

Online THM Analyzer Helps Utility Optimize Operation and Validate Laboratory Results

The Brunswick & Topsham Water District (BTWD) in Maine was receiving high trihalomethane (THM) results despite implementation of best practices. This led to split samples of monitoring and compliance samples that resulted in conflicting analytical results. The percent difference of results from two laboratories undertaking THM analysis for the utility ranged from 65-98%. At the same time, BTWD installed an online THM analyzer to study supply and distribution management impacts on THMs, which resulted in a better understanding of operational impacts on THMs. The analyzer was also used to help evaluate the analytical results and build confidence in data being received from laboratories. The online THM analyzer helped reveal a performance error contributing to data biased high at one laboratory and small adjustments at a second laboratory resulting in all three analyses finally being within 10% of each other.

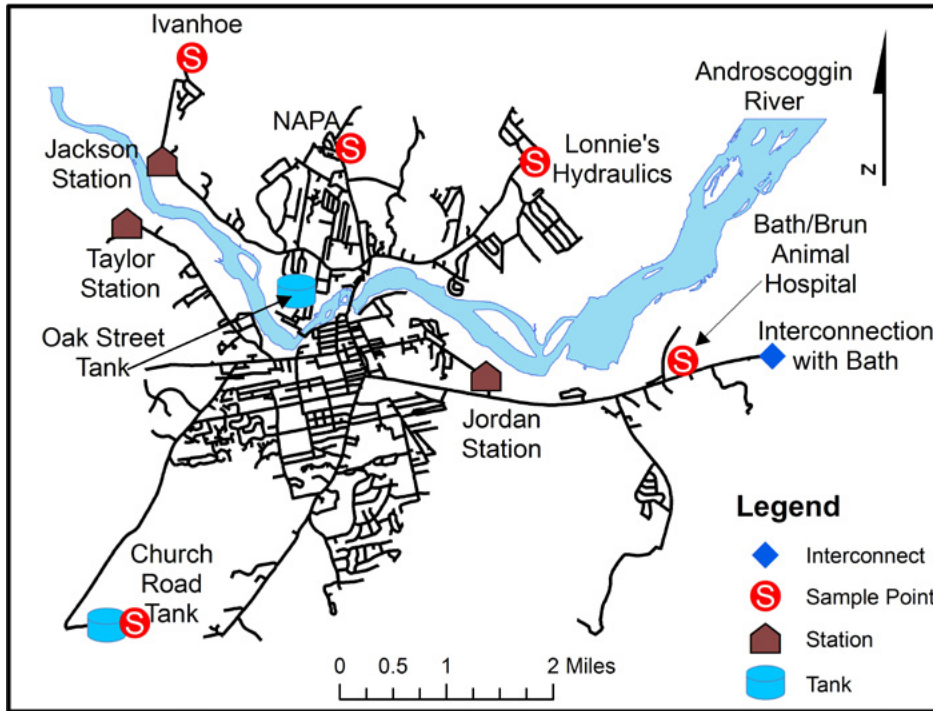


Background

The BTWD operates three facilities, including Jackson Station, a 3.5 mgd intermittently regenerated greensand treatment facility to meet the needs of approximately 30,000 residents in the towns of Brunswick and Topsham. In addition to the Jackson facility BTWD also operates the Taylor Station (2.5 mgd) and Jordan Station (1.5 mgd).

The District manages nearly 120 miles of water mains. One-third of the system is north of the Androscoggin River in Topsham and two-thirds of the system is south of the river in Brunswick (Figure 1). Water demands are distributed evenly across the system and the District maintains two river crossings between the communities. Since Jackson Station typically accounts for more than 50% of the District's production, water typically flows from the Oak Street Tank to Topsham and limited portions of Brunswick. The District has been monitoring five sampling locations as part of this effort; only Ivanhoe does not have an associated compliance site.

