

# FINDINGS AND RECOMMENDATIONS OF THE NORTH CAROLINA PER- AND POLYFLUOROALKYL SUBSTANCES TESTING NETWORK

FINAL REPORT TO THE NORTH CAROLINA GENERAL ASSEMBLY APRIL 15, 2021 Revised April 30, 2021



# FOREWORD

The North Carolina Per- and Polyfluoroalkyl Substances Testing Network (NC PFAST Network), was formed by the North Carolina Policy Collaboratory (Collaboratory) in July 2018 in response to a legislative mandate from the North Carolina General Assembly (NCGA). Within Session Law (S.L.) 2018–5, Section 13.1.(g), the NCGA directed the Collaboratory to:

"Identify faculty expertise, technology, and instrumentation...and coordinate these faculty and resources to conduct nontargeted analysis for PFAS, including GenX, at all public water supply surface water intakes and one public water supply well selected by each municipal water system that operates groundwater wells for public drinking water supplies..."

The NC PFAST Network is comprised of academic experts and their collaborative research teams from seven North Carolina universities, including faculty who have been studying the occurrence, effects, and remediation of PFAS exposures for several years prior to this legislation. Five million thirteen thousand dollars (\$5,013,000) in designated appropriation were provided in this legislation by the NCGA to the Collaboratory to fund the NC PFAST Network in accordance with Section 13.1.(i) of S.L. 2018–5:

"(i) to cover costs incurred as a result of activities conducted pursuant to this section, (ii) for acquisition or modification of essential scientific instruments, or (iii) for payments of costs for sample collection and analysis, training or hiring of research staff and other personnel, method development activities, and data management, including dissemination of relevant data to stakeholders."

The Collaboratory was also directed in Section 13.1.(j) of S.L. 2018-5 to: "*pursue* relevant public and private funding opportunities that may be available to address the impacts of PFAS...in order to leverage funds appropriated by this section, or any other funds provided to the Collaboratory." The Collaboratory had already funded three water-related emerging compounds (including PFAS) projects in FY 2017-18 ahead of this directive, totaling \$430,000. In addition, the Collaboratory utilized both its NCGA Challenge Grant and annual recurring appropriation to provide an additional \$1,724,587.82 (30 individual projects) in PFAS-related funding between FY 2018-19 and 2021-21. Therefore, the Collaboratory's 33 additional investigative grants totaling \$2,154,587.82, added to the \$5,0130,000 appropriated specifically for the PFAS Testing Network in FY 2018-19, represent a total state commitment dedicated to PFAS-related university research of \$7,167,587.82. This funding has been critical in supporting the creation of new PFAS datasets, research methods, mitigation technologies, substantial

stakeholder partnerships, and has directly and indirectly resulted in PFAST Network researchers receiving an additional \$24,046,393 in non-State PFAS research funding since the original Network appropriation.

In addition to baseline water sampling and analyses identified above, Section 13.1.(l) of S.L. 2018–5 further mandated the Collaboratory to coordinate research to:

"(i) develop quantitative models to predict which private wells are most at risk of contamination from the discharge of PFAS, including GenX; (ii) test the performance of relevant technologies in removing such compounds; and (iii) study the air emissions and atmospheric deposition of PFAS, including GenX. In addition, Collaboratory may, using relevant faculty expertise, technology, and instrumentation existing throughout institutions identified, evaluate other research opportunities and conduct such research for improved water quality sampling and analyses techniques, data interpretation, and potential mitigation measures that may be necessary..."

Furthermore in 2019 the NCGA enacted Session Law 2019-241 wherein Section 7.(a) directed the Collaboratory to "*create an inventory of aqueous film-forming foam* (*AFFF*) used or stored by fire departments in North Carolina operated, managed, or overseen by units of local government, including those located at or serving airports." It is well known that some older formulations of AFFF contain legacy PFAS such as the 8-carbon chain perfluoroalkyl octane sulfonate (PFOS) and shorter chain fluorinated components including the 6-carbon perfluoroalkyl hexane sulfonate (PFHxS), and that AFFF used in firefighting training and suppression of fuel-based fires and spills represents one important source of PFAS into the environment. At the discretion of the Collaboratory, this project was added to the NC PFAST Network.

Reporting requirements for PFAS testing and related research activities outlined in Section 13.1.(h) of S.L. 2018–5 include the following:

"Beginning October 1, 2018, the Collaboratory shall report no less than quarterly to the Environmental Review Commission, the Department of Environmental Quality, and the Department of Health and Human Services on all activities conducted pursuant to this section, including any findings and recommendations for any steps the Department of Environmental Quality, the Department of Health and Human Services, the General Assembly, or any other unit of government should take in order to address the impacts of PFAS..." In addition, Section 13.1(g) states, "No later than December 1, 2019, Collaboratory shall report the results of such sampling" to the reporting agencies.

In fulfillment of these reporting requirements, the NC PFAST Network submitted ten progress reports commencing October 1, 2018 and quarterly thereafter. Copies of

these reports have been archived and are available on the NC PFAST Network website at: <u>https://ncpfastnetwork.com/resources/</u>. At the request of NC PFAST Network and Collaboratory leadership, the NCGA approved an extension of research activities (without additional appropriations) to enable additional sampling of drinking water supply intakes during different seasons and provide more time for comprehensive analysis and interpretation of non-targeted data. Section 7.(d) of Session Law 2019-241, extended the deadline for submission of the Collaboratory's final NC PFAST Network report from December 1, 2019 to October 15, 2020. Subsequently, with the emergence of the COVID-19 pandemic in early 2020, sample collections, laboratory experiments, and in-person meetings were put on hold. As a result, the NCGA further extended the final report deadline to April 15, 2021 within Section 8.(a) of Session Law 2020-74.

The full legislative language from Session Law 2018-5 Section 13.(f)-(l), Session Law 2019-241 Section 13.1(a)-(d), and Session Law 2020-74 Section 8.(a) is provided for reference in Appendix I. A budget summary for the designated state appropriation for the NC PFAST Network is provided for reference in Appendix VI.

This final report dated April 15, 2021 is submitted to the North Carolina Environmental Review Commission, the North Carolina Department of Environmental Quality, the North Carolina Department of Health and Human Services, and the United States Environmental Protection Agency Region 4, on behalf of the members of the North Carolina PFAS Testing Network and the North Carolina Policy Collaboratory by:



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# EXECUTIVE SUMMARY

The North Carolina Per- and Polyfluoroalkyl Substances (PFAS) Testing Network, the **NC PFAST Network**, is a multi-university research collaboration convened by the North Carolina Policy Collaboratory (the Collaboratory) in response to legislative mandates from the North Carolina General Assembly (NCGA) to address public concerns regarding the occurrence of PFAS contaminants in North Carolina and their effects on humans, wildlife, and the environment.

PFAS are a very large group of currently unregulated, non-naturally occurring chemicals that do not break down easily in the environment. PFAS include the widelyrecognized perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and GenX as well as more than 7,800 other per- and polyfluorinated chemicals. They have been used in manufacturing and industrial processes since the 1940s and are components in some firefighting foams and many consumer products. The chemical properties of PFAS make them and products containing them resistant to water, oil, grease, stains, and heat. However, these very useful characteristics are offset by PFAS's extreme stability and tendency to persist in environmental media such as groundwater, surface waters, air, soil, and plants, and to biomagnify and bioaccumulate in animals (e.g., fish) and humans, leading to a number of adverse human health effects.

In 2016, the U.S. Environmental Protection Agency (EPA) established a lifetime health advisory level (HAL), which is not an enforceable regulatory standard (sometimes referred to as a maximum containment level, MCL), of 70 ng/L (or 70 parts per trillion, ppt) for the sum of PFOA and PFOS concentrations in drinking water. EPA is now moving forward to develop a national drinking water regulation under the Safe Drinking Water Act for PFOS and PFOA; however, all other PFAS, such as GenX and other legacy and emerging PFAS, are yet to be considered for regulation. Furthermore, current federally approved methods for measuring PFAS are limited to a subset of well-established compounds such as PFOS, PFOA, GenX and other PFAS with carbon chain lengths of 4 to 12. The development and application of highly sensitive, advanced analytical techniques at universities and other research institutions has revealed that there are many emerging (or previously unrecognized) PFAS present in drinking water sources and other environmental media throughout the state and across the globe.

North Carolina is an ideal location to study PFAS, given the presence of a fluoropolymer and specialty chemicals manufacturing facility (the Chemours Company Fayetteville Works site), large military bases, airports, and other users of fluorinated firefighting foams, and urban waste streams, all of which are potential sources for PFAS emissions into the state's environment. For example, in the seminal study by Sun et al. published in 2016 in the journal of *Environmental Science & Technology (ES&T) Letters*, it was demonstrated that EPA's HAL for the sum of PFOS and PFOA was exceeded on 57 of 127 sampling days in the Cape Fear River watershed. In raw water from a drinking water treatment plant downstream of the Chemours Company Fayetteville Works site, the average concentration of GenX, which is a replacement for PFOA, was determined to be 631 ng/L (or ppt). Importantly, six other emerging PFAS (i.e., of the perfluoroalkyl ether carboxylic acid (PFECA) class) were observed to have very large signatures (uncalibrated) relative to GenX, raising serious concerns that their concentrations were also well above the EPA's HAL of 70 ppt for the sum of PFOS and PFAS in drinking water sources. In fact, a follow-on publication by Zhang et al. published in 2019 in ES&T Letters showed the sum concentration of PFAS in a 2015 sample of the Cape Fear River at the intake to the Wilmington drinking water treatment plant exceeded 100,000 ng/L. In the absence of a national regulatory safe drinking water standard for PFAS chemicals, this ground-breaking work by Sun et al., and the available toxicity studies at the time, led the NC Department of Health and Human Services (DHHS) to set a provisional health goal of 140 ng/L (or ppt) for GenX in 2017. However, similar to the EPA's HAL for the sum of PFOS and PFAS, this is not an enforceable drinking water standard.

Notably, 5 other states with high levels of PFAS contamination, including Michigan, New Jersey, Vermont, New Hampshire, and Massachusetts, have adopted strict state-enforceable standards that are even lower than EPA's HAL of 70 ppt for the sum of PFOS and PFOA. For example, Michigan is one of the most restrictive states for selected and well-established PFAS; specifically, they set the limit on PFOA and PFOS at 8 ppt and 16 ppt, respectively, in drinking water, as well as limits on 5 other PFAS (i.e., PFNA, PFHxS, GenX, PFBS, and PFHxA). Likewise, Vermont and Massachusetts set limits below 20 ppt for the sum of 5 (VT) or 6 (MA) PFAS including PFOA and PFOS. Currently, no enforceable safe drinking water standard has been established by the state of NC, which is in part due to limited understanding of how extensive PFAS contamination is across the state's environment and the mechanisms and magnitude of toxicity associated with some PFAS that occur at the highest concentrations in NC.

In response to increasing public awareness of GenX and other emerging PFAS in the Cape Fear River watershed, and recognizing the serious threats PFAS pose to the environment and to the health and quality of life of all North Carolinians, the NCGA funded the NC PFAST Network in summer 2018 to help inform state regulators and policymakers regarding sources and levels of PFAS in the state's environment, strategies for reducing or eliminating PFAS exposures, and improved understanding of the toxic effects of PFAS. The NC PFAST Network is uniquely suited to carry out this important work by leveraging the collective expertise, technical resources, and advanced instrumentation of faculty and their research groups at NC State University, UNC Wilmington, UNC Chapel Hill, UNC Charlotte, Duke University, East Carolina University, and NC A&T University. The faculty and their respective research groups that make up the NC PFAST Network are leading environmental engineers, scientists and toxicologists that have strong national and international reputations in studying legacy and emerging PFAS in surface water, groundwater, air (i.e., fine particulates and rainwater), plants, wildlife and humans. In addition, since many PFAS are being identified for the first time, and analytical standards are not yet commercially available, the Network has utilized expertise in synthetic organic chemistry to devise novel synthetic routes to make some of these emerging PFAS for researchers. Furthermore, NC PFAST Network experts in science communication and stakeholder engagement have ensure research findings are accessible to all stakeholders. Descriptions of the research teams, copies of monthly newsletters, infographics and other useful information can be found on the NC PFAST Network website (https://ncpfastnetwork.com/). This report summarizes two and a half years of testing and research conducted by the NC PFAST Network and provides recommendations for additional monitoring efforts, research studies, and regulations.



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# SUMMARY OF KEY RECOMMENDATIONS

Based on research results (details are in subsequent sections) obtained over the 2.5-year NC PFAS Testing Network study, a total of 60 key scientific recommendations are summarized here focusing on the following PFAS topics: (1) water sampling and PFAS analysis of NC municipal drinking water sources; (2) private well contamination risk modeling; (3) PFAS removal technologies performance testing; (4) air emissions and atmospheric deposition of PFAS; (5) novel inputs of PFAS into the environment; (6) health effects following PFAS exposure; (7) bioaccumulation of PFAS in aquatic environments; (8) construction of computer-based predictive models; and (9) inventory of aqueous film forming foams (AFFF) used for firefighting. These 60 recommendations form the basis for 2 overarching (major) recommendations included at the end of this section.

#### **KEY SCIENTIFIC RECOMMENDATIONS**

#### Water Sampling and PFAS Analysis of NC Municipal Drinking Water Sources:

**Rec. 1:** Testing should be expanded to include additional groundwater sources to capture spatial variability among wells, and account for cases where municipalities draw from multiple groundwater well sources.

**Rec. 2:** Testing should continue to capture temporal variability of impacted sources (e.g., Pittsboro had summed PFAS concentrations = 54 ng/L in round 1, and 837 ng/L in round 2).

**Rec. 3:** Testing should be initiated to better understand PFAS sources in the Cape Fear and Neuse River basins, with special emphasis on the Haw River basin.

**Rec. 4:** Toxicological studies are urgently needed, especially beyond PFOS and PFOA, for: (1) PFAS most frequently detected; (2) PFAS detected at highest concentrations; and (3) PFAS studied in mixtures.

**Rec. 5:** Adsorbable Organic Fluorine (AOF) should continue as a valuable screening tool to prioritize drinking water samples for further analysis.

**Rec. 6:** Non-targeted chemical analysis should continue to be used to uncover unknown/emerging PFAS and their associated transformation products.

# Private Well Contamination Risk Modeling:

**Rec. 7:** Future work should further couple groundwater age-dating and PFAS analyses to better estimate timescales for natural flushing of PFAS from contaminated aquifers by groundwater flow.

**Rec. 8:** Gauging stations are needed on streams such as Georgia Branch and Willis Creek to monitor the rate of PFAS export to the Cape Fear River over time and during storms.

**Rec. 9:** Refinements should be made to the predictive model and additional private well testing in areas at highest risk, including data on well depth and year of construction.

# PFAS Removal Technologies Performance Testing:

# Ion Exchange (IX) Resins:

**Rec. 10:** PS-DVB (polystyrene divinyl benzene) resins are effective for PFAS removal in water treatment.

**Rec. 11:** Resins need to be changed frequently if the treatment goal includes removing short-chain PFAS.

**Rec. 12:** When using universal resins to remove PFAS, the impact of water matrix, such as inorganic anions or organic matter, needs to be further investigated.

**Rec. 13:** Disposal of exhausted resins need to be further explored.

# Granular Activated Carbon (GAC):

**Rec. 14:** Re-agglomerated, subbituminous coal-based GAC is recommended for PFAS removal.

**Rec. 15:** Increasing empty bed contact time (EBCT) from 10 to 20 minutes results in lower operation and maintenance costs because the GAC use rate is lower.

**Rec. 16:** Enhancing background organic matter removal from water prior to GAC treatment promotes PFAS removal by lowering GAC use rate and hence treatment costs.

**Rec. 17:** Management options for spent GAC need to be studied to assure that PFAS and other accumulated contaminants are not re-introduced into the environment.

# Membranes:

**Rec. 18:** Selection of membranes should strike a balance between required PFAS removal and water productivity (flow) for each use scenario.

**Rec. 19:** Further studies are needed to develop membrane modification methods that improve rejection of PFAS by high water flux membranes (e.g., nanofiltration) without detriment to water productivity.

#### Electrochemical Processes:

**Rec. 20:** Electrochemical reactors need to be designed with high anode area to sample volume ratio to ensure high PFAS destruction efficiency.

**Rec. 21:** Further studies are needed to resolve the unknown PFAS formed during electrochemical treatment.

#### Novel Ionic Fluorogels:

**Rec. 22:** Ionic fluorogel resins are a promising novel material for PFAS removal and should be investigated further.

**Rec. 23:** Further evaluation of ionic fluorogels in flow-through and up-scaled systems is needed.

#### Point-of-Use (POU) Systems:

**Rec. 24:** While not all POU filters are 100% effective, any activated carbon filter will remove some PFAS and reduce PFAS exposure; regular maintenance and frequent cartridge exchange are recommended.

**Rec. 25:** For homes served by public water systems, purchasing whole-house activated carbon filtration systems is not recommended to minimize bacterial buildup in pipes.

# Air Emissions and Atmospheric Deposition of PFAS:

**Rec. 26:** Continuous sampling should continue for a minimum of one year to better constrain PFAS deposition in specific air masses to calculate annual PFAS deposition.

**Rec. 27:** Investigation of atmospheric partitioning/deposition with synchronous sampling and analysis of aqueous-, particle-, and gas-phase samples is needed.

**Rec. 28:** Additional studies are needed to better constrain atmospheric PFAS sources through source tracking (e.g., isomers).

**Rec. 29:** Atmospheric PFAS transformations in controlled laboratory experiments should be studied to better understand sources and predict concentrations.

**Rec. 30:** Studies are needed to measure PFAS indoors (a major exposure location) since consumer product use might lead to elevated concentrations.

# Novel Inputs of PFAS into the Environment:

### Contributions from Municipal Solid Waste:

**Rec. 31:** POTW operators and landfill owners should be considered as part of a team that manages society's waste with leadership from the state Department of Environmental Quality.

**Rec. 32:** Regulatory support is needed to enable facility sampling, especially since several facilities denied requests to sample during this project.

**Rec. 33:** Public education is required to explain that PFAS are present in the products that we use in society and that POTWs and landfills do not themselves generate PFAS.

**Rec. 34:** In cases where landfill leachate is a significant contributor to PFAS, PFAS-specific treatment may be required on a case-by-case basis.

**Rec. 35:** Landfill operators should be required to report leachate quantity and flow data annually.

**Rec. 36:** The extent to which construction and demolition (C&D) landfills are resulting in surface and groundwater PFAS contamination should be assessed.

**Rec. 37:** The release of volatiles (gases) from landfills and from leachate evaporation systems should be quantified.

**Rec. 38:** Methods are needed to measure (and quantify) PFAS destruction efficiency in flares and engines typically used to treat landfill gas.

**Rec. 39:** Non-domestic PFAS sources in wastewater influent should be identified and pre-treatment requirements evaluated; other inputs to POTWs should also be analyzed.

**Rec. 40:** The impact of PFAS that are discharged from POTWs to surface water varies and site-specific/watershed-specific management strategies are appropriate.

**Rec. 41:** Estimates of wastewater releases from POTWs with non-discharge permits should be developed.

**Rec. 42:** In areas where POTW effluent is released to soil, samples of soil and vegetation on wastewater discharge area should be collected.

**Rec. 43:** An inventory of quantities and fates of wastewater treatment biosolids in NC should be developed, and vegetation, soil and wildlife impacted by land-applied biosolids should be analyzed for PFAS.

# Uptake and Distribution of PFAS in Crop Plants:

**Rec. 44:** Additional plant uptake studies, including those still in progress, are needed to evaluate plant species differences and translocation of PFAS to seed and fruit.

