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*"Quality services that ensure safe drinking water"*

MEMORANDUM

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**FROM:** Edward G. Means III
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**DATE:** December 10, 2004

**SUBJECT:** Disinfection Byproducts, Public Health, and the Role of Delta Water Quality

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The purpose of this memo is to document significant developments in disinfection by-product understanding and regulations since 1991, potential future drinking water regulations, and the source water quality issues that affect the ability of utilities treating Delta water to comply with disinfection byproduct (DBP) regulations and deliver safe drinking water to their customers.

**The key findings of this review are:**

- DBPs are a far larger issue today than they were in 1991 and there is an even greater need for improved source water from the Delta than in 1991.
- Information on the health effects of disinfection byproducts continues to increase, making it more likely that DBPs will be further and more stringently regulated in the future.
- Compliance with DBP regulations is likely to become more difficult and expensive for utilities treating Delta water and urban agencies will be forced to retrofit with DBP precursor removal technologies as DBP regulations become more stringent.
- Controlling DBP precursors (Total Organic Carbon (TOC) and bromide) in Delta source water must be one of the barriers of a multi-barrier approach to assist urban agencies in complying with safe drinking water regulations. Establishing 3.0 mg/L TOC and 50 µg/L

bromide as a narrative goal strikes a sensible balance between drinking water quality needs and water quantity realities.

## *1. Background*

Water utilities treating surface water must disinfect the water to control microbial contaminants, such as *Cryptosporidium*, *Giardia*, and other waterborne disease-causing microbes. We now know that disinfectants produce certain by-products of the disinfection process (disinfection by-products or DBPs) that are suspected human carcinogens or suspected causes of birth defects. DBPs are the reaction products of disinfectants like chlorine, ozone, chloramine[1], or chlorine dioxide with naturally occurring organic (humic and fulvic acids) and/or inorganic matter (bromide ion).

Utilities attempt to manage DBP formation by altering treatment or disinfection processes. However, competing treatment goals (i.e. achieving required disinfection and minimizing DBP formation) force utilities to carefully balance these goals to avoid non-compliance with drinking water regulations.

The two primary precursors to DBP formation in Delta water are total organic carbon (from natural sources and agriculture) and bromide (from seawater intrusion). Because the precursors to DBP formation can vary seasonally, so too can DBP formation in water treatment. U.S. Environmental Protection Agency's (USEPA's) Stage 1 Disinfectants/Disinfection By-Products Rule (D/DBPR) and the proposed Stage 2 D/DBPR, which will be discussed later, are intended to address the health effects of DBPs.

Chlorinated disinfection byproducts were first discovered in drinking water in 1974. Since then, toxicological studies have shown that several chlorinated DBPs (bromodichloromethane, bromoform, chloroform, dichloroacetic acid, and bromate) are carcinogenic. Other DBPs (chlorite, bromodichloromethane, and certain haloacetic acids) have been shown to adversely affect reproduction and development. Because DBPs are a concern to human health, the USEPA

[1]Chloramine is a combination of chlorine and ammonia.

currently regulates the following DBPs in drinking water under the 1998 Stage 1 Disinfectants/Disinfection Byproducts Rule:

- The sum of four Trihalomethanes (Total Trihalomethanes or TTHMs) which are formed during chlorination
- The sum of five Haloacetic Acids (HAA5) which are formed during chlorination,
- Bromate which is formed by the oxidation of bromide during ozonation, and
- Chlorite which is produced as an inorganic byproduct of chlorine dioxide application.

The relationships between DBP precursors, pathogens, disinfection and DBPs is summarized in Table 1.

**Table 1: Formation of DBPs as a Result of Drinking Water Treatment**

| **DBP Precursors** | | **Precursor and Pathogen Removal** | | **Disinfectants** | | **DBPs** |
|---|---|---|---|---|---|---|
| • Bromide<br>• TOC | → | • Membranes<br>• Coagulation[2]<br>• Ozone | → | • Chlorine<br>• Chloramine<br>• Ozone<br>• Chlorine Dioxide | → | • TTHMs<br>• HAA5<br>• Bromate<br>• Chlorite |
| **Pathogens**<br>• *Giardia*<br>• *Cryptosporidium* | → | • MIEX[3] | → | • UV Radiation | | |

Note disinfectants can be applied in as many as three stages: (1) early in the process (as pre-disinfection), (2) as the primary disinfection step, and (3) as secondary or post-disinfection to maintain disinfection and prevent microbial growth in the distribution system

Nationwide, 90-95% of all drinking water sources have lower levels of bromide than the Delta. Where Delta water is pumped to drinking water treatment plants, TOC concentrations range from

[2] Coagulation is the process of adding chemicals to cause particles to adhere together so they are easier to remove in subsequent treatment steps.
[3] MIEX (**M**agnetic **I**on **Ex**change) resin is an anionic exchange resin capable of adsorbing dissolved organic carbon and other negatively charged particles and ions.

3-7 mg/L and bromide concentrations range from 0.1-0.5 mg/L. Further, these concentrations exhibit fairly large swings seasonally. The agricultural drainage to the Delta contains high levels of humic substances, which have higher DBP formation potential than non-humic substances. Therefore, the high TOC, high reactivity, and resulting high disinfectant demand (because of the high TOC) combine together to increase the formation of DBPs in disinfected Delta water (Amy et al., 1998). As a result, DBP formation is a major concern for water utilities treating Delta water. TOC is being addressed by the Central Valley Regional Water Quality Control Board through the NPDES permitting process and development of the Central Valley Drinking Water Policy.

Controlling DBP precursors in the source water or improving treatment technologies are two ways to help protect the health of the 23.5 million Californians who rely on the Delta for drinking water. In anticipation of increasingly stringent DBP regulations, CALFED and the California Urban Water Agencies (CUWA) recently funded several studies and expert panel reviews focusing on DBP formation and control.

## *2. Delta Water Quality Objectives*

The 1978 Water Quality Control Plan for the San Francisco Bay/Sacramento-San Joaquin Delta Estuary established a water quality objective for chloride to protect municipal, industrial, and agricultural beneficial uses. In the 1987 Plan, the SWRCB set a maximum mean daily chloride[4] concentration objective of 250 mg/L to protect municipal and industrial beneficial uses. This objective is based on the USEPA's secondary maximum contaminant level for chloride, which is set at 250 mg/L for aesthetic (taste) reasons. This does not address the public health risk from the formation of DBPs, suspected carcinogens, during drinking water treatment.

In addition, the 1978 Plan required that a maximum mean daily concentration of 150 mg/L must be achieved on 240 days during wet years, 190 days during above normal years, 175 days during below normal years, 165 days during dry years, and 155 days during critical years to protect industrial beneficial uses (SWRCB and USEPA, 1995). This objective was based on the operational requirements for paper processing (SWRCB and EPA, 2004).

Since bromide ion is present at concentrations about 0.003 times the concentration of chloride ions in seawater, the chloride objective does result in some control of bromide and therefore provide ancillary protection of human health by decreasing DBP precursors. However, the bromide concentration in water with 150 mg/l of chloride is well above that recommended by CALFED, so this ancillary protection is not sufficient protection of human health.

