James R. Flechtner, PE
Executive Director
235 Government Center Drive
Wilmington, NC 28403
910-332-6625
jim.flechtner@cfpua.org

March 23, 2018

The Honorable Trudy Wade
North Carolina General Assembly
Legislative Building
16 West Jones Street
Raleigh, North Carolina 27601

RE: HB56 GenX Response Measures
Cape Fear Public Utility Authority (CFPUA) Final Report

Dear Senator Wade:

In accordance with House Bill 56 GenX Response Measures requirements, this final report summarizes the efforts to date of Cape Fear Public Utility Authority (CFPUA) to address water quality concerns in our water service area. Each of the progress reports and datasets included in this report has been shared with Pender and Brunswick counties, and we maintain an ongoing dialogue with their County Managers, and Public Utilities and Health departments.

Addressing the issue of emerging contaminants will require collaboration between public health experts, local utilities, water quality researchers and regulatory agencies. We are confident that the work we have done over the past year, aided in part by HB 56, effectively built the structure for such collaboration. We look forward to seeing that work evolve into a permanent network of water quality stakeholders.

Recognizing the complexity of the issue of emerging contaminants, CFPUA is taking a comprehensive approach that addresses both short-term and long-term concerns. It includes regular sampling; our work with researchers at the University of North Carolina Wilmington (UNCW); an ongoing pilot study at our Sweeney Water Treatment Plant to identify effective treatment technologies for emerging contaminants; free water stations available to the public from a groundwater source; and legal action.

As can be seen in Graph I on page four of this report, CFPUA continues to sample the finished water from the Sweeney Water Treatment Plant for GenX on a weekly basis. Levels of the compound have remained below the provisional health goal of 140 parts per trillion (ppt) set by the North Carolina Department of Health and Human Services since July 2017.

We know, however, that GenX is not the only emerging contaminant in the Cape Fear River. CFPUA has tested water samples from the Sweeney Plant for a wide array of unregulated compounds as part of its ongoing pilot study. As Graph II depicts, GenX accounts for only a small percentage of these compounds. Results from a screening of the twenty different per-fluorinated compounds with testing standards shows combined levels consistently above existing health goals for legacy compounds and for GenX (Graph III).

In addition, our ongoing partnership with UNCW has brought the existence of additional compounds to light. Scientists in the Department of Chemistry and Biochemistry at University of North Carolina Wilmington have been collecting raw and finished drinking water samples weekly from the Sweeney Water Treatment Facility since November 2017. To date, there are at least five new perflourinated alkyl substances (PFAS), not reported in the literature, that have been detected in both raw and finished drinking waters.

With this information in mind, CFPUA designed its pilot study to measure the potential of alternative treatment technologies in removing per-fluorinated compounds including, but not limited to, GenX. The most recent results of the pilot study may be seen in the enclosed Black & Veatch progress reports. We expect the pilot study to conclude this spring. CFPUA staff will use those findings to present a recommendation for water treatment enhancements to the Sweeney Water Treatment Plant to our Board.

Should Cape Fear Public Utility Authority choose to install additional treatment technology at the Sweeney Water Treatment Plant, design and construction of those upgrades will take several years. In the meantime, CFPUA has installed two water stations available for concerned customers to obtain water at no cost—both stations distribute groundwater that tested negative for GenX. These two water stations are located at either end of New Hanover County. Graph IV contains a map of their locations and recent water usage.

CFPUA is one of the first utilities in the country to pursue treatment of per-fluorinated compounds such as GenX. While much as been accomplished over the past year—challenges remain and much is still unknown. The absence of effective discharge controls and provisional health goals for many of these compounds adds a degree of difficulty in determining levels of treatment that are protective of public health. While industrial point source discharge is a known source of the compounds, researchers are still investigating the role of other potential sources such as air emissions, groundwater, rain, and storm water runoff.

As CFPUA moves forward in this process, we will continue to rely on State agencies for treatment guidance and public health expertise to ensure that we are providing safe and reliable drinking water to our community. We thank the General Assembly for the assistance it has provided, and for its continued attention to the issue of water quality in the Cape Fear Region.

If you have any questions, please do not hesitate to contact me at (910) 332-6669, or by email at jim.flechtner@cfpua.org.

Sincerely,

James R. Flechtner, P.E.
Executive Director

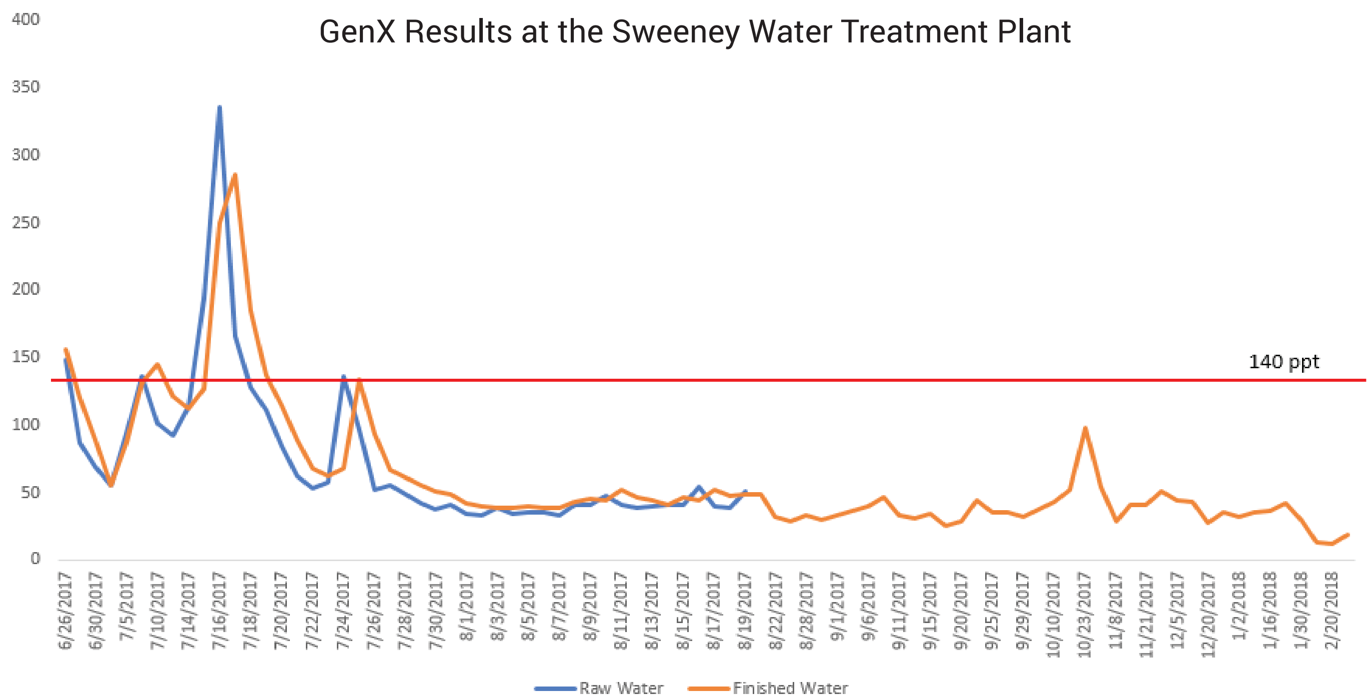
CC: Linda Miles, CFPUA Consulting Attorney
File

Enclosures (7):

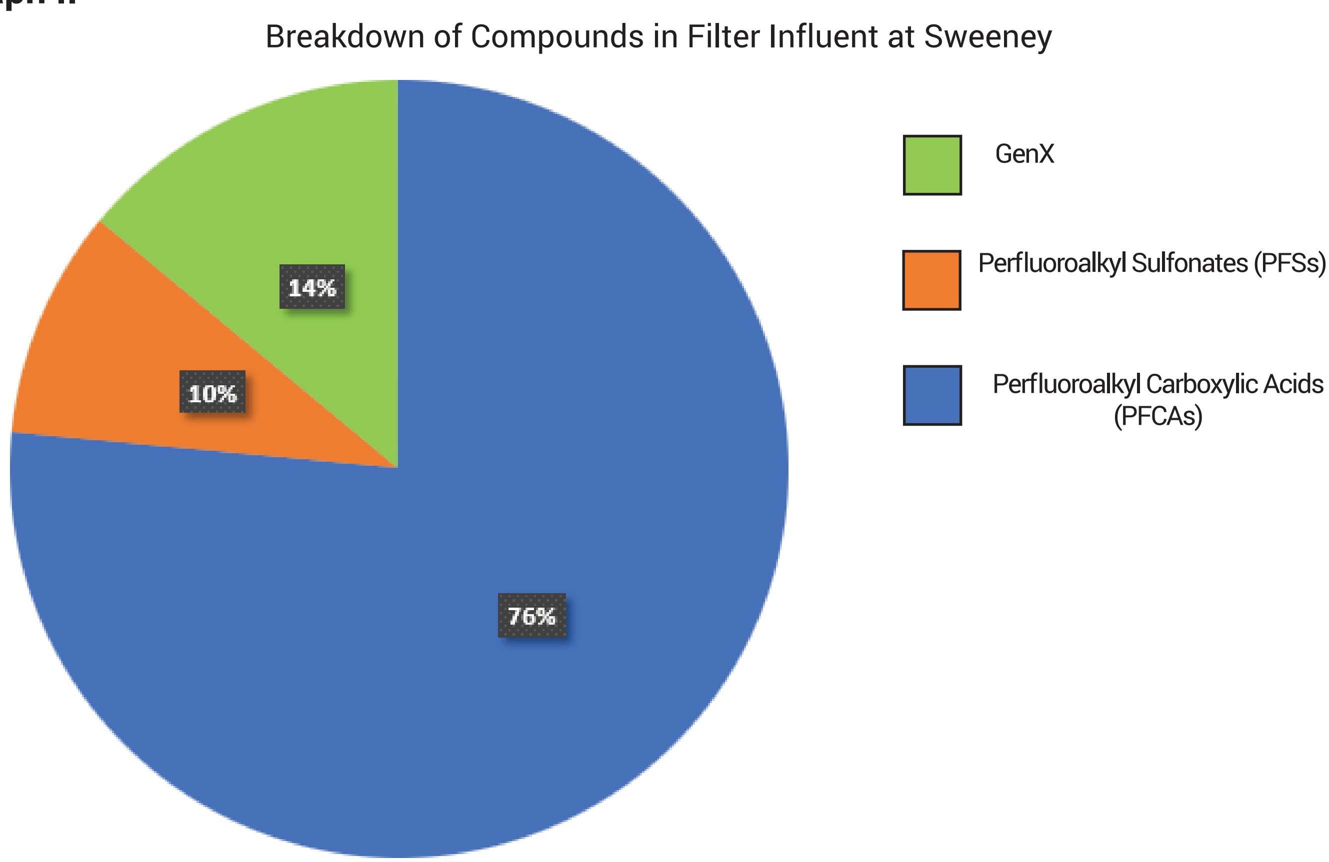
(1) HB 56 GenX Response Measures-Graphs
(2) Black & Veatch Progress Update Number 2
(3) Black & Veatch Progress Update Number 3
(4) Black & Veatch Progress Update Number 4
(5) University of North Carolina Wilmington Progress Update_January 2018
(6) University of North Carolina Wilmington Progress Update_March 2018
(7) University of North Carolina Rain Analysis for November and December 2017

