SOIL TESTING TO IDENTIFY SOURCES OF EMERGING AND LEGACY PFAS

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Preliminary Results- Do Not Cite or Quote

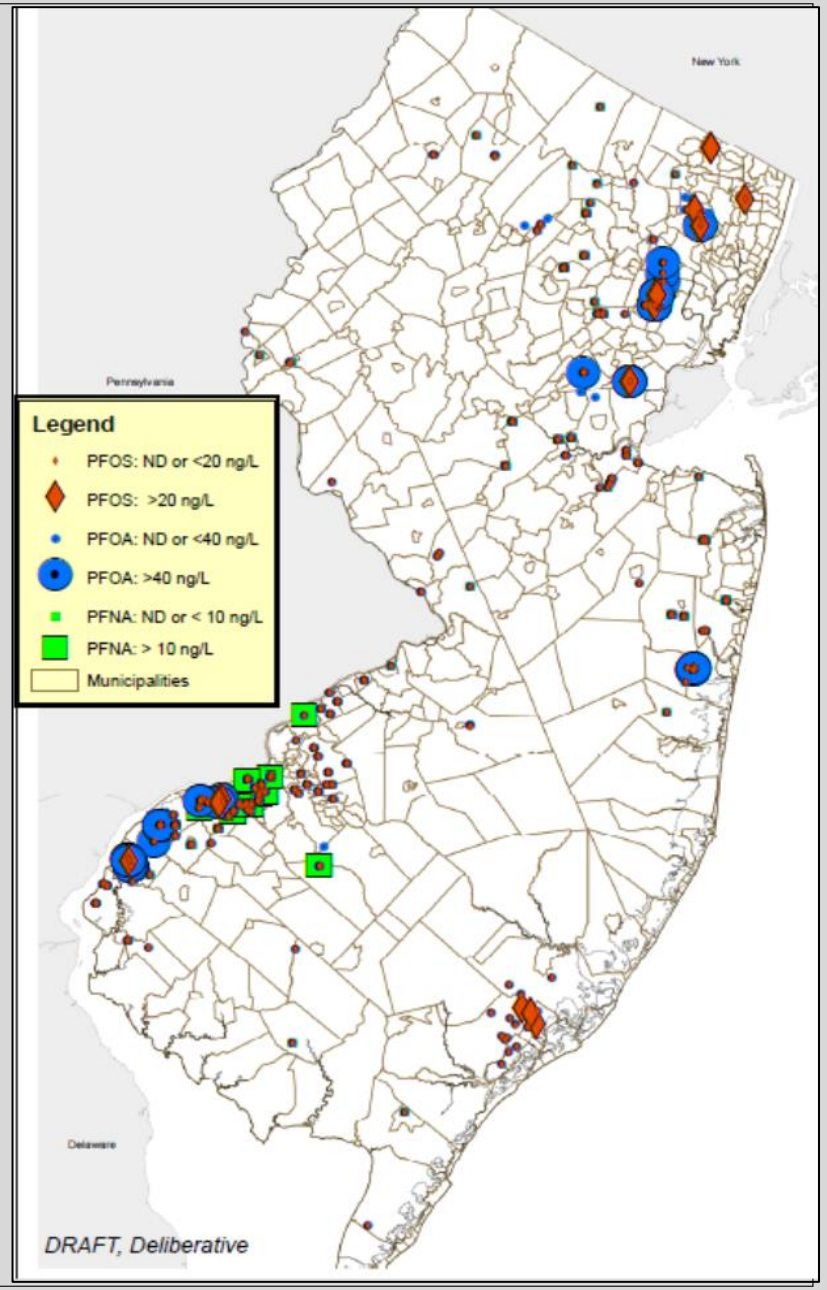
Background

- New Jersey has historical knowledge of private wells and municipal drinking water contaminated with perfluorooctanoic acid (PFOA, C8), perfluorononanoic acid (PFNA, C9), and other PFAS. Some sources have been identified, others remain uncertain.

- NJDEP has adopted MCLs for PFNA (13 ng/L), PFOA (14 ng/L) and PFOS (13 ng/L)

