UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

August 31, 2017

MEMORANDUM

SUBJECT: Laboratory PFAS Results for NC DEQ Cape Fear Watershed Sampling: Preliminary Non-Targeted Analysis

FROM: Timothy J. Buckley, Director
Exposure Methods and Measurements Division

THRU: Jennifer Orme-Zavaleta, Director
National Exposure Research Laboratory

TO: Linda Culpepper, Deputy Director
Division of Water Resources
North Carolina Department of Environmental Quality

Enclosed please find our fourth report of PFAS concentrations in Cape Fear River water samples collected under the direction of NC DEQ. This report includes preliminary findings from our non-targeted analyses. These results were presented and discussed during your visit August 28, 2017 to our Laboratory in Research Triangle Park, N.C.

Thank you for inviting us to be a part of this effort that addresses a very important public health concern in North Carolina. These results represent the effort of many within our lab, but I would especially like to acknowledge Drs. Mark Strynar, Andy Lindstrom, James McCord, and Seth Newton in conducting the laboratory analyses, Dr. Myriam Medina-Vera who provided invaluable support and coordination, and Ms. Sania Tong Argao who supported and oversaw quality assurance.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2454 or email buckley.timothy@epa.gov. I look forward to our continued work together.

Enclosure

CC: Becky B. Allenbach, USEPA Region 4
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Summary of Results

Our preliminary non-targeted results are limited to samples from the Chemours outfall and finished water from the Sweeney Water Treatment Plant for weeks 1 – 6. We chose these sites because we believe the concentrations observed bound this portion of the watershed. Furthermore, we did not want to delay our reporting due to the additional time required to assemble and interpret results from the other locations. We are continuing to work on a comprehensive report that will include targeted and non-targeted analysis results at all locations over the seven weeks of sampling.

We include five analytes in this initial non-targeted analysis report (Table 1). An important limitation to our non-targeted analysis results is that these results are considered semi-quantitative. We cannot know the exact concentration because no authentic standards are available for these chemicals. However, we are very confident of the chemical identity based on the high resolution mass spectrometry and knowledge of Chemours' chemical products.

Table 1. Analytes Measured Non-Targeted LC/TOFMS Analysis

Short Name	Chemical Name	Formula	CAS no.	Monoisotopic Mass (Da)
PFESA Byproduct 1	Perfluoro-3,6-dioxa-4-methyl-7-octene-1-sulfonic acid	$C_7HF_{13}O_5S$	29311-67-9	443.9337
PFESA Byproduct 2	Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-	$C_7H_2F_{14}O_5S$	749836-20-2	463.9399
PFMOAA	(2,2-difluoro-2-(trifluoromethoxy)acetic acid)	$C_3HF_5O_3$	674-13-5	179.9846
PFO2HxA	perfluoro-3,5-dioxahexanoic acid	$C_4HF_7O_4$	39492-88-1	245.9763
PFO3OA	perfluoro-3,5,7-trioxaoctanoic acid	$C_5HF_9O_5$	39492-89-2	311.9680

We provide semi-quantitative "concentrations" in two forms (Table 2). The first is the peak area that is associated with the monoisotopic mass for each compound. The peak area is generally proportional to the analyte concentration and it is useful in interpreting changes in concentration over time and between locations for a given analyte. For example, for PFMOAA measured in Sweeney Finished water, we see the peak area change from ~4.5 million to 3,000 counts from week 1 to 6. This can be interpreted as roughly a 1,500-fold decrease in concentration without knowing the exact concentration. The second way we provide a semi-quantitative estimate of concentration is to scale the non-targeted analyte based on the measured concentration of GenX.

$$[NTA] = [GenX] * \frac{NTA_{PA}}{GenX_{PA}}$$

Where: [NTA] is the concentration of the non-targeted analyte (ng/L)

[GenX] is the concentration of GenX (ng/L)
NTA_{PA} is the integrated peak area for the non-targeted analyte
$GenX_{PA}$ is the integrated peak area for GenX

In essence, we are assuming that the mass spectrometer responds to the non-targeted analyte as if it were GenX. The actual instrument response may be weaker or stronger resulting in an under- or over-estimation of the non-targeted concentration. Our experience with this class of analytes suggests that estimates of this fashion are accurate to within ~10-fold of the estimated value.