**Rec. 45:** Additional studies should probe PFAS occurrences in foods not studied here.

**Rec. 46:** Exposure models should incorporate diet in their assessment.

**Rec. 47:** Biosolids and irrigation water should be evaluated for their possible PFAS contribution to agricultural products.

#### Health Effects Following PFAS Exposure:

#### *Immunotoxicity in Laboratory Mice:*

**Rec. 48:** Additional studies are needed with underexamined PFAS (especially beyond PFOS and PFOA) that have been detected in NC.

**Rec. 49:** Mixtures studies should be conducted to better understand how these PFAS influence one another since real-world exposures are often to PFAS mixtures.

**Rec. 50:** Urinary PFAS concentrations need to be evaluated to estimate biological half-lives (blood concentrations were low).

**Rec. 51:** Further studies are needed to identify molecular changes associated with antibody suppression in understudied PFAS compared to changes induced by legacy PFAS.

# Impact of PFAS on Human Placental Health and Birth Outcomes:

Rec. 52: PFAS measurements needed in drinking water among pregnant women.

**Rec. 53:** PFAS effects on trophoblast stem cell differentiation *in vitro* should be investigated, and the mechanistic target needs to be determined.

**Rec. 54:** Studies are needed to measure PFAS-induced gene expression changes *ex vivo* using human placental explants.

**Rec. 55:** Investigate how PFAS change the molecular communication between trophoblasts and maternal immune cells (process may contribute to preeclampsia).

#### **Bioaccumulation of PFAS in Aquatic Environments (Fish and Alligator Exposures):**

**Rec. 56:** Studies should continue to measure PFAS exposure, bioaccumulation and biomagnification in consumed fish.

**Rec. 57:** Evaluation of immune and other adverse effects in Alligators at Greenfield Lake should continue.

**Rec. 58:** Analysis of alligator exposure monitoring and health effects should extend to all populations of alligators across the state of NC.

#### **Construction of Computer-Based Predictive Models:**

**Rec. 59:** Physiologically-based pharmacokinetic (PBPK) modeling efforts could be improved with additional time-course tissue-level or serum-level data.

#### Aqueous Film Forming Foam (AFFF) Inventory:

**Rec. 60:** NC Office of the State Fire Marshal should update and review annually their directory of fire departments and continue working with the Collaboratory to develop and implement an easy-to-use interface for any fire department using PFAS-containing AFFFs to report every incident of AFFF discharge. The state should also require annual inventory reporting of foam type and volume to help identify PFAS-containing foam that could be collected and disposed of properly.

# **OVERARCHING (MAJOR) RECOMMENDATIONS**

# **Rec. 1: Continued Funding for Statewide PFAS Research**

Additional funding to continue PFAS research is strongly suggested utilizing the expertise, instrumentation and collaborative enterprises at statewide universities. Additional sampling and analyses are needed to better understand spatial and temporal PFAS distributions found in surface waters and groundwater. Currently ongoing mammalian toxicology studies should be expanded to include lung cell models for assessing the adverse human health effects associated with inhalation exposures to airborne PFAS. These studies can provide health-based data that often form the basis for advisories and guidelines to protect human health.

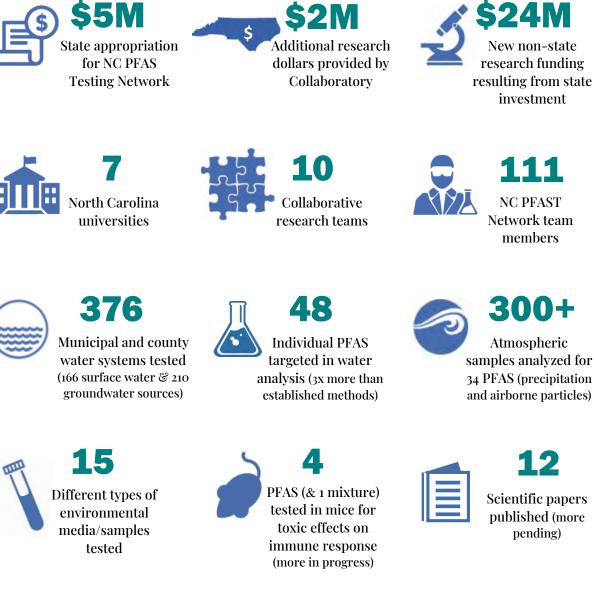
Research funding could focus on (at a minimum): (1) a basic program for statewide water sampling, testing, and monitoring; (2) coupled toxicology work in cellular and mammalian models based on the water and air results; and (3) support for data management and community engagement. In addition, continued efforts in chemical synthesis are critically needed in order to aid in these proposed areas of future research funding. Furthermore, regulatory and/or legislative action may be needed to ensure that researchers can gain access to starting materials needed to synthesize critical PFAS compounds. Many of these compounds are not readily available and manufacturers are not always able/willing to share/provide starting materials needed for synthesis.

Other PFAS research topics may include: air transport sampling, testing, and modeling to constrain sources of legacy PFAS and abiotic formation/degradation processes of emerging PFAS emitted into air; private well and groundwater sampling, testing, and modeling; PFAS signatures found in soils; performance testing of PFAS removal of existing technologies; continued development and testing of new PFAS removal technologies; and other projects of opportunity and collaborations with state and federal partners.

#### Rec. 2: Scientific Data Transparency

It is recommended that any future PFAS guidance, policies, or regulations clearly cite the data used to establish any numerical standards, limitations, thresholds, etc., by including a reference to the dataset(s) in the actual language of the regulation itself. As the scientific data and understanding of these compounds continues to grow, it will be more straightforward to identify when a regulation may have to be revised based on newer data and/or an evolving state of understanding of cited data. This broad philosophy for scientific transparency (e.g., raw data, processed data, study design, technology used for data measurements, concepts, original or alternate hypotheses, assumptions, etc.) utilized for policy-making decisions certainly can be extended beyond PFAS-related issues.

# NC PFAST NETWORK: BY THE NUMBERS







# **RESULTS AND KEY RECOMMENDATIONS BY PROJECT**



I. Water sampling and PFAS analysis of North Carolina municipal drinking water sources

# **Objective:**

To collect and analyze public water sources in NC to identify classes of PFAS and to quantify levels of PFAS using suspect screening, non-targeted analysis, total fluorine analysis, and quantitative (targeted) analysis.

#### **Proposed Aims:**

- Collect water samples during 2018/2019 at the intake of all 166 operational municipal/county surface water systems in NC and from one well each at all 210 operational municipal/county systems treating groundwater in NC. For systems with detectable PFAS, collect an additional set of samples during the third quarter of 2019.
- Quantify targeted PFAS in water samples using highly sensitive and specific tandem mass spectrometry approaches with authentic standards of known concentrations.
- Analyze all water samples using high-resolution mass spectrometry to identify PFAS via suspect screening for expected PFAS and non-targeted analysis of unknown abundant peaks.
- Complement non-targeted analyses with adsorbable organic fluorine (AOF) measurements to estimate what fraction of the AOF measurement can be

explained by quantifiable PFASs identified in targeted and non-targeted analyses.

#### Accomplishments:

• Two rounds of sample collection were completed from 376 county and municipal drinking water sources in NC. These included surface water intakes and one groundwater well selected by the utility operator (Fig. 1). The Data Science and Management team's Geospatial Analytics group at NC State University created optimized trips for the sampling campaigns.

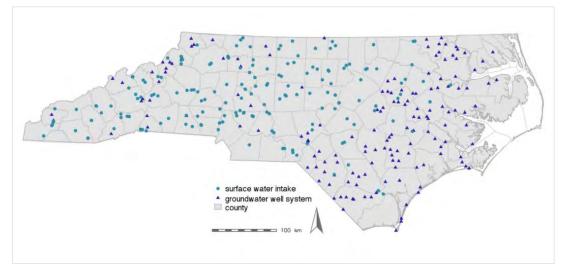


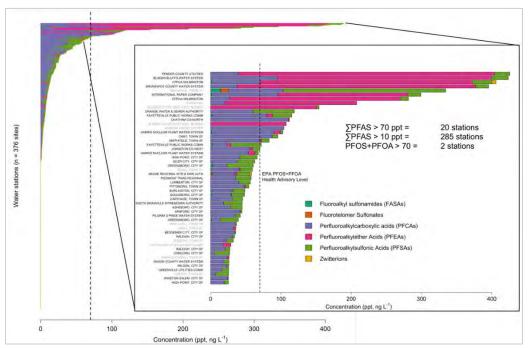
Figure 1: Surface (dots) and groundwater (triangles) sampling sites for drinking water sources

- Raw water samples were subjected to non-targeted analysis, suspect screening, and targeted analyses to identify and quantify the occurrence of PFAS in drinking water supplies around NC.
- Reports from the first round of sampling were provided to each water system showing concentrations of individual PFAS (including GenX) as well as the sum concentration of 48 targeted PFAS in the sample and the sum concentration of PFOA and PFOS.
- Adsorbable organic fluorine (AOF) concentrations were determined for the same samples to better understand the percentage of fluorinated compounds accounted for by the targeted analyses of 48 PFAS (a.k.a. fluorine mass balance).
- Non-targeted and suspect screening analyses were used to assess the presence and relative abundance of PFAS not included in the list of 48 targeted

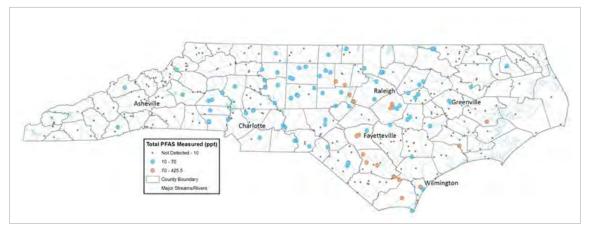
PFAS. Non-targeted analysis was completed for 141 samples from Round 1 of sampling, including all but 1 of the samples having measured summed PFAS > 70 ng/L. Samples were screened by high-resolution mass spectrometry using a comprehensive list of 7.267 known PFAS molecules and an additional 41.629 predicted chemical and biological transformation products of PFAS. Details of the structural database and in silico spectral library have been published in Analytical Chemistry: https://doi.org/10.1021/acs.analchem.oco4109, and the screening method using peak focusing, on-line solid phase extraction, and high resolution mass spectrometry for identification of PFAS in environmental waters has been reported in ACS ES&T Water: https://doi.org/10.1021/acsestwater.oco0309.

#### **Results:**

• Of the 376 water sources tested in round 1, 20 had a summed PFAS concentrations at or above the EPA health advisory limit for PFOA and PFOS of 70 ng/L (max 425 ng/L), 71 had summed PFAS concentrations in the range of 10–70 ng/L, and 285 had summed PFAS concentrations below 10 ng/L (Fig. 2).

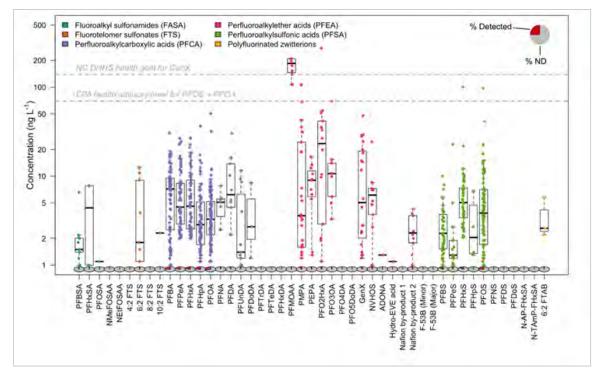


**Figure 2:** Summary of concentration distribution for 48 targeted PFAS in 376 North Carolina drinking water supplies. Inset shows detail for stations with  $\sum PFAS > 15 \text{ ng/L}$ . Water stations in black text indicate surface water supplies, while those shown in gray text represent groundwater sources.



**Figure 3:** Geographical distribution of targeted PFAS measurements in drinking water supplies of North Carolina from the first round of targeted analysis for 48 PFAS. Drinking water sources with summed PFAS concentrations > 10 ng/L were primarily located in central and southeastern NC (blue dots). A large majority of these sites represented surface waters. Groundwater sources in Eastern NC and surface water sources in Western NC typically had measured sum PFAS concentrations < 10 ng/L (small gray dots). Summed PFAS concentrations > 70 ng/L (orange dots) were exclusively found in the Haw, Cape Fear, and Neuse river watersheds, with the exception of two isolated groundwater sites in Eastern NC.

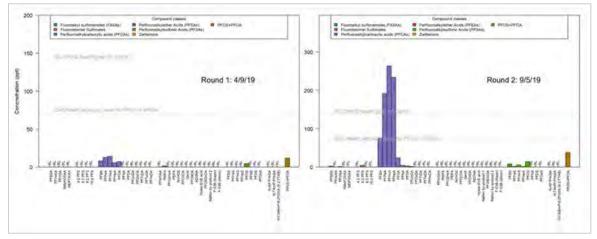
- Of the 10 sources with the highest total PFAS concentrations in round 1, 9 were in the Cape Fear River basin (Fig. 2 and 3).
- Summed PFAS concentrations in drinking waters from the lower Cape Fear region (Fig. 2) were considerably higher than maximum summed PFAS concentrations in drinking waters nationwide as reported by the Environmental Working Group (EWG). For the period of May December 2019, the maximum non-NC summed PFAS concentration reported by EWG was 110 ng/L (https://www.ewg.org/research/national-pfas-testing/).
- GenX was not detected above the NC DHHS provisional health goal of 140 ng/L in drinking water sources, but 3 perfluoroalkyl ether acids were measured above this level (PFMOAA, PFO2HxA, PMPA) (Fig. 4), and 8 out of 10 sources with the highest summed PFAS concentrations were impacted by perfluoroalkyl ether acids (Fig. 2).



**Figure 4:** Occurrence of 48 targeted PFAS in 376 North Carolina drinking water supplies. Colored dots represent concentrations detected for specific PFAS in individual samples. The red portion for each pie chart shows the fraction of all samples, in which the indicated PFAS was detected. The most frequently detected PFAS were the perfluoroalkyl acids (purple and green dots), with PFOS or PFOA detected above their reporting limits (1 ng/L) in approximately 25% of the 376 sites measured. The perfluoroalkyl ether acids (pink dots) were only found in the Cape Fear River watershed downstream and in the vicinity of Chemours' Fayetteville Works facility.

- PFOA+PFOS exceeded 70 ng/L in 2 drinking water sources. One was a groundwater source with a PFAS molecular signature suggesting contamination from firefighting foam. This source was taken out of service within one month upon notification. The second is a surface-water source likely impacted by runoff from land-applied biosolids. This drinking water source has been routinely treated with powdered activated carbon to bring PFOA+PFOS to below 70 ng/L in the finished drinking water.
- Important PFAS sources to drinking waters in NC are the Fayetteville Works site (Chemours), aqueous film forming foam (AFFF) used in firefighting (training) applications, municipal wastewater discharge, and runoff from fields that received biosolids.

- PFAS molecular profiles varied markedly among drinking water sources, highlighting the complex mixtures created by multiple sources of PFAS to the environment.
- Concentrations of PFAS in some drinking water sources varied markedly between measurements in Round 1 and Round 2 of sampling. This was particularly the case for surface water sources in areas that may receive variable inputs from upstream PFAS discharges (Fig. 5).



**Figure 5:** Temporal variability in PFAS concentrations measured in the Haw River at Pittsboro. In Round 1 sampling during May 2019 (left), PFAS molecular profiles in raw Pittsboro drinking water were dominated by short-chain (< 8 carbons) perfluoroalkyl acids, but summed PFAS concentrations were < 70 ng/L. During Round 2 sampling in September 2019 (right), the PFAS molecular profile was again primarily composed of short-chain perfluoroalkyl acids but the summed PFAS concentration was much higher (837 ng/L). This high temporal variability is reflective of fluctuating inputs of PFAS to the Haw River from discharges upstream of Pittsboro as well as fluctuations in stream flow.

- Adsorbable organic fluorine (AOF) concentrations were below the method reporting limit of 400 ng/L for 89% of tested sources and above 2000 ng/L (max. 6,700 ng/L) in 2% of sources tested in round 1.
- After analysis of 141 Round 1 samples by non-targeted and suspect screening for PFAS, 42 tentative "novel" PFAS compound annotations were obtained, none of which were measured at high abundance in samples. These compounds' identities could not be confirmed beyond match to computed mass spectra. In all cases, the dominant signals observed for PFAS during non-targeted analysis corresponded to PFAS already quantified through targeted analysis. This suggests that targeted PFAS analysis of samples in

Round 1 of analysis likely captured the majority of the analytically viable PFAS present in samples.

• No correlation was found between samples having high AOF measurements and abundant analytical signals for non-targeted PFAS.

#### **Recommendations:**

- 1. Testing should be expanded to include additional groundwater sources to capture spatial variability among wells and account for cases where municipalities draw from multiple groundwater well sources.
- 2. Testing should continue to capture temporal variability of impacted sources (e.g., Pittsboro had summed PFAS concentrations = 54 ng/L in round 1 and 837 ng/L in round 2).
- 3. Testing should be initiated to better understand PFAS sources in the Cape Fear and Neuse River basins with special emphasis on the Haw River basin.
- 4. Toxicological studies are needed for the compounds that were; (1) most frequently detected, and (2) detected at the highest concentrations.
- 5. Toxicological studies should consider that PFASs occur in mixtures.
- 6. Adsorbable Organic Fluorine (AOF) should continue as a valuable screening tool to prioritize drinking water samples for further analysis.
- 7. Non-targeted chemical analysis should continue to be used to assess completeness of PFAS quantitative analysis in targeted analyses, and to reveal novel PFAS molecules and transformation products.



II. North Carolina private well contamination risk modeling

#### **Objective:**

To understand factors influencing the risk of PFAS contamination in water supply wells near the Chemours plant by collecting and interpreting new data on the fate and transport of PFAS in contaminated groundwater near Chemours and by building and validating machine-learned Bayesian Network (BN) models for risk prediction.

#### **Proposed Aims:**

- Quantify the rate of PFAS (including GenX) flushing out of groundwater and into streams near Chemours, and the time it's expected to take for the main PFAS from Chemours to flush out of the groundwater following cessation of air emissions.
- Build machine-learned Bayesian Network models predicting private well contamination risk using new data and prior monitoring results provided by DEQ for 803 water supply wells, validate models, develop an interactive webbased version using *BayesiaLab*'s Web Simulator platform, and link the model to a GIS mapping application for easy visualization.

#### Accomplishments:

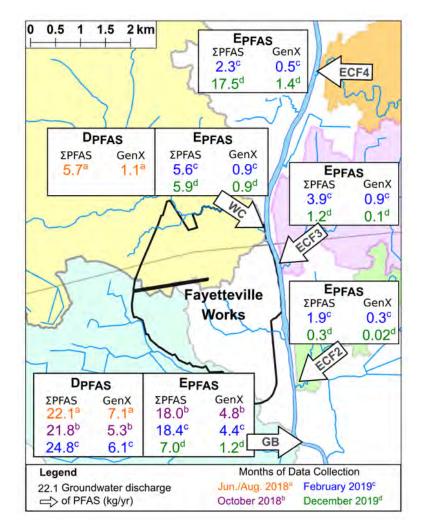
- Discharge of PFAS from groundwater to streams near Chemours was quantified using two different approaches under baseflow conditions:
  - 1. In two tributary watersheds west of the Cape Fear River, PFAS flux through the streambed was quantified at numerous points, and the mean flux was multiplied by the total streambed area to estimate the PFAS

discharge from groundwater to the stream, D<sub>PFAS</sub>. The two watersheds were Georgia Branch and Willis Creek, south and north of Chemours, respectively.

