GE
Water & Process Technologies
Analytical Instruments

Application Note

Today's TOC; Tomorrow's THMs

How Total Organic Carbon (TOC) Analysis Relates to Disinfection Byproducts such as Trihalomethanes (THMs) and the Corresponding EPA Regulations

Introduction

The US Environmental Protection Agency (EPA) amended the Safe Drinking Water Act (SDWA) in 1996 to balance the risks presented by microbial pathogens and by-products from the disinfectant used to destroy these microbes. The byproducts, called Disinfection Byproducts (DBPs), form from the interaction of the naturally occurring organic matter (NOM) in a treatment plant's source water and its disinfection process. NOM is typically measured as total organic carbon (TOC). DBPs, such as trihalomethanes (THMs), continue to form as water passes through a plant's distribution system and contact time increases. Therefore, it is said that the TOC measured in a plant today can be measured as DBPs tomorrow.

The EPA recently introduced new regulations to help further reduce health risks associated with DBPs. These changes will make meeting the DBP rules more difficult, and in turn make understanding a plant's TOC values and the correlation to DBP levels even more critical.

How TOC Relates to DBPs

TOC in drinking water is formed from the decay of naturally occurring vegetation, including algae, sediment, and particles in water. TOC content in water sources varies from region to region, by type of water body, and even seasonally within a water source. Algae blooms, for example, are usually more prominent in summer and early fall, and can increase the organics of a source water. TOC can also be increased in a raw water source through the transfer of other water sources, nearby wetlands, terrestrial runoff, or river channels. There are also quite a few man-made organic chemicals such as industrial solvents, hydrocarbons, pesticides, and herbicides derived from industrial sources and contributing to TOC.

Several DBPs have been linked to cancer in laboratory animals and are therefore regulated. Naturally occurring carbon compounds are not hazardous by themselves, but combined with a disinfectant they produce by-products, which pose a health concern. THMs, one class of DBPs, are formed from the interaction of TOC, naturally occurring bromide, and chlorine (see **Figure 1**).

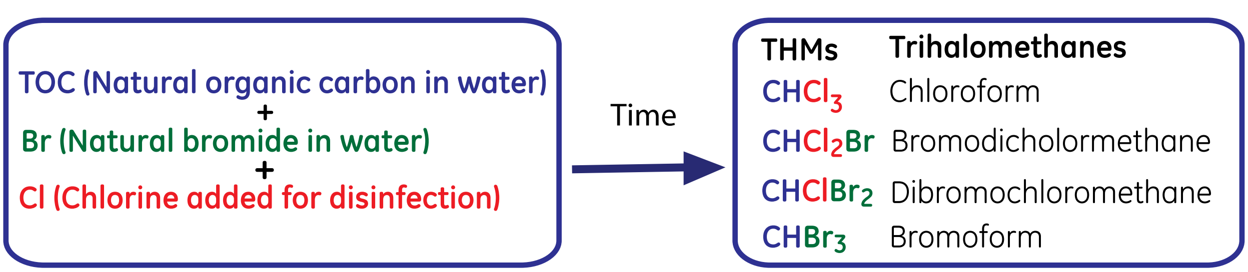

Figure 1. THMs formed from TOC, Bromide and Chlorine

Table 1
Stage 1 D/DBPR Regulated Contaminants for Surface and Ground Water Plants

Regulated Contaminants	Maximum Contaminant Level (MCL)	Maximum Contaminant Level Goal (MCLG)
Total Trihalomethanes (TTHM)	**80 ppb**	
Chloroform		70 ppb
Bromodichloromethane		zero
Dibromochloromethane		60 ppb
Bromoform		zero
Five Haloacetic Acids (HAA5)	**60 ppb**	
Monochloroacetic acid		70 ppb
Dichloroacetic acid		zero
Trichloroacetic acid		20 ppb
Bromoacetic acid		-
Dibromoacetic acid		-
Bromate (ozone plants)	**10 ppb**	zero
Chlorite (chlorine dioxide plants)	**1 ppm**	0.8 ppm

Chloroform, a specific type of THM, is known to depress the nervous system, and is a danger to health at much higher levels than present in drinking water. For these reasons, it is critical to ensure that the DBP precursors, or TOC, are removed to the lowest level possible.

Typical disinfection includes a primary and secondary disinfection, which can allow for the formation of DBPs many times over during the treatment process. Coagulation and filtration will not fully remove DBPs, especially with the secondary disinfection that occurs prior to release into the distribution system. The levels of DBPs can vary significantly from one point in a distribution system to another. Many continue to form as the water passes through the distribution system. DBP levels are generally higher in surface water systems because surface water usually contains higher DBP precursor TOC levels and requires stronger disinfection. Also, as previously stated, TOC can vary significantly, so to fully understand a water system's DBP level changes, TOC values must be monitored to understand fluctuations. Some plants have gone a step further to start TOC profiling their entire treatment plant. This is accomplished by testing TOC values at all points in a plant and each treatment train, determining where the majority of TOC reduction does or does not occur.

