Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water



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What are Per- and Polyfluoroalkyl Substances (PFAS)?

- 1000s of manufactured compounds.
 - Organic compounds with at least one totally fluorinated carbon atom.
 - Produced for over 70 years.
- Due to structure of molecule:
 - Repel oil & water.
 - Highly water soluble.
- C-F bond is one of strongest known.
 - Chemically & thermally non-reactive.
- Unique properties are the basis for:
 - Commercial & industrial uses.
 - Extreme environmental persistence.
- Most have little or no health effects data.
- Most not detected by routine lab methods.



Perfluoroalkyl Substances

- All carbons are fully fluorinated.
- Do not break down in the environment or the body.



Polyfluoroalkyl Substances

- One or more carbons not fully fluorinated
- Include "precursors" that transform to terminal <u>per</u>fluoroalkyl substances in the environment and the body.



Uses of PFAS

- Processing aid in production of fluoropolymer plastics used in:
 - Non-stick cookware
 - Waterproof/breathable clothing
 - Chemical/heat resistant industrial products.
- Water & stain resistant coatings

 For carpets & upholstery
- Grease-proof food packaging
- Aqueous film forming foams (AFFF)

....and many other uses not listed here







- Sources include:
 - Releases from industrial facilities where made or used.
 - Many types large and small.
 - Release of fire fighting foams.
 - Firefighter training sites.
 - Airports & military bases.
 - Wastewater treatment plants.
 - Discharge of treated wastewater.
 - Application of sludge/biosolids on agricultural land.
 - Leachate from landfills where products or waste containing PFAS are disposed.

...and other sources.









Transport in Groundwater

- Readily transported once in groundwater
 - Chain-length dependent
 - K_{oc} important, but not fully sufficient
- Composition may be impacted by remedial activities
- Partitioning at interfaces may further slow transport and contribute to retardation



ITRC PFAS-1 Technical Regulatory Document, Figure 2-17, CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission

Widespread Former Use in Aqueous Film Forming Foam

pubsacs.org/est

Military to check 664 sites for ^{III} water poisoning

Contamination may have come from foam used to fight fires

Albuquerque Journal 11 Mar 2016 +18 more

PROVIDENCE, R.I. — The military plans to examine hundreds of sites nationwide to determine whether chemiVa., and is testing wells in a nearby rural area after the discovery of perfluorinated chemicals in drinking water,



<u>Groundwater:</u>	Field Site 1	Field Site 2	
	ng/L	ng/L	
4:2 FtTAoS ^b	990	210	
6:2 FtTAoS	53,000	6,900	
4:2 FtS	230	7,500	
6:2 FtS	5,700	220,000	
8:2 FtS	11,000	370	
PFBS	64,000	43,000	
PFHxS	380,000	240,000	
PFHpS	60,000	11,000	
PFOS	1,100,000	78,000	
PFDS	ND	ND	
PFBA	6,100	24,000	
PFPeA	39,000	69,000	
PFHxA	27,000	130,000	
PFHpA	55,000	15.000	
PFOA	63,000	51,000	
Field & Porter, 2013	1,000	220	

Environmental Science & Technology

Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

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Initial Focus on Long-Chain Perfluoroalkyl Acids (PFAAs)

- PFAAs Most well-known PFAS subgroup.
 - Charged functional group:
 - Carboxylates (COO⁻)
 - Sulfonates (SO₃⁻)
 - Totally fluorinated carbon chain length varies.
- Long chain:
 - > 8 carbons carboxylates
 - > 6 carbons sulfonates.
 - Generally more bioaccumulative & toxic than short-chain.
- Considerable health effects data.
- Detected by commercial lab methods.
- Although use in by major U.S. manufacturers has ended.....
 - Do not break down "Forever Chemicals"
 - Environmental contamination persists indefinitely.
 - <u>Replacements</u> are of current concern.