- 2. In five tributary watersheds west and east of the Cape Fear River, the stream export of PFAS from each watershed, EPFAS, was determined as the product of the stream water PFAS concentration and the stream discharge measured at the same place and time. The five watersheds were Georgia Branch, Willis Creek, and 3 unnamed tributaries on the east side of the Cape Fear, designated here as ECF2, ECF3, and ECF4. Details about this study have been published in *Environmental Science & Technology*: https://doi.org/10.1021/acs.est.oco7978.
- A database was created with multiple factors that might influence GenX in well water. This included 422 data types for 1,207 private wells. Artificial intelligence algorithms were applied to generate a predictive model which was cross-validated with additional PFAS concentration data from well measurements. A web-based application was developed for users to predict contamination of untested wells and can be accessed through the NC PFAST Network website: <a href="https://ncpfastnetwork.com/genx-predictive-tool/">https://ncpfastnetwork.com/genx-predictive-tool/</a>. The results of this work have been published in the *Journal of Hazardous Materials*: <a href="https://doi.org/10.1016/j.jhazmat.2021.125075">https://doi.org/10.1016/j.jhazmat.2021.125075</a>.

#### **Results:**

• Base flow discharge of PFAS from groundwater to streams near Chemours is about 32 kilograms per year (see Fig. 6 below). Groundwater flow is a significant PFAS transport pathway and could contribute for many years to PFAS contamination in wells, streams, and the Cape Fear River.



**Figure 6:** Discharge of PFAS (kg/yr) from groundwater into streams during four different periods of data collection, in five tributary watersheds of the Cape Fear River: GB (Georgia Branch), WC (Willis Creek), ECF2, ECF3, and ECF4. To compare values within the same time period, compare numbers with the same font color. Values were calculated from point measurements of PFAS flux through the streambeds (D<sub>PFAS</sub>), and from measurements of stream export of PFAS (E<sub>PFAS</sub>).

• All 78 groundwater samples collected beneath streams in 2018-2019 were contaminated with PFAS. Given that 1980 is the year of first air emission of PFAS acknowledged by Chemours (for GenX at least), all of these samples likely represent groundwater recharged after 1980; in other words, groundwater less than 39 years old (older groundwater would be PFAS-free). The average transit time through groundwater from the water table to a

stream was likely 2-3 decades for the major PFAS (fluoroethers) at the site, though the full range of transit times is not yet clear.

- PFAS concentration was generally higher in younger groundwater, but even the oldest groundwater sample dated (29 years old based on tritium-helium age dating of the water) had 313 ng/L of total quantified PFAS. This sample represents groundwater recharged in 1990, showing that groundwater in the area had significant PFAS contamination within 10 years of the acknowledged start of air emissions in 1980.
- Overall, fluoroether PFAS from Chemours moved quickly from soil to groundwater to streams, in strong contrast to the much slower transport that is generally expected for other PFAS like PFOA and PFOS.
- Contamination risk of private wells can be predicted, even with limited data on well characteristics by incorporating large amounts of existing data available online into Bayesian Network machine-learned models. Although this project only had measurements for GenX, risks of new contamination from the massive group of more than 8,000 PFAS chemicals can be predicted using the same methodology.
- Air deposition rate and distance from Chemours were found to be the most influential variables in predicting the level of GenX which independently confirms previous research.

# **Recommendations:**

- 1. Future work should include further coupling of groundwater age-dating and PFAS analyses to better estimate the timescale for the natural flushing of PFAS from the contaminated aquifers by groundwater flow. This is an issue of major practical significance for homeowners with water supply wells, and for downstream users of the Cape Fear River.
- 2. Gauging stations are needed on streams such as Georgia Branch and Willis Creek to monitor the rate of PFAS export to the Cape Fear River over time, including during storms. This would better quantify the rate of PFAS flushing from contaminated aquifers and watersheds, and the rate of recovery in the quality of both surface water and groundwater.
- 3. Refinements to the predictive model and additional private well testing in areas at highest risk (northwest, northeast of Chemours) including data collection of well depth and year of construction.



# III. PFAS removal technologies performance testing

#### **Objective:**

To identify optimum technologies for removing both legacy and emerging PFAS from contaminated surface and ground waters in NC, as well as from finished drinking water and treatment waste streams, and to investigate electrochemical methods for PFAS destruction. This research involved multiple collaborating laboratories (Coronell, Sun, Knappe, Stapleton, Leibfarth) each focused on a particular technology.

# **Proposed aims:**

- Characterize PFAS removal from drinking water sources by a wide range of commercially available activated carbons, ion exchange (IX) resins, and high-pressure membrane filters.
- Characterize PFAS removal by electrochemical oxidation from waste streams generated during resin regeneration and membrane filtration and evaluate resulting degradation products.
- Characterize performance of in-home filters used at NC homes for removing PFAS from tap water.
- Evaluate enhancement of PFAS rejection by means of membrane modification to reduce contaminant permeation and passage.
- Develop an IX resin (Ionic Fluorogels) optimized for PFAS removal to overcome the limitations of activated carbon and ion-exchange technologies.

#### Accomplishments:

#### Ion exchange (IX) resins:

- PFAS removal from drinking water sources was evaluated using nine commercially available IX resins, including universal and PFAS-specific ones. Tests were conducted to determine PFAS removal kinetics and competitive adsorption by the IX resins.
- Rapid small-scale column tests were conducted to estimate the service life of IX resin for PFAS removal and the ease of resin regeneration. Practical approaches for regenerating exhausted IX resins were systematically investigated.

#### Granular activated carbon (GAC):

- Removal of 23 PFAS by five commercially available GACs was evaluated as well as the effects of background water matrix constituents on GAC effectiveness for PFAS removal.
- A scale-up approach was developed to predict PFAS removal in field-scale GAC filters.

#### Membranes:

- A wide range of high-pressure membranes were evaluated, including seawater, brackish water, and nanofiltration membranes, for their removal of a suite of legacy and emerging PFAS from groundwater collected near the Chemours fluorochemical plant.
- The effects of feed properties, including applied pressure and pH, on PFAS removal performance of different membranes and the effects of PFAS physiochemical characteristics, including p*Ka*, molecular weight, and functional groups, on membrane rejection efficacies were examined.

# Electrochemical processes for PFAS destruction:

- Three commercially available materials were compared for use as anodes in the PFAS mineralization reactor and the electrochemical mineralization of perfluorooctanoic acid (PFOA) and GenX were evaluated.
- The reactor design was optimized to minimize and capture aerosol-based PFAS losses during electrochemical treatment.

# Novel ionic fluorogels (IF):

- Ionic fluorogels for PFAS removal were synthesized and compared to existing materials.
- Two provisional patents were filed on complementary material compositions:
  - ✓ Fluorinated Ionic Polymer Networks, and Methods Relating Thereto.
    U. S. Provisional patent application # 62/891,111;
  - ✓ Fluoroether vinyl ether copolymer ionic fluorogels and methods of use thereof. U. S. Provisional patent application # 21-0073.

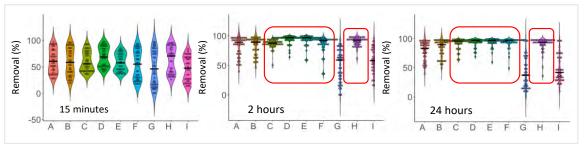
# Point-of-use (POU) systems:

- The effectiveness of POU treatments for residential removal of PFAS was investigated in 73 homes from two locations (central and southeastern NC).
- The filters studied included different types of granular activated carbon filters (e.g., pitcher and refrigerator filters), two-stage under-sink filters (sediment plus activated carbon block filters), under-sink reverse osmosis filters, and some whole house systems.

# **Results:**

# Ion exchange (IX) resins:

• The resin polymer type is the most important factor for PFAS removal, with multiple PS-DVB (polystyrene divinyl benzene) resins on the market capable of effectively removing most PFAS structures. In general, PFAS with long chains and sulfonic groups are better removed by resins when compared to short-chain or carboxylic groups (Fig. 7).



**Figure 7:** Removing 40 PFAS from Fayetteville groundwater with IX resins A through I: Five highlighted PS-DVB resins removed most PFAS in 2-24 hours. Resin dose = 5 mL/L. Initial PFAS concentration = 600 ng/L.

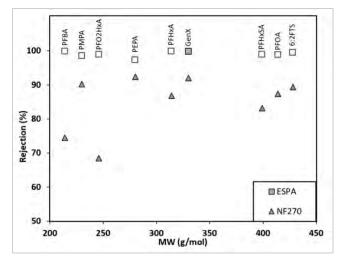
- The performance of PFAS-specific resins is barely affected by the water matrix, while the performance of universal resins decreased as concentrations of competitors increased. Furthermore, the PFAS-specific resins are capable of treating more water (longer operating time) than universal resins.
- PFAS-exhausted IX resins are not well regenerated when using organic solvents in the practical range (<20%), especially for PFAS-specific IX resins.

# Granular activated carbon (GAC):

- GAC effectiveness for PFAS removal depends on PFAS type, GAC type, and background organic matter concentration of the water. GAC consisting of reagglomerated, subbituminous coal (35-45% carbon) was more effective for PFAS removal than GAC prepared from coconut shells.
- GAC removed all studied PFAS to below the method reporting limit but loses its effectiveness relatively quickly for short-chain PFAS, such as perfluoromethoxyacetic acid (PFMOAA). In contrast, longer-chain PFAS can be removed to below the method reporting limit for a longer period of time.
- The GAC service life is longer when used to treat water with low background organic matter levels (e.g., groundwater from wells of residents living near Chemours) than from water with higher background organic matter levels (e.g., coagulated Cape Fear River water).
- Doubling the time water contacts the carbon bed (the empty bed contact time, or EBCT) from 10 to 20 minutes resulted in ~10% lower GAC use rates.

# Membranes:

• High-pressure membranes are effective for PFAS removal. The membranes used in this study displayed a broad range of performance when treating PFAS-contaminated groundwater, with PFAS rejection ranging from 49.6% to 99.9% (Fig. 8).



**Figure 8:** Comparison of PFAS rejection by Reverse Osmosis (ESPA: energy-saving polyamide) and Nanofiltration (NF270) membranes. RO membranes consistently showed >90% PFAS removal while NF membranes often showed <90% PFAS removal.

- PFAS rejection was highest among fully aromatic polyamide thin film composite (TFC) membranes (>93%) and lowest in semi-aromatic polyamide membranes. PFAS rejection performance displayed by a cellulose acetate membrane fell between that of those two groups.
- Membranes modified with additional polyamide growth exhibited increased PFAS rejection by up to 8.6%, but decreased water permeability by up to 91.6%. No extensive effort was made to optimize the membrane modification procedure for optimum membrane performance.
- Variability in PFAS rejection across membranes was greater for lower molecular weight (i.e., ≤300 g/mole) PFAS, and there was no correlation between PFAS functional groups and membrane rejection efficiency.
- Higher operational pressures and feed pH values resulted in slightly higher PFAS rejection.

#### Electrochemical processes:

- Boron doped diamond was the most effective anode material for PFAS destruction and high anode area to sample volume ratio resulted in better PFAS removal.
- Electrochemical treatment can achieve >80% PFOA and >60% GenX removal, but lead to formation of unknown PFAS as products.

• Complete fluorine mass balance was attained counting the formed fluoride and unknown PFAS (measured as adsorbable organic fluorine).

#### Novel ionic fluorogels (IF):

• A platform approach was developed to generate ionic fluorogel resins that contain a synergistic combination of fluorous and ionic components (Fig. 9). The IF resins selectively remove PFAS over background organic matter.

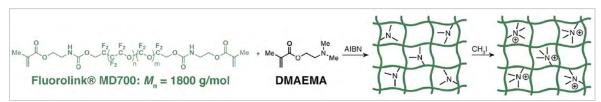
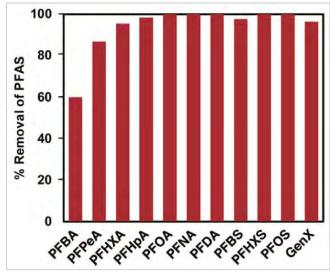


Figure 9: Scheme of polymerization and quaternization for preparation of Ionic Fluorogels.

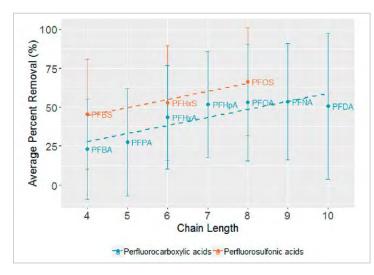
• Two unique ionic fluorogel compositions containing either ammonia or ammonium ions provide complementary performance for PFAS remediation from diverse water matrices (Fig. 10). Preparation of novel IF sorbents and the evaluation of PFAS removal have been published in *ACS Central Science*: https://dx.doi.org/10.1021/acscentsci.9bo1224.



**Figure 10:** Percent removal of individual PFAS after 2 h by Ionic Fluorogel containing 30% by weight ammonium co-monomer (IF-30+) from settled water collected at the Sweeney Water Treatment Plant in Wilmington, NC (TOC = 1.3 mg/L; pH = 6.2; sorbent conc. = 100 mg/L; PFAS initial conc. = 1  $\mu$ g/L each).

# Point-of-use (POU) systems:

• Common activated carbon based POU water filters (e.g., pitcher filters and inline refrigerator filters) did not completely remove PFAS and displayed a wide range of PFAS removal efficiencies (Fig. 11).



**Figure 11:** Average percent removal compared to chain length of PFAAs for activated carbon-based point-of-use filters.

The amount and size of the activated carbon in these filters is likely influencing the removal efficiency. Generally, longer chain PFAS were removed more efficiently than shorter chain PFAS.

- Upon prolonged use, some filters become saturated and start to leak PFAS back into to the filtered tap water.
- Under-sink reverse osmosis and two-stage filters performed very well in removing all types of PFAS analyzed in this study (~>99%).
- Results shown below (Fig. 12) from the evaluation of various POU and whole house filter options for removal of PFAS have been published in *Environmental Science* & *Technology Letters*: https://dx.doi.org/10.1021/acs.estlett.oco0004.

						Central NC				
		$\begin{array}{l} \text{counter} \\ \text{filter} \\ (n=0) \end{array}$	faucetfilter(n = 2)	pitcher filter (n = 13)	fridge filter $(n = 22)$	single-stage under- sink filter $(n = 5)$	whole-house, $GAC (n = 6)$	whole-house, GAC/CIX (n = 0)	two-stage filter $(n = 4)$	reverse osmosis (n = 11)
PFSA	PFBS	na	94%	65%	29%	>84%	18%	na	>92%	94%
	PFHxS	na	88%	54%	65%	>84%	32%	na	>95%	>96%
	PFOS	na	99%	71%	61%	>99%	67%	na	99%	100%
PFCA	PFBA	na	63%	36%	45%	15%	-34%	na	98%	>98%
	PFPA	na	67%	42%	35%	52%	-85%	na	>99%	>99%
	PFHxA	na	79%	43%	59%	53%	-63%	na	>97%	98%
	PFHpA	na	75%	43%	65%	52%	-37%	na	>97%	98%
	PFOA	na	84%	67%	71%	56%	19%	na	>99%	>92%
	PFNA	na	92%	>54%	72%	45%	28%	na	>99%	>88%
	PFDA	na	99%	>57%	57%	64%	44%	na	>99%	>93%
PFEA	GenX	na	63%	46%	56%	51%	21%	na	>99%	>99%
					So	utheastern NC				
		$\begin{array}{c} \text{counter} \\ \text{filter} \\ (n = 1) \end{array}$	faucetfilter(n = 0)	pitcher filter (n = 0)	fridgefilter(n = 3)	single-stage under- sink filter (n = 5)		whole-house, GAC/CIX (n = 5)	two-stage filter $(n = 3)$	reverse osmosi (n = 7)
PFEA	GenX	-146%	na	na	>78%	>74%	55%	-7%	>74%	>75%
	PFMOAA	-498%	na	na	92%	91%	40%	-106%	97%	97%
	PFO2HxA	-284%	na	na	98%	94%	54%	58%	>99%	97%
	PFO3OA	11%	na	na	>99%	97%	64%	60%	99%	>99%
	PFO4DA	70%	na	na	99%	99%	63%	69%	99%	99%
	Nation BP2	55%	na	na	97%	>99%	52%	1%	98%	99%

**Figure 12:** Average % Removal for PFAAs and PFEAs by Filter Class. All measurements displaying negative percent removal values experienced an increase in PFAS concentration after filtration.

#### **Recommendations:**

#### *Ion exchange (IX) resins:*

- 1. PS-DVB (polystyrene divinyl benzene) resins are more suitable choices for removing PFAS for water treatment.
- 2. Resins need to be changed frequently if the treatment goal includes removing short-chain PFAS.
- 3. When using universal resins to remove PFAS, the impact of water matrix, such as inorganic anions or organic matter, needs to be investigated.
- 4. Disposal of exhausted resins need to be further explored.

#### Granular activated carbon:

- 1. Re-agglomerated, subbituminous coal-based GAC is recommended for PFAS removal.
- 2. Increasing empty bed contact time (EBCT) from 10 to 20 minutes results in lower operation and maintenance costs because the GAC use rate is lower.
- 3. Enhancing background organic matter removal from water prior to GAC treatment promotes PFAS removal by lowering GAC use rate and hence

treatment costs. In addition, enhanced background organic matter removal would decrease disinfection by-product formation.

4. Management options for spent GAC need to be studied to assure that PFAS and other accumulated contaminants are not re-introduced into the environment.

## Membranes:

- 1. Selection of membranes should strike a balance between required PFAS removal and water productivity (flow) for each use scenario (e.g., community watertreatment plant, home system, water source, etc.). Two residential membranes evaluated in this project were generally suitable for removing PFAS from drinking-water sources.
- 2. Further studies are needed to develop membrane modification methods that improve rejection of PFAS by high water flux membranes (e.g., nanofiltration) without detriment to water productivity.

## Electrochemical processes:

- 1. Electrochemical reactors need to be designed with high anode area to sample volume ratio to ensure high PFAS destruction efficiency. Minimizing aerosolbased PFAS losses and proper mixing of the solution are key to achieving high PFAS removal electrochemically.
- 2. Further studies are needed to better understand the unknown PFAS formed during electrochemical treatment.

# Novel ionic fluorogels:

- 1. Ionic fluorogel resins are a promising novel material for removal of PFAS from water and should be investigated further.
- 2. Further evaluation of the ionic fluorogels in flow-through and up-scaled systems is needed for PFAS removal.

# Point-of-use (POU) systems:

1. While not all POU filters are 100% effective, any filter containing activated carbon will remove some PFAS and therefore reduce PFAS exposure; however, regular maintenance and frequent cartridge exchange are recommended to ensure filters don't lose their ability to remove PFAS.

- 2. For homes served by public water systems, purchasing whole-house filtration systems containing activated carbon is not recommended as these systems can remove helpful disinfectant residuals from the water that prevent the buildup of harmful bacteria in water pipes within the home.
- 3. To read more about this research and view a fact sheet with additional information on POU water filters and PFAS removal, please see the following website and click on "Resources": <u>https://sites.nicholas.duke.edu/pfas</u>.



# IV. Air emissions and atmospheric deposition of PFAS in North Carolina

#### **Objective:**

To better understand the composition, distribution and concentrations of airborne PFAS. There is limited data available regarding airborne legacy and emerging PFAS, and their sources, reactions, and deposition. Airborne PFAS have been found far from point sources due to limited environmental degradation (persistence) and ubiquitous release from consumer products and waste streams.