The new regulations may also encourage drinking water utilities to use chloramines and other alternatives to chlorine disinfection to control DBPs. Chloramines, formed from a reaction between chlorine and ammonia, dramatically reduce levels of regulated DBPs, but can be more costly and have other pitfalls such as leaching lead in pipes. There may also be more DBPs that have not yet been identified and tested for toxicity or cancer effects with the use of alternative disinfectants. In fact, there is very little known about DBPs derived from the newer alternative disinfectants, such as ozone, chlorine dioxide, and chloramine. Even with these alternative disinfectants, it is important to understand a plant's TOC levels and how they correspond to DBP levels.

DBP Regulation Overview

The Stage 1 Disinfectants and Disinfection By-products Rule (D/DBPR), promulgated in December 1998, was the first phase of the 1996 Amendments to the Safe Drinking Water Act. Stage 1 D/DBPR not only set limits at surface water and groundwater plants for the DBPs, such as THMs and haloacetic acids (HAA5) (see **Table 1**), but also established a TOC percentage removal requirement for utilities utilizing conventional treatment processes (see **Table 2**). Many surface water plants utilize conventional filtration, using coagulants to remove TOC, also termed "DBP precursors"[1] because of their interaction with a plant's disinfectant. The EPA uses the term "enhanced coagulation" to define the process of obtaining improved removal of TOC by conventional treatment in order to limit DBP formation.[2]

The Stage 2 D/DBPR, published on January 4, 2006, is meant to further reduce the potential health risks from DBPs beyond the Stage 1 regulation. The Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) is being implemented at the same time as Stage 2 D/DBPR to ensure drinking water is safe from both mi-

Table 2
TOC Requirement for Surface Water Plants Utilizing Conventional Treatment

Step 1 TOC Table- Required % Removal of TOC			
Source Water TOC (mg/L)	Source Water Alkalinity, mg/L as $CaCO_3$		
	0-60	>60-120	>120
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

crobial pathogens and DBPs. (The LT2ESWTR rules strengthen protection against microbial contaminants, especially Cryptosporidium.)[3] The Stage 2 D/DBPR does not replace the Stage 1 DBPR; instead it is an extension of the original rule. Systems must comply with all Stage 1 requirements, such as not exceeding maximum contaminant levels (MCL) for chlorite and bromate (see **Table 1**), and TOC removal requirements (see **Table 2**), as well as the Stage 2 regulations.

Various regulatory steps are required under the Stage 2 DBPR to ensure minimization of DBPs. Systems must conduct an initial distribution system evaluation (IDSE)[4] to identify compliance monitoring locations that represent high total THMs and HAA5 levels. In addition, the Stage 2 D/DBPR changes the way DBP sampling results are averaged for compliance. The Stage 2 D/DBPR regulation is based on a locational running annual average (LRAA) which means compliance must be met at each monitoring location, instead of the system-wide running annual average (RAA) used under the Stage 1 DBPR. Water plants are also required to conduct an operational evaluation if their DBPs are too high.

Plans for monitoring were due as early as 2006 for the largest municipalities. Compliance monitoring for Stage 2 begins in 2012 for the largest systems. By October 2013, all systems, regardless of size, must be in compliance. The frequency of monitoring for DBPs will be quarterly for most systems. However, small systems (Subpart H* systems with less than 500 in the population and groundwater systems with less than 10,000 in the population) will only be required to monitor yearly. The exact number of samples and number of sample locations depends again on the utility's community population size.

The requirements behind the Stage 2 D/DBPR forces a utility that has struggled in the past to meet the DBP requirements from Stage 1, to take even more steps to control DBPs. TOC monitoring is one way to better understand a plant's DBP levels and the changes that can be implemented to control TOC and therefore DBPs.

Conclusion

As the EPA continues updating the Safe Drinking Water Act to limit health risks surrounding DBPs, drinking water utilities remain challenged to meet the corresponding regulations. To maintain DBP levels below the acceptable limit, a water treatment plant must fully understand the characteristics of the DBP precursors in their source and distribution water. A large part of maintaining compliance with the D/DBPR rule involves monitoring organic levels and understanding how a treatment process impacts TOC. Knowing where TOC is or is not being removed within a plant will help a utility make the appropriate process changes to prevent today's TOC from becoming tomorrow's THMs.

References

[1]USEPA. *"Treatment technique for control of disinfection byproduct (DBP), Final Rule."* 40 CFR 141.135, June 1, 2006.

[2]USEPA. *Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual.* Office of Water, http:/www.epa.gov/safewater/mdbp/coaguide.pdf, May 1, 1999.

[3]USEPA. *Fact Sheet: Stage 2 Disinfectants and Disinfection Byproducts Rule.* Office of Water (4606) EPA 816-F-06-021, http://www.epa.gov/safewater/disinfection/stage2/pdfs/fs_st2_finalrule.pdf, June 1, 2006.

[4]USEPA. *Stage 2 DBPR IDSE Standard Monitoring Factsheet* http://www.epa.gov/safewater/disinfection/stage2/pdfs/fs_sm_fact_sheet_final.pdf, June 1, 2006.

** Subpart H systems are public water systems that use surface water or groundwater under the influence of surface water as a source.*

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