Mitigation of Constituents of Concern in St. Louis County Regional Landfill Leachate Using a Microcosm-Scale Hybrid Engineered Wetland Treatment System (EWTS)

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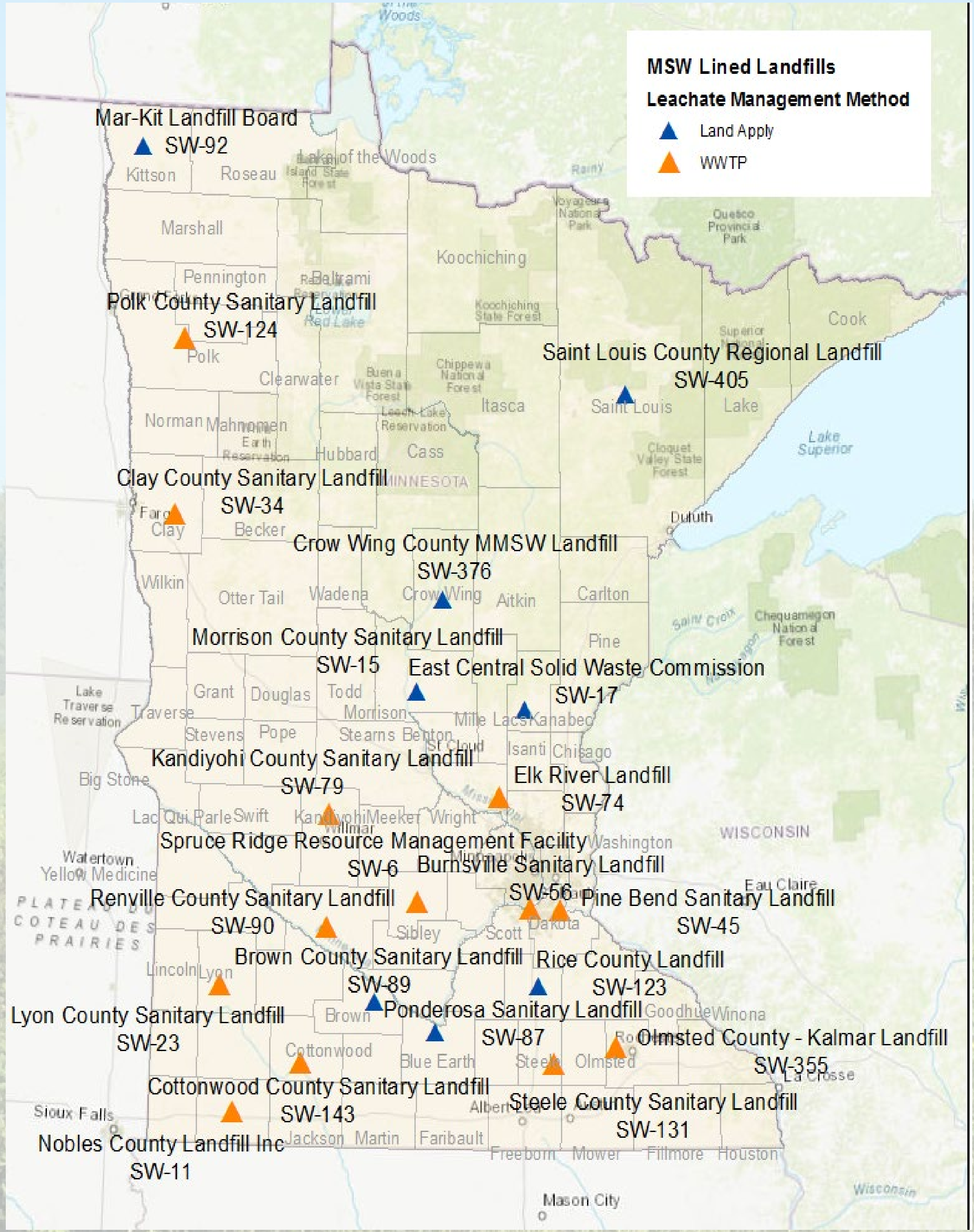
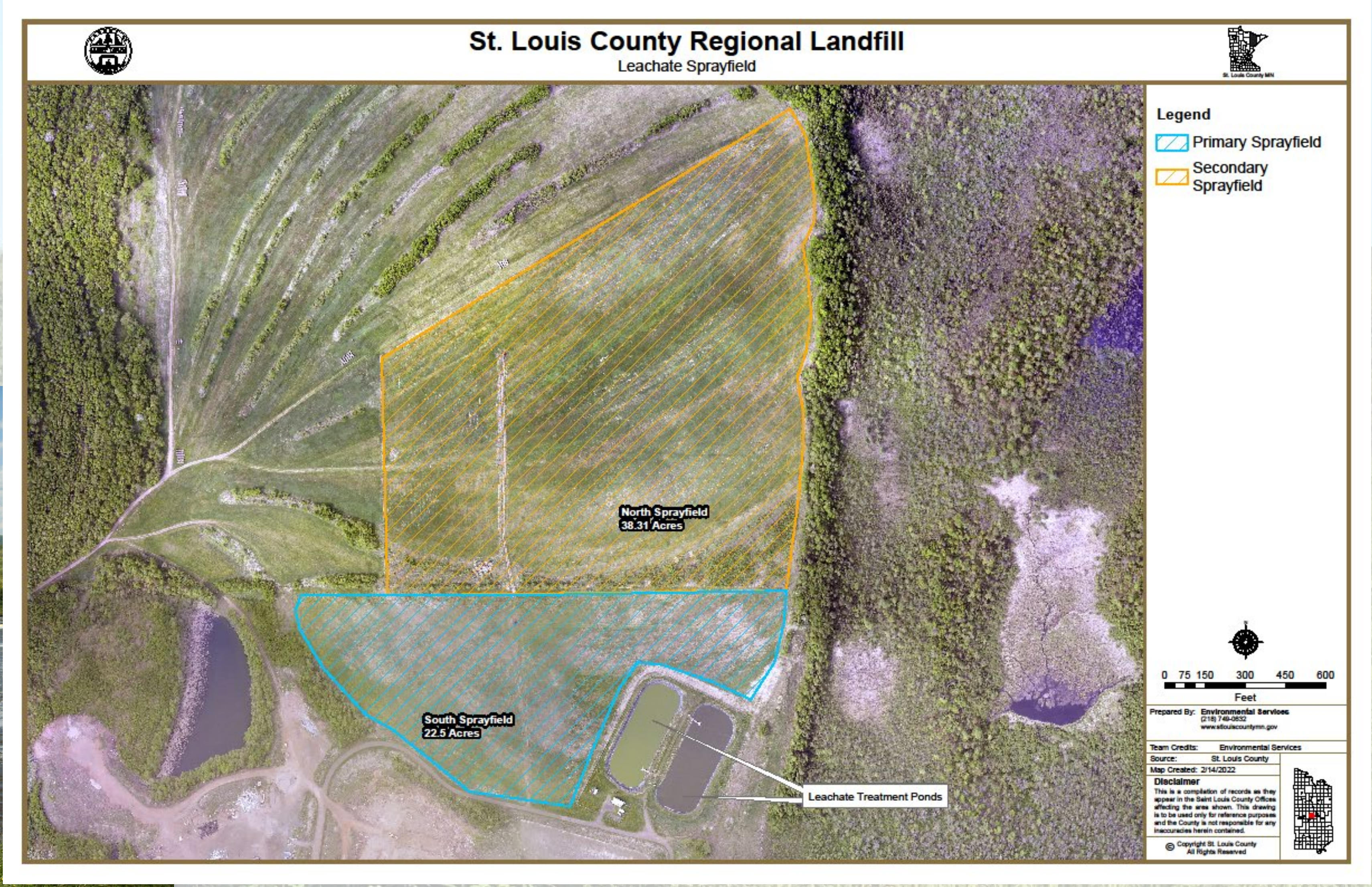
Current System SW-405

- Background
  - Last permitted MSW landfill in the state (1993)
  - Leachate treatment through land application
    - No intervention limit exceedances at compliance boundary
    - Proactive approach to groundwater compliance
    - Parametric loading limits within permit



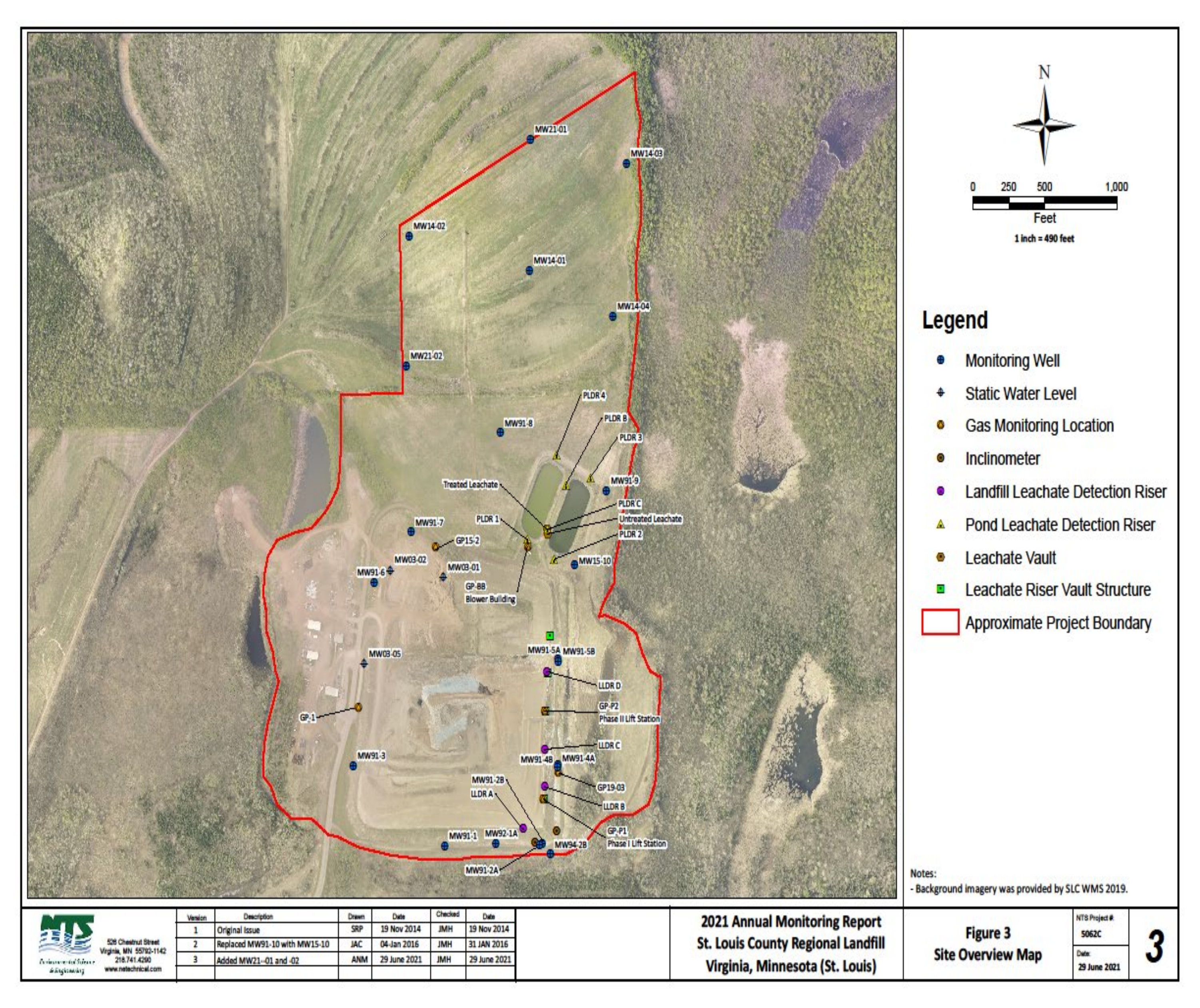
Current System SW-405

- Nitrogen Loading
  - In-pond Nitrogen treatment
  - Acquired additional acreage for spray field expansion