#### **Proposed aims:**

- Measure airborne PFAS compounds in Wilmington, Research Triangle Park, Charlotte, Greenville, and Fayetteville over a one-year period.
- Determine the concentration of PFAS in rainwater at the Wilmington site (intensive sampling) and examine the influence of air mass back-trajectory and season on the atmospheric concentration and distribution of PFAS.
- Determine PFAS concentration and distribution in wet and dry deposition at other selected locations on a less frequent basis (i.e., Greenville, Chapel Hill, Charlotte, Boone, and Bald Head Island).
- Determine the wet/dry areal deposition of HFPO-DA and other PFAS to surface waters including the Cape Fear River drainage basin.
- Measure near-source airborne PFAS species during a single, intensive field study.

• Conduct preliminary laboratory chamber experiments to examine multiphase chemistry (or reactive uptake) of hexafluoropropylene oxide (HFPO) with atmospheric aerosol.

#### Accomplishments:

- Statewide *ambient air* PFAS concentration measurements were completed in a one-year field campaign at five sites (Fayetteville, Charlotte, Research Triangle Park, Wilmington and Greenville) to determine PFAS levels in seasonally-composited (quarterly) samples of PFAS in airborne particles (PM<sub>2.5</sub>). Details about this study have been published in *Environmental Science: Processes & Impacts*: <u>https://doi.org/10.1039/DoEMo0497A</u>.
- Statewide *wet and dry deposition* sample analysis was conducted at remote monitoring sites (Charlotte, Research Triangle Park, Greenville, Wilmington, Boone, Bald Head Island) over winter/summer 2019. *Wet deposition* on event basis and *dry deposition* twice a month in Wilmington were studied for 1 year. Details about wet and dry deposition have been published in *Environmental Science & Technology Letters*: <a href="https://doi.org/10.1021/acs.estlett.1co0251">https://doi.org/10.1021/acs.estlett.1co0251</a>.



**Figure 13:** Map of sampling sites. Ambient air sites (Charlotte, Research Triangle Park, Greenville, Fayetteville, and Wilmington) and deposition sites (Charlotte, Chapel Hill, Greenville, Fayetteville, Wilmington, Boone, and Bald Head Island).

- An intensive, 6-month fence-line monitoring campaign using two high volume (HiVol) air samplers was conducted to measure weekly-averaged PFAS in airborne particles (PM<sub>2.5</sub>) at two locations close to the Chemours facility (near-field, within 1.5 km) and in line with the main wind directions (SSW and NNE).
- Laboratory chamber experiments to investigate HFPO chemistry have been initiated.

#### **Results:**

• Of 34 *ambient air* PFAS targeted statewide in PM<sub>2.5</sub> samples, only PFOS and PFOA were > 1pg/m<sup>3</sup> (Fig. 14). Concentrations above 1 pg/m<sup>3</sup> all occurred during the third quarter (July-Sept; PFOA in Charlotte; PFOS in Research Triangle Park and Wilmington). Geographic variability and seasonality of these legacy compounds is consistent with local atmospheric formation from more volatile PFAS compounds emitted (e.g., from contaminated sites, local sources or waste streams).

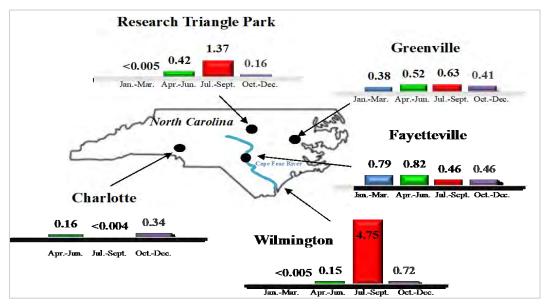
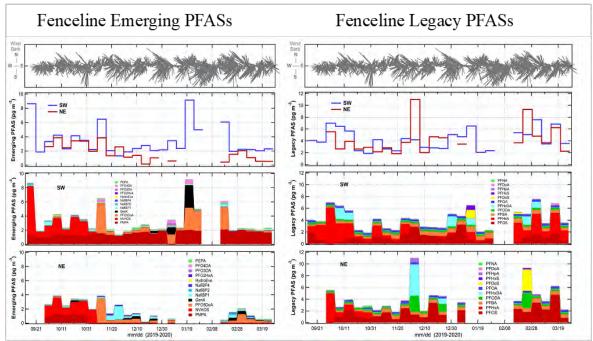


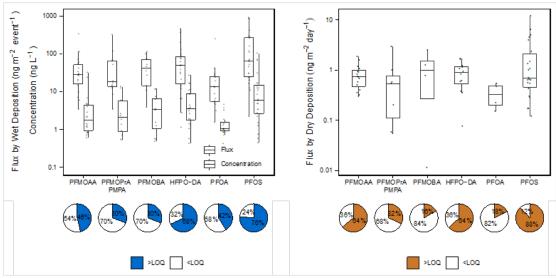
Figure 14: Particle-phase PFOS levels (pg/m<sup>3</sup>) measured in seasonally composited samples

• As seen in Figure 15 below, results from the intensive fence line monitoring showed that in *air*, 10 particulate PFAS were observed at >1pg/m<sup>3</sup> within 1.5 km of Chemours.



**Figure 15:** Emerging and Legacy PFAS measured in particles (PM<sub>2.5</sub>) within 1.5 km of southwest and northeast of Chemours.

• Legacy PFAS such as PFOS and PFOA are present in *wet and dry deposition* even though production has been phased out, and no impact of air mass origin on *deposition* concentrations or flux was observed (Fig. 16).



**Figure 16:** Detection frequencies of targeted analytes and detected concentration and flux in wet (left) and dry (right) deposition. LOQ stands for limit of quantification. Note that y-axes scales and units are different between wet and dry deposition.

• This study of atmospheric PFAS will increase awareness of the fate and transport of PFAS in the environment. Findings of detectable amounts of PFAS in wet and dry deposition across the state suggest that PFAS in the atmosphere could be introduced to rivers and groundwaters even far from a direct point source. Consumer product use, waste streams, and contaminated soils are also potential atmospheric PFAS sources. The detection of PFOS, no longer manufactured in the U.S., in air and wet and dry deposition may reflect long-range transport and/or the photochemical formation of PFOS from other PFAS compounds.

- 1. Continuous sampling should continue for a minimum of another year to better constrain deposition of the various PFAS compounds in specific air masses in order to calculate the annual deposition of PFAS compounds. Sampling should include sites up and downwind of Chemours as well as the now established regionally representative sites. Expand to include gas-phase PFAS measurements.
- 2. Investigation of atmospheric partitioning/deposition of PFAS with synchronous sampling and analysis of aqueous-, particle-, and gas-phase samples is needed.
- 3. Additional studies are required to better constrain atmospheric PFAS sources through source tracking (e.g., isomers).
- 4. Atmospheric transformations of PFAS in controlled laboratory chamber experiments should be studied to better understand sources and predict concentrations.
- 5. Studies are needed to measure PFAS indoors (a major exposure location) where consumer product use might lead to elevated concentrations and exposures.
- 6. Multiple-year studies should be conducted to assess temporal variations (outlier years) caused by climatological conditions such as El Niño events, high hurricane activity or drought. Typical rainwater studies last a minimum of 3-4 years. The net flux of the compounds can then be calculated using a volume-weighted approach, which is essentially the mathematical equivalent to combining all the rain events into one container at the end of the year and measuring the analyte.

V. Other applied research opportunities



A. Novel inputs of PFAS into the environment: contributions from municipal solid waste

## **Objective:**

To estimate the total mass of PFAS present in landfill leachate that is subsequently discharged to either Publicly Owned Treatment Works (POTWs) or to surface water after on-site treatment at a landfill.

## **Proposed aims:**

- Estimate the mass of PFAS that is discharged to POTWs by characterizing the PFAS fingerprint of municipal solid waste (MSW) landfill leachates.
- Estimate the mass of PFAS entering POTWs in North Carolina (NC) via municipal wastewater and assess the relative importance of MSW landfills as a source of PFAS to POTW influent.
- Estimate the release of PFAS to surface water by measuring PFAS in POTW effluent.
- Estimate the release of PFAS from landfills that receive construction and demolition (C&D) waste.

#### Accomplishments:

Samples were collected and analyzed from 16 MSW and 5 construction and demolition (C&D) waste landfills, as well as 31 wastewater treatment plants

(WWTPs) (influent and effluent) to estimate the total quantity of PFAS present in leachate that is subsequently discharged to either POTWs or to surface water after on-site treatment at a landfill. This work captured 37% of the statewide POTW design flow rate and considered release to 17 North Carolina river basins.

# **Results:**

- While there was wide variation in measured concentrations, the dominant compounds in landfill leachate included perfluorohexanoic acid (PFHxA), as well as 3 fluorotelomer carboxylic acids (5:3, 6:2 and 7:3).
- Using information on PFAS concentrations in the sampled landfills, the total constructed footprint of landfills in North Carolina and leachate flowrate data, it is estimated that 9 kg PFAS/yr (range of 6 11) are released from NC landfills to POTWs.
- The leachate from landfills that are permitted to receive only C&D waste contains PFAS at concentrations that are in some cases comparable to MSW landfill leachate.
- PFAS concentrations in POTW influent varied widely but are generally lower than leachate concentrations. On a mass basis, most of the POTWs are receiving less than 0.2 kg PFAS/yr although some facilities receive more than 0.8 kg PFAS/yr.
- The total PFAS concentrations in POTW influent and effluent were similar. This was expected because many PFAS are not attenuated in POTWs. Also, precursor compounds in POTW influent can be converted to some commonly targeted PFAS in POTWs. Similarly, on a mass basis, most of the POTWs are discharging less than 0.2 kg PFAS/yr although some facilities discharge more than 0.8 kg PFAS/yr.
- For a base case of a 100-acre landfill generating an average leachate volume (250 gallons per acre per day gpad), the leachate PFAS contribution to a 10 million gallon a day (MGD) POTW is about 10%. However, the base case is just that. The range of constructed footprints in NC is 10 to 280 acres, the range of leachate flowrates in the sampled landfills is 130 to 840 gpad, and the range in design flowrates of POTWs in NC is <1 MGD to 75 MGD. Thus, while statewide, leachate is a small contributor to landfill leachate, there is the potential for a specific landfill to be an important contributor to PFAS at an individual POTW. There is also the potential for a specific PFAS to be a significant contributor to POTW influent.

- 1. The presence of PFAS in landfill leachate has been well documented for many years. Many landfill owners are concerned that if their leachate is known to contain PFAS, then they would not have an outlet for leachate treatment. Landfills and POTWs are essential components of the waste management infrastructure in North Carolina and throughout the U.S. As such, POTW operators and landfill owners should be considered as part of a team that manages society's waste with leadership from the state Department of Environmental Quality.
- 2. Regulatory support is needed to enable facility sampling. Several facilities denied requests to sample during this project.
- 3. Public education is required to explain that PFAS are present in the products that we use in society and that POTWs and landfills do not generate PFAS.
- 4. In cases where landfill leachate is a significant contributor to PFAS at a specific POTW, PFAS-specific treatment may be required. However, leachate treatment requirements should be assessed on a case-by-case basis as a one size fits all policy will likely result in inefficient expenditures.
- 5. Landfill operators should be required to report leachate quantity and flow data annually. Such data are typically recorded by landfill operators and will prove useful for assessment of contaminant mass flows to POTWs.
- 6. Landfills that are permitted to receive construction and demolition waste are not typically lined in North Carolina. However, the leachate from C&D landfills was shown to contain considerable PFAS. Thus, the extent to which these landfills are resulting in surface and groundwater contamination should be assessed. This information should be used to evaluate whether steps should be taken to reduce contamination from C&D landfills.
- 7. The release of volatiles (gases) from landfills and from leachate evaporation systems should be quantified.
- 8. Methods should be developed to measure the destruction efficiency of PFAS in flares and engines that are typically used to treat landfill gas. These methods should then be used to quantify PFAS destruction efficiency at a range of NC landfills.
- 9. The non-domestic (i.e., industrial and commercial) sources of PFAS in wastewater influent should be identified and pre-treatment requirements evaluated. In addition to domestic wastewater, there are many other inputs to POTWs. These other inputs, should be analyzed to evaluate whether they are important sources of PFAS in POTW influent.

- 10. The impact of PFAS that are discharged from POTWs to surface water varies and site-specific/watershed-specific management strategies are appropriate.
- 11. Techniques should be developed to sample volatile PFAS compounds during wastewater treatment and quantify the release of volatiles (gases) from WWTPs.
- 12. Estimates of the wastewater releases from POTWs with non-discharge permits should be developed. The latest statewide report on non-discharge wastewater releases was published in 2013 with 2010 data. Due to increases in North Carolina's population, it is likely that these values are no longer representative.
- 13. In areas where POTW effluent is released to soil (i.e., non-discharge wastewater releases), samples of soil and vegetation on the area of the wastewater discharge should be collected. If PFAS are present, then animals that graze on such areas (e.g., dear, rabbits) should be sampled.
- 14. Wastewater treatment biosolids are known to contain PFAS but there is limited information. An inventory of the quantities and fates of biosolids in NC should be developed. Vegetation, soil and wildlife impacted by land-applied biosolids should be analyzed for PFAS.



B. Bioaccumulation of PFAS in aquatic environments: study of fish and alligator exposures in coastal North Carolina

#### **Objective:**

To Increase understanding of the potential for bioaccumulation and adverse impacts of PFAS, including GenX, on the health of the Cape Fear River aquatic ecosystem.

#### **Proposed aims:**

- Conduct untargeted analysis of alligator and striped bass serum samples collected from the Cape Fear River and Pamlico Aquaculture Facility.
- Collect and analyze liver and muscle of adult sunfish/bluegill and largemouth bass from other smaller water sources associated with known point source of PFAS (near Chemours).
- Develop detailed ecological models to help identify geographical areas of concern within the CF watershed and share derived data with NC DEQ and other regulatory agencies.

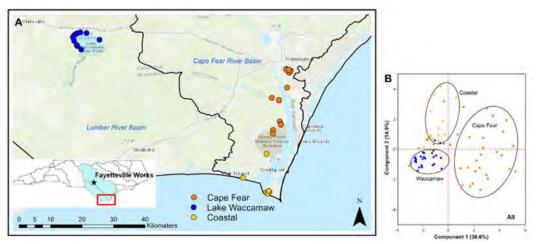
#### Accomplishments:

• Samples of blood/serum from striped bass (n=58) from the Cape Fear River were collected and analyzed and compared samples from controls (n=29) raised in Pamlico Aquaculture lab. Results have been published in *Environment International*: https://doi.org/10.1016/j.envint.2019.105358.

- Exposures and health outcomes of Cape Fear River Alligators were compared to that of low-exposure controls from Lumbar Watershed. Through 2021 ~150 alligators have been sampled (135 NC; 3 SC; 14 in FL).
- The SAFEwaterNC Study was expanded to include angler's questionnaire and evaluation of PFAS in consumed fish.

## **Results:**

- PFAS were detected in every sample with PFOS, PFNA, PFDA detected in every Striped Bass.
- Nafion BP2 was only detected in CFR samples (78%); GenX (50%) and PFHxS were highly enriched in CFR samples.
- PFOS accounted for 89% of targeted PFAS present in serum of Striped Bass from CFR.
- Differential accumulation was observed between Striped Bass serum and filet.
- PFAS exposure is associated with biomarkers of adverse effects on liver and immune function in CFR Striped Bass.
- In NC alligators, PFAS exposures are separable in to three groups 1) Cape Fear River; 2) Coastal golf courses; and 3) Lake Waccamaw (Lumbar River basin) as shown in Fig. 17.



**Figure 17:** A) Map showing locations of alligator sampling. B) Principal components analysis of PFAS exposure in alligator blood.

- PFAS exposure was elevated in alligators from the Cape Fear River.
- Those increases in PFAS exposure are associated with altered biomarkers of immune and kidney function.

- 1. Studies should be continued to measure PFAS exposure, bioaccumulation and biomagnification in consumed fish. This biomonitoring should be done continuously and use state-of-the-art non-targeted chemical approaches to identify new PFAS and targeted approaches to evaluate changes in known PFAS.
- 2. Evaluation of immune effects and other adverse effects in Alligators at Greenfield Lake should continue.
- 3. Analysis of alligator exposure monitoring and health effects should extend to all populations of alligators across the state of NC.



C. Health effects following PFAS exposure: immunotoxicity in laboratory mice exposed to PFAS

## **Objective:**

To evaluate immunotoxicity (changes in markers of innate and adaptive immune function) in mice exposed to PFAS.

#### **Proposed aims:**

- Determine effects of selected PFASs on major immune cell subpopulations in primary (thymus) and secondary (spleen) lymphoid organs.
- Assess functional responsiveness of the adaptive immune system (T celldependent antibody response targeting B cells) following exposure to selected PFAS.
- Assess functional responsiveness of the innate immune system (NK cell cytotoxicity) following exposure to selected PFAS.

## Accomplishments:

• In vivo immunotoxicity 30-day studies with PFMOAA (C3HF5O3), PFMOPrA (C4HF7O3), PFMOBA (C5HF9O3), and Nafion Byproduct 2 (C7H2F14O5S) were completed. Male and female mice were orally exposed to three different doses of these PFAS delivered in water and compared to an unexposed group. Daily body weights and in-life observations (appearance, behavior) were recorded throughout the dosing period and urine and feces collected 24-hr

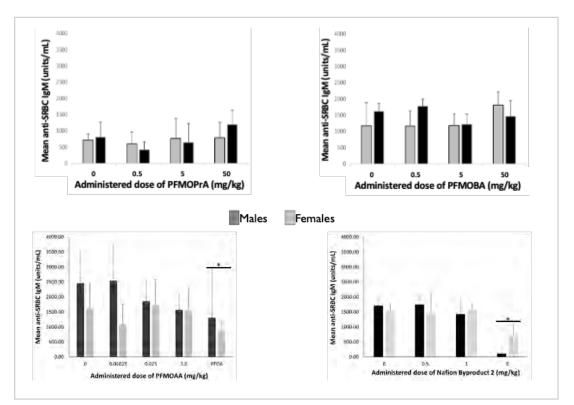
prior to dosing and after 1, 5, and 15 days of dosing. "Vaccinations" were given at 25th day of dosing to stimulate the antibody response.

- After the end of study on day 31, there was evaluation of basic measures of toxicity including organ weights as well as assessments of numbers of cells in immune organs, strength of antibody response, and natural killer (NK) cell cytotoxicity to assess the function of the adaptive and innate immune systems. Other data relevant to understanding PFAS toxicity included liver peroxisomal enzyme activity and liver histology for lipid accumulation. Some biological samples were sent to collaborators for independent analyses, including lungs (Dr. James Bonner at NC State University), brains (Dr. Todd Peterson at UNC-Wilmington), and feces (Dr. Carla Ng at University of Pittsburgh). Analyses of samples by these independent investigators is ongoing.
- Repeat 30-day in vivo studies of PFMOAA (at higher doses than the first study) and Nafion Byproduct 2 (at lower doses than the first study) and two 15-day in vivo studies of a mixture of PFMOAA and Nafion Byproduct 2 also were completed. These additional studies were supported, in part, with funds from another award from the Brody Brothers Foundation. While the initial plan with funds from the Network was to evaluate six different PFAS; funds from this other award were necessary to complete these repeat studies due to increases in animal costs, personnel costs, and other supplies.
- One manuscript on the initial studies with PFMOAA, PFMOPrA, and PFMOBA has been submitted and is under review by the journal *Toxics*. The Nafion Byproduct-2 study is in preparation for submission to *Toxicology*, the PFMOAA repeat study and the PFMOAA-Nafion Byproduct-2 mixtures studies are being analyzed and two separate manuscript submissions are anticipated.