HB56 GenX Response Measures - Graphs

Graph I

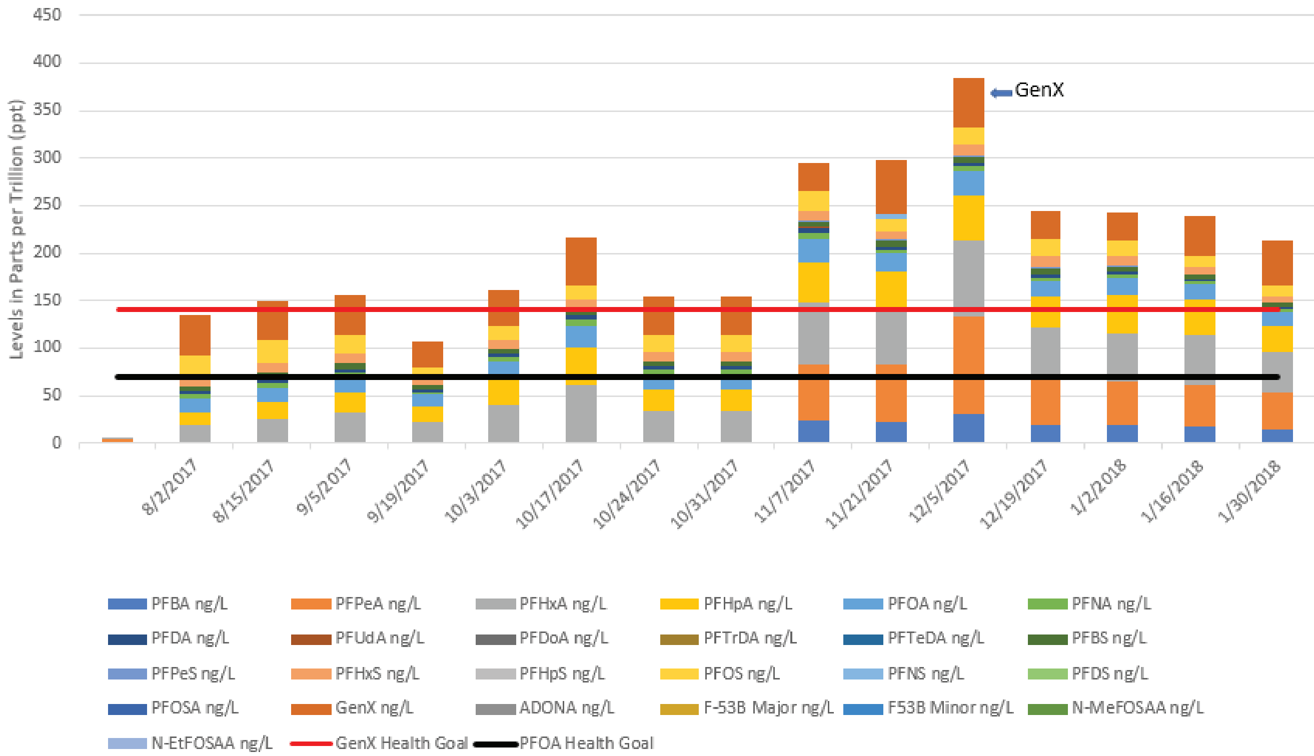


Graph II



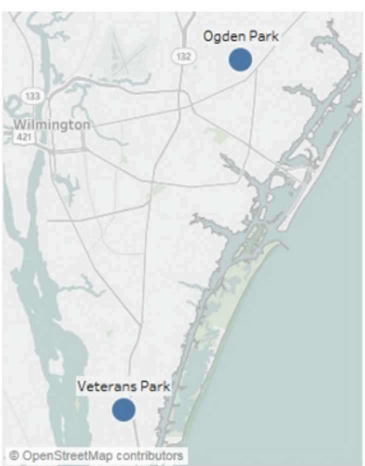
Graph III

Combined Levels of Compounds with Testing Standards in Water Entering Pilot Study

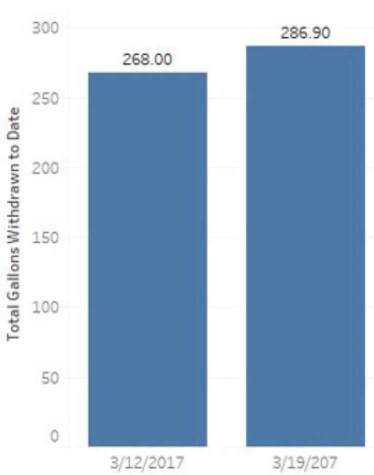


Graph IV

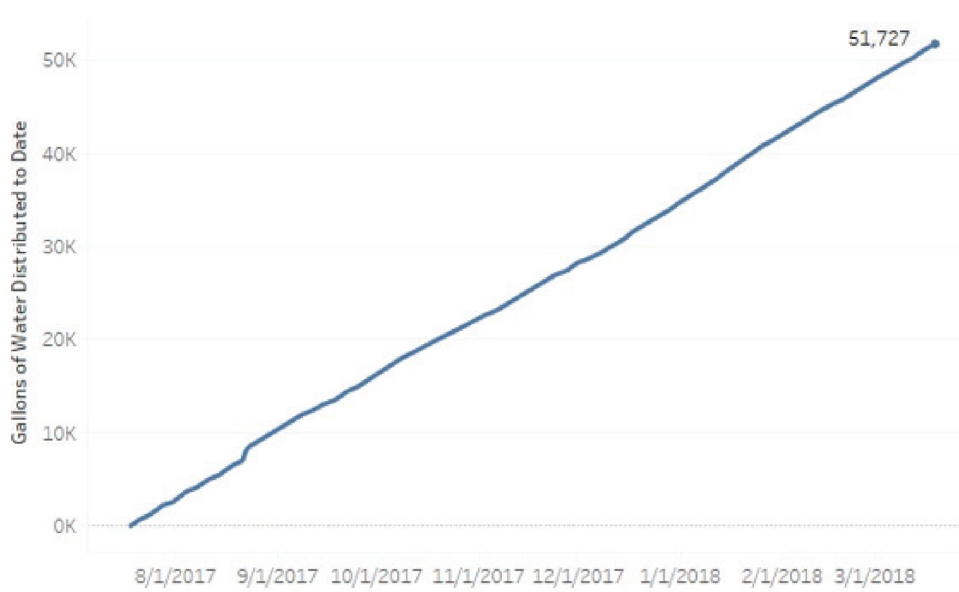
Water Station Data



Veteran's Park Water Station



Ogden Park Water Station



PROGRESS UPDATE NO. 2

Emerging Contaminants Treatment Strategy Pilot Study

B&V PROJECT NO. 196369

NORTH CAROLINA
PROFESSIONAL
SEAL
8749
ENGINEER
H. KEITH PROFFIT

H K Proffitt

12/05/17

PREPARED FOR

Cape Fear Public Utility Authority

5 DECEMBER 2017

BLACK & VEATCH

Table of Contents

LIST OF TABLES

1.0 Purpose

This document presents the status of ongoing bench- and pilot-scale testing to evaluate the performance of several proposed treatment technologies in their removal of perfluoroalkyl substances (PFASs), including perfluoro-2-propoxypropanoic acid (commonly known as GenX).

2.0 Introduction

PFASs have been detected in the Cape Fear River, which is the source of raw water for the Sweeney Water Treatment Plan (WTP). The Sweeney WTP provides drinking water to Cape Fear Public Utility Authority (CFPUA) customers in the city of Wilmington and New Hanover County in North Carolina.

In response to the detection of GenX and other PFASs in the Cape Fear River and because of concern over potential health effects, CFPUA is proactively investigating the feasibility and effectiveness of PFAS removal technologies. CFPUA is one of the first utilities in the United States to pursue treatment to target removal of these compounds. Initial evaluations performed by Black & Veatch were provided in Technical Memoranda 1 and 2. As a result of those evaluations, bench- and pilot-scale testing of granular activated carbon (GAC) filter media and ion exchange (IX) resins was initiated. The details of the bench- and pilot- scale testing are presented herein.

3.0 Testing and Analysis

Granular activated carbon filter media and ion exchange resin were selected for bench- and pilot-scale testing. Reverse osmosis/nanofiltration was excluded because of much higher life-cycle cost and potential challenges related to disposal of the concentrate, but the technology will be considered if testing of GAC and IX fail to meet testing goals. The following sections provide information on the testing.

3.1 TESTING GOALS

The primary goal of the testing is to establish the adsorption characteristics for PFASs and other contaminants of emerging concern (CECs) on GAC media and IX resin. These characteristics will be used to refine the previous study-related evaluations and identify the most advantageous short- and longer-term treatment strategies for removal of PFASs and CECs at the Sweeney WTP. The data will help define a design basis for full-scale implementation of the selected technology. Ancillary benefits are also being identified as part of the study, such as reductions in total organic carbon (TOC), disinfection byproduct (DBP) formation, and inorganic compounds.

3.2 MEANS AND METHODS

Means and methods for the bench- and pilot-scale testing were included in a previous progress report dated Nov. 3, 2017. Refer to the previous report for details.

CFPUA expanded the list of analyzed components to include additional per- and polyfluorinated components beginning with the November 7, 2017 samples. As a result, some additional components are presented herein that were not included in the previous report.

3.3 GAC INTERIM RESULTS TO DATE

Interim results of the ongoing pilot testing are presented in Table 3-1. All data is reported based on equivalent bed volumes of water treated.

Each GAC test column continues to exhibit gradual breakthrough of TOC and PFASs, led by shorter chain per- and polyfluorinated compounds. Each GAC media is exhibiting chromatographic peaking, which is the preferential adsorption of one molecule over another. As a result, shorter carbon chain molecules are being released by the GAC into the effluent contributing to greater than 100 percent breakthrough values. Results also continue to show that shorter carbon chains (PFBA, PFBS, GenX, etc.) are not as strongly adsorbed on the GAC media as the longer carbon chain molecules (PFDA, PFOS).

Table 3-1 Sampling Results as of November 7, 2017

	Column Influent	GAC-1	GAC-2	GAC-3	GAC-4	IX-1	IX-2
Bed Volumes	---	13,500	13,700	14,000	14,100	62,500	62,500
Empty Bed Contact Time (min)	---	10	10	10	10	1.5	1.5
Perfluoroalkyl Carboxylic Acids (PFCAs)	**ng/L**	**Percent Breakthrough**					
PFBA	23-24.3	114	104	114	110	97	91
PFPeA	55.6-58.7	101	102	120	119	70	109
PFHxA	64.5-65.2	83	90	105	110	26	12
PFHpA	42.3-42.6	74	74	98	113	6	ND
PFOA	23.3-23.7	64	70	83	97	ND	ND
PFNA	5.21-6.52	43	49	51	62	ND	ND
PFDA	4.68-5.91	27	31	32	31	ND	ND
PFUdA	ND-0.871	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	ND	ND
PFTrDA	ND	ND	ND	ND	ND	ND	ND
PFTeDA	ND	ND	ND	ND	ND	ND	ND
Perfluoroalkyl Sulfonates (PFSs)	**ng/L**	**Percent Breakthrough**					
PFBS	5.9-6.31	70	85	95	108	ND	ND
PFPeS	1.32-1.34	68	69	87	90	ND	ND
PFHxS	9.19-9.34	54	59	75	72	ND	ND
PFHpS	ND	ND	ND	ND	ND	ND	ND
PFOS	20.2-21.4	25	27	36	35	ND	ND
PFNS	ND	ND	ND	ND	ND	ND	ND
PFDS	ND	ND	ND	ND	ND	ND	ND
Perfluoroalkyl Sulfonamides (PFSAs)	**ng/L**	**Percent Breakthrough**					
PFOSA	ND	ND	ND	ND	ND	ND	ND

	Column Influent	GAC-1	GAC-2	GAC-3	GAC-4	IX-1	IX-2
Bed Volumes	---	13,500	13,700	14,000	14,100	62,500	62,500
Empty Bed Contact Time (min)	---	10	10	10	10	1.5	1.5
Perfluoroalkyl Ether Carboxylic Acids (PFECAs)	**ng/L**	**Percent Breakthrough**					
PFMOAA*	0.442-0.792	158	126	135	138	148	138
PFMOPrA*	ND	ND	ND	ND	ND	ND	ND
PFO2HxA*	23.8-88.4	106	97	109	120	153	191
PFMOBA*	1.74-2.13	111	110	107	114	75	38
PFO3OA*	12.1-71.7	129	98	123	132	28	30
PFPrOPrA/GenX	28.3-29	113	110	107	114	75	38
PFO4DA*	4.25-32.3	73	75	76	95	2	ND
Other Per- and Polyfluorinated Compounds	**ng/L**	**Percent Breakthrough**					
ADONA	ND	ND	ND	ND	ND	ND	ND
F-53B Major	ND	ND	ND	ND	ND	ND	ND
F-53B Minor	ND	ND	ND	ND	ND	ND	ND
Nafion Byproduct 1*	ND	ND	ND	ND	ND	ND	ND
Nafion Byproduct 2*	4.2-22.6	74	91	75	91	ND	ND
N-MeFOSAA	ND	ND	ND	ND	ND	ND	ND
N-EtFOSAA	ND	ND	ND	ND	ND	ND	ND

* Measurement is considered an estimate as the analytical lab does not have a standard for measurement of this compound.
ND – Not detected

3.4 IX INTERIM RESULTS TO DATE

Interim results of the ongoing pilot testing are presented in Table 3-1. Both ion exchange columns now show breakthrough of several shorter carbon chain molecules before 50,000 bed volumes. Both also appear to show chromatographic peaking for several perfluoroalkyl ether carboxylic acids.