Current System SW-405

- PFAS Loading
  - Loading limits included in 2106 Permit
  - Informed by regulator that land application won't be allowed in the future (2018)



Current System SW-405

- PFAS Loading (cont.)
  - Contingency action within permit all leachate hauled to nearest wastewater treatment plant – Duluth – Lake Superior

Background – How did all of this start?! 2019 CWTS

Short conversation going a bit off topic…lakes to leachate…go figure…

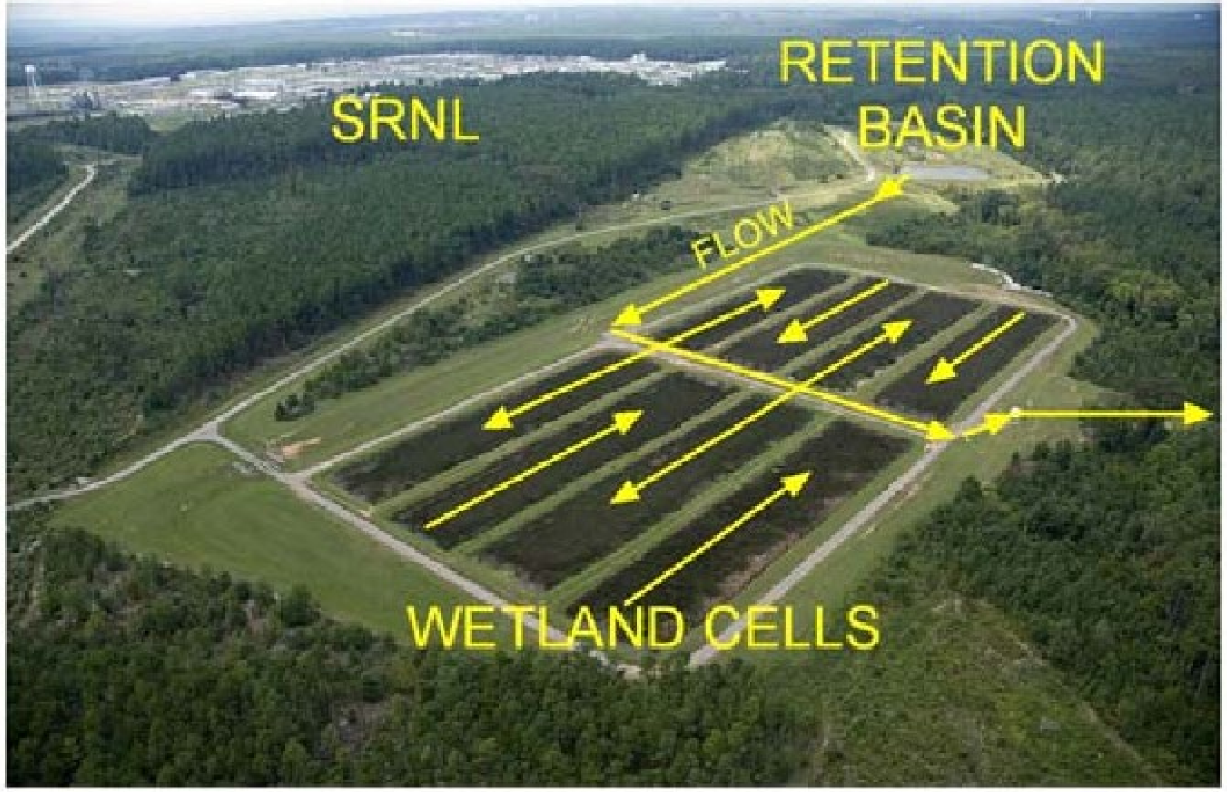
- Constituents of interest / concern
    - Nitrogen, per/polyfluoroalkyl substances (PFAS), boron, others??
- Multiple treatment options – R.O., ion exchg., activated carbon, even distillation!?...other physicochemical methods??
    - Costly to install, O&M; brines; solid-phase disposal; gunked-up filters…
- …however…what about constructed wetlands??...
- CWTS effective for mitigation of constituents of interest / concern in multiple industry influenced waters [even landfill leachates(!)]
    - Specific elements, compounds…and…PFAS(!)
    - Typical life expectancy = multiple decades with proper monitoring, maintenance

Basic Scientific Method

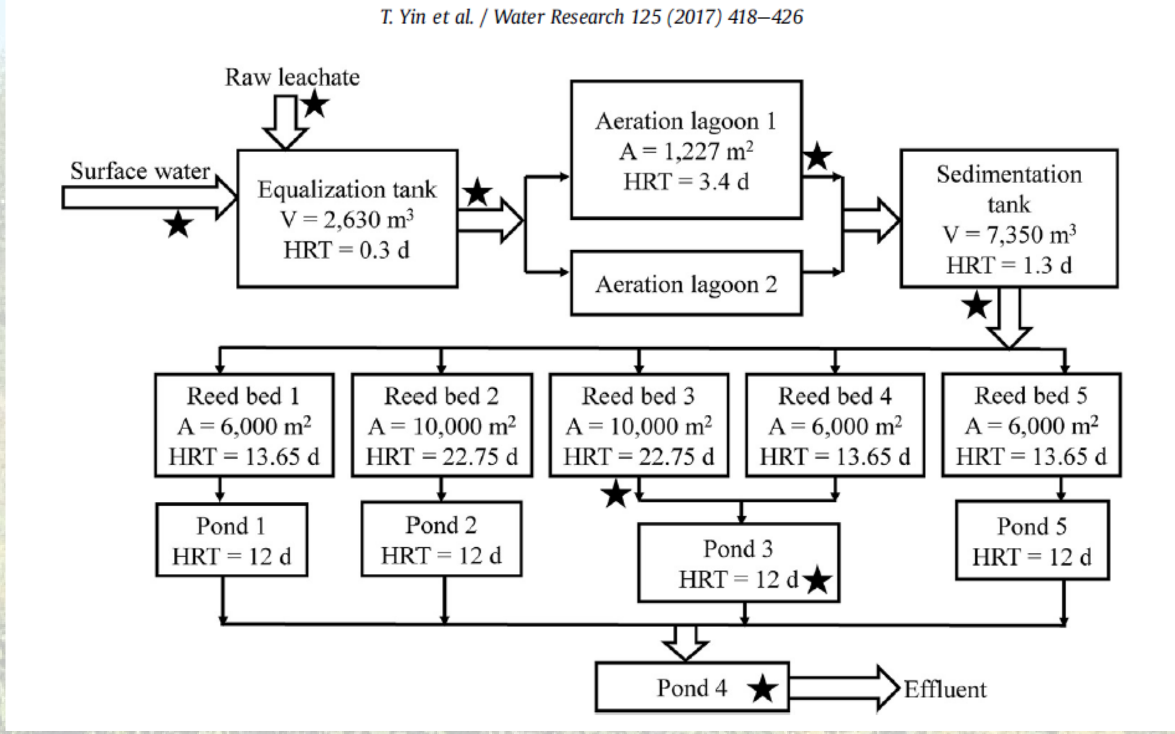
1. Observation / question
2. Testable / null hypothesis
3. Experimental design; obtain defensible data
4. Properly interpret data
5. Compose defensible conclusions…
6. Repeat…∞

Background - Savannah River National Laboratory CWTS (Clemson designed ☺; Nelson 2000): Hg, Cu, Pb, Zn Removal

Figure 2. Layout and water flow path through CWTS



Background - Field-Scale CWTS: PFAS Removal
Lorong Halus (Yin et al. 2017)



Background - Field-Scale CWTS: PFAS Removal Lorong Halus (Yin et al. 2017) (cont'd.)

424 T. Yin et al. / Water Research 125 (2017) 418–426

Table 3
Ranges of dissolved PFASs removals (%) during the treatment units employed at the Lorong Halus constructed wetland system.

Compounds	Aeration lagoon	Sedimentation tank	Reed bed	Polishing pond	Overall removal	Suggested removal process
Short-chain PFAAs (PFHxA, PFHpA, PFBS, PFHxS)	10–22	−3–4	43–49	−8–11	50–63	Weak sorption, high plant uptake
Long-chain PFAAs (PFOA, PFNA, PFDA, PFOS)	−5–19	17–40	42–46	−11–14	60–69	Strong sorption, low plant uptake
6:2 FTS	7	27	61	78	89	Biotransformation, photodegradation
5:3 acid	73	31	64	62	96	Biotransformation
N-MeFOSAA, N-EtFOSAA	55–72	5–23	75–76	1–32	84	Biotransformation
Total PFASs	22	7	44	7	61	

Note: Removal efficiency(%) $= \frac{C_{Influent} - C_{Effluent}}{C_{Influent}} * 100$.