## **Results:**

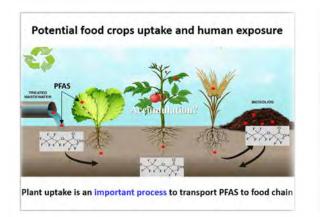
• At the doses administered, PFMOAA, PFMOPrA, and PFMOBA did not appear to produce overt toxicity and only mild immunotoxicity (none to minimal changes to immune cell numbers, NK cell activity, and antibody production) (Fig. 18). However, data from the repeat study of PFMOAA is still being analyzed. The repeat study included doses of PFMOAA that were higher than the first study and consistent with the doses administered for PFMOPrA and PFMOBA.

- At the doses administered in the first study, Nafion Byproduct 2 was overtly toxic and produced profound immunotoxicity. In the repeat study at lower doses, Nafion Byproduct 2 did produce overt toxicity but did induce suppression of the antibody response, which is a robust marker of immunotoxicity.
- The first mixture study of PFMOAA and Nafion Byproduct 2 produced greater overt toxicity than the individual compounds alone and doses were reduced by 10-fold after only three days of dosing males and one day of dosing females. However, the toxicity of the initially higher doses required terminating the study with males early for humane reasons. Immunotoxicological data from the females also was negatively impacted by the mixture overt toxicity. A repeat study with lower doses was conducted and evaluation of those data are ongoing; this lower dose mixture did not produce signs of overt toxicity.



**Figure 18:** Mean antibody responses of male and female mice dosed with PFMOPrA, PFMOBA, PFMOA, or Nafion Byproduct 2 at 4 concentrations (comparison to PFOA shown for PFMOAA).

- 1. Additional studies should be conducted with understudied PFAS that have been detected in NC. With recent additional Collaboratory funding, the following PFAS will be evaluated: 6:2 fluorotelomer sulfonic acid, ADONA, Perfluoropentanoic acid (PFPeA), and Perfluoropentanesulfonic acid (PFPeS).
- 2. Additional mixtures studies need to be conducted to better understand how these PFAS may influence one another since exposures are often to a mixture of PFAS.
- 3. Urinary PFAS concentrations need to be evaluated to estimate biological halflives (blood concentrations were low). This is being conducted by a colleague in the Chemistry Department at ECU.
- 4. Further studies are needed to identify molecular changes associated with antibody suppression in these understudied PFAS compared to changes induced by legacy PFAS.





D. Novel inputs of PFAS into the environment: uptake and distribution of PFAS in crop plants

## **Objective:**

To improve understanding of PFAS uptake and distribution within plant tissues and to explore how soil properties and management strategies may impact PFAS uptake and distribution.

#### **Proposed aims:**

- Measure uptake of PFAS compounds by two plants relevant to Eastern NC agriculture via greenhouse experiments and determine the effects of organic carbon content on PFAS availability by varying compost composition of the soil.
- Investigate the distribution and molecular associations of PFAS in plant tissues.

#### Accomplishments:

• A greenhouse study and sample analysis were completed to determine impact of compost additions on PFAS uptake by lettuce. Lettuce plants were grown in soil containing 0, 5, 10, or 20% compost. Spiking experiments were performed with 10 and 100 nanogram PFAS per gram soil, and samples were processed after 45 days.

- Methods were developed for sample extractions and analysis to measure PFAS (PFMOAA, GenX, PFBS, PFHxS, PFOS, 6:2FTS, 4:2FTS, and 8:2FTS) in lettuce leaves (shoots), roots, pore water, and soil.
- A greenhouse study was conducted to determine PFAS uptake by cucumbers, carrots, celery, and sweet potatoes from contaminated soil. The analyses in the analytical core facility are pending.

## **Results:**

- All PFAS studied were observed in the lettuce leaves.
- The short chain fluoroether acid compounds GenX and PFMOAA are transported to leaves to a greater extent than the legacy compounds PFOS and PFOA (Fig. 19).

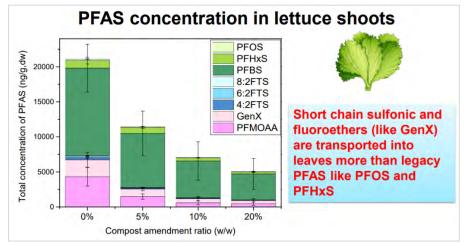


Figure 19: PFAS concentrations in lettuce, determined as nanograms per gram of dry weight

- Adding uncontaminated compost to soil dramatically reduces the uptake of PFAS by lettuce.
- Increasing compost content decreases the soluble PFAS concentration in soil by 68–96% (Fig. 20).

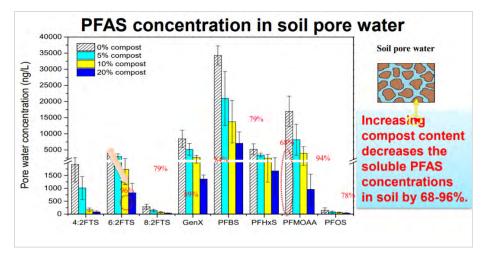


Figure 20: Effect of varying compost composition on PFAS concentrations in soil pore water

- 1. Additional plant uptake studies, including those still in progress are needed to evaluate plant species differences and translocation of PFAS to seed and fruit.
- 2. Additional studies should probe the occurrence of PFAS in other foods.
- 3. Exposure models should incorporate diet in their assessment.
- 4. Biosolids and irrigation water should be evaluated for their possible contribution of PFAS to agricultural products.

Do PFAS in drinking water pose a threat to pregnant women and could they affect the health and function of the placenta?

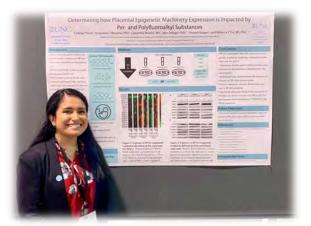


the placenta??





What is the effect of PFAS on placental health and function?



E. Health effects following PFAS exposure: impact of PFAS on human placental health and birth outcomes

## **Objective:**

To begin to understand the question: "do PFAS in drinking water pose a risk to pregnant women and could they affect the health and function of her placenta?"

## **Proposed aims:**

- Measure PFAS levels in placenta samples from pre-term birth cohort.
- Measure PFAS levels in drinking water from participants' homes.
- Measure PFAS response in placental cells in laboratory experiments (in vitro).
  - Assess migration and invasion of trophoblasts (placental cells).
  - Evaluate inflammation-related gene expression.
  - Evaluate invasion-related gene expression.

## Accomplishments:

- Levels of 26 PFAS were monitored in 122 placentas from high-risk pregnancies (UNC Hospital Preterm Biobank Study) and drinking water samples (n=68) from participants were analyzed for 12 PFAS.
- Response of placental cells (trophoblast migration and invasion) to PFAS treatment *in vitro* was measured and cellular pathways examined for altered gene expression (panel of 91 inflammatory genes expressed in the human placenta and involved in preeclampsia, cellular movement, or both and genes regulating invasion of trophoblasts).

## **Results:**

• In the placenta, 11 PFAS were detected in at least one sample; only 4 PFAS were detected above the limit of detection (LOD) in at least 50% of samples (PFOS >> PFHxS > PFUnA > PFHpS) (Fig. 21). None of the PFAS were associated with detrimental pregnancy health outcomes in this UNC-Chapel Hill cohort.

	PFPeS	PFHxS	PFHpS	PFOS	PFHxA	PFOA	PFNA	PFDA	PFUnA	PFTriA	PFTA
Chain length	5	6	7	8	6	8	9	10	11	13	14
%>LOD	31.1	74.6	54.9	99.2	1.6	27.0	21.3	39.3	49.2	29.5	6.6
Maximum	0.035	0.446	0.063	4.87	5.87	1.23	0.494	0.465	0.24	0.336	0.111
Minimum	< 0.005	< 0.033	< 0.008	< 0.001	< 1.32	< 0.290	< 0.148	< 0.030	< 0.033	< 0.050	< 0.049
Median	< 0.005	0.067	0.009	0.48	< 1.45	< 0.315	< 0.163	< 0.031	< 0.031	< 0.057	< 0.054
n	122	122	122	122	122	122	122	122	122	122	122

Figure 21: Detection frequency and concentration ranges of PFAS measured in human placental tissues.

• In drinking water, PFHxA and PFHpA were the most frequently detected, PFHxA and PFPeA had the highest concentrations, and 6 PFAS (PFHxS, PFNA, PFOS, PFDA, PFUdA, and GenX) were not detected (Fig. 22).

PFAS	Limit of Detection (LOD) ng/mL	Number of samples above LOD N (%)	Range of samples above LOD (ng/mL)
PFBA	0.02	2 (2.9%)	0.113-0.140
PFPeA	0.02	9 (13.2%)	0.032-0.350
PFBS	0.02	1 (1.5%)	0.052
PFHxA	0.02	17 (25%)	0.020-0.354
PFHpA	0.02	13 (19.1%)	0.020-0.213
PFOA	0.02	8 (11.8%)	0.022-0.057
PFHxS	0.1	0	-
PFNA	0.1	0	-
PFOS	0.5	0	-
PFDA	0.1	0	-
PFUdA	0.5	0	-
GenX	0.02	0	-

Figure 22: PFAS detection in drinking water of pregnant women in study

• In placental cells, PFOS, PFOA, and GenX decreased the rate of trophoblast migration (27.9%, 19.3%, and 31.2% respectively) and GenX decreased trophoblast invasion ~3-fold over PFOS (37.5% vs. 11.1%) while PFOA had no effect (Fig. 23). These results demonstrate that PFAS inhibit trophoblast migration and invasion and support previous reports of an association between placental PFAS content and the incidence of preeclampsia.

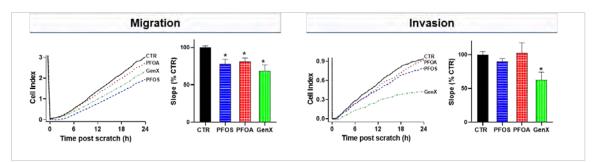
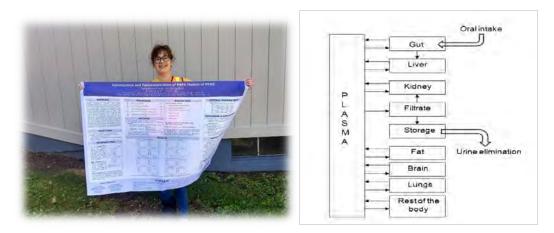


Figure 23: Trophoblast migration and invasion with PFAS treatment

- In placental cells, of the 91 inflammatory genes measured, 23 were significantly altered by one or more PFAS and represented 4 categories: chemokines, chemokine receptors, chemokine ligands, and enzymes. The results suggest that PFAS may modulate placental immune signaling.
- In placental cells, both PFOS and PFOA significantly inhibited transcription of matrix-metalloproteinase 2 (MMP2), and PFOS alone inhibited that of MMP9.
- Overall, these data indicate that in assessing the risk of PFAS, it is necessary to account for the increased susceptibility of their effects during pregnancy. Mechanistic insight gained could serve as the basis of future studies investigating preventative measures against PFAS-induced placental toxicity or identifying risk factors that increase individual susceptibility. Details of this research have been published in *Toxicological Sciences*: <a href="https://doi.org/10.1093/toxsci/kfaa043">https://doi.org/10.1093/toxsci/kfaa043</a> and in *Environmental Toxicology*: <a href="https://doi.org/10.1002/tox.23004">https://doi.org/10.1002/tox.23004</a>.

- 1. Testing for PFAS levels in drinking water among pregnant women in NC.
- 2. Effects of PFAS on trophoblast stem cell differentiation *in vitro* should be investigated, and the mechanistic target of PFAS in trophoblast cells needs to be determined.
- 3. Studies are needed to measure PFAS-induced gene expression changes *ex vivo* using human placental explants.
- 4. Additional studies should be conducted to investigate how PFAS change the molecular communication between trophoblasts and maternal immune cells. This system of interactions is central to regulating trophoblast invasion and may therefore be a critical mechanistic target of environmental toxicants that contribute to preeclampsia.



F. Construction of computer-based predictive models

## **Objective:**

To conduct quantitative analysis of experimental immunotoxicity and systemic toxicity data and construct computer-based models (Reference Dose and PBPK) to support derivation of health goals for measured PFAS.

# **Proposed aims:**

- Perform quantitative analysis of experimental immunotoxicity and systemic toxicity data generated by PFAST Network collaborators, including half-life estimates.
- Construct and apply physiologically-based pharmacokinetic (PBPK) model to predict ADME properties (absorption, distribution, metabolism, excretion) of emerging PFAS.
- Derive Reference Doses (RfDs) from experimental data (in collaboration with the DeWitt lab) using Benchmark Dose Modeling Software (BMDS, US EPA).
- Development of larger scale models to predict movement of emerging PFAS among environmental media.

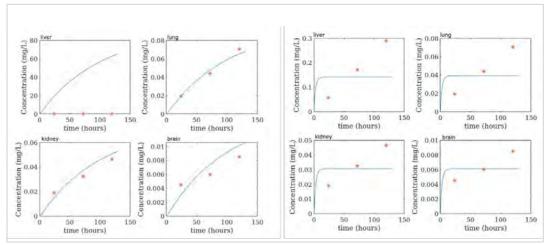
# Accomplishments:

• Examined previously published modeling efforts for PFAS, investigated a PBPK model for PFOS and PFOA, and searched for optimal parameters to fit the model to previously published data.

• Initial experimental data (8/2019) was not conducive to modeling efforts. Recent findings (1/2021) may be more suitable for Benchmark Dose Modeling. Efforts to construct model and analyze data are ongoing.

#### **Results:**

• Students were able to adequately fit previously published PFOS tissue-level concentrations in mice by optimizing the metabolic, resorption, and partition coefficient parameters from an established PBPK model. Results show that the shape of the curve is dependent on the parameterization of the model. Efforts should be extended to a more extensive data set for further investigation (Fig. 24).



**Figure 24**: Predicted tissue level concentrations of PFOS. The red asterisks represent the reported experimental data and the blue line represents the computational prediction based on an optimized PBPK model. These two sets of graphs represent the different shapes that were produced based on initial parameter selection in the optimization process.

• Efforts with Benchmark Dose Modeling are ongoing, with nothing to report at this time.

## **Recommendations:**

1. PBPK modeling efforts could be improved with additional time-course tissuelevel or serum-level data.



https://toxicfreefuture.org/safer-firefighting-foam-gear-drinking-water/

# VI. Collaboratory firefighting foam inventory project

## **Objective:**

To create an inventory of Aqueous Film Forming Foams (AFFF) being used and/or stored at fire stations throughout the state of North Carolina and to develop recommendations and estimated budget for tracking, collection, storage, and disposal of class B firefighting foams (AFFF) containing PFAS.

## **Proposed aims:**

- Work with Chief Deputy State Fire Marshal Robert Roegner and others from the NC Department of Insurance's (NC DOI) Office of the State Fire Marshal (OSFM) to identify county fire marshals and list of contacts for permanent and volunteer fire stations in all 100 North Carolina counties.
- Develop an electronic survey (Qualtrics) for each fire station to complete, providing the requested data such as fire station identifier, manufacturer, lot and product number, expiration date, volume stored, and volume used (where and when) and create instructions for firefighters to facilitate collection of pertinent information for the survey.
- Compile survey results and produce summary report including inventory of AFFF stored or in use, recommendations for collection, storage, and disposal of legacy AFFF, and projected costs.

# Accomplishments:

• An electronic survey (Qualtrics) was created and sent to all 100 North Carolina County Fire Marshals at the end of May 2020 in an attempt to collect relevant

data (fire station identifier, manufacturer, lot and product number, expiration date, volume stored, and volume used) for the state AFFF inventory. An introductory e-mail with a link to the survey and an accompanying set of instructional slides was provided to the county fire marshals to distribute to their respective fire departments.

- As of July 30, 2020 only 100 survey responses had been received, so the project team worked with the Office of the State Fire Marshal to prepare a memo signed by Chief State Fire Marshal Brian Taylor that was e-mailed to the County Marshals in August urging their participation in this state-mandated inventory project.
- Based on feedback from individual fire departments, the survey was redesigned to make completion easier, and follow-up requests were e-mailed to approximately 1200 individual North Carolina Fire Chiefs/Captains in September and again in October asking for their participation by December 2020.
- Data from the AFFF inventory survey have been compiled in a spreadsheet which will be provided to the NC Office of the State Fire Marshal and the NC Department of Environmental Quality and will be made available on the NC PFAS Testing Network website at: <u>https://ncpfastnetwork.com/afff-inventory-project/</u>.

## **Results:**

- There was overall low participation, with many fire chiefs/captains expressing concerns about the study and how the data will be used. Responses, either within the survey or via direct e-mail message to the graduate student assistant, were received from 436 out of a possible 1218 fire departments in North Carolina.
- Although Rescue, EMS, and Military stations with Fire Department ID (FDID) numbers listed in the OSFM directory were included in the survey request, all who responded indicated that they do not store or use AFFF. Therefore, they should not be included in future data collection efforts.
- A total of 230 fire departments responded that they do possess class B AFFF at one or more of their stations and 179 respondents indicated they do not have or use AFFF. A few fire chiefs also asked about plans for collection,

disposal and replacement of unwanted AFFF, and whether funding would be made available to them.

- The data received via the electronic survey was not uniform in terms of the AFFF brand names, locations and volumes of stocks entered and was challenging to summarize, highlighting the need for a better approach to data collection and analysis. Additional analysis of the existing data is needed.
- A separate report required by the NCGA for the Collaboratory Firefighting Foam Inventory project is available on the NC PFAS Testing Network website at: <u>https://ncpfastnetwork.com/afff-inventory-project/</u>.

- 1. An annual review and update of fire departments directory including points of contact is needed to ensure accuracy and facilitate communications.
- 2. A user-friendly tracking system for stations to report AFFF discharges should be developed and maintained by the Collaboratory in partnership with other supporting units (e.g. the UNC Institute for Convergent Science).
- 3. Additional inventory data must be collected from fire departments that did not respond to the survey to better estimate the total amount of PFAScontaining AFFF to be collected and disposed.
- 4. Funding should be provided for "turn-in" or replacement programs that will allow fire departments to more easily dispose of and/or exchange fluorinated AFFF stocks and associated equipment contaminated with PFAS.
- 5. Fluorine-free alternatives to PFAS-containing AFFF are now available from manufacturers and should be used in all firefighting training. A list of recommended products and vendors should be provided to fire stations.
- 6. Baseline biomonitoring of PFAS is highly recommended for NC firefighters exposed to PFAS via AFFF discharge and wearing of protective gear to assess firefighter exposure levels compared to the general public and to determine whether interventions are necessary to ensure occupational safety.

# CHEMICAL SYNTHESIS

All PFAS with carbon chain lengths greater than 2 are anthropogenic (nonnaturally occurring environmental pollutants that result from human activity) and are produced almost exclusively by one of two major manufacturing processes. Electrochemical fluorination (ECF) used since the 1970s produces mixtures of linear and branched PFAS isomers of approx. 70% and 30%, respectively, and Telomerization used since the 1950s, vields exclusively linear compounds. Reports on the synthesis of PFAS in academic literature are disproportionally rare, due primarily to proprietary protections and the fact that many emerging PFAS are unintended by-products. Lack of commercial availability of many PFAS standards, especially those that are newly discovered in the environment, is a significant limitation for researchers performing exposure and toxicity studies and makes laboratory synthesis an important tool for PFAS research. Because PFAS have extremely strong carbon-fluorine bonds and unique chemical-physical properties compared to typical organic compounds familiar to most organic chemists, the synthesis of PFAS standards is a very specialized area. Synthetic Chemistry efforts within the PFAST Network have led to the development of protocols for the synthesis of Nafion byproduct 1, Nafion byproduct 2, and Hydro-EVE acid:

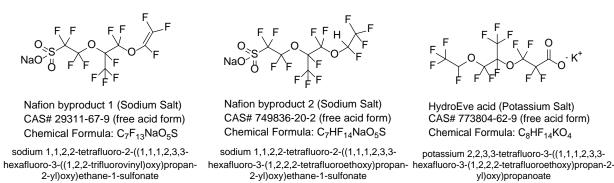


Figure 25: Chemical structures of Nafion byproducts 1 and 2, and Hydro Eve acid.