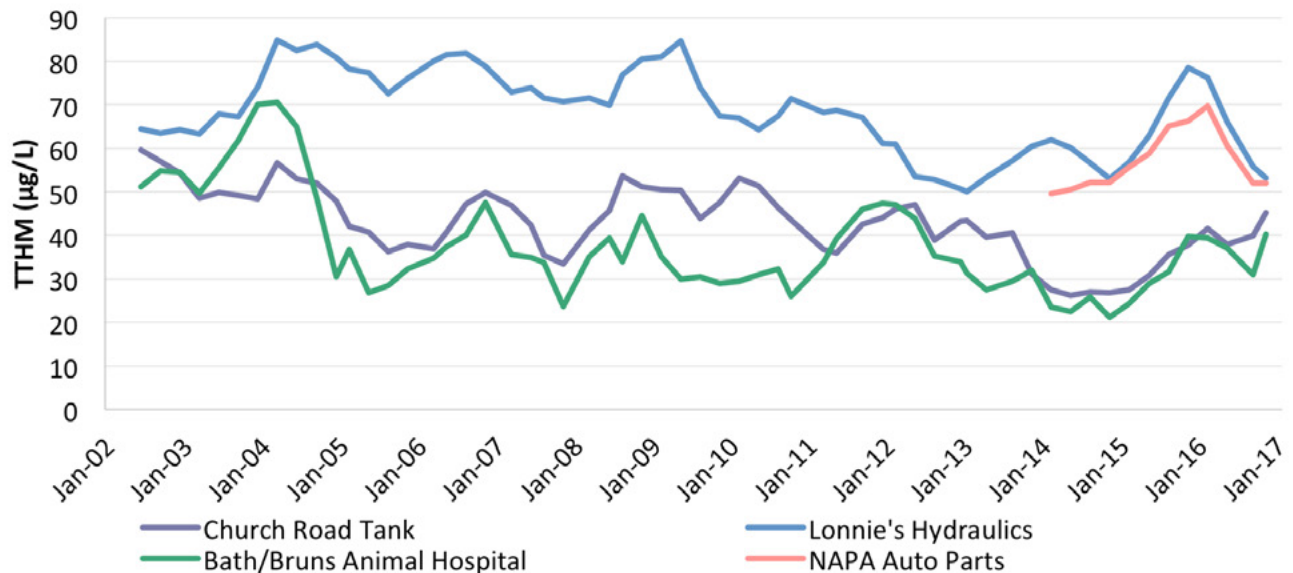
Figure 1: BTWD System Map Detailing Major Points of Interest



The source water at each BTWD station is relatively similar containing total organic carbon (TOC) ranging between 1.4 - 2.5 mg/L. Disinfection by-products (DBPs) such as THMs and haloacetic acids (HAAs) occur when natural organic matter reacts with a disinfection agent (for BTWD sodium hypochlorite) to form halogenated compounds. The District samples for total trihalomethanes (TTHMs) and HAA5s but for the larger objective of providing the best water to customers the District discusses THMs and HAAs, despite DBP compliance being based on TTHMs and HAA5s.

With the onset of the Stage 2 Disinfection and Disinfection By-Product Rule (Stage 2 DBPR) the District reanalyzed data collected during Stage 1 DBPR based on locational running annual averages (LRAAs) (Figure 2). This exercise highlighted the need for the District to be attentive to distribution operations as the Lonnie's Hydraulic site had time periods in violation based on LRAAs.

Figure 2: BTWD Historical TTHM Data Analyzed LRAAs



District staff used statistical analysis to try and link the LRAA peaks at the Lonnie’s Hydraulic site to facility selection, individual well selection, aquifer level, mean storage tank residence time, rainfall and facility production records. When no strong statistical correlation could be found, the District performed initial THM formation tests on treated water from the three sources and discovered the level at Jackson Station was three times that of the Taylor or Jordan supplies (Table 1) implying the formation potential could be three times higher¹.

Table 1: DBP Precursor Assessment of BTWD Source Water at Stations

Jackson Station	Parameter
4.7-4.0	SUVA Raw (L/mg·m)
3.1-2.0	SUVA Treated (L/mg·m)
1.7-2.5	TOC Raw (mg/L)
1.7-2.3	TOC Treated (mg/L)
12.9	Initial TTHM Formation (µg/L)
Jordon Avenue Station	
2.9	SUVA Raw (L/mg·m)
2.9	SUVA Treated (L/mg·m)
1.4-1.6	TOC Raw (mg/L)
1.4-1.6	TOC Treated (mg/L)
4.3	Initial TTHM Formation (µg/L)
Taylor Station	
3.0	SUVA Raw (L/mg·m)
2.4	SUVA Treated (L/mg·m)
1.7-1.9	TOC Raw (mg/L)
1.1-1.3	TOC Treated (mg/L)
3.6	Initial TTHM Formation (µg/L)

The District also collected data for specific ultraviolet absorbance (SUVA). SUVA is a predictive parameter for the ratio of humic to non-humic substances, which has implications on the treatability of the water matrix and can be indicative for DBP precursors². The SUVA values for the Jackson Station were found to be one and a half times those of the other two stations; indicating the greater presence of humic materials in the Jackson supply. Greater humic content compared to the other sources is another indication of Jackson’s higher THM formation potential.

The hydraulic model and anecdotal operation of the system showed District staff that the Church Road Tank and Bath/ Brunswick Animal Hospital were supplied predominately by the Taylor and Jordan Station respectively and Lonnie’s Hydraulics received its water predominately from the Jackson Station. Data from the initial TTHM formation testing, SUVA levels and LRAA calculations strongly indicated that water sourced at the Jackson Station was at the root of BTWD’s THM issues. The NAPA Auto Parts sample site, which also received its water predominately from the Jackson Station, would be added to compliance sampling under Stage 2 DBPR. Its TTHM values closely mirrored those of Lonnie’s Hydraulics, further validating concern of the Jackson supply.