- Lorong Halus (former landfill) field-scale CWTS evaluation
- Some PFAS removal in aeration basin
- PFAS sorption, plant (reed bed; multiple plant taxa) uptake more critical removal mechanisms depending on specific PFAS
- (Bio)Transformation also potential critical removal mechanism

2019 Design

- As a colleague would say – ‘quite rudimentary, yet functional!’
- Substrate, plants (bulrush, cattail) obtained onsite
- Specific plants [radial (root-zone) oxygen loss – ROL]
  - Bulrush = no ROL
  - Cattails = ROL
- Approximately 2.5 months of operation
- Plants loved it(!)
  - Rt. plant pic. 30d progression

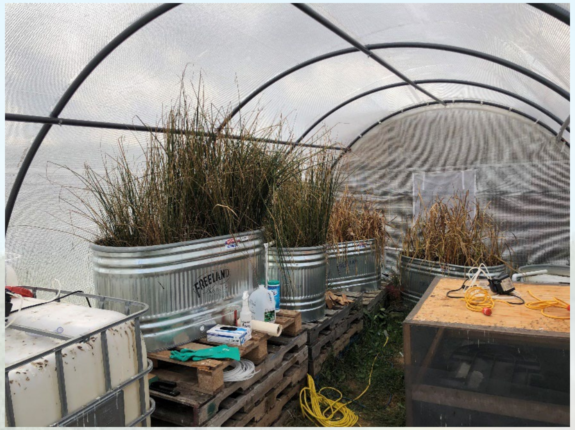
2019 CWTS PFAS Results

		Potential Target Conc. (ug / L)	May 01, 2019	Aug. 08, 2019			Aug. 28, 2019		Oct. 01, 2019		
			Treated Leachate	Secondary CWTS Inflow	Secondary CWTS Outflow	% Change	Secondary CWTS Outflow	% Change	Secondary CWTS Inflow	Secondary CWTS Outflow	% Change
Perfluorobutanesulfonic acid	**PFBS**	25% of HRL: 1.75	0.684	0.496	0.583	**-15**	0.523	5	0.557	0.508	**-9**
Perfluorobutanoic acid	**PFBA**	25% of HRL: 1.75	1.75	2.07	2.41	16	1.59	**-23**	0.881	0.94	7
Perfluorodecanoic acid	PFDA	NA	0.0308	0.0114	0.0054	**-53**	0.0077	**-32**	0.0211	0.0704	234
Perfluorododecanoic acid	PFDoA	NA	ND	ND	ND	NC	ND	NC	ND	ND	NC
Perfluoroheptanoic acid	PFHpA	GW Baseline: 0.050	0.798	0.999	1.08	8	0.782	**-22**	0.54	0.471	**-13**
Perfluorohexane sulfonate	**PFHxS**	GW Baseline: 0.033	0.763	0.712	0.777	9	0.607	**-15**	0.465	0.407	**-12**
Perfluorohexanoic acid	PFHxA	GW Baseline: 0.091	3.41	3.74	3.87	3	2.93	**-22**	2.69	2.16	**-20**
Perfluorononanoic acid	PFNA	NA	0.0691	0.0361	0.0302	**-16**	0.0305	**-16**	0.0456	0.0241	**-47**
Perfluorooctane Sulfonate	**PFOS**	I.L.: 0.075	0.162	0.0663	0.0417	**-37**	0.0569	**-14**	0.108	0.0345	**-68**
Perfluorooctanesulfonamidoacetate	PFOSA	NA	ND	ND	ND	NC	ND	NC	ND	ND	NC
Perfluorooctanoic acid	**PFOA**	25% of HRL: 0.00875	1.56	1.19	1.39	17	0.976	**-18**	0.888	0.699	**-21**
Perfluoropentanoic acid	PFPeA	GW baseline: 0.081	0.48	2.91	2.81	**-3**	2.46	**-15**	1.46	1.4	**-4**
Perfluorotridecanoic acid	PFTriA	NA	ND	ND	ND	NC	ND	NC	ND	ND	NC
Perfluoroundecanoic acid	PFUnA	NA	ND	ND	ND	NC	ND	NC	0.00252	**ND**	**NC**

2020 Design

June 12, 2020

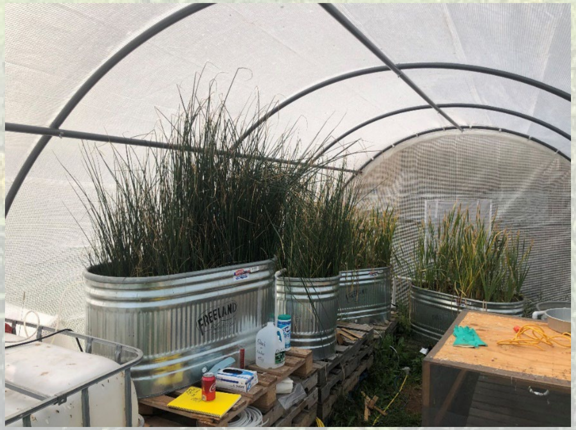
August 11, 2020



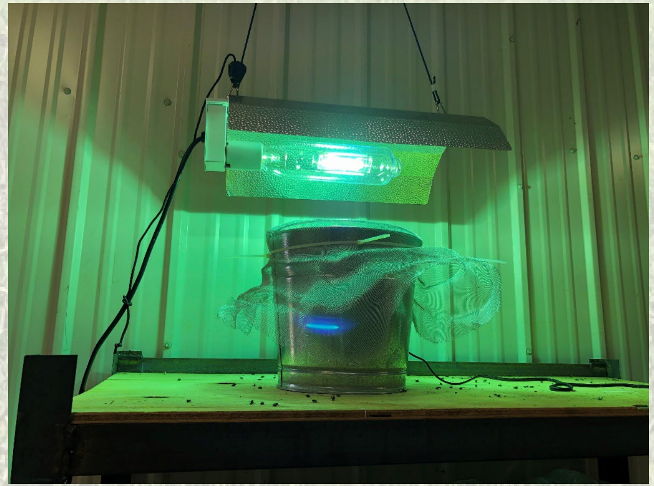
October 16, 2020

- Improved UV exposure chamber – amended to include granular H_2O_2 treatment / exposure and GAC filtration via fish-tank recirc. pump
- ‘H_2O_2-UV-GAC exposure chamber’

July 10, 2020

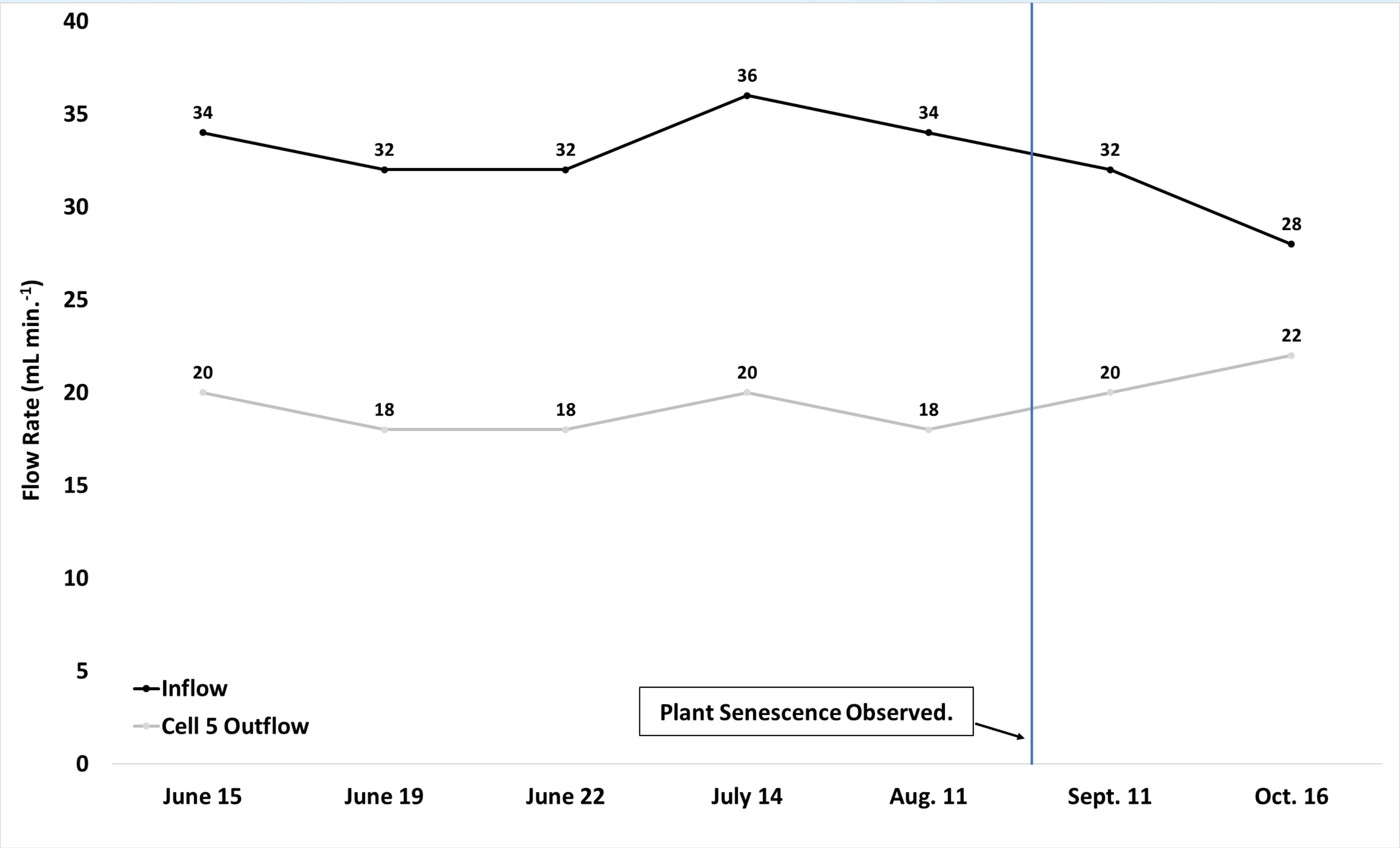


September 09, 2020.



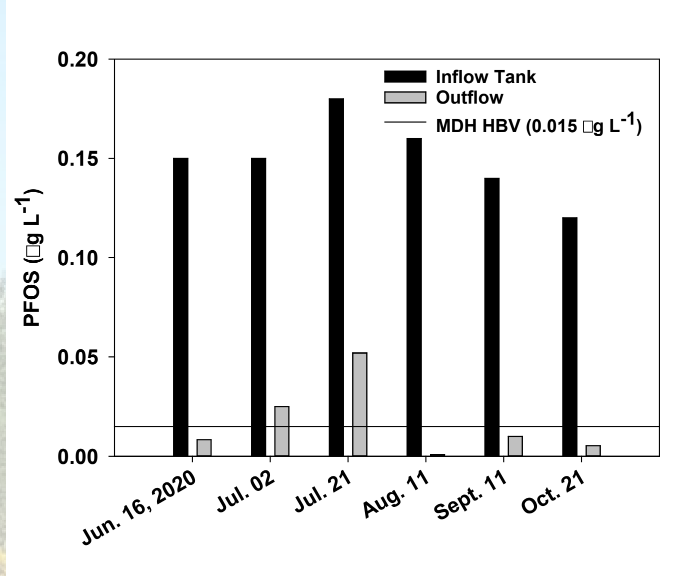
2020 Inflow-Outflow: Evapotranspiration

- Have to 'take the good with the bad'
- Evapotranspiration = water volume loss
- Lose water volume = less for disposal / irrigation
- BUT…tendency to concentrate dissolved ions, TOC, PFAS…

