

# Chemistry and Treatment of Disinfection Byproducts in Drinking Water

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Disinfection has been used for over a century and has almost eliminated biological waterborne-disease outbreaks in developed countries. However, in the 1970s scientists observed the formation of chlorinated organic materials in drinking water systems using chlorine and recognized their carcinogenic potential. Thus arose a need to balance the health benefits of disinfection to prevent waterborne disease outbreaks against the risk of cancer from long-term (chronic) exposure to disinfection byproducts (DBPs).

## Disinfection and Natural Organic Matter

All chemical disinfectants produce organic and/or inorganic DBPs of potential health concern (see table below). All disinfectants oxidize naturally occurring organic and inorganic material in water. Disinfectants react with precursors in drinking water to produce DBPs. The primary precursor is natural organic matter (NOM), which is generally measured as total organic carbon (TOC), and is comprised of roughly 50 percent carbon, 35 percent oxygen, 5 percent hydrogen, 3 percent nitrogen, and lower amounts of phosphorous, sulfur, and trace metals. Bromide is also an important

precursor, because bromide is easily oxidized to aqueous bromine (HOBr/OBr<sup>-</sup>), a mild disinfectant that can also react to form bromine-substituted DBPs such as

*Most THMs form within the water treatment plant; the remainder form in the water distribution systems.*

bromoform. Iodide undergoes similar reactions to produce HOI/OI<sup>-</sup>, and iodinated DBPs such as iodoform are also of potential health significance. Reactions between common disinfectants that provide residual disinfection capacity in water distribution systems, such as free chlorine, and precursors such as NOM lead to the formation of DBPs, particularly halogen-substituted organics.

## Factors of DBP Formation

Numerous water quality and treatment factors affect DBP formation. The rate and extent of DBP formation are higher as TOC, bromide, temperature, disinfectant dose, and contact time with the disinfectant increase. Several mechanistic and empirical models exist and account for these factors. For example, the following empirical

model predicts formation of the four regulated trihalomethanes (THM4):

$$\text{THM4} = 0.0412 [\text{TOC}]^{1.098} [\text{Cl}_2]^{0.152} [\text{Br}^-]^{0.068} [\text{Temp}]^{0.609} [\text{pH}]^{1.601} [\text{Time}]^{0.263}$$

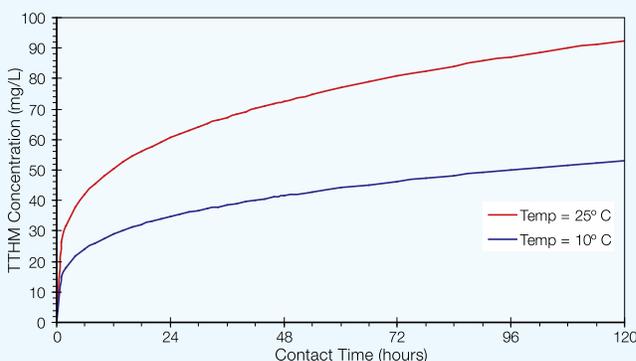
THM4 (in micrograms per liter, µg/L) is a function of chlorine dose (Cl<sub>2</sub> in milligrams per liter, mg/L), bromide concentration (Br<sup>-</sup> in µg/L), water temperature (degrees Celsius), pH, and contact time between the chlorine and water (hours).

The upper chart, next page, illustrates the effects of two key parameters, contact time and seasonal temperature, on THM4 formation. Water treatment plants (WTPs) commonly have 30 to 120 minutes of contact time with chlorine prior to entering the water distribution system (pipes, storage tanks, etc.) whereas contact times range from several hours to days as water is delivered to households, with typical lengths of 1 to 3 days. A significant percentage of the THM4 forms within the WTP (41 percent of THM4 formed within 4 hours in the chart), while the remainder form in the water distribution systems. Seasonal variations in water quality also impact DBP formation. For example, at common summertime temperatures of 25 C (78 F), THM4 concentrations are almost

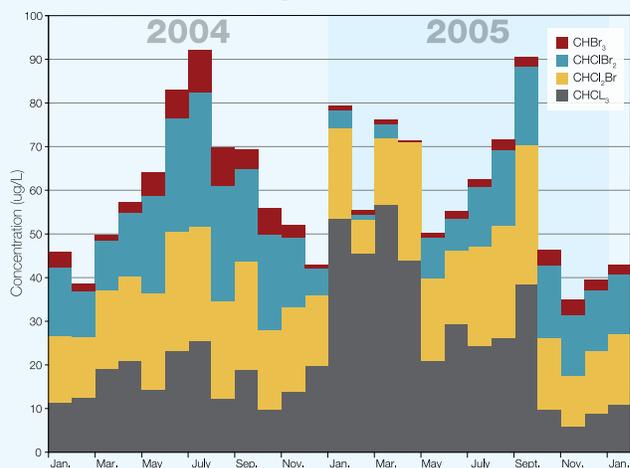
Disinfectant	Efficacy as a disinfectant	Provides disinfectant residual in water distribution system?	Dominant precursors for DBP formation	Dominant DBPs of regulatory concern
Ozone (O <sub>3</sub> )	high	no	bromide and TOC	bromate (BrO <sub>3</sub> <sup>-</sup> ) aldehydes
Free chlorine (HOCl/OCl <sup>-</sup> )	intermediate	yes	bromide and TOC	trihalomethanes and haloacetic acids
Monochloramine (NH <sub>2</sub> Cl)	intermediate	yes	TOC and organic nitrogen	nitrosamines
Chlorine dioxide (ClO <sub>2</sub> )	intermediate	no	decay of chlorine dioxide	chlorite and chlorate
UV irradiation	high	no	none	none