4.0 Discussion

- The bench-scale and pilot testing is ongoing and scheduled to continue through the first quarter of 2018 until testing goals are achieved.
- PFASs are being observed in the pilot GAC media effluent.
  - All columns are exhibiting effluent PFAS concentrations near or above the influent concentration for shorter carbon chain PFASs.
  - Longer carbon chain PFAS molecules continue to be partially removed.
- PFASs are being observed in the pilot IX resin effluent.

- Both columns are exhibiting effluent PFAS concentrations near or above the influent concentration for a few of the shortest carbon chain PFASs.
- Longer carbon chain PFAS molecules have yet to show any breakthrough.

- Testing will evolve as data is received to refine short- and long-term treatment strategies.
- Additional pilot columns are being considered for testing of other GAC and IX adsorbents.

5.0 Conclusions/Recommendations

The following conclusions and recommendations can be developed based on the interim testing results.

- Pilot testing is ongoing and should continue in order to fully characterize the performance of GAC and IX technologies for PFAS removal.
- With breakthrough occurring in the current GAC and IX pilot columns, the next round of pilot testing with additional media and longer empty bed contact time is being developed by the team with execution planned in the next few months.
- Additional piloting will create a competitive bidding environment and provide additional design and operating cost information in regard to EBCT. This information will optimize the design to lower operating cost.

FINAL

PROGRESS UPDATE NO. 3

Emerging Contaminants Treatment Strategy Pilot Study

B&V PROJECT NO. 196369

NORTH CAROLINA
PROFESSIONAL
SEAL
8749
ENGINEER
H. KEITH PROFFIT

01/09/2018

PREPARED FOR

Cape Fear Public Utility Authority

8 JANUARY 2018

BLACK & VEATCH

Table of Contents

LIST OF TABLES

1.0 Purpose

This document presents the status of ongoing bench- and pilot-scale testing to evaluate the performance of several proposed treatment technologies in their removal of perfluoroalkyl substances (PFASs), including perfluoro-2-propoxypropanoic acid (commonly known as GenX).

2.0 Introduction

PFASs have been detected in the Cape Fear River, which is the source of raw water for the Sweeney Water Treatment Plan (WTP). The Sweeney WTP provides drinking water to Cape Fear Public Utility Authority (CFPUA) customers in the City of Wilmington and New Hanover County in North Carolina.

In response to the detection of GenX and other PFASs in the Cape Fear River and because of concern over potential health effects, CFPUA is proactively investigating the feasibility and effectiveness of PFAS removal technologies. CFPUA is one of the first utilities in the United States to pursue treatment to target removal of these compounds. Initial evaluations performed by Black & Veatch were provided in Technical Memoranda 1 and 2. As a result of those evaluations, bench- and pilot-scale testing of granular activated carbon (GAC) filter media and ion exchange (IX) resins was initiated. The details of the bench- and pilot- scale testing are presented herein.

3.0 Testing and Analysis

Granular activated carbon filter media and ion exchange resin were selected for bench- and pilot-scale testing. Reverse osmosis/nanofiltration was excluded because of much higher life-cycle cost and potential challenges related to disposal of the concentrate, but the technology will be considered if testing of GAC and IX fail to meet testing goals. The following sections provide information on the testing.

3.1 TESTING GOALS

The primary goal of the testing is to establish the adsorption characteristics for PFASs and other contaminants of emerging concern (CECs) on GAC media and IX resin. These characteristics will be used to refine the previous study-related evaluations and identify the most advantageous short- and longer-term treatment strategies for removal of PFASs and CECs at the Sweeney WTP. The data will help define a design basis for full-scale implementation of the selected technology. Ancillary benefits are also being identified as part of the study, such as reductions in total organic carbon (TOC), disinfection byproduct (DBP) formation, and inorganic compounds.

3.2 MEANS AND METHODS

Means and methods for the bench- and pilot-scale testing were included in a previous progress report dated Nov. 3, 2017. Refer to the previous report for details.

3.3 GAC INTERIM RESULTS TO DATE

Interim results of the ongoing pilot testing are presented in Table 3-1. All data is reported based on equivalent bed volumes of water treated.

Each GAC test column continues to exhibit gradual breakthrough of TOC and PFASs, led by shorter chain per- and polyfluorinated compounds. Each GAC media is exhibiting chromatographic peaking, which is the preferential adsorption of one molecule over another. As a result, shorter carbon chain molecules are being released by the GAC into the effluent contributing to greater than 100 percent breakthrough values. Results also continue to show that shorter carbon chains (PFBA, PFBS, GenX, etc.) are not as strongly adsorbed on the GAC media as the longer carbon chain molecules (PFDA, PFOS).

Table 3-1 Sampling Results as of December 5, 2017

	Column Influent	GAC-1	GAC-2	GAC-3	GAC-4	IX-1	IX-2
Bed Volumes	---	17,340	17,640	18,000	18,050	90,900	90,900
Empty Bed Contact Time (min)	---	10	10	10	10	1.5	1.5
Perfluoroalkyl Carboxylic Acids (PFCAs)	**ng/L**	**Percent Breakthrough**					
PFBA	23-24.3	119	126	131	114	105	100
PFPeA	55.6-58.7	150	122	131	120	70	86
PFHxA	64.5-65.2	76	83	135	132	58	57
PFHpA	42.3-42.6	79	89	113	113	37	6
PFOA	23.3-23.7	90	102	105	88	15	ND
PFNA	5.21-6.52	69	80	93	104	ND	ND
PFDA	4.68-5.91	54	65	61	61	ND	ND
PFUdA	ND-0.871	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	ND	ND
PFTrDA	ND	ND	ND	ND	ND	ND	ND
PFTeDA	ND	ND	ND	ND	ND	ND	ND
Perfluoroalkyl Sulfonates (PFSs)	**ng/L**	**Percent Breakthrough**					
PFBS	5.9-6.31	81	86	105	109	ND	ND
PFPeS	1.32-1.34	69	67	76	85	ND	ND
PFHxS	9.19-9.34	59	66	75	84	ND	ND
PFHpS	ND	ND	ND	ND	ND	ND	ND
PFOS	20.2-21.4	45	53	55	59	ND	ND
PFNS	ND	ND	ND	ND	ND	ND	ND
PFDS	ND	ND	ND	ND	ND	ND	ND
Perfluoroalkyl Sulfonamides (PFSAs)	**ng/L**	**Percent Breakthrough**					
PFOSA	ND	ND	ND	ND	ND	ND	ND

	Column Influent	GAC-1	GAC-2	GAC-3	GAC-4	IX-1	IX-2
Bed Volumes	---	17,340	17,640	18,000	18,050	90,900	90,900
Empty Bed Contact Time (min)	---	10	10	10	10	1.5	1.5
Perfluoroalkyl Ether Carboxylic Acids (PFECAs)	**ng/L**	**Percent Breakthrough**					
PFMOAA*	0.442-0.792	116	115	123	120	112	113
PFMOPrA*	ND	118	115	111	107	104	109
PFO2HxA*	23.8-88.4	108	124	127	128	155	143
PFMOBA*	1.74-2.13	ND	ND	ND	ND	ND	ND
PFO3OA*	12.1-71.7	186	217	136	145	91	175
PFPrOPrA/GenX	28.3-29	98	94	101	95	71	82
PFO4DA*	4.25-32.3	153	169	95	121	30	5
Other Per- and Polyfluorinated Compounds	**ng/L**	**Percent Breakthrough**					
N-MeFOSAA	ND	ND	ND	ND	ND	ND	ND
N-EtFOSAA	ND	ND	ND	ND	ND	ND	ND

* Measurement is considered an estimate as there is currently no known authentic standard for measurement of this compound.
ND – Not detected

3.4 IX INTERIM RESULTS TO DATE

Interim results of the ongoing pilot testing are presented in Table 3-1. Both ion exchange columns now show breakthrough of several shorter carbon chain molecules before 50,000 bed volumes. Both also appear to show chromatographic peaking for nearly all perfluoroalkyl ether carboxylic acids. Perfluoroalkyl sulfonates continue to be completely removed.

4.0 Discussion

- The bench-scale and pilot testing is ongoing and scheduled to continue through the first quarter of 2018 until testing goals are achieved.
- PFASs are being observed in the pilot GAC media effluent.
  - All columns are exhibiting effluent PFAS concentrations near or above the influent concentration for all but the longest carbon chain PFASs.
  - Only the longest chain PFAS molecules continue to be removed.
  - Adsorption curves for each PFAS compound have been characterized for each column.
  - GAC columns 1 through 4 have reached the end of their useful life for the first phase of piloting and will be discontinued.
- PFASs are being observed in the pilot IX resin effluent.
  - Both columns are exhibiting effluent PFAS concentrations near or above the influent concentration for a few of the shortest carbon chain PFASs.

- Only PFASs with carboxylic acid functional groups have shown breakthrough.
- Longer carbon chain PFAS molecules have yet to show any breakthrough.
- PFAS molecules with sulfonate functional groups have yet to show any breakthrough.

- Additional pilot columns were installed for testing of other GAC and IX adsorbents.
  - Four new GAC pilot columns have been installed and will start operation mid-January. The four new pilot columns will be used to evaluate two more GAC media types and the effect of increasing the empty bed contact time on PFAS removal.
  - Three new IX pilot columns have been installed and will start operation mid-January. The three new pilot columns will be used to evaluate two more IX resins and the effect of increasing the empty bed contact time on PFAS removal.
- Testing will evolve as data is received to refine short- and long-term treatment strategies.

5.0 Conclusions/Recommendations

The following conclusions and recommendations can be developed based on the interim testing results.

- Pilot testing is ongoing and should continue in order to fully characterize the performance of GAC and IX technologies for PFAS removal.

FINAL

PROGRESS UPDATE NO. 4

Emerging Contaminants Treatment Strategy Pilot Study

B&V PROJECT NO. 196369

NORTH CAROLINA
PROFESSIONAL
SEAL
8749
ENGINEER
H. KEITH PROFFIT

02/26/2018

PREPARED FOR

Cape Fear Public Utility Authority

26 FEBRUARY 2018

BLACK & VEATCH

Table of Contents

LIST OF TABLES

1.0 Purpose

This document presents the status of ongoing bench- and pilot-scale testing to evaluate the performance of several proposed treatment technologies in their removal of perfluoroalkyl substances (PFASs), including perfluoro-2-propoxypropanoic acid (commonly known as GenX).

2.0 Introduction

PFASs have been detected in the Cape Fear River, which is the source of raw water for the Sweeney Water Treatment Plan (WTP). The Sweeney WTP provides drinking water to Cape Fear Public Utility Authority (CFPUA) customers in the city of Wilmington and New Hanover County in North Carolina.

In response to the detection of GenX and other PFASs in the Cape Fear River and because of concern over potential health effects, CFPUA is proactively investigating the feasibility and effectiveness of PFAS removal technologies. CFPUA is one of the first utilities in the United States to pursue treatment to target removal of these compounds. Initial evaluations performed by Black & Veatch were provided in Technical Memoranda 1 and 2. As a result of those evaluations, bench- and pilot-scale testing of granular activated carbon (GAC) filter media and ion exchange (IX) resins was initiated. The details of the bench- and pilot- scale testing are presented herein.

3.0 Testing and Analysis

Granular activated carbon filter media and ion exchange resin were selected for bench- and pilot-scale testing. Reverse osmosis/nanofiltration was excluded because of much higher life-cycle cost and potential challenges related to disposal of the concentrate, but the technology will be considered if testing of GAC and IX fail to meet testing goals. The following sections provide information on the testing.

3.1 TESTING GOALS

The primary goal of the testing is to establish the adsorption characteristics for PFASs and other contaminants of emerging concern (CECs) on GAC media and IX resin. These characteristics will be used to refine the previous study-related evaluations and identify the most advantageous short- and longer-term treatment strategies for removal of PFASs and CECs at the Sweeney WTP. The data will help define a design basis for full-scale implementation of the selected technology. Ancillary benefits are also being identified as part of the study, such as reductions in total organic carbon (TOC), disinfection byproduct (DBP) formation, and inorganic compounds.

