PFAS/PFOA
Other Contaminants

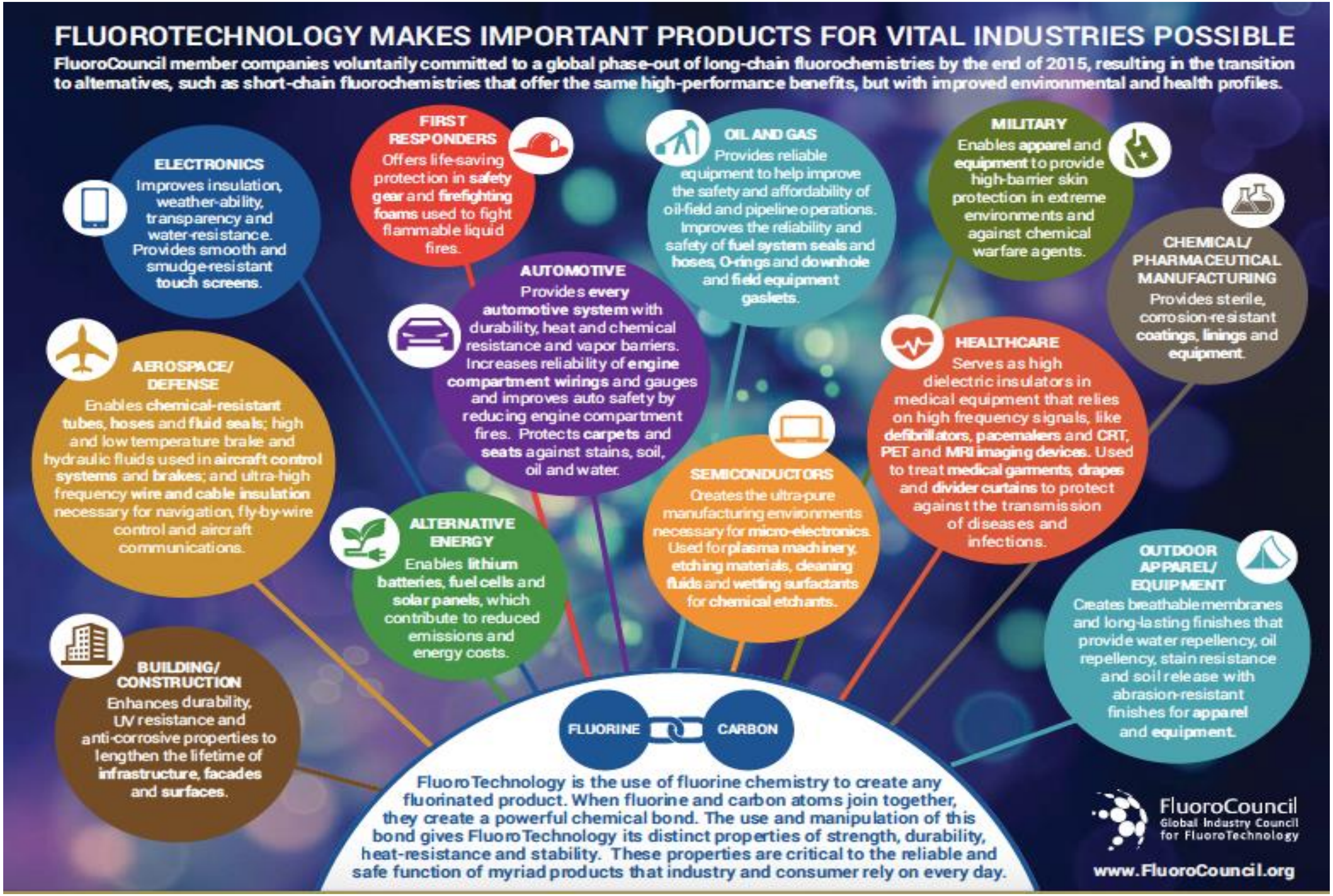
Jean Creech

Charlotte Water

Slides Courtesy of Ned Beecher and Northeast Biosolids Association

PFAS – The Basics

- Water soluble, hydrophobic, lipophobic, bind to proteins
- Persistent – C8 and lower versions do not degrade
- Not volatile, resists photolysis & hydrolysis
- Transport pathways: air deposition, leaching & groundwater, surface water
- Human exposure through drinking water (focus), food & food packaging, indoor dust & product exposure, use of consumer products
- Sorption & solubility differences
- 3000+ varieties, co-contaminants
- Destroyed at ~1000o C
- No natural counterparts


