Collection of Documents Relevant to the Use of Chloramine as a Drinking Water Disinfectant Prepared by SFDPH and SFPUC 2004-2013

- 1. SFPUC/SFDPH Comprehensive Q&A
- 2. Reviews of abstracts in the medical literature
- 3. Powerpoint presentation
- 4. Fact sheet about lead

## **Questions and Answers Regarding Chloramine**

In February 2004, after numerous studies and deliberation, the SFPUC implemented chloramination in the distribution system. The driver for changing the distribution system disinfectant from chlorine to chloramine was to comply with Federal and State water quality regulations. The primary objective was to reduce the formation of trihalomethanes (THMs), haloacetic acids (HAAs), and regulated chemical by-products of disinfection that may cause adverse health effects. Chloramine is very effective at limiting the formation of these by-products. In addition, due to the large size of the SFPUC water system, maintaining a small concentration of disinfectant throughout the pipe network and storage system is necessary to preserve water quality. Chloramine, since it is less reactive than chlorine, is ideal for meeting this secondary objective.

After the implementation of chloramination, the predicted improvements were realized (e.g., concentrations of THMs decreased by 50 percent) and extensive water quality monitoring was conducted as well as monitoring customer responses. Overall the results were positive. Some individuals, however, did express concerns about the amount of information available about health issues associated with chloramine, the decision to convert the system to chloramine and alleged effects such as skin rashes and digestive disturbances. Since these concerns were expressed, the SFPUC has met with and listened to concerned individuals, consulted with the medical community, held public meetings, reviewed the literature, conducted tests, engaged water professionals, surveyed other utilities, compiled analyses and posted information to the web-site. As a product of this effort, listed below are responses to frequently asked questions about chloramine and their researched responses. These responses are scientific in nature and are tailored to an informed audience while still providing general information for the average concerned citizen.

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Review by the above individuals in no way constitutes endorsement, nor reflects official positions of their respective organizations. The SFPUC is responsible for the contents of this document.

Note: Throughout the SFPUC FAQ regarding chloramine, the term chloramine refers to one of its species, monochloramine. Where it is important to distinguish between other species (i.e., dichloramine and trichloramine), the specific terms are used. Monochloramine is the dominant species found in SFPUC drinking water while dichloramine and trichloramine would be undetectable under the treatment conditions used.

## **GENERAL PUBLIC HEALTH**

# $Q\mbox{:}$ Have any independent health assessments been conducted on the use of chloramine for disinfection?

A: In 2005, the CCLHO reviewed current knowledge and evidence regarding the efficacy and safety of monochloramine in drinking water. CCLHO concluded that monochloramine is better than chlorine for maintaining a small (residual) amount of disinfectant in water distribution systems where high concentrations of trihalomethanes or haloacetic acids result from chlorination. Trihalomethanes and haloacetic acids are halogenated organic compounds that increase the risks of certain cancers.

## Q: Who is the CCLHO?

A: The California Conference of Local Health Officers is comprised of all legally appointed local Health Officers in California. In addition, physicians who are Deputy Health Officers or Assistant Health Officers may be appointed as non-voting associate members. The Conference was established by statute in 1947 to advise the California Department of Public Health (CDPH), other departments, boards, commissions, and officials of federal, state and local agencies, the Legislature and other organizations on all matters affecting health. For more information, please see: <a href="http://www.cdph.ca.gov/programs/cclho/Pages/default.aspx">http://www.cdph.ca.gov/programs/cclho/Pages/default.aspx</a>

## Q: What did the CCLHO find relative to chloramine in drinking water?

A: The CCLHO findings are documented in a March 8, 2005 letter

### Q: Did the CCLHO make any recommendations?

A: Yes, the CCLHO made five recommendations.

### Q: What is the SFPUC doing regarding the CCLHO recommendations?

- A: The SFPUC has actively addressed all of the recommendations of the CCLHO.
- 1) SFPUC has continued monitoring for recommended water quality parameters.
- 2) SFPUC conducted routine Lead and Copper Rule (LCR) compliance monitoring in 2004 and additional monitoring in 2006. Neither lead nor copper levels were affected by chloramination in the San Francisco Regional Water System (providing water to the local Bay Area water agencies) or in the San Francisco Water System (City system). Each permitted water system is individually responsible for LCR monitoring and compliance. SFPUC provides water that complies with CDPH approved corrosion control treatment.
- 3) SFPUC considers monitoring for new and emerging contaminants as suggested by the CCLHO recommendations. For example, after concerns were raised about the presence of iodinated disinfection by-products (DBPs), SFPUC participated in a 2006 USEPA survey of iodo-HAAs and iodo-THMs. These classes of iodinated DBPs are not currently regulated and are of research interest. SFPUC monitors quarterly for another DBP of research interest, N-nitrosodimethylamine (NDMA). In 2007, SFPUC monitored its system for algal toxins and dissolved inorganic nitrogen (DON) since these groups of contaminants are also of research

interest. SFPUC monitors for contaminants at ever lower analytical levels; e.g., arsenic is monitored at a detection limit five times lower than previously. SFPUC laboratory now has capabilities of molecular detection of various groups of bacteria in the source and treated water. In 2010, SFPUC began participation in another Water Research Foundation project: "Fate of Non-Regulated DBPs in Distribution Systems" conducted by CDM, University of Massachusetts and Yale University.

- 4) The SFPUC has actively promoted liaisons with the health departments in Alameda, San Francisco, San Mateo, Santa Clara and Tuolumne counties to monitor and communicate about emerging health issues potentially related to drinking water quality. In 2009, SFPUC completed Strategic Planning for San Francisco's Water Quality Future, engaging with federal, state and local health professionals as well as water agencies and citizens groups to scope out new and emerging water quality issues for a 30 year planning horizon. The report can be viewed at <a href="http://sfwater.org/detail.cfm/MC\_ID/13/MSC\_ID/166/MTO\_ID/581/C\_ID/4611">http://sfwater.org/detail.cfm/MC\_ID/13/MSC\_ID/166/MTO\_ID/581/C\_ID/4611</a>
- 5) The SFPUC communicates and cooperates routinely with local health departments, professional associations and national experts to address and monitor water quality issues, not only about disinfection practices, but many other issues such as cryptosporidiosis, mycobacterium avium complex, and emergency planning. SFPUC has requested a review of its chloramination practices by national experts and communicated the concerns to the health agencies and at professional conferences. The 2009 Strategic Planning for San Francisco's Water Quality Future is looking at a broad spectrum of possible emerging contaminants and issues that may become of importance in the future. Similarly, SFPUC has engaged national experts and received input from major water utilities in this endeavor.

## DRINKING WATER DISINFECTION

### Q: Why are disinfectants added to the water?

A: Untreated surface water is vulnerable to contamination by bacteria, viruses and parasites that may cause human illness. These disease-causing microorganisms are also referred to as pathogens. Standards have been developed within the US and elsewhere in the world defining minimum standards of disinfection to protect against contamination by pathogens.

In the US, all drinking water suppliers using surface water are required by the U.S. Environmental Protection Agency (USEPA) to use disinfectants to inactivate pathogenic microorganisms in drinking water. Currently, chlorine, chloramine, ozone, chlorine dioxide and ultraviolet (UV) light are approved by the USEPA for disinfection during treatment (termed primary disinfection) (USEPA, 1989a; USEPA 2006b). Utilities must also maintain a smaller amount of disinfectant throughout the drinking water distribution system to limit bacterial growth (termed "residual" or secondary disinfection). Currently, chlorine, chloramine, and chlorine dioxide are approved by the USEPA for disinfection systems. Chlorine dioxide is sometimes used for distribution system disinfection in smaller systems. Large systems typically do not use chlorine dioxide for distribution system disinfection because chlorine dioxide, like chlorine, is a strong oxidant and will not reach the most distant points in a large distribution system. Large water systems like the SFPUC must therefore choose between chlorine and chloramine for distribution system disinfection.

The USEPA's Stage 1 Disinfectants/Disinfection Byproducts Rule (Stage 1 D/DBPR) limits concentrations of disinfectants by establishing a Maximum Residual Disinfectant Level (MRDL) of 4 mg/L Cl<sub>2</sub> for chlorine and chloramine (USEPA, 1998). Water provided by the SFPUC meets all Federal and State drinking water regulations. Pathogens are controlled by watershed protection, disinfection with chlorine or ozone plus chlorine during treatment, distribution system disinfection with chloramine, cross-connection control, and other water quality maintenance practices.

# Q: What is the sequence of disinfectants applied at SFPUC for control of pathogenic microorganisms?

A: First, a strong disinfectant/oxidant is applied during water treatment for killing pathogens that might be present in the source water. SFPUC uses ozone and/or chlorine for this primary disinfection process. Beginning in 2011, UV light will be implemented for primary disinfection of Hetch Hetchy water source in addition to chlorine. Second, chloramine is formed to prevent microorganisms from growing in the pipes, which distribute water to the customers. Many large water systems with extensive service areas use chloramine instead of chlorine for distribution system disinfection because chloramine is less reactive and longer lasting in providing disinfection protection.

#### Q: What disinfection processes are available?

# A: Both chlorine and chloramine are proven disinfectants with considerable operating experience. Chlorine and chloramine are approved disinfectants, in addition to chlorine dioxide, ozone, and most recently ultraviolet light (UV) (USEPA 1989a, 2006b).

Each of these approved disinfectants has advantages and disadvantages in terms of: (1) disinfecting effectiveness for specific microorganisms, (2) reactivity with natural organic matter and associated formation of disinfection by-products (DBPs), (3) formation of inorganic DBPs (e.g.,

bromate, chlorate, chlorite), and (4) disinfectant persistence to provide lasting protection in the pipes and water storage reservoirs of the distribution system. Chlorine dioxide, ozone and UV cannot be used for secondary disinfection because of limited or no residual disinfectant provided by these processes. Chlorine dioxide is used by some utilities for secondary disinfection in the distribution system but this disinfectant has several drawbacks: (1) formation of chlorite which is regulated by the USEPA (1998), (2) possibility of creating "cat-urine" odors in customer homes, (3) greater reactivity and, therefore, lower persistence in the distribution system, and (4) high cost (USEPA, 1999).

The SFPUC continues to evaluate disinfection processes such as the planned use of UV light disinfection to augment chlorination and chloramination for the Hetch Hetchy source water to meet new drinking water regulations (i.e., the Long Term 2 Enhanced Surface Water Treatment Rule (USEPA, 2006b)). Potential disease-causing organisms (e.g., *Cryptosporidium*) have been found in the last 10 years to be resistant to chlorine disinfection but very sensitive to ultraviolet (UV) light. Consequently, the water industry is beginning to implement combinations of disinfectants (including UV light) to provide stronger defense against a variety of potential disease-causing microorganisms (Trussell, 2006). SFPUC has implemented a combination of disinfectants, chlorine followed by chloramine, to better disinfect the water. In the future, other disinfectants may be added to continually improve the disinfection process, meet future regulations and better serve SFPUC customers. For example, SFPUC plans on implementing UV disinfection for Hetch Hetchy water beginning in 2011, in addition to existing chlorination and chloramination. This project is estimated to cost approximately \$121 million, including construction and project delivery costs, and will provide additional barrier against microbial contamination.