PFNA (9 carbon carboxylate)

PFOS (8 carbon sulfonate)

Long-chain PFAAs found in blood serum of almost all U.S. residents:

- **PFOA:** Perfluorooctanoic acid, C8
- **PFNA:** Perfluorononanoic acid; C9
- **PFOS:** Perfluorooctane sulfonate, C8-S
- **PFHxS**: Perfluorohexane sulfonate, C6-S





Why Are Long-Chain PFAS of Particular Concern as Drinking Water Contaminants?

- Widespread drinking water occurrence.
- Do not break down in the environment "Forever Chemicals".
- Ubiquitous in human blood serum.
- Long human half-lives (~2-8 years).
 - Bioaccumulate.
 - Remain in the body for many years after exposure ends.
- Multiple types of animal toxicity,
- Evidence for multiple human health effects from low exposures.
- Low drinking water levels can dominate other exposures (e.g. food/food packaging, consumer products).
 - Unlike other persistent, bioaccumulative, and toxic (PBT) chemicals (PCBs & dioxins) –
 Drinking water is not an important exposure route for these.
- Higher drinking water exposures to infants, a sensitive subgroup.
- Overall suggests need for caution about exposure from drinking water.







Overview - NJ Response to PFAS in Drinking Water

- NJDEP scientists recognized PFOA & other PFAS as contaminants of particular concern.
 - Based on previous experience with many other drinking water contaminants.
 - Due to their environmental persistence, bioaccumulation from drinking water, low dose toxicity, and associations with human health effects.
- 2005-2006: PFOA detected in tap water (2005) and wells (2006) of a NJ public water system (PWS) near an industrial source.
- **2007:** NJDEP issued PFOA **chronic (lifetime) drinking water guidance** of 40 ng/L at request of affected PWS.
- 2006 & 2009: NJDEP conducted first statewide studies of PFAS in drinking water in the U.S.
- 2013-15: PFOA and PFNA found much more frequently in NJ public water systems than nationally in national USEPA study (UCMR3).
- 2014: NJDEP Commissioner asked DWQI to recommend MCLs for PFNA, PFOA & PFOS.
- 2018-2020: Adopted MCLs for PFNA (13 ng/L), PFOA (14 ng/L), and PFOS (13 ng/L) and added them to Private Well Testing Act (PWTA) after proposal and public comments.
 - New Jersey's PFNA MCL was first MCL for any PFAS in the United States.
- **Present time:** Continuing to evaluate information on other PFAS that may be present in NJ drinking water.
 - UCMR5 will include 29 PFAS (with lower reporting levels than UCMR3).

MCLs Were Developed to Address Detections of PFOA, PFOS and PFNA (C9) in NJ Public Water Systems (PWS)

2006 Study



- First state to conduct statewide PFAS occurrence studies.
 - 2006 study: 23 water systems PFOA and PFOS.
 - In response to 2006 detection of PFOA in PWS near NJ industrial site
 - 2009-10 study: 31 water systems 10 PFAAs.
 - Reporting Levels 4-5 ng/L (ppt)
- Multiple PFAS (up to 8) found in many water systems.
 - **PFOA** most frequent, ~60% of systems.
 - **PFOS** 30% of systems.
 - PFNA Paulsboro, Gloucester County (Southwestern NJ)
 - Highest level reported in drinking water worldwide.
 - Industrial source was identified.

2009-10 Study



New Jersey vs. National PFAS Drinking Water Occurrence: 2013-15 EPA Unregulated Contaminant Monitoring Rule 3 (UCMR3)

Compound	Reporting	New J Public Wate	ersey er Systems	U.S. Public Water Systems Other than NJ	
	Level (ng/L)	# Detects*	% Detects	# Detects	% Detects
PFOA (C8)	20	19/175	10.9%	98/4745	2.1%
PFNA (C9)	20	4/175	2.3%	10/4745	0.2%
PFOS (C8-S)	40	6/175	3.4%	89/4745	1.9%
PFHxS (C6-S)	30	2/175	1.1%	53/4745	1.1%
PFBS (C4-S)	90	0/175	0%	8/4745	0.2%
PFHpA (C7)	10	6/175	3.4%	80/4745	1.7%

- All large (>10,000 users) and a few small U.S. public water systems.
- Much higher reporting levels than NJDEP studies, but allows for comparison of NJ and national occurrence on same basis.
- **PFOA and PFNA** much more frequent in NJ than nationally.
 - *PFNA Southwestern NJ (Gloucester and Camden Counties).*
 - PFOA Various locations statewide.