FLUOROTECHNOLOGY MAKES IMPORTANT PRODUCTS FOR VITAL INDUSTRIES POSSIBLE
FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemistries by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemistries that offer the same high-performance benefits, but with improved environmental and health profiles.
ELECTRONICS
Improves insulation, weather-ability, transparency and water-resistance. Provides smooth and smudge-resistant touch screens.
FIRST RESPONDERS
Offers life-saving protection in safety gear and firefighting foams used to fight flammable liquid fires.
OIL AND GAS
Provides reliable equipment to help improve the safety and affordability of oil-field and pipeline operations. Improves the reliability and safety of fuel system seals and hoses, O-rings and downhole and field equipment gaskets.
MILITARY
Enables apparel and equipment to provide high-barrier skin protection in extreme environments and against chemical warfare agents.
CHEMICAL/ PHARMACEUTICAL MANUFACTURING
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Provides every automotive system with durability, heat and chemical resistance and vapor barriers. Increases reliability of engine compartment wirings and gauges and improves auto safety by reducing engine compartment fires. Protects carpets and seats against stains, soil, oil and water.
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HEALTHCARE
Serves as high dielectric insulators in medical equipment that relies on high frequency signals, like defibrillators, pacemakers and CRT, PET and MRI imaging devices. Used to treat medical garments, drapes and divider curtains to protect against the transmission of diseases and infections.
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Creates the ultra-pure manufacturing environments necessary for micro-electronics. Used for plasma machinery, etching materials, cleaning fluids and wetting surfactants for chemical etchants.
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FluoroCouncil
Global Industry Council for FluoroTechnology
www.FluoroCouncil.org

EPA reaches new C8 deal with DuPont

on January 16, 2017 at 4:54 pm

The Washington Works DuPont plant in Parkersburg, West Virginia, on Wednesday, August 5, 2015. Photo: Maddie McGarvey for The Intercept/Investigative Fund

PARKERSBURG, WV — "Less than two weeks before the Obama administration leaves office, the U.S. Environmental Protection Agency on Monday said it had reached a new agreement with DuPont Co. regarding pollution of drinking water in the Mid-Ohio Valley with the toxic chemical C8 from the company's manufacturing plant near Parkersburg.

EPA said in a news release that it had amended its 2009 agreement with DuPont to reflect a lower level of C8 exposure recommended in an EPA health advisory issued last year. While more protective than the previous agreement with DuPont, the new number would allow larger

LAWSUITS CHARGE THAT 3M KN ABOUT THE DANGERS OF ITS CHI

Sharon Lerner

April 11 2016, 9:42 a.m.

FOR DECADES, 3M was the primary producer of C8, or PFOA, and was the sole producer of a related chemical known as PFOS. But while DuPont was caught up in a massive class-action suit over C8, 3M has largely avoided public scrutiny and serious legal or financial consequences for its role in developing and selling these industrial pollutants.