### Q: Why is disinfection important?

A: Disinfection is proven to stop and prevent disease. Just a hundred years ago, waterborne typhoid fewer was a leading cause of death in the United States. Less than fifty years before that, the major cities in Europe and North America were ravaged by waterborne cholera (Morris, 2007). The importance of disinfection is exemplified by the dramatic reductions in typhoid in the early 20<sup>°</sup> century after widespread implementation of water treatment, including drinking water disinfection practices. In addition, when disinfection is discontinued due to operational failures, disease outbreaks have occurred. For example, an outbreak of E. Coli 0157:H7 occurred in Canada when chlorination of wells was interrupted (O'Connor, 2002).

Chemical disinfection became an integral part of municipal drinking water treatment over 100 years ago as a vital means for protection of public health. By the late 1880s it was clear that a number of important epidemic diseases were often waterborne, cholera, typhoid fever, and amoebic dysentery, among them. The twentieth century began with the development of continuous chlorination as a means for bacteriological control (Crittenden et al., 2005). McGuire (2006) listed "eight revolutions in the history of North American drinking water disinfection":

- 1) Application of chlorine for full-scale disinfection in Jersey City, NJ, in 1907. It took a court dispute and a legal deadline to clear away the objections and to apply what was until then only an experimental treatment method. Chemical treatment was involved and popular prejudice against its use was strong.
- 2) In 1914, the Secretary of Treasury established a standard for the coliform bacteria concentration in each sample.

- 3) In 1917 in Ottawa, Ontario, a combination of chlorine and ammonia was implemented to produce chloramine to solve taste and odor problems related to chlorine. The ammonia-chlorine process also produced stable chlorine residuals that persisted far into the distribution system. Denver Water has used the ammonia-chlorine process continuously since 1917. Chloramine disinfection was also applied in San Francisco prior to World War II (SFPUC, 1941). In Southern California in 1941, when the Colorado River water was first imported, chloramine was necessary to ensure that a residual could be maintained in the furthest reaches of the distribution system.
- 4) The discovery in 1974 of trihalomethanes (THMs) and the resulting regulation in 1979 limited THM levels to 100 ug/L (micrograms per liter, equivalent to ppb, or parts per billion). THMs are organic compounds produced from the chlorination of natural organic matter in drinking water, considered probable carcinogens. Subsequent to the identification of THMs, many other organic and inorganic "disinfection by-products" (DBP) have been discovered (Krasner et al., 2006).
- 5) Application of the product of C x T concept (disinfectant concentration C after the contact time T) in 1989 to be achieved during treatment of surface waters on a daily basis. The target organisms of USEPA Surface Water Treatment Rule (SWTR) were viruses and the protozoan microorganism Giardia lamblia (USEPA, 1989a).
- 6) The change in focus from coliform bacteria concentration to presence-absence in no more than 5% positive coliform samples in any monthly set of distribution system samples, as mandated in 1989 by the USEPA Total Coliform Rule (TCR, USEPA, 1989b).
- 7) Regulations balancing the risk from microbial contamination and risks of disease from the disinfection by-products (DBPs): in 1998 Stage 1 Disinfectant/DBP Rule (USEPA, 1998) and in 2006 Stage 2 Disinfectant/DBP Rule (USEPA, 2006a). These two rules added new regulated DBPs and attempted to minimize peak concentrations of these compounds in the distribution system.
- 8) The cryptosporidiosis outbreak in Milwaukee, WI, in 1993 resulted in the promulgation in 2006 of the USEPA Long Term 2 Enhanced SWTR (USEPA, 2006b) specifying the degree of inactivation of protozoan microorganism Cryptosporidium or other protective measures to reduce the likelihood of an outbreak of cryptosporidiosis. The discovery in 1996 that ultraviolet light (UV) can economically disinfect Cryptosporidium, Giardia, and other pathogens will dramatically change how water is disinfected in the United States.

Within six years of implementing chlorination in Jersey City, half of the water treatment plants in the United States were using chlorine to disinfect water. By 1924 three thousand cities had turned to chlorine. The occurrence of serious waterborne diseases declined and diseases like cholera, typhoid and amoebic dysentery which had been common became rare. In 1900 an average American had a 5 percent chance of dying of a gastrointestinal infection before the age of seventy. By 1940 that likelihood had dropped to 0.03 percent and by 1990 it had fallen to about 0.00005 percent (Morris, 2007). Evidence clearly demonstrates that implementing disinfection has reduced waterborne disease and that failures in disinfection can result in increased levels of disease.

### Q: What is chloramine?

A: Chloramine is a disinfectant added to water for public health protection. It is a combination of chlorine and ammonia that is currently considered best technology for controlling the formation of certain regulated organic disinfection byproducts. Chloramine is formed at the SFPUC treatment plants following treatment with ozone (at one SFPUC

# treatment plant) and with chlorine (at all SFPUC treatment plants). Chloramine is used as a distribution system disinfectant.

The SFPUC began using chloramine for distribution system disinfection for the second time in its history in February 2004. The SFPUC had used chloramine for disinfection from 1935 to 1944 (SFPUC Annual Reports; White, 1999) but stopped during WW II due to ammonia shortages.

Chloramine is formed at the treatment plants by combining chlorine and ammonia at a weight ratio of 5:1 or slightly less – this maximizes formation of monochloramine, which is not volatile. Initially, for a few weeks early in 2004, chloramine target was as high as 3.5 mg/L Cl<sub>2</sub>, and was subsequently decreased to 2.3 mg/L Cl<sub>2</sub>. The current chloramine target concentration in the SFPUC system is 2.3 mg/L Cl<sub>2</sub> in plant effluent and slightly less in the distribution system. In the past, before chloramine was used in the SFPUC distribution system, the levels of chlorine in plant effluents ranged from 1.0 to 1.5 mg/L Cl<sub>2</sub>. Thus chloramine levels are relatively higher than chlorine. Although chloramine is less reactive than chlorine and more stable from a practical water supply point of view, it is not a persistent chemical and eventually breaks down by itself (Valentine, 1998). Chloramine does not bioaccumulate or transfers up the food chain (Environment Canada, 2002).

# Q: What is the history of chlorine and chloramine use for drinking water disinfection in the United States?

A: Both chlorine and chloramine have been used for disinfection for about the same length of time. The first regular use of chlorination in the United States was in 1908 (AWWA, 1998). It actually required a court dispute and a legal deadline to clear away the objections for applying chlorine (McGuire, 2006). By 1917, chlorine disinfection was adopted by hundreds of US water utilities and issues emerged with chlorine taste and odor. Chlorine readily combines with phenol to produce a wide variety of chlorophenols that at low concentrations impart a strong medicinal odor to water. In addition, chlorine itself has a significant, penetrating, and disagreeable odor (McGuire, 2006).

In 1917 in Ottawa, Ont., a combination of ammonia and chlorine was implemented to solve flavor and odor problems related to chlorine (McGuire, 2006). Chloramine has been used for disinfection in the United States since that time (USEPA, 1999; Kirmeyer et al, 2004). Chloramination enjoyed its greatest popularity between 1929 and 1939. In 1938, based upon replies to a questionnaire from 2,541 water suppliers in 36 states, 407 utilities reported using ammonia with chlorine. Denver, CO, has used a chloramination process continuously since 1917 (McGuire, 2006). The San Francisco Hetch Hetchy Aqueduct was chloraminated from 1935 until the ammonia supply became scarce during World War II in 1944 (SFPUC, 1941; White, 1999). The Metropolitan Water District of Southern California (MWDSC) implemented the use of chloramination in 1941 when Colorado River water was first delivered to Southern California. Chloramine disinfection was used so that a sufficient residual could be carried to the furthest reaches of the MWDSC distribution system (McGuire, 2006).

A survey in 1938 (AWWA, 1941) indicated that 33 of 36 surveyed states had a least one water supply that used chloramine. In California, 190 water supplies were reported to use chlorine and 35 chloramine, which was the second largest use of chloramine in any state after New York, where 69 water supplies were chloraminated. By 1936, 16% of all U.S. water treatment facilities were using chloramine. Due to the scarcity of ammonia during World War II use of chloramine declined until 1960s to a low of 2.6% facilities. After the enactment of the Federal Safe Drinking Water Act (SDWA) by the US Congress in 1974 and its subsequent Amendments, interest in using

chloramine was renewed due to increasing focus on microbiological safety and reduction of DBPs. About 20% of treatment facilities used chloramine in 1990 (Kirmeyer et al., 2004). In 1996, approximately 6.9 million Canadians were supplied with chloraminated drinking water (Environment Canada, 2001). Many utilities in California serving a total population of over 20 million have been using chloramine for over 20 years. Chloramine is used worldwide on four continents.

### Q: What is the history of chloramine application by SFPUC?

# A: Chloramine was successfully applied at SFPUC for control of biofilm in the tunnels and pipelines as well as in the distribution system to improve water quality for about 10 years after Hetch Hetchy supply was first introduced into the system, from 1935 through 1944.

Hetch Hetchy water was first delivered from the Sierra Nevada Mountains to Crystal Springs Reservoir in San Mateo County on October 28, 1934. The most serious issue for the Water Department when the Hetch Hetchy supply was first delivered was the appearance of *Crenothrix*, an iron bacteria. These non-pathogenic bacteria formed a "slimy growth" in the aqueduct impacting water flows and causing an objectionable taste. Testing was performed to control *Crenothrix* (SFPUC, 1935). From October 28, 1934 until June 6, 1935, the Hetch Hetchy water was chlorinated with a portable chlorinating unit. On June 6, 1935, a new permanent chlorinator started operation at the Irvington Portal. On June 15, 1935, an ammoniator was installed at Irvington to control the growth of *Crenothrix*.

*Crenothrix* in the Hetch Hetchy Aqueduct continued to be the most serious problem confronting the Water Department in 1935/1936 (SFPUC, 1937). Inspection revealed 1/8-inch slimy growth, which decreased the water flow, imparted taste and odor, and decreased dissolved oxygen in Hetch Hetchy water by 50%. Treatment with chlorine and ammonia (since June 17, 1935) at Irvington Portal had been most effective in removing the growth inside the entire Bay Crossing Pipeline, and did not generate taste or odor. A similar chlorine and ammonia facility was designed for Tesla Portal (at the entrance to the Coast Range Tunnel). There were 19 chlorinators and 3 ammoniators installed that year at 11 different locations. An ammoniator was also installed at College Hill Reservoir to overcome algal taste due to algae growth in this open reservoir and to reduce stagnation in the dead ends of the distribution system, which was the cause of customer complaints (SFPUC, 1937).

The new chloramination station located at Tesla Portal was completed on the Hetch Hetchy Aqueduct in FY1936/1937 and reported to be the largest chloramine treatment plant in the world at the time. There were a total of 23 chlorinators and 6 ammoniators at 12 different stations throughout the system. Chlorine and ammonia treatment of Calaveras water was initiated at the reservoir outlet on October 29, 1936 and determined effective for *Crenothrix* control (SFPUC, 1938).

Nelson A. Eckart, General Manager and Chief Engineer of the San Francisco Water Department reported in 1940 (Eckart, 1940) that chlorination and ammoniation reduced raw water bacteria from 12-15% positive for coliform organisms to 0-1.4 %, well under the 10% allowable under federal requirements of the day. Dosages averaged 0.3 mg/L, with chlorine to ammonia ratio of 5:1 (Eckart, 1940).