The cumulative knowledge and fact that the Jackson Station was approaching full depreciation lead the District to undertake a study in 2010 resulting in a plan to replace the facility in a ten-year period. The plan addressed THM precursors, but was reliant on the District maintaining compliance in the interim ten-year period to allow for proper development of the new facility.

THMs Start to Rise Unexpectedly

Things progressed well with the plan until early 2015 when TTHMs began to rise. By late 2015 the District staff was deeply concerned the TTHM LRAA at Lonnie's Hydraulics would be exceeded. Three proactive steps were taken:

- Operating levels were dropped by 10 feet in both of the District's water storage tanks resulting in a 25% decrease in stored water.
- Three bleeder vaults (Figure 3) were installed at the end of the three longest main runs that were fed by the Jackson facility Ivanhoe, Main St (NAPA Auto Parts) and Middlesex Rd (Lonnie's Hydraulics).
- Facility operations were adjusted to maximize production from the Taylor and Jordan Facilities and minimize production from the Jackson Facility.

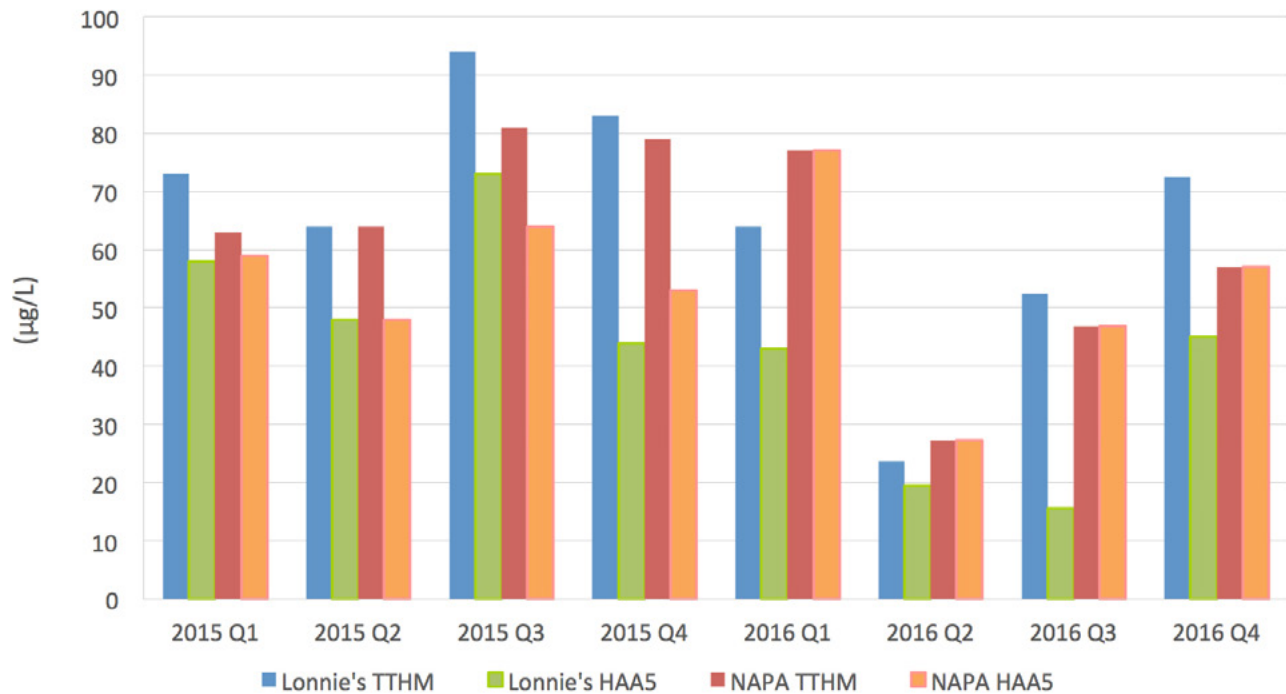


Figure 3: Typical Bleeder Vault Installation

Each of the vaults is installed with a throttling valve, dechlorinator, meter and backflow device (blocked from view by the dechlorinator). Staff is able to refill the dechlorinator with a non-permit confined space entry. The meter is connected to the District's remote read system.

These proactive steps implemented before quarter one 2016 compliance sampling seemingly had little effect on TTHM values. Especially alarming to staff was the increase in HAA5 values. This can be seen in the District compliance data (Figure 4), specifically the NAPA Auto Parts sample site between quarter four 2015 and quarter one 2016. The TTHM values held practically constant at 79 and 77 $\mu\text{g}/\text{l}$, while the HAA5 values increased from 53 to 77 $\mu\text{g}/\text{l}$. The increase in HAA5's clearly indicated a decrease in water age, but then why were the TTHMs holding steady? The groundwater quality was very stable based on data going back to 1971; it was difficult for staff to believe the TOC matrix had changed so rapidly in a single quarter to provide such results.

