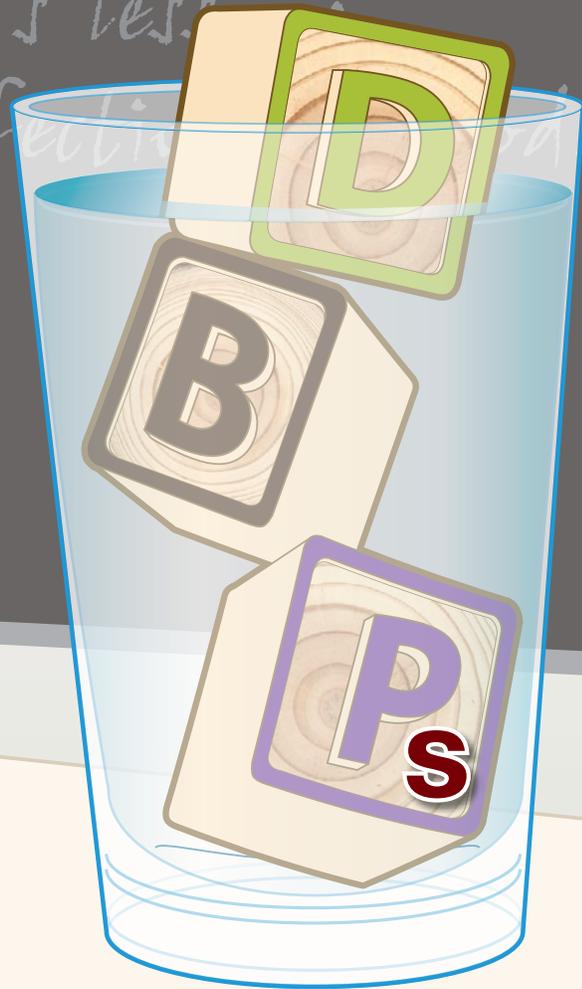
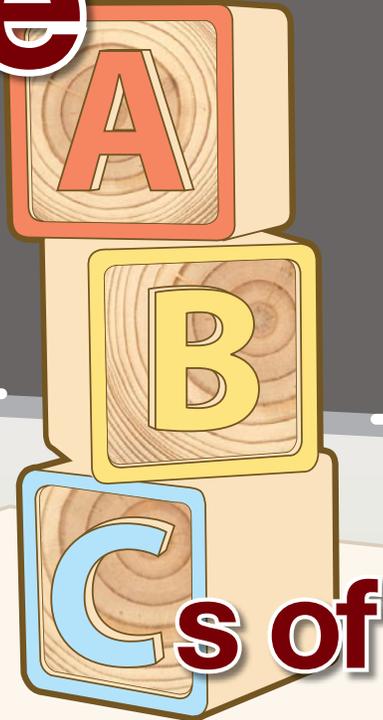


The



Today's lesson
Disinfection byproducts

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Without doubt, disinfection of drinking water has vastly improved human health. However, while not posing nearly the same health risks as untreated drinking water, disinfection byproducts (DBPs) resulting from common disinfection practices do warrant attention. Certain DBPs have been associated with adverse health effects, notably cancers and reproductive and developmental disorders (see sidebar, opposite page).

Disinfection is the process of chemically inactivating disease-causing microorganisms present in raw water supplies. DBPs are formed by reactions between disinfecting agents and natural organic matter (NOM) and bromide, both

of which occur naturally and harmlessly in groundwater and surface water supplies. DBPs are found in all water supplies that are chlorinated, ozonated, or treated with other chemical disinfectants.

Among the thousands of DBPs that can form, the most studied (due to health effects and analytical capabilities) are the halogenated compounds, so named because they contain chlorine, bromine, and less commonly iodine. Among these are the trihalomethanes (THMs) and haloacetic acids (HAAs), which form when chlorine is used as a disinfectant. THMs are formed when individual carbon atoms in NOM are attacked by halogen disinfectants. Small hydrocarbon chains are cleaved from NOM molecules, and the

reaction of the halogen species continues until THMs are formed. HAAs are formed in a similar manner. Other halogenated DBPs include bromate, formed when ozone is used to disinfect bromide-containing source waters, and chlorite, formed when chlorine dioxide is used.

What Affects DBP Formation?

DBP formation depends upon the quality of the source water and the types of treatment used. In general, waters with high levels of natural organic carbon concentrations (total organic carbon greater than about 5 milligrams per liter, mg/L, see sidebar, far right) and high bromide concentrations (greater than about 0.10 mg/L) tend to have high

levels of DBPs unless these precursors are removed prior to adding the disinfectant. Other factors influencing their formation are listed below.

pH: As pH increases, the overall formation of halogenated organic compounds decreases. Above pH 8, many of the halogenated DBPs hydrolyze, except for THMs.