In the 1991 Water Quality Control Plan, the SWRCB reviewed potential objectives for disinfection byproducts, but concluded that technical information on disinfection byproducts at that time was not sufficient to set objectives. The 150 mg/L chloride objective was however maintained to provide some ancillary protection of municipal and industrial uses until such time as trihalomethane and other disinfection byproduct objectives are established. Due to concerns of DBPs in treated drinking water from the Delta, the State Board in the 1991 Water Quality Control Plan found that municipal water agencies should "strive to obtain bromide levels of 0.15 mg/l or less (about 50 mg/l chloride in the Delta)."

The CALFED drinking water quality program is aimed at providing safe, reliable, and affordable drinking water in a cost-effective way. In order to provide safe drinking water, the 2000 CALFED Bay-Delta Program Record of Decision established a target of 50 µg/L of bromide (equivalent to chloride levels of <20 mg/L) and 3.0 mg/L of total organic carbon (TOC) or an "equivalent level of public health protection using a cost-effective combination of alternative source waters, source control and treatment technologies." These standards were based upon the recommendations of a CUWA expert panel (Owen et al., 1998). The expert panel determined the water quality criteria for TOC and bromide in the Delta that would be needed to enable water utilities to comply with current and predicted future drinking water regulations for THMs and bromate.

Although CALFED (now the California Bay-Delta Authority) has set target bromide and TOC concentrations in the Delta, the SWRCB has yet to adopt specific water quality objectives for disinfection byproducts, their precursors, or pathogens. The current 1995 WQCP municipal and

[4] Chloride is a major component of salinity

industrial chloride objectives were not designed to and do not provide sufficient source water quality to protect human health.

## *3. CUWA Expert Panel*

An objective of the CALFED Bay-Delta Program is to continuously improve quality of water diverted from the Delta to meet drinking water needs. To accomplish this, CALFED must select a long-term solution that provides reasonably consistent quality source water that urban water providers can treat with reasonable cost to meet current and future federal and state health-based drinking water standards.

In 1998, CUWA employed the services of an expert panel (Owen et al.), to evaluate specific source water quality characteristics to permit diverted water from the San Francisco Bay/Sacramento-San Joaquin River Delta to be used for meeting potential public health related water quality standards under defined treatment conditions. The expert panel was charged with:

1. Developing potential future regulatory scenarios
2. Defining appropriate drinking water treatment process criteria for coagulation, ozonation, granular activated carbon and membrane treatment processes
3. Estimating source water quality diverted from the Delta that would allow users implementing the defined conventional treatment technologies to comply with the regulatory scenario

The expert panel developed two potential regulatory scenarios based on the then proposed Stage 1 of the Disinfectant/Disinfection By-Product Rule (D/DBPR), the Interim Enhanced Surface Water Treatment Rule, Stage 2 of the D/DBPR and the Long Term Enhanced Surface Water Treatment Rule. The expert panel concluded that various treatment processes could be considered to comply with the respective regulatory scenarios. Treatment processes included: the use of alum in the coagulation process, followed by a chlorine and/or chloramines residual; the use of specific ozone to TOC ratios followed by chloramines residuals; or the use of post-filter granular activated carbon adsorbers in combination with ozone, membrane filtration, and free chlorine. The expert panel concluded that to allow maximum flexibility and to enable urban

water agencies to comply with the expected future regulations, a Delta water quality target for bromide concentrations of less than 50 µg/L and TOC concentrations less than 3.0 mg/L could be feasibly treated. Future treatment technology additions (e.g. granular activated carbon, ultraviolet disinfection, or membranes) may allow increased source water flexibility but were generally concluded as not affordable or feasible on the scale need for municipal treatment in California.

The CUWA expert panel's findings suggest that significantly better source water quality is needed in the Delta to fully protect public health, in the future, even with advances in treatment technologies.

Since that time, many utilities treating Delta supplies for drinking water have moved towards advanced water treatment technologies. Contra Costa Water District (CCWD) supplies treated water to the Diablo Water District (DWD), which serves customers in Oakley from the Randall-Bold Water Treatment Plant, jointly owned by CCWD and DWD. The Randall-Bold facility, completed in 1992, is a 40 MGD direct/deep-bed filtration plant and utilizes both pre- and post-ozonation. In 1999, CCWD completed upgrading its older 75 MGD Bollman Water Treatment Plant in Concord to include ozonation. The Metropolitan Water District of Southern California is retrofitting all five water treatment plants with ozone to help manage disinfection by-product formation. Inaction would have certainly brought non-compliance with the Stage 2 DBP Rule (USEPA expects to promulgate this rule in Summer 2005). Santa Clara Valley Water District is retrofitting plants with ozone as well. This is not fail-safe however, as ozone DBPs caused by bromide occurrence pose vexing challenges to these utilities and argue for minimizing bromide levels in State Project water.

CCWD and the USEPA have assembled an innovative partnership with the American Water Works Association Research Foundation (AwwaRF) and the Santa Clara Valley Water District, Alameda County Water District, Zone 7 Water District, the City of Napa, and Solano County Water Agency to study the effectiveness of advanced treatment technologies to increase disinfection potential and reduce DBP formation during treatment of Delta water. Total funding for the project is $1,040,300, including $715,300 from U.S. EPA and $100,000 from AwwaRF.

Innovative technologies to be tested include the synergistic effects of using multiple disinfectants such as ozone, chlorine dioxide, chloramines, chlorine, potassium permanganate, and ultraviolet disinfection. Additionally, advanced filtration technologies such as membranes, MIEX resin, and granular activated carbon filters will be investigated.

## *4. CALFED Bromide Expert Panel*

In 1998, CALFED convened an expert panel (Amy et al.) to advise CALFED on the effects of bromide in water treatment and controlling bromide concentrations in the Delta. In their report, the CALFED expert panel:

1. Defined the sources and occurrence of bromide in the Delta and provided source management options,
2. Summarized present drinking water regulations and projected future regulations,
3. Described the health effects of bromide in disinfected drinking water and identified ongoing/future studies,
4. Identified and compared drinking water treatment options for controlling brominated DBPs,
5. Contrasted treatment versus source management approaches, and
6. Recommended short and long-term treatment and source management practices and identified research needs.

Some of the expert panel's findings were:

1. Options exist for minimizing bromate formation during ozonation or for removing bromate after it is formed; however, due to water quality and technology-development constraints, management of bromide may require a combination of treatment and source control (referred to as a multi-barrier approach)
2. Short-term options for controlling bromide should place more emphasis on treatment with some possibilities for source control
3. Long-term options should focus on source management, which is possible with implementation of alternative water conveyance through the Delta

a. Alternative 1– the existing system with storage
b. Alternative 2 – improvements to the through-Delta transfer facility. The panel concluded that this alternative would provide more benefit at certain export points
c. Alternative 3 – a dual system (through Delta and an isolated facility with a 7,500 cfs capacity.) The panel concluded that this would provide the most benefit for drinking water quality. (CALFED did not select this for a variety of reasons.)

The panel recommended that CALFED:

1. Follow and promote health effects research with a focus on brominated DBPs
2. Develop DBP models that assess treatment and source control options
3. Develop an inventory of natural organic matter to determine its spatial and seasonal distribution
4. Obtain information on microbial contamination in the Delta (e.g. *Giardia, Cryptosporidium*)
5. Obtain information on the co-occurrence of bromide, TOC, and microbes in the Delta
6. Determine the extent to which pathogens and DBP precursors can feasibly be reduced in source waters
7. Nanofiltration and ultrafiltration membrane processes should be assessed for their ability to remove bromide, TOC, and microbes from source water

The expert panel findings suggest that both short-term (treatment upgrades) and long-term (source management) strategies are necessary for utilities to deal with bromide-related drinking water issues.

