City of Paso Robles Uses Online Monitor to Detect Low-Level of THMs in Treated Wastewater

The City of Paso Robles, California used an online water quality instrument to characterize and monitor low-levels of bromodichloromethane (BDCM) and dibromochloromethane (DBCM) in their treated wastewater for ground water recharge (GWR) use. The high frequency of reliable and accurate trihalomethane (THM) data provided by the online instrument proved essential to the City's disinfection by-product (DBP) strategy to obtain regulatory compliance with NPDES permit levels.

The City of Paso Robles operates a 4.9 mgd activated sludge wastewater treatment plant (WWTP) to meet the needs of 36,000 plus residents and a number of local vineyards and wineries. Treated wastewater from the facility is used for GWR to replenish the Paso Robes water basin and Salinas River. The facility faces stringent NPDES permit restrictions on effluent levels of total nitrogen (TN), microbiology and THMs.

Prior to 2015 the Paso Robles WWTP encountered routine TN and toxicity violations. The trickling filter plant and use of effluent settling ponds provided minimal nitrogen removal treatment, while large levels of effluent ammonia reacting with the disinfectant chlorine (indirect chloramination) assured THM compliance. The State Water Board instructed the city to remediate TN and toxicity violations with a plant upgrade that would better address nitrogen removal treatment to meet the TN 10 mg/L maximum requirement.

BNR Upgrade Leads to Increased THM Formation

As a result of the recommendation from the State Water Board the Paso Robles WWTP underwent a $47 million dollar upgrade to a biological nutrient removal (BNR) process in 2015 in efforts to achieve compliance. The upgrade helped the facility reduce TN by using bacteria to convert ammonia in the treated effluent into nitrogen gas, which is lost, and other nitrogen species. However, an unexpected consequence of the upgrade was an increase in THM formation (Figure 1).

By effectively reducing ammonia levels, the chlorine disinfectant injected prior to effluent discharge reacted with the residual organic matter leading to elevated THM levels. Whereas Total THM (TTHM) levels were below practical quantitation limits (PQL) prior to the installation of the BNR process, following the upgrade levels averaged approximately 60 ppb. The facility faced quarterly fines up to $12,000 as a result of the THM violations.

Figure 1: City of Paso Robles WWTP Effluent Parameters Before & After BNR Upgrade

Regulated Contaminant	NPDES Limit	Before BNR Upgrade	After BNR Upgrade
Total-Nitrogen	10 ppm	~40 ppm [2]	~10 ppm [4]
Total Coliforms	23 MPN [1]	In & Out of Compliance	Routinely at Method Detection Limit (1.8 MPN)
THMs	0.56 ppb BDCM 0.40 ppb DBCM	Non-Detect [3]	TTHM ~60 ppb [5] BDCM ~15 ppb

1. MPN - most probable number in 100 mL over a 7 day median
2. Almost all as ammonia
3. Very low levels due to large excess of ammonia pre-disinfection with Cl_2
4. Mostly nitrate, ~ 0 ppm ammonia
5. Before implementing chloramination

Chloramination Trial to Mitigate THM Formation

In an effort to reduce THM levels without compromising disinfection and TN limits the WWTP facility trialed the use of chloramination.

The chloramination evaluation began in March 2016 and was operated under the following conditions:

- Cl_2 dosing to maintain residual of 9 ppm
- Ammonium sulfate (15-30%) dosing upstream of Cl_2 disinfection
- NH_3 and Cl_2 dosing pump speeds respond to process flow volumes and residual BNR ammonia
- Disinfection contact time ~50 minutes
- Final neutralization of excess Cl_2 with $NaHSO_3$
- THM compliance point at discharge into Salinas River after a weir and a polishing channel that further reduces concentrations of THMs by volatilization and evaporation

Polishing channel enabling aeration and evaporation to further reduce THM concentrations

The facility relied on standard laboratory methods to quantify TTHM levels at the start of the chloramination trial. However, obtaining a high frequency of grab samples results needed to facilitate the optimization of the chloramination process became impractical. Using an analytical laboratory, it would take up to two weeks to obtain results, cost $250/sample, and the facility would receive dated results of water quality that had already been discharged.

Looking for more timely results, the facility decided to pilot a new online low-level THM monitor manufactured by Aqua Metrology Systems (AMS) that would allow them to accelerate the optimization of the chloramination process by providing high frequency, real time and reliable data on TTHM, DBCM and BDCM levels.