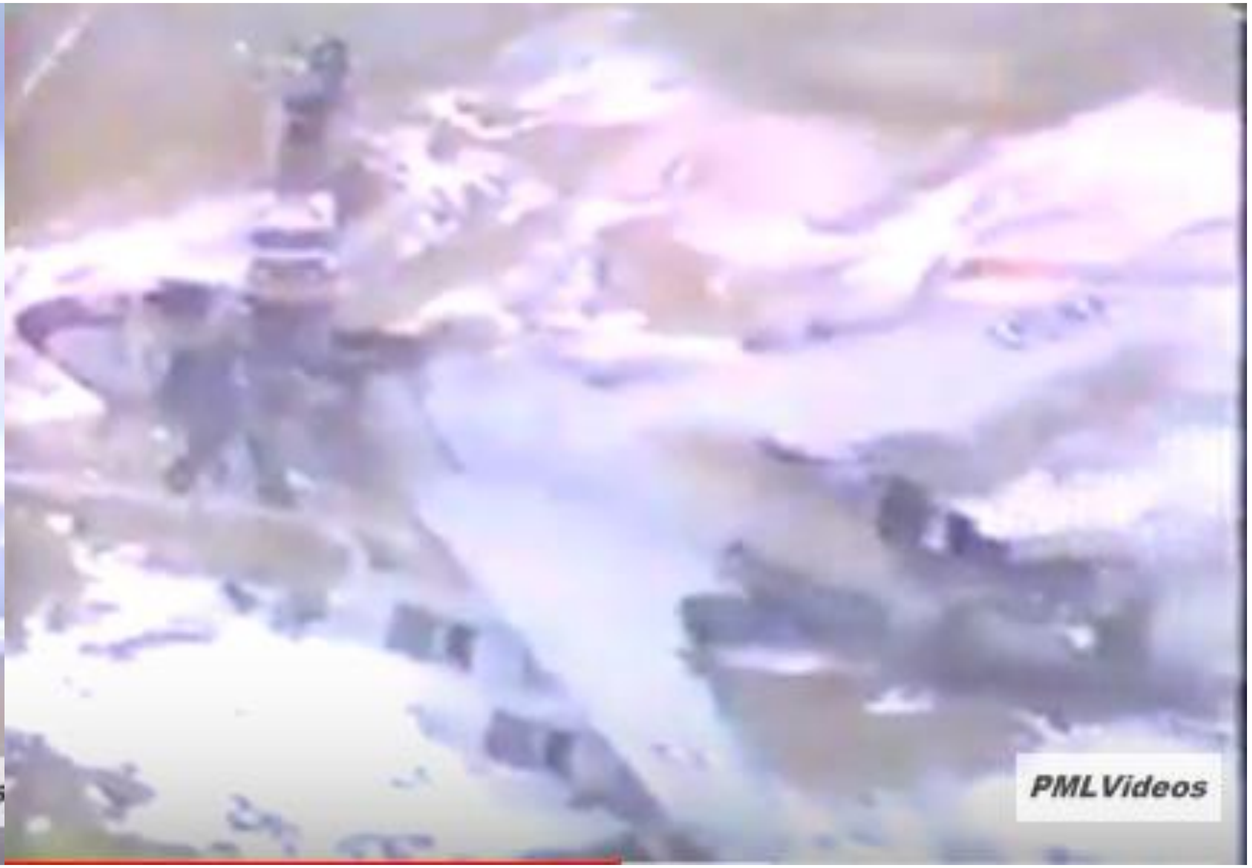
In February, however, a state court in Minnesota, where the company is headquartered, allowed a lawsuit against 3M to move forward. And late last year, lawyers filed a class-action suit in Decatur, Alabama, home to one of 3M's biggest plants. Both lawsuits charge that 3M knew about the health hazards posed by the perfluorinated chemicals it was manufacturing and using to make carpet coating, Scotchgard, firefighting foam, and other products – and that the company knew the chemicals were spreading beyond its sites. With PFCs cropping up in drinking water around the country and all over the world, the two lawsuits raise the possibility that 3M may finally be held accountable in a court of law.

State Attorney General Lori Swanson first filed the lawsuit against 3M on behalf of the people of Minnesota in 2010, claiming that the company polluted more than 100 square miles of groundwater near its plant in Cottage Grove, Minnesota, as well as four aquifers serving as drinking water for some 125,000 people in the Twin Cities. The suit charges that the company piped PFC-polluted wastewater into a stream that flows into the Mississippi River and disposed of it on land near the river, which allowed it to leach into the river.