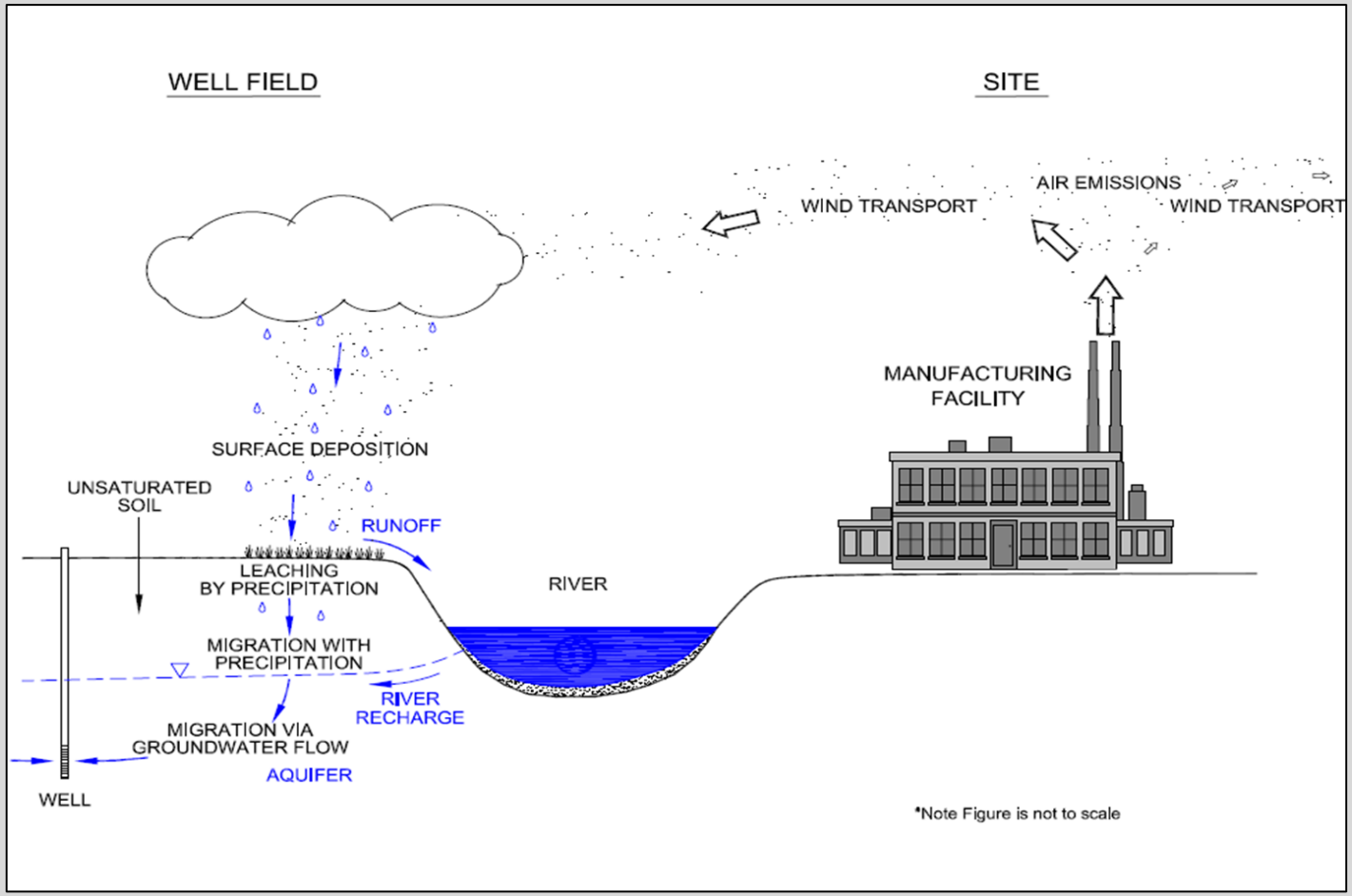
- The Solvay fluoropolymer site in West Deptford released large amounts of PFNA to air and surface water. Historically it has been a primary source of PFNA to the Delaware River and its tidal tributaries, and contributed to widespread contamination of drinking water sources. The impact of airborne releases continues to be investigated.

- Airborne PFAS is a well established source of drinking water contamination. For example, PFOA and HFPO-DA (GenX) from fluoropolymer site in Parkersburg, WV contaminated drinking water wells over wide area.



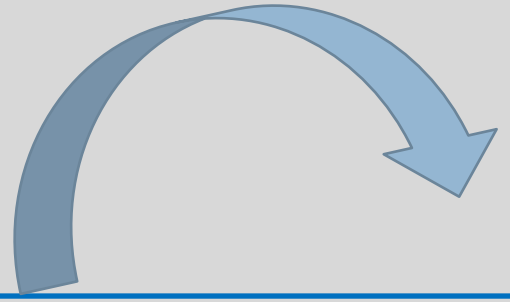
PFAS emissions and air dispersion

- Since there are no environmentally relevant mechanisms of PFAA destruction, migration through soils with percolation leads to contamination of groundwater.
- Davis et al., 2007: Air transport found to be the most likely, and the primary, transport pathway of PFOA from the Parkersburg WV facility to surrounding areas.
- Shin et al., 2011, found that groundwater used for drinking water was contaminated with PFOA up to 20 miles or more from the emission source.
- Galloway et al., 2020 concluded that air emissions of PFOA and HFPO-DA impact environmental media > 40 km from the source.



Davis et al. Chemosphere 67 (2007) 2011–2019

2015 Air Modeling Report from Solvay Specialty Polymers



Facility used **Surflon** to aid in the production of the fluoropolymer polyvinylidene fluoride (PVDF) from 1985 to 2010. Surflon© S-111 is a commercial mixture of three perfluoroalkyl acids **PFNA (C9,~74%), PFUnDA (C-11, ~20%), PFTrA (C13, ~5%**). (Prevedouros, 2006). The facility also reported using sodium perfluorooctanoate (NaPFO) in smaller quantities from 1995 to 2003.

The air modeling study (using AERMOD) performed by the facility **concluded that all PFNA emitted from facility was only distributed only to areas within the fence line** of the facility. The fence line is approximately 1000 feet from the building with the emission stacks.

