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INITIAL DISTRIBUTION SYSTEM EVALUATION GUIDANCE MANUAL

FOR THE FINAL STAGE 2 DISINFECTANTS AND DISINFECTION BYPRODUCTS RULE

APPENDIX A

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http://www.epa.gov/safewater/disinfection/stage2/compliance.html

Appendix A

Formation of Disinfection Byproducts

A.1 Introduction

The formation of disinfection byproducts (DBPs) is a function of many factors, including:

- precursor concentration,
- disinfectant dose,
- water pH,
- temperature,
- contact time, and
- bromide ion concentration.

The purpose of this appendix is to provide a brief summary of the factors that affect DBP formation in water treatment processes and distribution systems. More detailed information on this subject can be found in other existing literature, including the following EPA guidance documents:

- *Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual,* available from EPA (Document #815-R-99-012)

- *Controlling Disinfection By-Products and Microbial Contaminants in Drinking Water,* available from EPA (Document #600-R-01-110)

- *Alternative Disinfectants and Oxidants Guidance Manual*, available from EPA (Document #815-R-99-014)

- *Microbial and Disinfection Byproduct Rules: Final Simultaneous Compliance Guidance Manual*, available from EPA (Document #)

Moreover, it should be noted that the book entitled *Formation and Control of Disinfection By-Products in Drinking Water* (Singer et al., 1999) contains a detailed compilation of the chemistry of DBP formation in Chapter 3 (Krasner, 1999). The references for that chapter represent the seminal works in the literature. Additional references are also presented in the following discussion.

A.2 Formation of DBPs

Organic DBPs (and oxidation byproducts) are formed by the reaction between organic substances, inorganic compounds such as bromide, and oxidizing agents that are added to water during treatment. In most water sources, natural organic matter (NOM) is the major constituent of organic substances and DBP precursors. Total organic carbon (TOC) is typically used as a surrogate measure for precursor levels and is used in the Stage 1 DBPR to determine precursor removal compliance. Dissolved organic carbon (DOC) and UV absorption at 254 nm [UV_{254}] are also often used as surrogate parameters for monitoring precursor levels. The following are the major factors affecting the type and amount of DBPs formed.

- Type of disinfectant, dose, and residual concentration
- Concentration and characteristics of precursors
- Water temperature
- Water chemistry (including pH, bromide ion concentration, organic nitrogen concentration, and presence of other reducing agents such as iron and manganese)
- Contact time and mixing conditions for disinfectant (oxidant), coagulant, source water, and other treatment chemicals

A summary for each of these factors follows.

A.2.1 Impact of Disinfection Method on Organic DBP Formation

Organic DBPs can be subdivided into halogenated and non-halogenated byproducts. Halogenated organic disinfection byproducts are formed when organic and inorganic compounds found in water react with free chlorine, free bromine, or free iodine. The formation reactions may take place in the treatment plant and the distribution system. Free chlorine can be introduced to water directly as a primary or secondary disinfectant, or as a byproduct of the use of chlorine dioxide and chloramines.

Reactions between precursors, bromide and iodide ions, and chlorine lead to the formation of a variety of halogenated DBPs including THMs and HAAs. The presence of bromide can affect both the rate and the yield of DBPs, and if the ratio of bromide to precursors (measured as TOC) increases, the percentage of brominated DBPs also increases (Krasner, 1999 and references therein). Similarly, the presence of iodide may result in the formation of mixed chlorobromoiodomethanes byproducts (Bichsel and Von Gunten, 2000).

The following is an overview of disinfectants including chlorine, chloramines, chlorine dioxide, ultraviolet (UV) irradiation, and ozone and their potential impacts on the formation of THMs and HAAs. Some discussion is also included of potential issues associated with the use of these disinfectants.

Chlorine

Most water systems that disinfect use either liquid or gaseous chlorine as their disinfectant. Halogenated byproducts are formed when free chlorine reacts with natural organic matter. In addition, brominated byproducts are formed when source water containing bromide is chlorinated. Chlorine reacts with natural organic matter in the water to form THMs, HAAs and other disinfection byproducts.

Water systems using chlorine can modify their treatment to reduce TTHM and HAA5 concentrations in the finished water. Treatment modifications include moving the point of chlorination downstream in the water treatment plant, optimizing coagulation to enhance removal of DBP precursors, and using another disinfectant or oxidant to supplement or replace the use of free chlorine. Moving the point of chlorination downstream in the treatment train allows the concentration of disinfection byproduct precursors to be reduced before chlorine is added and may be implemented seasonally. Systems that are required to develop a disinfection profile must calculate a disinfection benchmark for the treatment configuration in place before making any changes to their disinfection practices.