Disinfection practice changed at SFPUC between 1942 and 1944 as a result of World War II: higher dose of chlorine was applied, primarily at Tesla and Calaveras and fewer disinfection stations were in operation. Biofilm control in the tunnels and pipelines was provided by either chlorination or chloramination (SFPUC, 1943a and 1943b). Chloramination was discontinued

some time in 1944 due to ammonia shortages. High chlorine doses were needed for biofilm control (SFPUC 1947) and to maintain adequate chlorine residuals (SFPUC, 1949).

### Q: What is the history of regulatory approval of chloramine?

A: Chloramine has been used as a municipal drinking water disinfectant for over 90 years. Chloramine is an approved treatment and distribution system disinfectant by the USEPA (USEPA, 1990). The World Health Organization (WHO, 1996) states that chloramine is useful for maintaining a disinfectant in distribution systems.

The Stage 1 Disinfectant and Disinfection By-Product Rule (USEPA, 1998) established maximum residual disinfectant levels for chlorine and chloramine of 4 mg/L Cl<sub>2</sub> in the distribution system. Residuals higher than 4 mg/L Cl<sub>2</sub> levels of chlorine or chloramine are allowed for short-term distribution system disinfection.

The use of chloramine as a disinfection agent, when compared to chlorine, reduces the formation of disinfection byproducts (DBPs). The reduction in DBPs is an improvement in public health protection. DBPs are currently regulated by the USEPA under Stage 1 and Stage 2 D/DBP Rules (USEPA, 1998 and 2006a). The Surface Water Treatment Rule (USEPA, 1989a), SWTR, established the C x T values (concentration, C, after given contact time, T, with the disinfectant) required for disinfection of *Giardia* and viruses during treatment with chlorine, chloramine, ozone, or chlorine dioxide. The SWTR also established that the minimum disinfectant residual should be detectable in the distribution system for either chlorine or chloramine.

### Q: What is the current and future use of chloramine for drinking water disinfection?

A: Chloramine is a proven disinfectant used extensively in the Bay Area, California, across the US and worldwide. Most major utilities in California use chloramine as a final drinking water disinfectant. In the Bay Area, Santa Clara Valley Water District (since 1984), Contra Costa Water District (since 1981), Alameda County Water District (since 1985), Marin Municipal Water District (since 1995), Zone 7 Water Agency in Livermore, Pleasanton and Dublin (since 1990) and the East Bay Municipal Utility District (since 1998) have provided chloraminated water to their customers. The Metropolitan Water District of Southern California has provided chloraminated water in the 1940's and then again since the mid 1980s and the City of San Diego since 1982. More than one in five Americans use drinking water treated with chloramine. (USEPA, 2009)

USEPA's Information Collection Rule data (2002) indicated that of 353 treatment plants examined 34.7% of the systems used chloramine with some combination of chlorine pretreatment, while 11.5% of the systems used chloramine with chlorine dioxide or ozone pretreatment.

Seidel et al. (2005) conducted the most recent chloramine survey in 2004 (363 utilities from 50 states responded to the survey, including SFPUC) with the following results: 29% of community water systems used chloramine for secondary disinfection and another 3% were in the process of switching to chloramination, about 12% contemplated the switch in the near future. The proportion of utility respondents that intended to or considered switch to chloramine, increased with system size. More than 25% of utility respondents that served more than 100,000 customers indicated that they intended to or seriously considered switch to chloramine.

The reported median target chloramine concentrations were 2.7 mg/L at the plant effluent location, 2.0 mg/L at the distribution system average residence time location, and 1.0 mg/L at the distribution system maximum residence time location (Seidel et al., 2005).

In 2007, the AWWA Disinfection Systems Committee conducted its fourth survey of drinking water disinfection practices. Chlorine gas remained the predominant disinfectant; however its use decreased from 70% of all surveyed systems in 1998 to 63% of respondents in 2007 because many utilities changed from gas to bulk liquid chlorine and on-site generation. Use rates of chloramine (30%), chlorine dioxide (8%), ozone (9%), and ultraviolet light (2%) increased from the prior 1998 survey (AWWA, 2008a). The planned future changes to free chlorine alternatives were estimated as follows: 10% of respondents planned change to chloramine, 16% planned to add UV, 7% planned to add ozone, and 4% chlorine dioxide (AWWA, 2008b).

### Q: What are the types of chloramines that can be formed under special circumstances?

A: There are three inorganic chloramines that can be theoretically formed under different conditions of water pH and/or chlorine to ammonia weight ratio: monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) and trichloramine (NCl<sub>3</sub>). Under the conditions existing in full-scale drinking water distribution systems at pH values above 8 (pH in the SFPUC system varies between 8.6 and 9.4, depending on the water source) and chlorine to ammonia weight ratios of 5:1 or below, monochloramine is the only observed chloramine species (100%).

While not formed in the SFPUC system, dichloramine and trichloramine could be formed if the SFPUC were to significantly increase the chlorine to ammonia ratios and lower pH values. Above pH 7.5, trichloramine is not detectable at any chlorine to ammonia ratios (USEPA, 1994; White, 1999; Environment Canada, 2001).

While dichloramine and trichloramine likely have good disinfecting capabilities, they cause taste and odor. In addition, they are much less stable than monochloramine; therefore, their formation should be avoided. Trichloramine, which in its pure form is very volatile and pungent, cannot exist in chloraminated water systems without the presence of chlorine and it has been known to form in the chlorinated distribution systems long after leaving the treatment plant. This situation is corrected by converting the chlorine residual to monochloramine (White, 1999).

Trichloramine may occur during the practice of "breakpoint chlorination" (i.e., when excess amounts of chlorine are added to the water containing chloramine and/or ammonia to develop chlorine residual). Trichloramine may form in swimming pools if pH and chlorine dose are not properly maintained. It is also a nuisance chemical in wastewater treatment. It is so volatile and unstable that is it difficult to quantify by analytical methods (White, 1999).

Small amounts of organic chloramines may also form in chlorinated or chloraminated water if certain organic nitrogen compounds, including amino acids and nitrogen heterocyclic aromatics, are present (Environment Canada, 2001; White, 1999, Lee and Westerhoff, 2009). Chlorine forms organochloramines almost instantaneously, whereas monochloramine reacts slower. With very few exceptions, all organochloramines are nongermicidal and nontoxic to aquatic life (White, 1999, Amiri et al., 2010). Experience indicates that trace levels of organochloramines can be formed in all treated natural waters. Available data indicate that inorganic monochloramine is predominant chloramine in SFPUC system.

Throughout this document, the term chloramine refers to monochloramine. Where it is important to distinguish between monochloramine, dichloramine, and trichloramine, the specific terms are used. Due to concerns expressed by some customers about the potential presence of dichloramine and

trichloramine in our chloraminated distribution system, SFPUC requested an independent opinion on chloramine speciation. The opinion by a recognized chemistry expert can be found on SFPUC website at http://sfwater.org/detail.cfm/MC\_ID/13/MSC\_ID/166/MTO\_ID/399/C\_ID/3408.

# Q: What was the reason for changing distribution system disinfectant from chlorine to chloramine at SFPUC as well as at many other water utilities?

A: Two properties of chloramine enable the SFPUC to minimize potential for microbial contamination and comply with Federal regulations. First, because chloramine is longer lasting than chlorine, it helps achieve compliance with the Surface Water Treatment Rule. Second, chloramine forms much lower levels of regulated DBPs than chlorine, thus enabling compliance with Federal rules governing DBPs.

The SFPUC implemented chloramination in the distribution system in February 2004. The primary driver for changing the distribution system disinfectant from chlorine to chloramine was to reduce the formation of trihalomethanes (THMs) and haloacetic acids (HAAs). In the late 1970s and early 1980s it was discovered that chlorine reacts with naturally occurring organic matter to form THMs, HAAs and other disinfection by-products (DBPs). Subsequent research showed that exposure to THMs over a lifetime may statistically increase the rates of some cancers. To protect public health, the USEPA began regulating four THMs in 1979, with a maximum contaminant level (MCL) of 100 ug/L (or one hundred parts per billion). Chloramine reduces the formation of these potentially carcinogenic DBPs and therefore makes water safer for human consumption. In 1998 (USEPA, 1998), the MCL for four THMs was further reduced to 80 ug/L and new MCLs were promulgated by the USEPA for five haloacetic acids (60 ug/L HAA) and other inorganic DBPs bromate (resulting from ozonation) and chlorite (resulting from chlorine dioxide application).

The choice of disinfectant(s) depends on many factors. Utilities must balance many considerations to simultaneously fulfill the requirements of numerous drinking water quality regulations. The change of disinfectants or treatment process is always preceded by careful planning, testing, and review of similar practices at other water utilities. In California, the application of any proven or new drinking water treatment processes must be approved by the California Department of Public Health (CDPH), a primacy agency for the State of California, to assure the compliance of public water systems with the requirements of the Safe Drinking Water Act (SDWA) and its Amendments. Chloramination is not simply an add-on process at the end of the treatment plant but must be fully integrated into the design and the operation of the water treatment facilities and the distribution system (Kirmeyer et al., 2004).

### Q: What are the benefits of using chloramine instead of chlorine in the distribution system?

A: The benefits of chloramine compared with chlorine for distribution system disinfection are: (1) longer lasting disinfectant and ability to reach remote areas, (2) effectiveness as a disinfectant for biofilms, (3) tendency to form lower levels of regulated DBPs (e.g., THMs and HAAs), which are probable carcinogens (USEPA, 1998), and (4) ability to minimize chlorinous or other objectionable taste and odors.

Chloramine is more stable and lasts longer in the water in the distribution system because it is less reactive than chlorine. The water agencies that have converted to chloramine report that customers note an improvement to flavor of the water. Research on the taste-and-odor quality of drinking water has demonstrated the benefits of monochloramine over chlorine. The San Francisco Public Utilities Commission's (SFPUC's) change to chloramine helps ensure compliance with more

stringent federal and state drinking water quality regulations. In San Francisco, chloramination has virtually eliminated the presence of *Legionella* species in large building hot water heaters (Flannery et al., 2006).

# Q: What are the drawbacks of using chloramine instead of chlorine in the distribution system?

A: The drawbacks of using chloramine compared with chlorine for distribution system disinfection are: (1) potential temporary deleterious effects on older elastomeric materials sometimes used in some home appurtenances and plumbing fixtures, (2) vulnerability to the microbiological process known as nitrification, (3) potential formation of chloramine related DBPs if precursor material is present in the source water (Kirmeyer et al., 2004).

The treatment precautions for hemodialysis clinics and fish cultures must be taken both with chlorine and with chloramine (Amato, 2005). Certain natural rubber products and their derivatives used in household appliances (e.g., toilet tank valves, hot water heater dip tubes) will deteriorate faster with chloramine than with chlorine (Reiber, 1993). If such effects are experienced, replacing these items with alternative materials available in the plumbing and hardware stores will eliminate this temporary nuisance rubber deterioration. Chlorine tablets for toilet water tanks may significantly increase the corrosion of submerged rubber parts in these appliances and plumbers typically do not recommend their use.

