TREATMENT MITIGATION STRATEGIES FOR POLY- AND PERFLUOROALKYL CHEMICALS

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SOUTHERN NEVADA WATER AUTHORITY

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Water Research Foundation

SOUTHERN NEVADA WATER AUTHORITY

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Objective

Evaluate the ability of a wide spectrum of full-scale drinking water treatment techniques to remove poly- and perfluoroalkyl substances (PFAS) from raw water or potable reuse sources.

Approach: PFAS

Compounds	Inclusion in This Study	Inclusion in CCL3	Inclusion in UCMR3
Perfluoro Carboxylic Acids			
Perfluorobutyric acid (PFBA)	✓		
Perfluoropentanoic acid (PFPnA)	✓		
Perfluorohexanoic acid (PFHxA)	✓		
Perfluoroheptanoic acid (PFHpA)	✓		✓
Perfluorooctanoic acid (PFOA)	✓	✓	✓
Perfluorononanoic acid (PFNA)	✓		✓
Perfluorodecanoic acid (PFDA)	✓		
Perfluoroundecanoic acid (PFUnA)	✓		
Perfluorododecanoic acid (PFDoA)	✓		
Perfluoro Sulfonic Acids			
Perfluorobutane sulfonic acid (PFBS)	✓		✓
Perfluorohexane sulfonic acid (PFHxS)	✓		✓
Perfluorooctane sulfonic acid (PFOS)	✓	✓	✓
Perfluorodecane sulfonic acid (PFDS)	✓		

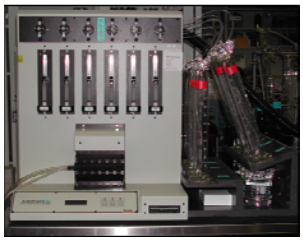
Approach: PFASs

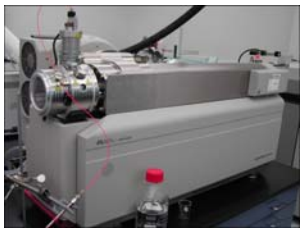
PFAS Classes	Chemical Name	Abbreviation	# of Carbons	M.W. (g/mol)
Perfluorocarboxylic Acids (PFCAs)	Perfluorobutyric acid	PFBA	4	214
	Perfluoropentanoic acid	PFPeA	5	264
	Perfluorohexanoic acid	PFHxA	6	314
	Perfluoroheptanoic acid	PFHpA	7	364
	Perfluorooctanoic acid	PFOA	8	414
	Perfluorononanoic acid	PFNA	9	464
	Perfluorodecanoic acid	PFDA	10	514
	Perfluoroundecanoic acid	PFUnA	11	564
	Perfluorododecanoic acid	PFDoA	12	614
Perfluorosulfonic Acids (PFSAs)	Perfluorobutane sulfonic acid	PFBS	4	300
	Perfluorohexane sulfonic acid	PFHxS	6	400
	Perfluorooctane sulfonic acid	PFOS	8	500
	Perfluorodecane sulfonic acid	PFDS	10	600

Other PFASs: perfluorooctane sulfonamide (FOSA), 2 perfluorosulfonamidoacetic acids, 4 fluorotelomer unsaturated carboxylic acids and 3 fluorotelomer sulfonic acids

Analytical Methods

- Automated Solid-Phase Extraction - Dionex AutoTrace 280 workstation
- Isotopic Dilution LC/MS-MS - API 4000™
- Minimum Reporting Levels: range from 0.1 to 5.0 ng/L