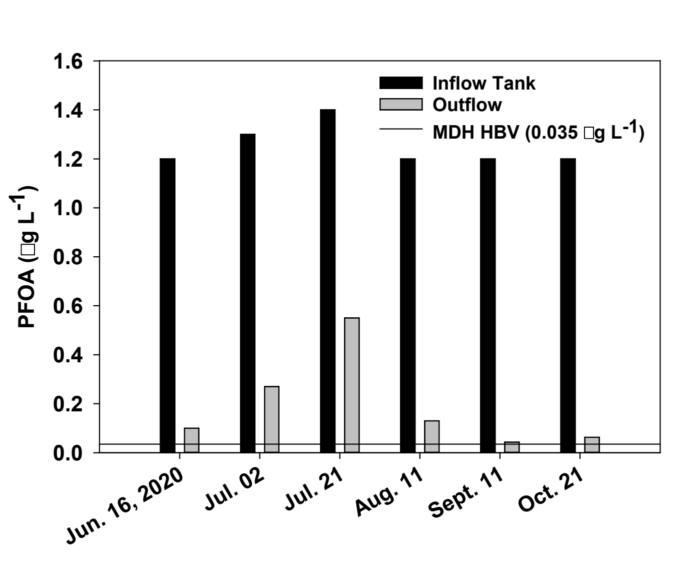


	June 15	June 19	June 22	July 14	Aug. 11	Sept. 11	Oct. 16
Inflow (mL $min.^{-1}$)	34	32	32	36	34	32	28
Cell 5 Outflow	20	18	18	20	18	20	22
Percent Decrease	41	44	44	44	47	38	21

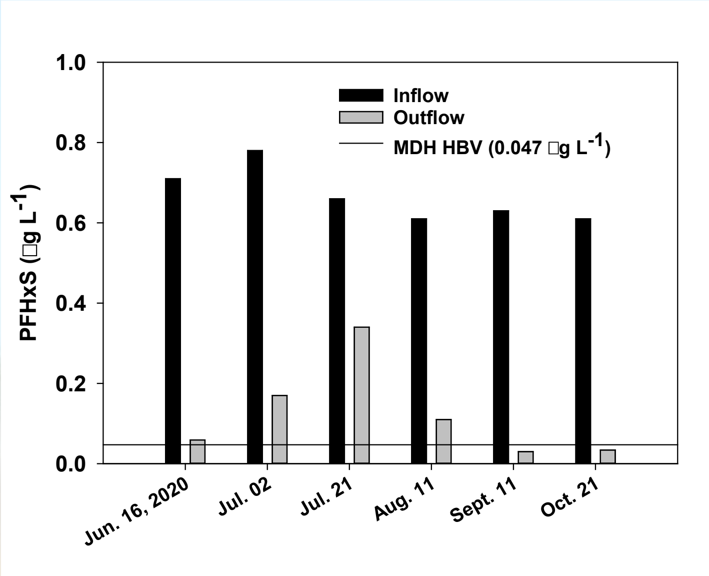
2020 PFAS



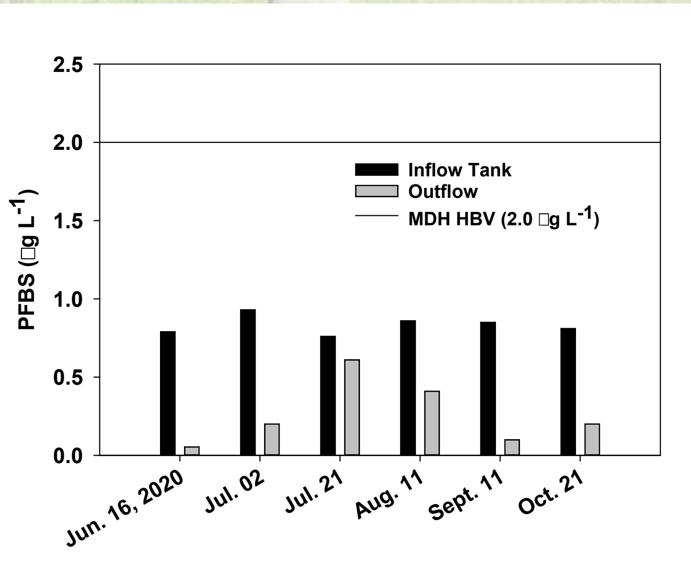
Inflow Tank
Outflow
MDH HBV (0.015 □g L-1)
PFOS (□g L-1)
0.20
0.15
0.10
0.05
0.00
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21



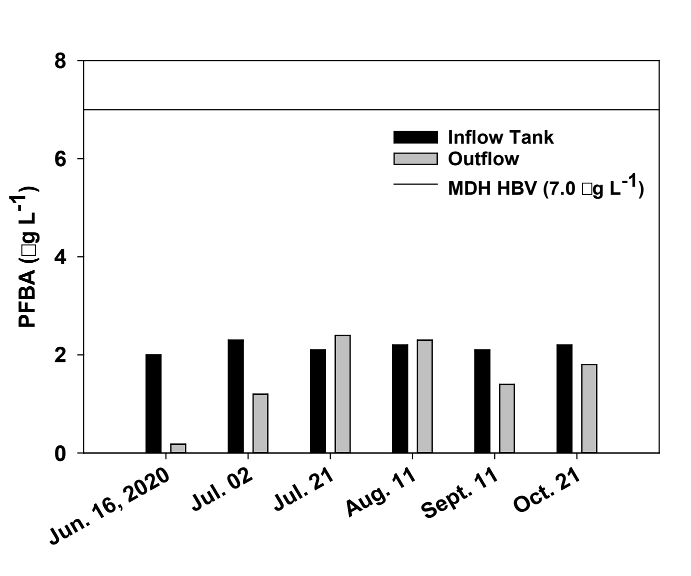
Inflow Tank
Outflow
MDH HBV (0.035 □g L-1)
PFOA (□g L-1)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21



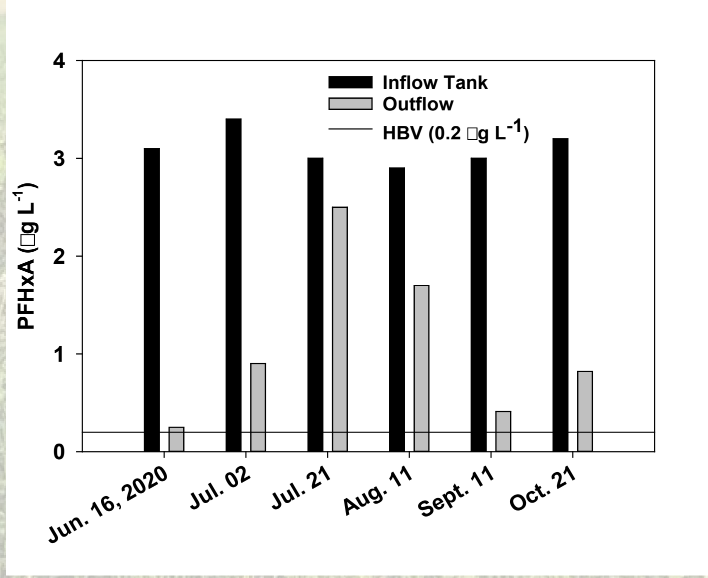
Inflow
Outflow
MDH HBV (0.047 □g L-1)
PFHxS (□g L-1)
1.0
0.8
0.6
0.4
0.2
0.0
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21



Inflow Tank
Outflow
MDH HBV (2.0 □g L-1)
PFBS (□g L-1)
2.5
2.0
1.5
1.0
0.5
0.0
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21

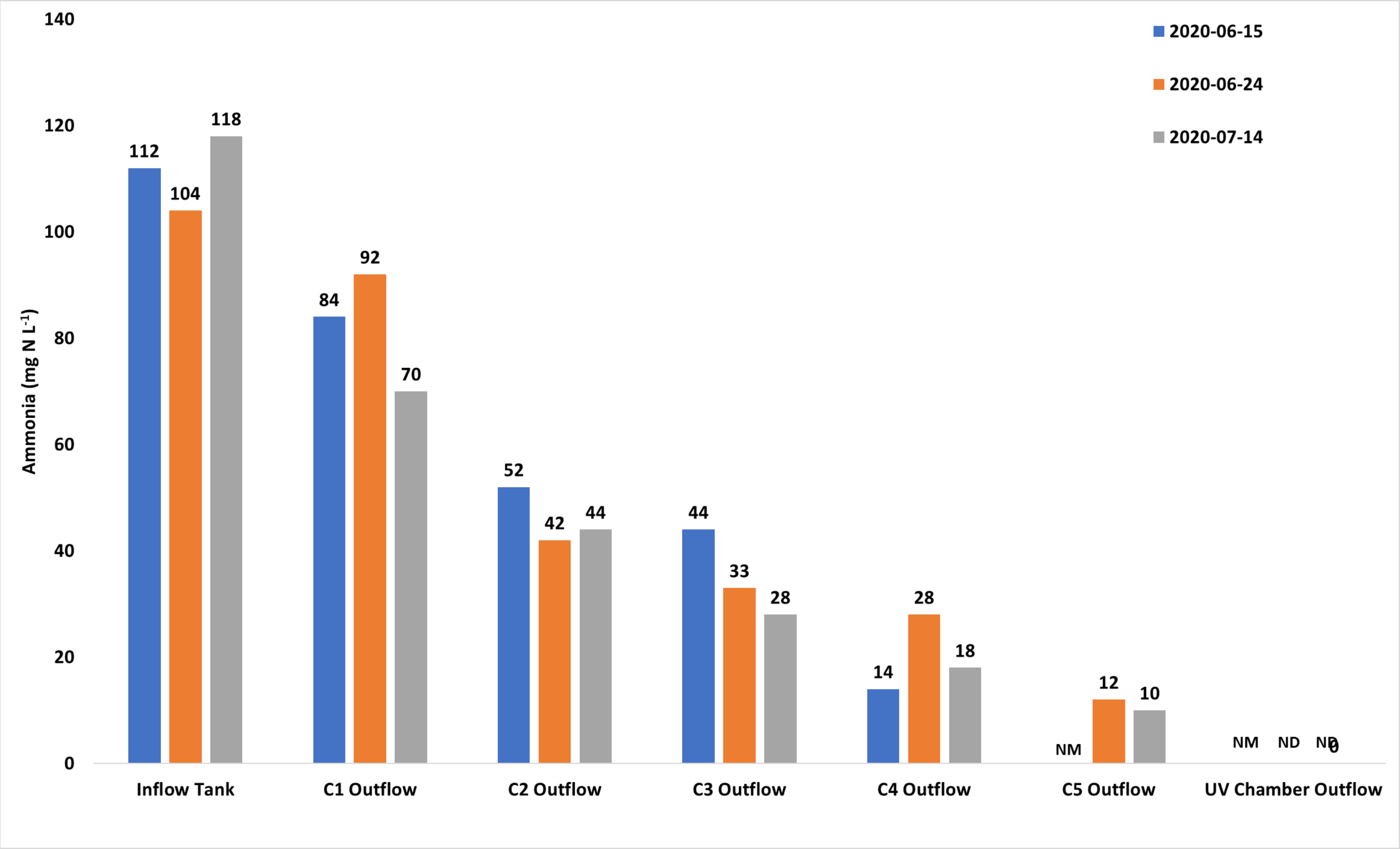


Inflow Tank
Outflow
MDH HBV (7.0 □g L-1)
PFBA (□g L-1)
8
6
4
2
0
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21

