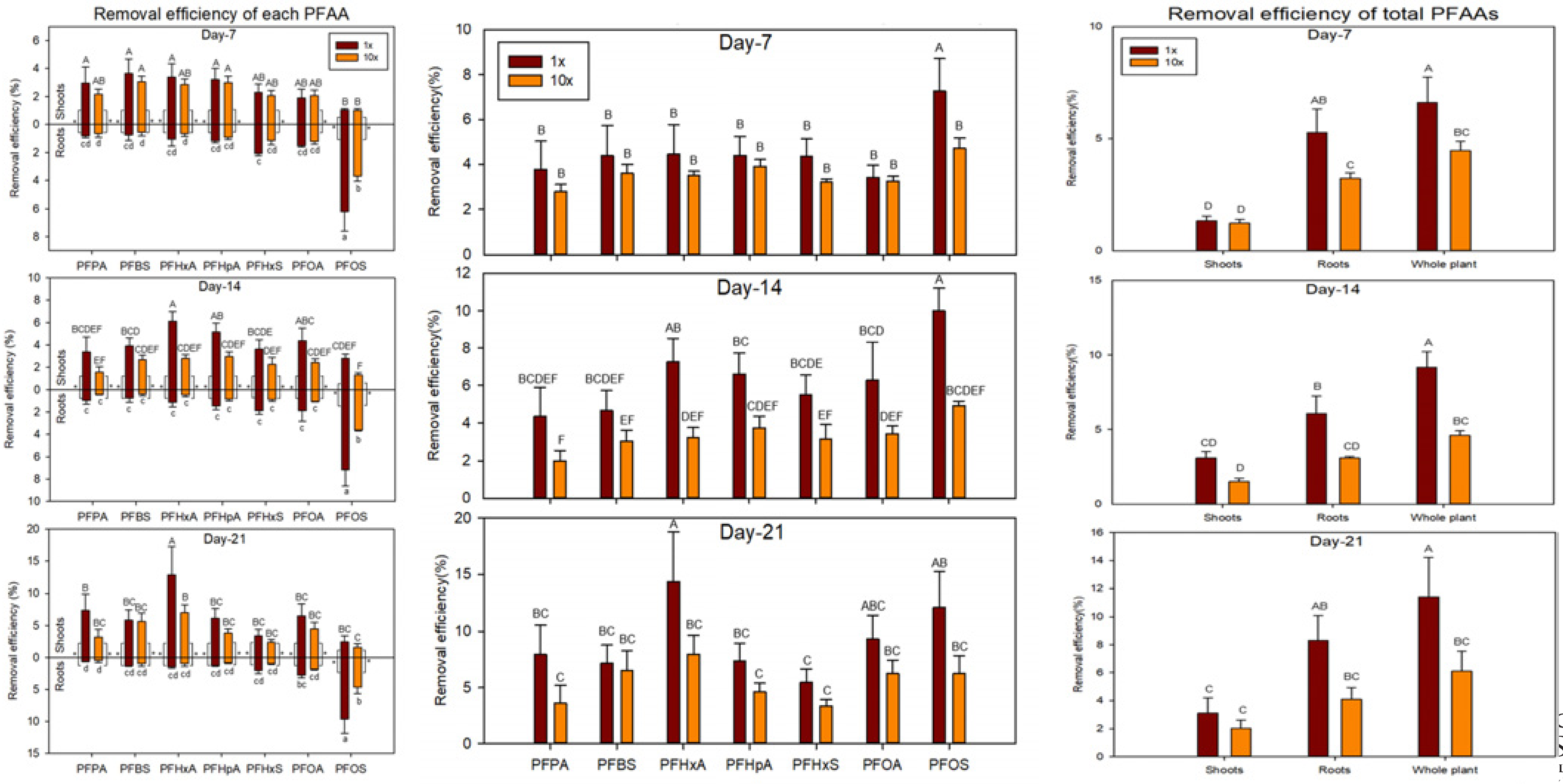
PFAAs removal efficiency



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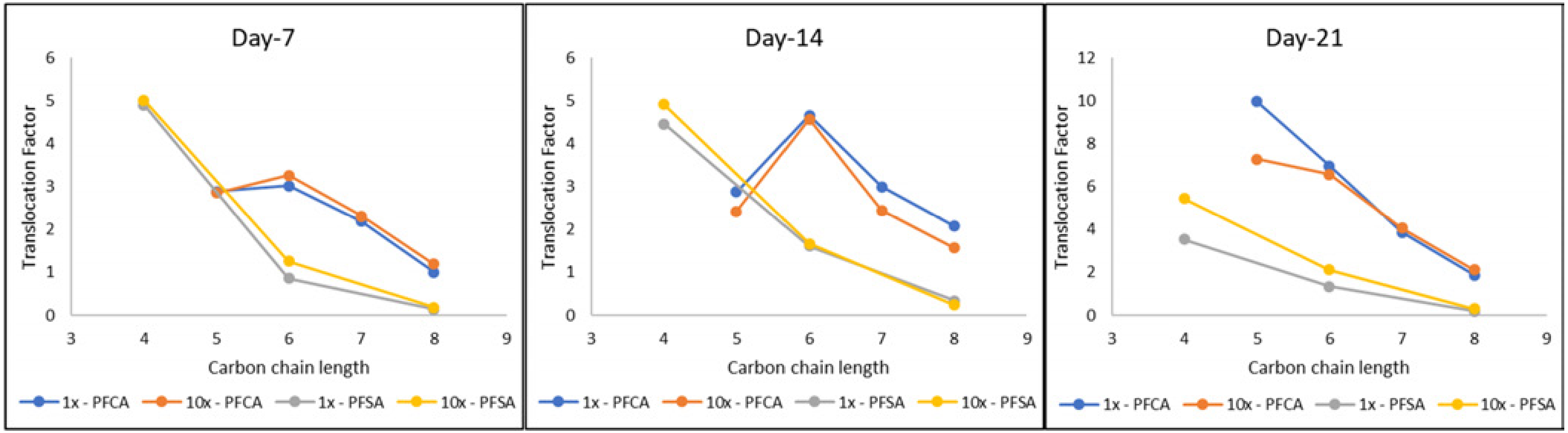
Correlation between carbon chain