The novel synthetic strategies for generating these emerging PFAS in gram quantities are described in more detail on the NC PFAST Network website at: <u>https://ncpfastnetwork.com/final-report/</u>.

# COMMUNITY ENGAGEMENT AND COMMUNICATIONS

With increasing public awareness and concern over exposure to PFAS environmental pollutants and the associated effects on wildlife, human health and development, timely and effective communications have been critical to the success of the NC PFAST Network. The Network's Communications team addressed an important need to engage stakeholders such as citizens, grassroots organizations, advocacy groups, educators, clinicians, public utilities, legislators, and state environmental quality and human health agencies with PFAS Network subject matter and technical experts and worked with the scientists to make complex information accessible, understandable, and relevant to the people of North Carolina. The Network also received guidance from an Executive Advisory Committee of academic PFAS experts and valuable feedback from a Community Stakeholders Advisory Committee comprised of community partners actively involved in increasing the collective understanding of PFAS exposures and impacts in North Carolina and who advocate for solutions to protect our environment and health. Notable public events and other significant contributions of the Communications team included:

- The fall 2018 research symposium was held Sep. 28, 2018 at the Washington Duke Inn. The focus was "Emerging Contaminants (including PFAS) in the Ambient Environment: Perspectives to Guide North Carolina's Per- and Polyfluoroalkyl Substances (PFAS) Monitoring Network." The event was well attended with 216 participants representing academia, government, nonprofit and private sector entities. An edited recording of the event is available at: https://www.youtube.com/watch?v=7rdEJFaZoDI&feature=youtu.be.
- The fall **2019 research symposium** was co-hosted with the Research Triangle Environmental Health Collaborative (RTEHC) as a 1.5-day PFAS summit held October 23-24, 2019 at the NC Biotech Center in RTP. The event brought together 154 researchers, elected officials, regulatory agencies, environmental nonprofits, and residents of communities impacted by PFAS contamination to discuss how to limit exposure to PFAS in North Carolina, with a focus on the research occurring in the NC PFAST Network.
- The fall **2020 virtual seminar series** was held in lieu of a third in-person symposium and was presented as 4-part series:
  - (1) Sep. 18, 2020– PFAS in Drinking Water Sources, featuring Detlef Knappe and Helena Mitasova (62 attendees).

- (2) Oct. 9, 2020- PFAS and Contamination Reduction, featuring Morton Barlaz and Mei Sun (62 attendees).
- (3) Oct. 23, 2020– PFAS in Plants and Fish, featuring Owen Duckworth and Scott Belcher (46 attendees).
- (4) Nov. 6, 2020– PFAS and Health (How Toxic are PFAS?), featuring Jamie DeWitt and Rebecca Fry (45 attendees).

Together these webinars reached over 200 participants, and recordings are available at this link: <u>https://ncpfastnetwork.com/resources/</u>.

- Two of 3 planned **Science Cafés** were held at the North Carolina Museum of Natural Sciences in Raleigh (one canceled due to unexpected circumstances).
  - (1) Mar. 21, 2019– "What Have You Been Drinking?" featuring Scott Belcher (114 attendees).
  - (2) Jun. 20, 2019- "Toxic Chemicals and Human Health" featuring Lee Ferguson and Jamie DeWitt (71 attendees).
- **Beer-Reviewed Science** event (similar format to science cafés) was held at the Transfer Food Hall in Raleigh, NC on Jul. 23, 2019 featuring Detlef Knappe and Scott Belcher (~30 attendees).
- An on-line **public forum** sponsored by the North Carolina Coastal Federation and their partners was held on Oct. 22, 2020. This event had 213 attendees including 3 news outlets and several elected officials.
- A **community meeting** at Fayetteville State University was held on Feb. 26, 2020, highlighting network research on food crops and ground water. This evening event was moderated by Jory Weintraub and featured PFAST Network researchers Owen Duckworth, David Genereux, and Jackie MacDonald Gibson. Approximately 70 people were in attendance including several members of the media as well as elected officials.
- The **Duke Science & Society Initiative** Science Communication Monthly Lunchand-Learn Series held on Jan. 22, 2020 at Duke University featured Kathleen Gray and Lee Ferguson who presented "Water, Water Everywhere: Testing North Carolina's Drinking Water and Communicating Risk" (100 attendees).

 $\underline{https://scienceandsociety.duke.edu/engage/events/scicomm-lunch-and-learn/.}$ 

• NC School of Science and Math's Science Day held on October 5, 2019 included a presentation about the PFAST Network to ~40 students to increase PFAS awareness

among the public. Resources were also shared with the School Dean of Sciences to share with environmental sciences teachers.

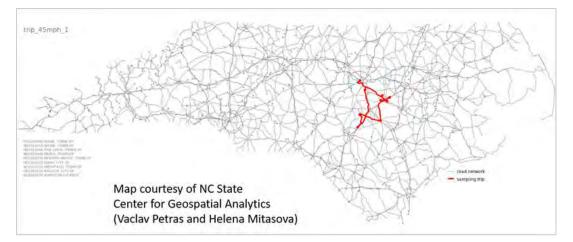
- A **webinar for educators** titled "Per- and Polyfluoroalkyl Substances (PFAS) What are they and how are NC scientists investigating their prevalence in the environment and their potential impacts to humans and wildlife?" was held on Oct. 3, 2019. Network presenters Wanda Bodnar, Jamie DeWitt, and Scott Belcher joined Dana Haine of the UNC Institute for the Environment to provide background about PFAS and to explain how scientists are studying potential health effects of PFAS, impacts of PFAS on ecosystems & wildlife (e.g., bioaccumulation) and what can be done to minimize exposure.
- A **public meeting** was held in Maysville, Jones County, NC on June 13, 2019 to present results of PFAS profiles in water sampling analysis, answer questions, and discuss options for remediation.
- A **public forum** was held on May 31, 2019 at the University of North Carolina Wilmington with the NC Coastal Federation to introduce the PFAST Network projects' objectives and preliminary results.
- An overview of the PFAST Network and associated communications activities was presented at an October 1, 2018 meeting in Raleigh, NC organized by the **League of Municipalities** for its members, which included local governments and water utilities.
- The NC PFAST Network website (https://ncpfastnetwork.com) was developed and released. From launch in Apr. 2019 through Mar. 15, 2021, the website had 7,616 unique users and over 27,000 page views. Team descriptions and other useful resources including monthly newsletters and progress reports, FAQs, infographics and links to results and publications are available.
- **Science communication training** was provided to scientists to enhance their skills for communicating effectively with non-technical audiences.

# DATA SCIENCE AND MANAGEMENT

The research teams of the NC PFAS Testing Network have generated large amounts of heterogeneous data related to sample collection and analysis for the determination of PFAS concentrations in more than a dozen different types of environmental media and biological specimens. The Data Science and Management team which includes members of the Center for Geospatial Analytics (CGA) at NC State University and the Renaissance Computing Institute (RENCI) and School of Information and Library Science (SILS) at UNC Chapel Hill has provided support to each research team for the management and public dissemination of the their PFAS data and results. Specific contributions of the team are summarized below.

#### **Sample Collection:**

• A sampling optimization and routing tool was developed to support sample collection of nearly 400 drinking water sources across the entire state of NC by the research labs based at NC State and Duke Universities over relatively short period time with specific requirements in terms of trip duration, sampling time and a complex structure of water resources. Lack of unique identifiers for each drinking water source (except for the EPA source ID) and uncertainty of which groundwater well would be selected for sampling by each municipality were limiting factors. A procedure had to be developed to match the sampling points with DEQ records using GPS coordinates. The tool was implemented in open source GRASS GIS as module: <u>v.net.tripplanner</u>. One water sampling trip is shown here for illustration:



**Figure 26:** A representative trip from the 27 total trips made in Round 1 of water sampling. Each trip consisted of 6-17 sites over a period of 1-3 days.

• Considerable effort was devoted to identification and geo-referencing the sampling sites, especially those associated with water systems with multiple sources. The geocoding procedure facilitated matching of drinking water sampling locations with DEQ records and improved the accuracy of monitoring results data and mapping. Photo documentation of selected sampling locations across the teams was collected and workflows were developed to create a consistent geo-referenced data set of sampling locations for input into the DataHub. Future development of official unique identifiers for each drinking water source in collaboration with state and federal agencies (e.g. adopt the EPA source ID) would support efficient repeat sampling and aid data management and analysis.

## Data Management:

- Relevant database models were surveyed for potential use for storing the highly heterogeneous Network data and associated metadata. The Observations Data Model2 (ODM2: <u>http://www.odm2.org/</u>) was selected because it provided the requisite level of detail and flexibility for the various data types being generated within the NC PFAST Network. The ODM2 data model was adapted with specialized vocabularies relevant to the PFAST Network to facilitate data integration across research teams. Research teams were also consulted to determine a common PFAS naming convention while allowing for some flexibility and variation to accommodate individual team's needs.
- Data management policies and procedures were established to ensure data integrity, and tools for uploading and tracking data were developed and implemented. Project-relevant data catalogs, data package descriptions, and a workflow and tools catalog were developed, and metadata and document support was also provided. Once verified and released by each team, data are uploaded and stored in a professionally managed relational database with routine backups.

## Data Visualization:

• The current version of the NC PFAST Network DataHub is undergoing final testing and fixes. The team plans to officially launch the DataHub by the end of May. Users will access the DataHub via a link on the NC PFAST Network website under "Data and Tools" and will be able to search for and view data of interest in a variety of ways.

The main entry page (Fig. 27) has an option to search for data by location, and presents a snapshot of recently added data. The DataHub provides a user interface and web-based user experience that facilitates end-use. This includes DataHub look and feel, features, information organization, and documentation.

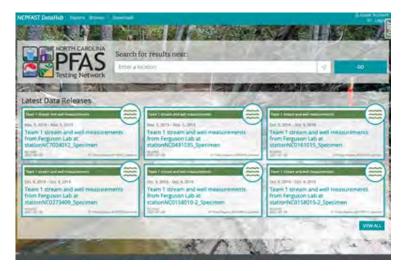


Figure 27: NC PFAST Network DataHub current landing page.

• In addition to the various data search options (by compounds, datasets, or sampling location), the DataHub also provides a map interface (Fig. 28) with graphical elements Fig. 29). Users can see at a glance where research teams have conducted which sampling, and the list of available datasets is displayed beneath the map for the locations shown in the map window.

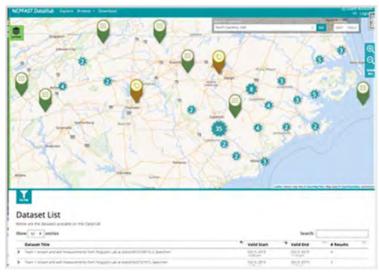


Figure 28: NC PFAST Network DataHub Map Interface.



Fig. 29: Graphical Elements and Color Scheme for NC PFAST Network DataHub

• The map interface allows users to select among viewable layers and to add a data layer of interest on the fly using the GeoJSON protocol. For example, state legislative <u>district boundaries</u> were added as shown in blue in the figure below.

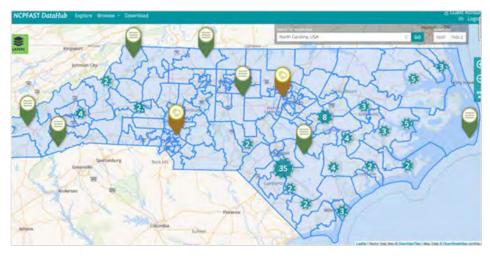


Figure 30: DataHub showing legislative districts added via GeoJSON.

• Results can be viewed in a variety of formats, including a graphical summary view and a table view. Data from the table view is downloadable in a variety of formats.

Result	Compound	ŧ.	Compound Full Name	4	Date To	Value	Unit
10167	Poly(1,1-difluoroethylene/1,1,3,3,3- pentafiuoropropene /tetrafluoroethylene/trifluoromethyl trifluorownyl ether)		Poly(1,1-difluoroethylene/1,1,3,3,3- pertafluoropropene /tetrafluoroethylene/trifluoromethyl trifluorovinyl ether)	1	Aug 13, 2019 12:00 pm	0.12	PEU/100 L
10171	Poly(1,1-difluoroethylene/1,1,3,3,3- pentafluoropropene /tetrafluoroethylene/trifluoromethyl trifluorovnyl ether)		Poly(1,1-difluoroethylene/1,1,3,3,3- pentafluoropropene /tetrafluoroethylene/trifluoromethyl trifluorovinyl ether)		Aug 13, 2019 12:00 pm	1 256	PFU/100
46628	PFOZHVA		Perfluoro-3,5-dioxahexanoic acid		Aug 6, 2019 12:00 pm	1.1	ppt
46735	PFUnDA		Perfluoroundecanoic acid		Jul 16, 2019 12:00 pm	1	ppt

Fig. 31: DataHub table view.

### ACKNOWLEDGEMENTS

The NC PFAS Testing Network would like to recognize and thank the following groups and individuals for their support, insights, and contributions toward the mission of addressing and taking steps to eliminate PFAS exposures in the state of North Carolina.

North Carolina General Assembly North Carolina Policy Collaboratory NC PFAST Network Executive Advisory Committee NC PFAST Network Community Stakeholders Advisory Committee North Carolina Department of Health and Human Services North Carolina Department of Environmental Quality **Division of Water Resources** Division of Air Quality **Division of Waste Management** North Carolina Department of Insurance Office of the State Fire Marshal US EPA Office of Research and Development **NIEHS National Toxicology Program** North Carolina State University **Center for Geospatial Analytics** Center for Human Health and the Environment Department of Civil, Construction, and Environmental Engineering Department of Crop and Soil Sciences Department of Marine, Earth, and Atmospheric Sciences **Department of Biological Sciences** Superfund Center for Environmental and Health Effects of PFAS University of North Carolina at Chapel Hill **Department of Chemistry** 

Department of Environmental Sciences and Engineering
Gillings School of Global Public Health
Institute for the Environment
Renaissance Computing Institute
School of Information and Library Science
UNC Hospital
Duke University
Department of Civil & Environmental Engineering
Nicholas School of the Environment
Pratt School of Engineering
Superfund Research Center
Duke Initiative for Science & Society
University of North Carolina Wilmington
Department of Chemistry & Biochemistry
University of North Carolina Charlotte
Department of Civil & Environmental Engineering
East Carolina University
Brody School of Medicine
Department of Pharmacology ど Toxicology
North Carolina Agricultural and Technical State University
Department of Mathematics
North Carolina Coastal Federation
Clean Air Carolina
North Carolina Haw River Assembly
Research Triangle Environmental Health Collaborative

## APPENDIX I North Carolina General Assembly's Legislations Pertaining to PFAS

### Session Law 2018-5, Sections 13.1.(f)-(l), effective June 12, 2018

### FUNDING TO ADDRESS PER- AND POLY-FLUOROALKYL SUBSTANCES, INCLUDING GENX/USE OF EXPERTISE AND TECHNOLOGY AVAILABLE IN INSTITUTIONS OF HIGHER EDUCATION LOCATED WITHIN THE STATE

**SECTION 13.1.(f)** The General Assembly finds that (i) per- and poly-fluoroalkyl substances (PFAS), including the chemical known as "GenX" (CAS registry number 62037-80-3 or 13252-13-6), are present in multiple watersheds in the State, and impair drinking water and (ii) these contaminants have been discovered largely through academic research not through systematic water quality monitoring programs operated by the Department of Environmental Quality or other State or federal agencies. The General Assembly finds that the profound, extensive, and nationally recognized faculty expertise, technology, and instrumentation existing within the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions of higher education located throughout the State should be maximally utilized to address the occurrence of PFAS, including GenX, in drinking water resources.

SECTION 13.1.(g) The North Carolina Policy Collaboratory at the University of North Carolina at Chapel Hill (Collaboratory) shall identify faculty expertise, technology, and instrumentation, including mass spectrometers, located within institutions of higher education in the State, including the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions, and coordinate these faculty and resources to conduct nontargeted analysis for PFAS, including GenX, at all public water supply surface water intakes and one public water supply well selected by each municipal water system that operates groundwater wells for public drinking water supplies as identified by the Department of Environmental Quality, to establish a water quality baseline for all sampling sites. The Collaboratory, in consultation with the participating institutions of higher education, shall establish a protocol for the baseline testing required by this subsection, as well as a protocol for periodic retesting of the municipal intakes and additional public water supply wells. No later than December 1, 2019, Collaboratory shall report the results of such sampling by identifying chemical families detected at each intake to the Environmental Review Commission, the Department of Environmental Quality, the Department of Health and Human Services, and the United States Environmental Protection Agency.

**SECTION 13.1.(h)** Beginning October 1, 2018, the Collaboratory shall report no less than quarterly to the Environmental Review Commission, the Department of Environmental Quality, and the Department of Health and Human Services on all activities conducted pursuant to this section, including any findings and recommendations for any steps the Department of Environmental Quality, the Department of Health and Human Services, the General Assembly, or any other unit of government should take in order to address the impacts of PFAS, including GenX, on surface water and groundwater quality, as well as air quality in the State.

**SECTION 13.1.(i)** Five million thirteen thousand dollars (\$5,013,000) of the funds appropriated in this act for the 2018-2019 fiscal year to the Board of Governors of The University of North Carolina shall be allocated to the Collaboratory to manage and implement the requirements of this section, which shall include distribution to the Collaboratory and participating institutions of higher education (i) to cover costs incurred as a result of activities conducted pursuant to this section, (ii) for acquisition or modification of essential scientific instruments, or (iii) for payments of costs for sample collection and analysis, training or hiring of research staff and other personnel, method development activities, and data management, including dissemination of relevant data to stakeholders. No overhead shall be taken from these funds from the participating institutions that receive any portion of these funds. Funds appropriated by this section shall not revert but shall remain available for nonrecurring expenses.

**SECTION 13.1.(j)** The Collaboratory should pursue relevant public and private funding opportunities that may be available to address the impacts of PFAS, including GenX, on surface water and groundwater quality, as well as air quality, in order to leverage funds appropriated by this section, or any other funds provided to the Collaboratory, including the Challenge Grant authorized in Section 27.5 of S.L. 2016-94, as amended by Section 10.4(a) of S.L. 2017-57.

**SECTION 13.1.(k)** In the event that the United States Environmental Protection Agency no longer provides access to its analytical instrumentation at no cost to the State for water quality sampling analysis related to per- and poly-fluoroalkyl substances (PFAS), including the chemical known as "GenX" (CAS registry number 62037-80-3 or 13252-13-6), or if the Department of Environmental Quality determines that such analysis is not being performed in a sufficiently timely manner, the Collaboratory shall coordinate such analysis in the most cost-effective manner using relevant faculty expertise, technology, and instrumentation, including mass spectrometers, existing throughout institutions of higher education located throughout the State, until such time as the Department of Environmental Quality is able to perform such analysis with instrumentation acquired pursuant to subsection (q) of this section. The Collaboratory, in consultation with the Department and relevant experts across institutions of higher education in the State, including the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions, shall establish a protocol for delivery of such samples taken by the Department to the entity designated to perform analysis of the samples, chain of custody protocols, and other matters to

ensure proper handling and processing of the samples, which protocols shall be subject to approval by the United States Environmental Protection Agency, if such approval is required pursuant to authority delegated from the United States Environmental Protection Agency to the Department to administer federal environmental law.

