UNCW Water Quality Research Plans (Related to HB56) DRAFT – September 25, 2017

1. Work on existing contract with CFPUA to analyze both raw and treated water.

Purpose of Work:

As a public utility, CFPUA is committed to providing its customers the highest quality water possible. Recent studies suggest there may be unregulated compounds and chemicals in the Cape Fear River that may be difficult for CFPUA to remove and that may have unknown health effects. This study will help identify those emerging contaminants and provide a scientific basis for state and federal regulatory agencies to determine whether discharge controls would be appropriate.

Proposed Work:

Building upon previous published research UNCW will focus its efforts on two goals listed below.

Goal 1: Establish a method at UNCW for the analysis of PFAS in raw and finished drinking water using published methodology (e.g. Nakayama et al 2010). Quality assurance and control is vital and will be monitored using established procedures, including spike recoveries and internal standards. When appropriate, selected samples will be split and sent to Dr. Mark Strynar's (EPA Research Triangle Park) laboratory for analysis to test the accuracy of the method.

Deliverable 1: A brief report that summarizes the methods developed, sampling strategies, QA/QC procedures, results, and possible additional research needs. After Goal 1 is approved by both parties, UNCW will move to Goal 2.

Goal 2: Once UNCW is confident in the analytical methodology, a sampling campaign of raw and finished drinking water will begin. Weekly raw and finished water samples will be collected for 8 months using the optimized method developed in goal 1. Building upon Sun et al. (2016) and Newton et al. (2017), PFAS will be identified and where appropriate, quantified when authentic standards are available. If an authentic standard is not available, high-resolution mass spectrometry and multidimensional mass spectrometry will be used to propose a tentative structure for unknown PFAS. Additional purification and pre-concentration may be used for fluorine and proton nuclear magnetic resonance (NMR) spectrometry for structural elucidation.

Deliverable 2: A brief report that summarizes the sampling plan, sampling procedures, results, findings and recommendations.

The UNCW Marine and Atmospheric Chemistry Research Laboratory or MACRL Group will complete this project over 12 months (September 1, 2017 – August 31, 2018).

2. Develop and implement the analysis of sediments, as in HB56.

The sedimentary fate of GenX is currently unknown and poses a potential risk to the citizens of North Carolina. The research group at UNCW are experts in the fate, transport and remobilization of pollutants such as GenX from sediments. GenX may persist in riverine sediments like the Cape Fear River even if point sources are eliminated. This research will shed light into the potential reintroduction of legacy

GenX into the water column of the Cape Fear River and potentially into CFPUA input water even if current discharge is eliminated. Based upon the behavior of legacy (e.g. C8) compounds, it is possible that GenX may show an affinity for sediments also. We are currently developing the capability to measure GenX in sediments of the Cape Fear watershed. Once the methodology is developed, the temporal and spatial variability of GenX in sediments of the Cape Fear will be determined. Spatial variability will be addressed by collection of sediments at a variety of locations within the Cape Fear River. Samples in the estuarine portion of the watershed will be collected via a grab sampler on the RV Cape Fear at seven locations within the estuary beginning at the seawater end member near the city of Southport, NC, following a salinity transect to the freshwater end member north of the port of Wilmington. Additional samples will be collected in the freshwater portion of the river, including sites upstream and downstream of the Chemours facility. Transects will be collected during different seasons in order to evaluate the temporal variability of GenX within sediments of river.

The Lower Cape Fear River Program at the UNC Wilmington Center for Marine Science will provide its boats, vehicles and personnel to collect water, sediments, and biological samples for other UNCW researchers as needed throughout the basin. The UNCW Marine and Atmospheric Chemistry Research Laboratory or MACRL Group will complete this project.

3. Conduct biodegradation studies in sediments, as in HB56.

Limited studies suggest little or no degradation of GenX via hydrolysis in standardized testing over 28 days. However, to the best of our knowledge, no biodegradation studies have been conducted with authentic sediments that have been exposed to GenX over a long period of time. Often microbial communities present in sediments and exposed to specific substances are able to alter these substances. Our research team will conduct long term (1 year) incubation experiments with sediments exposed to GenX to monitor loss of the compound over time. Depending on the results of our spatial sediment GenX survey, sediments will either be monitored for loss of in situ levels of GenX or loss of GenX spiked into the sediments. The UNCW Marine and Atmospheric Chemistry Research Laboratory or MACRL Group will complete this project.

4. Bioaccumulation in ecosystem, as in HB56.

Perfluorooctonoic compounds (PFOA) like GenX has the potential to affect marine organisms. While high concentrations and acute exposures may result in death, most of the time in nature, these compounds exist in low concentrations and thus organisms are more prone to chronic exposure to low levels. Chronic exposure of PFOAs while not resulting in death, at least in adult organisms, may affect various physiological activities of organisms including growth, survival and reproduction. Some of the PFOAs behave as endocrine disrupting chemicals thus impacting reproduction and growth. This is especially pertinent and acute in early life stages of organisms since these are more susceptible to environmental and chemical perturbations.

The choice organism for the study is the eastern oyster Crassostrea virginica - an organism that is ubiquitous in the estuarine and nearshore environments. In addition to being economically important, oysters are more valuable for ecological reasons. They form reefs that serve as a buffer against waves and boat wakes protecting shoreline, provide food, shelter and habitat for over 300 species and clear water from algae, detritus, sediment, contaminants, microorganisms, and thus promote growth of sea grasses and benthic microalgae.

Given that oysters filter 4-40L/oyster/hr, potential for bioaccumulation and bioconcentration of chemicals present in the water (like PFOAs) is very high and may thus have impacts to human health upon consumption of contaminated oysters or may result in biomagnification when contaminated oysters are eaten by other predators (e.g., crabs) and make their way up the food chain. We will examine the natural concentrations of GenX in oysters from various field sites in Cape Fear region, examine the impacts of GenX on early life stages (e.g., gametes, embryos, larvae, juveniles and adults) of oysters. Responses could include cellular responses, clearance/filtration rates, disease susceptibility, lipid peroxidation, and reproductive development.

This study would be conducted in collaboration with faculty in Chemistry and Biochemistry, as well as Biology and Marine Biology. Experiments would be conducted at the UNCW Center for Marine Science.

5. Economic Impacts & Household Filtration Effectiveness and Household Risk Perception

Additional projects have been discussed that could address questions related to human health and behaviors.

One possible research study could identify filtering devices used by residential customers in order to determine the efficacy of household filtering devices at removing Gen-X from drinking water, with the goal of providing residents with information about the most effective filtration systems (i.e., reverse osmosis, carbon filters, ion-exchange, etc.) for removing Gen-X from their water source. The water samples would be extracted using flash columns, eluted with an organic solvent and then analyzed using a Sciex Triple Quad QTRAP Mass spectrometer. Samples would be quantified using linear regression analysis of known Gen-X standards.

A second possible project, probably after additional scientific research and other actions have been completed, might be a survey to understand: (1) household perceptions of Gen-X risk; (2) household behavioral responses and adaptation to the presence of Gen-X (and related chemicals); and (3) the economic impacts of behavioral adaptations.

Scientists from the Center for Marine Science and a natural resource economist in the Department of Environmental Sciences would conduct these studies, respectively.