Low-level Online THM Detection Methodology

The standard configuration of the online THM-100™ analyzer uses a "purge-and-trap" method to extract the THMs from a 250 mL sample, followed by their desorption into a chemical mixture that generates a colored product when heated. Once heated, a time-resolved spectrophotometric analysis of the reaction kinetics is performed since the four THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform) react at different rates. The reaction absorbances for the sample and calibration parameters derived from the onboard THM standard are then used to calculate the sample's composition and concentrations of THM species and their total.

The low-level wastewater application at Paso Robles demanded the development of three new modifications to the THM-100 platform:

1. Pre-concentration: THMs from as many as four online samples can sequentially be transferred by "purge-trap-desorb" into the *same* chemical mixture before starting the reaction. This affords an increase in sensitivity up to four-fold.

2. Enhance optical detector sensitivity: The length of the flow-cell was increased three-fold (from 2 to 6 cm) to provide a longer path for light to travel, resulting in higher absorbances more differentiated from the blanks.

3. DBCM & BDCM reporting: A refined calculation method for quantifying the DBCM & BDCM species was developed, and their concentrations were outputted to SCADA and the shared THM result files in the cloud.

The low-level detection THM analyzer was installed in June 2016 at the sampling location post-disinfection and pre-dechlorination. Data from the online monitor was expected to run slightly higher than compliance sample readings due to placement of the instrument upstream of the weir and polishing channel and their THM-reducing volatilization and evaporation effects.

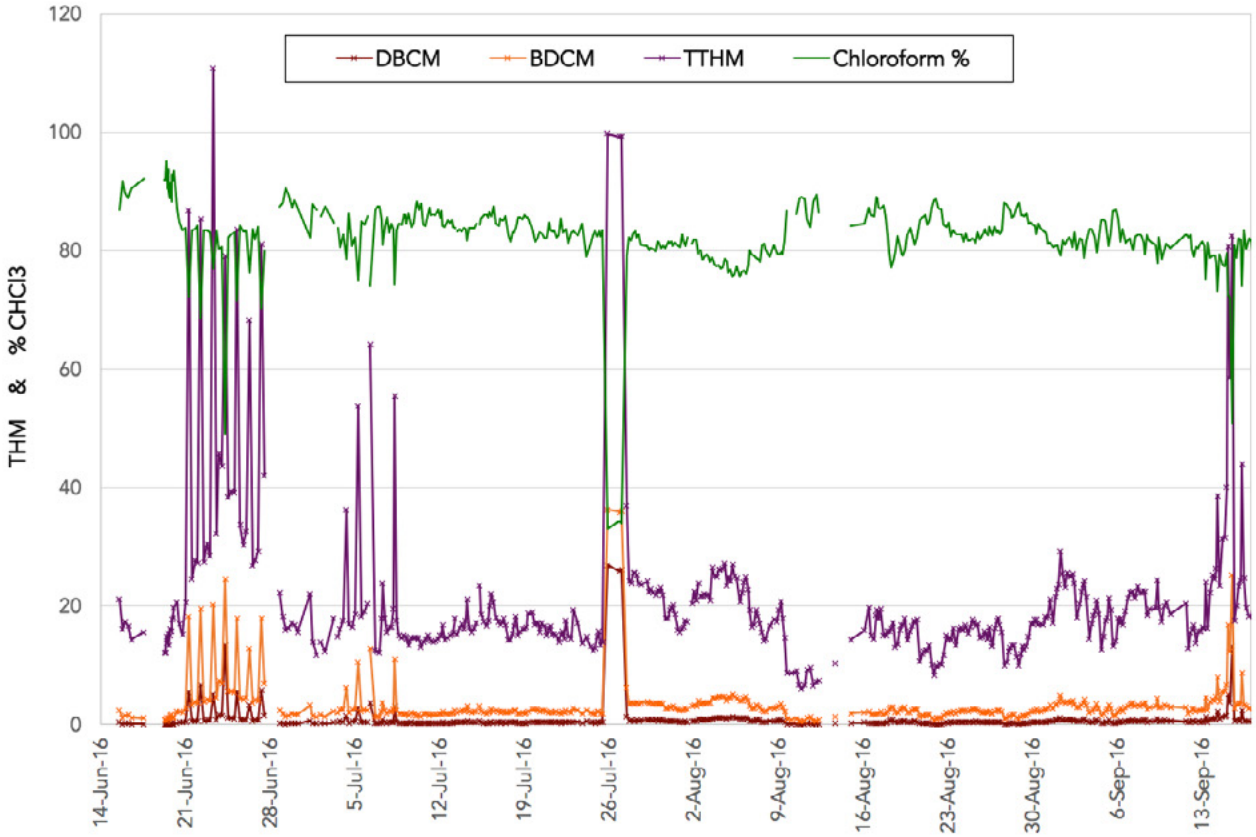
Chloroform ($CHCl_3$) is the predominant THM species at the Paso Robles WWTP, in the range of 75-95% of the TTHM. As a result, TTHM levels of approximately 2 ppb would need to be accurately quantified to understand if the chloramination successfully reduced the BDCM levels to below 0.56 ppb. If effective, DBCM compliance below the 0.4 ppb NPDES limit would automatically be guaranteed considering the THM speciation profile in this discharge water, with a typical BDCM : DBCM ratio of approximately 6 : 1.