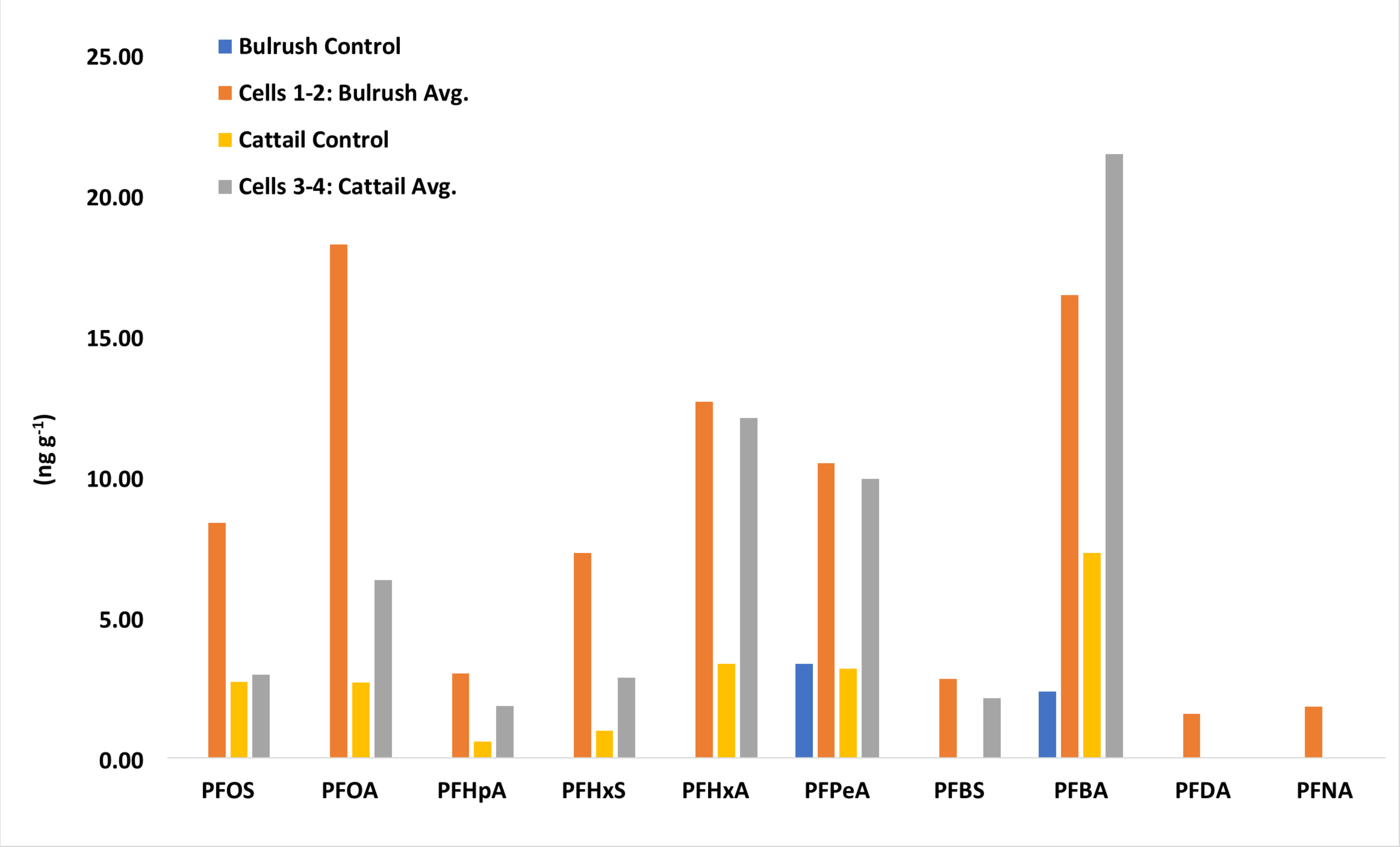


Inflow Tank
Outflow
HBV (0.2 □g L-1)
PFHxA (□g L-1)
4
3
2
1
0
Jun. 16, 2020
Jul. 02
Jul. 21
Aug. 11
Sept. 11
Oct. 21