Figure 4: BTWD Compliance Data for TTHMs and HAA5s 2015-16



With the initial three proactive steps not resulting in any improvement, the District began planning for the worst in 2016. From the staff's perspective there were four options that needed to be pursued simultaneously to try and get ahead of an emerging THM crisis:

- Since the predominant species was chloroform, the District would pursue an aeration system for the Oak Street Tank.
- Install an online THM analyzer to better understand the nature of THMs leaving the plant and if possible run grab samples from the distribution system to better understand THM behavior in the system.
- Reactivate the altitude valve at the Church Road Tank at a lower set point to help push more water towards the Jackson Station side of the system.
- Run split samples for monitoring and compliance sample locations to ensure the values being received were indeed valid.

These items were pursued simultaneously; ultimately the aeration system was set aside by late summer of 2016 as the other three initiatives revealed such a system was not necessary. Split samples from monitoring sites that mirrored the compliance locations were completed in March of 2016 (Table 2). The sampling included an additional site Ivanhoe, the third large diameter dead-end leg that mirrors the existing compliance sites of Lonnie's Hydraulics and NAPA Auto Parts in terms of water age and being supplied by the Jackson Station.

Table 2: TTHM Split Samples for Monitoring Sites March 2016

	Lab 1	Lab 2
Lonnie’s Hydraulics*		
Chloroform (µg/L)	46	22
Total THMs (µg/L)	57	30.5
TTHM Percent Difference	87%	
NAPA Auto Parts*		
Chloroform (µg/L)	65	33
Total THMs (µg/L)	79	44
TTHM Percent Difference	80%	
Ivanhoe		
Chloroform (µg/L)	79	41
Total THMs (µg/L)	94	53.3
TTHM Percent Difference	76%	
*The monitoring locations have been renamed to match the compliance sites for the clarity of the reader, but the sites were in fact different sites than the compliance sites.		

The results from March 2016 (Table 2) were a big moment for District staff because it confirmed a growing but unsubstantiated belief that Lab 1, which was running compliance samples for the District, might be in error. The problem now was determining which was the true TTHM value — Lab 1, Lab 2 or some other value? How would the District determine the true value?

The third prong of the District’s additional steps was to install an online THM analyzer. The District selected an analyzer manufactured by Aqua Metrology Systems, the THM-100™, which was installed at the Jackson Station in the first week of May 2016 in advance of quarter two compliance sampling.

The THM-100 is an automated system using a “purge-and-trap” method for TTHM extraction of the sample (common to many standard methods for THM analysis), followed by desorption into a chemical mixture that generates a colored product and time-resolved spectrophotometric analysis for detection and determination of THM levels. In addition to the online samples, manually collected ‘grab’ samples from other locations in the BTWD network could be collected and analyzed alongside samples taken automatically by the monitor in its online mode at the Jackson Station. This allowed for analysis at the station and throughout the distribution system. On average the THM-100 analyzes six online samples daily and five grab samples per week for BTWD.

Three Different TTHM Values for One Sample

The District was working with the Maine Drinking Water Program and the Maine Laboratory Certification Officer through this process. There was significant anticipation for quarter two compliance sampling; to see what values returned from the split samples given to the two certified laboratories and the online analyzer (Table 3) and how they would compare to monitoring results compiled in March 2016.

Table 3: TTHM Split Samples Compliance Second Quarter 2016

	Lab 1	Lab 2	Online BTWD
Lonnie's Hydraulics			
Chloroform (µg/L)	24	12	17.7
Total THMs (µg/L)	31	16.1	25
TTHM Percent Difference*	93%		
NAPA Auto Parts			
Chloroform (µg/L)	26	14	18.6
Total THMs (µg/L)	34	20.6	26.7
TTHM Percent Difference*	65%		
Church Road Tank			
Chloroform (µg/L)	24	12	N/A
Total THMs (µg/L)	31	17	N/A
TTHM Percent Difference*	82%		
Bath/Brun Animal Hospital			
Chloroform (µg/L)	21	9.9	N/A
Total THMs (µg/L)	26	13.1	N/A
TTHM Percent Difference*	98%		
* Percent difference between the two certified laboratories.			

The quarter two compliance results created even more questions than the District had going into the round of sampling. The results varied greatly, showing a percent difference ranging from 65-98% between Lab 1 (original) and Lab 2 (new). The variance was predominantly in chloroform values, which is the most prevalent THM speciation found in water at the BTWD.