Some Likely Sources of PFAS in NJ Public Water Systems

• **PFOA and PFOS in Northeast NJ**

- Sources unknown for most sites.
- Efforts to identify sources are ongoing.

• **PFOA & PFNA in Southwest NJ.**

- Two large industrial sites (Chemours & Solvay).
- Current NJDEP multi-media study with USEPA ORD using research analytical methods.

• **PFOA in surface water source**

- Small industrial facility upstream of river intake (Procopio et al., 2017).

- Multiple PFAAs (carboxylates & sulfonates)
 - Military use of aqueous film forming foam.



(Raw and finished water sampling locations shown; multiple data points shown for some public water systems. Does not include 2019 PFAS MCL monitoring data that has been reported to NJDEP)

Development of PFAS Maximum Contaminant Levels (MCLs) Continues NJDEP and NJ DWQI Work on Emerging Drinking Water Contaminants since 1980s

- 1984 New Jersey Safe Drinking Water Act Amendments established Drinking Water Quality Institute (DWQI) to recommend Maximum Contaminant Levels (MCLs) to NJDEP.
 - Appointed members from environmental health community, academia, and water purveyors.
 - Ex officio members from NJDEP and NJ Dept. of Health.
- DWQI and NJDEP have evaluated many types of drinking water contaminants since 1984.
- 2014 NJDEP Commissioner asked DWQI to recommend MCLs for PFNA, PFOA and PFOS

Public Participation in NJ DWQI & DEP MCL Development Process



Current Status of NJDEP PFAS Regulations

PFNA (rule adopted in 2018):

- MCL & Ground Water Quality Standard 13 ng/L.
 - First MCL in the nation for any PFAS.
 - Phased-in monitoring by all community and nontransient noncommunity systems in 2019 and 2020.
- Added PFNA to NJ Hazardous Substances List.

PFOA & PFOS (ruled adopted in 2020):

- MCLs & Ground Water Quality Standards: PFOA 14 ng/L; PFOS 13 ng/L.
 - Monitoring by all community and nontransient noncommunity systems starting 1st quarter 2021.
- Added PFOA and PFOS to NJ Hazardous Substances List.
- Added PFOA, PFOS and PFNA to NJ Private Well Testing Act.

NJ Public Water System (PWS) Quarterly Monitoring Data as of 8/10/21

<u># of Systems</u>	PFNA (13 ng/L)	PFOA (14 ng/L)	PFOS (13 ng/L)	
Submitting Results	1262	1254	1254	
Detection(s) > MCL	21 (1.6%)	141 (11.2%)	109 (8.7%)	
	184 (14.5%)			
Detection(s) > 1 or more MCL(s)	89 community water systems (CWS),			
	1 transient non-community systems (NTNC),			
Detection(s) >	,	20 (20 (1.6%)	
USEPA PFOA/PFOS Health Advisory (70 ng/L total for both)	n/a	9 CWS, 11 NTNC		
In violation of MCL	15 (1.1%)	13 (1%)*	18 (1.4%)*	
In violation of 1 or more MCL	41 (3.2%) 14 CWS, 27 NTNC			

• Monitoring for PFNA was required starting in January 2019, and for PFOA and PFOS starting in January 2021.

Some systems began treating for PFAS before required monitoring began.

*Based on running annual average of 2 quarters (or, in a few cases, 3 quarters) starting in January 2021.