## *5. Equivalent Level of Public Health Protection Concept*

As part of its mission to protect drinking water supplies and provide safe and cost effective water, in 2002 CALFED Bay-Delta Drinking Water Subcommittee was tasked with developing a strategic water quality plan and providing a definition of equivalent level of public health protection (ELPH). The strategy was based on the CALFED drinking water goal of either (a) average concentrations at Clifton Court Forebay and other southern and central Delta drinking

water intakes of 50 μg/L bromide and 3.0 mg/L total organic carbon, or (b) an equivalent level of public health protection using a cost-effective combination of alternative source waters, source control, and treatment technologies.

The water quality criteria were developed based on the recommendation of the 1998 CUWA expert panel that assessed DBP formation during typical treatment processes of Delta water. The 50 μg/L bromide and 3.0 mg/L total organic carbon (referred to as the 50/3 target) goal was set as a reasonable source water quality goal that would minimize DBP formation and therefore protect public health. The ELPH concept was developed in response to the concerns of stakeholders that these TOC and bromide criteria were inflexible, possibly not attainable in the near or intermediate term in the Delta and would not provide them with opportunities to adequately provide customers with sufficient water.

The ELPH concept could allow water purveyors that perceive the 50/3 target as unattainable on a consistent basis for their location/situation to provide an equivalent level of public health protection through treatment technology upgrades, source water quality improvements, blending with higher quality sources, and conveyance and storage improvements. To do this effectively, an accurate risk assessment database is needed to allow water purveyors to characterize and quantify the level of public health protection (acute and chronic) the 50/3 target would provide, and a defensible characterization and quantification of the level of public health protection that they propose to provide. The technical implementation of risk trade-off calculations to provide such a balance is complicated and fraught with uncertainty. For example, how do you factor in the health effects of the uncharacterized disinfection by-products like iodinated DBPs, some of which are now being found in water treated with chloramines?

The health effects are poorly understood yet treatment trade-offs to avoid the "understood" risks are made. What we know today may be fundamentally altered tomorrow as further research is conducted. The original 1979 THM rule was established based upon the suspected health effects of chloroform (one of the four THMs regulated today). Subsequent research has shown that chloroform is virtually irrelevant from a human health risk standpoint given levels in drinking water.

The concept of ELPH will forever be constrained by the limits of our knowledge regarding the health effects of DBPs. Systems must, at minimum, react to what is known and regulated. Beyond that, systems are free to implement additional treatment safeguards although costs often prohibit going far beyond the regulatory requirements. It may well turn out that the ELPH protection to a 50/3 target is ultimately more costly than providing the source control measures.

## *6. Regulations*

The 1996 Safe Drinking Water Act amendments authorized the USEPA to promulgate a national drinking water regulation and publish maximum contaminant level goals for contaminants that may have an adverse effect on human health. Described below are a suite of regulations that address the potential trade-offs between health risk from microbial contamination of drinking water (considered acute or short-term exposure risks) and health risk from byproducts formed from disinfection practices (considered chronic or long-term exposure risks) aimed at controlling microbe concentrations (USEPA, 2003a).

Currently, most water systems treating Delta water are able to meet the regulatory requirements by 1) switching to chloramines instead of chlorine disinfection or 2) optimizing their treatment operations and using ozone as a primary disinfectant followed by chloramines as a secondary disinfectant (Amy et al, 1998). This combination of disinfectants currently enables urban agencies to meet the currently regulated DBPs but could act synergistically to produce other DBPs with unknown health impacts. Degradation of Delta water quality, and more stringent regulations, will make it increasingly difficult for water systems treating Delta water to meet future regulations.

### 1979 Total Trihalomethane Rule

The first rule to regulate DBPs was the Total Trihalomethane Rule, promulgated in 1979 by the EPA. This rule set an interim TTHM (the sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform) MCL of 0.10 mg/L for community water systems serving more than 10,000 people. Compliance was calculated based upon a running annual average of quarterly system-wide TTHM averages.

**1989 Surface Water Treatment Rule and 1989 Total Coliform Rule**

In June 1989, under the SWTR, the EPA set a Maximum Contaminant Level Goal (MCLG) of zero for *Giardia lamblia*, viruses, and *Legionella* to protect against adverse health effects. In June 1989, the EPA also promulgated the Total Coliform Rule, which set an MCLG of zero for total and fecal coliform, in order to protect from microbial contamination of drinking water. These two rules were meant to reduce exposure to pathogenic organisms. But, they also resulted in increased use of disinfectants in some public water systems, which resulted in increased formation of disinfection byproducts in some systems.

**1992 Regulatory Negotiation**

In 1992, due to concerns about the health risk tradeoffs between DBPs and pathogens, the EPA initiated a negotiated rulemaking process under the Federal Advisory Committee Act to develop regulations for DBPs (referred to as the Reg-Neg process). Representatives from state, local, and regulatory agencies, public water systems, elected officials, consumer groups, and environmental groups met from November 1992 to June 1993 and recommended the development of the Information Collection Rule (ICR), a two-stage Disinfection Byproduct Rule (DBPR), and an interim Enhanced Surface Water Treatment Rule. The Metropolitan Water District of Southern California, which relies on Delta water for much of its drinking water supply, participated in this process.

**1996 Information Collection Rule**

The ICR, published in 1996, required that large water systems gather data on DBPs and pathogens, which resulted in new data on DBP exposure and control and on pathogen occurrence and treatment. Three conclusions were drawn from the ICR data that resulted in the recommendation of further control of DBPs:

1) DBP MCL compliance based on running annual averages of all monitoring locations in the system allows the occurrence of elevated DBP levels at some locations in the distribution system.

2) Customers can receive water with DBP concentrations up to 75% above the MCLs, even when the system is in compliance.
3) The highest TTHM and HAA concentrations do not always occur at the locations of maximum residence time.

**1998 Interim Enhanced Surface Water Treatment Rule (IESWTR)**

The IESWTR was published at the same time as the 1998 Stage 1D/DBPR to ensure simultaneous compliance. This rule addresses the risk tradeoffs between exposure to DBPs and pathogens, so that attempts to control DBPs will not compromise the disinfection or removal of pathogens. The IESWTR was intended to improve the control of pathogens in drinking water and applies to water systems that treat surface water and serve more than10,000 people.

**1998 Stage 1 Disinfectants/Disinfection Byproducts Rule**

The Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) was finalized in December 1998 and lowered the TTHM Maximum Contaminant Level (MCL) and established new MCLs for chlorite, bromate, and five Haloacetic Acids (HAA5), as shown in Table 1. In addition, the Stage 1 D/DBPR applied to all public water systems that treat their water with a chemical disinfectant for either primary or residual treatment. Water systems serving ≥10,000 people had to comply with the Stage I D/DBPR as of January 1, 2002. Small water systems, serving <10,000 people had to comply with the rule as of January 1, 2004. Compliance of the TTHM and HAA5 MCLs is based on the running annual average of quarterly averages of all samples collected in a distribution system.