Chloramines

Studies have documented that chloramines produce significantly lower THM and HAA levels than free chlorine, and there is no clear evidence that the reaction of precursors and chloramine leads to the formation of THMs (Singer and Reckhow, 1999; USEPA, 1999). Predictions of an empirical DBP formation model calibrated using ICR data indicated that under chloraminated conditions, THMs and HAAs are formed in full-scale plants and distribution systems at a fraction of the amount that would be expected based on observations of DBP formation under free chlorine conditions. The amount of formation with chloramines varied from 5% to 35% of that calculated for free chlorine, depending on the individual DBP species (Swanson et al., 2001). When chloramination is used, it is possible that DBPs might form if chlorine is added before ammonia. If the mixing process is inefficient, it is also possible that DBPs might form during the mixing of chlorine and ammonia. In this case, free chlorine might react with precursors before the complete formation of chloramines. In addition, monochloramine slowly hydrolyzes to release free chlorine in water. This free chlorine may contribute to the formation of small amounts of additional DBPs in the distribution system.

Additional issues should be considered prior to switching to chloramination. For example, systems using chloramines that have excess ammonia, warm temperatures, long distribution system residence times, and low chloramine residuals may experience nitrification in their distribution systems. Also, systems should be aware that switching from chlorine to chloramines in the distribution system can also change the oxidation reduction potential of the water. The *Microbial and Disinfection Byproduct Rules: Final Simultaneous Compliance Guidance Manual* includes a detailed discussion of factors to consider prior to switching to chloramines.

Chlorine Dioxide

The application of chlorine dioxide does not produce significant amounts of THMs and HAAs unless chlorine is formed as an impurity in the generation process. However, THMs and HAAs will form if excess chlorine is added to water to ensure complete reaction with sodium chlorite during the production of chlorine dioxide.

Chlorine dioxide can also oxidize bromide ions to bromine. The bromine can then react with organic matter to form brominated DBPs. Systems with high bromide concentrations that are near the Stage 2 DBPR limits for THMs or HAA5 should take this into account.

When chlorine dioxide is used as a disinfectant, chlorite is formed. The MCL for chlorite was set at 1.0 mg/L by the Stage 1 D/DBPR. Systems using chlorine dioxide must monitor daily at the entrance to the distribution system for chlorite. They must also collect 3 chlorite samples per month in the distribution system. As much as 70 percent of the chlorine dioxide added to water can break down to form chlorite. This limits the dose of chlorine dioxide that can be used and therefore the amount of inactivation that can be achieved.

Chlorite can react with excess chlorine to reform chlorine dioxide. Some systems may opt to boost with chlorine to maintain a residual in the distribution system. Systems that use chlorine dioxide and then boost with chlorine in the distribution system are required by the Stage 1 D/DBPR to monitor the chlorine dioxide residual in the distribution system. If doses are high enough, systems could exceed either the chlorine dioxide MRDL or the chlorite MCL. Reformed chlorine dioxide can also volatilize at consumer's taps and react with volatile organics to cause odor problems.

Ultraviolet Irradiation

To date, there is no evidence to suggest that ultraviolet irradiation results in the formation of any disinfection byproducts; however, little research has been performed in this area. Most of the research regarding application of UV and DBP formation has focused on chlorinated DBP formation as a result of UV application prior to the addition of chlorine or chloramines (Malley et al., 1995). Studies comparing the effects of UV light followed by chlorination versus chloramination suggest UV does not affect DBP formation in either of these two cases (Malley et al., 1995).

A main drawback with UV is the possibility of microbes passing through at times the lamp is operating off specification. At low UV intensities, some microbes have shown the ability to repair damage done by UV light. Because of this, even drops in lamp intensity not enough to cause a violation of disinfection requirements may allow microbes into the distribution system where they can repair themselves, colonize biofilms, and cause problems with TCR compliance. Therefore any periods of the lamp operating off specification should be minimized.

Because UV disinfection relies on UV light interacting with the organism's genetic material to be effective, any substance that either absorbs or refracts the UV light can interfere with disinfection. Compounds with the potential to do this include dissolved organic carbon (DOC), iron, manganese, calcium, aluminum, and ozone. EPA has developed an *Ultraviolet Disinfection Guidance Manual* that discusses these issues in detail.

Ozone

Ozone does not directly produce chlorinated DBPs. However, if chlorine is added before or after ozonation, mixed bromo-chloro DBPs as well as chlorinated DBPs can form. Ozone can alter the characteristics of precursors and affect the concentration and speciation of halogenated DBPs (THMs and HAAs) when chlorine is subsequently added downstream. In waters with bromide concentrations, ozonation can lead to the formation of bromate and other brominated DBPs. Bromate, like TTHM and HAA5, is a regulated DBP.

Ozonation of natural waters also produces aldehydes, haloketones, ketoacids, carboxylic acids, and other types of biodegradable organic material. The biodegradable fraction of organic material can serve as a nutrient source for microorganisms, and should be removed to prevent microbial regrowth in the distribution system. AOC is a measure of the organic carbon readily available as food for microorganisms. Some systems that have added ozone without biological filtration have experienced increased AOC and microbial growth in the distribution system. Increased biological growth in the distribution system may result in increased corrosion, taste and odor problems, as well as potential health risk.

A.2.2 Disinfectant Dose

As the concentration of chlorine or chloramines increases, the production of DBPs increases. Formation reactions continue as long as precursors and disinfectant are present (Krasner, 1999 and references therein).