Input parameters of concern:

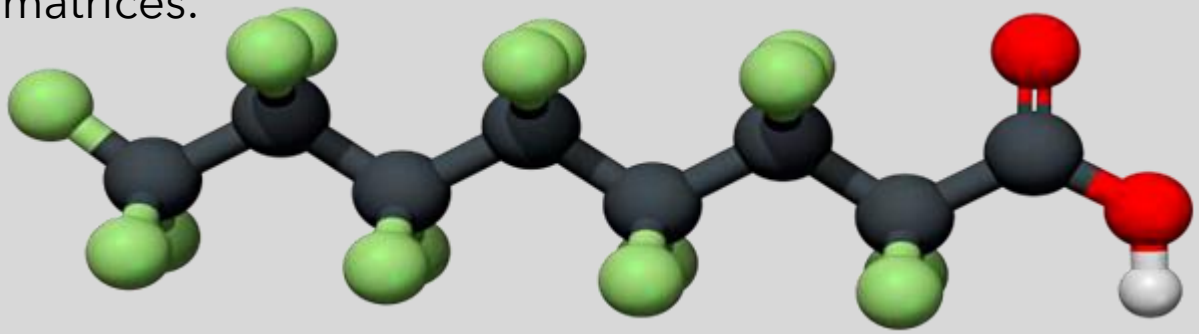
- **Particle size** distribution skewed strongly to larger particles, ignoring established mass fractions of emissions that included a higher percentage of smaller particles. The model also did not consider aerosols or vapors.
- Used **averages** of wind speeds, particle size distribution, stack velocities, and emission concentrations, so that no peak values were considered
- Scenarios evaluated in **sensitivity analysis** lacked relevance and focused on the evaluation of larger particles and removal of buildings (to evaluate downwash).

Phase-out of Long-Chain PFAS

- **USEPA PFOA Stewardship Program** with 8 major manufacturers specified voluntary elimination of "long-chain" perfluoroalkyl carboxylic acids (PFCAs), (including PFNA,) and their precursors by 2015 (PFCAs as long or longer than **PFOA** – 7 or more contiguous perfluorinated carbons) due to concerns about their presence and persistence in the environment and people and their potential health effects.

- The Solvay fluoropolymer plant in West Deptford used a technical mixture of long-chain PFCAs containing primarily **PFNA** (Surflon) as a processing aid until 2010. Phase out of **Surflon** and use of alternative aids that conformed with EPA Stewardship Program was implemented.

- There developed a need to investigate legacy and replacement PFAS used as fluoropolymer processing aids, and determine if emissions have occurred and impacted surface water, groundwater, drinking water, soil, plants, and other matrices.



PFOA (perfluorooctanoic acid) molecule, in its acid form.

Source: Manuel Almagro Rivas (Own work using: Avogadro, Discovery Studio, GIMP) [CC BY-SA 4.0] (https://creativecommons.org/licenses/by-sa/4.0)], via Wikimedia Commons.
https://commons.wikimedia.org/wiki/File:PFOA-3D.png

Research Basis and General Procedures

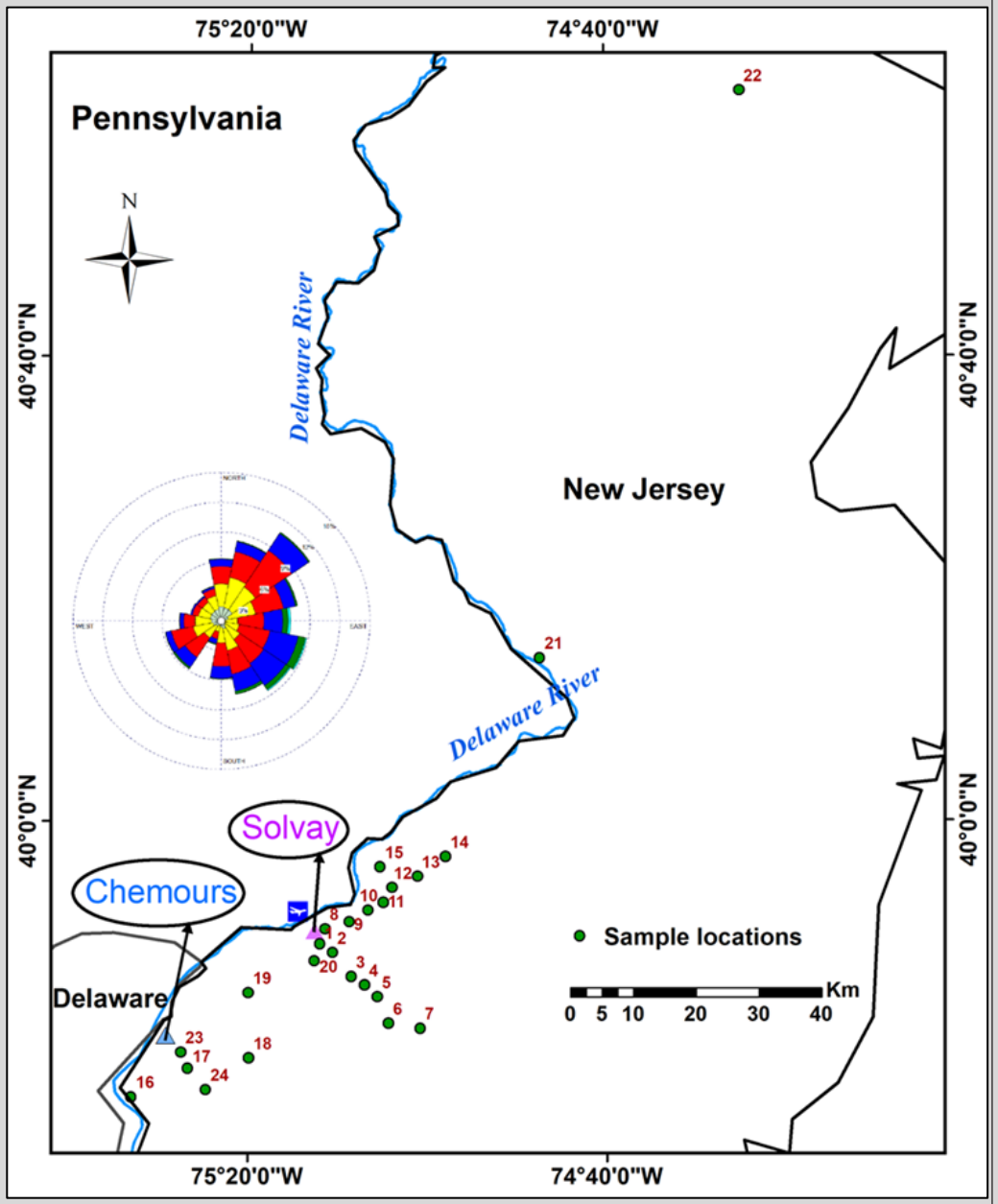
- The study area covered Gloucester and Salem counties, and included area surrounding both the Solvay facility and the DuPont/Chemours facility.
- It was learned that PFNA was released by airborne emissions from Solvay for two decades, but the extent of impacted area was unknown.
- A newer proprietary PFAS that was not included in the EPA Stewardship program has been used as substitute in the same polymer production process.
- There was a need to identify replacement compound(s) and evaluate the potential for contamination of water resources, soils, and air.