3.2 MEANS AND METHODS

Means and methods for the bench- and pilot-scale testing were included in a previous progress report dated Nov. 3, 2017. Refer to the previous report for details.

3.3 PILOT MODIFICATIONS

The configuration of the pilot columns was modified for the second phase of testing in mid-January. The second phase of pilot testing is aimed at refining the basis for a full-scale design and to identify configurations with the lowest life-cycle cost. A flow diagram for the new configuration is included in Figure 3-1.

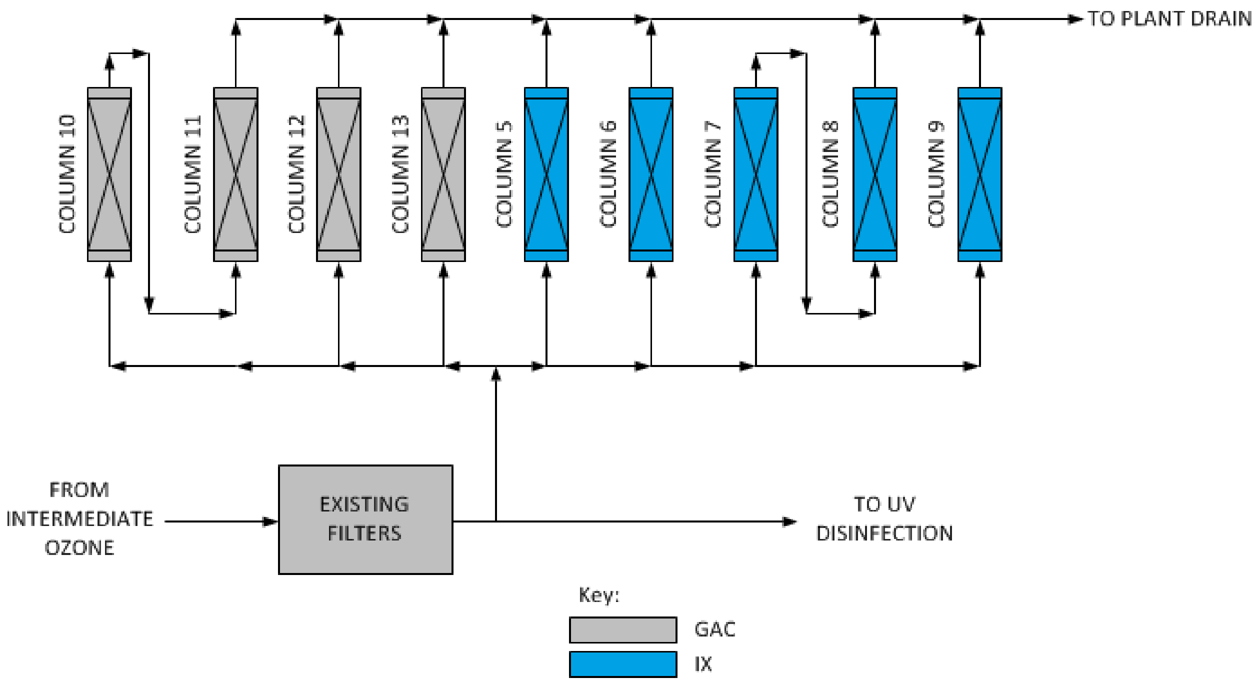


Figure 3-1 Pilot Test Flow Diagram

Columns 10 through 13 include new GAC media. Columns 5 and 6 are the remaining two ion exchange columns from the initial phase of piloting that are still in service. Columns 7 through 9 include new ion exchange resins. The media and resins contained in each pilot column are shown in Table 3-1 and Table 3-2.

Columns 10 and 11 are operated in series to evaluate the effects of a longer empty bed contact time (EBCT) on adsorption characteristics of GAC. Columns 7 and 8 are also operated in series in the same manner for ion exchange resins.

Table 3-1 Pilot Modifications – GAC Media

Column No.	10	11	12	13
EBCT, min	10	10	10	10
Supplier	Calgon	Calgon	Cabot	Cabot
Media/Resin	Filtrasorb 400	Filtrasorb 400	Hydrodarco 4000	GAC 400

Table 3-2 Pilot Modifications – IX Resins

Column No.	5	6	7	8	9
EBCT, min	1.5	1.5	1.5	1.5	1.5
Supplier	Evoqua	Calgon	Purolite	Purolite	Calgon
Media/Resin	DOWEX PSR-2 Plus	CalRes 2304	Purofine PFA694E	Purofine PFA694E	CalRes 2301

3.4 GAC INTERIM RESULTS TO DATE

The initial phase of piloting for GAC consisted of four pilot columns that all began operation on Aug. 2, 2017. Operation of those columns was terminated in December and final results were reported in Progress Update No. 3, dated Jan. 8, 2018.

The second phase of piloting for GAC consists of four new pilot columns that will test some new GAC media as well longer empty bed contact times. Operation of the second phase of piloting for GAC began on Jan. 16, 2018. Testing results for these pilot columns have not yet been received as of the date of this report.

3.5 IX INTERIM RESULTS TO DATE

Interim results of the ongoing pilot testing are presented in Table 3-3. Breakthrough of perfluoroalkyl carboxylic acids appears to be consistently expanding to include the longer chain molecules. Perfluoroalkyl sulfonates continue to be completely removed. The capacity of each ion exchange resin to adsorb PFPrOPrA/GenX has been exhausted. The performance of each resin for removal of other PFECAs and Nafion byproducts is unknown at this time as the estimated results for such compounds, which have no known authentic standard, are inconsistent with previous testing results.

Table 3-3 Sampling Results as of January 16, 2017

	Column Influent	IX-1	IX-2
Bed Volumes	---	133,400	133,400
Empty Bed Contact Time (min)	---	1.5	1.5
Perfluoroalkyl Carboxylic Acids (PFCAs)	**ng/L**	**Percent Breakthrough**	
PFBA	18	119	113
PFPeA	43	110	144
PFHxA	53	78	106
PFHpA	37	62	27
PFOA	16	53	ND
PFNA	3	ND	ND
PFDA	2.4	ND	ND
PFUdA	ND	ND	ND
PFDoA	ND	ND	ND
PFTrDA	ND	ND	ND
PFTeDA	ND	ND	ND

	Column Influent	IX-1	IX-2
Bed Volumes	---	133,400	133,400
Empty Bed Contact Time (min)	---	1.5	1.5
Perfluoroalkyl Sulfonates (PFSs)	**ng/L**	**Percent Breakthrough**	
PFBS	4.9	ND	ND
PFPeS	ND	ND	ND
PFHxS	7.8	ND	ND
PFHpS	ND	ND	ND
PFOS	11	ND	ND
PFNS	ND	ND	ND
PFDS	ND	ND	ND
Perfluoroalkyl Sulfonamides (PFSAs)	**ng/L**	**Percent Breakthrough**	
PFOSA	ND	ND	ND
Perfluoroalkyl Ether Carboxylic Acids (PFECAs)	**ng/L**	**Percent Breakthrough**	
PFMOAA*	2900 (Est.)	100	100
PFMOPrA*	ND	ND	ND
PFO2HxA*	98 (Est.)	184	163
PFMOBA*	ND	ND	ND
PFO3OA*	22 (Est.)	191	500
PFPrOPrA/GenX	44	86	100
PFO4DA*	7.9 (Est.)	124	67
Other Per- and Polyfluorinated Compounds	**ng/L**	**Percent Breakthrough**	
ADONA	ND	ND	ND
F-53B Major	ND	ND	ND
F-53B Minor	ND	ND	ND
Nafion Byproduct 1*	ND	ND	ND
Nafion Byproduct 2*	20 (Est.)	ND	ND
N-MeFOSAA	ND	ND	ND
N-EtFOSAA	ND	ND	ND

* Measurement is considered an estimate as there is currently no known authentic standard for measurement of this compound.
ND – Not detected
Est. – Estimated

4.0 Discussion

- The bench-scale and pilot testing is ongoing and scheduled to continue through the first quarter of 2018 until testing goals are achieved.

- The first phase of piloting of GAC media (columns 1 through 4) has been completed.
- PFASs are being observed in the pilot IX resin effluent.
  - Both columns are exhibiting effluent PFAS concentrations near or above the influent concentration for the shortest carbon chain PFASs.
  - Only PFASs with carboxylic acid functional groups have shown breakthrough.
  - Longer carbon chain PFAS molecules have yet to show any breakthrough.
  - PFAS molecules with sulfonate functional groups have yet to show any breakthrough.
  - The capacity of both ion exchange resins for adsorption of GenX has now been exhausted.
- Additional pilot columns were installed for testing of other GAC and IX adsorbents.
  - Four new GAC pilot columns have been installed and started operation on Jan. 16, 2018. The four new pilot columns will be used to evaluate two more GAC media types and the effect of increasing the empty bed contact time on PFAS removal. Results from these new columns have not yet been received.
  - Three new IX pilot columns have been installed. Column 9 was started on Jan. 16, 2018. Columns 7 and 8 were started on Jan. 17, 2018. The three new pilot columns will be used to evaluate two more IX resins and the effect of increasing the empty bed contact time on PFAS removal. Results from these new columns have not yet been received.
- The most recent testing results for compounds which have no currently known authentic standard are inconsistent with past results. This includes the testing results for most of the listed PFECAs and both Nafion byproducts. The project changed analytical labs prior to the most recent testing, which is likely a contributing factor to the observed differences. Test methods will be reviewed to clarify observed differences.
- Testing will evolve as data is received to refine short- and long-term treatment strategies.

5.0 Conclusions/Recommendations

The following conclusions and recommendations can be developed based on the interim testing results.

- Pilot testing is ongoing and should continue in order to fully characterize the performance of GAC and IX technologies for PFAS removal.

Cape Fear Public Utility Authority

Project update for the period covering December 1, 2017 through January 18, 2018

Notice:

Where an authentic standard is not available the concentrations must be considered semi-quantitative. When interpreting the molecular formulas generated by high resolution mass spectrometry, caution is advised when considering health impacts, if any, until a complete structural elucidation and appropriate health studies are performed.

Weekly sampling of raw and finished waters began November 15, 2017 and has continued through the week of January 15^{th}, 2018. Targeted quantification of perfluoroalkyl substances (PFAS) are presented in table 1 where authentic standards are available for each of the compounds. The concentration of GenX varied in the finished water samples collected. All but one (12/21/17) were below the health advisory goal of 140 ppt. We are currently analyzing the duplicate sample that was collected and will report that analysis when it is complete. The raw water in several of the samples was elevated in concentration compared to the finished drinking water. There appeared to be a spike in the concentration of GenX in the sample collected 11/28/17 and a decrease over the following two weeks. The raw water collected 1/3/18 appears to be increasing in concentration as well.

There were also other PFAS compounds detected in both the raw and finished waters that have been reported previously. The concentrations of these non-targeted compounds should be considered semi-quantitative since no authentic standards are available. This is an important consideration given the different response factors for the unknown compounds relative to

GenX. The concentrations reported were determined using equation number 1 (EPA report to NC DEQ 2017) :

Equation 1: $$[Unknown] = [GenX] * \frac{Unknown\ peak\ area}{GenX\ peak\ area}$$

where:

[Unknown] is the concentration of non-targeted analyte in ng/L
[GenX] is the concentration of GenX in ng/L

Figures 2 through 6 compare the concentrations of the individual non-targeted compounds in the raw and finished drinking water. The compound concentrations were variable in the raw and finished waters over the time frame collected so far. Caution, however, is advised in that the raw and finished water samples may not represent the exact same water mass as it moves through the facility.

No PFAS were detected in the field and laboratory blanks illustrating no contamination took place for each sampling event. Sample processing and QA/QC procedures were followed as described in Nakyama et al. (2010)[1] and Strynar et al. (2015)[2]. Briefly, external calibration curves using authentic standards, when available, were used to quantify each analyte by LC-MS/MS. Each sample was spiked with a recovery surrogate standard; recoveries ranged from 65 to 111%.