twice those measured at 10 C for a 24-hour contact time.

The four trihalomethanes regulated by the U.S. EPA are chloroform ( $\text{CHCl}_3$ ), dichlorobromomethane ( $\text{CHCl}_2\text{Br}$ ), chlorodibromomethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ). The lower chart at right summarizes the THM4 concentrations leaving a conventional water treatment plant for one water utility in central Arizona over a two-year period, along with the distribution of individual THM species. High THM4 concentrations generally occur in the summer, as expected due to warmer water temperatures. However, during the early winter of 2005, heavy rain and snow led to significant runoff and flooding. As a result, the dissolved organic concentrations increased from less than 3 mg/L in 2004 to greater than 4 mg/L in 2005 due to solubilization of soil organic matter; TOC concentrations exceeded 10 mg/L. As a result, THM4 concentrations were higher due to TOC in the runoff. In addition, the runoff diluted the salts in the surface water sources, which lowered the bromide concentration more than 50 percent. As a consequence



Formation of total trihalomethanes as a function of time and water temperature (based upon equation in text, assuming 3 mg/L TOC, 5 mg/L  $\text{Cl}_2$  dose, 150  $\mu\text{g/L}$   $\text{Br}^-$ , pH 7.5).



Sum of four THM species (THM4) from effluent of a water treatment plant in central Arizona.

of lower bromide levels, the distribution of chlorinated and brominated THMs shifted during the early 2005 runoff period, resulting in greater chloroform production.

### Regulatory Drivers

Regulatory mandates drive WTP operations and technology changes. Traditionally,

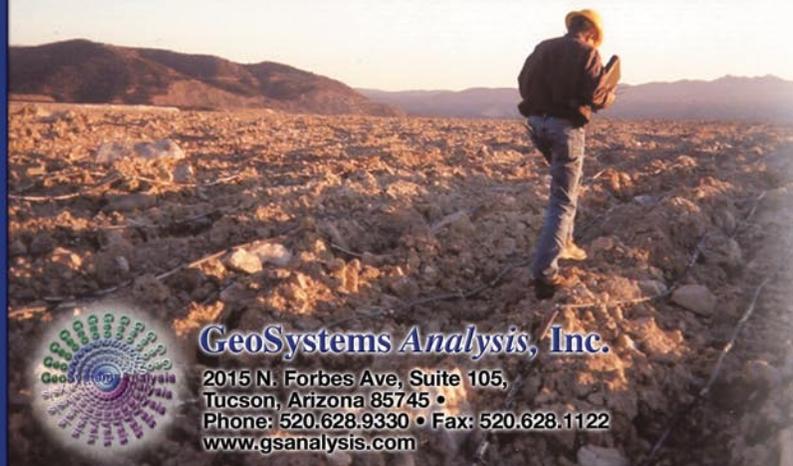
THMs, haloacetic acids (HAAs), and many other DBPs were viewed as posing only chronic health risks. As such, THM and HAA compliance depended on meeting regulatory levels based on usually four samples collected throughout the water distribution system on a quarterly basis. All the samples were then averaged on a running annual average to comply with the THM and HAA regulations. This permitted averaging of high summer DBP levels with low winter levels, and locations in the distribution system with shorter (low DBP levels) and longer (high DBP levels) contact times. Recent concerns over possible acute health risks from DBPs (such as spontaneous abortions in women, which refined epidemiology studies are now finding unsubstantiated) and social justice issues have resulted in new THM and HAA regulations that do not permit averaging of concentrations across the entire water distribution system. The standards must be met at each sampling location on a running annual average basis. Updates on the newest DBP regulations can be found at [www.epa.gov/ogwdw/disinfection/stage2/](http://www.epa.gov/ogwdw/disinfection/stage2/).

### Treatment Technologies Evolve

Over the past 10 to 20 years, DBP regulations have become increasingly stringent. In response, WTP operations and technology selection have evolved. Most WTPs control DBP formation by reducing DBP precursors—removing

see Treatment, page 33

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## Protecting the Public

In the 1970s, the first link between consumption of chlorinated water and cancers of the digestive and urinary tracts was made. During the same decade, THMs became the first class of halogenated DBPs to be identified and regulated in treated drinking water.