The non-targeted analyte estimated concentrations are particularly uncertain at the Chemours outfall during weeks 1-3. Concentrations were so high that even after samples were diluted 20X, we exceeded our calibration curve for GenX and were also likely saturating the mass spectrometer for both GenX and non-targeted analytes. The semi-quantitative estimate for the non-targeted analytes are particularly uncertain and likely underestimated. These results are shown in Table 2 and have been flagged accordingly.

Whether considering peak area or estimated concentration, the non-targeted results show two very different time profiles. For three of the analytes, concentrations at the outfall and Sweeney finished water show a precipitous drop very similar to what was observed for GenX (Figures 1-4). These results suggest that whatever mitigation strategy used to reduce GenX, was also effective for these three chemicals. The second time profile is for two perfluoroethersulfonic acid (PFESA) byproducts. We believe these chemicals are a byproduct of Nafion production. In contrast to the GenX-related chemicals, for these two chemicals, we do not observe a clear decreasing trend in concentration (Figures 5 & 6). These results suggest the discharge of these chemicals was unaffected by whatever strategies were used to mitigate GenX discharge. Concentrations of the PFESAs range from 2,900 to 73,900 ng/L at the Chemours outfall and 53 to 7,860 ng/L in Sweeney finished drinking water. Note that these concentrations are in the same range as GenX originally noted in Sun et al., 2016.[1]

In Figure 7, the plots show the two different types of time profiles for the six analytes. Each analyte is graphed as a relative percentage of its maximum intensity over the sampling period. For the PFESAs byproducts, this maximum period occurred in the middle of sampling, while for the other analytes, the maximum was during the first week.

As with GenX, our QA/QC results for the non-targeted results are within expected tolerances. We did not detect any of the analytes in field blanks, indicating that no field or lab contamination took place. Because there are no standards for these analytes, we have no assessment of accuracy, but duplicate analyses were within 20 percent. The laboratory methods for the results reported here are described in Sun *et al.,* 2016[1] and Strynar *et al.,* 2015[2].

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[1] Sun M; Arevalo E; Strynar M; Lindstrom A; Richardson M; Kearns B; Pickett A; Smith C; Knappe DRU: Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. Environmental Science & Technology Letters. 2016

[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). Environ Sci Technol. 2015

Table 2. Semi-Quantitative Estimates of GenX and Non-Targeted Analyte Concentrations (ng/L) Measured at Chemours Outfall and Sweeney Finished Drinking Water During Sampling Weeks 1 – 6.

Non-Target Analyte	Location	Sample Week	NTA Area	GenX Area	GenX Conc. (ng/L)	NTA Conc. (ng/L)	Flag
PFMOAA	Chemours Outfall 002	1	63,712,278	10,363,496	21,760	134,000	1
PFO2HxA	Chemours Outfall 002	1	182,599,647	10,363,496	21,760	383,000	1
PFO3OA	Chemours Outfall 002	1	51,940,394	10,363,496	21,760	109,000	1
GenX	Chemours Outfall 002	1	10,363,496	10,363,496	21,760	21,800	1
PFESA Byproduct 1	Chemours Outfall 002	1	1,380,791	10,363,496	21,760	2,900	1
PFESA Byproduct 2	Chemours Outfall 002	1	14,039,048	10,363,496	21,760	29,500	1
PFMOAA	Sweeney	1	4,560,543	293,854	726	11,300	2
PFO2HxA	Sweeney	1	3,594,341	293,854	726	8,880	2
PFO3OA	Sweeney	1	1,265,760	293,854	726	3,130	2
GenX	Sweeney	1	293,854	293,854	726	726	2
PFESA Byproduct 1	Sweeney	1	21,356	293,854	726	53	2
PFESA Byproduct 2	Sweeney	1	664,104	293,854	726	1,640	2
PFMOAA	Chemours Outfall 002	2	37,373,851	8,345,860	15,250	68,300	1
PFO2HxA	Chemours Outfall 002	2	71,331,553	8,345,860	15,250	130,000	1
PFO3OA	Chemours Outfall 002	2	19,111,355	8,345,860	15,250	34,900	1
GenX	Chemours Outfall 002	2	8,345,860	8,345,860	15,250	15,300	1
PFESA Byproduct 1	Chemours Outfall 002	2	1,895,442	8,345,860	15,250	3,460	1
PFESA Byproduct 2	Chemours Outfall 002	2	13,230,172	8,345,860	15,250	24,200	1
PFMOAA	Sweeney	2	1,059,209	10,129	100	10,500	
PFO2HxA	Sweeney	2	738,362	10,129	100	7,290	
PFO3OA	Sweeney	2	251,372	10,129	100	2,480	
GenX	Sweeney	2	10,129	10,129	100	100	
PFESA Byproduct 1	Sweeney	2	14,447	10,129	100	143	
PFESA Byproduct 2	Sweeney	2	437,286	10,129	100	4,320	
PFMOAA	Chemours Outfall 002	3	11,265,308	9,390,564	21,530	25,800	1
PFO2HxA	Chemours Outfall 002	3	10,284,502	9,390,564	21,530	23,600	1
PFO3OA	Chemours Outfall 002	3	1,545,961	9,390,564	21,530	3,540	1
GenX	Chemours Outfall 002	3	9,390,564	9,390,564	21,530	21,500	1
PFESA Byproduct 1	Chemours Outfall 002	3	5,721,468	9,390,564	21,530	13,100	1
PFESA Byproduct 2	Chemours Outfall 002	3	17,252,514	9,390,564	21,530	39,600	1