**SECTION 13.1.(I)** The Collaboratory shall identify faculty expertise within institutions of higher education in the State, including the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions, and use technology and instrumentation existing throughout the institutions to conduct the following research (i) develop quantitative models to predict which private wells are most at risk of contamination from the discharge of PFAS, including GenX; (ii) test the performance of relevant technologies in removing such compounds; and (iii) study the air emissions and atmospheric deposition of PFAS, including GenX. In addition, Collaboratory may, using relevant faculty expertise, technology, and instrumentation existing throughout institutions identified, evaluate other research opportunities and conduct such research for improved water quality sampling and analyses techniques, data interpretation, and potential mitigation measures that may be necessary, with respect to the discharge of PFAS, including GenX.

### Session Law 2019-241, Sections 7.(a)-(d), effective Nov. 6, 2019

## AN ACT... TO AMEND CERTAIN REPORTS OF THE NORTH CAROLINA POLICY COLLABORATORY TO THE GENERAL ASSEMBLY...

### COLLABORATORY/FIREFIGHTING FOAM

**SECTION 7.(a)** The North Carolina Policy Collaboratory at the University of North Carolina at Chapel Hill (Collaboratory) shall create an inventory of aqueous film-forming foam (AFFF) used or stored by fire departments in North Carolina operated, managed, or overseen by units of local government, including those located at or serving airports. This inventory shall include, at a minimum, the following:

(1) The name and address of each fire department that owns or otherwise has on the premises of a fire station a firefighting vehicle that carries AFFF or a storage tank or other vessel for AFFF.

(2) The volume, trade name, and CAS number of AFFF used by each department in 2018 for fighting fires or firefighter training.

(3) The number of firefighting vehicles carrying AFFF and the volume of AFFF carried by each vehicle.

(4) Each fire department's annual cost of acquiring AFFF and last known purchases of AFFF.

(5) The volume, trade name, and CAS number of AFFF stored by each fire department or unit of local government for firefighting use and the portion of these AFFFs that are no longer utilized and could be removed from inventory for disposal.

(6) Other data deemed relevant by the Collaboratory to establish a statewide inventory of AFFF used for fighting fires or firefighter training.

The Office of the State Fire Marshal of the Department of Insurance and all units of local government shall provide any assistance requested by the Collaboratory to acquire and compile the data required by this section.

**SECTION 7.(b)** The North Carolina Policy Collaboratory at the University of North Carolina at Chapel Hill (Collaboratory) shall develop a proposal for identifying and collecting AFFF that is expired or no longer needed or wanted by each fire department in North Carolina operated, managed, or overseen by units of local government, including those located at or serving airports. This proposal should include recommendations on which State agency or agencies could oversee such a collection effort and cost estimates on this collection, stockpiling, and disposal. The Department of Insurance Office of the State Fire Marshal, the Department of Environmental Quality, the Department of Health and Human Services, and the Department of Public Safety shall provide any assistance requested by the Collaboratory to acquire and compile the data required by this section.

**SECTION 7.(c)** The Collaboratory shall submit an interim report with the results of the studies required by subsections (a) and (b) of this section no later than April 1, 2020, and a final report no later than October 15, 2020, to the Joint Legislative Oversight Committee on Agriculture and Natural and Economic Resources and the Environmental Review Commission.

**SECTION 7.(d)** Section 13.1(g) of S.L. 2018-5 reads as rewritten:

"SECTION 13.1.(g) The North Carolina Policy Collaboratory at the University of North Carolina at Chapel Hill (Collaboratory) shall identify faculty expertise, technology, and instrumentation, including mass spectrometers, located within institutions of higher education in the State, including the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions, and coordinate these faculty and resources to conduct nontargeted analysis for PFAS, including GenX, at all public water supply surface water intakes and one public water supply well selected by each municipal water system that operates groundwater wells for public drinking water supplies as identified by the Department of Environmental Quality, to establish a water quality baseline for all sampling sites. The Collaboratory, in consultation with the participating institutions of higher education, shall establish a protocol for the baseline testing required by this subsection, as well as a protocol for periodic retesting of the municipal intakes and additional public water supply wells. No later than December 1, 2019, October 15, 2020, the Collaboratory shall report the results of such sampling by identifying chemical families detected at each intake to the Joint Legislative Oversight Committee on Agriculture and Natural and

<u>Economic Resources</u>, the Environmental Review Commission, the Department of Environmental Quality, the Department of Health and Human Services, and the United States Environmental Protection Agency."

### Session Law 2020-74, Section 8.(a), effective July 1, 2020

## AN ACT TO PROVIDE FURTHER REGULATORY RELIEF TO THE CITIZENS OF NORTH CAROLINA.

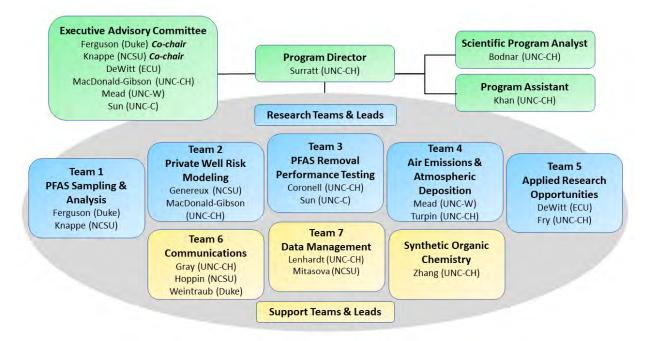
### COLLABORATORY REPORTING CHANGES

**SECTION 8.(a)** Section 13.1(g) of S.L. 2018-5, as amended by Section 7(d) of S.L. 2019-241, reads as rewritten:

"SECTION 13.1.(g) The North Carolina Policy Collaboratory at the University of North Carolina at Chapel Hill (Collaboratory) shall identify faculty expertise, technology, and instrumentation, including mass spectrometers, located within institutions of higher education in the State, including the Universities of North Carolina at Chapel Hill and Wilmington, North Carolina State University, North Carolina A&T State University, Duke University, and other public and private institutions, and coordinate these faculty and resources to conduct nontargeted analysis for PFAS, including GenX, at all public water supply surface water intakes and one public water supply well selected by each municipal water system that operates groundwater wells for public drinking water supplies as identified by the Department of Environmental Quality, to establish a water quality baseline for all sampling sites. The Collaboratory, in consultation with the participating institutions of higher education, shall establish a protocol for the baseline testing required by this subsection, as well as a protocol for periodic retesting of the municipal intakes and additional public water supply wells. No later than October 15, 2020, April 15, 2021, the Collaboratory shall report the results of such sampling by identifying chemical families detected at each intake to the Joint Legislative Oversight Committee on Agriculture and Natural and Economic Resources, the Environmental Review Commission, the Department of Environmental Quality, the Department of Health and Human Services, and the United States Environmental Protection Agency."

### APPENDIX II

### THE NC PFAST NETWORK ORGANIZATION



### LIST OF MEMBERS

PROGRAM MANAGEMENT		
Name	Role	Institution
Jason D. Surratt, PhD	Director	UNCCH
Wanda Bodnar, PhD	Scientific Program Analyst	UNCCH
Manal Khan, MPA	Program Coordinator	UNCCH
Erin Hong, DDS, MS	Grad Student Temp	UNCCH
Hope Thomson	Grad Research Assistant	UNCCH
TEAM 1		
Name	Role	Institution
Detlef Knappe, PhD	Co-Lead	NCSU
Lee Ferguson, PhD	Co-Lead	Duke
Mei Sun, PhD	Co-PI	UNCC
Yuling Han, PhD	Postdoc	UNCC
Abigail Joyce, PhD	Research Scientist	Duke
Gordon Getzinger, PhD	Cheminformatics Scientist	Duke
Patrick Faught	Technician	Duke

Noelle DeStefano, PhD	Postdoc	NCSU
Rebecca Weed, PhD	Research Scientist	NCSU
Kasia Grzebyk	Technician	NCSU/Duke
TEAM 2		
Name	Role	Institution
David Genereux, PhD	Co-Lead	NCSU
Jackie MacDonald Gibson, PhD	Co-Lead	UNCCH
Detlef Knappe, PhD	Collaborator	NCSU
Marie-Amélie Pétré, PhD	Postdoc	NCSU
Javad Roostaei, PhD	Postdoc	UNCCH
Sandrine Duboscq	Grad Student	NCSU
Lydia Koropeckyj-Cox	Grad Student	NCSU
Riley Mulhern	Grad Student	UNCCH
TEAM 3		
Name	Role	Institution
Orlando Coronell, PhD	Co-Lead	UNCCH
Mei Sun, PhD	Co-Lead	UNCC
Detlef Knappe, PhD	Co-Investigator	NCSU
Frank Leibfarth, PhD	Co-Investigator	UNCCH
Heather Stapleton, PhD	Co-Investigator	Duke
Kasia Grzebyk	Grad Student	UNCCH
Mikayla Armstrong	Grad Student	UNCCH
Guan Pin (Nick) Chew, PhD	Postdoc	UNCCH
Vivek Pulikkal	Grad Student	UNCC
Yen-Ling Liu, PhD	Postdoc	UNCC
Zachary Hopkins	Grad Student	NCSU
Lan Cheng	Grad Student	NCSU
Rebecca Weed, PhD	Research Scientist	NCSU
Elango Kumarasamy, PhD	Postdoc	NCSU
Robert Johnson	Grad Student	NCSU
George Tait	Research Technician	Duke
David Bollinger	Research Technician	Duke
Sharon Zhang	Research Associate	Duke
Kate Hoffman, PhD	Research Professor	Duke
TEAM 4		
Name	Role	Institution
Ralph Mead, PhD	Co-Lead	UNCW
Barbara J. Turpin, PhD	Co-Lead	UNCCH
G. Brooks Avery, PhD	Investigator	UNCW
Robert Kieber, PhD	Investigator	UNCW

Steve Skrabal, PhD	Investigator	UNCW
Karsten Baumann, PhD	Investigator	UNCCH
Mei Sun, PhD	Investigator	UNCCH
Jason D. Surratt, PhD	Investigator	UNCCH
Joan Willey, PhD	Investigator	UNCW
Megumi Shimizu, PhD	Postdoc	UNCW
Jiaqi Zhou, PhD	Postdoc	UNCCH
Rachel Mott	Grad Student	UNCW
Isabel Srivoraphan	Undergrad Student Assistant	UNCC
Dave Tilley	Undergrad Student Assistant	UNCC
Samuel Vance	Undergrad Student Assistant	ECU
Mark Ibrahim	Undergrad Student Assistant	ECU
Jeffery Ayala	Undergrad Student Assistant	ECU
TEAM 5A		
Name	Role	Institution
Morton Barlaz, PhD	Co-Lead	NCSU
Jean-Rene Thelusmond, PhD	Postdoc	NCSU
James Levis, PhD	Investigator	NCSU
TEAM 5B		
Name	Role	Institution
Scott Belcher, PhD	Co-Lead	NCSU
Theresa Guillette, PhD	Postdoc	NCSU
Matthew Guillette, PhD	Consultant	NCSU
Madison Polera	Grad Student	NCSU
TEAM 5C		
Name	Role	Institution
Jamie DeWitt, PhD	Co-Lead	ECU
Tracey Woodlief, PhD	Postdoc	ECU
Samuel Vance	Grad Student	ECU
Kathleen Ferris	Undergrad Student	ECU
Emma Tobin	Grad Student	ECU
Jeffery Ayala	Undergrad Student	ECU
Mark Ibrahim	Undergrad Student	ECU
TEAM 5D		
Name	Role	Institution
Owen Duckworth, PhD	Co-Lead	NCSU
Stephen Broome, PhD	Co-Lead	NCSU
Detlef Knappe, PhD	Co-Lead	NCSU
Yuanbo Li, PhD	Postdoc	NCSU
Alison Plumbley	Undergrad Student	NCSU

Cecile Zhi, PhD	Postdoc	NCSU	
Sarah Doydora, PhD	Postdoc	NCSU	
Ying Ding	Undergrad Student	NCSU	
TEAM 5E			
Name	Role	Institution	
Rebecca Fry, PhD	Co-Lead	UNCCH	
Tracy Manuck, MD, MS	Co-Lead	UNCCH	
Matthew Lockett, PhD	Co-Lead	UNCCH	
Stephanie Sun	Clinical Research Assistant	UNCCH	
Jacqueline Bangma, PhD	Postdoc	UNCCH	
Martha Scott Tomlinson, PhD	Postdoc	UNCCH	
John Szilagyi, PhD	Postdoc	UNCCH	
Lauren Eaves	Grad Student	UNCCH	
Kirsi Oldenburg	Undergrad Student	UNCCH	
Aja Crayton	Work Study Student	UNCCH	
TEAM 5F			
Name	Role	Institution	
Nick Luke, PhD	Lead	NC A&T	
Jarel McFadden	Undergrad REU Participant	NC A&T	
Ilana Goldin	Undergrad REU Participant	Mt. Holyoke College	
TEAM 6			
Name	Role	Institution	
Kathleen Gray, PhD	Co-Lead	UNCCH	
Jane Hoppin, ScD	Co-Lead	NCSU	
Jory Weintraub, PhD	Co-Lead	Duke	
Ariana Eily, PhD	Postdoc	Duke	
Karl Bates	Media Contact	Duke	
Katlyn May	Community Engagement	NCSU	
Tracey Peake, MA	Media Contact	NCSU	
Marisa Incremona, MA	Science Communicator	NCSU	
Nicole Wilkerson	Media Contact	NCSU	
Caylen Best	Undergrad Student	NCSU	
Victoria Triana	Research Assistant	UNCCH	
Amanda Crowe	Media Contact	UNCCH	
Megan Rodgers	Research Assistant	UNCCH	
TEAM 7			
Name	Role	Institution	
Chris Lenhardt	Co-Lead	UNCCH/RENCI	
Helena Mitasova, PhD	Co-Lead	NCSU/CGA	
Tielena Mittasova, Tilb	eo Leua	11050/0011	

James McManus	Developer	UNCCH/RENCI	
Patrick Patton	Project Manager	UNCCH/RENCI	
Zachary Arcaro	Geospatial Data Tech.	NCSU/CGA	
Arcot Rajasekar, PhD	Information Scientist	UNCCH/SILS	
Mohammad Jarrahi, PhD	Information Scientist	UNCCH/SILS	
Praveen Wunnava	Grad Student	UNCCH/SILS	
Eliscia Kinder	Grad Student	UNCCH/SILS	
Tripp Tuttle	Grad Student	UNCCH/SILS	
Blake Baines	Grad Student	NCSU/CGA	
Stacie Reckling	Grad Student	NCSU/CGA	
Vaclav Petras, PhD	Software Engineer	NCSU/CGA	
CHEMISTRY SUPPORT			
Zhenfa Zhang, PhD	Synthetic Organic Chemist	UNCCH	







4 North Carolina Agricultural and Technical State University

## APPENDIX III PFAS TARGETED ANALYTES

Abbreviation	Analyte Chemical Name	CAS #			
Perfluoroalkylcarboxylic acids					
PFBA	Perfluorobutanoic acid	375-22-4			
PFPeA	Perfluoropentanoic acid	2706-90-3			
PFHxA	Perfluorohexanoic acid	307-24-4			
PFHpA	Perfluoroheptanoic acid	375-85-9			
PFOA	Perfluorooctanoic acid	335-67-1			
PFNA	Perfluorononanoic acid	375-95-1			
PFDA	Perfluorodecanoic acid	335-76-2			
PFUnA	Perfluoroundecanoic acid	2058-94-8			
PFDoDA	Perfluorododecanoic acid	307-55-1			
PFTrDA	Perfluorotridecanoic acid	72629-94-8			
PFTeDA	Perfluorotetradecanoic acid	376-06-7			
PFHxDA	Perfluorohexadecanoic acid	67905-19-5			
	Perfluoroalkylsulfonic acids	•			
PFBS	Perfluorobutanesulfonic acid	375-73-5			
PFPeS	Perfluoropentanesulfonic acid	2706-91-4			
PFHxS	Perfluorohexanesulfonic acid	355-46-4			
PFHpS	Perfluoroheptanesulfonic acid	375-92-8			
PFOS	Perfluorooctanesulfonic acid	1763-23-1			
PFNS	Perfluorononanesulfonic acid	68259-12-1			
PFDS	Perfluorodecanesulfonic acid	335-77-3			
PFDoS	Perfluorododecanesulfonic acid	79780-39-5			
	Perfluoroalkylsulfonamides				
NEtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6			
NMeFOSAA	N-methyl perfluorooctanesulfonamidoacetic acid	2355-31-9			
PFOSA	Perfluorooctane sulfonamide	754-91-6			
NEtFOSE	N-ethylperfluorooctane sulfamidoethanol	1691-99-2			
NMeFOSE	N-methylperfluorooctane sulfamidoethanol	24448-09-7			
NEtFOSA	N-ethylperfluorooctane sulfamide	4151-50-2			
NMeFOSA	N-methylperfluorooctane sulfamide	31506-32-8			
	Fluorotelomer sulfonic acids	- -			
4:2 PFS (4:2 FTS)	4:2 Fluorotelomer sulfonic acid	757124-22-4			

6:2 PFS (6:2 FTS)	6:2 Fluorotelomer sulfonic acid	27619-97-2
8:2 PFS (8:2 FTS)	8:2 Fluorotelomer sulfonic acid	39108-34-4
10:2 PFS (10:2 FTS)	10:2 Fluorotelomer sulfonic acid	120226-60-0
	Perfluoroalkyl ether carboxylic and sulfonic acids	
HFPO-DA (GenX)	Perfluoro-2-propoxypropanoic acid	13252-13-6
ADONA	Dodecafluoro-3H-4,8-dioxanonanoic acid	958445-44-8
F-53B (Major)	Potassium-9-chlorohexadecafluoro-3-oxanonane-1- sulfonate	73606-19-6
F-53B (Minor)	Potassium-11-chloroeicosafluoro-3-oxanonane-1- sulfonate	83329-89-9
PFMOAA	Perfluoro-2-methoxyacetic acid	674-13-5
PMPA	Perfluoro-2-methoxypropanoic acid	13140-29-9
PEPA	Perfluoro-2-ethoxypropanoic acid	267239-61-2
PFO2HxA	Perfluoro(3,5-dioxahexanoic) acid	39492-88-1
PFO3OA	Perfluoro(3,5,7-trioxaoctanoic) acid	39492-89-2
PFO4DA	Perfluoro(3,5,7,9-tetraoxadecanoic) acid	39492-90-5
PFO5DoDA	Perfluoro(3,5,7,9,11-pentaoxadodecanoic) acid	39492-91-6
Nafion by-product 1	Ethanesulfonic acid, 2-[1-[difluoro[(1,2,2- trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]- 1,1,2,2-tetrafluoro-	29311-67-9
Nafion by-product 2	Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2- tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]- 1,1,2,2-tetrafluoro-	749836-20-2
Nafion by-product 4	2,2,3,3,4,5,5,5-4-(1,1,2,2-tetrafluoro-2- sulfoethoxy)pentanoic acid	2416366-18-0
Hydro-EVE acid	Propanoic acid, 3-[1-[difluoro(1,2,2,2- tetrafluoroethoxy)methyl-1,2,2,2-tetrafluoroethoxy]- 2,2,3,3-tetrafluoro-	773804-62-9
NVHOS	1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonic acid	1132933-86-8
Zwitter	ions (contain both positively and negatively charged groups)	
N-AP-FHxSA	N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexane- sulfonamide	50598-28-2
N-TAmP-FHxSA	N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]- N,N,N-trimethylammonium	38850-51-0
N-CMAmP-6:2FOSA (6:2 FTAB)	N-(carboxymethyl)-N,N-dimethyl-N-[3-(1H,1H,2H,2H- perfluoro-1-octanesulfonamido)propan-1-yl]ammonium	34455-29-3