**Table 1 MCLs and MCLG[5]s for DBPs**

| Regulated Contaminants | MCL (µg/L) | MCLG (µg/L) |
|---|---|---|
| **Total Trihalomethanes (TTHM)** | 80 | |
| Chloroform | | - |
| Bromodichloromethane | | zero |
| Dibromochloromethane | | 60 |
| Bromoform | | zero |
| **Five Haloacetic Acids (HAA5)** | 60 | |

[5] MCLG = Maximum Contaminant Level Goal

| | | |
|---|---|---|
| Monochloroacetic acid<br>Dichloroacetic acid<br>Trichloroacetic acid<br>Bromoacetic acid<br>Dibromoacetic acid | | -<br>zero<br>300<br>-<br>- |
| **Bromate** | 10 | zero |
| **Chlorite** | 1000 | 800 |

The Stage 1 D/DBPR was enacted to reduce health risks associated with exposure to DBPs formed from ozone, chlorine dioxide, and chlorine. The requirement that water systems using surface water (or groundwater influenced by surface water) must remove a percentage of TOC in the source water by enhanced coagulation or enhanced softening was implemented to reduce overall exposure to non-specified DBPs. In the Regulatory Impact Analysis for the Stage 1 D/DBPR, the USEPA estimated that the rule would lower TTHM levels by 24% and decrease exposure to DBPs to more than 140 million people; lowering their risk of cancer and developmental and reproductive problems. As a result of the Stage 1 D/DBPR, many systems using Delta water began converting to ozone and chloramine disinfection to minimize the formation of TTHMs. This strategy has grown very complex because bromide variations in source water have a major impact on bromate formation in ozone disinfection systems.

It is important to note that the bromate MCL was set at 10 μg/L or at the 1 in 5000 cancer risk level. This is half the normal public health protection USEPA typically allows in setting MCLs for suspected human carcinogens (which is typically set between a 1 in 10,000 risk level and as low as a 1 in a million risk level). USEPA established this "more lenient" standard because they recognized the benefits of ozone, there are few technology alternatives in the "tool box" and future research might determine better ways to manage bromate formation. The bromate standard could be reduced in the future as health effects studies continue.

**2001 Filter Backwash Rule and 2002 Long Term 1 Enhanced Surface Water Treatment Rule**

The purpose of the Filter Backwash Rule (FBR) and the Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR) is to balance the risk of microbial and DBP exposure. The FBR was promulgated by the EPA in 2001 and the LT1ESWTR was promulgated in 2002. The

purpose of the FBR is to control the re-entry of pathogens and DBPs into the treatment process when backwash water is returned to the front of the treatment process. The purpose of the LT1ESWTR is to increase protection against *Cryptosporidium* and other disease-causing bacteria. LT1ESWTR applies to all water systems treating surface water, regardless of size.

**Stage 2 Disinfectants/Disinfection Byproducts Rule (expected to be promulgated in 2005)**

The Stage 2 D/DBPR was proposed by the EPA on August 18, 2003. The results of the ICR led to changes in monitoring requirements for DBPs proposed in the Stage 2 D/DBPR. This rule requires an initial distribution system evaluation to identify areas in distribution systems with high TTHM and HAA5. In order to ensure the reduction of peak DBP concentrations, compliance is based on a *locational running annual average* (compliance must be met at each monitoring location) instead of a system-wide running annual average. This is significantly more stringent than the Stage 1 Rule and, from the standpoint of driving water treatment technology changes at utilities, is basically equivalent to setting the Stage 1 TTHM MCL at 40 µg/L (or half the level that was set) because DBPs must be reduced system-wide to meet pre-existing criteria at problem locations.

In addition, systems must conduct a "significant excursion" evaluation if DBP levels are significantly higher than the MCL. EPA is proposing that states develop criteria for determining whether a system has a significant excursion. EPA draft guidance states that a system that has a significant excursion must: 1) evaluate distribution system operational practices to identify opportunities to reduce DBP levels (such as tank management to reduce residence time and flushing programs to reduce disinfectant demand), 2) prepare a written report of the evaluation, and 3) no later than the next sanitary survey, review the evaluation with their state.

This rule is expected to be promulgated by USEPA in 2005. USEPA is convening special discussions among stakeholders in January 2005 to evaluate the significance of recent birth defect/DBP studies with regard to whether the standards are adequate and continue discussions regarding "significant excursions".

In the Stage 2 D/DBPR, the USEPA is proposing a new MCLG for chloroform of 0.07 mg/L, a new MCLG for monochloroacetic acid of 0.03 mg/L and a lower MCLG of 0.02 mg/L for trichloroacetic acid.

The main benefit of the Stage 2 D/DBPR is the reduction of DBP-related bladder cancer. This rule may reduce bladder cancer by up to 182 cases per year. In addition, this rule may potentially reduce adverse reproductive and developmental effects (such as miscarriage, stillbirth, neural tube defects, heart defects, and cleft palate), as well as other forms of cancer. It is estimated that this rule will prevent up to 47 premature deaths per year (USEPA, 2003b).

**Table 2 Proposed USEPA MCLs and MCLGs for DBPs**

| Regulated Contaminants | MCL (ug/L) | MCLG (ug/L) |
|---|---|---|
| **Total Trihalomethanes (TTHM)** | 80 | |
| Chloroform | | 70* |
| Bromodichloromethane | | zero |
| Dibromochloromethane | | 60 |
| Bromoform | | zero |
| **Five Haloacetic Acids (HAA5)** | 60 | |
| Monochloroacetic acid | | 30* |
| Dichloroacetic acid | | zero |
| Trichloroacetic acid | | 20* |
| Bromoacetic acid | | - |
| Dibromoacetic acid | | - |
| **Bromate** | 10 | zero |
| **Chlorite** | 1000 | 800 |

*New MCLGs proposed in the Stage 2 D/DBPR

**Long Term 2 Enhanced Surface Water Treatment Rule**

The LT2ESWTR was proposed in August 2003 and was negotiated along with the Stage 2 D/DBPR. It is expected to be finalized in the summer of 2005. The purpose of this rule is to provide additional protection against *Cryptosporidium*. The amount of additional treatment required will be based on the levels of *Cryptosporidium* present in the source water.

## *7. Factors Affecting Disinfection Byproduct Formation*

Total Trihalomethanes (TTHMs) and Haloacetic Acids (HAAs) are DBPs formed by chlorination, bromate is formed by ozonation, and chlorite is formed through chlorine dioxide oxidation. Summaries of some observations regarding THM and DBP formation follow:

Chlorination, chloramination, and ozonation can form brominated DBPs when bromide ion is present in the source water. Chlorination forms brominated DBPs such as the brominated THMs and HAA5 species and ozonation forms bromate. In 1989, it was already known that THM concentrations increase more rapidly in chlorinated water containing bromide than in water lacking bromide (Aizawa et al., 1989). In fact, chlorination preferentially forms brominated THMs when the source water contains bromide. Because bromide ion has a higher molecular weight than Cl (80 versus 35.5), total trihalomethane concentrations, which are based on weight, can be up to two times higher when bromide is present (WRCB, 1991). More recently, HAA5 have also been shown to shift speciation[6] and increase in concentration when bromide is present (Pourmogahaddas et al., 1993; Cowman and Singer, 1996).

Temperature, pH, chlorine dose, bromide concentration, TOC, and reaction time all positively influence TTHM formation. HAA5 formation is similarly influenced, except for pH which inversely effects the formation of certain species, such as trichloroacetic acid. Bromate formation is positively influenced by temperature, pH, ozone dose, and bromide ion concentration (Amy et al, 1998).