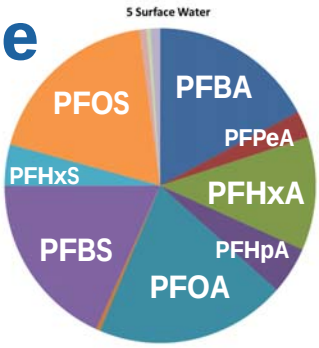


Approach: Utility Sites

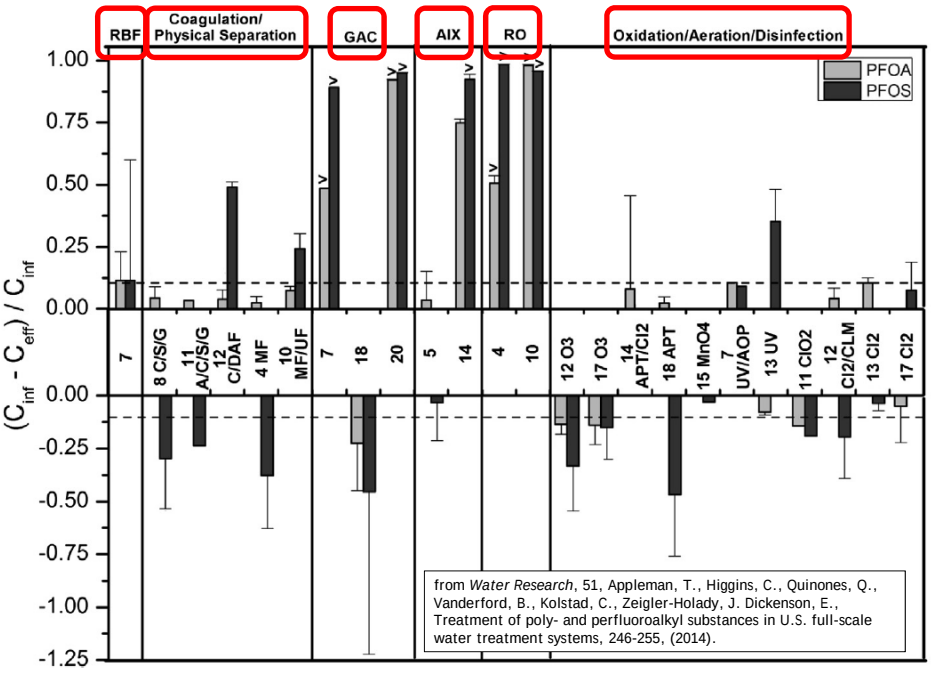
Utility ID	State	Source Water	Treatment Train	Source Water Sampling Dates	Treatment Train Sampling Dates
1	WI	SW		8/9/2011	
2	OK	SW		8/23/2011	
3	AK	SW		8/22/2011	
4	CA	2º TWW	MF/RO/UV-AOP/DI/Cl_2	8/8/2011	12/6/2011, 2/22/2012
5	AL	SW	AIX/COAG/FLOC/SED/MF/Cl_2	8/15/2011	12/13/2011, 3/20/2012
6	CO	SW		4/9/2012	
7	CO	SW	RBF/ARR/SOFT/SCC/UV-AOP/G-FIL(Biological)/GAC	9/13/2011	5/1/2012, 6/19/2012, 8/21/2012
8	OH	SW	SED/COAG/FLOC/SED/G-FIL/GAC/Cl_2	8/9/2011	12/12/2011, 2/22/2012
9	NV	SW		9/19/2011	
10	CA	3º TWW	MF/UF/RO/UV-AOP	10/4/2011	1/9/2012, 3/6/2012
11	NJ	SW/GW	AER/COAG/FLOC/SED/G-FIL/ClO_2		12/6/2011, 3/14/2012
12	NJ	SW	O_3/DAF/Cl_2/CLM		3/21/2012, 5/23/2012
13	NJ	GW	UV/Cl_2		3/21/2012, 5/23/2012
14	NJ	GW	AIX/APT/Cl_2		5/30/2012, 9/19/2012
15	NJ	GW	Cl_2/MnO_4/G-FIL		12/13/2011
16	NJ	GW	ClO_2/Cl_2		11/29/2011
17	NJ	SW	MnO_4/O_3/Cl_2		12/14/2011, 4/3/2012
18	NJ	SW	APT/GAC/Cl_2		11/22/2011, 4/3/2012
19	NJ	GW	Cl_2		11/29/2011
20	MN	GW	GAC/Cl_2		10/26/2006 to 06/20/2011
21	NC	SW	COAG/FLOC/SED/G-FIL/CLM	9/22/2011	9/22/2011

Results: Occurrence

- Detected PFAS were in the low ng/L
- Highest levels were in treated wastewater samples:
  - PFPeA = 370 ng/L
  - PFOA = 220 ng/L
- Highest level in drinking water was:
  - PFHxA = 62 ng/L



- PFBA, PFHxA and PFPeA were frequently detected, but they were not included in UCMR3
- Longer chain PFCAs were detected less frequently.
- The longer chain PFSA, perfluorodecane sulfonic acid, and fluorotelomer carboxylic and sulfonic acids were not detected.
- Perfluoro-sulfonamides were not detected in ground waters, but were in 3 surface waters and treated wastewater effluents.



