NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Non-Targeted Analysis for Discovery of Chemicals of Emerging Concerns in Treated Water for Drinking and Source Investigation

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Background and Introduction

Overview: The purpose of this research project is to use non-targeted analysis to assess any harmful chemicals found within the samples taken from a river in northeastern US. One of the limitations of quantization based analytical chemistry techniques is that you can only measure what you hypothesize. By using a non-targeted analysis, chemicals not targeted can be screened.

Water samples were taken in a river and drinking water facilities in northeastern US by the EPA and sent to us. The sampling location is confidential. Each 1L of water sample was split into two 500 mL samples each, totaling in twelve samples; before the effluent of a Wastewater Treatment Plant (WWTP), the effluent of the WWTP, downstream the river, the mix zone of the river, the influent of the Treated Drinking Water Plant (TDWP) and end result of the treated water for drinking. Water was extracted by Oasis HLB (Waters) Solid Phase Extraction (SPE) to catch a wide range of chemicals in the samples. After further concentration, the final extracts were injected to comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC/TOF-MS). The GC×GC/TOF-MS has higher separation power due to GC×GC compared to single-dimensional GC and collects full scan mass spectra from the beginning of data acquisition to the end of running. The collected data are currently analyzed by using the instrument software and add-in statistical compare function to identify the chemicals present within the samples.

Hypothesis and goals/objectives: My researches objectives are to identify potentially hazardous organic compounds including disinfection by-products (DBPs) in treated drinking water and the source of the compounds. The goals of this project is to find the harmful chemicals that currently exist in the river and identify persistent compounds from the effluent of the WWTP, throughout the river (from upstream to downstream) until the TDWP intake; as well as DBPs formed after treatment. In addition, potential sources of the chemicals identified in the treated drinking water will be investigated.

Needs research addresses: This research is part of inter-laboratory collaborating project led by Dr. Glassmeyer at the EPA. Several laboratories from the government (EPA and USGS) and academic institutions are participating in this project. The EPA collected water samples in a river, effluent of WWTP, and TDWP in northeastern US and provided the water samples to the laboratories. The laboratories are providing chemical and biological analyses. These include hazard analyses currently

required for drinking water (regulatory tests) and analyses for potential hazardous chemicals, called "chemicals of emerging concern (CECs)". There are known CECs; however, there are unknown CECs that are present in treated water. Unidentified DBPs are part of unknown CECs as well. My research will provide non-targeted analysis for organic compounds in the provided water samples. I will be focusing on discovering organic compounds, which are not screened by the targeted analyses conducted by the other laboratories. At the same time, it will be a great opportunity to evaluate application of the non-targeted analysis in water quality by comparing with the targeted analyses' results. In addition, a laboratory participating in this project will test the water samples for biological activity using in-vitro bioassays. Therefore, the results from the wide range of testing and analyses will provide an opportunity to evaluate overall water quality, and suggest solutions and directions for proper water quality.

Progress to Date

Experimental Design: The research plan is primarily to analyze the samples using GC×GC/TOF-MS and its data analysis software, LECO ChromaTOF. The water samples were collected in a river in eastern U.S. The sampling locations are described in Figure 1: upstream and downstream in a river, effluent from WWTP, mixing zone of the effluent and river stream, intake and effluent of TDWP. 1L of water was collected at each location and shipped to our laboratory via overnight shipping in a cooler with ice. Dr. Glasmeyer and her team at the EPA handled water collection; field blank water samples were also collected. When the water samples arrived in our laboratory, each water sample was split to two, 500 mL each. And then, each 500 mL of water was extracted right away through Oasis HLB SPE. The final extractions were injected in the GC×GC/TOF-MS.

In addition to the water samples, we received extract of samples collected by polar organic chemical integrative sampler (POCIS) in the same location during the same sampling time. POCIS is a passive water sampler that can absorb organic chemicals in water. Therefore, chemicals are accumulated at high concentrations in the sorbent. We expect to identify additional chemicals, which are not detected in the water samples.

Data Collection and Analysis: Data analysis has been conducted by using the instrument's software, ChromaTOF and its add-in feature, "Statistical Compare". The ChromaTOF searches for GC peaks based on criteria of peak intensity and other conditions. This produces thousands of peaks and their mass spectra in full scan per sample. The ChromaTOF compares each mass spectrum with NIST mass spectral database containing hundreds of thousands compounds and then ranks the identified compounds based on mass spectral similarity. Manual review is necessary confirm whether a selected compound with highest similarity score is actually the same as the compound. Through the process, each peak is identified. The "Statistical Compare" feature can compare GC peaks among groups of samples and then determine which GC peaks are identical or different among groups of samples. The "Statistical Compare" feature is essential for the data analysis to isolate chemicals present in samples only not in field blank samples. Also using the feature, chemicals among the water samples can be compared. However, manual review is critical because there can be false positive.

Objectives of Research: This study will test a recently developed method; non-targeted analysis based on GC×GC/TOF-MS to screen a wide range of organic chemicals in the water samples provided by EPA. The water samples were carefully collected in a river from upstream to downstream near a drinking water facility, wastewater effluent to the river, and influent and effluent of the drinking water facility. The non-targeted analysis will enable to discover chemicals not screened by the regular analyses

and the provided samples will help to determine the fate of chemicals in river, and water treatment.

Discussion of Results: Analysis of the water samples taken at six locations in the river have been completed and a list has been created to show compounds found in the water samples; as well as constant compounds found throughout the river samples. There is one compound that has been found in all six locations. The wastewater effluent has produced the greatest amount of compounds, and some of which are known pharmaceuticals and organic compounds. The area of the river that receives the wastewater effluent is concerning for exposure to this compounds. As the effluent makes its way down the river, the natural degradation of the river seems to do its work. There are fewer compounds found at the treated drinking water intake, showing the rivers natural degradation. The amount of compounds found after treatment compared to prior to treatment increased significantly. Known and unknown disinfection byproducts were found in the treated drinking water, as well as other organic compounds.

Conclusions

Why the reader should care and serving the greater good: This research will enable to discover and identify previously unrecognized chemicals in treated water for drinking by using a non-targeted analysis. Previously unidentified DBPs are part of the expected chemicals identified in this study. Chlorination is one of the leading disinfection processes that WWTPs and TDWPs use in the US. Chlorine has been known to cause DBPs in our water supplies, whether it come from WWTPs or TDWPs. Chlorine is used to disinfect the majority of organisms we try to protect the public from including, bacteria such as Leginolella and E. coli, Giardia, and some viruses. While known DBPs posse potential health effects, such as Bromoform, Chloroform, and Dibromochloromethane can cause cancer, liver and kidney effects, and even nervous system and reproductive effects; directly from chlorination and chloramination by-products. More specifically halogenated organic by-products like these posse the greatest risk to the publics' health. It is important to identify these DBPs and other CECs to ensure public health.

Next Steps

The next phase of my research is to conduct the statistical comparison of the polar organic chemical integrative sampler (POCIS). After the conducting this comparison I expect to identify additional chemicals from these samples that were not found in water samples. The comparison will be conducted the same way as the grab water samples, by comparing each sample to the field blank given. Therefore, showing what is in the sample that is not in field blank. After doing so I will do further analysis of the samples to identify similar compounds or different compounds from the previous set of samples. In the end I will have roughly three tables, one showing the compounds found in each of the six grab samples and compounds found throughout all six samples, the same for the POCIS samples, and potentially a third table with similar compounds found in both sets of samples (to be determined).

Figure 1. Water sampling location in a river, a wastewater treatment plant, and drinking water treatment plant.