aqua metrology systems

APPLICATION BRIEF

Research Shows That AMS' Online THM Monitoring Technology Is a Viable Method to Accurately Predict THM Precursor Content and Network THM Levels

Figure 1. Mill River Monitoring System

Summary

A research project collaboration between the Water and Energy Technology (WET) Center at the University of Massachusetts (UMass) in Amherst, Ma., and Aqua Metrology Systems (AMS) tested a novel method for near real-time analysis of disinfection byproduct (DBP) precursors and natural organic matter (NOM) properties in water supplies. AMS' online trihalomethane (THM) and THM Formation Potential (THM-FP) monitoring technology was shown to be a viable method to accurately predict THM precursor content and network THM levels. The collaboration was funded by the Massachusetts Clean Energy Center.

Background

UMass' WET Center is a pilot-scale testing facility owned and operated by the UMass Environmental Engineering research group. The facility is deeply integrated with the nearby College of Engineering's Elab Environmental Engineering Research Laboratory which focuses on bench-scale treatment and trace analytical testing.

The WET Center is the only university-based testing facility in the U.S. with direct, continuous piped access to municipal drinking water, wastewater and raw surface water for testing and evaluation purposes. The Center has access to raw, primary, and secondary wastewater from the Town of Amherst's municipal wastewater treatment; in addition to local surface (Mill River) and potable water (Amherst, MA., Tap Water).

Dating back to the 1970s, the facility has a long history in research and has played a key role in the advancement of what are now considered classical water treatment technologies to support the protection of public and environmental health.

DBP Precursor Monitoring System

Today, the WET Center tests new technological innovations for purifying contaminated water with a focus on methods and devices that can be used in public water supplies and wastewater treatment systems, as well as sensors for monitoring contaminants in those waters.

One of the various research projects currently underway is the WET Center Project #1 – DBP Precursor Monitoring System.

David Reckhow, Professor of Civil and Environmental Engineering at UMass Amherst, believes that developing a better understanding of DBPs and their precursors is a major thrust of drinking water research. "Naturally-occurring trace organic constituents in water react with chlorine to produce a wide array of carcinogenic DBPs, including the THMs. There are approximately 700 known DBPs and this work will help us to advise on methods for monitoring precursors to THMs and other DBPs, both regulated and emerging."

Regulators have chosen THMs as the leading indicator of the broad group of DBPs present in consumers' water supplies. Water utilities struggle to limit the presence of THMs, and other DBPs, because raw water quality is highly variable and the amount of THMs fluctuate as a result. Online analyzers for monitoring THM-FP in distribution systems have been adopted in the U.S. and Europe to provide utilities with continuous real-time THM-FP data of drinking water once chlorinated. While this data are of value to utilities because they predict the presence of THMs in water before it reaches the consumer, utilities have not had access to timely, reliable and continuous predictive data of the potential formation of THMs from raw (untreated) water before it is chlorinated.

Reliable, continuous real-time THM precursor data are of significant value to utilities with multiple raw water sources because they can inform the optimal source-water blend to use on any given day to minimize the formation of DBPs during chlorination and, with it, the costs of protecting the consumer. For utilities dependent on a single water source with a limited ability to remove DBP precursors, THM precursor data can be used to better inform their water storage strategy, or to better adjust dosing of coagulants/flocculants, etc. This data can help them to maximize the use of water storage capacity for water produced during favorable raw water conditions and using this storage to minimize production when precursor data anticipates a deterioration in THM levels in water before chlorination takes place.

Research Project

Starting in 2017, the Massachusetts Clean Energy Center funded a collaboration between the WET Center and AMS to undertake a long-term study of an online THM-FP instrument developed by AMS.

AMS has been producing on-line THM analyzers using purge and trap technology along with time-resolved colorimetric detection (Fujiwara reaction). More recently, the company has developed a high-temperature chlorine dosing system to rapidly convert organic precursors to THMs, followed by their automated quantitation.