Non-Target Analyte	Location	Sample Week	NTA Area	GenX Area	GenX Conc. (ng/L)	NTA Conc. (ng/L)	Flag
NOTE: For week#3, there was insufficient sample available for a Sweeny finished water analysis. For week#4, there was insufficient sample available for a Chemours outfall 002 water analysis.							
PFMOAA	Sweeney	4	82,181	21,348	81	312	
PFO2HxA	Sweeney	4	210,440	21,348	81	798	
PFO3OA	Sweeney	4	168,842	21,348	81	641	
GenX	Sweeney	4	21,348	21,348	81	81	
PFESA Byproduct 1	Sweeney	4	31,581	21,348	81	120	
PFESA Byproduct 2	Sweeney	4	622,627	21,348	81	2,360	
PFMOAA	Chemours Outfall 002	5	558,337	287,302	713	1,390	3
PFO2HxA	Chemours Outfall 002	5	366,856	287,302	713	910	3
PFO3OA	Chemours Outfall 002	5	175,874	287,302	713	436	3
GenX	Chemours Outfall 002	5	287,302	287,302	713	713	3
PFESA Byproduct 1	Chemours Outfall 002	5	1,797,348	287,302	713	4,460	3
PFESA Byproduct 2	Chemours Outfall 002	5	15,762,943	287,302	713	39,100	3
PFMOAA	Sweeney	5	3,405	8,630	95	37	
PFO2HxA	Sweeney	5	100,174	8,630	95	1,100	
PFO3OA	Sweeney	5	63,750	8,630	95	702	
GenX	Sweeney	5	8,630	8,630	95	95	
PFESA Byproduct 1	Sweeney	5	14,352	8,630	95	158	
PFESA Byproduct 2	Sweeney	5	713,541	8,630	95	7,860	
PFMOAA	Chemours Outfall 002	6	113,443	16,637	102	696	
PFO2HxA	Chemours Outfall 002	6	70,333	16,637	102	431	
PFO3OA	Chemours Outfall 002	6	14,038	16,637	102	86	
GenX	Chemours Outfall 002	6	16,637	16,637	102	102	
PFESA Byproduct 1	Chemours Outfall 002	6	2,569,948	16,637	102	15,800	
PFESA Byproduct 2	Chemours Outfall 002	6	12,055,574	16,637	102	73,900	
PFMOAA	Sweeney	6	3,312	11,030	70	21	
PFO2HxA	Sweeney	6	185,715	11,030	70	1,170	
PFO3OA	Sweeney	6	123,515	11,030	70	778	
GenX	Sweeney	6	11,030	11,030	70	70	
PFESA Byproduct 1	Sweeney	6	11,504	11,030	70	72	
PFESA Byproduct 2	Sweeney	6	741,742	11,030	70	4,670	

Flag

1 = Sample was diluted 20X and diluted sample exceeded the calibration curve for GenX