Table 1: Concentrations of targeted PFAS compounds in raw (RW) and finished (FW) waters collected at the Sweeney Water Treatment Plant. Structures for each of the compounds can be found in the appendix. The date refers to when the sample was collected and bdl is below detection limit.

	11/15/17		11/28/17		12/6/17		12/13/17		12/21/17		12/27/17		1/3/18	
ng/L	RW1	FW2	RW3	FW4	RW4	FW5	RW5	FW7	RW6	FW9	RW7	FW11	RW8	FW13
PFMOBA	bdl	bdl	0.6	0.9	0.2	5.2	5.3	3.8	5.6	bdl	bdl	5.8	4.9	6.3
PFPrOPrA	8	41	999	52	94	83	606	17	62	253	110	66	363	137
PFOA	bdl	1	40	40	28	11	72	7	21	103	38	bdl	10	27
PFOS	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl

Figure 1: The concentration of PFPrOPrA (GenX) in raw and finished water collected at Sweeney Water Treatment Plant.

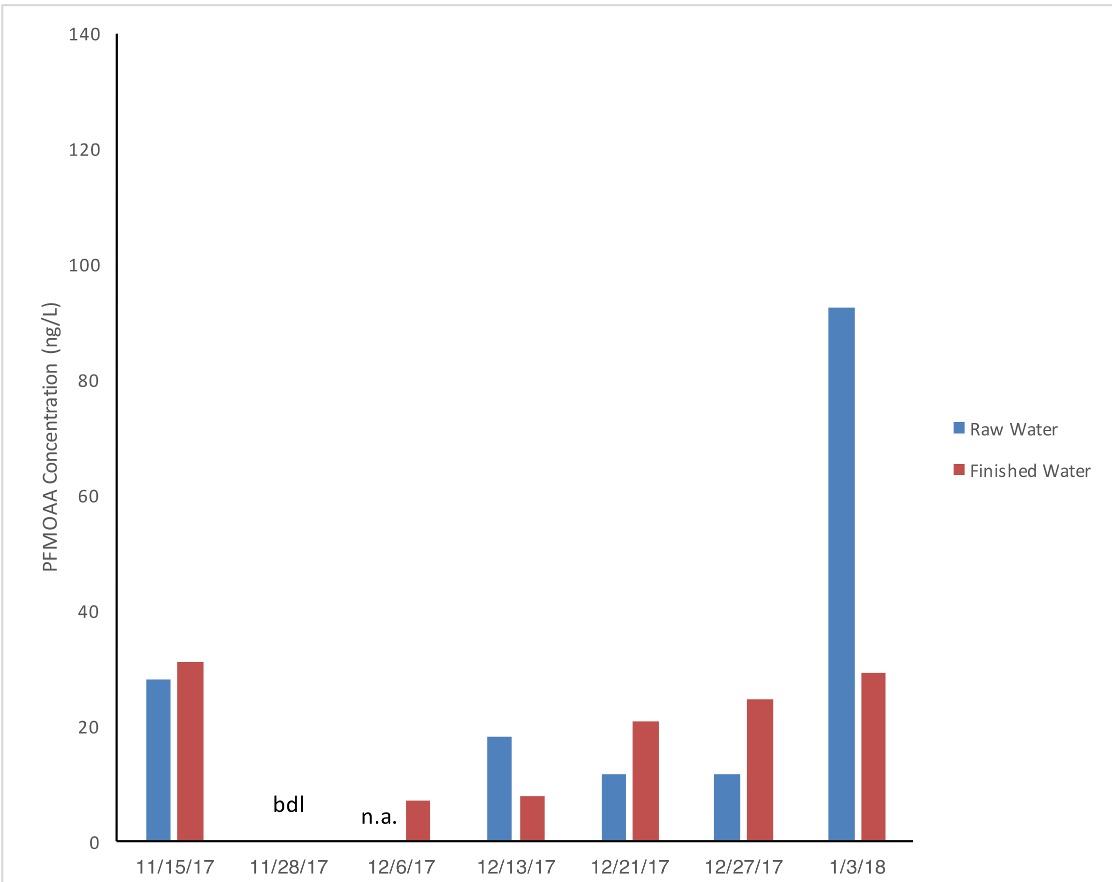


Figure 2: Semi-quantitative concentrations of other non-targeted perfluorinated compounds detected in raw and finished waters collected at Sweeney Water Treatment Plant. (bdl= below detection limit and n.a. is not analyzed)

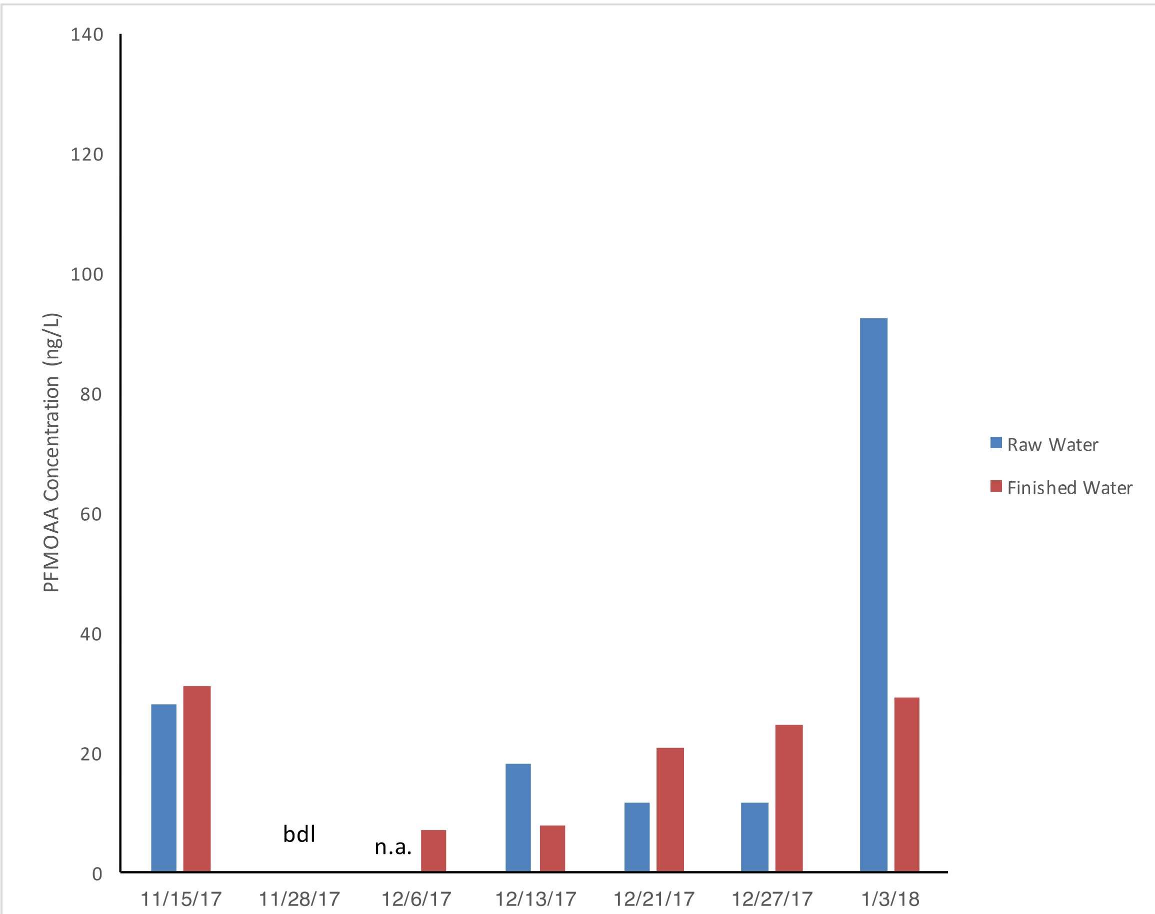


Figure 3: Semi-quantitative concentrations of other non-targeted perfluorinated compounds detected in raw and finished waters collected at Sweeney Water Treatment Plant. (bdl= below detection limit and n.a. is not analyzed)

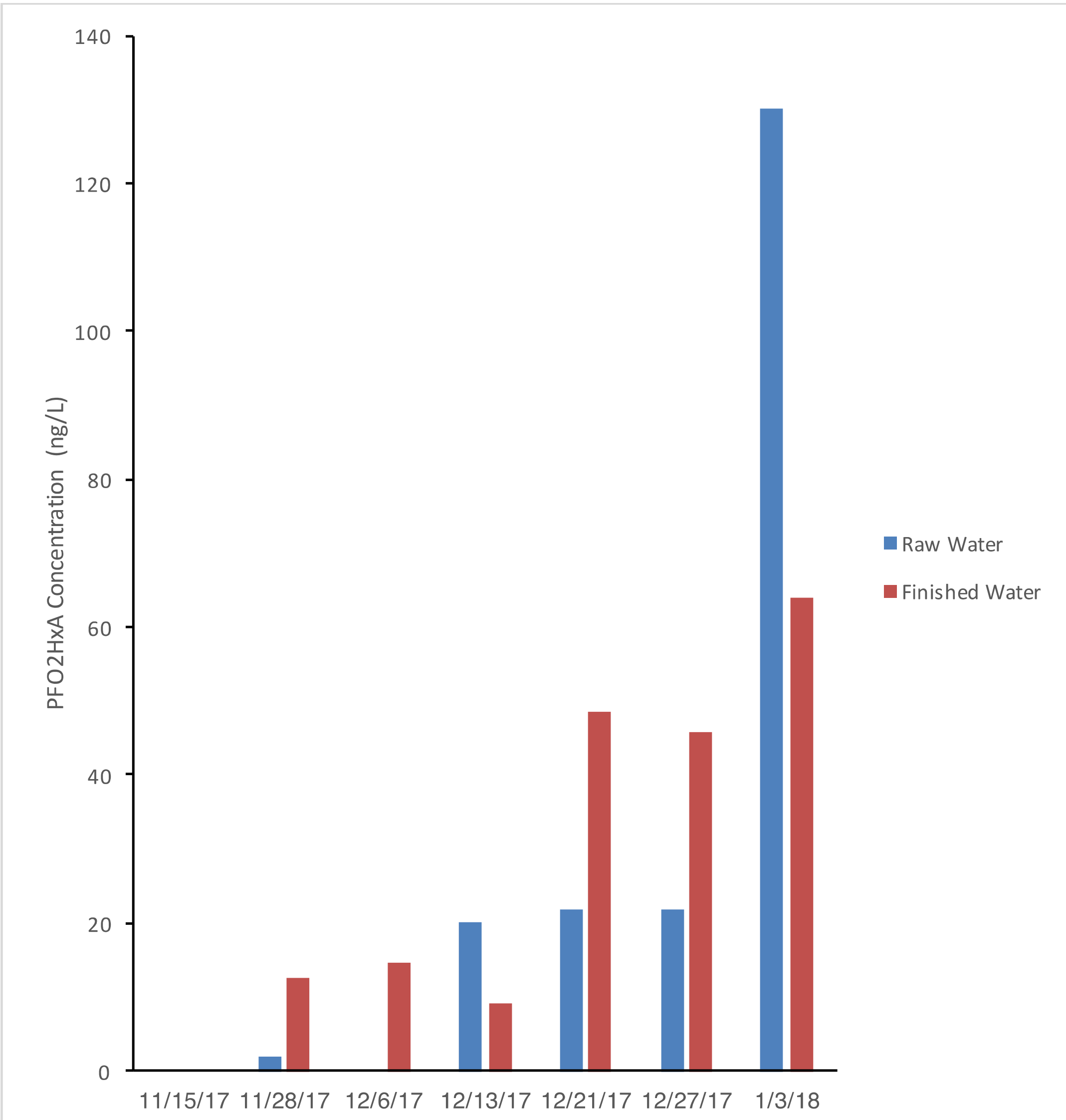


Figure 4: Semi-quantitative concentrations of other non-targeted perfluorinated compounds detected in raw and finished waters collected at Sweeney Water Treatment Plant. (bdl= below detection limit and n.a. is not analyzed)