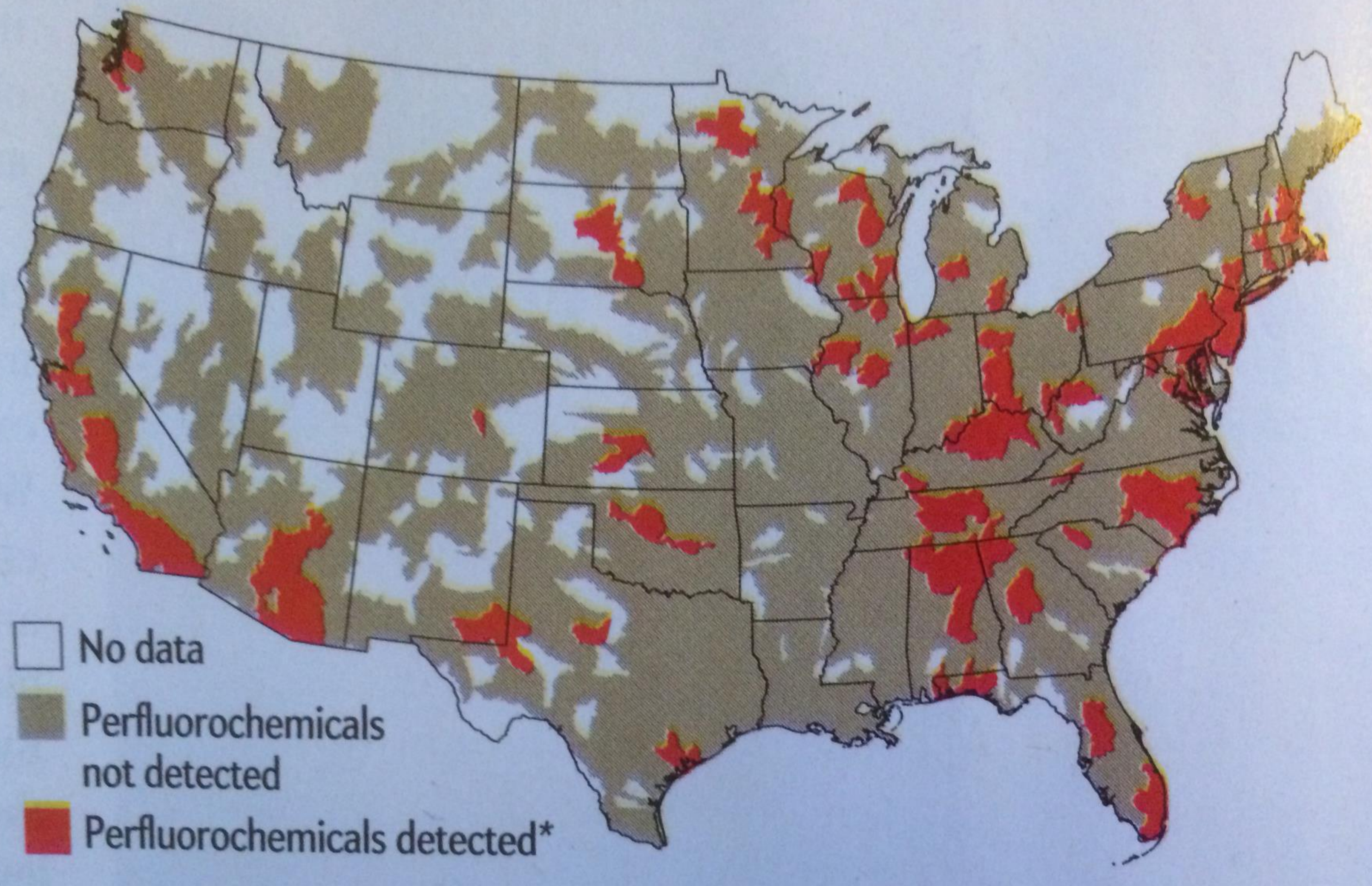
Based on the company's own research, the complaint argues, 3M "knew or should have known" that PFCs harm human health and the environme Flip Pl that the chemicals would leach from their disposal sit

Major source of PFAS in the environment:
AFFF, Pease AFB, NH

All the white is AFFF
(PFAS-containing foam)



Known U. S. PFAS hot spots, 2016. More found since.



*Zip codes where the chemicals were detected in one or more water samples that were at or above the minimum reporting levels required by the EPA (2013–2015). Not all drinking-water sources within a zip code necessarily have high levels.