As part of the Information Collection Rule an 18-month monitoring program was implemented that monitored DBPs and treatment parameters in 296 water systems nationwide (McGuire and Graziano, 2002). Some of the results of the data analysis portion of this study regarding TTHM formation are:

- Chloroform is the dominant TTHM species found in drinking water

6 Speciation of a chemical is a specific form of an element defined as to isotopic composition, electronic or oxidation state, or molecular structure.

- Correlation analyses showed that TTHM concentrations in distributions systems were not well predicted by TOC concentrations alone; but appear to be dependent on both bromide ion and TOC influent concentrations.
- No clear trend was evident between the type of disinfectant used and TTHM effluent concentrations; this was attributed to aggressive treatment strategies employed by the various water systems to comply with existing MCL requirements.

As part of this same data analysis effort the following conclusions were made regarding bromate (Moll and Krasner, 2002):

- Chlorine dioxide disinfection does not produce significant concentrations of bromate
- Increases in bromide ion concentration in source water and ozone dosage resulted in increased bromate formation
- No association was found between bromate formation and TOC, acidity (pH), temperature, or ammonia concentration, ozone residual, or ozone CT[7]; a lack of correlation of some of these parameters and bromate formation can probably be attributed to the wide range of water system types included.

The 1995 CUWA study on the Strategies for Removing Bromate from Drinking Water (Siddiqui and Amy, 1995) investigated factors effecting bromate formation during ozonation. This study found that:

1) Bromate formation increases with increasing pH
2) As ozone dose increases, bromate formation increases as long as sufficient bromide is present
3) Initial bromide ion concentration is important. As bromide ion increases, formation of bromate increases (when ozone and dissolved organic matter remain the same)
4) Alkalinity enhances formation of bromate

7 CT is defined as the disinfectant concentration multiplied by contact time, and represents the amount of disinfection obtained.

## *8. Treatment Methods for Controlling DBPs*

There are several treatment options for controlling brominated disinfection byproducts:

- Removal of bromide prior to disinfection
- Removal of organic precursors prior to disinfection
- Removal of DBPs after formation
- Altering treatment conditions to limit DBP formation
- Use of alternation disinfectants

**Removal of Bromide**

There are limited treatment options for removing bromide from drinking water. Reverse osmosis, and to a much lesser extent, nanofiltration are the only practical processes shown to remove bromide. These membrane processes are expensive, require conventional treatment prior to use and have low recovery (significant water is wasted). Ion exchange can remove bromide, but most resins are not selective for bromide (Amy et al, 1998). Because bromide currently cannot be cost-effectively removed prior to disinfection, source water control programs (minimizing seawater intrusion) are a critical element in managing this precursor.

**Removal of Organic Precursors**

Conventional (coagulation, sedimentation, and filtration) or advanced processes (granular activated carbon and membrane) can be optimized to remove TOC prior to disinfection. Typically high dosages of coagulants and chemicals to lower pH (which optimizes TOC removal) are required and production of significant additional sludge results. Use of acids to reduce pH increases the total dissolved solids level of the drinking water which can, in the end, affect the uses recycled water produced by wastewater utilities. These issues add cost and complexity to the challenge of producing potable water. Further, frequent variations in water quality require frequent fine-tuning of coagulant addition and is, from a process quality control standpoint, very undesirable; stable consistent source water quality will allow a treatment plant to produce the best, consistent finished water quality.

Removing DBP precursors also decreases disinfectant demand, which lowers the formation of DBPs. However, conventional processes do not remove bromide so removing TOC increases the

bromide/TOC ratio. Although DBP formation is reduced, the risk to public health may not be decreased because a higher bromide/TOC ratio can result in greater brominated DBP (versus chlorinated DBP) formation, which some believe presents a greater health risk (Amy et al., 1998).

**Removal of DBPs After Formation**

Removal of DBPs after formation is rarely practiced as it is more often cost-effective to minimize their formation to begin with. THMs, which are the only volatile halogenated DBPs, can be removed by air stripping as well as adsorption on carbon but this is rarely done as it is not economical. Several HAAs, unlike THMs, are biodegradable and can be removed by passing pre-chlorinated water through a biologically active filter bed. Haloacetonitriles are unstable at high pH, but high pH promotes THM formation. Since no single treatment strategy can remove all DBPs, alternative disinfectants or precursor removal are the best methods of DBP control (Amy et al, 1998).

One exception is bromate removal; several treatment techniques exist for removing bromate from drinking water (although none are used in routine surface water treatment for removal of bromate to my knowledge). Bromate can be minimized during ozonation using low-pH ozonation, or it can be removed after formation using chemical reduction (for example, ferrous salts) (Amy et al, 1998). A CUWA study (Siddiqui and Amy, 1995) investigated potential strategies (ferrous iron reduction, powdered activated carbon- PAC, granular activated carbon, and ultraviolet irradiation) for removing bromate from drinking water.

This study found that for all processes, chemical reduction of bromate to bromide is the significant mechanism of removal, and adsorption onto iron floc is insignificant. In addition, reduction of bromate is dependent on pH, alkalinity, dissolved organic matter, temperature, and dissolved oxygen.

Ferrous iron reduces 30-50% of the bromate, but must be followed by clarification or filtration to remove the ferric hydroxide precipitate. As a result, ferrous iron treatment must occur early in the drinking water treatment train.

Removal of bromate using PAC and GAC depended on the type of carbon, pH, and contact time. PAC resulted in a 10-30% reduction of bromate; whereas GAC resulted in a 50-100% reduction. Preliminary results also indicated that 30-40% of bromate could be continuously removed for two months using a GAC column. Because granular activated carbon has a limited capacity to absorb bromate, it must be replaced frequently.

Removal of bromate by UV was not effective when low-pressure mercury lamps were used and very high contact times were needed to reduce bromate under normal disinfection conditions. Medium pressure mercury lamps were more effective, reducing bromate by 80%.

**Altering Treatment Conditions**

Decreasing the pH during ozonation decreases the formation of bromate. However, with enhanced coagulation, significant amounts of acid (or carbon dioxide) must be added to the high-alkalinity waters to reduce the pH. Implementing pH depression on a large scale, e.g., MWD's 760 MGD Jensen Treatment Plant, would require huge quantities of acid or carbon dioxide to be produced or delivered daily to the treatment plant. The acid addition raises the total dissolved solids content of the water; impacts to recycled water salt loads can occur. Another option to control bromate formation is applying ozone in several stages, instead of just the first stage of treatment. Hydrogen peroxide and ammonia addition can also potentially decrease bromate formation (Amy et al, 1998).

**Alternative Disinfectants**

Disinfection in water treatment occurs in two stages. Primary disinfection refers to the application of an oxidant to achieve basic inactivation of pathogens and the production of water that is "safe" to drink. Disinfectants that are used for this purpose include ozone, chlorine, chlorine dioxide and UV. Secondary disinfection is used to ensure that the water contains a "residual" disinfectant as it courses out into the water distribution system. There are only two secondary disinfectants in use in California: chlorine and chloramines. Many systems treating Delta water have shifted to the use of chloramines as a secondary disinfectant to minimize DBP formation or to ozone/chloramines for primary/secondary disinfection. Ozone is an

exceptionally effective disinfectant for *Cryptosporidium* inactivation and provides significant taste and odor control. Bromate formation in bromide containing waters places significant operational constraints on the use of ozone.