So…

- Nontargeted screening with high resolution mass spectrometry was recognized as the best approach for identifying replacement compounds and other unknown PFAS that may be in the waste streams.
- Identification of “new” PFAS and determination of their concentrations in important exposure-related media will help establish priorities for continued research in NJ and worldwide, and may identify exposure that are of potential public health concern.

Experimental Design

- Samples of multiple media were collected in area of two facilities involved with the PFOA Stewardship program in south-western NJ.
- Media
  - Soil
    - 24 Surficial Soil Samples
    - 4 Core Soil Samples
    - Sediments (20, collected at surface water sites)
  - Surface Water
    - Tidal and non-tidal (20 samples)
    - Inland freshwater impoundments (11 samples)
  - Groundwater (25 private wells)
  - Vegetation (24, collected at Soil Sampling locations)
- Locations
  - Soil samples collected along transects characterizing the predominant downwind direction
  - Originating at two known, identified facilities that use or manufacture PFAS

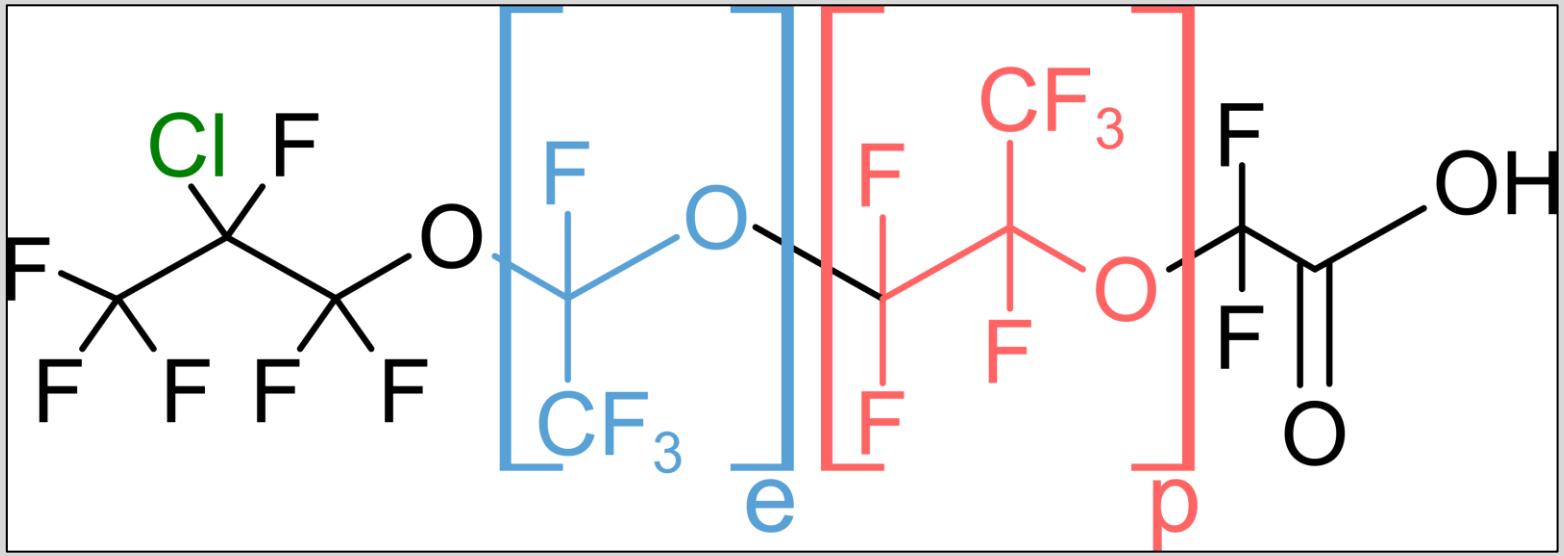


Analysis: EPA National Exposure Research Laboratory

- All samples were sent to EPA ORD located in Athens, Georgia and Research Triangle Park, North Carolina
- **Targeted** mass spec analyses for known legacy PFAS
- **Nontargeted**, high resolution mass spectrometry (HRMS) analyses has been used to determine formulas and likely structures from molecular-precursor and fragment data. (X.Lim, Nature 566. 26-29 (2019), and S. Newton et al., ES&T 51, 1544-1552 (2017).
- The research team at EPA NERL employed an "***ultra-performance liquid chromatograph (UPLC) coupled to a quadrupole time-of flight (QToF) mass spectrometer*** *operating in negative electrospray ionization (ESI), Ms^{e} no mass filtering mode. Output data were sorted by signal intensity, high intensity molecular feature were plotted on mass-defect plots*" (Washington et al., Science 368, 1103-1107 [2020], also see Newton et al., ES&T 51, 1544-1552 [2017])