The grab samples given to the online analyzer nearly split the difference between the two certified laboratories indicating both certified laboratories might be having an issue. Even more interestingly it seemed that the initial and secondary proactive steps, that were now fully implemented, had dramatically decreased THMs in the system based on the data from either laboratory.

The months following quarter two compliance sampling and analysis resulted in very detailed reviews of both certified laboratory's quality assurance/quality compliance (QA/QC) programs, as well as a review of USEPA method 524.2. It should be noted that USEPA method 524.2 allows for 20% error for THM values during laboratory validation and 30% error for laboratories during routine operations. This is a significant point of note for any utility seeking to maintain regulatory compliance.

The variability of TTHM values from certified laboratories are discussed by Saini et al.³ Based on the data presented therein and the allowable variance provided for in USEPA method 524.2, the District set a target of 10% variance in TTHM samples. The goal was to try to resolve the differences between the values received from the certified laboratories and the values from the THM-100 analyzer with which the District was having increasing confidence.

These investigations were still ongoing when quarter three compliance samples were taken (Table 4). This time the sample was split five ways and the values were generally grouped closer together. Interestingly Lab 2 values were now higher than the value received from the online THM-100 analyzer (possibly due to an adjustment made at the laboratory). Additionally after this round, Lab 1 notified the District they had identified a cause for their high values. They reported their ion source was deteriorating. Every gas chromatography mass spectrophotometer (GC-MS) instrument has an ion source that ionizes the molecules after they have traveled the length of the column. As the particles enter into the sensor of the mass spectrometer, the ionized particles are then detected by an electron multiplier diode; that turns the ionized mass fragment into an electrical signal that is then detected. Their ion source was no longer in specifications (an unusual event) and was biasing their results and spiked recoveries high, complicating the identification of the issue.

By the time quarter four 2016 compliance samples were taken the two laboratories and the grab samples from the online analyzer were all within the District's 10% goal of each other (Table 5).

Table 4: TTHM Split Samples Compliance Third Quarter 2016

	Lab 1	Lab 2	Online BTWD	Online AMS**	GC/MS AMS***
Lonnie's Hydraulics					
Chloroform (µg/L)	42	36	29.6	28.7	30.4
Total THMs (µg/L)	55	49.9	41	39.9	41
Percent Difference*	34%	22%		-3%	0.0%
NAPA Auto Parts					
Chloroform (µg/L)	38	31	27.2	25.5	27.1
Total THMs (µg/L)	50	43.7	37.8	35.8	36.5
Percent Difference*	32%	16%		-3%	-5%
Church Road Tank					
Chloroform (µg/L)	37	30	26.1	23.7	26.2
Total THMs (µg/L)	53	46.1	39.9	35.8	38.9
Percent Difference*	33%	16%		-10%	-3%
Bath/Brun Animal Hospital					
Chloroform (µg/L)	26	18	17.9	17.1	19.0
Total THMs (µg/L)	32	23.2	23.3	22.6	24.4
Percent Difference*	37%	-0.4%		-3%	5%

*Percent difference between the laboratories and Online BTWD.

** Grab sample through a THM-100 located in Sunnyvale, CA.

*** Non-certified GC/MS located in Sunnyvale, CA.

Table 5: TTHM Split Samples Compliance Fourth Quarter 2016

	Lab 1	Lab 2	Online BTWD
Lonnie's Hydraulics			
Chloroform (µg/L)	42	36	29.6
Total THMs (µg/L)	55	49.9	41
Percent Difference*	34%	22%	
NAPA Auto Parts			
Chloroform (µg/L)	38	31	27.2
Total THMs (µg/L)	50	43.7	37.8
Percent Difference*	32%	16%	
Church Road Tank			
Chloroform (µg/L)	37	30	26.1
Total THMs (µg/L)	53	46.1	39.9
Percent Difference*	33%	16%	
Bath/Brun Animal Hospital			
Chloroform (µg/L)	26	18	17.9
Total THMs (µg/L)	32	23.2	23.3
Percent Difference*	37%	-0.4%	
* Percent difference between the laboratories and Online BTWD.			

Information Learned from the Distribution Grab Samples Taken

The District learned a significant amount of information from the grab samples processed by the online THM-100 analyzer. The District created a weekly profile of TTHM values throughout the system for the better part of 2016 (Figure 5).

Several things were learned in this process. While District staff understood that each step taken to improve water quality would have an impact on THM values observed in the system, using the online analyzer really allowed staff to appreciate the impact of each operational change. As noted in the figures not all of the changes were elective, some of the changes observed were forced, by the availability of wells or failure of motors, rendering some sources or stations unavailable for periods of time. But those changes resulted in a corresponding increase or decrease to distribution THM values.

The reliance on Jackson Station due to mechanical and maintenance needs has shifted the District's overall production ratio significantly towards Jackson Station in the latter part of 2016 (Figure 6). This has resulted in an increase in distribution THMs; however, the District expects that once repairs are made THM values will decrease to early 2016 levels.