Reliable Data from Online THM Monitor Helps Optimize Treatment Plant

The automated online monitor analyzed six samples daily from June through September 2016. The monitor captured fluctuations in TTHM, DBCM, and BDCM levels at the Paso Robles WWTP resulting from daily cycles, process changes, plant maintenance activities, and unexpected operational failures.

The online THM data proved fundamental for understanding the impact of chloramination ratios and THM speciation and levels. An increase to the ammonia : chlorine ratio leads to a decrease in TTHM levels and an increase in the percentage of $CHCl_3$; in combination these two effects further suppressed the regulated brominated THMs (Figure 2).

Figure 2: City of Paso Robles WWTP Online THM Data (June-September 2016)



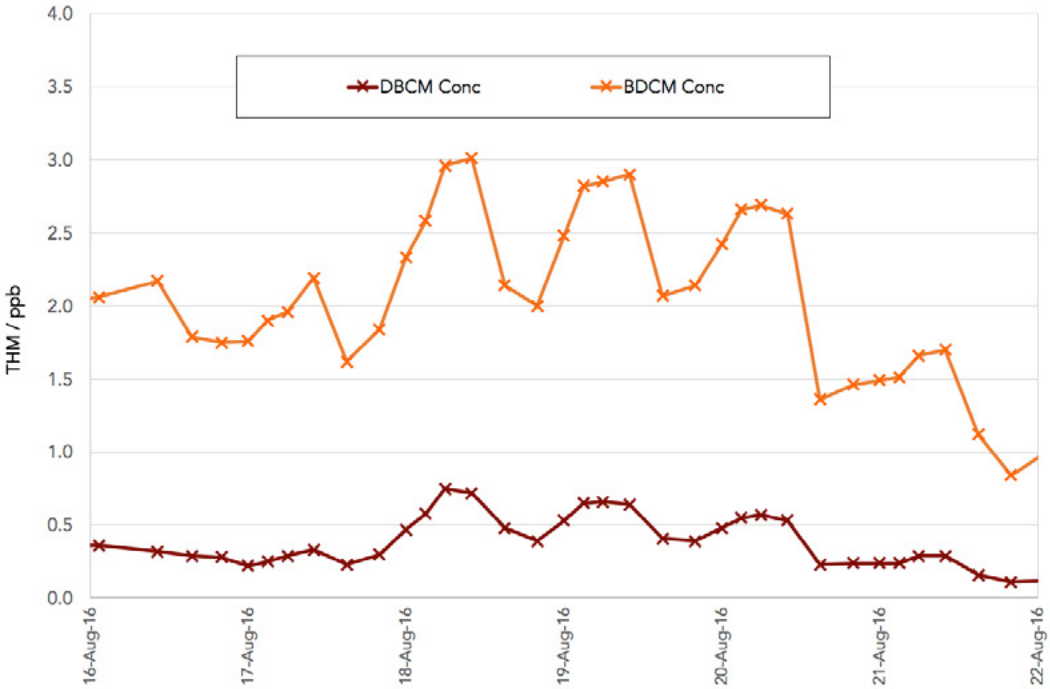
Aside from the prolonged periods of routine plant operation, the online THM monitoring revealed a few abnormal events that would otherwise have gone unnoticed. Two significant operational failures were identified:

1. Nightly events of extremely high THMs in late-June, early-July and mid-September were caused by under-dosing ammonium with the peristaltic pump when the flexible tubing was worn out. The severity of the failure increased with a reduction in pump dosing rates, which correlated with the nightly low-flows of wastewater at the plant.

2. On 26 July 2016 an online monitor of BNR residual ammonia fell out of calibration, falsely reporting elevated levels. In response, an operator manually turned off the ammonium sulfate dosing pumps. Without any ammonia residual from the BNR or by ammonium dosing the chloramination effort was undermined, and BDCM levels rose to over 35 ppb as the residual organic matter combined with the more reactive chlorine.

Under routine plant operating conditions, the online monitor revealed daily cyclic THM levels. THM concentrations peaked in the 10:00 am sample, but six hours later they dropped to the lowest daily levels, a pattern that correlated with plant flow rates and automated treatment operations. The online monitor reliably captured these diurnal fluctuations for DBCM at extremely low levels, between 0.1 and 0.7 ppb (Figure 3).