length of PFAAs and translocation factors (TF)



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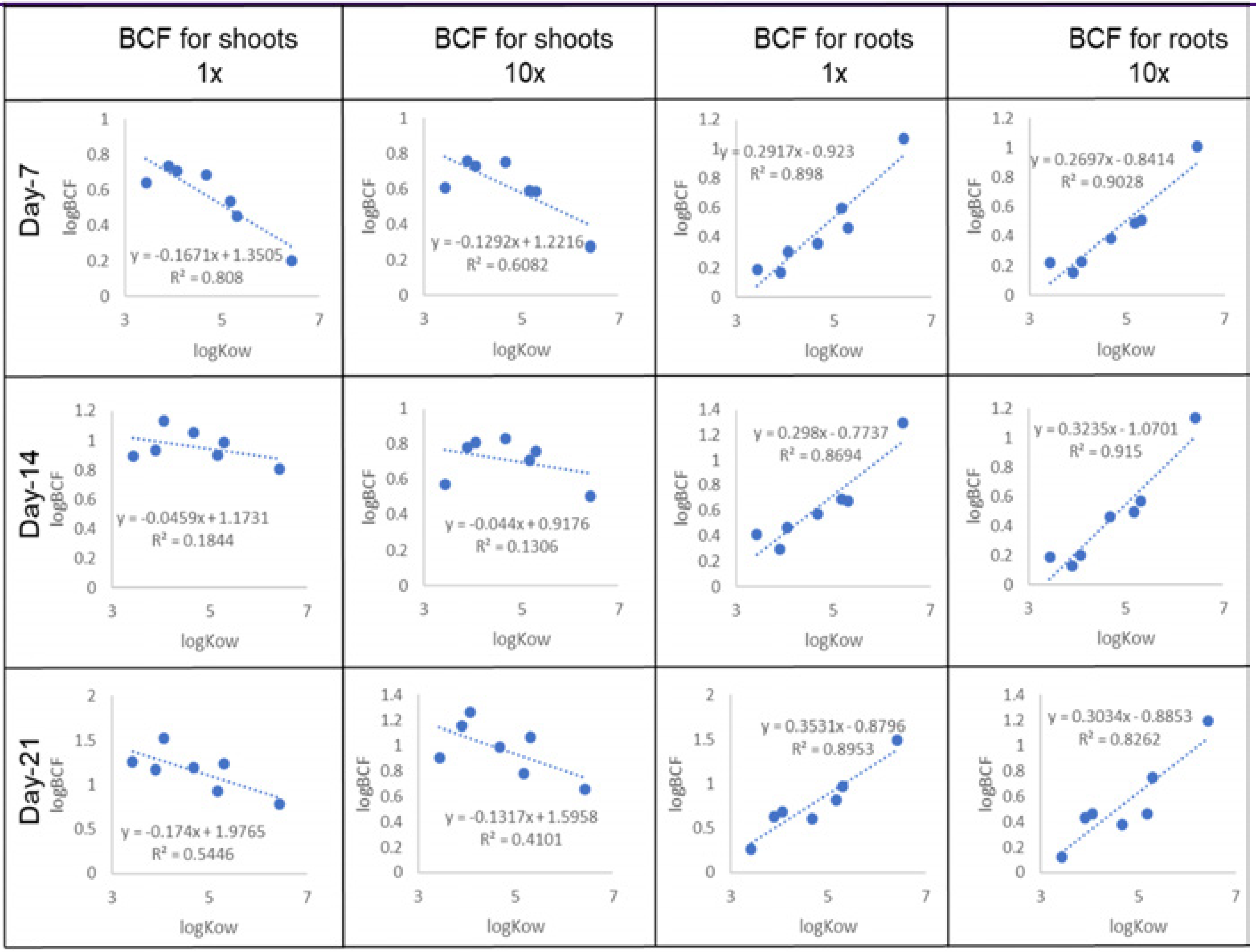
Correlation between log*Kow* and logBCF of PFAAs