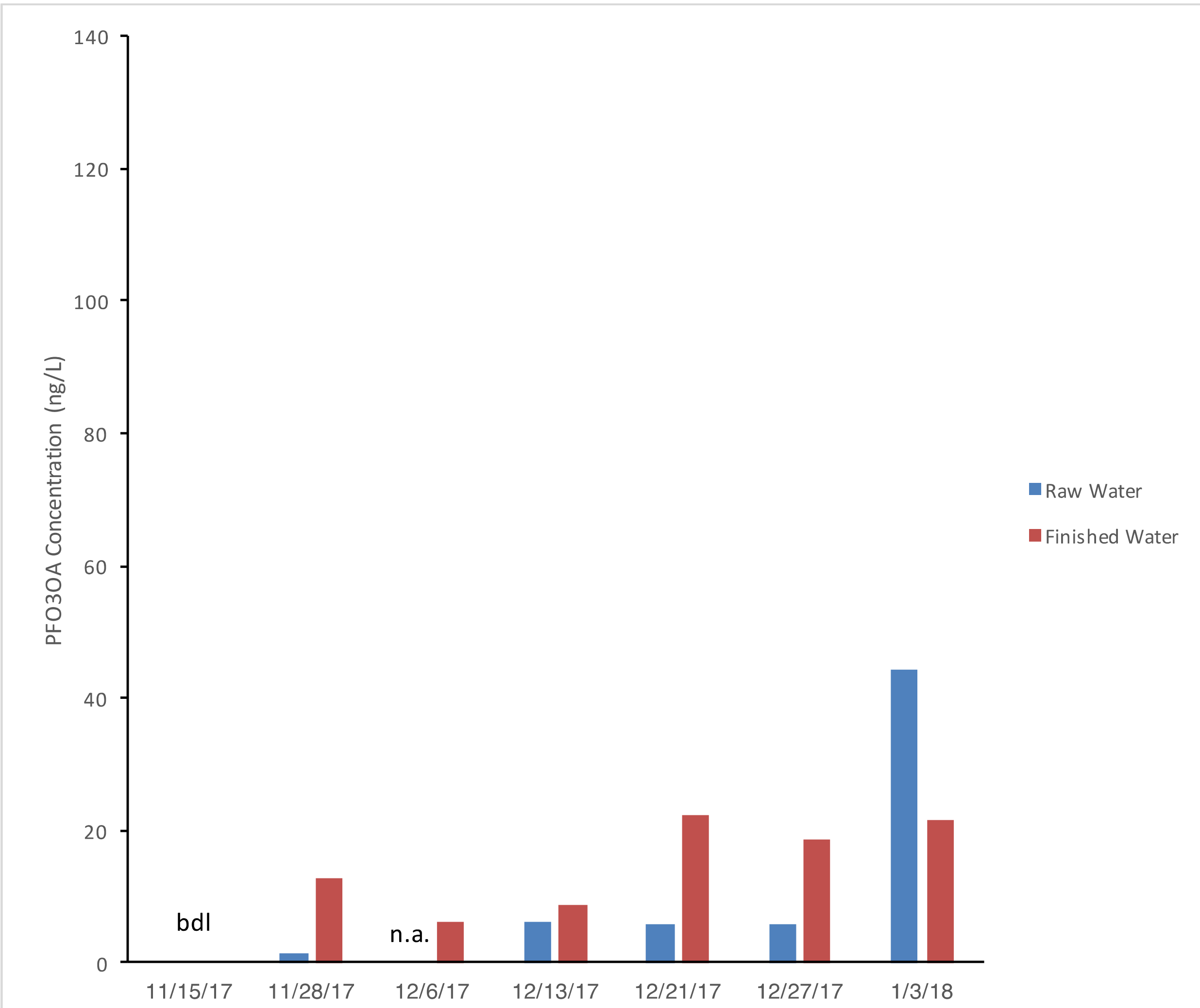


Figure 5: Semi-quantitative concentrations of other non-targeted perfluorinated compounds detected in raw and finished waters collected at Sweeney Water Treatment Plant. (n.a. is not analyzed)

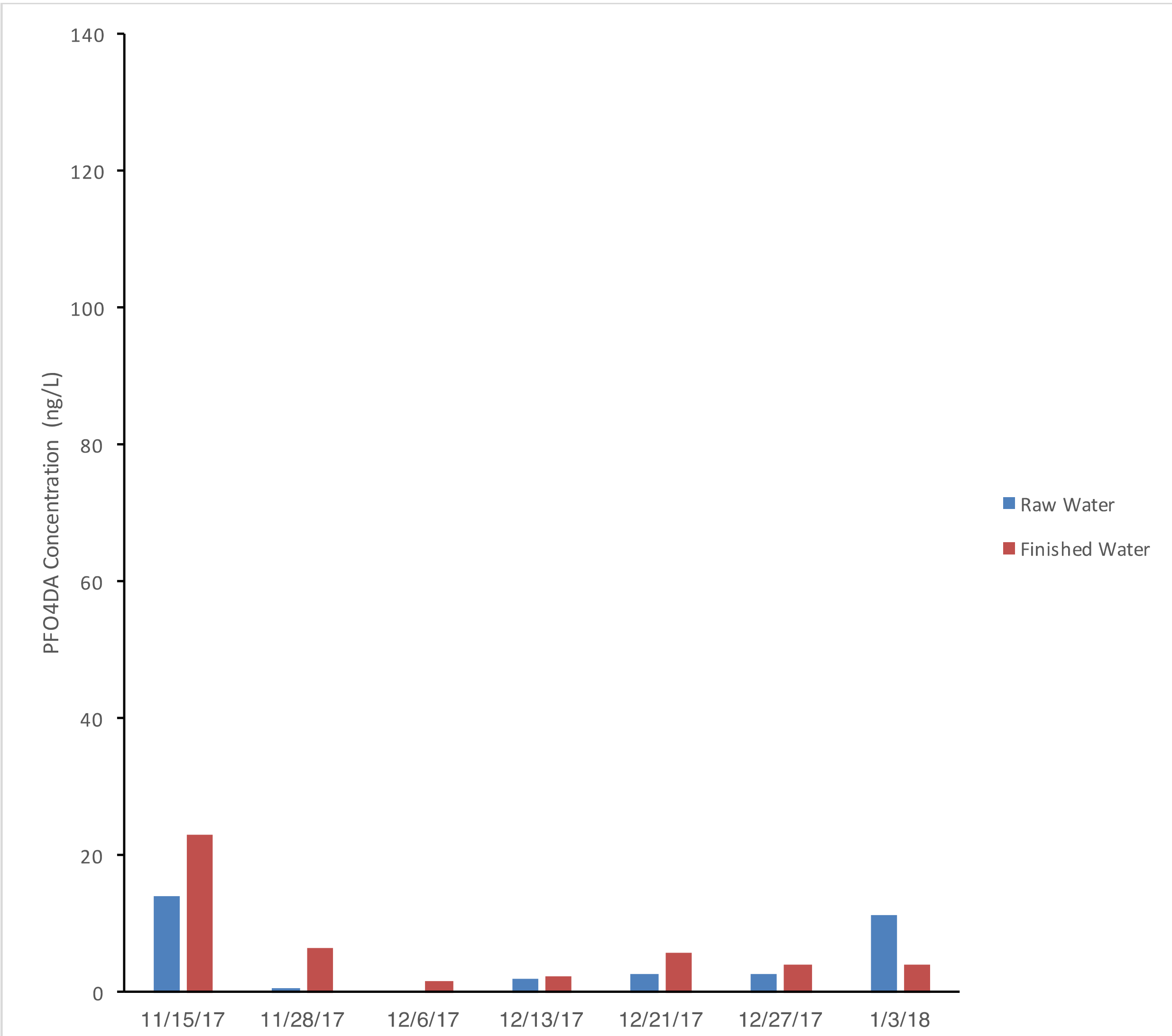
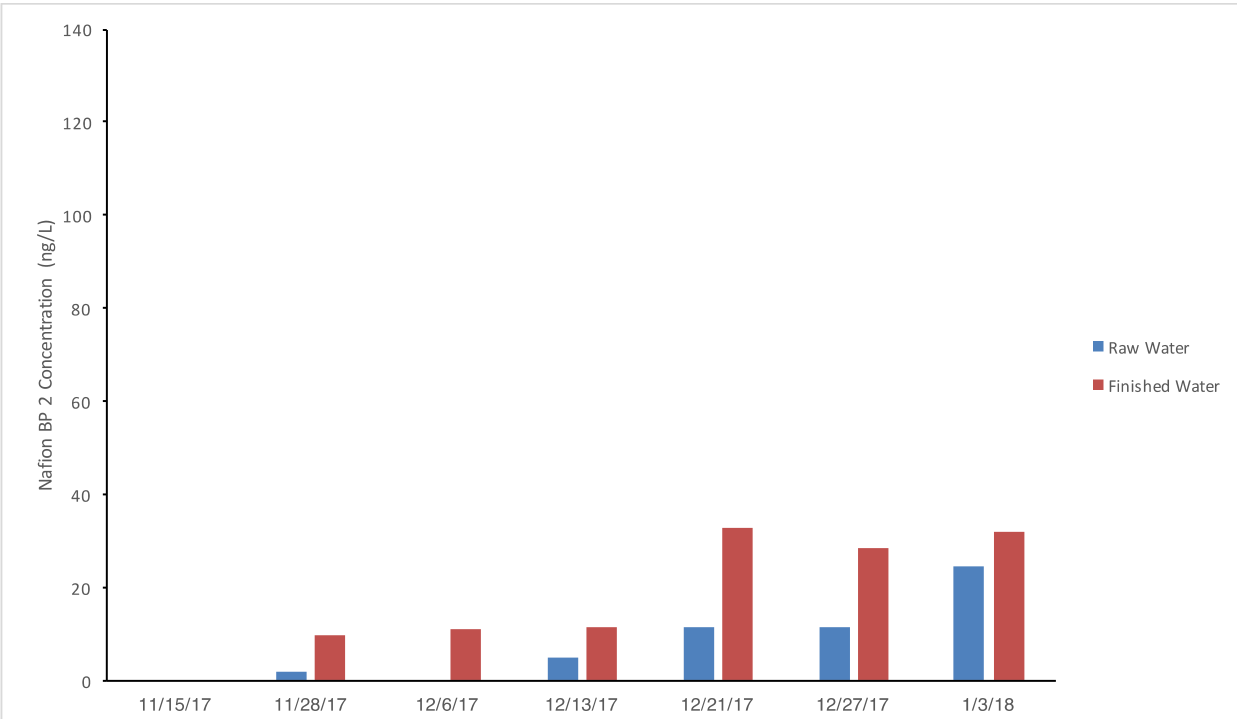
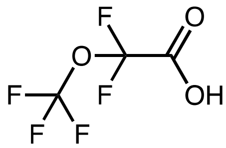


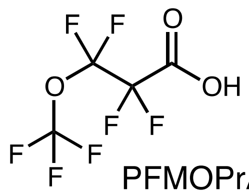
Figure 6: Semi-quantitative concentrations of other non-targeted perfluorinated compounds detected in raw and finished waters collected at Sweeney Water Treatment Plant. (bdl= below detection limit and n.a. is not analyzed)



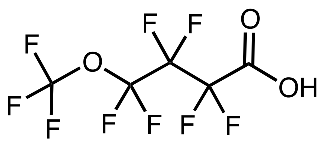
Appendix:



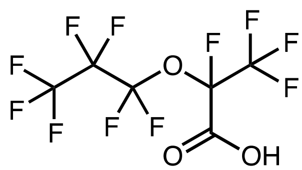
PFMOAA



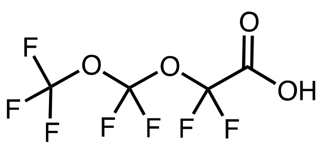
PFMOPrA



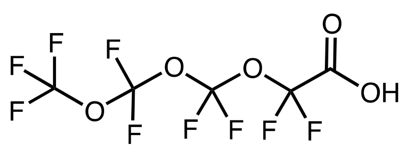
PFMOBA



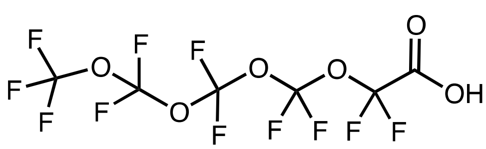
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

Cape Fear Public Utility Authority

Project Report

1.0 Introduction:

The focus of this report is to present and describe, to date, the non-targeted screening of perfluorinated alkyl substances (PFAS) in raw and finished water collected on a weekly basis from the Sweeney Water Treatment facility. The workflow involves isolating PFAS from water samples with subsequent analysis by LC/QTOF. The chromatogram is explored for non-targeted compounds by hand as well as statistically to identify new compounds.