UMass proposed to help identify the best reaction conditions, and then test this new instrument with a flashy river source. In addition, the results of the online THM-FP-Raw method would be compared against other online methods that have been used to characterize and quantify the organic precursor content of an untreated or partially treated water. These other options include UV-VIS spectroscopy, TOC analysis, and various forms of chemical or electrochemical oxidant demand. These were all compared to the conventional lab-based THM precursor analysis, also referred to as THM-FP.

The research was conducted at the WET Center which is adjacent to the Mill River in Hadley, MA., near the western border of Amherst. This small river is typified by base flows of about 4 cubic feet per second (cfs) under drought conditions with annual high flood flows above 200 cfs.

A small in-stream pump station that delivers Mill River water directly to the center's analytical lab (Figure 1) was constructed. This system became fully operational in February 2017.

For about two years, the AMS prototype analyzed for THM precursors every four to five hours, resulting in many hundreds of unattended measurements. Other instruments were plumbed to the same interior circulation loop, so that real-time comparisons could be made among the various candidate sensors. The only pretreatment applied to the raw sample stream was 50 micron filtration, which was primarily of benefit to the UV-VIS spectrophotometric instrument.

Initial work was devoted to identifying the best set of conditions (e.g., heated temperature and chlorine dose) for the AMS prototype so that the accelerated system was detecting about the same amount of precursor as the standard laboratory THM-FP method. It was not considered necessary that the two produce the same concentrations. However, the UMass and AMS teams felt that if the two methods were to be expected to reflect the same precursor structures in natural organic matter, they should result in similar levels of THM production.

A three-day test run at 25°C and dosed with sufficient chlorine to maintain a residual of 1 mg/L at the end of the three-day incubation period was used. Samples were then quenched and analyzed by conventional GC/ECD (EPA method 551.1). Timed grab samples were collected during both dry and wet weather. These were used for laboratory analysis of THM-FP, as well as conventional and rapid chlorine demand tests (Table 1).

Using well-tested models as a guide (e.g., Amy et al., 1987; Harrington et al., 1992), it was determined that 50°C and a 40 mg/L chlorine dose should produce about the same level of THM in 1 hour as a 25 °C low dose test would after 72 hours. Later testing would show this to be high for the Mill River NOM (~60% above), but still acceptable.

Category	Procedure	Detection
THM-FP	25°C, 72 hr, 1 mg/L chlorine residual	GC/ECD
Chlorine Demand - Standard	25°C, 72 hr, 1 mg/L chlorine residual	DPD Titration
Chlorine Demand - Accelerated	50°C, 1 hr, 30 mg/L chlorine dose	DPD Titration

Table 1. Off-Line Measurements

Also, during this early testing, it was discovered that lower chlorine doses would produce anomalous results due to premature loss of residual, probably by consumption with ammonia or low-oxidation metals and other inorganics. Once enough chlorine had been added to maintain a residual for the full one hour, further elevating the dose had little effect.

For various reasons, TOC has been viewed as a robust, albeit imperfect, predictor of THM precursor content. Figure 2 shows that the AMS prototype tracks TOC quite well, both during dry and wet weather. It should be noted that the TOC trace exhibits vertical spikes, an expected result of the occasional electrical or flow disturbances. Nevertheless, the rise and fall of TOC is clearly linked to changes in rainfall and river discharge, with higher TOCs at times of higher flow.

The AMS prototype matches this as well and it is expected that TOC would be a good predictor of THM precursors in a flashy river system such as this one. The reason is that most of the precursor material is of terrestrial origin and consistent in chemical structure. This is in contrast with reservoir sources that can fluctuate between terrestrial and algal source dominance. In those cases, TOC may not be as useful a predictor of THM precursors because of the differences in NOM characteristics between allochthonous and autochthonous sources (e.g., Stepczuk et al., 1998; Zhao et al., 2018).