Vulnerability of chloramine to nitrification can be remedied by several practices, including: a) reducing the detention time of water in the drinking water storage reservoirs and low-use pipelines, b) keeping the system clean of deposits, which may harbor bacteria, c) flushing when necessary, and d) monitoring the system. All these actions have an additional benefit for customers by providing fresher, shorter "shelf age" water. Typically, a change to chloramine has been preceded and followed by distribution system capital improvements aimed at decreasing water age such as: seasonal or permanent outages of water tanks, improving mixing within the tanks, redesign of pressure zones for better interconnectivity, changing pumping schedules to improve stored water turnover, or installation of new water quality monitoring stations (Wilczak et al., 1996, Odell et al., 1996; AWWA 2006a).

### Q: What is nitrification and how does it impact water quality?

## A: Nitrification is a microbial process by which ammonia is sequentially oxidized to nitrite and nitrate ions. In extreme cases, nitrification may cause a depletion of chloramine disinfectant thus allowing bacterial regrowth.

Every utility using chloramine needs to assess nitrification potential and implement proper control measures. Nitrite and nitrate ions produced due to nitrification are of no water quality significance in SFPUC system. Other impacts of nitrification may include some decrease in alkalinity, pH, and dissolved oxygen (Wilczak et al., 1996; Kirmeyer et al. 2004).

Nitrification is a utility operational issue and does not pose any health concerns. Nitrification results from metabolism and growth of harmless non-pathogenic nitrifying bacteria that are ubiquitous in soils and water. Utilities implement operational control measures, including decreased water age and enhanced monitoring to limit the extent of nitrification (AWWA, 2006a). After this optimization period the customers benefit from fresher water that was stored for a shorter period of time in the distribution system. Nitrification can sometimes increase soluble lead contamination of potable water by reducing pH (Zhang et al. 2009). SFPUC has implemented a vigorous nitrification

monitoring and control program and has been successful in controlling the nitrifying bacteria and maintain stable pH in our system.

For example, nitrification occurred in two small fire storage tanks in San Francisco due to a long water detention time in these facilities. SFPUC has already redesigned piping in these storage tanks thereby completely eliminating nitrification at these sites. No nitrification was observed in any of the large water storage reservoirs in San Francisco in six years after chloramine conversion, likely due to a combination of low water temperature and large solar-powered water mixers installed in these facilities, which eliminated any stagnation. In the fall of 2009 SFPUC started addition of a small amount of chlorine to a pipeline serving water to Treasure Island to control nitrification.

### Q: What are the disinfecting properties of chloramine as compared with chlorine?

A: Chlorine is a stronger oxidant/disinfectant than chloramine and acts more rapidly as a primary disinfectant (e.g. to inactivate pathogenic microorganisms). Chloramine lasts longer than chlorine as a residual disinfectant. These differences account for how the SFPUC uses each in combination.

Disinfection of pathogens is achieved by holding a target microorganism in contact with a minimum level of chemical disinfectant concentration (C) for a minimum length of time (T) to obtain a certain level of kill (or inactivation). This is referred to as the CT concept. Promulgation of the Surface Water Treatment Rule (SWTR) in 1989 specified for the first time CT values for treatment of surface waters. The SWTR's main target organisms were viruses and the protozoan microorganism *Giardia lamblia* (McGuire, 2006). Additionally, the SWTR mandates maintaining disinfectant residual in the distribution system.

SFPUC relies on chlorine for disinfection of pathogenic cysts, bacteria, and viruses at three of its treatment facilities. One SFPUC treatment facility uses a combination of ozone followed by chlorine for disinfection. Chlorine is also used by SFPUC for pipeline disinfection and water tank disinfections after outages or construction. Chloramine is formed at the end of the treatment process to maintain disinfection throughout the distribution system. Chloramine is an approved treatment and distribution system disinfectant by the USEPA (USEPA, 1990). The World Health Organization (WHO, 1996) states that chloramine is useful for maintaining a disinfectant in distribution systems.

Chloramine is a less reactive (weaker) oxidant and disinfectant than chlorine, which is actually an advantage in the distribution system because chloramine lasts and disinfects longer. The disinfection effectiveness of chloramine should not be discounted. Studies have shown that chloramine matches the effectiveness of chlorine when contact times are sufficiently long. Additionally, chloramine has shown superior performance for the disinfection of biofilms. These results have led to the wide use of chloramine as disinfectant in distribution systems (AWWA, 2006b).

In the slightly alkaline pH range typical for drinking water distribution systems, the disinfecting effectiveness of chlorine is diminished for inactivation of bacteria, cysts and viruses, whereas the effectiveness of chloramine is not impacted (USEPA, 1990; White, 1999). This is because chlorine (hypochlorous acid) dissociates to hypochlorite ion at higher pH while chloramine remains as monochloramine as long as pH is above neutral. Disinfection with chloramine in the distribution system is superior to chlorine, which is also evident from SFPUC water quality monitoring. It must

be recognized that, regardless of the disinfectant chosen, the water distribution system can never be regarded as biologically sterile.

The use of multiple disinfectants in sequence improves disinfection effectiveness, because synergistic effects may occur. For example, the exposure of *E. coli* bacteria to mixtures of chlorine and chloramine resulted in a greater inactivation than would be predicted by their individual effectiveness. Similarly, the combinations of disinfectants (chlorine followed by chloramine, ozone followed by chlorine or chloramine, chlorine dioxide followed by chlorine or chloramine) may offer a greater level of inactivation of the *Cryptosporidium* protozoan oocysts (AWWA, 1999; West et al. 1998; Li et al, 2001).

## Q: What is the mechanism of chlorine and chloramine disinfection and is there a benefit of applying two different disinfectants instead of one?

A: Rates of microbial inactivation depend upon several factors including: the type and concentration of the disinfectant, contact time with the disinfectant, temperature, type and number of microorganisms, pH, and disinfectant demand (Jacangelo et al., 1987). It has been suggested that chlorine and chloramine act by two different mechanisms. Chlorine is a very reactive molecule and rapidly reacts with nucleic acids, most nucleotides, purine and pyrimidine bases, proteins and amino acids. Carbohydrates and lipids are generally unreactive to chlorine. Chloramine reacts rapidly only with the sulfur-containing amino acids, and the heterocyclic aromatic amino acid, tryptophan. Slow reactions of chloramine were observed with nucleic acids, purine and pyrimidine bases and the alpha amino group of amino acids. These slow reactions may become important when the rapidly reacting materials are masked or buried (Jacangelo et al., 1987). Most studies on the mode of action of chlorine in bacteria have implicated the disruption of the cell membrane. Chloramine does not severely damage the cell envelope. Chloramine inactivation has been suggested to occur through the blockage or destruction of several enzymes and cofactors. The mode of action of chloramine appears to involve multiple hits by the disinfectant on the bacterial cell and reactions at several sensitive sites in the bacteria, which precede inactivation (Jacangelo, et al., 1987).

Some studies have shown that chlorination followed by chloramination is more effective for disinfection of the protozoan *Cryptosporidium parvum* oocysts than chlorine alone (West et al., 1998). The future of drinking water disinfection will rely on multiple disinfectants applied in sequence (Trussell, 2006).

# Q: How has chloramine performed in SFPUC distribution system so far in terms of control of microorganisms?

A: Monitoring results indicated that the incidence of positive coliform bacteria samples decreased by 75 percent and that the heterotrophic plate count bacteria levels decreased by as much as a factor of ten comparing with free chlorine. A significant decrease in *Legionella* levels in San Francisco hot water heaters is an additional important benefit of chloramination. At the same time, growth of nitrifying bacteria in the distribution system has been controlled.

SFPUC monitors its distribution system for coliform bacteria as mandated by the Total Coliform Rule (TCR, USEPA, 1989b). Additionally, although not required, SFPUC monitors its distribution system for heterotrophic plate count (HPC) bacteria using the sensitive R2A method. Chloramination has improved TCR compliance and lowered the levels of HPC bacteria in the

distribution system by a factor of 10, as compared with chlorine. This is likely due to higher and longer-lasting disinfectant residuals provided by chloramine. Similarly, chloramination has virtually eliminated the presence of *Legionella* species in San Francisco in hot water heaters (Flannery et al., 2006). *Legionella* bacteria were found to be much more resistant to chlorine than *E. coli* and other coliforms that have been used as indicator organisms to monitor potable water quality (Kim et al., 2002). *Legionella* bacteria have been known to cause pneumonic legionellosis and severe influenza-like illness. Hospitals supplied with drinking water disinfected with chloramine are less likely to have Legionnaires' disease outbreaks than those that use water containing chlorine (Kim et al., 2002). In an independent opinion by a leading medical university professor posted on SFPUC website indicates that control of *Legionella* is a significant public health benefit.

Immunocompromised individuals may consider boiling drinking water regardless of the disinfectant applied, depending on recommendations from their physician. It is technologically impossible to provide sterile drinking water by any utility.

### Q: Why doesn't the SFPUC use ozone or ultraviolet light instead of chloramine?

A: SFPUC applies ozone and chlorine for primary disinfection at one of its treatment plants. Chlorine alone is used for primary disinfection at the remaining treatment facilities. Ultraviolet light will be used for treatment of Hetch Hetchy water to augment current chlorine disinfection beginning in 2011. However, ozone and ultraviolet light do not provide lasting disinfectant in the water and cannot be used as disinfectants in the distribution system.

# Q: Why doesn't SFPUC remove organic matter before disinfection and use chlorine for disinfection?

A: Chemical pretreatment and filtration are already used at two SFPUC treatment plants. This treatment lowers but does not prevent THMs or other chlorinated DBPs from forming during chlorination. The removal of a portion of natural organic matter (NOM) from the Hetch Hetchy water would require chemical pretreatment by adding aluminum or iron coagulant salts and filtration of 300 million gallons of water per day. A facility capable of this type of treatment would cost billions of dollars to build and have operating costs on the order of millions of dollars per year, based on recent general cost estimates from AWWA for membrane filtration plants (AWWA, 2005a) and other estimates from the California Resource Agency (Environmental Defense, 2006). There would be significant operational impacts of filtration, including loss of gravity system and the need for pumping of all water delivered to the Bay Area.

There is no guarantee that even such costly treatment would allow SFPUC and its retail customers to remain in compliance with DBP regulations with chlorine disinfection in the distribution system. Disinfection by-product (DBP) precursor removal efficiencies are site-specific and vary with different source waters and treatment techniques. Many utilities use coagulation and filtration to remove a portion of natural organic matter (NOM) present in the source water and still need to use chloramine for DBP minimization; this has been true for all large utilities in California. Large systems with large emergency water storage volume are unlikely to be able to control DBPs unless they use chloramine in the distribution system. SFPUC continues to apply chlorine at the treatment plants for disinfection of protozoan cysts, bacteria, and viruses. Chlorine is also used by SFPUC for pipeline disinfection and water tank disinfections after outages or construction. Chloramine is used for residual disinfection in the distribution system.

DBP precursor removal may also carry unintended effects. Because coagulation and filtration remove total organic carbon (TOC) but not bromide, in some waters containing high levels of bromide there may be an increase in the bromide-to-TOC ratio and a shift to more brominated species during chlorination (although this would not be expected in SFPUC waters). Brominated DBPs may be of higher health concern than the chlorinated species within the same class (Bull et al. 2001). The addition of salts could increase the corrosivity of Hetch Hetchy water.