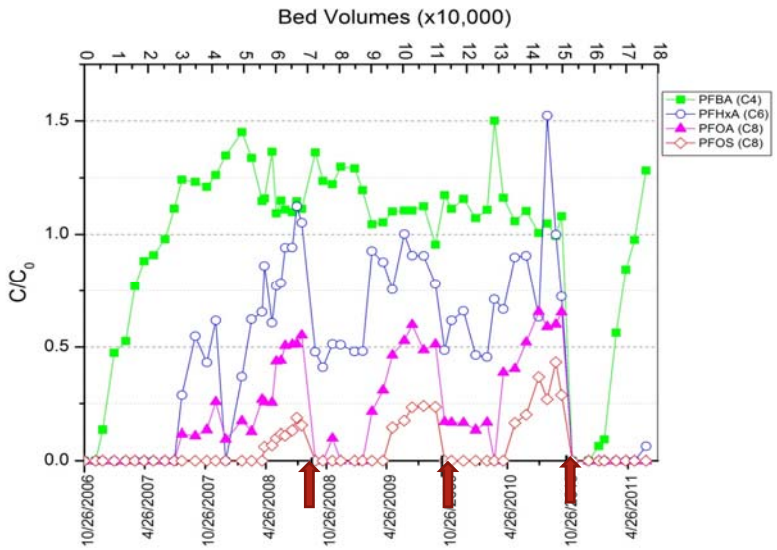
Results: Full-Scale Treatment

	Site:	4	5	7	8	10	11	12	13	14	15	16	17	18	19	20	21
Treatment	n=	CA	AL	CO	OH	CA	NJ	NJ	NJ	NJ	NJ	NJ	NJ	NJ	NJ	MN	NC
RBF	1			No													
AIX	2		No							Yes							
AER	2									No				No			
$KMnO_4$	2										No		No				
O_3	2							No					No				
COAG/FLOC/SED	1		No														
COAG/FLOC/SED/G-FIL	3				No		No										No
SOFT	1			No													
COAG/DAF/G-FIL	1							No									
M-FIL or U-FIL	3	No	No			No											
RO	2	Yes				Yes											
UV-AOP	1			No													
GAC	4			Yes	No									No		Yes	
UV	1								No								
ClO_2	2						No					No					
Cl_2	9		No					No	No	No	No	No	No	No	No		
CLM	2							No									No

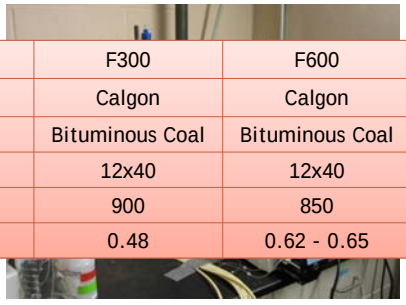
Results: Full-Scale GAC and AIX

Utility	# of Carbons	#7	#20	#14	#14
Treatment		GAC	GAC	AIX	AIX
Sample Date		8/21/2012	4/25/2007 – 4/22/2008	5/30/2012	9/19/2012
PFBA	4	33%	-17%	-9%	0%
PFPeA	5	74%	> 22%	0%	0%
PFHxA	6	91%	> 68%	14%	-14%
PFHpA	7	> 89%	N/A	54%	38%
PFOA	8	> 48%	> 92%	76%	73%
PFNA	9	> 37%	N/A	N/A	> 67%
PFBS	4	> 96%	N/A	83%	80%
PFHxS	6	> 96%	> 41%	> 97%	> 98%
PFOS	8	> 89%	> 95%	> 90%	> 94%

Results: Full-Scale GAC



Methods: Bench-Scale GAC

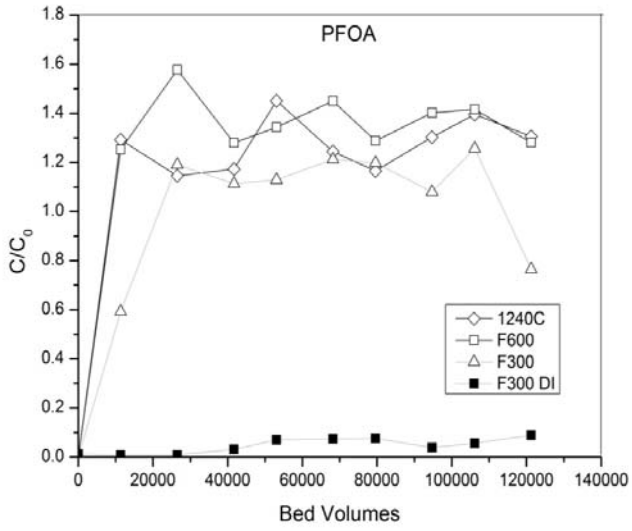


	F300	F600	1240C
Manufacturer	Calgon	Calgon	Siemens
Carbon Type	Bituminous Coal	Bituminous Coal	Coconut Shell
Mesh Size, U.S. Sieve	12x40	12x40	12x40
Iodine No., mg I_2/g	900	850	1100
Apparent Density, g/cc	0.48	0.62 - 0.65	0.46 - 0.52

Water Source	Spiked DI	Filtered (1 µm) and spiked Clear Creek Water		
PFAA Concentrations (ug/L)	1.0	1.0		
# of Columns	3	2	2	2
Carbon	F300	F300	F600	1240C
Column Width (cm)	0.7	0.7	0.7	0.7
Carbon Depth (cm)	1	1	1	1
Flow Rate (mL/min)	1	1	1	1
EBCT (min)	0.38	0.38	0.38	0.38
Duration (days)	43	32	52	38