Figure 5: Monitoring Data for TTHM and HAA5's for BTWD 2016

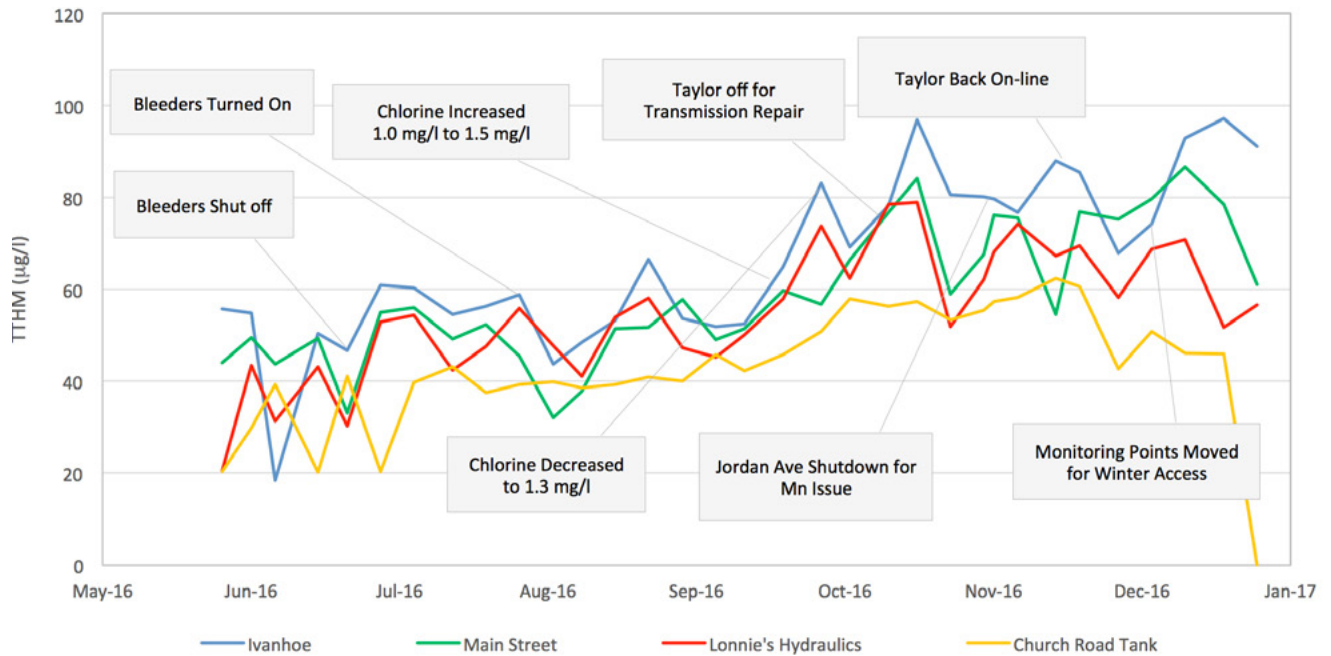
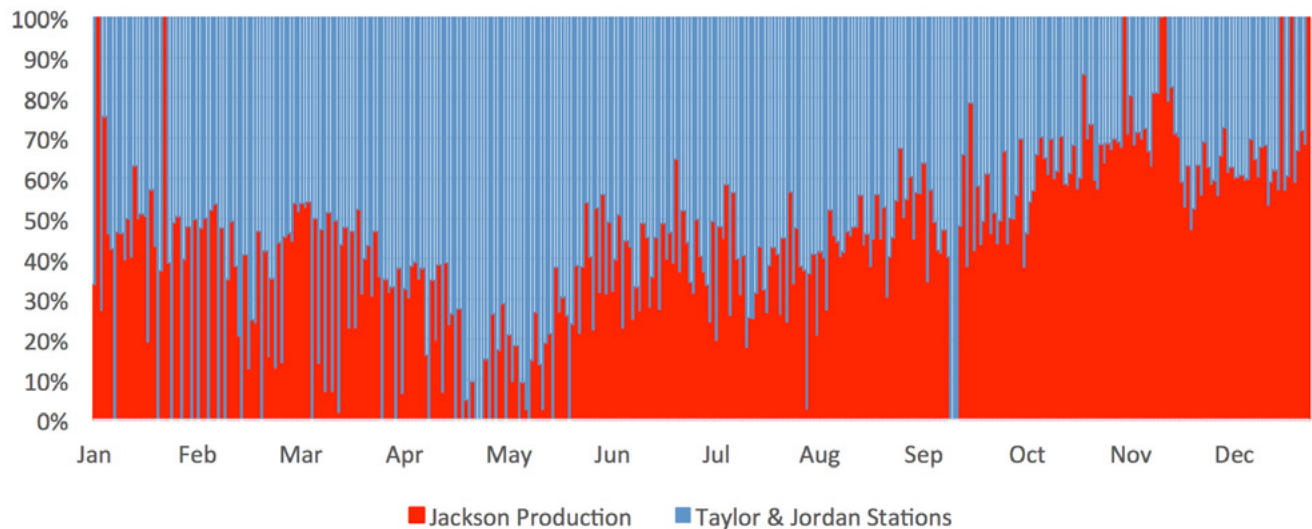