PFOA, PFOS, & PFNA: Health Effects Summary

- In <u>laboratory animal studies</u>, multiple types of toxicity including some at very low doses:
 - Liver
 - *Immune system*
 - Developmental
- Metabolic Neurobehavioral

 \checkmark vaccine response

• Thyroid

- *Reproductive*
- Tumors (PFOA & PFOS; PFNA not yet studied)
- In human studies, evidence for health effects from PFOA, PFOS, and PFNA in the general population and/or communities with contaminated drinking water including:
 - **↑** cholesterol
 - \uparrow uric acid
- ↑ infectious disease Testicular and kidney cancer (PFOA)
- \uparrow liver enzymes
- \checkmark birth weight

....and others



Similarities in Toxicity Among PFAS in Laboratory Animal Studies

	# of Carbons	Liver	Develop- mental	Repro- ductive	Immune	Hema- tologic	Thyroid	Neuro- behavioral	Tumors
			Pe	erfluoroal	kyl Carbox	ylates			
PFBA	4								
PFPeA	5								
PFHxA	6								🗆 (Negative)
PFHpA	7								
PFOA	8								
PFNA	9								
PFDA	10								
PFUnA	11								
PFDoA	12								
			ŀ	Perfluoroo	alkyl Sulfor	ates	-		
PFBS	4								
PFHxS	6								
PFOS	8								
Per- & Polyfluoroalkyl Ether Replacements									
ADONA	6								
GenX	6								



Effect reported in one or more laboratory animal study

Effect was evaluated but not found, or effect has not been evaluated

Low Drinking Water Levels of PFOA, PFOS & PFNA Can Dominate Other Exposure Sources





Greater Increases in Blood Serum PFAA Levels in Infants

- Higher exposures to infants from breast milk or prepared formula:
 - PFAAs level in breast milk
 in maternal drinking water.
 - Infants ingest much more fluid per body weight
- Sensitive subpopulation for developmental & other short-term effects.





Human Health Basis of New Jersey MCLs for PFOA, PFOS and PFNA

- Developed following USEPA risk assessment guidance.
- Protective for lifetime (chronic) exposure.
- Primary basis is animal toxicology data.
- Multiple human health effects at low exposures support a protective approach.
- Animal-to-human comparison accounts for much higher blood PFAS levels in humans than animals from the same dose of PFAS.
- Primary basis is non-cancer effects:
 - Most sensitive effects that are well established, adverse/precursor to adverse, relevant to humans.
 - **PFOA:** Liver toxicity (primary basis).
 - Delayed mammary gland development at very low doses (accounted for by uncertainty factor).
 - **PFOS:** Decreased immune system response (analogous to decreased vaccine response in humans).
 - **PFNA:** Liver toxicity.
- Cancer risk was also evaluated:
 - PFOA and PFOS: "Suggestive evidence of carcinogenicity."
 - MCL based on non-cancer effects also protective for cancer effects at 1-in-1 million lifetime cancer risk level used by New Jersey.
 - **PFNA:** Cancer effects have not been studied.

Exposure Assumptions for NJDEP Health-based MCLs for PFOA & PFOS

Health-based MCL =

<u>Reference Dose (mg/kg/day) x Body Wt. (kg) x Relative Source Contribution (%)</u> Drinking Water Consumption (L/day)

Water ·

2 ng/kg/day

Other Sources -

8 ng/kg/day

Drinking Water Ingestion Rate (L/kg/day)

- NJDEP used **default adult assumptions** (70 kg body wt.; 2 L/day).
- Minnesota Dept. of Health (Goeden et al., 2019) model that accounts higher exposure in breastfed infants (recently used by MN and other states) was not available.