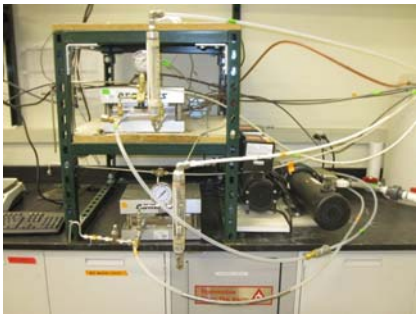
—Surface water: DOC = 1.7 mg/L, pH = 6.5

Results: Bench-Scale GAC



Methods: Bench-Scale Nanofiltration

- Set-up
  - Two flat-sheet NF270 membranes in sequence
  - Flow-through operation
  - 1 L/min, 18°C, pH of 6.7
  - Five 30 min increments
- Initial experiment:
  - Spiked DI water feed (1 ug/L)
  - Pressures tested from 25-125 psi
- Second experiment:
  - Spiked artificial ground water used for feed (1 ug/L)
  - Membranes were fouled to 65% capacity (DOC = 2.5 mg/L)
  - Experiment was repeated with fouled membranes with constant flux



Component	Concentration (mg/L)
$MnSO_4 \cdot H_20$	1
Na_2SO_4	180
NaCl	113
$NaHCO_3$	40

Results: Bench-Scale Nanofiltration

	Permeate Flux (LMH)	PFBA (214)	PFPeA (264)	PFHxA (314)	PFOA (414)	PFNA (464)	PFDA (514)	PFBS (300)	PFHxS (400)	PFOS (500)
AGW-Virgin	17	> 94	> 97	> 95	> 97	> 98	> 97	> 99	> 99	> 99
	33	> 94	> 97	> 95	> 97	> 97	> 97	> 99	> 99	> 99
	50	> 94	> 97	> 95	> 97	> 98	> 97	99	> 99	> 99
	59	> 95	> 97	> 95	> 97	> 98	> 97	98	> 99	> 99
	75	> 94	> 97	> 95	> 97	> 98	> 97	98	> 99	> 99
AGW-Fouled	17	> 95	> 97	> 95	> 97	> 98	> 97	> 99	> 99	> 99
	33	> 94	> 97	> 95	> 97	> 97	> 97	> 99	> 99	> 99
	50	> 94	> 97	> 95	> 97	> 97	> 96	> 99	> 99	> 99
	59	> 94	> 97	> 95	> 97	> 98	> 97	> 99	> 99	> 99
	75	> 94	> 97	> 95	> 97	> 98	> 97	> 99	> 99	> 99
DI-Virgin	20	> 93	> 97	> 95	> 97	> 98	> 97	97	> 97	> 99
	28	> 93	> 97	> 95	> 97	> 98	> 98	98	98	> 99
	44	> 93	> 97	> 95	> 95	> 97	> 97	96	97	> 99
	59	> 94	> 97	> 95	> 97	> 98	> 98	96	96	> 99
	70	> 93	> 97	> 95	> 97	> 97	> 98	95	96	> 99

Results: Treatment Summary

	M.W. (g/mol)	AER	COAG/ DAF	COAG/ SED/ G- or M-FIL	AIX	GAC	NF	RO	$KMnO_4$, O_3, ClO2, Free Cl2, NH2Cl, UV, UV/AOP
PFBA	214	assumed	assumed						
PFPnA	264								
PFHxA	314								
PFHpA	364								
PFOA	414								
PFNA	464		unknown		assumed	assumed			
PFDA	514		unknown		assumed	assumed			
PFBS	300								
PFHxS	400								
PFOS	500								
FOSA	499	unknown	unknown		unknown	assumed	unknown	assumed	unknown
***N*-MeFOSAA**	571	assumed	unknown		assumed	assumed	assumed		unknown
***N*-EtFOSAA**	585		unknown		assumed	assumed	assumed	assumed	unknown

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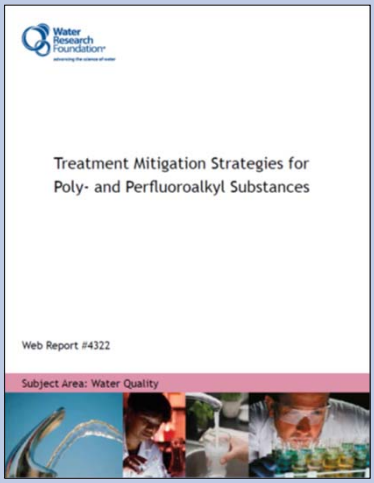

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Appleman, T., Higgins, C., Quinones, Q., Vanderford, B., Kolstad, C., Zeigler-Holady, J. Dickenson, E. Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems, *Water Research*, 51, 246-255, **2014**.

Appleman, T., Dickenson, E., Bellona, C., Higgins, C. Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids, *Journal of Hazardous Materials*, 260, 740-746, **2013**.