In 1979, the U.S. EPA promulgated the Interim Trihalomethane Rule, establishing a maximum contaminant level (MCL) of 100 micrograms per liter ( $\mu\text{g/L}$ ) for the sum of the concentrations of four THMs (THM4). The THMs are chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ). Compliance was based on a running annual average of four quarterly samples collected at four locations in the distribution system of each plant: three locations of “average” residence time and one remote location. The rule applied only to community water systems that served 10,000 people or more because of concerns that smaller systems might compromise their disinfection practices in an attempt to comply with the rule. The 100  $\mu\text{g/L}$  MCL was considered achievable with the best water treatment technology available at the time and at reasonable cost, without compromising protection from pathogenic microorganisms.

In 1989, in response to Safe Drinking Water Act requirements and the identification of hundreds of other DBPs, EPA renewed its focus on DBP regulation. But establishing appropriate regulations was complicated by the fact that alternative disinfectants to chlorine, such as ozone and chlorine dioxide, were coming into use, and they formed disinfection byproducts of their own, also with adverse health effects. Furthermore, conclusive evidence linking DBPs with adverse health affects was lacking. Due to these complexities, EPA utilized a negotiated rule-making process in 1993, which resulted in the eventual promulgation of an Information Collection Rule (ICR) in 1996 and a two-stage Disinfectants/Disinfection By-Products (D/DBP) Rule in 1998.

The Stage 1 D/DBP Rule reduced the MCL for THM4 to 80  $\mu\text{g/L}$  and established an

MCL for five HAAs (HAA5) of 60  $\mu\text{g/L}$ . Unlike the 1979 rule, the Stage 1 D/DBP Rule applied to all community water systems, including small systems.

Meanwhile, the ICR provided for the collection of a large array of water quality, treatment, and DBP data, including THM4 and HAA5 concentrations within water treatment plants and in their distribution systems. The new data showed that the running annual average compliance calculation allowed a significant amount of sampling locations within the distribution system to have DBP levels appreciably above the MCLs, even in systems fully compliant with Stage 1 D/DBP. Likewise, appreciable DBP levels in excess of the MCL were observed at different times of the year. Over the next several years, these data, combined with new health studies linking acute DBP exposure to reproductive and developmental health effects, led EPA to establish the Stage 2 D/DBP Rule in 2006.

Under Stage 2, the THM4 and HAA5 MCLs remain the same, but concentrations are regulated as a locational running annual average of four locations in the distribution system for each treatment plant, rather than a system-wide running annual average. Additionally, new sampling locations are to be determined at which maximum levels of THM4 and HAA5 concentrations are expected. This is anticipated to provide for equity in terms of DBP exposure, and a reduction in DBP concentration peaks.

## Gaining Perspective

Few issues in our professional lifetime have had such an impact on raw water source selection, watershed management, water treatment plant design and operation, and the distribution of finished drinking water as the occurrence of DBPs. Our knowledge of DBP formation and health impacts, as well as efforts to protect public health, advanced significantly during the past three decades, but we still have much to learn. Both control of pathogenic microorganisms by disinfection and control of disinfection by-product formation are critical to safe drinking water.

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TOC—or by using alternative disinfection practices. To remove TOC, most WTPs add metal salt coagulants (alum, ferric sulfate) that precipitate as solids and adsorb TOC. However, in the southwestern United States, the characteristics of NOM and high alkalinity of surface waters result in only modest TOC removal by that method. Consequently, WTPs in the Southwest must consider other technologies that can adsorb (granular activated carbon), biodegrade (biofiltration), or separate TOC (ultra- or nano-filtration) before the addition of chlorine.

Utilities are also considering alternative disinfectants to chlorine, such as ozone, ultraviolet (UV) irradiation, chloramines, and chlorine dioxide. However, each of these options has unique DBP issues, such as bromate formation during ozonation, or the fact that UV irradiation does not provide residual disinfection capability in water distribution systems. As regulations change, these and other technologies will be required in order to control DBP formation. Although a few research studies are currently underway in the Southwest (such as AwwaRF Project 3103: Localized Treatment for Disinfection By-products), removal of DBPs after they have formed is generally not considered economically favorable.

DBPs will continue to be present in all waters containing chemical disinfectants. The U.S. Environmental Protection Agency and other researchers have identified more than 500 DBPs, although fewer than a dozen are currently regulated. Ongoing toxicity testing with these emerging DBPs indicates that nitrogen-containing DBPs, including nitromethanes and nitrosamines, pose a significantly greater risk than currently regulated THMs or HAAs. Furthermore, switching from chlorine to chloramines and other strategies implemented to control THMs or HAAs may create higher levels of these potentially more toxic nitrogen-containing DBPs. As a result, control of DBP formation will continue to be a pressing issue for the water industry.

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