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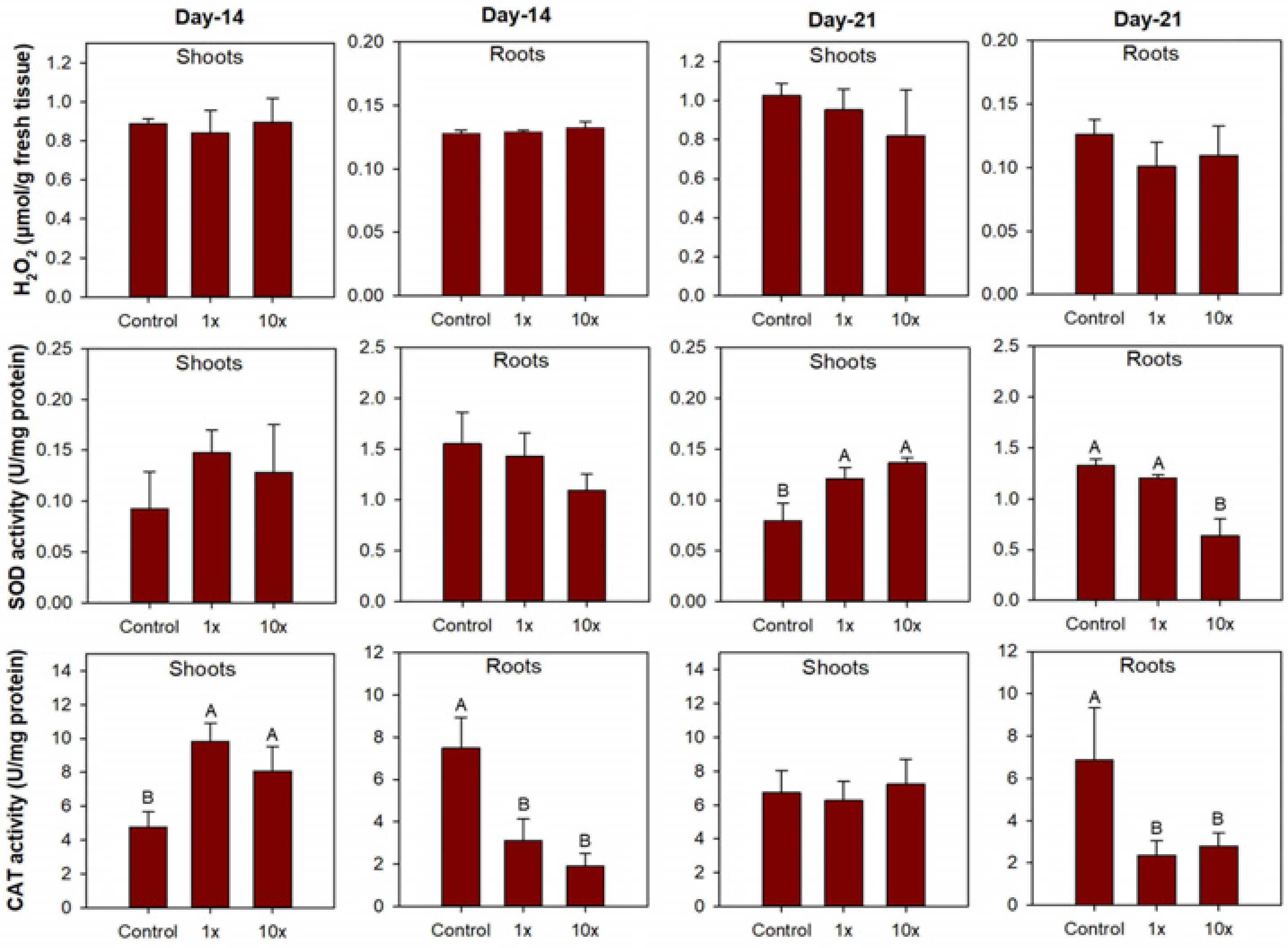
Plant response



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Results

- Approximately 11.4% of spiked PFAAs were removed by *J. effusus* when it was exposed to PFAAs at a total of 4.635 mg/L for 21 days.
- Except PFOS, the other six PFAAs had higher concentrations in the shoots than those in the roots.
- Accumulation in shoots increased with decreased carbon-chain length.
- No visible impacts to plant growth was observed.
- Exposure to PFAAs stimulated anti-oxidative defense system in *J. effusus* shoots but inhibited the superoxide dismutase (SOD) and catalase (CAT) activities and damaged the anti-oxidative defense system in *J. effusus* roots.

Further studies

- Since this study was performed in December with a daylight time of < 9 hours, it would be interesting to evaluate plant uptake in summer.
- Plant uptake with a longer duration needs to be investigated.
- Real PFAS-contaminated water needs to be studied considering the possible presence of other non-PFAS compounds.
- Other plant species needs to evaluated for PFAS remediation.
- Plant-microbe-soil interactions deserve to be studied.

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