- "Using low collision energy pre-cursor masses, a distinctive mono-chloro M+2 spectral feature, and carbon-isotopic ratios, **the research group was able to tentatively identify a molecular feature as a chloroperfluoropolyether carboxylate (ClPFPECA) that is described in the literature as "Solvay's product" (CAS No. 329238-24-6) (Wang et al., Environ. Int. 60, 242-248 [2013] and as reported in a product assessment to the European Food Safety Authority (EFSA, EFSA J. 8, 1519 [2010]"** (Washington et al., 2020).

NTA Determined Apparent Structure: Chloroperfluoropolyether carboxylate (ClPFPECA)

- Cl=Chloro
- Nine congeners were tentatively identified
- 0-2 perfluoro ethyl groups
- 1-4 perfluoro propyl groups
- Separated by ether linkages



Note: Multiple lines of evidence exist to support this determination, including the publication of this structure as "Solvay's Product" (Wang et al., 2013) and the detection of five of these congeners in surface water samples collected downstream of Solvay Specialty Polymers, Italy (Washington et al., 2020)

MS/MS Features of ClPFPECA Congeners

Carbon Chain Length	Anion Formula	Number of Ethyl, Propyl Groups	Molecular Mass (g/mol)	Precursor	Fragment	Elution Time (m) Soils (Plants)
7	$C_7ClF_{12}O_4$	1,0	410.9294	316.9447	200.9542	2.3 (2.3)
8	$C_8ClF_{14}O_4$	0,1	460.9262	366.9395	200.9542	2.6 (2.6)
9	$C_9ClF_{16}O_5$	2,0	526.9179	432.9312	200.9542	3.4 (3.4)
10	$C_{10}ClF_{18}O_5$	1,1	576.9147	482.9280	200.9542	3.9 (3.9)
11	$C_{11}ClF_{20}O_5$	0,2	626.9115	532.9249	200.9542	4.6 (4.23)
11	$C_{11}ClF_{20}O_6$	3,0	642.9064	548.9198	200.9542	4.9 (4.47)
12	$C_{12}ClF_{22}O_6$	2,1	692.9032	598.9166	200.9542	5.5 (5.25)
13	$C_{13}ClF_{24}O_6$	1,2	742.9000	648.9134	200.9542	6.1 (6.1)
14	$C_{14}ClF_{26}O_6$	0,3	792.8968	698.9102	532.9249	6.7 (6.4)

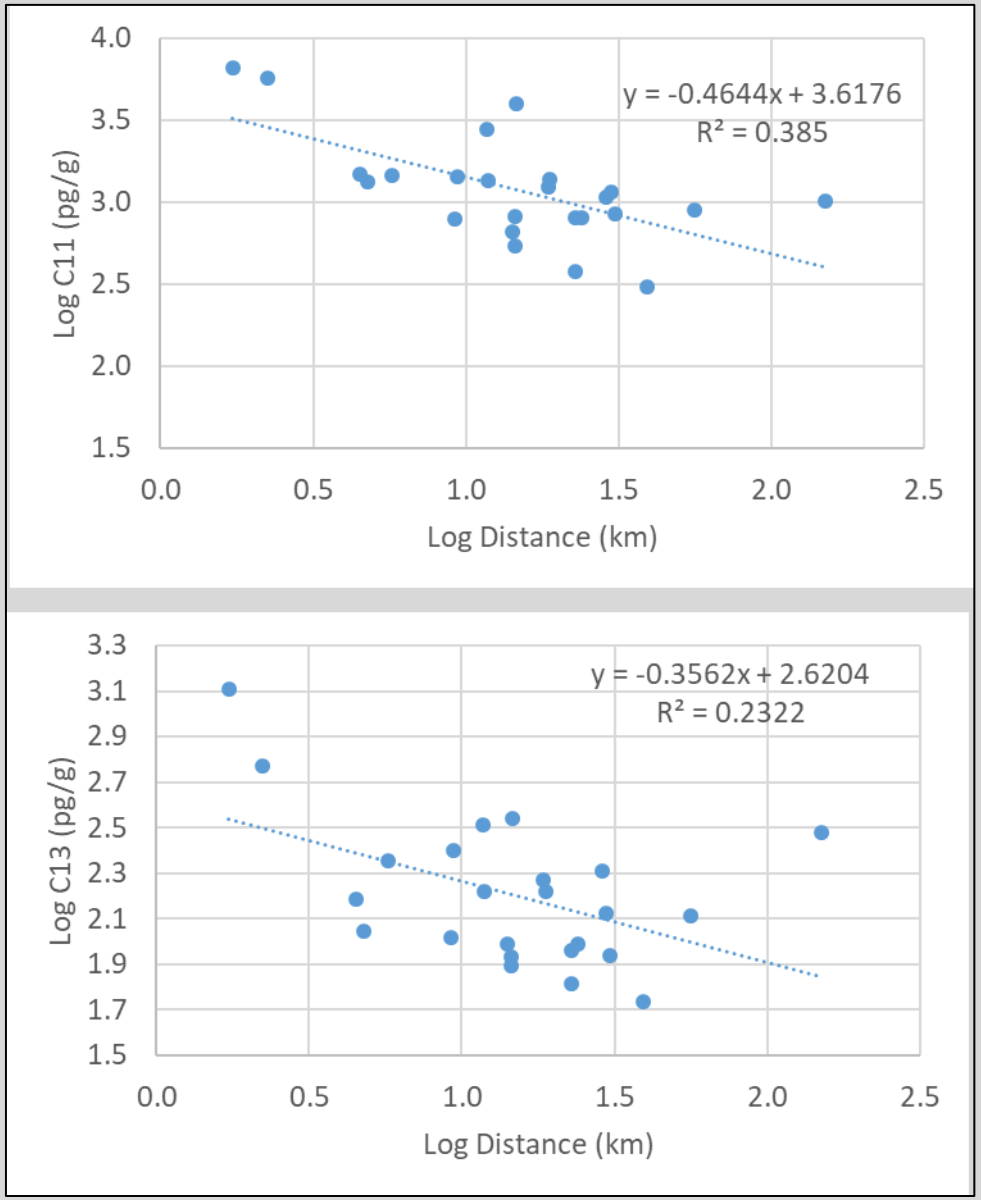
- A lab standard of the alternate Solvay product has not been made available to NJDEP or US EPA.
- Therefore, semi-quantitative concentrations were determine for each soil sample through peak area ratios with known mass labeled internal matrix standards.
- Of the 10 congeners identified, 6 were expected on the basis of the EFSA information
- The 0,1 and 1,1 were found to dominate concentrations found in the soil samples