Relative Source Contribution (RSC):

- Accounts for non-drinking water exposures (e.g. food, consumer products).
 Higher RSC → higher drinking water level:
 - NJDEP used **default RSC of 20%** most stringent option.
 - Assumes 20% of Reference Dose from drinking water; 80% from other sources.
 - While not explicit intent, 20% default also partially accounts for higher exposures in breastfed and formula-fed infants who don't have additional dietary exposures

Factors Considered in NJ DWQI PFAS MCL Recommendations

- Health-based MCL
- Practical Quantitation Level (PQL)
 - Level reliably measured by drinking water laboratories.
- Availability of treatment removal technology
- * Health-based MCL is the goal *
 - PFAS MCLs not limited by analytical or treatment factors.
- Therefore, PFAS MCLs were set at Health-based MCLs.

(Units: ng/L)	Health-based MCL	Analytical PQL	Treatment Removal	Recommended MCL
PFOA	14	6	Not limiting	14
PFOS	13	4.2	Not limiting	13
PFNA	13	5	Not limiting	13

NJ, USEPA, CDC Agency for Toxic Substances & Disease Registry (ATSDR), & European Food Safety Authority (EFSA) PFOA and PFOS Toxicity Factors

		<u>PFOA</u>		<u>PFOS</u>	
Agency	Species	Basis	Toxicity Factor (ng/kg/day)	Basis	Toxicity Factor (ng/kg/day)
USEPA Reference Dose		Developmental: Delayed bone development & earlier male puberty	20	Developmental: ↓ offspring body wt.	20
NJ Reference Dose	Animal	 ↑ Liver weight: • With uncertainty factor of 10 for delayed mammary gland development. 	2	Immune suppression	1.8
ATSDR Minimal Risk Level		Developmental: Behavioral & skeletal changes	3	 Offspring body wt. With uncertainty factor of 10 for immune toxicity 	2
EFSA Tolerable Daily Intake	Human	Maternal exposure resulting in decreased vaccine response in 1 year old breastfed children			0.63 (Total of PFOA, PFOS, PFNA, PFHxS)



"NJ Drinking Water Quality Institute Health Effects Subcommittee concludes that these [blood serum PFAS] increases [at 70 ng/L] are **not desirable and may not be protective of public health.**"

State and USEPA PFOA & PFOS Drinking Water Guidelines Over Time (note logarithmic scale)



Current Issue: Replacements for Phased Out Long-Chain PFAAs

- Use of long-chain PFAAs (e.g. PFOA, PFNA, PFOS, PFHxS) and their precursors phased out in U.S.
- 100s of new PFAS/replacements approved by USEPA.

USEPA 2018

- Most are short-chain PFAAs (e.g. PFBS) or short-chain PFAS with other structures (e.g. GenX).
- Intended advantage is more rapid excretion (shorter half-lives) –



- However, some have similar toxicity to long-chain PFAS.
 - e.g. GenX similar toxicity in rats and mice as PFOA, and same tumor types in rats as PFOA
 - And, like long-chain PFAS, do not break down.

- Detected in environmental media in NJ and elsewhere.
- Current topic of major scientific, regulatory, and public interest.





Chloroperfluoropolyether Carboxylates



- Replacement for PFNA and PFOA, but, unlike other replacements, <u>not</u> short-chain.
 - 7 to >14 carbons, plus ether oxygens.
 - Equally or more bioaccumulative and toxic than PFOA and PFNA.
- Used and discharged to air and water by industrial facility in West Deptford since late 1990s.
- Detected in private wells, soil and other environmental media with non-target analysis in joint NJDEP/EPA Office of Research & Development study.
 - Private wells in study already had treatment to remove PFNA.
 CIPFPECAs were also removed not detected in finished water.



Thank you!