### APPENDIX IV

### LIST OF SCIENTIFIC PEER-REVIEWED PUBLICATIONS

# Note: List of oral and poster presentations is available on the NC PFAST Network website at: <u>https://ncpfastnetwork.com/final-report/</u>

Environmental Science & Technology Letters (February 2020)

Assessing the Effectiveness of Point-of-Use Residential Drinking Water Filters for Perfluoroalkyl Substances (PFASs)

Nicholas J. Herkert, John Merrill, Cara Peters, David Bollinger, Sharon Zhang, Kate Hoffman, P. Lee Ferguson, Detlef R. U. Knappe, and Heather M. Stapleton. https://dx.doi.org/10.1021/acs.estlett.0c00004

### ACS Central Science (February 2020)

**Ionic Fluorogels for Remediation of Per- and Polyfluorinated Alkyl Substances from Water** Elango Kumarasamy, Irene M. Manning, Leonard B. Collins, Orlando Coronell, and Frank A. Leibfarth.

https://dx.doi.org/10.1021/acscentsci.9b01224

### Environment International (March 2020)

**Elevated levels of per- and polyfluoroalkyl substances in Cape Fear River Striped Bass** (*Morone saxatilis*) are associated with biomarkers of altered immune and liver function T. C. Guillette, James McCord, Matthew Guillette, M. E. Polera, Kyle T. Rachels, Clint Morgeson, Nadine Kotlarz, Detlef R. U. Knappe, Benjamin J. Reading, Mark Strynar, and Scott M. Belcher.

https://doi.org/10.1016/j.envint.2019.105358

Toxicological Sciences (June 2020)

Per- and Polyfluoroalkyl Substances Differentially Inhibit Placental Trophoblast Migration and Invasion In Vitro

John T. Szilagyi, Anastasia N. Freedman, Stewart L. Kepper, Arjun M. Keshava, Jackie T. Bangma, and Rebecca C. Fry.

https://doi.org/10.1093/toxsci/kfaa043

### Environmental Toxicology (August 2020)

An assessment of serum-dependent impacts on intracellular accumulation and genomic response of per- and polyfluoroalkyl substances in a placental trophoblast model Jacqueline Bangma, John Szilagyi, Bevin E. Blake, Cinthya Plazas, Stewart Kepper, Suzanne E. Fenton, and Rebecca C. Fry. https://doi.org/10.1002/tox.23004 Environmental Toxicology and Chemistry (November 2020)

## PFAS Exposure Pathways for Humans and Wildlife: A Synthesis of Current Knowledge and Key Gaps in Understanding

Amila O. De Silva, James M. Armitage, Thomas A. Bruton, Clifton Dassuncao, Wendy Heiger-Bernays, Xindi C. Hu, Anna Kärrman, Barry Kelly, Carla Ng, Anna Robuck, Mei Sun, Thomas F. Webster, and Elsie M. Sunderland.

https://doi.org/10.1002/etc.4935

Journal of Hazardous Materials (January 2021)

## Predicting the risk of GenX contamination in private well water using a machine-learned Bayesian network model

Javad Roostaei, Sarah Colley, Riley Mulhern, Andrew A. May, and Jacqueline MacDonald Gibson.

https://doi.org/10.1016/j.jhazmat.2021.125075

### Analytical Chemistry (January 2021)

Structure Database and In Silico Spectral Library for Comprehensive Suspect Screening of Per- and Polyfluoroalkyl Substances (PFASs) in Environmental Media by High-resolution Mass Spectrometry

Gordon J. Getzinger, Christopher P. Higgins and P. Lee Ferguson. https://doi.org/10.1021/acs.analchem.0c04109

### Environmental Science: Processes & Impacts (March 2021)

PFOS Dominates PFAS Composition in Ambient Fine Particulate Matter (PM<sub>2.5</sub>) Collected Across North Carolina Nearly 20 Years After the End of Its US Production Jiaqi Zhou, Karsten Baumann, Ralph N. Mead, Stephen A. Skrabal, Robert J. Kieber, Gene Avery, Megumi Shimizu, Jamie C. DeWitt, Mei Sun, Samuel A Vance, Wanda Bodnar, Zhenfa Zhang, Leonard B. Collins, Jason D. Surratt, and Barbara J. Turpin. https://doi.org/10.1039/D0EM00497A

Environmental Science & Technology (April 2021)

### Per- and Polyfluoroalkyl Substance (PFAS) Transport from Groundwater to Streams near a PFAS Manufacturing Facility in North Carolina, USA

Marie-Amélie Pétré, David P. Genereux, Lydia Koropeckyj-Cox, Detlef R.U. Knappe, Sandrine Duboscq, Troy E. Gilmore, and Zachary R. Hopkins. https://doi.org/10.1021/acs.est.0c07978

https://doi.org/10.1021/acs.est.0c0/9/

### ACS ES&T Water (April 2021)

High-Throughput Trace-Level Suspect Screening for Per- and Polyfluoroalkyl Substances in Environmental Waters by Peak-Focusing Online Solid Phase Extraction and High-Resolution Mass Spectrometry

Gordon J. Getzinger and P. Lee Ferguson. https://doi.org/10.1021/acsestwater.0c00309

#### Environmental Science & Technology Letters (April 2021)

## Atmospheric deposition and annual flux of legacy perfluoroalkyl substances and replacement perfluoroalkyl ether carboxylic acids in Wilmington NC, USA

Megumi S. Shimizu, Rachael Mott, Ariel Potter, Jiaqi Zhou, Karsten Baumann, Jason D. Surratt, Barbara Turpin, G. Brooks Avery, Jennifer Harfmann, Robert J. Kieber, Ralph N. Mead, Stephen A. Skrabal, and Joan D. Willey.

https://pubs.acs.org/doi/10.1021/acs.estlett.1c00251

Environmental Science & Technology Letters (submitted)

### Per- and Polyfluoroalkyl Substances (PFASs) in Airborne Particulate Matter (PM<sub>2.0</sub>) Emitted During Floor Waxing

Jiaqi Zhou, Karsten Baumann, Naomi Chang, Glenn Morrison, Wanda Bodnar, Zhenfa Zhang, Joanna Atkins, Jason D. Surratt, and Barbara J. Turpin.

#### Atmospheric Environment (in preparation)

## Atmospheric Wet depositional Flux of Per- and polyfluoroalkyl Substance during Hurricanes

Megumi S. Shimizu, Rachael Mott, Ariel Potter, Jiaqi Zhou, Karsten Baumann, Jason D. Surratt, Barbara J. Turpin, G. Brooks Avery, Jennifer Harfmann, Robert J. Kieber, Ralph N. Mead, and Stephen A. Skrabal.

AWWA Water Science (in preparation)

# Predicting removal of per- and polyfluoroalkyl substances in field-scale granular activated carbon adsorbers from rapid small-scale column tests

Zachary R. Hopkins and Detlef R.U. Knappe.

#### Journal TBD (in preparation)

**Per- and polyfluoroalkyl Substances (PFAS) in Airborne Particles Near a Manufacturing Plant** 

Jiaqi Zhou, Karsten Baumann, John Offenberg, Ralph N. Mead, Wanda Bodnar, Zhenfa Zhang, Jason D. Surratt, and Barbara J. Turpin.

### APPENDIX V

### ADDITIONAL FUNDING RECEIVED FOR PFAS RESEARCH

Supplementing and leveraging the state appropriation to the NC Policy Collaboratory for the NC PFAS Testing Network, the following grants were received by Network researchers (\*) for additional PFAS research.

Morton A. Barlaz\*, Jennifer A. Field and Stacy Simonich, "Characterization and Quantification of per- and polyfluoroalkyl substances in landfill gas and estimate of emissions from US Landfills," U.S. EPA, 9/19 – 8/22, *\$419,992 to NCSU out of \$900,000 total* 

Jacqueline MacDonald Gibson\* and Jennifer Redmon, "Predicting and Communicating PFAS Exposure Risks from Rural Private Wells," U.S. EPA Science to Achieve Results (STAR) Program, 9/1/2020 – 8/27/2023, *\$1,584,420* 

Jamie DeWitt\*, "Do Per- and Polyfluoroalkyl Substances Found in the Cape Fear River of North Carolina Pose a Risk to the Immune System?" Brody Brothers Endowment, 1/1/20-12/31/21, *\$32,000* 

Carolyn Mattingly, Detlef Knappe\*, Jane Hoppin\*, Suzanne Lea, Jamie DeWitt\*, Scott Belcher\*, Mort Barlaz\*, et al, "Center for Environmental and Health Effects of PFAS," NIEHS Superfund Research Program, 2/28/20–2/27/25, *\$*7,408,011

Frank Leibfarth\* and Orlando Coronell\*, "Ionic Fluorogels as a Flow-Through Resin Technology for PFAS Remediation from Water," NC Policy Collaboratory and UNC Institute for Convergent Science, 3/1/20-6/30/22, *\$225,000* 

Mei Sun\*, Frank Leibfarth\*, Jinyong Liu and Jia Niu, "Passive Samplers for Per- and Polyfluoroalkyl Substances with Innovative Sorbents," U.S. DOD, 5/1/20-7/31/24, *\$887,556* 

Barbara J. Turpin\*, Glenn Morrison\*, Jason D. Surratt\*, Zhenfa Zhang\* and Joanna Atkin, "Probing the Behavior of Emerging Water-Soluble Organic Compounds in Indoor Air," Alfred Sloan Foundation, 7/1/20-6/30/23, *\$500,000* 

Scott Belcher\*, Theresa Guillette\* and Katy May\*, "Exploring fish consumption as a route of PFAS exposure," NCSU CHHE Pilot Grant Program, *\$38,875* 

Robyn Tanguay, Lisa Truong, Jennifer Field, Carla Ng, David Reif, and Jamie DeWitt\*, "System toxicological approaches to define and predict toxicity of per- and polyfluoroalkyl substances," U.S. EPA, 5/1/19-4/30/22, *\$465,000 to ECU out of \$1,984,400 total* 

Stephanie Kulesza, Owen Duckworth\*, Detlef Knappe\* and Aziz Amoozegar, "Occurrence and Fate of Per- and Polyfluoroalkyl Substances (PFAS) in North Carolina Agricultural Systems," NC Department of Justice, 01/01/21 – 12/31/23, *\$242,021* 

Mei Sun\*, "Evaluate the impact of land-applied biosolids on the occurrence of per- and polyfluoroalkyl substances (PFAS) in North Carolina water sources," NC Department of Justice, 4/1/21-3/30/22, *\$101,792* 

Mei Sun\*, "Heat-Activated Persulfate Regeneration of Ion Exchange Resins for Per- and Polyfluoroalkyl Substances Treatment," NC Urban Water Consortium, 3/1/21-2/28/22, *\$120,000* 

Heather Stapleton\*, P. Lee Ferguson\*, Kate Hoffman, Kateri Salk-Gundersen, Liping Feng and Amy Pickle, "Drinking Water Contamination in NC: Water Use, Human Health and Going Beyond GenX," Duke Provost Collaboratory Funding Program, 7/1/19 – 6/30/22, *\$494,921* 

Morton Barlaz\*, Detlef Knappe\* and James Levis, "Development of a perfluoroalkyl substances (PFAS) systems analysis tool (SAT) to assist in prioritization of destruction research and management decisions," US EPA, <u>Part 1:</u> 6/1/20-9/30/20, *\$124,999*; <u>Part 2:</u> 4/1/21-10/30/21, *\$105,978* 

Helena Mitasova\* and Jane Hoppin\*, "A Web Platform for Mapping Global, Publication-based, Spatial and Temporal Distributions of Per- and Polyfluoroalkyl Substances (PFAS)," NCSU CHHE Pilot Grant Program, 4/15/2020-4/15/21, *\$23,633* 

Marc Deshusses and P. Lee Ferguson\*, "Supercritical Water Oxidation (SCWO) for Complete PFAS Destruction," Environmental Security Technology Certification Program, 6/2020-5/2021, *\$646,335* 

Heather M. Stapleton\*, P. Lee Ferguson\* and Heileen Hsu-Kim, "Duke Environmental Analysis Laboratory," NIEHS, 9/2019-5/2024, *\$5,000,000* 

Detlef Knappe\*, "Occurrence of PFAS in US Wastewater Treatment Plants," CDM-Smith/The Water Research Foundation, 3/26/20-7/1/22, *\$46,600 to NCSU* 

Detlef Knappe\*, "Thermal Reactivation of Spent GAC from PFAS Remediation Sites," U.S. DOD, 12/16/20-6/16/22, *\$250,000* 

Detlef Knappe\*, Heather Stapleton\*, Jane Hoppin\*, Owen Duckworth\*, et al, "PFAS-UNITEDD: Poly- and Perfluoroalkyl Substance – U.S National Investigation of Transport and Exposure from Drinking Water and Diet," Colorado School of Mines/U.S. EPA, 5/1/19-4/30/22, \$700,000 to NCSU and Duke out of \$1,964,375 total

Detlef Knappe\*, Chris Bellona, Eric Dickenson, Erik Rosenfeldt, Charles Schaefer, et al, "Investigation of Treatment Alternatives for Short-Chain Poly- and Perfluoroalkyl Substances," The Water Research Foundation, 3/1/19-2/28/22, *\$350,000* 

Detlef Knappe\*, "Field Demonstration and Comparison of Ex-Situ Treatment Technologies for Poly- and Perfluoroalkyl substances (PFASs) in Groundwater," The Water Research Foundation/U.S. DOD, 5/16/18-7/31/22, *\$200,011 to NCSU out of \$481,250 total* 

Wei Gao and Detlef Knappe\*, "Collaborative Research: Cyclodextrin-Based 2D Materials for the Treatment of Legacy and Emerging Perfluoroalkyl Substances," National Science Foundation, 8/15/18-7/31/21, *\$180,000 to NCSU out of \$397,352 total* 

James Bomer, Jamie DeWitt\* and Jane Hoppin\*, "Assessing the Consequences of Inhalation Exposure to GenX on the Pulmonary Immune Response of Mice to Allergens and Microbial Agents," NCSU CHHE Pilot Grant Program, *\$25,000* 

Yujie Men, Wei Zheng, Mei Sun\*, John Scott and Elizabeth Meschewski, "Systematic Understanding of PFAS Sources and Mobility to Water Resources from Biosolids Land Application and Water Reuse in the US Rural Areas," U.S. EPA, 9/1/2020 – 8/31/2023, *\$1,604,211* 

Mei Sun\*, "Heat-Activated Persulfate Regeneration of Ion Exchange Resins for Per- and Polyfluoroalkyl Substances Treatment," U.S. DOD, 5/1/2021-4/31/2022, *\$150,857* 

Douglas Call and Detlef Knappe\*, "An Electroactive Point-of-Use Filter for Per- and Polyfluoroalkyl Contaminant Removal," U.S. EPA, 10/1/19-9/30/21, *\$25,000* 

Jamie DeWitt\* and Tracey Woodlief\*, "Uncovering PFOA-induced Metabolic Changes and Their Association with B-cell Metabolic Function," NCSU CHHE Pilot Grant Program, 4/15/2020-4/15/2021, *\$36,875* 

Erin Baker, Jane Hoppin\*, Detlef Knappe\*, Nadine Kotlarz and Catherine LePrevost, "Investigating PFAS Occurrence in Private Wells in North Carolina Uniquely Impacted by Landapplied Biosolids Using a Novel Non-targeted Analytical Workflow," NCSU CHHE Pilot Grant Program, 4/15/2020-4/15/2021, *\$25,000* 

Jane Hoppin\*, Nadine Kotlarz, Dereje Jima and Jamie DeWitt\*, "Investigating Immune System Impacts of PFAS in a Uniquely Exposed Population in North Carolina," NCSU CHHE Pilot Grant Program, 4/15/2020-4/15/2021, *\$25,000* 

## APPENDIX VI Network Budget Summary

### **BUDGET OVERVIEW**

North Carolina Policy Collaboratory (Collaboratory) selected UNC Gillings School of Global Public Health (Gillings) to manage the overall North Carolina PFAST Network. In partnership with the Collaboratory, Gillings convened a pan-campus, interdisciplinary team of nationally and internationally recognized academic experts from UNCCH, UNCW, NCSU, NCA&T, UNCC, ECU, and Duke University to establish the NC PFAST Network. The budget presented below was prepared by the Collaboratory and Gillings in cooperation with the Investigators for each of these campus teams. Indirect/overhead costs are specifically disallowed by the state appropriation and, therefore, not included. Additionally, per Section 13.1.(j) of S.L. 2018-5, "The Collaboratory should pursue relevant public and private funding opportunities that may be available to address the impacts of PFAS, including GenX, on surface water and groundwater quality, as well as air quality, in order to leverage funds appropriated by this section, or any other funds provided to the Collaboratory, including the Challenge Grant authorized in Section 27.5 of S.L. 2016-94, as amended by Section 10.4(a) of S.L. 2017-57." Therefore, the Collaboratory in some instances supplemented funding for a PI or project during the course of this research period, but that supplemental funding from other state sources is not reflected here as this budget summary reflects allocations using the state mandate and appropriation provided *specifically* for the NC PFAST Network (see Appendix I).

been rounded to the nearest dollar.					
UNIVERSITY	AMOUNT				
University of North Carolina at Chapel Hill	\$1,889,652				
University of North Carolina at Wilmington	\$299,942				
North Carolina State University	\$1,550,762				
North Carolina A&T State University	\$20,521				
University of North Carolina at Charlotte	\$341,406				
East Carolina University	\$171,068				
Duke University	\$739,649				
TOTAL	\$5,0130,000				

Breakdown of budget allocations for each campus involved in the NC PFAST Network. Numbers have been rounded to the nearest dollar.

Table 1. Total Budgeted Expenditures per University

### Table 2. Total Budgeted Expenditures per Team

Breakdown of budget allocations for each team (which can include multiple campuses) in the NC PFAST Network. Numbers have been rounded to the nearest dollar.

Network. Numbers have been rounded to the nearest dollar.								
TEAM	UNCCH	UNCW	NCSU	NCA&T	UNCC	ECU	DUKE	TOTAL
Project Mgmt	\$715,924	\$0	\$0	\$0	\$0	\$0	\$0	\$715,924
Team 1 H2O sampling	\$0	\$0	\$502,075	\$0	\$171,478	\$0	\$582,906	\$1,256,459
Team 2 well risk models	\$137,100	\$0	\$240,927	\$0	\$0	\$0	\$0	\$378,027
Team 3 PFAS removal	\$256,882	\$0	\$126,907	\$0	\$166,928	\$0	\$99,689	\$650,406
Team 4 air deposition	\$235,246	\$299,942	\$0	\$0	\$3,000	\$3,000	\$0	\$541,188
Team 5 applied R&D	\$199,207	\$0	\$510,857	\$20,521	\$0	\$168,068	\$0	\$898,653
Team 6 communication	\$61,054	\$0	\$57,054	\$0	\$0	\$0	\$57,054	\$175,162
Team 7 data mgmt	\$284,239	\$0	\$112,942	\$0	\$0	\$0	\$0	\$397,181
TOTAL	\$1,889,652	\$299,942	\$1,550,762	\$20,521	\$341,406	\$171,068	\$739,649	\$5,013,000