SFPUC thoroughly evaluated all alternative methods to comply with DBP regulations. Water utilities do not conduct basic health research to test water disinfectants. Decisions are based on USEPA and CDPH approved technologies and cost considerations. Chloramine has performed very well in the SFPUC distribution system, significantly reducing the formation of regulated disinfection by-products and allowing SFPUC to meet current and future USEPA regulations. At the same time, chloramine has improved control of biofilm in the SFPUC distribution system, lowering the incidence of coliform positive samples, reducing heterotrophic plate count (HPC) bacteria by up to an order of magnitude, and virtually eliminating *Legionella* from the hot water heaters in large buildings.

## **DISINFECTION BY-PRODUCTS**

## Q: What are the disinfection by-products of chlorine and chloramine?

# A: Chlorine and chloramine produce similar types of disinfection by-products though the concentrations tend to be much lower when using chloramine.

Chloramine like chlorine can react with naturally occurring material and treatment chemicals to produce disinfection byproducts. Thus, utilities must carefully balance the application of these disinfectants with the formation of by-products of potential health concern, including trihalomethanes (THMs), haloacetic acids (HAAs), and other halogenated and non-halogenated compounds. THMs and HAAs constitute the two largest groups of DBPs by weight and other DBPs typically form at lower levels (Krasner et al., 2006). Chloramine is not as strong an oxidant as chlorine and it generally forms less by-products than chlorine and thus enhances public health protection.

In general, chloramine forms halogenated by-products to a much lower extent than chlorine (Speitel et al., 2004; Baribeau et al., 2006). Specifically, chloramine reduces the production of THMs and HAAs that are formed by chlorine. Typically, HAA formation during chloramination is 5 to 20% of that observed with chlorination (Speitel et al., 2004). Therefore, chloramination improves public health protection by minimizing the formation of regulated THMs and HAAs. SFPUC made the decision to convert to chloramine disinfectant in the distribution system to maintain compliance with the federal drinking water regulations (USEPA 1998 and 2006a).

One possible by-product of using either chlorine or chloramine for disinfection is Nnitrosodimethylamine, or NDMA, typically found at levels 10,000 times lower than THMs. There is no drinking water quality standard set for this compound though California has proposed a Public Health Goal of 3 nanograms per liter (ng/L, parts per trillion). The biggest sources of human exposure to NDMA are tobacco smoke, chewing tobacco, bacon and other cured meats, beer, cheese, toiletries, shampoos, cleansers, interior air of cars, and household pesticides.

Chloramine has greater tendency to participate in chlorine substitution reactions, rather than oxidation reactions, in comparison with chlorine. Substitution reactions are especially prevalent with organic nitrogen compounds (Singer, 1999). Chloramine chemistry is fairly well understood. Although considerable information is available, the complexities of chloramine chemistry with respect to DBP formation are not fully understood (Singer, 1999).

Total Organic Halides (TOX) formation with chloramine ranges from 10 to 20 percent of that observed with chlorine, when chlorine and ammonia are added concurrently (Singer, 1999). At least some of halogenated products are different than those found from chlorination. Overall, DBP formation from chloramination can be minimized by maintaining the distribution system pH as high as practical (Singer, 1999), something that SFPUC has done continually.

Q: How has chloramine performed in SFPUC distribution system so far in terms of control of disinfection by-products?

# A: Monitoring results indicate that since 2004 the concentrations of THMs were reduced in the SFPUC system by at least 50% and high THM and HAA peaks were eliminated. Chloramination has effectively decreased levels of regulated DBPs.

Total regulated four THMs (THM4) concentration was reduced from a maximum of 150 ug/L in individual samples in 2001 and 2003 (free chlorine) collected in the San Francisco Water System down to at less than 60 ug/L (chloramine). The average concentrations of THM4 measured in SFWS since 2004 have been consistently below 45 ug/L. Chloroform is the predominant of four THMs formed in SFPUC system, while the remaining regulated THMs were near or below detection.

The total concentration of five regulated HAAs (HAA5) did not change significantly between 2000 and 2010, regardless of chlorine or chloramine. Levels for individual samples were at or below 40 ug/L and the average is consistently below 30 ug/L. Trichloroacetic acid was the predominant HAA with chlorine, while dichloroacetic acid was the predominant HAA with chloramine. This shift in HAA species is expected and well documented in the literature (Pope et al., 2006; Hong et al., 2007). Pope et al. (2006) pointed out that most dichloroacetic acid formation occurs within treatment facilities that prechlorinate before chloramination, therefore, HAA control strategies in such systems should focus on the chlorination step.

## Q: What is the epidemiological significance of disinfection by-products?

A: There have been numerous epidemiological studies exploring the potential health effects of DBPs in human populations. Consumption of water containing these byproducts has been associated with cancer (Doyle et al, 1997; Bull et al, 1995; Morris et al, 1992) and adverse reproductive outcomes (King et al, 2000; Nieuwenhuijsen et al 2000; Gallagher et al, 1998; Reif et al, 1996; Savitz et al, 1995; Bove et al, 1995; Aschengrau et al, 1993; Fenster et al, 1992; Kramer et al, 1992; Zierler et al, 1992), although some of these studies have not found significant associations with specific outcomes. EPA and CDC believe the benefits of drinking water disinfection outweigh the potential risks from disinfection byproducts. (USEPA, 2009)

Several epidemiologic studies have specifically explored the relationship between THMs and pregnancy loss. (Waller et al, 1998; Swan et al, 1998) More recently a large study did not find an association between THMs exposure and pregnancy loss in three study sites, two of which used chloramination (Savitz et al, 2005). SFPUC is not aware of any studies linking chloramination or specific chloramination byproducts to this health outcome. Chloramination is very effective in controlling THM and HAA formation.

The SFPUC has moved to chloramine as a precautionary measure since it is better than chlorine for controlling the formation of regulated DBPs for which there is evidence of adverse human health effects. Please see the expert opinion on health effects at: <u>the expert opinion on health effects at sfwater.org.</u>

### Q: What is the significance of cyanogen chloride?

A: Cyanogen chloride is a DBP whose formation has been associated with the use of chloramine. However, it will be formed in the presence of any combination of a strong oxidant, ammonia, aromatic amino acids, and chloride. Cyanogen chloride is a respiratory irritant at concentrations in the air above 0.75 mg/m<sup>3</sup>. The small concentrations produced in water treatment would be unlikely to produce these levels in air even in enclosed places such as a shower. The concentrations of cyanogen chloride in drinking water do not approach levels necessary to produce thyroid effects (Bull et al, 2001). Cyanogen chloride is currently unregulated, but the probable regulatory range for cyanogen chloride has been estimated at 60 to 600 ug/L.

In a survey of 35 utilities, the systems that prechlorinated and postammoniated had a cyanogen chloride median of 2.2 ug/L versus 0.4 ug/L for systems that used chlorine only. The concentrations in chloraminated plant effluents ranged from 1 to 11 ug/L versus 0 to 4 ug/L in chlorinated plant effluents (Krasner et al, 1989). Krasner et al (1989) also found that certain DBPs (i.e., haloacetonitriles, haloketones, chloral hydrate, and cyanogen chloride) were not stable in the distribution system where the pH is relatively high (e.g., pH 9) (Singer 1999). Therefore, cyanogen chloride is of no significant concern to SFPUC.

### Q: What are the emerging classes of disinfection by-products of chlorine and chloramine?

A: The research community is focusing on new classes of disinfection by-products that are now detectable in drinking waters thanks to advances in analytical technology. An area of particularly active research in the first decade of the 21<sup>st</sup> century is nitrogenous DBPs, specifically nitrosamines, brominated and iodinated-DBPs. EPA scientists coordinate their research on disinfection byproducts with scientists from many organizations. In accordance with the Safe Drinking Water Act, EPA scientists and decision makers review regulations of disinfection byproducts every six years to determine if they need to be revised. (USEPA, 2009)

### Q: What is the occurrence of nitrosamines in drinking water?

# A: Chloramination has not resulted in increased NDMA levels and NDMA is not an issue for SFPUC based on available data.

Nitrosamines, and the related nitrosamides including the nitrosoureas, are carcinogens that have been recognized as environmental contaminants of potential importance since the 1960s. These compounds have been most closely associated with the use of nitrite salts in food preservation. Active compounds in this class appear to induce tumors in virtually all species in which testing has been conducted (Bull et al., 2001). The occurrence and control of nitrosamines in drinking water is a relatively new research issue and a considerable amount of information is being collected (Najm and Trussell, 2001; Siddiqui et al, 2001; Mitch et al, 2003, Krasner 2009). Nitrosamines in drinking water form at such minute concentrations (parts per trillion) that their detection only recently became possible.

Both chlorination and chloramination have been implicated in reaction mechanisms that result in Nnitrosodimethylamine (NDMA) formation from natural precursors. Furthermore, field observations do not indicate that one method of disinfection necessarily leads to lower NDMA formation and therefore should be preferred (Valentine et al., 2005). A recent national survey of NDMA occurrence and formation detected NDMA in 18 of 21 utilities disinfected with either chlorine or chloramine. The use of chloramine in the distribution system correlated with slightly higher NDMA levels than the use of chlorine: the median for treated drinking water distribution samples was less than 2 ng/L (parts per trillion) for chloraminated water and less than 1 ng/L for chlorinated water (Barrett et al, 2003; Valentine et al., 2005). Baribeau et al (2006) investigated formation of DBPs in chlorinated and chloraminated systems. There were no obvious differences between the concentrations of NDMA measured in chlorinated and chloraminated systems. No particular trend in NDMA concentrations could be identified with increasing water age in a chloraminated system or a chlorinated system. In Scotland, Goslan et al (2009) investigated the occurrence of DBPs in seven chlorinated or chloraminated drinking water systems, finding NDMA at only one chloraminated plant during one season; levels of other N-containing DBPs did not differ between the works using chlorination or chloramination.. Wilczak et al (2003a) observed that sequential application of chlorine followed by chloramine at the treatment plant minimized the formation of NDMA in the distribution system, which is typical practice for SFPUC and many other utilities.

SFPUC voluntarily monitored NDMA in 1999, 2000 and on a quarterly basis since 2004 (immediately following the conversion from chlorine to chloramine). From August 2004 to August 2010, NDMA was detected in 19 of 197 samples (approximately 10 percent of the samples). Of the detections, NDMA levels ranged from 1.3 ng/L to 4.6 ng/L, all below California Notification Level (NL) of 10 ng/L. No federal standard exists for NDMA. One sample in May 2010 of 12 ng/L exceeded California NL. This sample was collected at the treatment plant effluent which was not chloraminated. The sample was collected right after plant startup when higher dose of polymer was applied; therefore it does not represent routine operation. NDMA was not detected in a follow-up sample.

NDMA has not been detected in the Hetch Hetchy raw and treated water regardless of the disinfectant used in the distribution system (either chlorine or chloramine) during the entire monitoring period 1999 - 2010. This is due to the excellent quality of this pristine source water low in organic nitrogen and free from agricultural or municipal run-off. NDMA precursors present in pristine or NOM- or algal-impacted waters are insufficient to generate significant NDMA concentrations (Mitch et al., 2009). NDMA has been detected twice in the treated Harry Tracy WTP water (in 10% of the samples both with free chlorine and chloramine, last time in 2004) at very low levels near the detected three times in the treated Sunol Valley WTP water (in 14% of the samples all with free chlorine, last time in 2010). NDMA has been detected in approximately 25% of the distribution system samples, regardless of the disinfectant used in the distribution system (either chlorine or chloramine), although the levels detected in chloraminated water appear slightly higher than when the system was chlorinated. The source of NDMA is likely the cationic polymer that is necessary for turbidity control at the treatment plants.