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NJDEP PFAS Publications in Peer-reviewed Scientific Journals

- McCord, J.P., Strynar, M.J., Washington, J.W., Bergman, E.L., Goodrow, S.M. (2020). Emerging Chlorinated Polyfluorinated Polyether Compounds Impacting the Waters of Southwestern New Jersey Identified by Use of Nontargeted Analysis. Environ. Sci. Technol. Lett. Online Sept. 22, 2020.
- Post, G.B. (2020). Recent U.S. state and federal drinking water guidelines for per- and polyfluoroalkyl substances (PFAS). Environmental Toxicology and Chemistry. Online August 26, 2020. Open access at https://setac.onlinelibrary.wiley.com/doi/epdf/10.1002/etc.4863
- Washington, J. W., Rosal, C. G., McCord, J. P., Strynar, M. J., Lindstrom, A. B., Bergman, E. L., Goodrow, S. M., Tadesse, H. K., Pilant, A. N., Washington, B. J., Davis, M. J., Stuart, B. G., Jenkins, T. M. (2020). Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils. Science 368: 1103–1107.
- Goodrow, S. M., Ruppel, B., Lippincott, R. L., Post, G. B., Procopio, N. A. (2020). Investigation of levels of perfluoroalkyl substances in surface water, sediment and fish tissue in New Jersey, USA. The Science of the total environment, 729, 138839
- Pachkowski, B., Post, G.B., Stern, A.H. (2019). The derivation of a Reference Dose (RfD) for perfluorooctane sulfonate (PFOS) based on immune suppression. Env. Research 171:452-469
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- Post, G.B., Louis, J.B., Lippincott, R.L., and Procopio, N.A. (2013). Occurrence of perfluorinated chemicals in raw water from New Jersey public drinking water systems. Env. Sci. Technol. 47 (23):13266-75.
- Post, G.B., Cohn, P.D., and Cooper, K.R. (2012). Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature. Env. Res. 116: 93-117.
- Post, G.B., Louis, J.B., Cooper, K.R., Boros-Russo, B.J., and Lippincott, R.L. (2009). Occurrence and potential significance of perfluorooctanoic acid (PFOA) detected in New Jersey public drinking water systems. Environ. Sci, Technol. 43: 4547–4554.

NJ Drinking Water Quality Institute Maximum Contaminant Levels PFAS Recommendation Documents

• <u>Perfluorooctane Sulfonate</u> (PFOS), June 2018

<u>Appendix A</u> – Health-Based Maximum Contaminant Level Support Document for PFOS

<u>Appendix B</u> – Report on the Development of a Practical Quantitation Level for PFOS in Drinking Water

<u>Appendix C</u> – Second Addendum to Appendix C: Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

<u>Appendix D</u> – Responses to Comments on DWQI Health Effects Subcommittee Report: "Public Review Draft - Health-Based Maximum Contaminant Level Support Document: PFOS"

• Perfluorooctanoic Acid (PFOA), March 2017

<u>Appendix A</u> – Health-Based Maximum Contaminant Level Support Document" PFOA

Appendix B – Report on the Development of a Practical Quantitation Level for PFOA in Drinking Water

<u>Appendix C</u> – Addendum to Appendix C: Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

<u>Appendix D</u> – Responses to Comments on DWQI Health Effects Subcommittee Report: "Public Review Draft-Health-Based Maximum Contaminant Level Support Document: PFOA"

• Perfluorononanoic Acid (PFNA), July 2015

Appendix A – Health-Based Maximum Contaminant Level Support Document: PFNA

Appendix B – Report on the development of a Practical Quantitation Level for PFNA

<u>Appendix C</u> – Recommendation on Perfluorinated Compound Treatment Options for Drinking Water

NJDEP PFAS MCL Rule Proposals and Adoptions

• PFOA and PFOS MCL Rule

– Proposal (4/1/2019)

https://www.nj.gov/dep/rules/proposals/20190401a.pdf

- Adoption (6/1/2020)

https://www.nj.gov/dep/rules/adoptions/adopt_20200601a.pdf

- PFNA MCL Rule
 - Proposal (8/7/2017)
 https://www.nj.gov/dep/rules/proposals/20170807b.pdf
 - Adoption (9/4/2018)

https://www.nj.gov/dep/rules/adoptions/adopt 20180904a.pdf