Target Analysis: Distribution of Legacy PFAS

- Graphs to the right: PFUnA and PFTrA Soil concentration with distance (log transformed).
- Both C11 and C13 (components of the Solvay Surflon product) are highly statistically correlated with distance from Solvay.
- Results of the regressions indicate that C9 (PFNA) was ***not*** correlated with distance from Solvay.

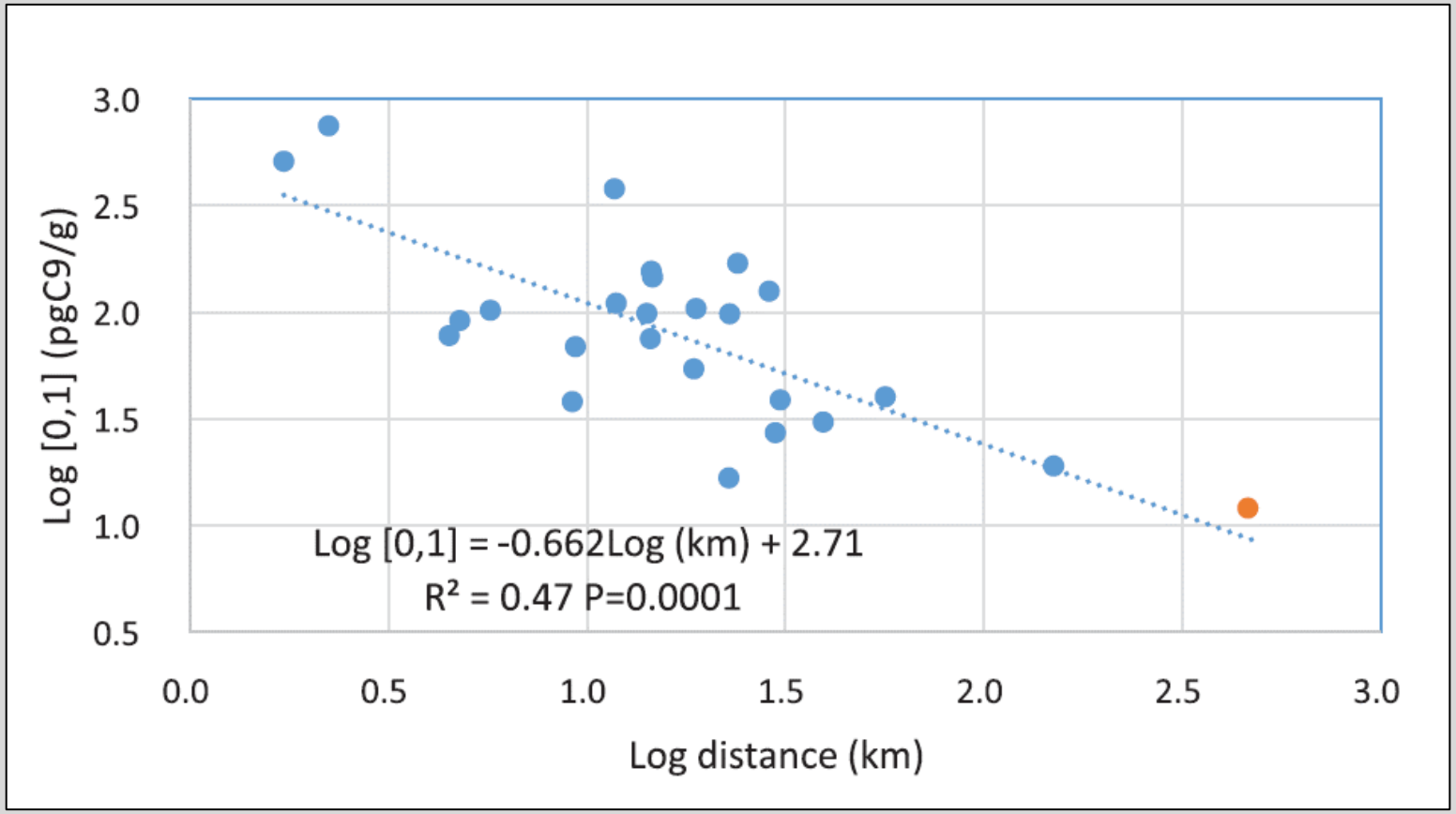
WHY?