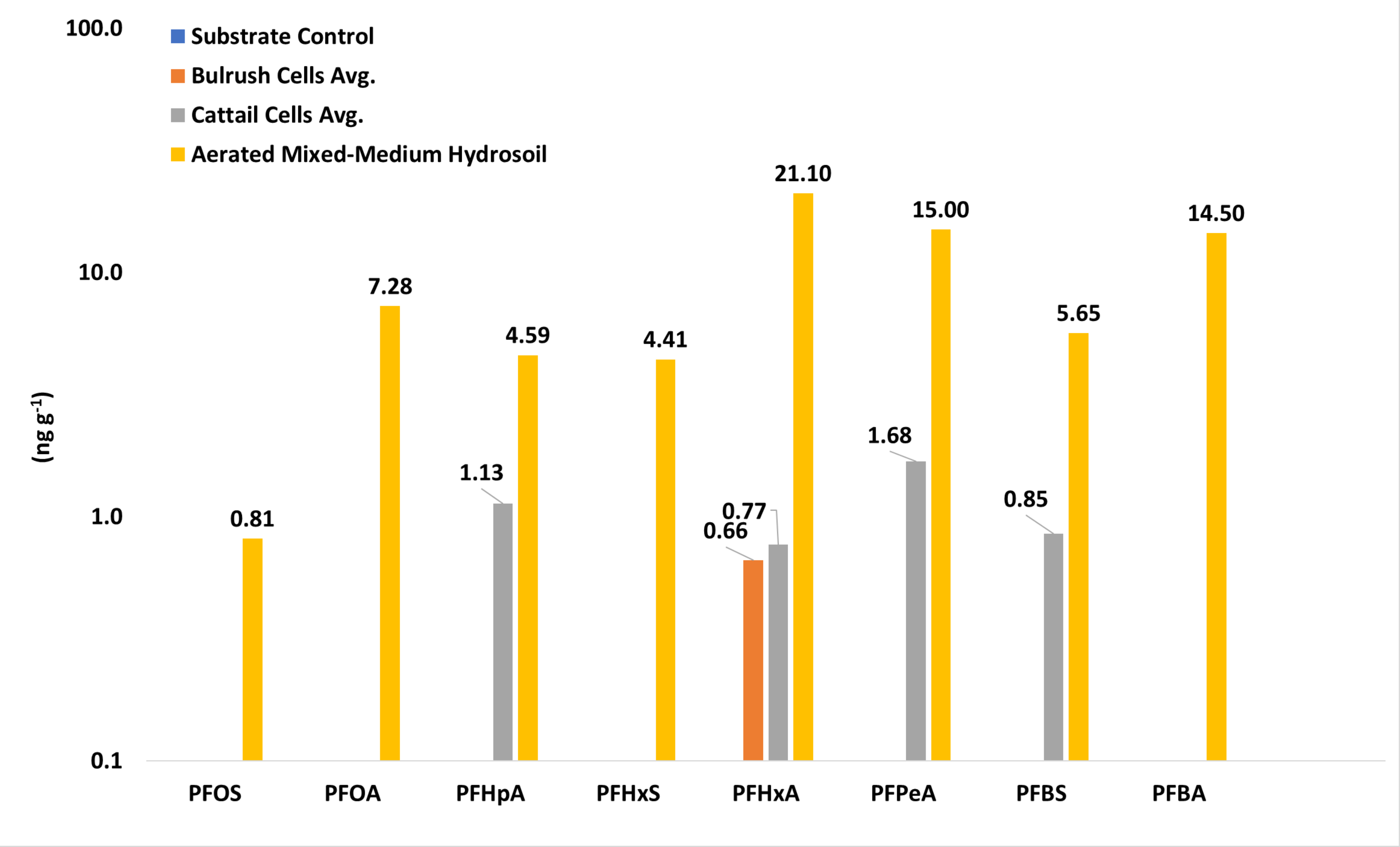
2020 Between-Cell NH_3-N



2020 Plant PFAS



2020 Substrate PFAS

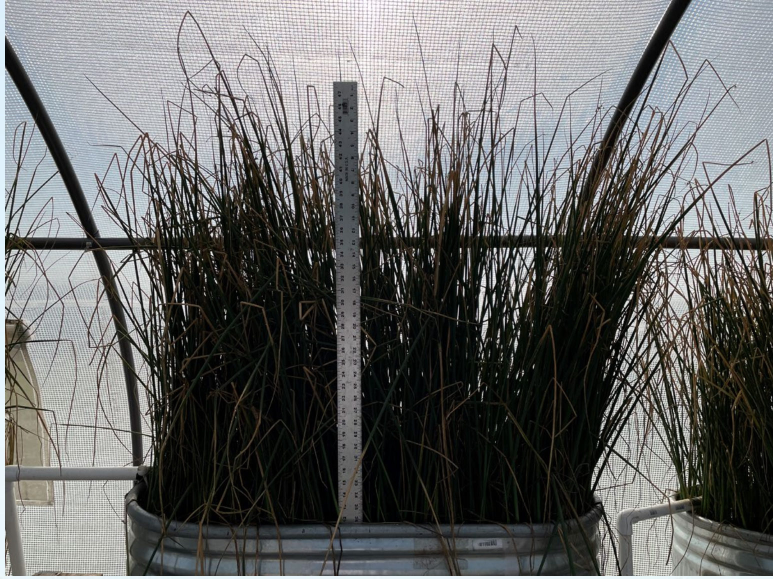


2021 Design

June 16, 2021

June 25, 2021

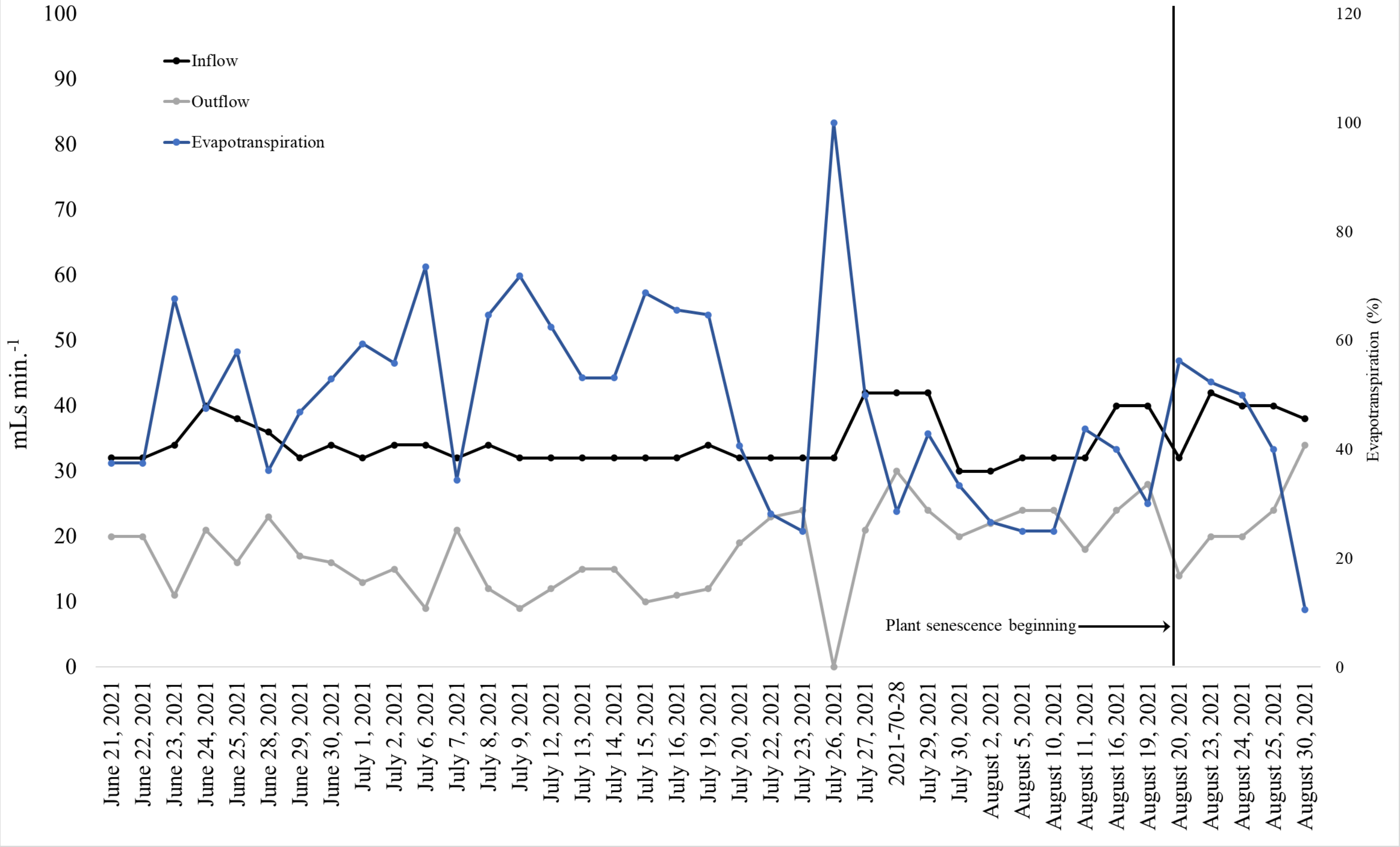
June 25, 2021



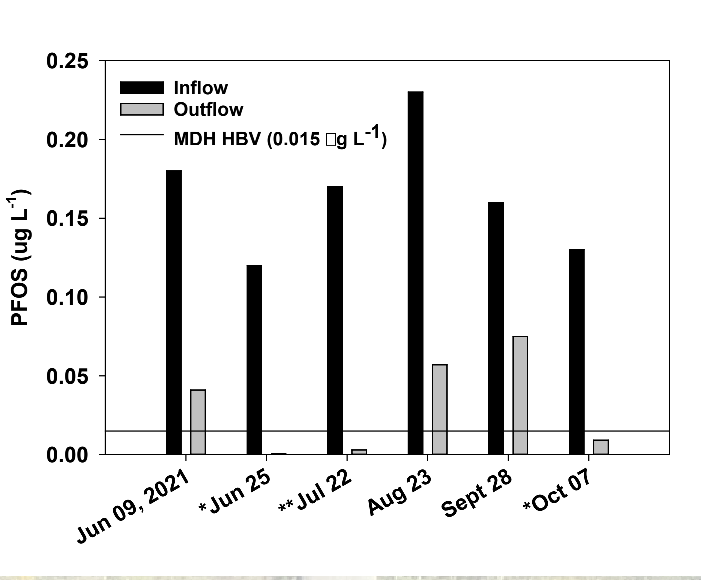
August 30, 2021

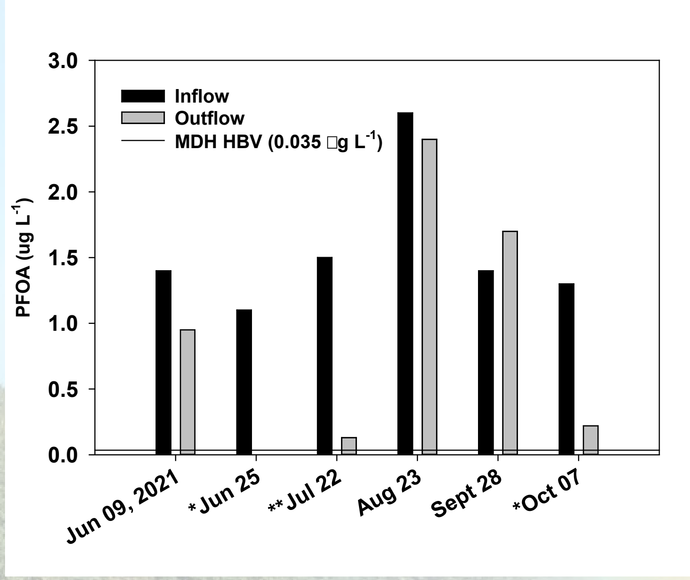
August 30, 2021

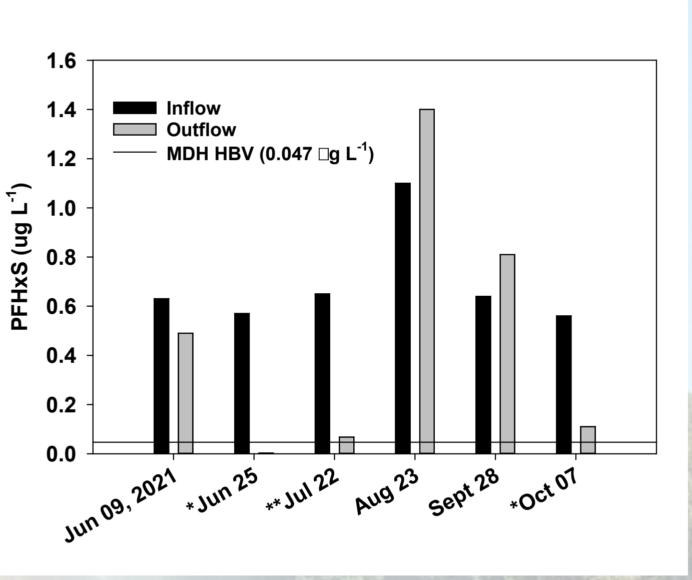
2021 Inflow-Outflow: Evapotranspiration

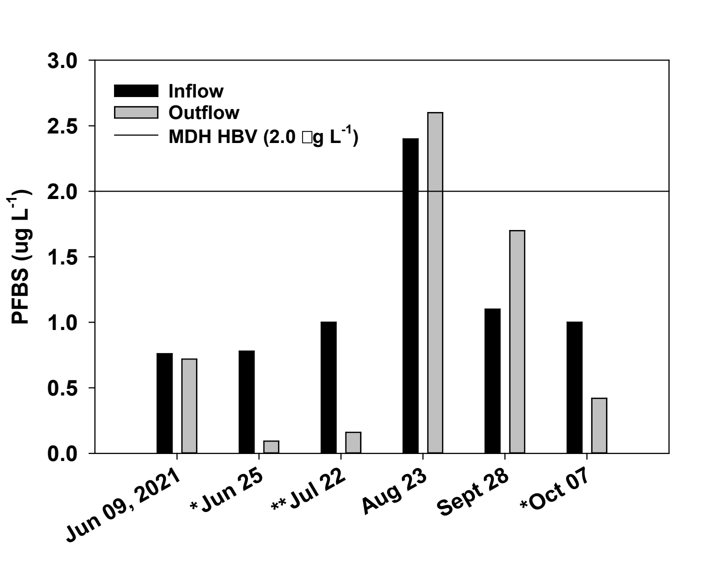


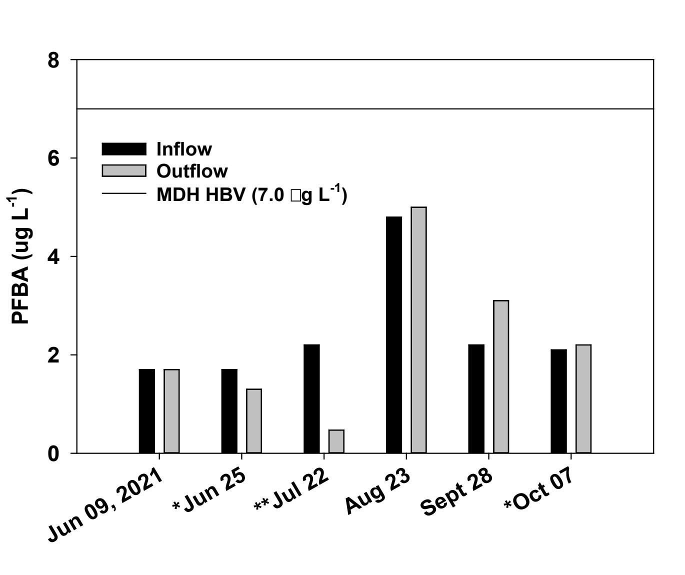
2021 PFAS

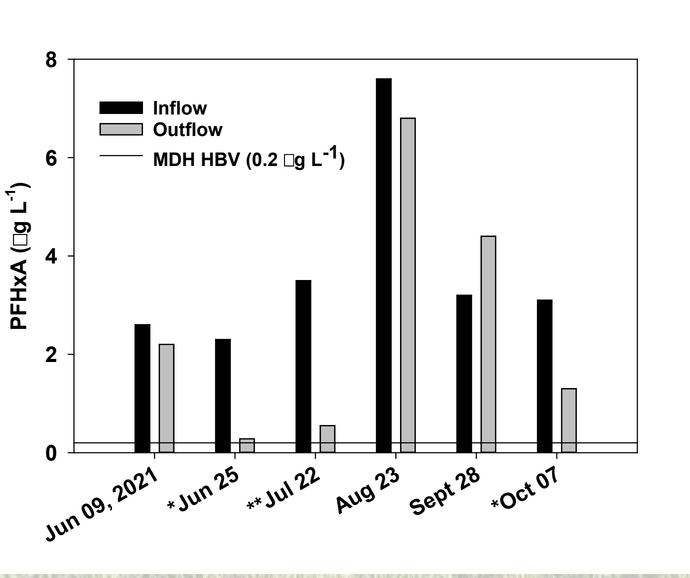

PFOS (ug L-1)
Inflow
Outflow
MDH HBV (0.015 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07


PFOA (ug L-1)
Inflow
Outflow
MDH HBV (0.035 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07