Other nitrosamines have not been extensively studied in drinking water; however, recent research suggests that NDMA is the most prevalent nitrosamine, and that the other nitrosamines form at levels that are an order of magnitude or more lower than NDMA. In addition to the voluntary NDMA sampling, NDMA and five other nitrosamines were monitored quarterly in the San Francisco system in 2008 under USEPA UCMR-2. None of the six nitrosamines (NDEA, NDMA, NDBA, NDPA, NMEA, and NPYR) were detected during UCMR-2 sampling. Special sampling was conducted for N-nitrosodiphenylamine, a CCL3 contaminant, in 2003 and 2009. These data were also nondetect.

### Q: What is the occurrence of iodinated disinfection by-products in drinking water?

A: SFPUC system is unlikely to have significant levels of iodo-DBPs because of the low concentrations of bromide and iodide in the raw water. In 2006 SFPUC collected samples from the Harry Tracy Water Treatment Plant (HTWTP) influent and effluent as part of USEPA research survey. Iodo-DBPs are a class of emerging disinfection byproducts, currently of research interest, that may be formed during disinfection if iodide is present in the source

water. Iodoacetic acid (iodo-HAA) and bromochloroiodomethane (iodo-THM) were not detected in the SFPUC treated chloraminated sample. Four other iodoacids and dichloroiodomethane (iodo-THM) were detected in the SFPUC sample at parts per trillion levels near method detection limits. The results obtained in HTWTP water were one of the lowest in the USEPA survey of 23 both chlorinated and chloraminated sampling sites nationwide. Future research could be conducted pending the development of analytical methods and better understanding of the significance of these groups of compounds.

Iodo-DBPs are a new group of disinfection by-products for which the level of toxicity is not well understood. For years scientists have known that all chemical disinfectants will result in the formation of DBPs at some level. More than 500 disinfection by-products have been reported in the literature for the major chemical disinfectants currently used (chlorine, ozone, chlorine dioxide, chloramine), as well as their combinations (Weinberg et al., 2002). The formation of iodinated DBPs is recognized as an important research finding because iodide is present in drinking water supplies throughout the world; for example iodinated THMs have been found in the United States (Weinberg et al., 2002), Australia (Hansson et al., 1987), France (Bruchet et al., 1989), and Spain (Richardson, 2004).

In 2002, the US Environmental Protection Agency conducted a nationwide DBP occurrence study (Weinberg et al., 2002). This study evaluated the occurrence of six iodinated THMs and was also the first to demonstrate the formation of iodinated acids. Iodoacids were detected at one utility that treats high-bromide water and uses chloramine both for disinfection during treatment and for maintaining disinfectant in the distribution system. Plewa et al. (2004) postulated that chloraminated drinking waters that have high bromide and iodide concentrations in the source waters might contain these iodoacids and other iodo-DBPs. Plewa et al. (2004) observed that one of these acids (iodoacetic acid) was more genotoxic to mammalian cells than other DBPs that have been studied in their assay.

These research findings are not of immediate public health concern to SFPUC because: (1) iodoacids have been detected only in one water system with high bromide and likely high iodide content (iodide is not commonly measured while the bromide occurrence database is well developed), (2) iodoacids were detected at a utility that applied chloramine only and it is believed that the use of chlorine before applying chloramine (as the SFPUC does) will allow the chlorine to react with iodide to form iodate and stop iodoacids formation (Plewa et al., 2004, Richardson, 2004). Iodate is not a health concern as it is transformed back to iodide after ingestion (von Gunten, 2003). The study of iodoacids toxicity by Plewa et al. (2004) used *in-vitro* isolated mammalian cells and not *in-vivo* animal or human subjects. This testing approach is typically used as a screening tool to determine candidate chemicals for future *in-vivo* toxicity testing.

lodide occurrence in drinking water sources and its influence on the formation of iodinated DBPs are currently not known. Methods for quantification of iodoacids are under development by the USEPA (Richardson, 2004) and any further studies depend on our ability to measure concentrations of these compounds at the levels of potential concern. Further toxicological studies are warranted (Plewa et al., 2004).

The SFPUC system is unlikely to have significant levels of iodoacids because of the low concentrations of bromide and iodide in the raw water. All waters treated by the SFPUC are chlorinated prior to ammonia addition and chloramine formation, which will further preclude or minimize the formation of iodoacids.

#### Q: What is the occurrence of hydrazine in drinking water?

# A: The SFPUC has not measured levels of hydrazine in its water but, based on the mechanisms of formation, believes that hydrazine formation would be of no significant concern in its chloraminated water.

Najm et al. (2006) evaluated the formation of hydrazine as chloramine by-product. This is the first known study on the subject in drinking water. The project team found that "In a laboratory experiment performed under water and wastewater chloramination conditions, hydrazine formation was below detection when free ammonia was less than 0.2 mg/L." The SFPUC treatment target for free ammonia is 0.03 mg/L, which is consistently met; levels up to 0.10 mg/L are occasionally observed, but less frequently. Based on the report findings hydrazine does not appear to pose a concern. Commercial labs do not test for hydrazine at such low levels (below 10 ng/L) in drinking water. Therefore, Najm et al. (2006) used a computer model simulation to evaluate the impact of major water quality parameters on hydrazine formation. Consistent with the lab results, the model predicted that at pH < 9.5 and free ammonia less than 0.5 mg/L N hydrazine formation would be of no significant concern in chloraminated water. SFPUC operating targets are well below these levels.

## HOUSEHOLD WATER USE

# Q: Does the water chemistry (pH, mineral content) change as a result of chloramine addition?

A: Chloramination, as practiced by the SFPUC, does not affect pH or mineral content.

# Q: Why aren't tap water and bottled water monitored by the same agency? Is bottled water better than tap water?

A: Soft drinks and bottled water are monitored by the federal Food and Drug Administration (FDA) and the California Department of Public Health (CDPH). Tap water is regulated by the USEPA and the CDPH. The act of bottling the water legally makes the water a packaged product, and legally these are all regulated by the FDA, rather than the USEPA and the CDPH. The FDA and USEPA standards can differ and the USEPA regulations and the testing requirements are more stringent than those required of the bottled water by the FDA. Bottled water is oftentimes tap water that has been passed through additional filtration, GAC adsorption, and disinfection steps. However, this does not mean that bottled water is necessarily better than tap water.

50 million empty water bottles are thrown away or recycled every day in America (Morris, 2007), which equals over 18 billion water bottles annually. The manufacture of a single bottle requires more water than the bottle will ultimately hold. The transport of these bottles over hundreds or even thousands of miles adds to the disproportionate ecological impact of bottled water. Many brands of bottled water are superior to tap water and can offer a valuable alternative, particularly when traveling or after a disaster (e.g., earthquake). But economically, environmentally, and in many cases even with respect to disease prevention, they fall short as a replacement for tap water (Morris, 2007). Many plastic water bottles end up in landfills and in the oceans where biodegradation may literally take thousands years contributing to environmental pollution and degradation. SFPUC has designed, built and operates a very efficient water conveyance system, which additionally produces hydroelectric power.

# Q: How much bleach should be added to water for emergency storage? How long to keep water in a closed container as part of earthquake preparedness?

A: Emergency preparedness recommendations are to store an appropriate amount of tap water (as specified by the emergency preparedness brochure) in plastic, airtight, clean containers in a dark cool place. Tap water may be stored without bleach addition and kept for up to six months before it should be replaced. At the time of usage 16 drops of bleach should be added to each gallon of water. The water should be mixed and left to stand for 30 minutes prior to use. In case chlorine odor is objectionable, lemon, lime, or orange juice or fruit (all of which remove chlorine) may be used to improve flavor after allowing 30 minutes for disinfection.

# Q: According to labels for household products, mixing bleach and ammonia is dangerous. Why is it safe for drinking water?

A: Levels of ammonia and chlorine in household products are extremely concentrated (i.e., several orders of magnitude higher than in tap water). It is always dangerous to mix concentrated chemicals together because proportions of the chemicals and the conditions of chemical reactions cannot be controlled in a household setting. Many side reactions can occur when mixing

concentrated household cleaning products and irritants may be formed in these side reactions. That is why these products are clearly labeled with warnings. Conversely, trained and licensed operators carefully add chlorine and ammonia sequentially into the large volumes of continually flowing water at a treatment plant so that the chemical concentrations at the point of mixing are already low and stable. Dissolution of chemicals and formation of chloramine is almost instantaneous and easy to control using on-line instrumentation for the water and chemical flows, pH, and the resulting disinfectant concentration. Water delivered to customers has chlorine concentrations of less than or equal to 2.3 mg/L Cl<sub>2</sub> (parts per million), and ammonia approximately 0.5 mg/L NH<sub>3</sub>-N to ensure slight excess of ammonia to stabilize monochloramine. These are current SFPUC chlorine and ammonia target levels, which may change depending on the operational needs.

### Q: Can one be exposed to chlorine disinfectants in public swimming pools?

# A: Yes, one can be exposed to irritants in swimming pools. Dichloramine and trichloramine may be present in swimming pools where chloramine needs to be converted back to chlorine to provide a stronger biocide necessary for water in contact with multiple bathers.

Chlorine is a stronger disinfectant than chloramine, especially at lower pH. Pool water differs from drinking water because it receives a great many nitrogen compounds in the form of perspiration and urine. From these materials, urea is hydrolyzed to form ammonia compounds. Pool may exhibit chlorine odors and users may experience stinging of the eyes especially in indoor pools and at the water surface in outdoor pools. The chlorine odor and eye stinging are often attributed to overchlorination. In actuality, chlorine odor in pools is a symptom of inadequate chlorine feed rate and chlorine dose, and to operate the pool in the chlorine residual range. Pool odor is an indicator of improper treatment with chlorine and may be a symptom of insufficient pool chemistry management (Connell, 1997). A recent study of indoor and outdoor recreational swimming pools did not detect monochloramine (the distribution system disinfectant used by SFPUC) in samples from laboratory experiments or swimming pools (Li and Blatchley, 2007).

Current research supports the relationship between exposure to trichloramine in indoor swimming pools and adverse effects such as asthma and upper respiratory tract irritation in recreational swimmers, lifeguards and pool attendants.(Li and Blatchley, 2007; CDC, 2007; White, 1999; Bernard et al., 2003; Thickett et al., 2002), The exposure of bathers to chlorine compounds in public swimming pools can usually be minimized by proper pool maintenance, although additional treatment may be necessary (Li and Blatchley, 2007). Proper ventilation at indoor pools and proper chemistry (pH between 7.2 and 7.5 and sufficient chlorine dose to convert to chlorine) minimizes this exposure. Showering before entering the pool reduces the input of contaminants in public pools. In addition, some pools use more expensive disinfection processes such as ozone or UV to reduce exposure to irritants altogether.