C9 has a higher mobility in soils than either C11 or C13, both of which can partition more strongly to soils. Therefore, it is likely that the more soluble C9 percolated through the soil with the rain over the years. This conclusion is supported by the detection of PFNA in groundwater samples.



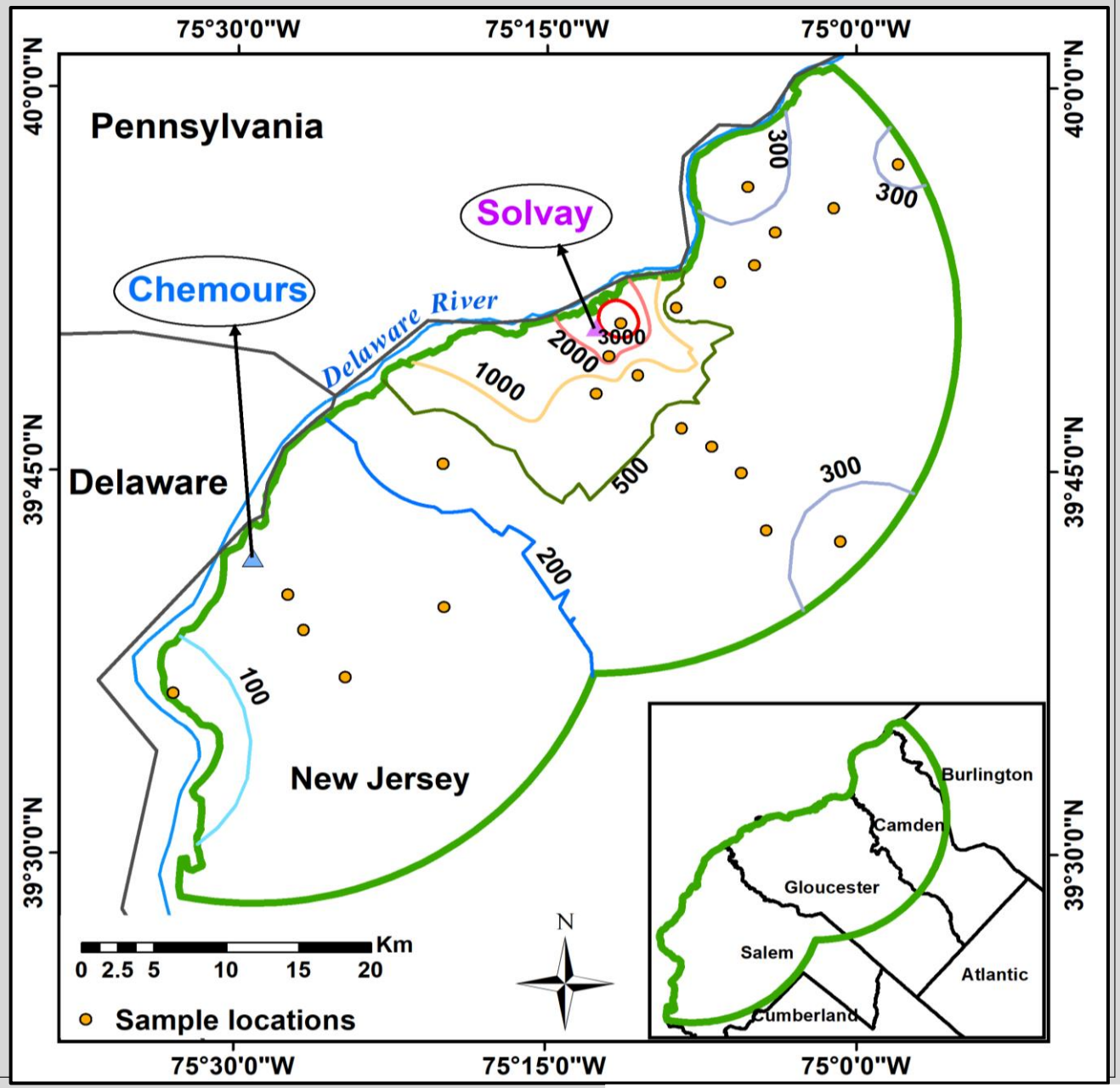
Non-target analysis: Distribution of ClPFPECA (0,1)

- Soil concentrations of 8 of the 9 congeners were regressed against distance from Solvay (the remaining congener was only rarely detected)
- All 8 congeners decreased with distance from Solvay
- Red dot is representative of downwind soil concentration of ClPFPECA (0,1) detected in Merrimack, N.H.
- Analysis of upwind sample (Conyers, GA) did not find detectable levels of these compounds.
  - The more distant samples have higher uncertainty as to correlation to Solvay and require additional study.