2 = Sample was diluted 5X

3 = Sample was diluted 20X

Figure 1. GenX Concentration (ng/L) Profile

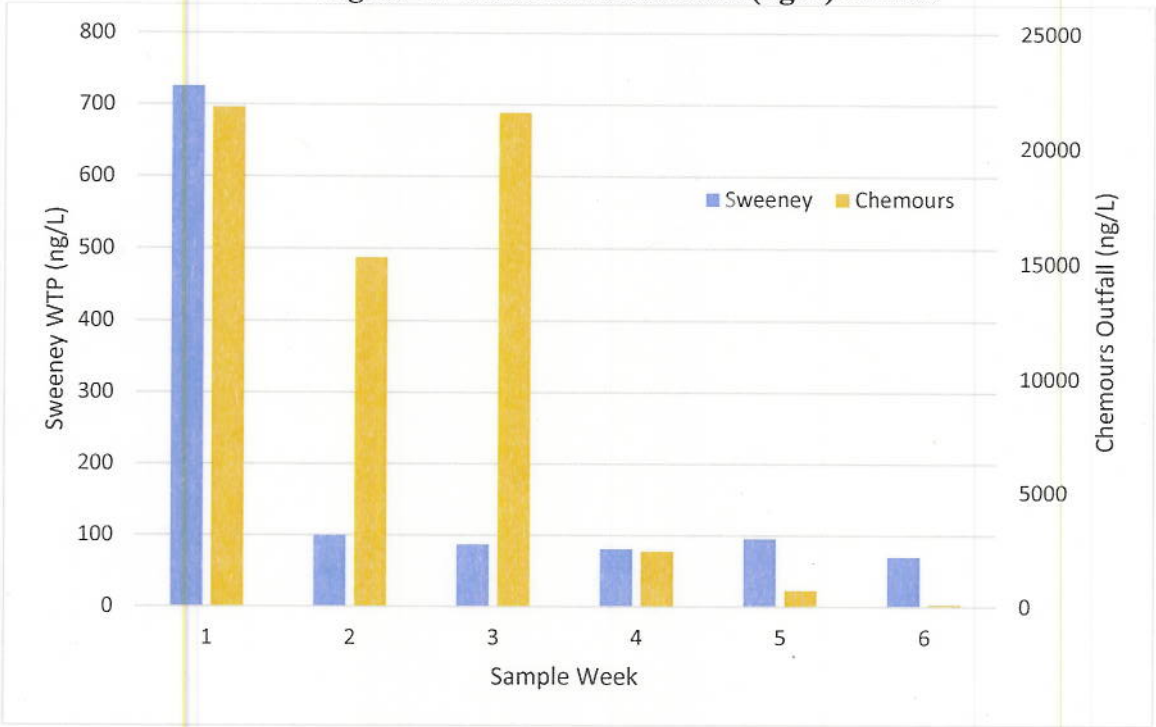

Figure 2. PFMOAA Concentration (ng/L) Profile

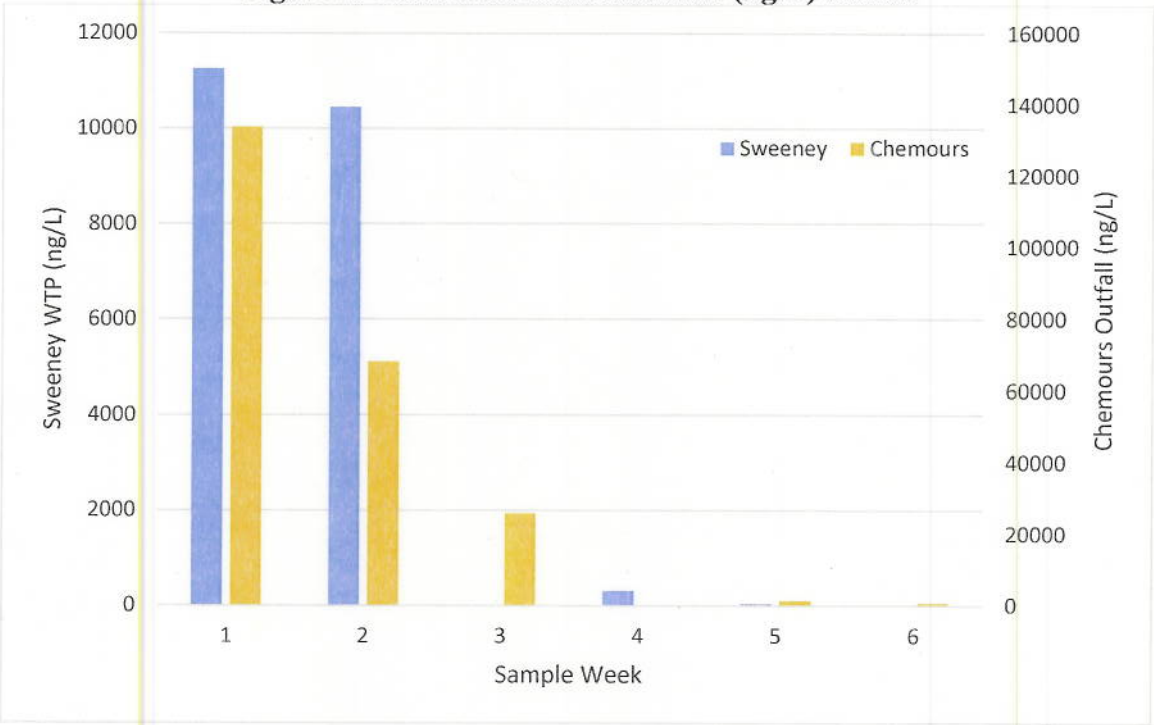