Figure 3: City of Paso Robles WWTP Daily Cyclic THM Data



The online THM monitor also captured the effect of BNR maintenance on THM levels (Figure 4), which temporarily dropped at the post-dechlorination location to below the NPDES limits enforced at the site of GWR discharge. When one of the two BNR tanks was brought off-line for maintenance on 9 August, it caused a net reduction in the conversion of influent ammonia to other nitrogen species (N_2 and nitrate). Although the plant was now out of compliance for TN, the increase in ammonia carry-over into the disinfection system brought about an elevated ammonia : chlorine ratio, leading to a reduction in THM formation by this 'enhanced' chloramination.

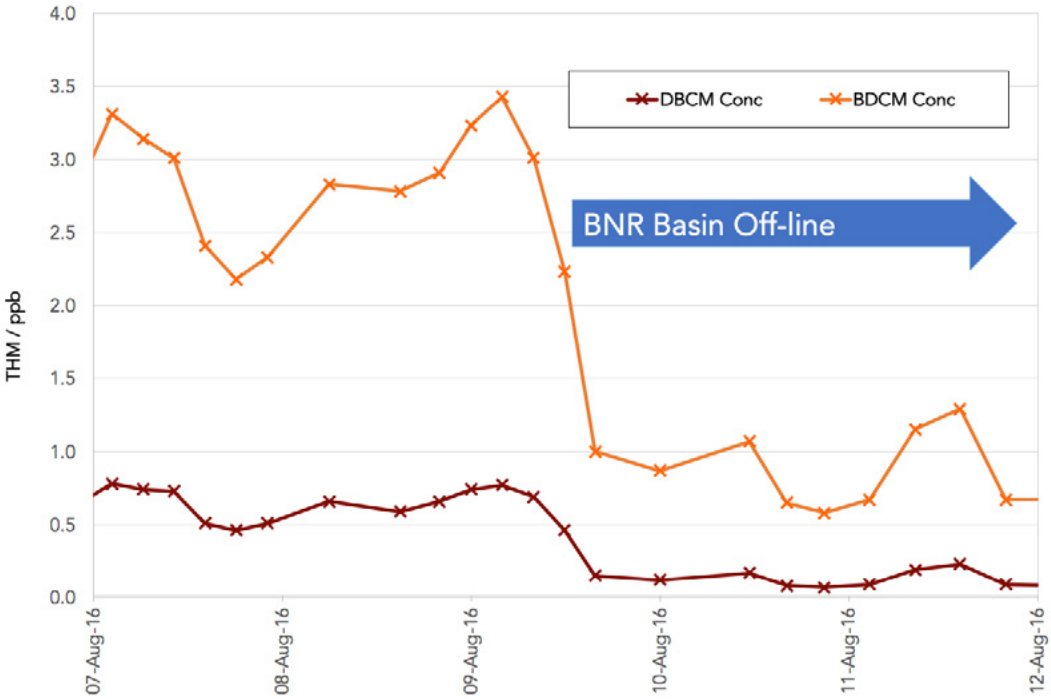


Figure 4: City of Paso Robles WWTP BNR Maintenance Effect on THMs

THM Compliance Samples During Chloramination Study

On 16 June and 8 August 2016, NPDES compliance samples from the GWR discharge location were submitted to the analytical laboratory. Figure 5 shows the results in which the lab reported that BDCM and DBCM were 'in compliance' by being below the lab's PQL of 0.5 ppb for these two THMs.

Figure 5: City of Paso Robles WWTP Compliance Samples

		NPDES THM Limits (Daily Average) [1]			
Date	**Sample Type & Location**	**$CHCl_3$ —**	**BDCM 0.56 ppb**	**DBCM 0.40 ppb**	**$CHBr_3$ —**
6/16/2016	Compliance Grab Sample [1]	10.3	ND	ND	ND
	Online Monitoring [2]	15.6 - 12.9	1.64 - 1.12	0.21 - 0.10	ND
8/8/2016	Compliance Grab Sample [1]	Not Reported	ND	ND	1.2
	Online Monitoring [2]	15.2 - 11.4	2.91 – 2.78	0.66 - 0.59	ND

1. At location of GWR discharge into Salinas River (after weir and polishing channel)
2. At location post-disinfection (upstream of weir and polishing channel)

ND for Non-Detect.

There are several interesting observations to be made about the reported THM values and the NPDES limits. This commentary is not intended to specifically criticize this laboratory, but to emphasize the general principal that it is challenging for an analytical technique to accurately quantify species whose concentrations approach the method's PQL.

