# Detecting Low-Level of THMs in Treated Wastewater Using Online THM Monitor

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**ABSTRACT:** 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 its treated wastewater for groundwater 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.

## INTRODUCTION

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

Before 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.

## BIOLOGICAL NUTRIENT REMOVAL UPGRADES LEAD TO INCREASED THM FORMATION

As a result of the State Water Board's recommendation, the Paso Robles WWTP underwent a 47-million-dollar upgrade to a biological nutrient removal (BNR) process in 2015 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.

The chlorine disinfectant injected prior to effluent discharge effectively reduced ammonia levels. However, the residual organic matter reacted with the disinfectant, leading to elevated THM levels. While 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. As a result of the THM violations, the facility faced quarterly fines up to $12,000.

The City of Paso Robles WWTP effluent parameters before and after the BNR upgrade are detailed in the following table:

| | 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<br>0.40 ppb DBCM | Non Detect [3] | TTHM ~60 ppb [5]<br>BDCM ~15 ppb |

1: MPN (most probable number) in 100 mL over 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

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 a 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

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 sample 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 AMS. This monitor would allow them to accelerate the optimization of the chlorination 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 were expected to run slightly higher than compliance sample readings due to the instrument's placement 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 1).

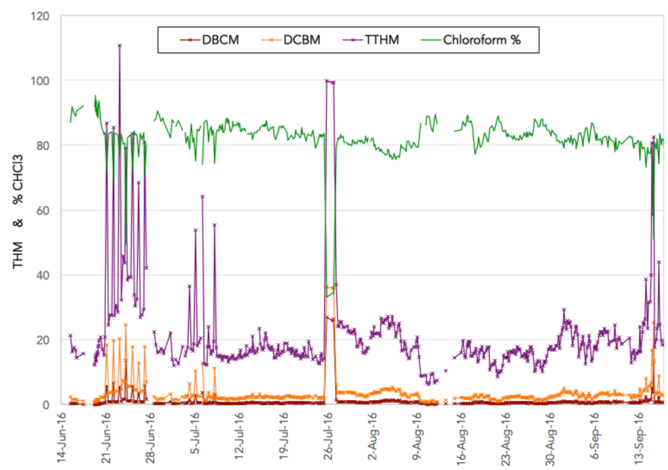


Figure 1- City of Paso Robles WWTP Online THM Data (June-September 2016)

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 2).

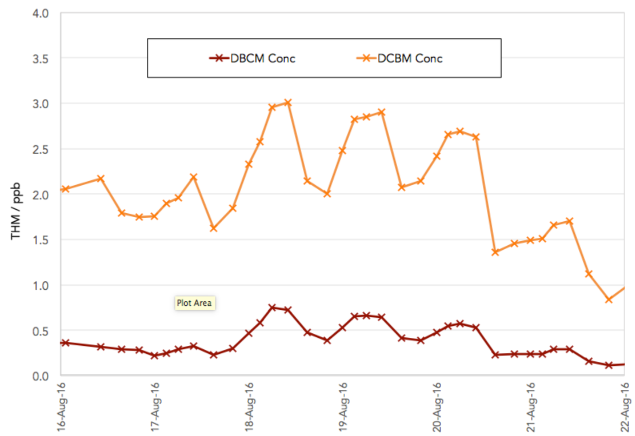


Figure 2- City of Paso Robles WWTP Daily Cyclic THM Data

The online THM monitor also captured the effect of BNR maintenance on THM levels (Figure 3), 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.

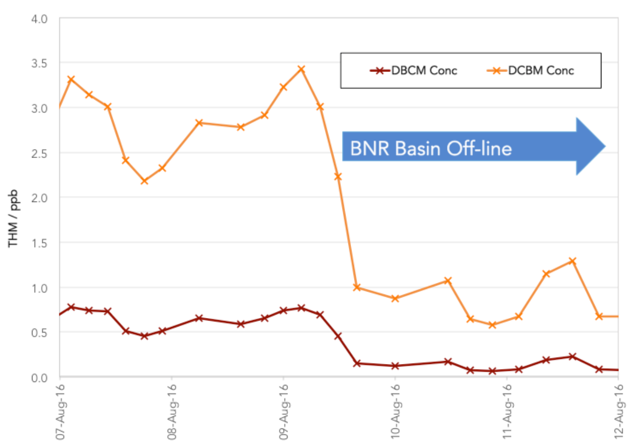


Figure 3- City of Paso Robles WWTP BNR Maintenance Effect on THMs

## THM COMPLIANCE SAMPLES DURING THE CHLORAMINATION STUDY

On 16 June and 8 August 2016, NPDES compliance samples from the GWR discharge location were submitted to the analytical laboratory, results are of the City of Paso Robles WWTP compliance samples are in the following table:

| | | NDPDES THM Limits (Daily Average) [1] | | | |
|---|---|---|---|---|---|
| Date | Sample Type & Location | $CHCl_3$ | BDCM 0.56 ppb | DBCM 0.40 ppb | $CHBr_3$ |
| 16 Aug 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 Aug 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

## CONCLUSION

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 evaluate the DBP prevention strategy and ensure the quality of treated wastewater used in the GWR program.