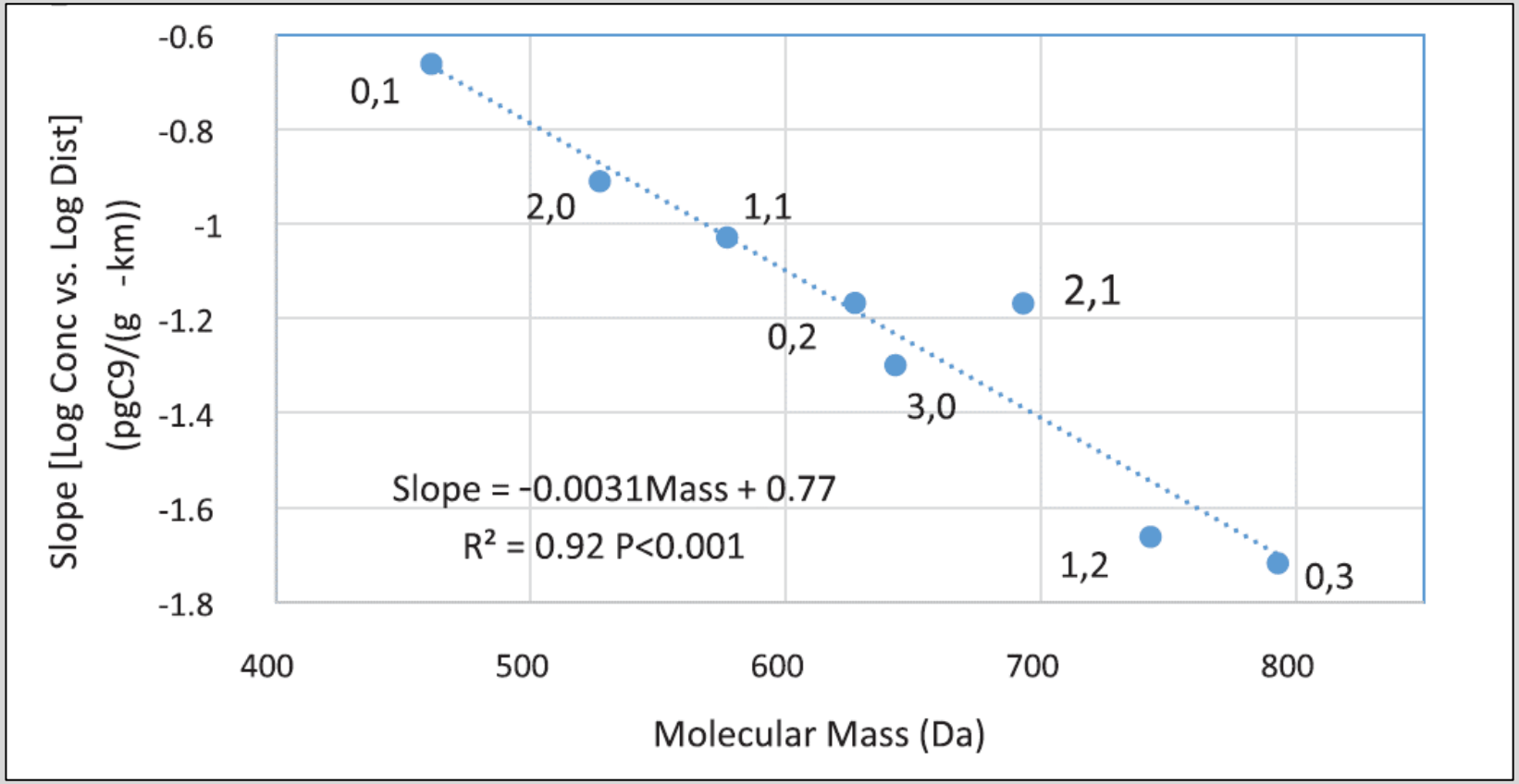
Concentration Contours

- Calculated contour lines depicting total **ClPFPECAs** in surface soils (estimated, ppt)
- Notes:
  - Algorithm using weighted data points according to inverse-square distance
  - Presence of some geographic sporadicity in the data
  - Presence of artifacts where data are sparsely space
- Depicts clear pattern of increasing total ClPFPECAs with proximity to Solvay



Transport Sorting by Mass

The slope of the diminishing concentration with distance from Solvay increases with molecular mass (P<0.001) suggesting that the smaller congeners are dispersed more widely than the larger congeners.



Summary, Next Steps, Conclusions

- Results of this study
  - Distinct chemical formulas and structures, as well as geographic distribution suggest airborne transport of both legacy and alternative PFAS from an identified industrial source.
  - Lighter congeners dispersed more widely than heavier congeners.
- General Statements/Next steps
  - Long-chain PFCAs (e.g. PFOA, PFNA) have been phased out and replaced with PFAS with other structures. Often, the precise structure of these alternatives are a trade secret and difficult to detect in environmental samples
  - The availability of non-target analysis is largely limited to research facilities, due to availability of equipment and technical expertise, but has the potential for a wider application in the future.
  - Data sets are inherently complicated, representing multiple mechanisms of distribution in the environment according to varied physical and chemical characteristics. A thorough review of the analytical results for multiple media will provide additional information needed to fully characterize distribution in the environment.

For More Information:

Washington, John W., Charlita G. Rosal, James P. McCord, Mark J. Strynar, Andrew B. Lindstrom, Erica L. Bergman, Sandra M. Goodrow, Haile K. Tadesse, Andrew N. Pilant, Benjamin J. Washington, Mary J. Davis, Brittany G. Stuart, Thomas M. Jenkins, *"Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey Soils"*, **Science** 368, 1103-1107 (2020).

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