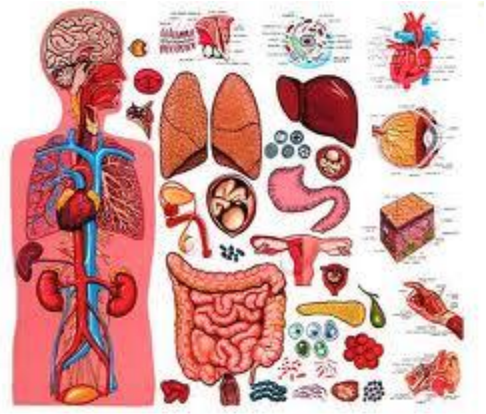
PFAS Health Effects – Summary 1

Animal toxicity

- Causes liver, immune system, developmental, endocrine, metabolic, and neurobehavioral toxicity.
- PFOA and PFOS caused tumors in chronic rat studies.

Human health effects associated with PFC(s) in the general population and/or communities with contaminated drinking water include:

- ↑ cholesterol
- ↑ uric acid
- ↑ liver enzymes
- ↓ birth weight
- ↓ vaccine response
- Thyroid disease
- Osteoarthritis
- Diabetes
- Testicular and kidney cancer
- Pregnancy-induced hypertension
- Ulcerative colitis
- Effects in young adulthood from prenatal exposures
  – *Obesity in young women.*
  – ↓ *sperm count in young men.*



Slide by A. Lindstrom, U. S. EPA, March 2018

PFAS Health Effects – Summary (2)

- Toxicity of PFOA & PFOS and other PFAS have uncertainties
  - Epidemiological studies and laboratory animal studies have not shown consistent and conclusive findings
  - Cancer incidence studies in NY, NH, and MN not indicative of PFAS effects
  - If PFAS is causing health effects, the effects appear to be subtle
  - Current risk-based standards/guidelines for PFOA and PFOS are protective (e.g. EPA's PHA, Health Canada's numbers)
- Reasons for concern
  - PFAS in drinking water elevates PFAS in blood
  - Little data for PFAS other than PFOA and PFOS; unknowns à caution

Slide courtesy Steve Zemba, Sanborn Head

Sources of PFAS Exposure for Humans

from EPA

- Best documented source is contaminated drinking water near industrial production facilities or waste disposal e.g., Cottage Grove, Minnesota; Parkersburg, West Virginia; Dalton, Georgia; Decatur, Alabama; Arnsberg, Germany; Osaka, Japan *Lindstrom et al. 2011, Environ. Sci. & Technol. (45) 8015 – 8021*
- Food is also implicated in many studies, especially fish from contaminated waters, items contaminated by food packaging, and breast milk *Fromme et al. 2009, Inter. J. Hyg. & Envr. Heath (212) 239-270; Mogensen et al. 2015 , Environ. Sci. & Technol. (49) 10466 - 10473*
- House dust may also be an important route of exposure – especially for children who ingest relatively higher levels of dust via hand-to-mouth activity *Shoeib et al. 2011, Environ. Sci. & Technol. (45) 7999 - 8005*
- Workplace exposures significant for some sectors: manufacturing or services making or directly using PFAS, apparel sales, waste treatment *Nilsson et al. 2013 Environ. Sci.: Processes Impacts, 15, 814-822*

Slide by Mark Strynar, U. S. EPA
October 17, 2017

US Environmental Protection Agency
PFOA Stewardship Program

In January 2006, USEPA started this program to help minimize impact of PFOA in the environment

Eight major international companies have agreed to participate (including 3M, DuPont, Asahi Glass, Daikin)

Agreement to voluntarily reduce factory emissions and product content of PFOA and related compounds* on a global basis by 95% no later than 2010

Agreement to work toward total elimination of emissions and product content of these compounds by 2015

Based on emissions and content determinations made for 2006

* Includes PFOA, precursor chemicals that can break down to PFOA, higher homologues (C9 and larger)