Figure 3. PFO2HxA Concentration (ng/L) Profile

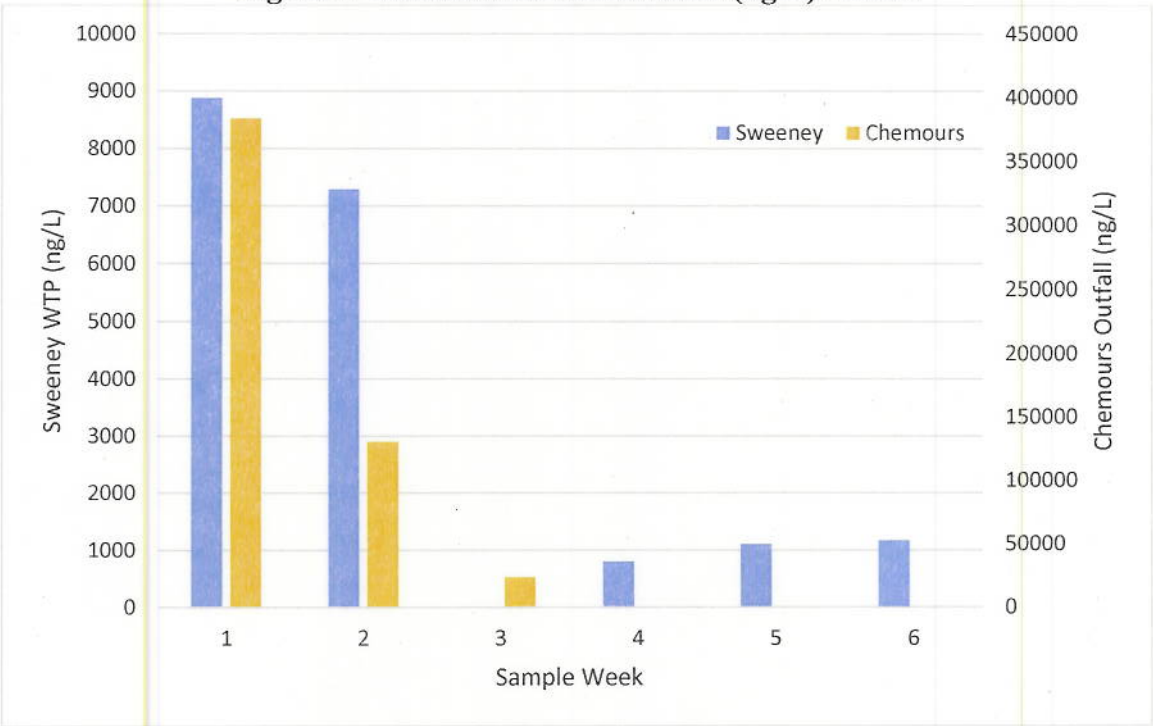

Figure 4. PFO3OA Concentration (ng/L) Profile

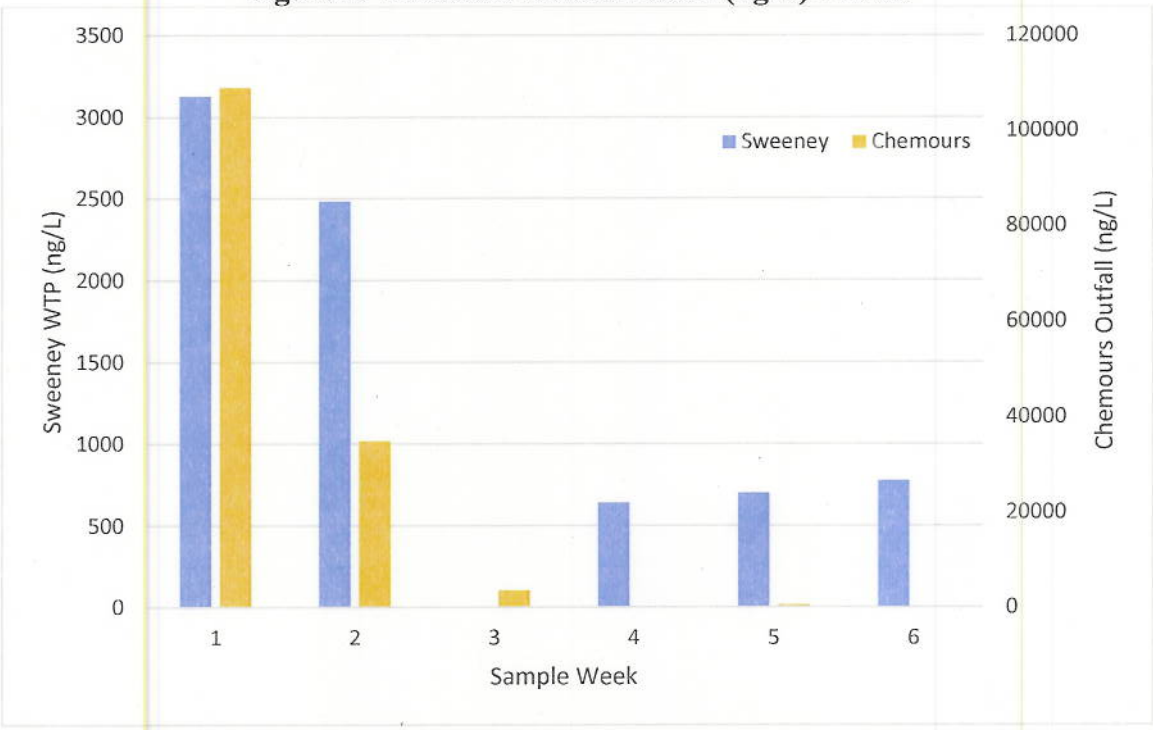

Figure 5. PFESA Byproduct 1 Concentration (ng/L) Profile