Full scale UV-disinfection has not been shown to be practical for cyst inactivation; although new technologies are still being developed.

**Microfiltration to Remove Pathogens**

Microfiltration is capable of removing *Giardia* and *Cryptosporidium* but not viruses. Nano- and micro-filtration are applicable for this purpose. These membrane processes are typically more expensive than conventional processes and significant water must be wasted or recovered at added expense. Alternatively, post-chlorination can be employed, but this can still form DBPs, especially in water containing elevated levels of bromide (Amy et al., 1998).

In summarizing this short review of water treatment, several points are key:

1. Conventional water treatment processes and disinfection strategies were designed to protect against pathogens.
2. USEPA regulation of DBPs has forced many utilities to retrofit conventional plants with a variety of "add-on" processes to meet DBP standards. In most utilities treating Delta water, the processes implemented have included ozone, enhanced coagulation, and, chloramines. Expensive processes like reverse osmosis and granular activated carbon have generally not been selected.
3. All water treatment processes have limits to their effectiveness and trade-offs (like cost, formation of other DBPs, water waste, need for media regeneration, high energy costs, high sludge volume production, etc.).
4. Wide variations and swings in source water quality (ie. bromide and TOC) present a serious treatment challenge to many operators of treatment plants seeking to provide consistent high quality water to California citizens.
5. Pending regulations (and potential future regulations) will increase the seriousness of that challenge.

## *9. DBP Occurrence*

Although over 500 disinfection byproducts have been identified, many have not yet been chemically defined. Less than 50% of chlorination DBPs, about 17% of chloramine DBPs, about 8% of ozone DBPs, and about 28% of chlorine dioxide DBPs have been identified (Plewa et al, 2004). Because so many agencies are converting to ozone, the fact that over 90 % of the ozonated DBPs are unknown, and may need to be regulated in the future, is a potential concern.

Because of the lack of information on DBPs, the EPA conducted a study in 2002 to quantify their occurrence (Weinburg et al., 2002). Because of the uncertainty of the identity and levels of DBPs in drinking water, and because only a limited number of DBPs have been associated with adverse health effects, it is impossible to say whether unregulated DBPs pose an adverse health risk. The EPA study chose approximately 50 DBPs that were potentially the most toxic and not included in the EPA's Information Collection Rule. The following are DBPs found at high levels during the study:

*Iodoacids*

During this study, iodoacids were discovered for the first time, including iodoacetic acid, iodobromoacetic acid, iodobromopropenoid acid, and 2-iodo-3-methylbutenedioic acid. Iodoacids were only detected in finished water from treatment plants treating water containing elevated levels of bromide with only chloramine disinfection.

*Haloaldehydes*

Dihaloacetaldehyde and brominated analogues of trichloroacetaldehyde were detected in many samples. The highest levels of dichloroacetaldehyde were found at a plant that disinfects with chloramines and ozone.

*Halomethanes and Haloketones*

Mono-, di-, tri-, and/or tetra- halomethanes and haloketones were detected at low µg/L levels (i.e. at levels comparative to the levels of commonly measured DBPs). Carbon tetrachloride, a halomethane, was detected at levels as high as 0.8 µg/L. The highest levels of iodo-trihalomethanes (iodo-THMs), trihalomethanes containing iodine, were found at a plant that used

chloramines without pre-chlorination. Levels of individual iodo-THMs ranged from 0.2 to 15 µg/L. The highest brominated nitromethane concentration was 3 µg/L.

*Halogenated furanones*

3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) was widely observed during the occurrence study at levels much higher than previously reported. Prior to the study, MX concentrations had not been observed above 90 ng/L. However, in this study MX levels were often significantly greater than 100 ng/L. The highest concentration (310 ng/L) was observed at a treatment plant disinfecting high TOC water with chlorine dioxide, chlorine, and chloramines.

Brominated MX (BMX) was also widely observed during the study. The highest concentrations of BMX-1 and BEMX-3 (both brominated forms of MX) were 170 ng/L and 200 ng/L, respectively. As with MX, these peak concentrations were observed at a treatment plant disinfecting high TOC water with chlorine dioxide, chlorine, and chloramines. This study found MX concentrations that were much higher than had previously been reported. These results also indicate that chlorine dioxide disinfection does not destroy MX precursors. It was concluded that MX and BMX formation was highest at plants treating source water high in TOC and bromide, respectively.

*Halonitromethanes*

Concentrations of individual species of halonitromethanes ranged from 0.1 to 3 ug/L. In some cases, pre-ozonation increased the formation of brominated halonitromethanes.

*Brominated Acids*

Many brominated acids were identified at plants treating source waters with elevated levels of bromide. Several were newly discovered, including brominated propanoic, propenoic, butanoic, butenoic, oxopentanoic, heptanoic, nonanoic, and butenedioic acids.

***Implications***

One conclusion is that "this study revealed that some of our previous understanding of the formation and control of DBPs with alternative disinfectants was not complete" (Weinburg,

2002). It had previously been assumed, based on THM data, that alternative disinfectants control other potentially harmful DBPs. The discovery of DBPs, such as dihalogenated DBPs and iodo-THMs, at plants treating with chloramines led to the realization that control of the four regulated THMs does not necessarily guarantee control of other halogenated DBPs. In addition, alternative disinfection (such as chloramines and ozonation, technologies that utilities have shifted to in order to reduce formation of regulated brominated DBPs) can apparently increase the concentration of some DBPs (such as iodo-THMs and dihaloacetaldehydes) when compared to chlorination. So, although alternative disinfectants control regulated THMs, they may not necessarily control all DBPs of concern. This underscores the importance of maintaining good source water quality to minimize known and unknown DBP formation, consistent with a multi-barrier approach.

## *10. DBP Health Risks*

In 1976, the discovery that chloroform is an animal carcinogen raised questions about the risk trade-off of drinking water disinfection. Because disinfection byproducts may have carcinogenic, mutagenic, or reproductive effects, there are concerns about the public health risk of DBPs in drinking water. By 1991, the USEPA had classified brominated THMs as probable or possible human carcinogens. At that point, it was already believed that brominated THMs, such as bromodichloromethane and bromate, pose a greater health risk than chlorinated THMs (WRCB, 1991). Although the health risks associated with DBPs have been researched since 1976, some uncertainty in the health effects and risk of exposure to low levels of DBPs still remains; therefore research is still ongoing.

### Cancer Risk

Toxicological studies have shown several DBPs (bromodichloromethane, bromoform, chloroform, dichloroacetic acid, and bromate) to be carcinogenic in laboratory animals. Many of the studies were conducted at high concentrations, but the USEPA believes they provide sufficient evidence that DBPs pose a potential health risk.

Human epidemiology studies have been conducted to determine the association between chronic exposure to chlorinated drinking water and cancer. In 1994, when the Stage 1 D/DBP rule was

proposed, the EPA could not conclude, based on the studies, that there is a link between chlorinated drinking water and cancer. But, a number of epidemiological studies (Shy, 1985; Cantor et al, 1985; 1987, 1990; McGeehin, 1993) have shown an association between bladder, rectal, and colon cancer and exposure to chlorinated surface water. Other studies have shown an association between TTHM exposure and bladder, colon, and rectum cancer (King and Marrett, 1996; Doyle et al, 1997).