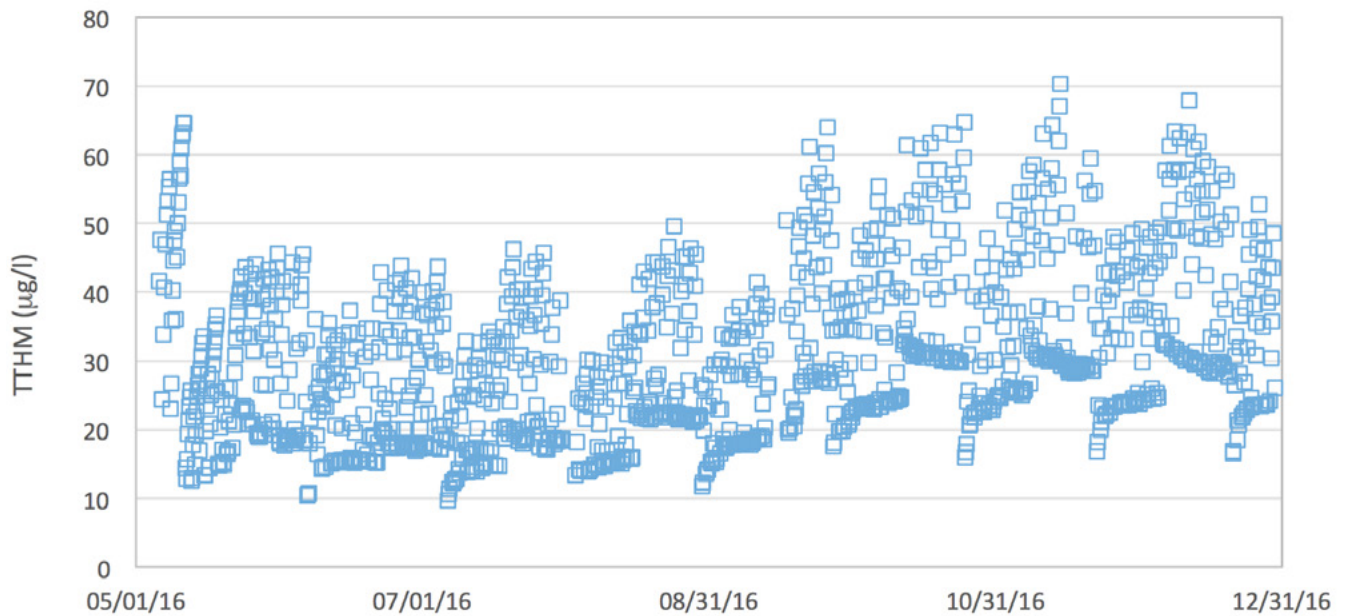
Figure 6: Jackson Production Ratio versus Taylor and Jordan in 2016



Data from the Online Analyzer

The data presented to this point has focused on the grab samples analyzed on the THM-100. The automated online analyzer has also provided a significant amount of information on the current treatment process. The data from the online analyzer was at first difficult to interpret (Figure 7). To interpret this data, understand that the lowest highly overlapped data points are from when the station is online. The data points above these reflect the water quality coming back to the station over time from the Oak Street Tank.