Slide by A. Lindstrom, U. S. EPA, March 2018

US Environmental Protection Agency
Health Advisories

Health Advisory levels for PFOS and PFOA in drinking water

PFOS alone = 70 ng/L

PFOA alone = 70 ng/L

PFOS + PFOA = 70 ng/L

* Some experts calling for further reduction in these standards to be truly protective for long term exposures

PFOS = 1 ng/L PFOA = 1 ng/L

"Protective" long term (chronic) exposure level

- Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children
- Grandjean, P ; Budtz-Jorgensen, E ;Environmental Health (12:35) DOI: 10.1186/1476-069X-12-35, APR 19 2013

Slide by A. Lindstrom, U. S. EPA, March 2018

PFAS in wastewater - ppb

(presence further confirmed, 2017 NH DES data)

	PFBA C4	PFHPA C7	PFHXS C6-S	PFHXA C6	PFNA C9	PFOA C8	PFOS C8	PFPEA C5
Small City Influent	13	<4	<4	7	<4	6	6	5
Small City Effluent	7	<4	<4	46	<4	6	7	21
Mid-size City Influent	<9.6	7	7	10	<4.8	15	22	29
Mid-size City Effluent	<9.6	5	8	20	<4.8	15	14	9
Municipality with industrial impacts Influent	56	8	<4	49	<4	50	4	36
Municipality with industrial impacts Effluent	73	19	<4	195	<4	49	<4	101

A few biosolids around the U.S. are impacted at levels raising regulatory concern when an industry discharges large amounts of PFAS to a sewer.

Solution: Apply pretreatment and source control.

- Decatur, AL (2000s) Dupont related
- Lapeer, MI (2017)
- Maine farm (2019) – issue is not municipal biosolids

Large majority of biosolids average ~2 – 30 ng/g or ppb for each PFAS.

EPA Technical BRIEF

www.epa.gov/research

INNOVATIVE RESEARCH FOR A SUSTAINABLE FUTURE

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)

Methods and guidance for sampling and analyzing water and other environmental media

Background

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of manufactured compounds used in a variety of industries, such as aerospace, automotive, textiles, and electronics, and are used in some food packaging and firefighting materials. For example, they may be used to make products more resistant to stains, grease, and water. In the environment, some PFAS break down slowly, if at all, allowing bioaccumulation (concentration) to occur in humans and wildlife. Some have been found to be toxic to laboratory animals, producing reproductive, developmental, and systemic effects in laboratory tests.

The U.S. Environmental Protection Agency's (EPA) methods for analyzing PFAS in environmental media are in various stages of development. EPA is working to develop validated robust analytical methods for groundwater, surface water, wastewater, and solids, including soils, sediments, and biosolids.

Drinking Water

Analysis using EPA Method 537

To assess for potential human exposure to PFAS in drinking water, EPA-approved commercial drinking water laboratories successfully analyzed finished (treated) drinking water samples for six PFAS monitored under the third Unregulated Contaminant Monitoring Rule (UCMR3). For the UCMR3 analyses, laboratories used EPA Method 537, which also includes eight additional PFAS analytes not listed on the UCMR3.

Health Advisories

In May 2016, EPA issued drinking water health advisories for two types of PFAS: perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). EPA's health advisories are non-enforceable and non-regulatory, and provide technical information to state agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination.

Method Development & Validation

Currently, there are no standard EPA methods for analyzing PFAS in surface water, non-potable groundwater, wastewater, or solids. For non-drinking water samples, some U.S. laboratories are using modified methods based on EPA Method 537. These modified methods have no consistent sample collection guidelines and have not been validated or systematically assessed for data quality.

EPA formed a cross-Agency method development and validation workgroup to provide sampling guidance and validated methods for sample types other than drinking water, which will fill this sampling and analytical gap. The workgroup will develop SW-846 analytical methods for quantifying 24 PFAS analytes. The method development process will occur in a phased approach.

Phase I EPA labs tested an existing direct injection analytical protocol for preparing and analyzing 24 PFAS analytes in groundwater, surface water, and wastewater. Labs completed this phase in winter 2017, and results warranted moving to Phase II.
EPA has also drafted a solid-phase extraction/isotope dilution (SPE-ID) method. Pending an acceptable Phase I outcome, this method will be internally validated in fall 2018 for inclusion into Phase II.