In general, the impact of chlorine concentration is greater during primary disinfection than during secondary disinfection. The amount of chlorine added during primary disinfection is usually less than the long-term demand, therefore, the concentration of chlorine is often insufficient to react with all DBP precursors in the water. On the contrary, during secondary disinfection, DBP formation is often limited by the concentration of DBP precursors since excess disinfectant is added to the water to maintain a residual concentration in the distribution system (Singer and Reckhow, 1999).

Distribution system

In distribution systems, DBP formation reactions can become limited by the disinfectant concentration when the free chlorine residual drops to low levels. As a rule of thumb, Singer and Reckhow (1999) suggest this event takes place when the chlorine concentration drops below approximately 0.3 mg/L.

In many systems booster disinfection is applied to raise disinfectant residual concentration, especially in remote areas of the distribution system or near storage tanks where water age may be high and disinfectant residuals can be low. The additional chlorine dose applied to the water at these booster facilities may increase THM and HAA levels. Further, booster chlorination can maintain high HAA concentrations because the increased disinfection residuals can prevent the biodegradation of HAAs. However, booster chlorination can also be useful in decreasing DBP levels by reducing the concentration of secondary disinfectant needed in the finished water leaving the plant.

A.2.3 Time Dependency of DBP Formation

The longer the contact time between disinfectant/oxidant and precursors, the greater the amount of DBPs that can be formed. Generally, DBPs continue to form in drinking water as long as a disinfectant residual and precursors are present. After formation, THMs and HAAs are generally chemically stable as long as a significant disinfectant residual is still present (Singer and Reckhow, 1999). As a consequence, high concentrations of DBPs can accumulate in water with old age.

High THM levels usually occur where the water age is the oldest. Conversely, HAAs cannot be consistently related to water age because HAAs are known to biodegrade over time when the disinfectant residual is low. This might result in relatively low HAAs concentrations in areas of the distribution system where disinfectant residuals are depleted.

A.2.4 Concentration and Characteristics of Precursors

The formation of THMs and HAAs is related to the concentration of precursors at the point of disinfection. In general, greater DBP levels are formed in waters with higher concentrations of precursors. Therefore, removing DBP precursors prior to disinfectant addition is one of the most effective approaches to DBP control.

Studies conducted with different fractions of NOM have indicated the reaction between disinfectant and NOM with high aromatic content tends to form higher DBP levels than NOM with low aromatic content. For this reason, UV_{254}, which is generally linked to the aromatic and unsaturated components of NOM, is considered a good predictor of the tendency of a source water to form THMs and HAAs (Owen et al., 1998; Singer and Reckhow, 1999).

Specific ultraviolet light absorbance (SUVA) is also often used to characterize aromaticity and molecular weight distribution of NOM. This parameter is defined as the ratio between UV_{254} and the dissolved organic carbon (DOC) concentration of water (Letterman et al., 1999). It should be noted that the more highly aromatic precursors in source waters, characterized by high UV_{254}, are more easily removed by coagulation. Thus, it is the UV_{254} measurement immediately upstream of the point(s) of disinfection within a treatment plant that is more directly related to THM and HAA formation potential.

A.2.5 Water Temperature

The rate of formation of THMs and HAAs increases with increasing temperature. Consequently, the highest THM and HAA levels may occur in the warm summer months. However, water demands are often higher during these months, resulting in lower water age within the distribution system which helps to control DBP formation. Furthermore, high temperature conditions in the distribution system promote the accelerated depletion of residual chlorine, which can mitigate DBP formation and promote biodegradation of HAAs unless chlorine dosages are increased to maintain high residuals (Singer and Reckhow, 1999). For these reasons, depending on the specific system, the highest THM and HAA levels may be observed during months which are warm, but not necessarily the warmest. Higher DBP precursor levels in the fall or spring may also cause the highest THM and HAA levels to be observed in cooler months.

Seasonal trends affect THM and HAA concentrations differently. For example, when water is colder, microbial activity is typically lower and DBP formation reactions are slower. Under these conditions, the highest THM and HAA concentrations might appear in the oldest water in the system. In warmer water, the highest HAA concentrations might appear in fresher water, which is likely to contain higher disinfectant residuals that can prevent the biodegradation of HAAs.

A.2.6 Water pH

In the presence of DBP precursors and chlorine, THM formation increases with increasing pH, whereas the formation of HAAs decreases with increasing pH. The increased THM production at high pH is likely promoted by base hydrolysis (favored at high pH). HAAs are not sensitive to base hydrolysis but their precursors are. Consequently, pH can alter their formation pathways, leading to decreased production with increasing pH (Singer and Reckhow, 1999).

Water pH also affects the balance of hypobromite and hypobromous acid formation during the ozonation of waters containing significant concentrations of bromides. At low pH, the equilibrium shifts to the less reactive hypobromous acid. Consequently, the overall formation of bromate decrease as the pH decreases (Singer and Reckhow, 1999). However, the hypobromous acid at low pH can react with NOM to form HAAs and THMs. This may occur if systems using ozone operate at low pH to control bromate formation. In addition, systems may maintain a low pH to achieve the required inactivation.

A.3 References

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