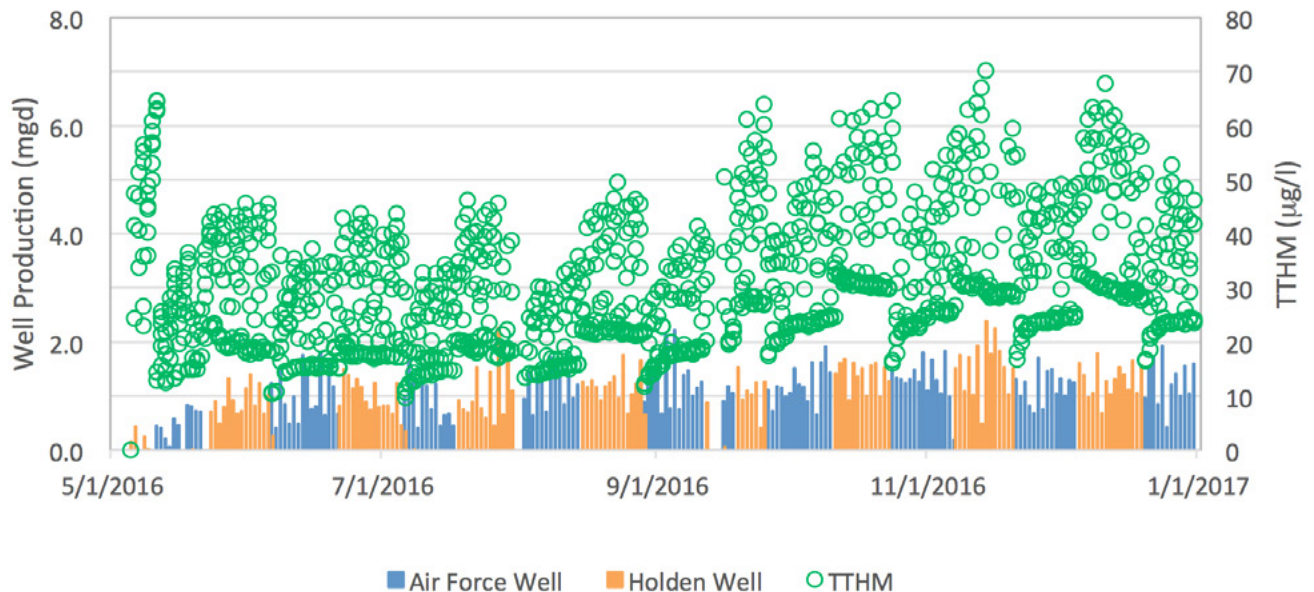
Figure 7: Online TTHM Data at Jackson Station



Initially staff thought that THM-100 analyzer had a calibration issue because there were curves in the TTHM monthly data that seemingly matched the unit’s automated calibrations. It wasn’t until the District did a closer study and overlaid the THM-100’s data with District SCADA data (Figure 8) that staff realized the data fluctuations were due to the switching of wells and not automated calibrations.

The Jackson Facility can be supplied by either the Holden or Air Force well. These wells are swapped on a bi-weekly basis. Although these wells are less than fifty feet apart and screened in the same layer of the aquifer, the wells have differing THM profiles. This will be a significant piece of knowledge for the District as staff moves forward with the replacement of Jackson’s treatment processes. Knowing the wells have varying THM formation potential depending on their operation will allow the District to pilot more conservatively to assure the new facility is able to meet its TOC removal objectives.

Figure 8: Well Production Overlaid with Online TTHM Data from Jackson Station



Discussion

1. Utilities need to collect more data to better optimize distribution system operations. While BTWD was able to leverage its vast history of compliance data, when it came to making operational changes quarterly sampling data was difficult to use. By looking at weekly values it was easier to identify secondary causes of data fluctuations (e.g. a well pump under repair, changes to operating points or distribution maintenance). Without a consistent baseline of data it is nearly impossible to understand what the impact is of the multitude of changes that occur between quarterly samples.

2. Utilities and regulators need to have a greater appreciation for the analytical limitations of the methods being used.

One of the biggest eye openers so far has been the acceptable variability in TTHM and HAA5 data. Except for those responsible for the instruments that measure these parameters few people understand that USEPA Method 524.2 allows for non-certification values to be within 30%. Certainly there needs to be some allowances when readings are made in the parts per billion and parts per trillion range, but too often the profession takes the laboratory data at face value, when that may not be the case.

3. There are more opportunities to use the online analyzer moving forward. In addition to helping maintain compliance while the new facility is being designed, the District also plans to use the analyzer's grab sample capability for the pilot phase of the new facility. The investment in the analyzer will allow for significantly more simulated THM holds to better understand which prospective treatment process provides the best treatment for the District moving forward. Another benefit/opportunity is the short sample turnaround time. In either the online or grab sample mode, samples are processed in 2 hours. This allows for quicker response, system adjustments and follow-up samples than the typical 1-2 week time frame for an outside laboratory.

Conclusions

The use of an online THM analyzer has proven a valuable tool enabling BTWD to optimize operations, better understand treatment processes, resolve THM compliance concerns and validate laboratory performance and results. These results are likely the beginning of many more discoveries that will hopefully ensure that THM issues become a problem of the past for the District.

References

- 1 Gallard, H.; & Gunten, U.V., 2002. Chlorination of natural organic matter: kinetics of chlorination and of THM formation. *Water Research Foundation*, 36:65-74.
- 2 Singer, P. C., 1999. Humic Substances as Precursors for Potentially Harmful Disinfection By-Products. *Water and Science Technology*, 40:9:25-30.
- 3 Harmesh, S.; West, M.; Qin, W.; Garvey, J.; & Mui, R., 2013. An Evaluation of the Accuracy of On-line THM Monitoring. *Journal AWWA*, 105:11:28-33.