At the time the Stage 1 D/DBPR was proposed, members of the Reg-Neg negotiating committee disagreed as to whether or not the toxicological studies provided sufficient evidence that exposure to DBPs in drinking water results in an increase risk of cancer. Therefore, the USEPA agreed to review additional research and conducted two expert panel workshops (USEPA, 1997).

The July 1994 Workshop concluded that many of the epidemiological studies had methodological problems or systematic biases that limited the interpretation of the results and recommended further research. The October 1995 Workshop panel concluded that bladder and colorectal epidemiological studies have shown an increased risk of cancer due to consumption of chlorinated surface water and recommended further research.

The USEPA recognizes the data deficiencies of health effects from DBPs, but believes the weight of evidence supports a potential health concern and warrants regulation of DBPs. A major component in assessing risk for a contaminant is the number of people exposed. In the case of DBPs, over 200 million people are exposed to disinfected drinking water. In 1992, a controversial meta-analysis (Morris et al, 1992) estimated that 10,000 cancer cases each year could be attributed to consumption of chlorinated drinking water and disinfection byproducts.

Between the Stage 1 D/DBPR and the proposed Stage 2 D/DBPR, new information on health effects of DBPs became available. Health studies were published that continued to support the association between DBPs and bladder, colon, and rectal cancers. In addition to cancer effects, recent studies (discussed below) report associations between chlorinated drinking water and several reproductive and developmental problems such as spontaneous abortion, stillbirth, neural tube defects, pre-term delivery, intrauterine growth retardation, and low birth weight.

**Pregnancy Risk**

During a 1980-1981 epidemiological study by the Department of Health Services in Santa Clara County (Deane et al, 1989), it was observed that pregnant women who drank tap water had a higher frequency of spontaneous abortion than women who drank bottled water. This study led to additional studies investigating the association between acute exposure to disinfection byproducts and birth outcomes. As a result of the differences in design and methodology between the studies, the findings of the various studies have been inconsistent. In addition, epidemiology studies have raised questions about the toxicity of byproduct mixtures compared with the toxicity of individual byproducts.

In 1998, a study (Waller et al, 1998) showed a two to three fold increased risk of spontaneous abortion among pregnant women drinking ≥5 glasses of tap water with high concentrations (≥75 ug/L) of THMs. Of the four individual trihalomethanes tested, spontaneous abortion was only associated with high bromodichloromethane concentrations (≥18 ug/L). An earlier study (Savitz et al, 1995) had found a smaller (20%) increase in spontaneous abortion in relation to trihalomethane consumption. A third study (Kanitz et al, 1996) found possible association between consumption of drinking water disinfected with chlorine dioxide and/or sodium hypochlorite and somatic parameters (i.e. birthweight, body length, cranial circumference, and neonatal jaundice). Although most of the studies focus on TTHMs, between 1995 and 1997, several studies showed the potential for different HAAs (including dichloroacetic acid and brominated HAAs) to cause developmental and reproductive effects.

At the time the Stage 1 D/DBPR was proposed, the USEPA could not conclude, based on available studies, that there is an association between DBP exposure and reproductive and developmental effects. But, in 1997, a review panel concluded that the results of several studies showed a small to moderate risk of adverse reproductive or developmental effects associated with consumption of disinfected water. Note that, unlike chlorination, no epidemiological studies have been conducted to suggest that ozonation carries a cancer risk in humans.

In 1998, a USEPA expert panel reviewed toxicological and epidemiological studies of reproductive and developmental effects associated with DBPs. Prior to 1998, the USEPA

focused on the carcinogenetic properties of DBPs. The expert panel recommended further studies to determine reproductive and developmental effects of DBPs (Zavaleta et al, 1999).

After the Stage 1 D/DBPR rule was promulgated, a study (Hwang et al, 2002) found that chlorinated byproducts were associated with birth, cardiac, respiratory, and urinary tract defects. In 2003, another study (Windham et al, 2003) suggested that THM exposure might affect ovarian function. Because this is the first study investigating menstrual cycle variations, further research is needed to confirm the relationship.

By 2003, when the Stage 2 D/DBPR was proposed, the EPA had concluded, based on the epidemiological studies, that DBPs pose a potential developmental and reproductive health hazard. However, the data was not yet suitable for a quantitative risk assessment.

**Health Risk of Brominated DBPs**

In the past, human health studies have focused on the health risks of consumption of chlorinated drinking water or the risk of exposure to TTHMs, some animal toxicology studies have focused specifically on brominated DBPs. However, brominated DBPs comprise a major portion of the byproducts not tested for adverse health effects. Studies on bromodichloromethane, bromoform, and to a lesser extent dibromochloromethane have shown evidence of carcinogenicity in rats and mice. Dibromochloromethane increases liver tumors, bromodichloromethane increases colon, kidney, large intestine, and liver tumors, bromoform increases colon and intestinal tumors, and bromate increases kidney and other tumors (Zavaleta et al, 1999).

Reproductive studies have shown bromodichloromethane, bromoacetic acid, dibromoacetic acid, and bromate to be associated with impairments to sperm mobility, morphology, and maturation in laboratory animals. Other studies have shown bromodichloromethane and bromoform to be associated with miscarriage in rats. Offspring of pregnant rats exposed to brominated acetic acids exhibit heart defects. In addition, bromodichloromethane exposure has also been associated with early-term miscarriage in one human epidemiology study (Zaveleta et al, 1999).

There remains uncertainty about the conduct of the toxicological studies and the mode of administration of the chemicals. Rodents are administered disinfection byproducts in corn oil, instead of in drinking water, and it has not been demonstrated that this means of administration does not, in itself, cause tumors. Because of these uncertainties, the U.S. Environmental Protection Agency and the National Toxicology Program are currently evaluating the carcinogenicity of bromodichloromethane administered to animals via drinking water. In addition, further study is underway to confirm the carcinogenicity of bromate (Zavaleta et al, 1999).

**Recently Discovered DBPs**

Many water utilities are switching to chloramines instead of chlorine as a disinfectant, because they can substantially reduce levels of chlorinated disinfection byproducts. Epidemiological studies have shown that people who drink chlorinated water have a higher risk of cancer than those who drink chloraminated water (Renner, 2004). But, recent studies have revealed that alternative disinfectants can form highly toxic DBPs.

In 1988 MX (3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) had been determined to be the most mutagenic DBP, as well as being carcinogenic to laboratory animals. MX comprises 20-50% of the mutagens in chlorinated water. Brominated MX is of special concern, because brominated DBPs have been shown to be significantly more mutagenic than their chlorinated analogues (Weinburg et al, 2002). By 2002, brominated nitromethanes were shown to be more than an order of magnitude more genotoxic than MX and also more genotoxic than MX. As of 2004, iodoacetic acid is the most cytotoxic and mutagenic DBP known. Iodoacetic acid is 93 times more cytotoxic and 28 times more mutagenic than MX (Renner, 2004).

The 2002 EPA DBP occurrence study (Weinburg et al, 2002) revealed that DBPs containing iodide (iodinated DBPs) were being formed in drinking water at concentrations around 10 ug/L (Renner, 2004). Iodinated DBPs are formed when water with high bromide and iodide concentrations are disinfected with chloramines. The EPA survey led to another study (Plewa et al, 2004), which showed that iodinated DBPs are significantly more cytotoxic and genotoxic than

their chlorinated analogs. The authors noted that their results were from treatment plants using chloramines only.