1. There is inherent unreliability in the accuracy of analyte levels close to a laboratory method PQL (or MDL). Whereas the NPDES limits may be derived from a careful analysis of the available health science and the water discharge environment, assuring compliance is unreliable without the support of a reliable laboratory analytical methods with detection limits considerably below the regulatory levels.

   Specifically in this case, the lab analytical method has a PQL of 0.5 ppb for DBCM, but the regulatory limit is lower at 0.4 ppb. A sample containing 0.45 ppb would technically be out of compliance, but the lab analysis should be reported as 'Below PQL' – and therefore probably in NPDES compliance – whether accurately detected or not.

2. There are some internal inconsistencies in the THM results reported by the laboratory. The $CHCl_3$ concentration in the sample of 16 June was reported at 10.3 ppb. If it is accepted that this value is reliable, and that other lab samples and online THM analyses over this period were typically speciated with 90% $CHCl_3$, it should be expected that the BDCM concentration for this sample would be about 1.0 ppb, double the PQL (and not 'Non-Detected' as reported).

   In comparison with the online THM monitor, the BDCM results for this date were between 1.6 and 1.1 ppb, at the location upstream of the THM-volatilization action of the weir and polishing channel, which are expected to reduce the BDCM level to ~1 ppb at the compliance sample location but *unlikely* (as other measurements have shown) to drop the concentration below the PQL level of 0.5 ppb.

3. For the 8 August 2016 compliance sample, it is *unexpected* that the concentration of bromoform would have been measured as high as 1.2 ppb. This is inconsistent with the characteristic THM speciation in this discharge water of ~90% chloroform, with a ~10% sum of BDCM, DBCM and bromoform in progressively smaller amounts.

   For example, a water sample with this speciation and a TTHM level of 10 ppb is expected to contain ~9.0 ppb $CHCl_3$, ~0.85 ppb BDCM, ~0.12 ppb DBCM, and bromoform at ~0.03 ppb or less. Moreover, in more than 20 samples from this site of 10-20 ppb TTHM analyzed at the AMS's laboratory (by Standard Method 524.4), bromoform was always below their PQL of 0.2 ppb. Furthermore, it is highly improbable that the detected bromoform originated in the raw water arriving at the WWTP, without being accompanied by a significant quantity of DBCM that was not detected.

   In fact, the predominant THM in the Paso Robles drinking water supply is BDCM, and bromoform is the least dominant THM species. As a possible explanation, it is plausible that the detected bromoform in the 8 August 2016 sample could have as its source method carry-over from the preceding analytical sample or quality control standard.

Summary: Regulatory Compliance and Ensured Water Quality

Accurate and reliable high frequency water quality data was imperative for Paso Robles WWTP to control the chloramination process and ensure regulatory compliance. The facility faced stringent limits on DBCM (0.40 ppb) and BDCM (0.56 ppb) and timely analytical results were necessary. Standard laboratory analysis became impractical and the facility pilot tested the efficacy of a new commercially available online THM monitor capable of low-level real-time detection of DBCM and BDCM.

The online monitor provided accurate and reliable low-level detection of DBCM and BDCM formation at-or-below NPDES permit limits. The high frequency data helped The City to evaluate the DBP prevention strategy and ensure the quality of treated wastewater used in the GWR program.

Through the adoption of a BRN treatment system, chloramination and online THM monitoring the Paso Robles WWTP obtained regulatory compliance by being below NPDES permit limits for TN, microbiology and THMs at the June and August 2016 sampling dates.

Footnote

Although the June and August 2016 compliance samples were below the NPDES THM limits, the Central Coast Regional Water Quality Control Board (CCRWQCB) and The City of Paso Robles have since entered into a time-schedule order agreement for THM compliance, giving the Paso Robles WWTP the opportunity to consider alternative plant upgrades and treatment methods, which must bring the plant into compliance by June 2021. The City had been planning on investing in the infrastructure for recycled water and was open to switching disinfection methods if chloramination was unfeasible with the goals of the recycled water project.

The City sought relief from the current low-level THM limits during design and construction. The CCRWQCB revised and relaxed The City of Paso Robles NPDES THM limits on 27 July 2016. New interim BDCM and DBCM limits of 10 and 5 ppb respectively are now in effect. Paso Robles WWTP must report on the preparation and implementation of a pollution prevention plan for THMs, with a strategy to achieve full compliance of the original NPDES regulations by June 2018. While the City is still evaluating options for THM control, the exceptional quality of work performed by AMS and the reliable data from the online monitor have helped Paso Robles to solve their THM problem.

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