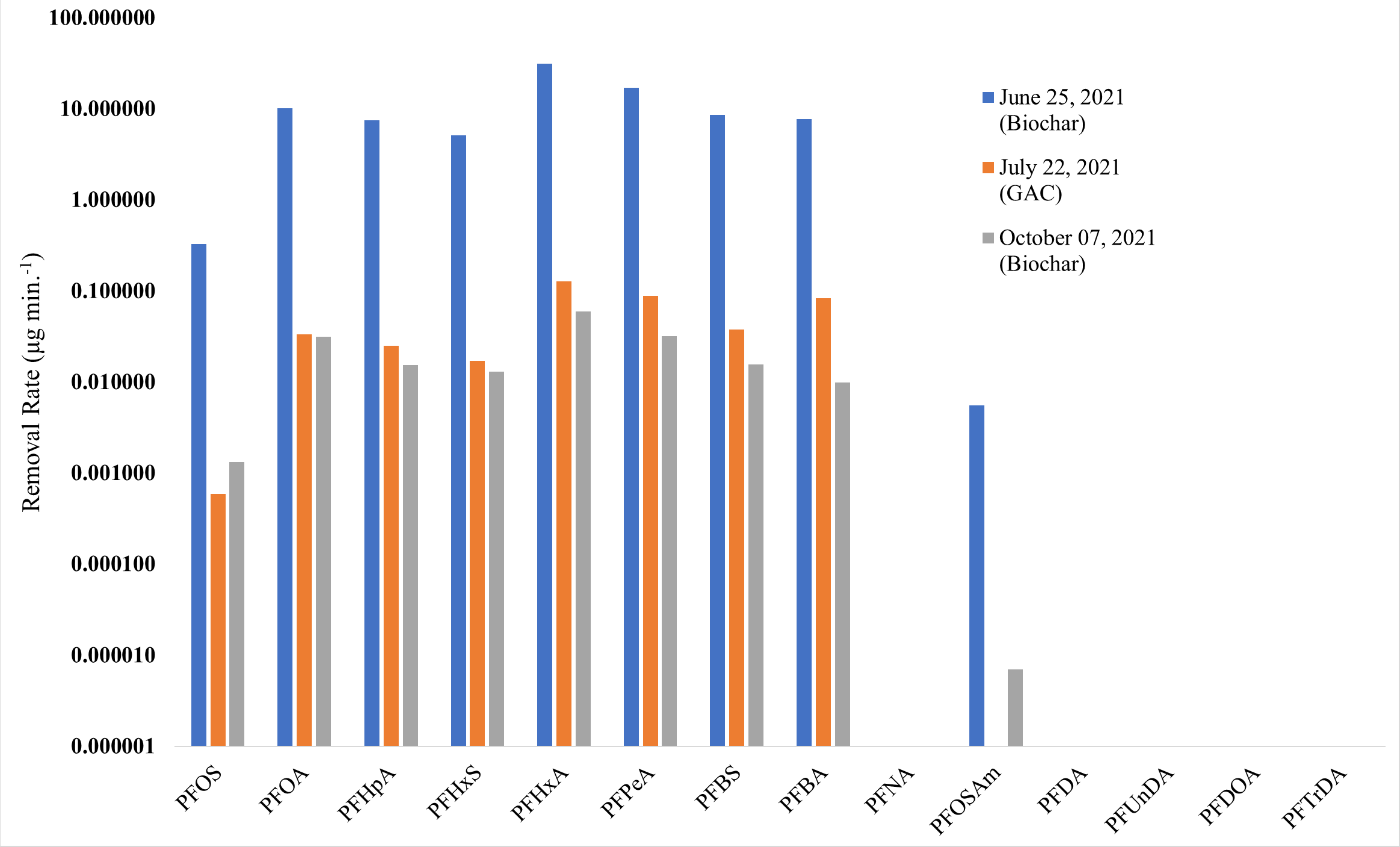

PFHxS (ug L-1)
Inflow
Outflow
MDH HBV (0.047 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07


PFBS (ug L-1)
Inflow
Outflow
MDH HBV (2.0 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07

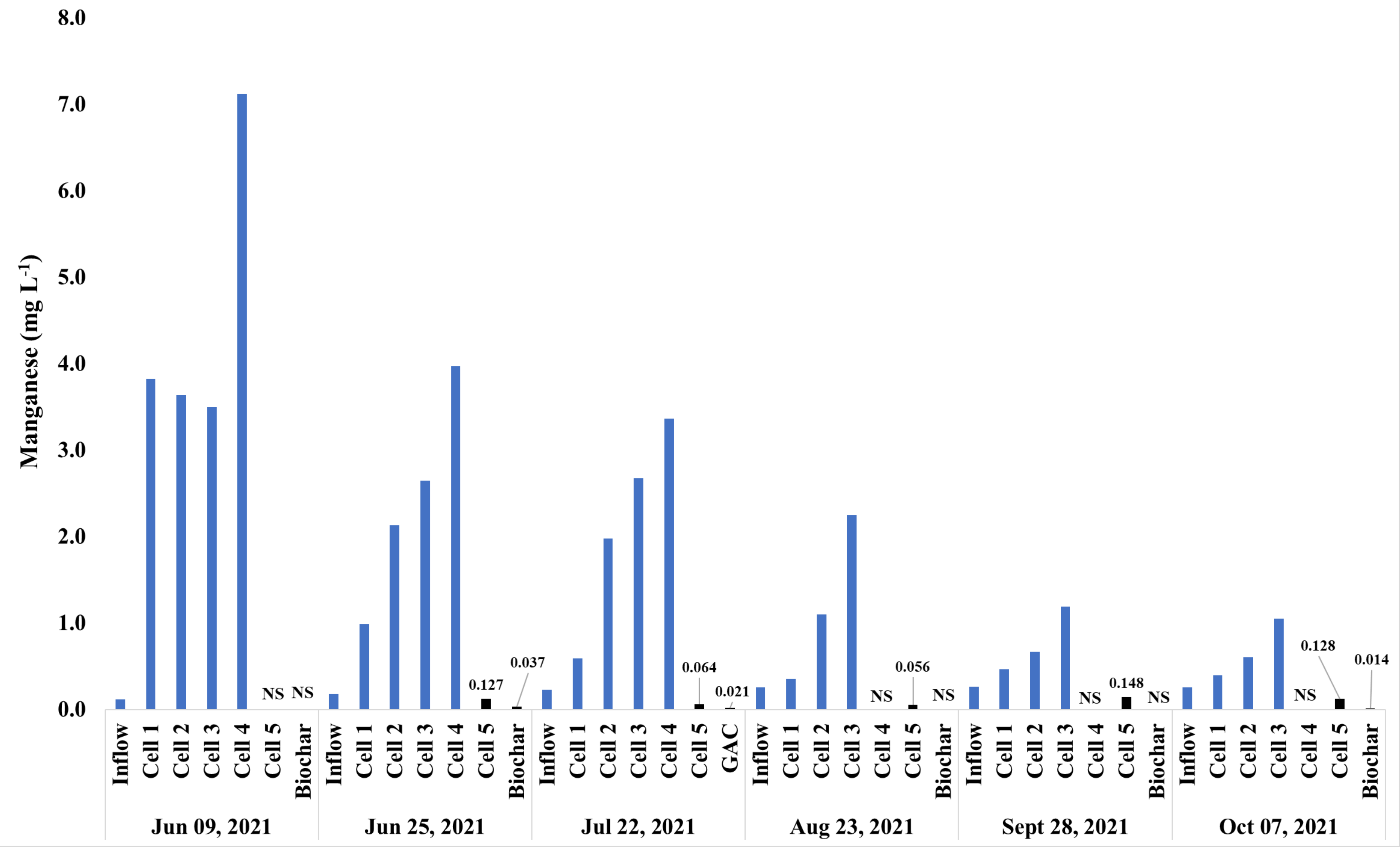

PFBA (ug L-1)
Inflow
Outflow
MDH HBV (7.0 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07


PFHxA (□g L-1)
Inflow
Outflow
MDH HBV (0.2 □g L-1)
Jun 09, 2021
* Jun 25
** Jul 22
Aug 23
Sept 28
*Oct 07

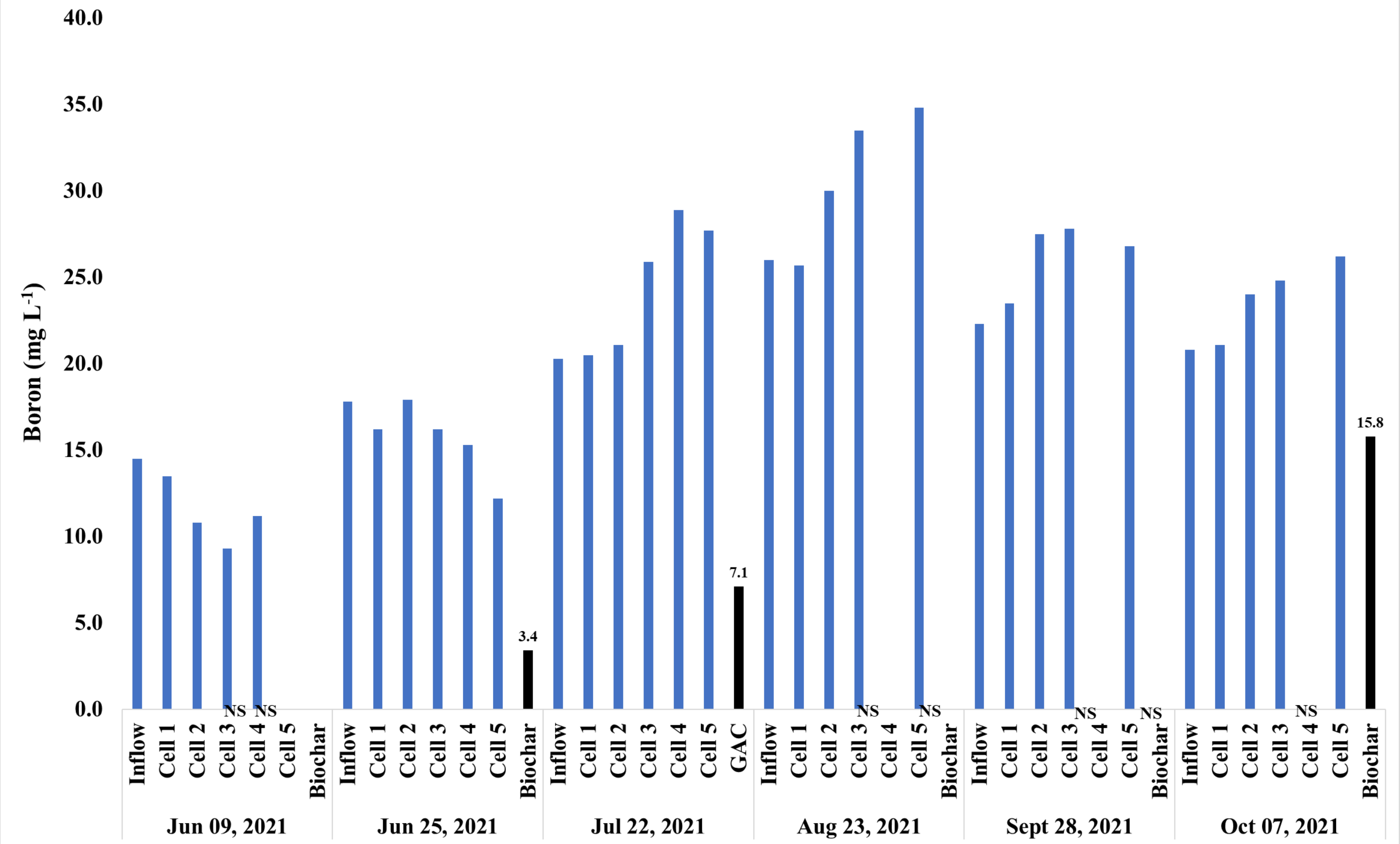
2021 Calc. Biochar / GAC PFAS Removal Rates