2.0 Methods:

Water samples are collected in HDPE containers that are pre-rinsed with methanol prior to filling. Sample processing and QA/QC procedures were followed as described in Nakyama et al. (2010)[1] and Styrnar et al. (2015)[2]. No PFAS compounds were detected in field blanks and laboratory blanks indicating that no contamination took place.

2.1 High Resolution Mass Spectrometric Analysis:

Non-targeted analysis of each sample was carried out using an Agilent 1290 LC coupled to a Bruker quadrupole time of flight high resolution mass spectrometer. An electrospray ionization source operated in the negative mode was used for all analysis. During each analysis the mass axis was calibrated using the Agilent low tune mix. Molecular formulas were generated after calibration using Bruker Data Analysis package 4.2 with general elemental composition limits of: carbon 1-60, hydrogen 0-60, fluorine 0-100, oxygen 0-15, nitrogen 0-1, sulfur 0-1 and Na 0-1. These were refined depending on several observations such as isotope patterns. One atom of Cl would be included in the formula generation if the isotope pattern of 3:1 was observed for the $[M+]^-$ and $[M+2]^-$.

3.0 Results and Discussion:

Table 1 presents the non-targeted PFAS compounds that have been reported in previous updates to CFPUA. These compounds have been detected and described elsewhere[2]. Perfluoro-2-methoxyacetic acid has been successfully synthesized; therefore, we currently have a standard for quantification and structure confirmation. This standard has been shared with Dr. Mark Strynar at EPA. We have also obtained from Dr. Strynar standards for Nafion byproducts 1 and 2. All of these authentic standards are important for accurate identification and quantification.

Additional non-targeted compounds have been detected and are presented in Table 2. These compounds are unreported to the best of our knowledge in the literature. The molecular formula generated was used to search databases for possible matches. Compounds 1 and 2 have CAS numbers whereas compound 3 does not. It is important not to assume the structure given by the CAS number matches what was observed in the samples until further experiments are performed. Structure elucidation is ongoing and standards are being purchased, when available, to aid in identification.

To guide the non-targeted screening in raw and finished drinking water, the seven raw and seven finished waters were treated statistically to construct a volcano plot (Figure 1). The volcano plot is a type of scatter plot used to aid in the identification of changes in large data sets composed of replicate measurements. The replicates in this case are the weekly sampling of raw and finished waters. The assumptions are that the raw source waters do not change and finished water is treated consistently. The data are then plotted with the factor of change on the x-axis versus the statistical significance (probability, p) on the y-axis. A volcano plot combines the statistical t-test with the magnitude of the change enabling visual identification of points that show large magnitude changes that are statistically significant. The negative log of the p-value on the y-axis (base 10) is plotted resulting in low p values (high significance) towards the top of the plot. The x-axis is the log of the fold change of the two conditions, in this case raw and finished drinking water. By using the log fold change, data points that are in both directions appear equidistant from the center. Therefore, two regions of interest appear: those points that are found toward the top of the plot that are far to either right or left hand side (orange color-coded on the plot). These represent data points that display large magnitude fold change (i.e. left or right of center) as well as high statistical significance (towards the top of the plot).

The high resolution mass spectrometric data used to generate Figure 1 consisted of 75,466 individual time and m/z steps of which 14,025 are significant ($p<0.05$). The significance arises from differences in organic compounds detected by the LC/QTOF raw and finished waters that were analyzed exactly the same way. This post treatment of data will help guide further study of these compounds. An important consideration is that not all these significant compounds will be related to PFAS or contain a fluorine atom but post treatment allows for quickly visualizing the data and guidance.

4.0 Future Directions:

Our current analytical workup focuses on the retention of fluorinated compounds that contain an acidic functional group. We will be opening the analytical window to other organic fluorine molecules with functional groups other than acids. We will focus on using a fluorine specific solid phase extraction procedure that selectively extracts fluorine-containing organic compounds. This procedure will preconcentrate analytes prior to analysis and will be selective to organic compounds that contain at least one fluorine atom.

We will also use a reverse phase solid phase extraction procedure to isolate more non-polar organic compounds from water and analyze by GC/MS. This will allow us to investigate less polar compounds that might be present in the water and not amenable to (-) ESI source. These additional screening methodologies are significant because they may identify additional fluorinated compounds not detected with current techniques widely used in the analysis of fluorine compounds in drinking water.

1. Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B., *Environ. Sci. Technol.* **2010,** *44*, 4103.
2. Strynar, M.; Dagnino, S.; McMahen, R.; Liang, S.; Lindstrom, A.; Andersen, E.; McMillan, L.; Thurman, M.; Ferrer, I.; Ball, C., Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS). *Environmental Science & Technology* **2015,** *49* (19), 11622-11630.

Table 1: Non-targeted compounds detected in raw and finished water collected to date. We have recently obtained authentic standards for CAS numbers 674-13-5,29311-67-9 and 749836-20-2. There is not an authentic standard for the remaining compounds.

Compound	Molecular Formula	M	[M-H]- m/z	CAS Number	Reference
Ether compounds					
perfluoro-2-methoxyacetic acid	C3HF5O3	179.9845	178.9767	674-13-5	Strynar et al., 2015;Sun et al. 2016
perfluoro(3,5-dioxahexanoic)acid	C4HF7O4	245.9762	244.9684	39492-88-1	Strynar et al., 2015;Sun et al. 2016
perfluoro(3,5,7-trioctanoic)acid	C5HF9O5	311.9679	310.9601	39492-89-2	Strynar et al., 2015;Sun et al. 2016
perfluoro(3,5,7,9-tetradecanoic)acid	C6HF11O6	377.9596	376.9518	39492-90-5	Strynar et al., 2015;Sun et al. 2016
Perfluorosulfonic acids					
PFESA Byproduct I	C7HF13O5S	443.9337	442.9264	29311-67-9	Strynar et al., 2015
PFESA Byproduct II	C7H2F14O5S	463.9399	462.9326	749836-20-2	Strynar et al., 2015

Table 2: Non-targeted compounds detected in raw and finished water collected to date. The formula and associated error is for the deprotonated species. Until the structure is elucidated these are considered tentative.

Compound Number	[M-H]- m/z	Formula	err [ppm]	err [mDa]	Example CAS Number	Commercial Vendor
1	362.96972	C 7 F 13 O 2	-0.3	-0.1	15899-29-3	Yes
2	506.95306	C 10 F 17 O 4	0.1	0.9	87944-97-6	No
3	698.91672	C 13 H 3 Cl F 19 O 9	0.1	0.05		

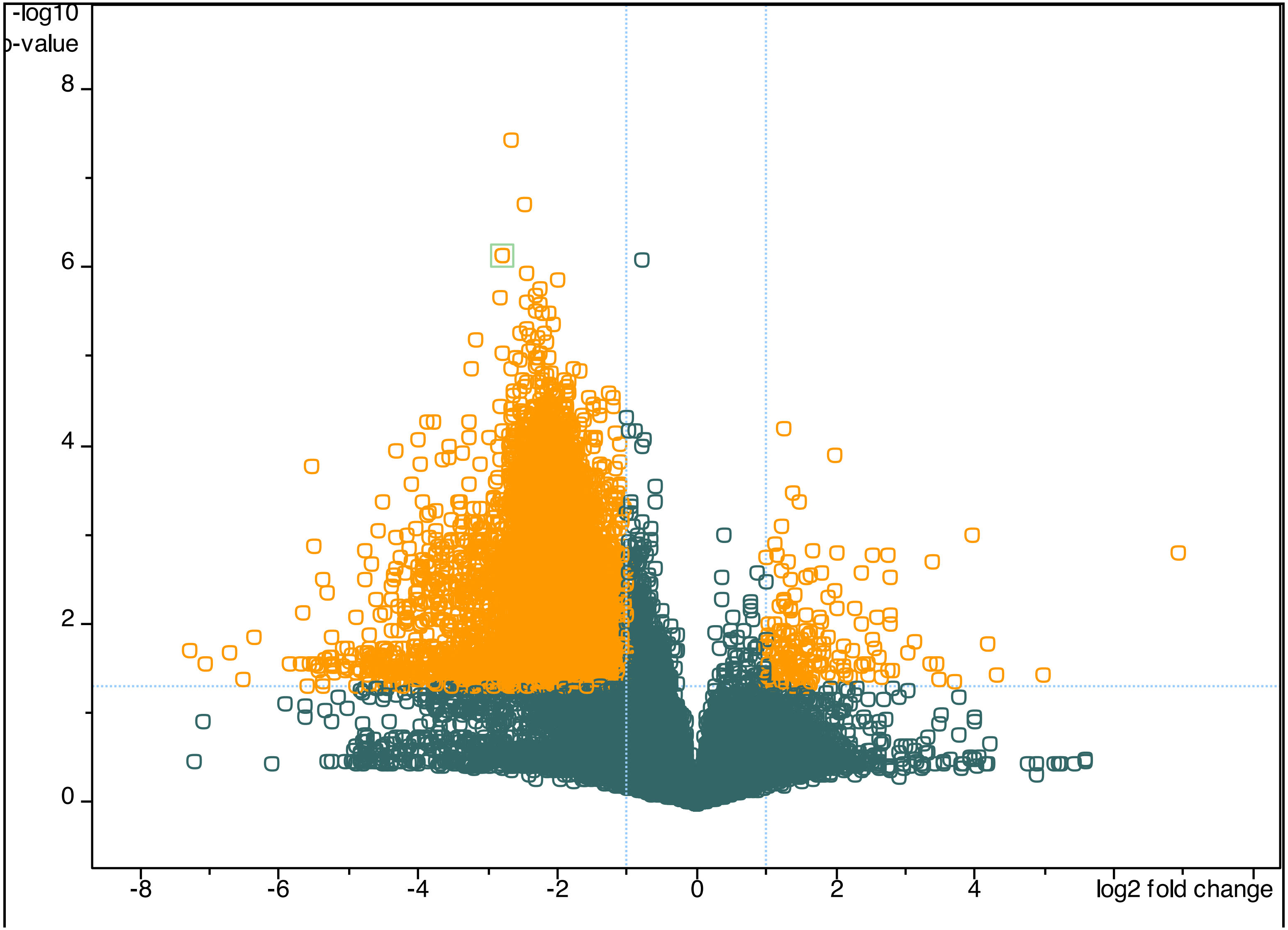
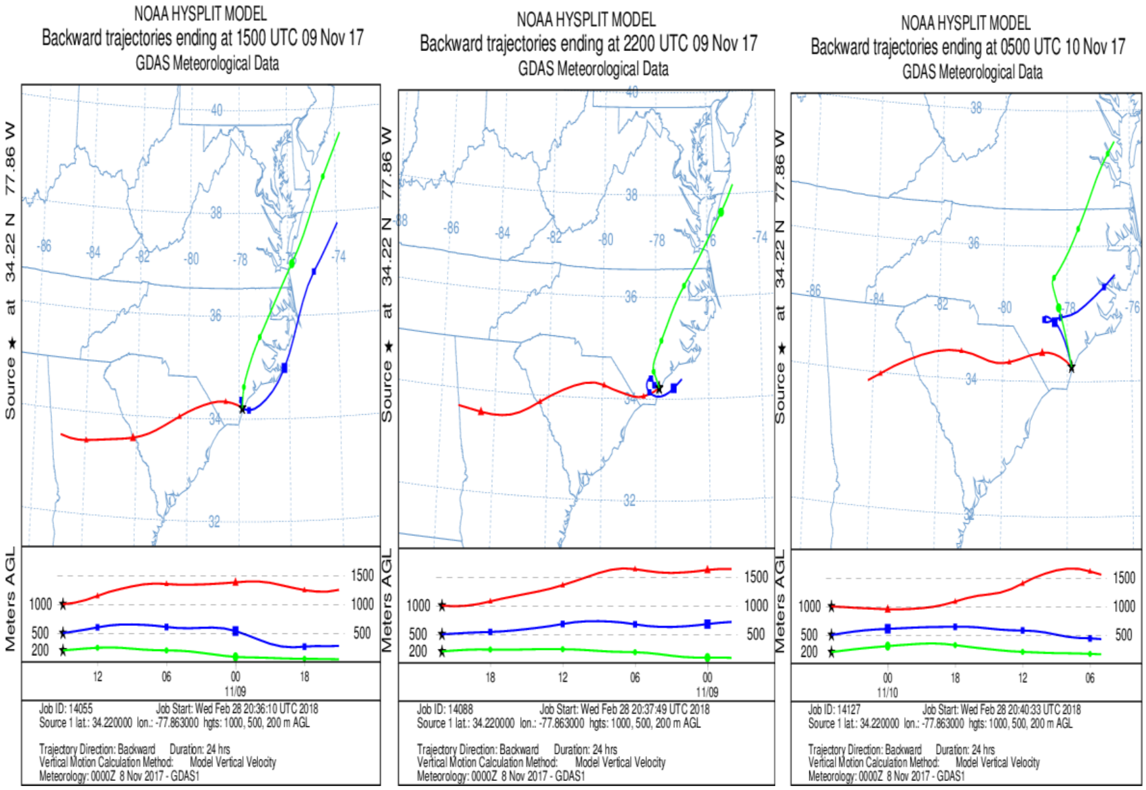
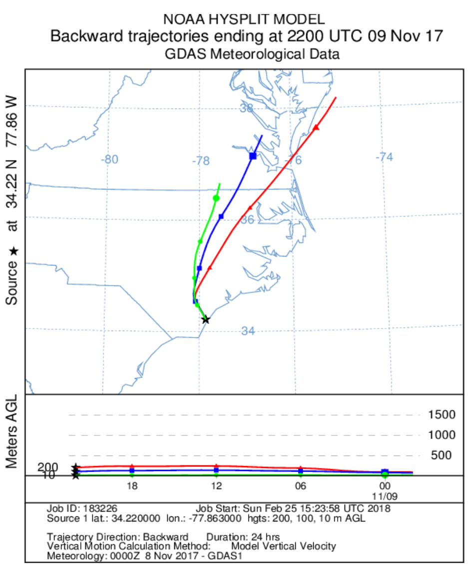