Time: Generally, THM and HAA formation increases as contact time between the disinfectant and NOM-containing water increases. Therefore they continue to form in the water distribution system as long as free chlorine residuals persist. However, some halogenated DBPs, such as haloacetonitriles and halo ketones, may form rapidly upon chlorination but then decay in the distribution system due to hydrolysis and continuing reactions with residual chlorine.

Season: The rate and extent of DBP formation may be markedly affected by seasonal factors and meteorological conditions. In the warmer summer months,

faster reaction kinetics means that more chlorine is consumed, more is required

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to achieve disinfection, and consequently more DBPs are produced. The composition of organic precursors and bromide concentration may also vary seasonally, for example with increased spring runoff or saltwater intrusion during drier periods.

NOM characteristics: The composition of NOM also influences the extent of DBP formation. NOM contains both hydrophobic and hydrophilic organic material arising from the decay of

vegetative matter, with hydrophobic material favoring greater DBP formation. The nature and distribution of the organic materials depend on the type of vegetation in the watershed and the species of algae in the water.

Chlorine: The rate, extent, and distribution of DBPs are impacted by the chlorine dose and free chlorine residual. Higher doses and residuals favor the formation of HAAs over THMs, the formation of the trihalogenated HAAs over the di- and mono-halogenated HAAs, and the formation of the chlorinated THMs and HAAs over their brominated and mixed bromo-chloro counterparts. THM and HAA formation stops when the free chlorine residual is depleted, although some DBPs continue to be formed to a limited degree as a result of hydrolysis reactions.

Bromide: Bromine incorporation into halogenated DBPs increases with higher bromide ion concentrations.

see ABCs, page 33

DBPs: How Bad Are the Risks?

Studies evaluating the health risks of DBPs, particularly THM4 and HAA5, have been monitored by the U.S. EPA, World Health Organization (WHO), and Lenntech in the Netherlands. Findings from the last decade are summarized here.

Cancer Risks

Many studies have evaluated the risks of increased bladder, anal, and intestinal cancer. Meta-analysis of studies indicates that a direct relation between the development of cancer and drinking of chlorinated water is unproven. However, DBP exposure from drinking water has been attributed as the cause of nine percent of human bladder cancers and 15 percent of anal cancers. Moreover, these risks increase after lengthy exposure to chlorinated drinking water. Too little evidence exists to link intestinal cancer to exposure to chlorinated drinking water.

New research (see pages 22-23 and 33) now suggests that emerging DBPs may

have greater toxicity than those currently regulated.

Reproductive and Developmental Effects

Studies on reproductive and developmental effects have almost exclusively used lab animals. DBP concentrations that have been linked to birth defects and spontaneous abortion (see page 19) are many times larger than those that can cause cancer after lengthy exposure.

Epidemiological studies suggest a connection between exposure to trihalomethanes and spontaneous abortion, birth defects, and growth delay. DBP exposure before and during pregnancy is likely related to low birth weight and growth delay.

Treatment versus Nontreatment

A 1993 study by Regli and others compared the risk from known pathogens in untreated drinking water to the risk of getting cancer from DBPs in treated water:

- the risk of death from pathogens is 100 to 1,000 times greater;
- the risk of illness from pathogens is 10,000 to 1 million times greater.

Regli, S., P. Berger, B. Macler, and C. Hass, 1993. Proposed decision tree for management of risks in drinking water: considerations for health and socioeconomic factors. In Craun, G.F., ed., Safety of Water Disinfection: Balancing Chemical and Microbial Risks, LSI Press.

Organic Material: How Much Is A Lot?

Natural organic matter is a precursor to DBP formation. It is typically measured in water as total organic carbon (TOC) or dissolved organic carbon (DOC). Concentrations of TOC greater than about 5 milligrams per liter (mg/L) are considered relatively high with respect to DBP formation. What are typical concentrations?

Colorado River: 3 to 4 mg/L

Central Arizona Project water: 2.4 to 10 mg/L

Stormwater runoff: 10 to 2,400 mg/L

Municipal wastewater: 10 to 25 mg/L; up to 300 mg/L

Tucson-area groundwater: generally less than 0.2 mg/L

AZ municipality drinking water: average 3.7 mg/L, maximum 8.9 mg/L

Las Vegas Wash: 5 mg/L

CA State Water Project (Delta) water: 3 to 4 mg/L

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 (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl), and bromoform (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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