

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE: May 8, 2017

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: This study is part of inter-laboratory collaborating project led by Dr. Glassmeyer at the Environmental Protection Agency (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 wastewater treatment plant (WWTP), and treated drinking water plant (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 disinfection by-products (DBPs) are part of unknown CECs as well.

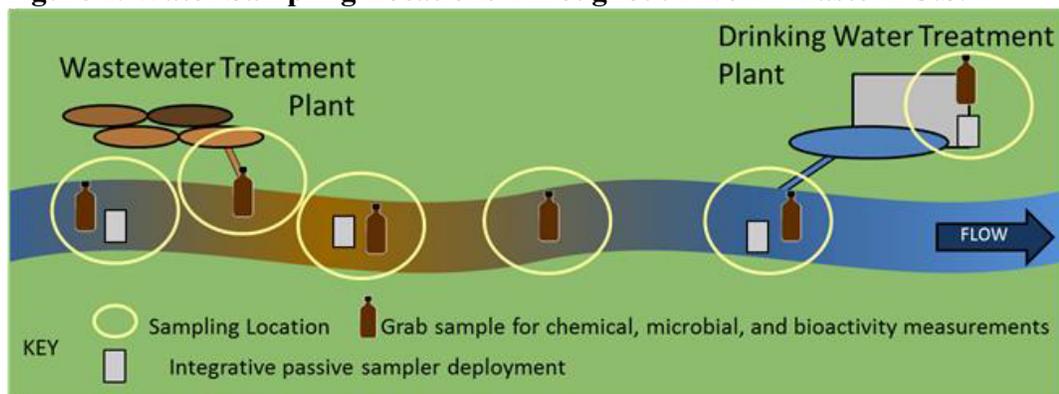
Hypothesis/Objectives and Goals: My researches objectives are to identify potentially hazardous organic compounds including disinfection by-products (DBPs) in treated drinking water and the source of the compounds. The goals of this project is to find the harmful chemicals that currently exist in the 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 Served: The purpose of my thesis is to assess harmful chemicals found within the water samples by using the non-targeted analysis. In this way, I was able to screen a wide range of chemicals, discover and identify previously unrecognized chemicals, and compare the chemicals in the water before, and after treatment. It is important to not only follow the treated drinking waters processes from influent to effluent, but to also find where these chemicals are being introduced; specifically before the effluent of the WWTP, the chemicals already present in the river, and if they react with the byproducts from the WWTP. Also, to see if the river is capable of naturally degrading the chemical byproducts significantly enough before entering the TDWP, and what the concentration of chemicals are at the TDWP influent and after treatment. Are the TDWPs creating more or less byproducts, and where are the potential problems throughout this process?

Progress to Date:

Experimental Design: The water samples were collected in a river in northeastern 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 as described in Figure 1. One liter 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. Then, each 500 mL of water was extracted right away through Oasis HLB Solid Phase Extraction (SPE). The SPE was done prior to my start of this project; as well as the final extractions being injected in the GC×GC/TOF-MS.

Figure 1. Water Sampling Locations Throughout River in Eastern U.S.



Data Collection and Analysis: The data generated by the GC×GC/TOF-MS was processed by the instrument's software, LECO ChromaTOF (version 4.50.8.0 optimized for Pegasus) 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 of each compound was done to 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 based on their mass spectra and GC×GC retention times. 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. Each sample was compared to the field blank given, but out of the six samples only three of them have field blanks.

Discussion of Results: After careful analysis of all six sampling locations, each sample was separated into two sub-groups, one that of high identification and one of low identification from the set criteria. A total of 48 compounds, 20 high identified and 28 low identified were detected from the upstream (US) sample location. A total of 240 compounds, 80 high identified and 160 low identified were detected from the wastewater effluent (WWE) sample location. A total of 22 compounds, 15 high identified and 7 low identified were detected from the MZ sample location. A total of 29 compounds, 7 high identified

and 22 low identified were detected from the DS sample location. A total of 26 compounds, 5 high identified and 21 low identified were detected from the DWI sample location. A total of 17 compounds, 8 high identified and 9 low identified were detected from the TDW sample location. A total of 382 compounds, 135 high identified and 247 low identified were detected after final analysis. Along with the findings, there was also a pattern of compounds that were found in multiple locations throughout the river, a total of 20 compounds found in more than one location throughout the river, whether they are high or low identified compounds and in what location they were found. There is only one compound that was found in all six sampling locations.

Conclusions:

The implementation of sample collection, sample preparation and data analysis were crucial to quality and successful achievement of the project's objectives. Although the aim of the research was met, some limitations were unavoidable.

- The exact sampling location of the water samples is confidential, therefore limiting the knowledge of the rivers environment.
- The SPE Oasis HLB cartridges and GC×GC/TOF-MS analysis were limited to detect volatile/semi-volatile compounds. Therefore, non-volatile compounds would not be detectable.
- This was a qualitative study that only tentatively identified the chemicals in each sample based on their match with compounds in the NIST library. For future quantitative analysis, authentic standards can confirm chemicals and support concentration computations.

Why the reader should care and serving the greater good: This study showed that the non-targeted analysis was able to discover and identify previously unrecognized chemicals in several types of water bodies. In addition, the non-targeted analysis can provide overview of chemical profiles through the water stream (including natural process and water treatments). This study shows that the non-targeted analysis can be a part of monitoring to improve water quality.

Next Steps: The tentatively identified compounds will be confirmed by authentic standards if commercially available. This project is part of the on-going inter-laboratory project led by EPA. Therefore, we could not share the list of compounds right now because of confidentiality required by the EPA. However, once the whole project is complete, results of this study will be published.