These differences can be captured slightly better by UV absorbance monitors, but these are sometimes affected by high turbidities or elevated iron concentrations. While some manufacturers have developed site-specific algorithms using absorbance at multiple wavelengths, to avoid these problems, this was not a part of this study.

Despite the excellent agreement between TOC and the AMS prototype, the real test comes from a comparison with the widely accepted lab-based THM-FP (referred to in Figure 3 as the "Standard Lab THM" test). Not surprisingly, these show all five tests to produce data that correlates well with THM-FP (Figure 3). However, three of them (AMS, TOC and the three-day chlorine demand) are clearly stronger than the other two. Of those three, only AMS and TOC are "real-time," and based on this dataset, the AMS prototype does a bit better than TOC (e.g., higher r^2).

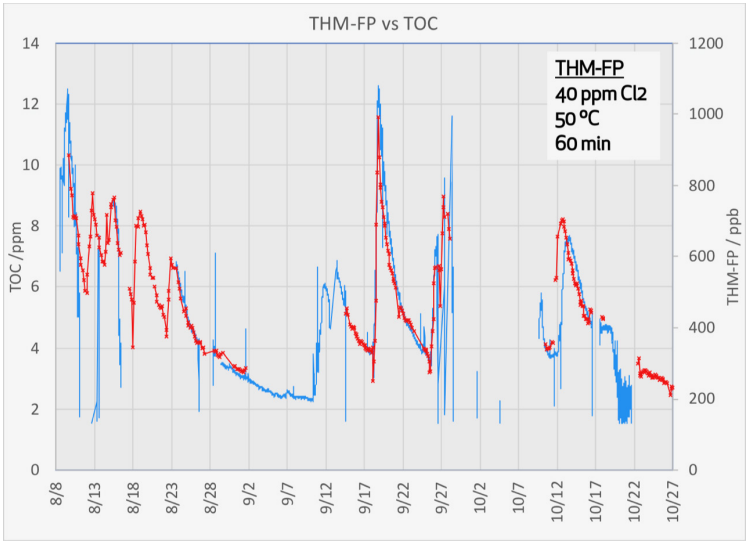

Figure 2. Comparison of TOC with the Accelerated Online Precursor Analyzer (AMS prototype) for Late Summer and Fall 2018

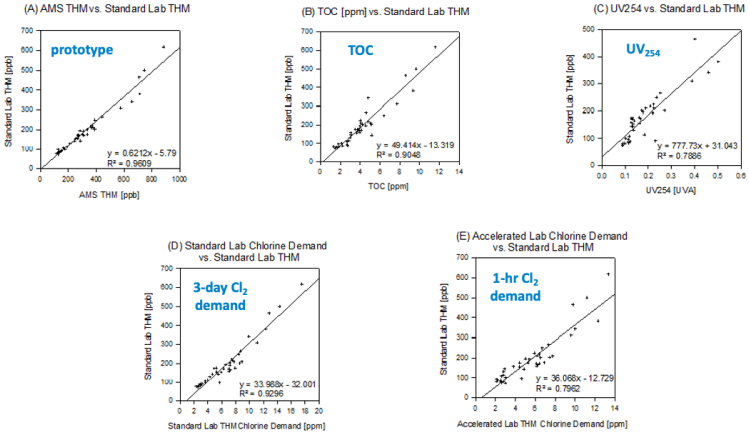

Figure 3. Correlations Between Some of the Study Parameters and Laboratory Measurements of THM Precursors

Conclusion

This research project shows that incorporating automated chlorine dosing with an accelerated THM formation step into an existing THM analyzer is a viable concept that results in near-real-time measurements that can accurately predict THM precursor content, demonstrating that AMS' online THM and THM-FP monitoring technology is a viable method to accurately predict THM precursor content and network THM levels. This idea has shown itself to result in a robust method, compatible with instrumentation that is easy to use and trouble-free. In the study using the Mill River, the analyzer has been shown to work well on a flashy source dominated by allochthonous organics.

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