Phase II In October 2018, seven external labs are validating the direct injection method. The target timeframe for publishing a validated SW-846 direct injection method (Draft Method 8327) for public review is winter 2018. Following internal testing in fall 2018, the SPE-ID protocol (Draft Method SW-846 8328) will be externally validated, with a target start time in winter 2018. Draft Method 8328 will include solid matrices in addition to non-drinking water aqueous matrices. Additionally, an analytical method for short-chained PFAS in drinking water is under development and planned for external validation and publication for public review by early 2019.

Developing Sampling & Storage Methods

EPA ran time-based studies on degradation or loss of target analytes during sample storage (45 days) and assessed the effects of different sample vessel materials (e.g., plastic, glass) on analyte recovery. Based on these studies, the SW-846 methods under development will utilize PFAS-free, high-density polyethylene containers; whole sample preparation; and sample holding times of 28 days. EPA will also develop guidelines for field sampling, which are critical for minimizing sample contamination and optimizing data quality for site characterization and remediation.

Due to the widespread use of PFAS, many materials normally used in field and laboratory operations contain PFAS. For example, polytetrafluoroethylene products (tubing, sample containers, and sampling tools) are often used in sampling; however, since these products can contain PFAS, they cannot be used in sampling for PFAS. In addition, many consumer goods, such as water-resistant jackets or fast food wrappers, brought to a sampling site may contain PFAS that can contaminate samples. Proper field sampling and laboratory hygiene protocols are critical to ensuring that testing results reflect actual PFAS levels in the analyzed media.

PFAS – we have to figure this out

1. Wastewater contains PFAS in 1s to 10s of ppts. Biosolids contain PFAS in 1s to 10s ppbs. Even food waste composts are in the 1s ppbs+ range.
2. Some states (e.g. NH) are creating low drinking water & groundwater & other standards for the two prominent PFAS – PFOA & PFOS – in the 10s of parts per trillion (e.g. VT's 20 ppt). Some are scrutinizing other PFAS too.
3. Because PFAS are persistent and can leach some, biosolids may convey traces of PFOA and PFOS (and precursors) to surface or groundwater at levels relevant to these low advisory levels or standards.
4. State regulatory overreactions – very low numerical standards for waters & soils – can lead to significant disruptions and eroded confidence in wastewater, septage, biosolids, residuals, & composts.

Summary: Wastewater & biosolids convey PFAS, but…

PFAS are ubiquitous. Even wastewater & biosolids with no industrial inputs have 1's to 10's parts per billion (ppb*). Wastewater & biosolids are not sources, but transfer routes for PFAS.

Presence does not necessarily mean risk. For wastewater & biosolids, there is no dermal, inhalation, or ingestion risk. The indirect pathway of leaching to waters (groundwater) is the only possible human health concern, and that will depend on the endpoint screening levels set for ground- and surface waters.

Data for biosolids sites show groundwater impacts directly under several worst-case-scenario legacy biosolids sites, but minimal to no exceedance of EPA's health advisory levels in drinking water. Biosolids & soils bind longer-chain PFAS.

PFOA & PFOS are at lower levels in modern wastewater & biosolids than in the past, due to phase-outs. Wastewater & biosolids returning to the environment today are conveying significantly less PFOA & PFOS (~1/10th).

Data are inadequate for robust modeling of leaching potential from biosolids applied to soils. Most states recognize this. There are no approved EPA analytical methods for PFAS in anything but drinking water. Efforts are underway for regional &/or national studies to address data gaps.

Environmental impacts: Wastewater & biosolids have contained PFAS for 50+ years – including PFOA & PFOS at higher levels than today. Bioassays of uses of effluent & biosolids have not found significant negative impacts, only benefits.

How much will society – your municipality & state – spend chasing trace PFAS in waste streams & the environment? And what is the public health benefit compared to use of those resources elsewhere? Prioritize the obvious, highly-impacted industrial & military sites. Careful thinking is needed as screening levels & standards are set.