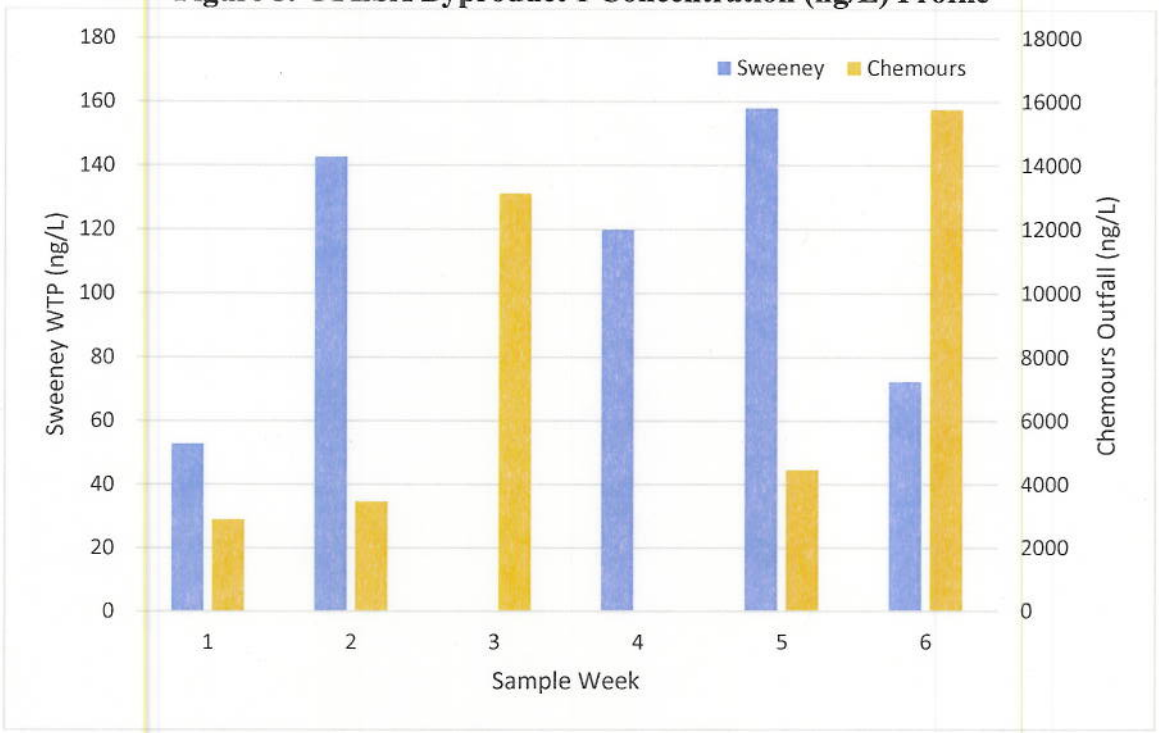

Figure 6. PFESA Byproduct 2 Concentration (ng/L) Profile

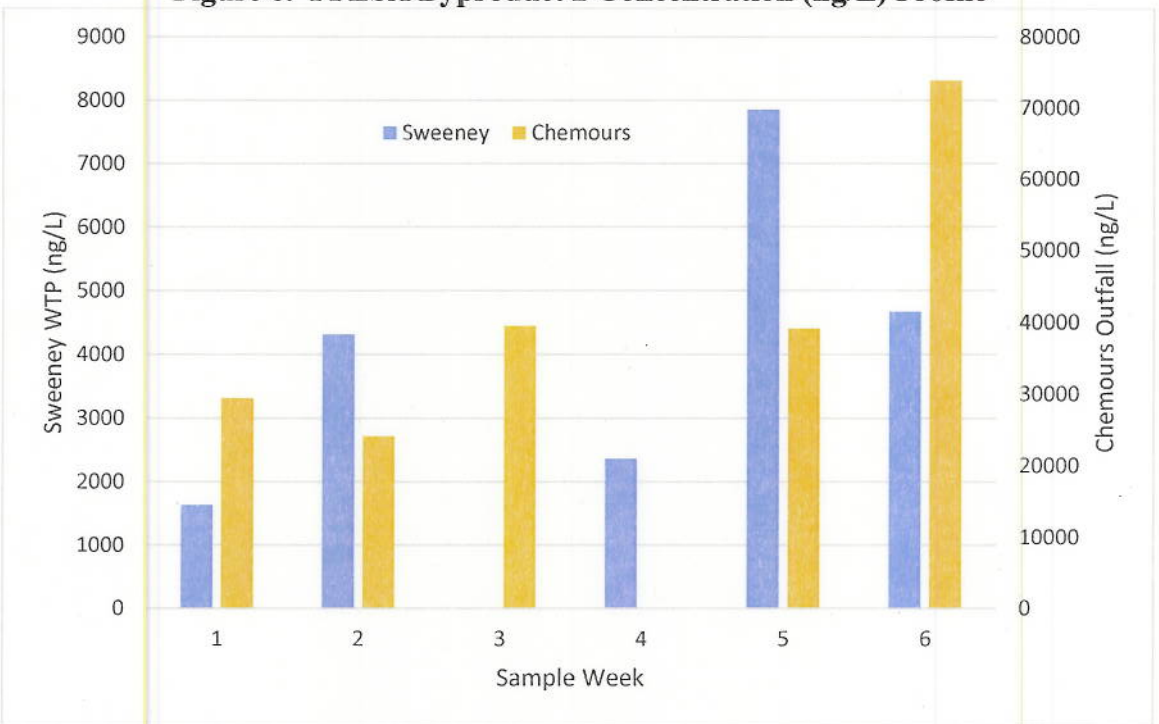

Figure 7. Relative change (compared to highest measured value) in PFAS concentration over weeks 1 – 6 for GenX and NTAs at the Chemours outfall and Sweeney Finished Drinking Water. GenX and NTAs in Panels A,D,E, & F show a consistent decreasing profile. The PFESA Byproduct concentrations are variable and do not show a clear trend.