### Q: Can one be exposed to chlorine disinfectants in the home shower or bath?

A: Exposures via respiration do not occur from bathing or showering with chloraminated drinking water. Under the slightly alkaline pH conditions typical for drinking water systems, neither chlorine nor chloramine present in drinking water at low concentrations should be appreciably lost to the air from the water in the shower or bath. Showering with chloraminated water poses little risk because monochloramine does not easily enter the air. (USEPA, 2009)

Chloramine is completely dissolved in the water and chlorine would be primarily in its dissolved ionized form of hypochlorite ion. Neither chlorine nor chloramine is highly volatile under these conditions even in hot water. Tests conducted by SFPUC in chloraminated bath and shower water at moderate bathing temperature (100 F, 38 C) indicate a loss of total chlorine of only 3% in the bath to 6% in the shower. This is consistent with expected results for monochloramine. In

cold water (67 F, 20 C), the loss of chloramine in the shower or bath was within the measurement error (i.e., insignificant). Conversely, the loss of chlorine in similar tests was 12 - 18%, at water temperatures between 65 and 105 F. In very hot water directly from the heater at  $135^{\circ}$ F, 100% chlorine was lost in the shower versus only 14% chloramine. Monochloramine is much less volatile, as compared with dichloramine, trichloramine or chlorine. Dichloramine is somewhat volatile (20%) but cannot form under typical conditions in the distribution system. Trichloramine is 100% volatile but cannot form in the chloraminated drinking water in the absence of chlorine (White, 1999). Other reactions may be taking place when water is exposed to air in the shower; for example, reactions with oxygen in the air could be responsible for measured differences.

Chloramination is expected to reduce an overall exposure of the bathers to residual chlorine from the water in home bathrooms, as compared with chlorinated distribution systems. Chloramination is also effective in controlling the formation of volatile trihalomethanes (THMs) such as chloroform, a chlorination by-product. People may get significant inhalation exposure to THMs when showering in water with high concentrations of chloroform (Backer et al., 2007). Chloroform concentrations in San Francisco's water were reduced at least 50% as a result of chloramination.

Water at home contains relatively low concentrations of the disinfectants. Any concerns about exposure can be further minimized by increasing ventilation in the bathroom (e.g., opening a window in the bathroom), taking a bath instead of a shower (less contact between water and air), and reducing water temperature (i.e., taking a warm shower or bath instead of using hot water).

### Q: Is there a Material Safety Data Sheet for chloramine?

A: There is no Material Safety Data Sheet (MSDS) for chloramine because chloramine is not sold commercially and is not available in a concentrated form either as a liquid or solid. In the SFPUC system, chloramine is generated on-site from chlorine and ammonia; therefore SFPUC does not need to have an MSDS for chloramine but does have the MSDS for chlorine and ammonia, as these are the materials that employees handle. SFPUC currently adds 2.3 mg/L of chlorine and

0.5 mg/L of ammonia to form a target chloramine residual of 2.3 mg/L. To put the MSDS information in its proper context, the maximum levels for these chemicals in the drinking water will likely not exceed 4 mg/L for chlorine and 1 mg/L for ammonia. The concentration of chlorine that employees work with is about 13% or 163,000 mg/L, and for ammonia is about 19.0% or 176,000 mg/L.

Information contained on MSDS sheets should be interpreted in context. The US Occupational Safety and Health Administration (OSHA) requires companies to provide an MSDS if they use a material in their workplace. The MSDS is aimed at protecting workers from acute exposure to concentrated chemicals, and has little relevance for drinking water consumers. In addition, there is very little oversight in the quality of data contained in an MSDS and the mere existence of an MSDS does not imply high quality of information. Customers have sometimes brought up an MSDS for chloramine-T, which comes up in Internet searches for chloramine. Chloramine-T is sold commercially, but it is an antiseptic with a different chemical formula of (sodium p-toluenesulfonchloramine), and it is not used for drinking water disinfection.

#### Q: Can chloramine promote the growth of bacteria in home point of use devices?

## A: Regrowth of bacteria in *well-maintained* point-of-use devices (POUD) should not be a concern within the SFPUC service area.

The regrowth of bacteria in customers' plumbing is controlled if there is adequate disinfectant residual (no stagnation and proper maintenance of point of use devices). Based on the review of SFPUC water quality data, chloramine disinfectant residuals are more stable in the San Francisco water system than chlorine and chloramine better controls regrowth of coliform and heterotrophic plate count (HPC) bacteria in the distribution system than chlorine. The study of *Legionella* occurrence in SFWS conducted by the Centers of Disease Control and Prevention (CDC), SFPUC, SF Department of Public Health, California Department of Health Services and the California Emerging Infections Program reported by Flannery et al. (2006) showed that chloramine virtually eliminated *Legionella* in large buildings in San Francisco.

Strickhouser et al. (2006) evaluated the regrowth of *Legionella pneumofila* and *Mycobacterium avium* under conditions of increased temperature of 37 C simulating the conditions of the water heaters. The samples were spiked with domestic water heater water and outdoor pond water. No regrowth of bacteria was detected for samples with chlorine above 0.25 mg/L and chloramine above 0.4 mg/L. The regrowth of bacteria occurred in samples without the disinfectant and especially for samples with the high levels of free ammonia (1 mg/L), simulating the conditions of stagnant water with no disinfectant residual.

The Surface Water Treatment Rule (SWTR, USEPA 1989a) specifies a minimum disinfectant residual of 0.2 mg/L for chlorine and 0.4 mg/L for chloramine in the distribution system. These disinfectant concentrations may control bacterial growth in the bulk water but may be inadequate to control biofilm bacterial growth. There is evidence that a chloramine residual can exert better control of biofilm bacterial growth than does chlorine (Flannery et al, 2006). Maintaining an adequate disinfectant residual limits the extent of development of a biofilm, but the disinfectant residual necessary to do so varies with changes in source water quality and with the performance of treatment processes in removing particulates, nutrients, and microorganisms. Maximum biofilm bacterial densities occur when disinfectant residuals in the bulk water are maintained within 1.6 to 1.8 mg/L (AWWA, 2006c). SFPUC maintains chloramine disinfectant in San Francisco Water System storage reservoirs between 1.5 and 2.3 mg/L. Typical levels of free ammonia in the SFPUC distribution system are less than 0.1 mg/L N. Given these results, regrowth of bacteria in well-maintained point-of-use devices (POUD) should not be a concern within the SFPUC service area.

## CHLORINE AND CHLORAMINE REMOVAL FROM WATER

Q: Is it necessary to remove disinfectants from drinking water in a home setting?

A: No, chlorinated and chloraminated water is safe for people and animals to drink, and for all other general uses including bathing. EPA believes that drinking water disinfected with monochloramine that meets regulatory standards is safe to use and it does not need to be removed. (USEPA, 2009) The removal of either chlorine or chloramine from drinking water is not necessary for public health but some customers may elect to do so for common household purposes based on personal preference.

Chloramine is not a persistent disinfectant and decomposes easily from a chemistry point of view (Valentine et al, 1998) but for water supply purposes chloramine is stable and it takes days to dissipate in the absence of substances exerting chloramine demand (Wilczak et al., 2003b). Therefore, it is not practical to remove chloramine by letting an open container of water stand because it may take days for chloramine to dissipate.

However, chloramine is very easily and almost instantaneously removed by preparing a cup of tea or coffee, preparing food (e.g., making a soup with a chicken stock). Adding fruit to a water pitcher (e.g., slicing peeled orange into a 1-gal water pitcher) will neutralize chloramine within 30 minutes. If desired, chloramine and ammonia can be completely removed from the water by boiling; however, it will take 20 minutes of gentle boil to do that. Just a short boil of water to prepare tea or coffee removed about 30% of chloramine. Conversely, chlorine was not as consistently removed by boiling in SFPUC tests.

If desired, both chlorine and chloramine can be removed for drinking water purposes by an activated carbon filter point of use device that can be installed on a kitchen faucet. If desired, both chlorine and chloramine can be removed for bathing purposes by dissolving Vitamin C in the bath water (1000 mg Vitamin C tablet will neutralize chloramine in an average bathtub). SFPUC does not recommend that customers remove disinfectants from drinking water. Customers desiring to do so should consult with their physician.

Q: Why is it important to remove both chlorine and chloramine from the tap water used for hemodialysis treatment of kidney dialysis patients?

A: While tap water is safe for drinking, bathing and other household uses, it is not acceptable for use in hemodialysis. People can safely drink chloraminated water because their digestive process neutralizes chloramine before it enters the bloodstream. But, just like with fish that take chloramine directly into their bloodstream through their gills, the membranes used for hemodialysis do not remove chloramine. In fact, the hemodialysis fluid must be free of even traces of compounds that are safe to drink.

Residual disinfectants, particulates, organics, ions and remaining microorganisms are removed prior to hemodialysis units. The average person consumes approximately 2 liters of water per day in different forms (juice, coffee, etc.), whereas a patient on hemodialysis uses anywhere from 90 to 190 liters of water (in the dialysate) per treatment. In the dialyzer the blood is separated from the dialysate by a semi-permeable membrane, which is only selective with respect to molecular size but is not contaminant specific. The recommended maximum concentrations for hemodialysis water are 0.5 mg/L chlorine and 0.1 mg/L chloramine (Amato, 2005).

Carbon adsorption is used to remove either chlorine or chloramine because both of them destroy red blood cells. Chlorine and chloramine are not removed by the reverse osmosis membrane and can also damage the membrane. At least two carbon beds in series are required for a total of 10 minutes empty bed contact time at the maximum flowrate to remove either chlorine or chloramine, followed by a 1 to 5-um filter to remove carbon fines before the reverse osmosis unit (Amato, 2005).

### Q: Why are some industrial users advised to remove chloramine but people are not?

A: Chloramine is added to the water for public health protection. Distilled or deionized water is required for many industrial processes and products. On the other hand, distilled or deionized water would not be appropriate for distribution and consumption due to its corrosivity, taste, and health impacts. Three special user groups, kidney dialysis patients, aquarium owners, and businesses or industries that use water in their manufacturing processes may need to remove chloramine from the water prior to use as they did with chlorine. Products to remove or neutralize chloramine are readily available.

Biotechnology companies and breweries must take treatment precautions for both chlorine and chloramine. Beer manufacturers must remove chlorine and chloramine because either will inhibit the growth of yeast. Photo labs may need to remove chlorine or chloramine from the water because it may interfere with the chemicals used to develop the film and may adversely impact the colors in the final print. Chip manufacturers and pharmaceutical companies have very specific water quality requirements for their manufacturing process.

### Q: What methods are used by the industry to remove chloramine and ammonia?

A: In the water industry, the most widely practiced methods of dechlorination are the addition of reducing agents, for example, sulfite compounds, hydrogen peroxide and ascorbic acid - Vitamin C (Tikkanen et al., 2001). Granular activated carbon (GAC) filters are also used for dechlorination (Kirmeyer et al., 2004). Breakpoint chlorination is used routinely by some utilities to remove chloramine and/or ammonia in the source water or to avoid blending chlorinated and chloraminated water. During breakpoint chlorination, excess chlorine in chloraminated water consumes the available ammonia and the remaining disinfectant residual exists as chlorine.

### Q: How much time will it take for chlorine and chloramine to dissipate when left standing?

A: While both chlorine and chloramine residuals decrease with time, chloramine decreases more slowly than chlorine. Chlorine may take days to dissipate in a pitcher left on a counter and it will take longer for chloramine. The decomposition rate will be faster when the water is exposed to air and sunlight (Wilczak et al., 2003b). Chloramine, like chlorine, will eventually dissipate completely over time but it is not practical to let the water sit for it to dissipate. Other methods may be used to remove chloramine if desired for aesthetic reasons.