Best practical option: Phase out any PFAS that are particularly toxic, persistent, &/or bioaccumulative. This is the proven, most-effective way to reduce potential risk.. But we will not get to zero PFAS in wastewater and biosolids and the environment anytime soon.

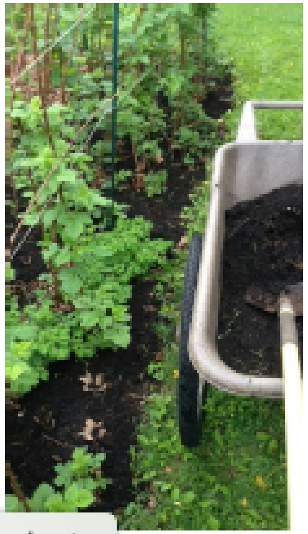
***1 ppb = 1 sec. in 31.7 years / 1 ppt = 1 sec. in 31,700 years**

Interim best management

Best Management Practices – PFAS and Biosolids and Residuals

The regulatory requirements and best management practices (BMPs) routinely followed by professionals managing biosolids, residuals, digestates, and composts also reduce any potential risk of PFAS leaching from land application programs. Leaching to groundwater and/or surface water is the *only* potential significant risk from PFAS in these materials. Here's what you can do, even as research and understanding continue to advance:

- *Continue to apply biosolids, residuals, and composts (including Class A / EQ) in accordance with the agronomic rate. This controls the amount of any traces of chemicals thus conveyed to the environment, including PFAS. Healthy soils break down and sequester most trace chemicals. Limited research shows that longer-chain PFAS, such as PFOA and PFOS, are more likely to be bound in the soil; shorter chain PFAS leach more easily.*
- *Near surface waters, maintain reasonable setback distances and create/maintain vegetated buffers. Setbacks protect against nutrient pollution of waters and also protect against any trace PFAS migration to surface water.*
- *Evaluate potential sources of PFAS in wastewaters, biosolids, residuals, digestates, and compost. Look upstream for industries that use any of these chemicals. Evaluate waste streams, such as landfill leachate, which may convey PFAS. Sample and test and consider reducing any significant industrial inputs of PFAS. Sampling and testing for PFAS is challenging. NEBRA has sampling and analysis guidance. Consult experts and understand the limitations of PFAS lab analysis.*
- *Consider testing your program's biosolids, residuals, digestate, and/or compost products for PFOA and PFOS and other PFAS. Be careful, because these chemicals are everywhere and the analytical levels (ppt) are challenging, especially when testing solids. Be a savvy lab customer and proceed thoughtfully.*
- *Honestly communicate with your residuals management employees and customers (farmers, landowners) about traces of chemicals – including PFAS – in various media, including biosolids, residuals, composts, digestates, animal manures, and soils. Honor their questions and address them as best you can. Offer to provide further information. See NEBRA info and contact NEBRA for assistance, if needed (https://www.nebiosolids.org/resources/#/microconstituents/).*
- *Communicate with regulatory agencies and monitor research and the development of legislation and regulation. Discourage jurisdictions from setting regulatory standards for drinking water, groundwater, surface waters, and soils without careful consideration of the implications for management of wastewater and the uses of biosolids, residuals, digestates, and composts. Very low standards may create severe impediments and significant costs to municipalities and ratepayers.*
- *Support targeted, practical field research on PFAS in residuals and soils.*
- *Support societal efforts to reduce the use of PFAS – at least any persistent, bioaccumulative (e.g. longer-chain) versions. Support source reduction and pollution prevention.*



Screenshot

Additional Information

PFAS in Your Environment:epa.gov/pfas

Clean-Up Information:clu-in.org/

EPA Method 537:nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100EQ6W.txt

SW-846 (Compendium):epa.gov/hw-sw846/sw-846-compendium

Drinking Water Health Advisoriesfor PFOA and PFOS: epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

Third Unregulated ContaminantMonitoring Rule (UCMR3):epa.gov/dwucmr/third-unregulated-contaminant-monitoring-rule

EPA’s Water Research: epa.gov/water-research

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THANK YOU!

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