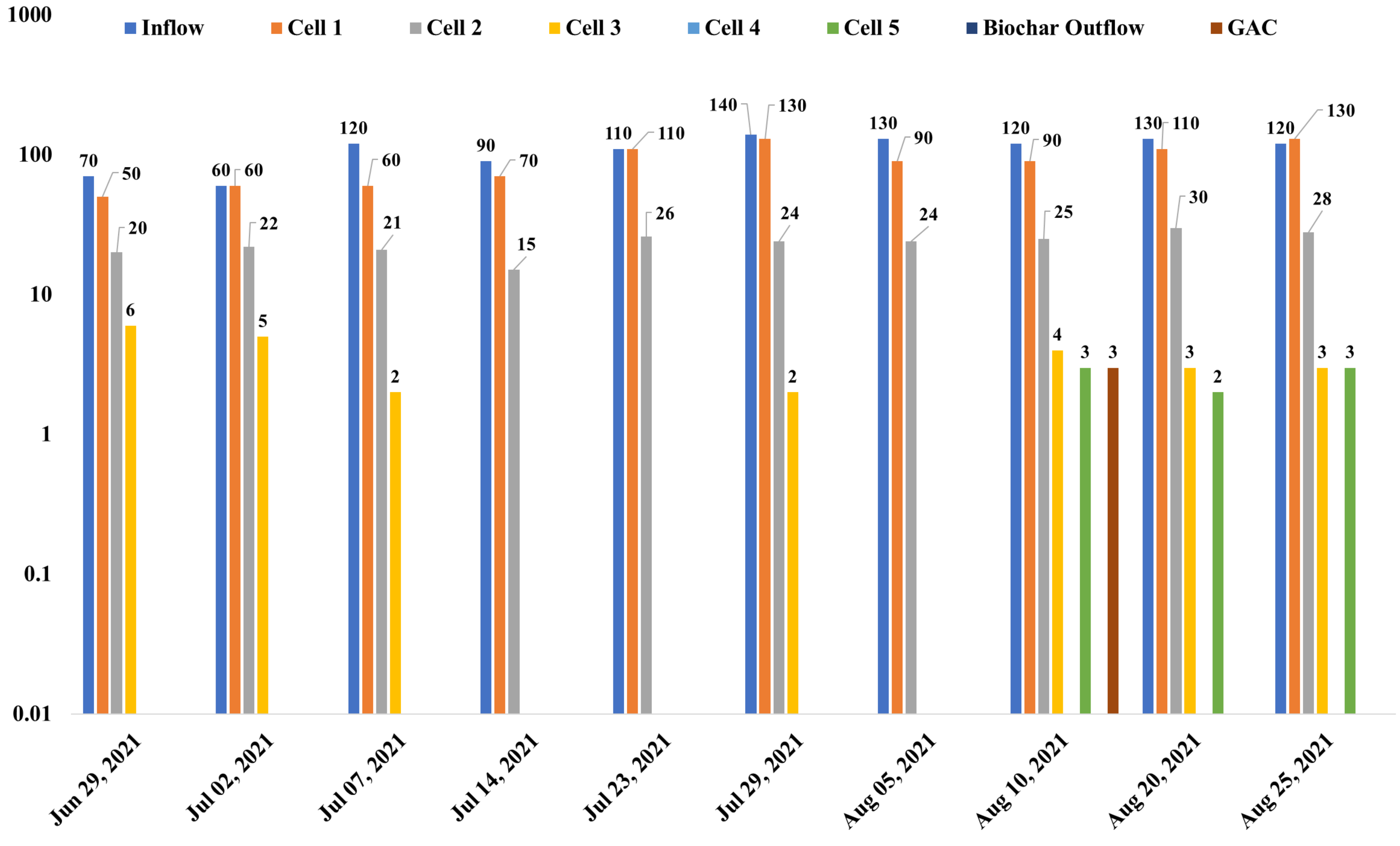
2021 Between-Cell Manganese



2021 Between-Cell Boron



2021 Between-Cell NH_3-N



2019 Conclusions

Rudimentary, but functional!

- Decreased concentrations of multiple PFAS
  - Mechanism?? Sorption? Plant uptake? Degradation?
  - All possible based on existing pubs.
- Decreased concentrations of NH3-N; N overall
  - Plant, biological consumption – assimilatory / dissimilatory reduction
- Increased Mn conc. likely due to reductive (re)mobilization
  - Can be mitigated with oxidizing cell / conditions
- Flow rate was ~10x too high (300-500 mL $min.^{-1}$; gravity feed system)
- Inflow / Outflow differences sufficient to result in additional 2020 evaluation(!!)

2020 Conclusions

Here we are…something VERY POSITIVE about 2020!

- Although variable, overall PFAS removal achieved to greater extent than 2019
  - Consistent(!) PFAS removal (example: August, September, October 2020 PFAS Data)
- Overall N removal achieved to greater extent than 2019; 90-100% (based on HRT)
  - Consistent N (as NH_3) removal
- Mn removal achieved
  - Consistent Mn removal
- B removal initially achieved, not maintained (likely sorption mechanism)
  - Could test simultaneous with TOC…
- TOC removal initially achieved, not maintained (sorption mechanism?)
  - Could test simultaneous with boron…

2021 Conclusions

EVEN BETTER THAN 2020!

- Although variable, overall PFAS removal greater than 2019; hybrid version better than 2020
- Mn removal achieved; consistent with oxidizing cell, Biochar, GAC
- B removal achieved w/ Biochar, GAC – likely sorption mechanism
- TOC removal achieved w/ Biochar, GAC – likely sorption mechanism
- Overall N removal achieved similar to 2020; 90-100% (based on HRT)
  - Consistent N (as NH_3) removal
- Emphasizes CWTS can do a lot, but not everything…
- Need for modular hybrid system – more consistent to greater extent

Acknowledgements

- St. Louis County (SLC) Commissioners
- Funded by SLC Environmental Services
  - Mark St. Lawrence, David Fink
- Other County Personnel
  - Anita, Ken (in absentia), Mark, Brian, others??
- NTS Colleagues
  - Rick C., Nick J., Nick M., Jeff K., Karissa V., Mike H., Jordan E., Corey A., Ian S., Jon N., Catherine H., Evan J.
- Pace Analytical, TestAmerica – analytical support

Rocky Dog

Jack Dog


Comments?
Questions?

2021 Between-Cell PFAS (% Dec.)

		June 09, 2021						June 25, 2021						*July 22, 2021					
		% Change						% Change						% Change					
		Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Biochar	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Biochar	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	GAC
1	PFOS	-28	-82	-84	-77	NS	NC	-8	-45	-75	-76	-78	-100	-29	-69	-71	-78	-83	-98
2	PFOA	-14	-34	-40	-32	NS	NC	-9	0	-15	-13	-28	-100	7	-7	7	27	7	-91
3	PFHpA	-9	-22	-29	-20	NS	NC	-10	12	5	12	0	-98	10	18	28	67	54	-86
4	PFHxS	5	-27	-41	-22	NS	NC	-5	-2	-12	-14	-30	-100	9	5	11	35	26	-90
5	PFHxA	4	-8	-12	-15	NS	NC	-9	13	13	17	17	-88	3	17	46	63	74	-84
6	PFPeA	0	0	-6	-11	NS	NC	-6	12	18	24	18	-60	9	22	48	87	87	-81
7	PFBS	3	-5	-12	-5	NS	NC	-5	9	6	17	-3	-88	10	30	50	80	80	-84
8	PFBA	0	6	6	0	NS	NC	-12	6	12	18	12	-24	9	23	45	82	86	-79
	PFNA	-18	-62	-69	-59	NS	NC	-17	-37	-67	-67	-73	NC	-10	-50	-43	-57	-68	-97
	PFOSAm	-40	NC	NC	NC	NS	NC	-27	-60	-78	-80	-88	-98	-35	-81	-79	-84	NC	-85
	PFDA	-41	-91	-91	-85	NS	NC	-48	-83	-92	-92	-91	NC	-44	-89	-95	-95	-94	NC
	PFUnDA	-19	NC	NC	NC	NS	NC	NC	NC	NC	NC	NC	NC	-35	NC	NC	NC	NC	NC
	PFDOA	NC	NC	NC	NC	NS	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
	PFTrDA	NC	NC	NC	NC	NS	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC

		August 23, 2021						September 28, 2021						October 07, 2021					
		% Change						% Change						% Change					
		Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Biochar	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Biochar	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Biochar
1	PFOS	18	24	-35		-66	NC	0	-25	-39	NS	-53	NC	-15	-33	-43	NS	-42	-93
2	PFOA	47	60	93		60	NC	14	14	36	NS	21	NC	8	0	15	NS	38	-83
3	PFHpA	54	67	105		118	NC	12	27	33	NS	47	NC	1	4	4	NS	29	-72
4	PFHxS	38	69	100		115	NC	14	30	30	NS	27	NC	11	0	18	NS	36	-80
5	PFHxA	51	69	97		94	NC	13	22	22	NS	38	NC	3	3	19	NS	39	-58
6	PFPeA	43	78	113		130	NC	14	27	36	NS	55	NC	5	14	29	NS	48	-29
7	PFBS	50	90	120		160	NC	9	36	36	NS	55	NC	10	10	20	NS	20	-58
8	PFBA	41	77	109		127	NC	14	18	27	NS	41	NC	5	5	19	NS	29	5
	PFNA	39	24	13		-31	NC	3	3	8	NS	-15	NC	-10	-11	-10	NS	6	-92
	PFOSAm	-3	-60	-81		-87	NC	-9	-64	NC	NS	NC	NC	-21	-61	-79	NS	-85	-92
	PFDA	0	-53	-86		-94	NC	0	-50	-78	NS	-87	NC	-27	-54	-78	NS	-82	-98
	PFUnDA	-35	NC	NC		NC	NC	NC	NC	NC	NS	NC	NC	-37	NC	NC	NS	NC	NC
	PFDOA	NC	NC	NC	NC	NC	NC	NC	NC	NC	NS	NC	NC	-8	NC	NC	NS	NC	NC
	PFTrDA	NC	NC	NC	NC	NC	NC	NC	NC	NC	NS	NC	NC	NC	NC	NC	NS	NC	NC