The Stage 2 D/DBPR will likely encourage many treatment plants to switch to chloramines. But, many plants will use chloramines for secondary disinfection only. Research is currently being conducted to determine the levels at which iodinated DBPs occur and to access their health risk. While stakeholder meetings are scheduled to be held on January 18, 2005 to gauge the significance of the birth defect data and how to handle "significant excursions" in the distribution system, the EPA does not currently plan on delaying finalizing the Stage 2 D/DBPR based on these studies (Renner, 2004). However there is no sign that USEPA will soften preamble language that cites birth defect health risks.

The greatest implication of recent health risk research to utilities treating high bromide water is that switching to alternative disinfectants to reduce regulated DBP concentrations may promote formation of DBPs that pose a greater health risk.

## *11. Future Research Needs*

**DBP Health Risk Research Needs**

In 1995, a workshop was held to discuss the emerging health effects data (Zavaleta et al, 1999). Major conclusions from the workshop include:

- Efforts to reduce the risk posed by DBPs should not compromise the microbial quality of the water
- Although the risks from DBPs appear low, they are still important because of the large number of people potentially exposed (>200 million)
- Additional byproducts need to be identified, because only about half of the halogenated compounds in chlorinated drinking water have been identified
- It is critical for future research to focus on byproducts that pose the greatest health concerns

- Studies on interactions and mixtures of DBPs should focus on byproducts for which the mode of action has been established

In 2001 McGuire Environmental Consultants, Inc. (MEC) led a three-day workshop in Vail, Colorado with over 40 drinking water experts. The purpose of this workshop was to characterize the current state of understanding regarding various DBP related topics and to define areas of DBP research where there was an incomplete scientific basis for regulatory and other decision making processes (MEC, 2001). Regarding health effects of DBPs the following was found:

- Mixed opinions were found regarding both the sufficiency and quality of information on microbial occurrence, reproductive, and developmental health effects from DBPs and the risks associated with microbial exposure levels.
- In general, consensus was found regarding the sufficiency of information to support carcinogenic health consequences associated with DBP exposure.
- In the area of unresolved issues related to chlorination byproducts, the group identified a need for improved method for exposure assessment as well as a number of assessments of reproductive and developmental consequences and evaluations of risk based on genetic factors and exposure routes.
- Toxicological studies on the biological plausibility for bladder and colon cancer are high priority. Projects to develop a process for identifying potentially important uncharacterized DBPs are also high priority.
- Additional and confirmatory toxicological and epidemiological research on the reproductive and developmental effects associated with DBP exposure, including mixture effects.
- Chemistry, occurrence, and fate of emerging DBPs that could represent important health consequences.

**Formation and Occurrence Research Needs**

As part of the 2001 three-day workshop led by MEC a characterization and assessment was made regarding the state of current research and future research needs regarding various DBP

related topics and to define areas of DBP research where there was an incomplete scientific basis for regulatory and other decision making processes (MEC, 2001).

Overall there was a consensus of opinion that there was sufficient information available and it was of good quality regarding the information resources available on DBP occurrence and treatment and cost information available for both DBPs and microbial parameters. The notable exceptions were in the following areas:

- DBP occurrence patterns for small systems, whether surface of groundwater;
- Microbial control via inactivation by such key technologies as UV and chlorine dioxide; and
- Predicted formation of bromate by ozone with the available modeling tools.

Some of the high priority research needs for future regulatory negotiation efforts identified by the workshop interviewees included:

- Better understanding of short-term variability of DBP occurrence in distribution systems;
- Small system DBP occurrence levels and patterns;
- Modeling robustness for DBP formation and control at the individual system level to improve national assessments of technology selection forecasts;
- Improved and/or new algorithms for DBP species, bromate, and other DBP compounds of interest under future regulatory development efforts;
- In the area of DBP Occurrence and Control, problems arising from systems moving to chloramination.
- The occurrence and formation of organic nitrogen DBPs and the kinetics of DBP formation during chloramination.
- Engineering of chloramination practices to minimize DBP formation, including the formation of organic nitrogen DBPs and other newly discovered DBPs, and extending to source water management for DBP control.

- The fate of contaminants, effects of distribution system materials on water quality, characterizing distribution system intrusion events, the stability of DBPs in distribution systems, and modeling of the distribution system for water quality and biostability.

In addition, interviewees all identified distribution system issues as important and critical to future regulatory development, but believed that the state of the science is still too immature to meaningfully move forward in the near term on drinking water standards.

## *13. Conclusions*

The following conclusions need to be taken into account when reviewing municipal and industrial objectives for the Bay-Delta system and the need for new drinking water protection objectives

**DBPs are a far larger issue today than they were in 1991.** The Stage 2D/DBPR will require compliance at individual sample locations as opposed to system-wide averaging. This increased emphasis on individual sample locations is the result of increasing concern over potential reproductive risks associated with exposure to brominated DBPs. Much of this concern has arisen since 1991. USEPA is scheduled to hold stakeholder talks to weigh the value of further regulation of DBPs (e.g. to define the meaning of "significant excursion" in the draft rule) due to reproductive risk in January 2005. EPA staff has indicated that their goal for the Stage 2 D/DBPR promulgation is the summer of 2005. High quality source water is even more important than it was in 1991.

**The weight of evidence of health effects continues to build.** Cancer and toxicological studies are continuing to add to the findings of previous studies. The pivotal issue is associated with the nature and extent of the reproductive risk posed by brominated DBPs (such as can be formed treating Delta water containing bromide from seawater intrusion). In addition, recent research has been focusing on identifying new DBPs and determining their cancer and developmental risk. Of particular interest are disinfection by-products associated with alternative disinfectants such as chloramines, ozonation, and chlorine dioxide as many utilities are shifting to these

technologies to minimize regulated DBPs in their treated water. While there is considerable debate about the specific health effects of human exposure to various DBPs, water utilities generally pursue cost-effective operational and treatment strategies to minimize DBP formation. In my opinion, the troubling studies regarding brominated DBP health effects makes it more likely that such DBPs will be further regulated in the future. This again points to the need for improved source water quality from the Delta.

**Compliance with DBP regulations is likely to become more difficult and expensive for utilities treating Delta water.** Stage 2 "locational running annual averages" will likely require greater removal of TOC and/or bromide to ensure **all** locations in the water distribution system comply. These standards are slated for promulgation in Summer 2005. Broad scale use of alternative disinfectants will occur. Short of controlling DBP precursors in the source water, utilities will be increasingly constrained in their treatment and operational flexibility as they simultaneously seek to ensure compliance with the DBP regulations. Wide swings in water quality make process selection and compliance even more difficult. In the absence of source control of TOC and bromide, treatment plants will be forced to retrofit with precursor removal technologies as DBP regulations grow more stringent.

**Controlling DBP precursor (TOC and bromide) in Delta source water must be one of the barriers of a multi-barrier approach to assist utility compliance with the DBP regulations.** Utilities will not be able to rely on water treatment technologies alone for several reasons:

1. These alternative compliance technologies have environmental and public health trade-offs of their own
2. Regulations are likely to become more stringent in the future, and
3. The cost of these technologies generally rise as the source water quality degrades, and
4. The effectiveness of treatment technologies in providing uniform quality and compliance is a function of source water quality. Large variations in quality risk non-compliance.

Given what is known about health effects, treatment complexity, and the regulatory calendar, establishing 3.0 mg/L TOC and 50 µg/L bromide as narrative goals strikes a sensible balance between drinking water quality needs and water quantity realities.

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