Figure 1: LC/QTOF data from seven raw and seven finished waters presented in a volcano plot. The higher the points on the y-axis the more significant the difference between the samples.



E1775 Storm November 9, 2017. NOAA HYSPLIT 24 hour air mass back trajectories for the beginning, middle and end of the rain event. Heights are 200m (green), 500m (blue) and 1000m (red) above ground level. Times are Coordinated Universal Time (UTC) which is equivalent to GMT, currently 5 hours ahead of Wilmington, NC.

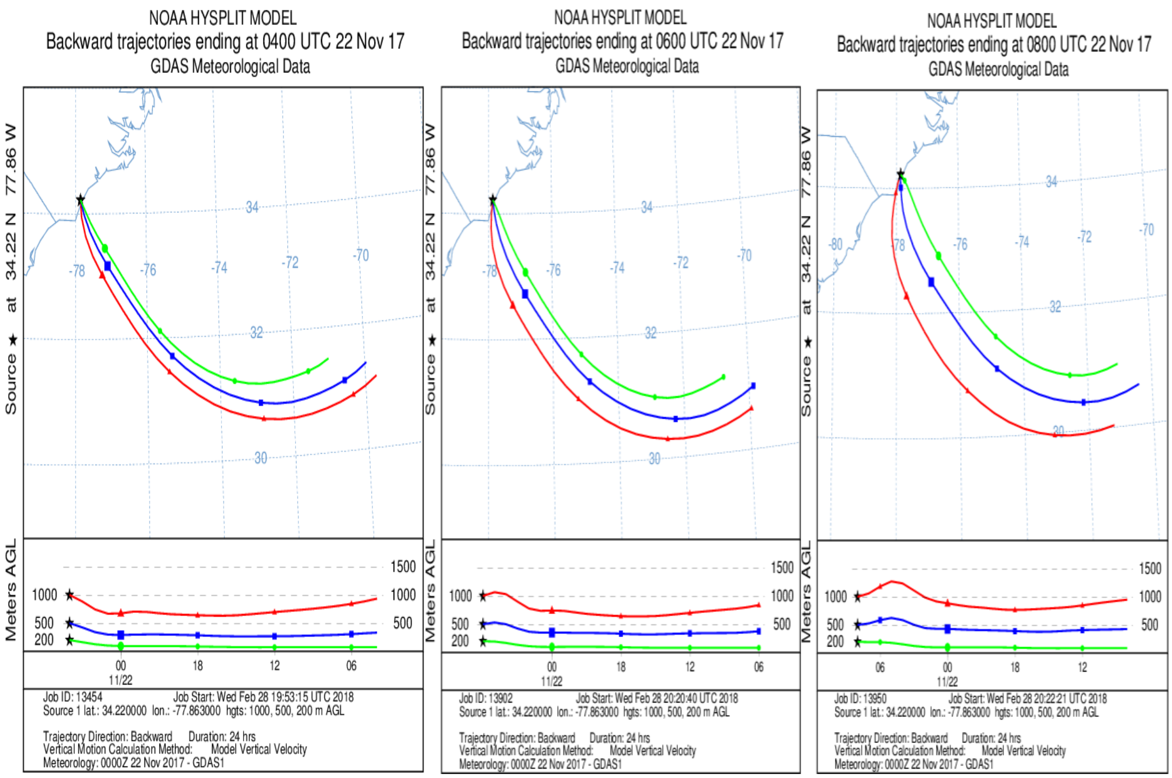
Rain Event 1775 had 24 ppt GenX (24 ng/L). UNCW received 0.78 inches of rain. The pH was 5.24.



Low level air mass back trajectories for the middle of rain event E 1775. Heights are 10m (green), 100m (blue) and 200m (red) above ground level.

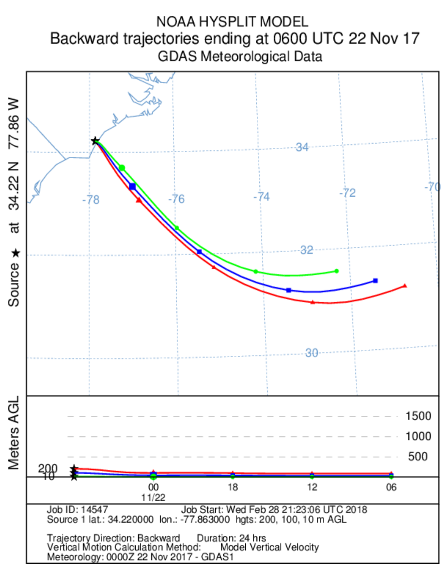
Joan D. Willey, Robert J. Kieber, Ralph N. Mead, G. Brooks Avery and Stephen A. Skrabal, Department of Chemistry and Biochemistry, University of North Carolina Wilmington

Draxler, R.R., Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, College Park, MD. https://ready.arl.noaa.gov/HYSPLIT_traj.php



E1778 Marine Storm November 21 - 22, 2017. NOAA HYSPLIT 24 hour air mass back trajectories for the beginning, middle and end of the rain event. Heights are 200m (green), 500m (blue) and 1000m (red) above ground level. Times are Coordinated Universal Time (UTC) which is equivalent to GMT, currently 5 hours ahead of Wilmington, NC.

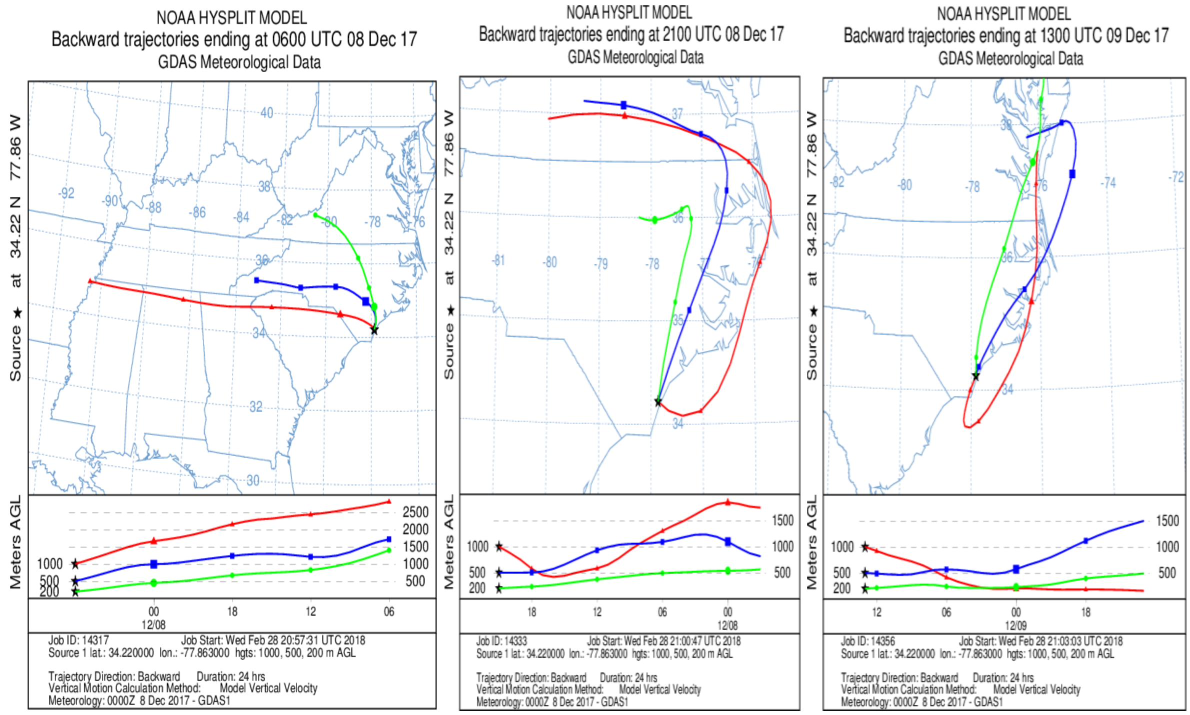
Rain Event 1778 had none detectable GenX (< 3 ppt, less than 3 ng/L). UNCW received 0.26 inches of rain. The pH was not analyzed.



Low level air mass back trajectories for the middle time of rain event E1778. Heights are 10m (green), 100m (blue) and 200m (red) above ground level.

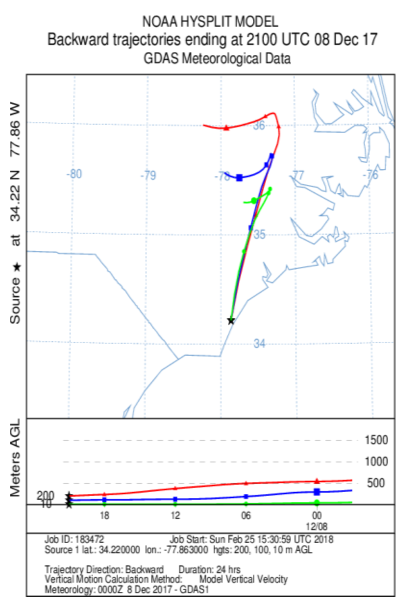
Joan D. Willey, Robert J. Kieber, Ralph N. Mead, G. Brooks Avery and Stephen A. Skrabal, Department of Chemistry and Biochemistry, University of North Carolina Wilmington

Draxler, R.R., Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, College Park, MD. https://ready.arl.noaa.gov/HYSPLIT_traj.php



E1781 Storm December 8 – 9, 2017. NOAA HYSPLIT 24 hour air mass back trajectories for the beginning, middle and end of the rain event. Heights are 200m (green), 500m (blue) and 1000m (red) above ground level. Times are Coordinated Universal Time (UTC) which is equivalent to GMT, currently 5 hours ahead of Wilmington, NC.

Rain Event 1781 had > 500 ppt GenX (greater than 500 ng/L). This concentration was above the highest standard in the calibration curve used on the day of analysis. UNCW received 1.80 inches of rain. The pH was 4.68.



Low level air mass back trajectories for the middle time of rain event E1781. Heights are 10m (green), 100m (blue) and 200m (red) above ground level.

Joan D. Willey, Robert J. Kieber, Ralph N. Mead, G. Brooks Avery and Stephen A. Skrabal, Department of Chemistry and Biochemistry, University of North Carolina Wilmington

Draxler, R.R., Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, College Park, MD. https://ready.arl.noaa.gov/HYSPLIT_traj.php