### Q: Can chlorine and chloramine be removed by boiling?

A: Boiling the water for 20 minutes will remove chloramine and ammonia. SFPUC does not recommend for customers to boil water for such long periods of time because it is not necessary from a public health perspective and poses risk of scalding. However, such tests demonstrate that chloramine is not a persistent chemical, which does not remain in the water after cooking.

Additionally, many foods and drinks rapidly neutralize chloramine without the necessity of boiling (e.g., tea, coffee, chicken stock, orange juice, etc.).

#### Q: Can charcoal filters remove chloramine?

A: Charcoal or granular activated carbon (GAC) filter can reduce chloramine concentrations of 1 to 2 mg/L to less than 0.1 mg/L. The GAC filter may be followed by a reverse osmosis (RO) filter to remove the carbon fines. RO should not be used alone as chloramine will pass through the membrane and may damage the RO membrane elements (some RO units are resistant to chlorine and chloramine). A GAC filter will remove chloramine, allowing RO to effectively remove other constituents.

#### Q: Are GAC filters certified and if so by whom?

A: As a public agency, the SFPUC does not test, endorse or recommend specific water filtration products. Contact the NSF International, a nonprofit organization that independently tests and certifies drinking water filtration products. Website: <u>NSF International</u>, phone: 800-673-8010.

The removal of chloramine is not necessary from a public health perspective; however, some customers may chose to remove either chlorine or chloramine for drinking purposes. Several units are certified and listed on the NSF International website <a href="http://www.nsf.org/Certified/DWTU/">http://www.nsf.org/Certified/DWTU/</a> (accessed August 2010) for the removal of chloramine: smaller units certified at flows below 1 gpm (service cycle from 300 to 1600 gal) are appropriate for drinking water applications at a kitchen faucet, larger units certified at 5 gpm (service cycle from 15,000 to 84,000 gal) could be used for other uses if desired. NSF International verifies claims of 85% chloramine removal of 3 mg/L. GAC filters, if desired, need to be installed on the kitchen sink cold water tap as filter effectiveness decreases in warm or hot water. The removal of disinfectant from the water may increase the potential of bacterial regrowth in plumbing.

#### Q: Can Vitamin C be used to remove chlorine and chloramine for bathing purposes?

A: Exposures via respiration do not occur from use of chloraminated drinking water. Based on personal preference, some individuals may choose to reduce exposure to chlorine or chloramine. Vitamin C (ascorbic acid) has recently been included in AWWA Standard (AWWA, 2005b) as one of the methods for dechlorination of disinfected water mains. SFPUC and other utilities have used Vitamin C for dechlorination prior to environmental discharges of chlorinated and chloraminated water. Since ascorbic acid is weakly acidic, the pH of water may decrease slightly (Tikkanen et al., 2001). Ascorbic acid has been used for a long time as one of the dechlorinating agents for preservation of chlorinated or chloraminated water samples for laboratory analysis.

The removal of chloramine is not necessary from a public health perspective; however, some customers may chose to remove either chlorine or chloramine for bathing purposes. There are no NSF International certified point of use devices utilizing Vitamin C; however SFPUC determined that 1000 mg of Vitamin C (tablets purchased in a grocery store, crushed and mixed in with the bath water) remove chloramine completely in a medium size bathtub without significantly depressing pH. Shower attachments containing Vitamin C can be purchased on the Internet, as well as effervescent Vitamin C bath tablets. The 1000 mg effervescent Vitamin C tablets dissolved readily without residue but may depress pH more than regular Vitamin C tablets purchased in grocery stores. Some shower attachments with Vitamin C marketed on the Internet are effective in removing chloramine; however, the claims posted on the Internet as to their replacement frequency

appear to overestimate the duration when the shower attachment is effective. There are reports of the benefits of Vitamin C for skin care (Griffith, 1998) and various cosmetics are available in stores that contain Vitamin C. SFPUC does not recommend for customers to use Vitamin C for bathing purposes and anyone desiring to do that should consult with their physician.

### Q: What are other simple methods to remove chloramine for drinking water purposes?

A: The removal of chloramine is not necessary from a public health perspective; however, some customers may choose to remove chloramine for aesthetic reasons. Placing a few slices of fruit (e.g., orange, lime, lemon, mango, strawberries) or vegetable (cucumber) in a water pitcher will effectively dechlorinate the water within a few hours. A peeled and sliced medium size orange can be used for a 1-gal water pitcher and will completely dechlorinate the water in 30 minutes. The fruit can then be removed from the water. The water pH will become closer to neutral or acidic (if lime or lemon is used). The ammonia will not be removed but most of the fruits contribute some or more ammonia than the drinking water.

Preparing a cup of tea (black, green, caffeinated, decaffeinated, and herbal) also removes chloramine, as does coffee prepared in a common coffee maker.

### Q: What are the methods for removing chloramine from fish aquariums?

A: Just as with chlorine, chloramine can harm saltwater and freshwater fish, reptiles, shellfish, and amphibians that live in water, because they take chloramine directly into their bloodstream through their gills. People and animals that don't live in water can safely drink chloraminated water because their digestive process neutralizes chloramine before it enters the bloodstream. Effective procedures are available to remove chloramine and ammonia. Commercial establishments and hobbyists involved in fish rearing need to take precautions to prevent losses. There are two methods that can be used to remove or neutralize chloramine before adding water to a fish tank, pond, or aquarium: (1) GAC filtration system specifically designed to remove chloramine, or (2) conditioner or additive that contains a dechloraminating chemical for both ammonia and chlorine. Products are available at local pet and aquarium supply stores. Residential and commercial fish owners are advised to verify which method is best for them with their pet store or aquatic/aquarium retailer.

If too much dechlorinating agent is added to the aquarium or pond water, it may bind up the oxygen in the water. In this case, the fish may suffocate. It is important to carefully follow the label instructions.

## HUMAN PHYSIOLOGY

# Q: What is the position of the regulatory agencies on the use of chloramine for drinking water disinfection?

A: The California Conference of Local Health Officers (CCLHO) joined the California Department of Public Health and the US Environmental Protection Agency (USEPA) in endorsing the use of chloramine as a safe alternative to chlorine in the residual disinfection of public drinking water supplies. In February of 2004, the San Francisco Public Utilities Commission (SFPUC) changed the drinking water residual disinfectant from chlorine to chloramine. Using chloramine in SFPUC drinking water results in lower levels of potentially harmful disinfection by-products than were present with the use of chlorine.

Chloramine is a more effective distribution system disinfectant than chlorine. It has been used extensively in California, the U.S., and around the world for decades. SFPUC was the last major water agency in the Bay Area to switch to chloramine in February 2004. Using chloramine as a distribution system disinfectant allows SFPUC to comply with the USEPA regulations regarding allowed levels of disinfection by-products in drinking water. The decision to change to chloramine was made in conjunction with 29 wholesale water agencies represented by the Bay Area Water Supply and Conservation Agency (BAWSCA) after careful analysis of current scientific information about the risks and benefits of chlorine and chloramine.

### Q: What happens when chloramine is ingested?

A: When people ingest chloramine, the chloramine is broken down quickly in the digestive system to chloride and ammonia. The chloride is eliminated through the urine, and the ammonia is transformed to urea in the urea cycle. Whether it comes from the breakdown of chloramine or the breakdown of proteins in foods like hamburger or tofu, ammonia is transformed to urea in the urea cycle. Ammonia does not bioaccumulate.

#### Q: Is there an impact of chloramine on human metabolism?

A: There is evidence that chloramine in the concentrations that are present in drinking water has no effect on human metabolism. A study conducted in 1993 and published in the peer-reviewed journal Environmental Health Perspectives showed no effects of chloramine ingestion at levels of 2 mg/L. Healthy men were randomized to consume 1.5 liter per day of either distilled water, water containing 2 mg/L chloramine, or water containing 15 mg/L chloramine for four weeks. At the end of the study, the men who were drinking 2 mg/L chloramine, showed no difference in total cholesterol, triglycerides, HDL cholesterol, LDL cholesterol, apolipoproteins A1, A2, or B, compared to the men drinking distilled water. The 2 mg/L study group had no difference in thyroid metabolism compared to the distilled water group. The men who drank 15 mg/L chloramine had no differences except that their plasma apolipoprotein B levels, (a protein associated with LDL cholesterol) had risen by about 10%, whereas the men drinking distilled water and the men drinking water with 2 mg/L chloramine had their plasma apoliporotein B levels drop slightly. The authors suggested that this finding may be due to chance (Wones et al., 1993). EPA's standard for monochloramine is set at a level where no digestive problems are expected to occur. An important characteristic of monochloramine is that any amount ingested quickly leaves the body. (USEPA, 2009)

Another study found that 10 healthy male volunteers experienced no biochemical or physiochemical response after drinking water treated with chloramine at concentrations up to 24 mg/L and compared to a control group (Lubbers et al., 1981). Typical levels of chloramine in drinking water in SFPUC system are between 1 and 2 mg/L Cl<sub>2</sub>.

### Q: What happens when chloramine is inhaled?

# A: Monochloramine is preferentially created in the SFPUC disinfection process, and this compound is soluble and stable in the water. Monochloramine does not volatilize to any significant extent in a shower or bathing environment.

Vikesland et al (2001) showed that at 35 C and pH 7.5, monochloramine has a half-life of 75 hours. With this long half-life, the concern about inhalation exposures is unwarranted. The half-life of chloramine can be even longer (several weeks) in high quality waters at lower temperatures and slightly alkaline pH values typical for drinking water distribution systems (Wilczak et al., 2003b).

The Occupational Safety and Health Administration (OSHA) documents for concentrated chemicals and studies investigating exposure to chlorine and trichloramine at swimming pools in Europe are not relevant to drinking water. Monochloramine is highly soluble in water and loss to evaporation is minimal. Dichloramine is a little more volatile but it is not present in SFPUC drinking water-- based on the presence of free ammonia, the pH range, and the extent of loss of disinfectant due to aeration. It is impossible for highly volatile trichloramine to exist in a chloraminated drinking water system without free chlorine (White, 1999). There is no record of inhalation concerns in the water industry.

SFPUC performed bench top tests to estimate how much chlorine or chloramine may be lost to volatilization or reactions with the air or other constituents in a bath or shower, finding that chloramine loss in the shower or bath was minimal as compared with chlorine, which was more volatile at all tested temperatures. At shower temperature of 100  $^{\circ}$ F (38  $^{\circ}$ C), which is typical for bathing, less than 8% of chloramine was lost from the water in the bath or shower, which is consistent with the literature. In chlorinated water, 12 to 94% of the chlorine was lost in the shower or bath was within the measurement error (i.e., insignificant). Relatively less chloramine was lost in the shower compared with chlorine.

### Q: Can chloramine be absorbed through skin during bathing?

A: There have been no published studies on the absorption of chloramine through the skin, in either animals or humans (USEPA 1994). This is likely because there is no evidence that chloramine would come out of solution in the water to enter through the skin.

### Q: What is the damage to blood cells by chloramine?

A: If chloramine enters the blood stream directly, it combines with hemoglobin (red blood cells) so it can no longer carry oxygen. This can occur if chloramine is not removed from water used in dialysis machines but cannot happen by drinking chloraminated water. Both chlorine and chloramine need to be removed from kidney dialysis water.

### Q: Can one safely wash an open wound with chloraminated water?

A: Yes. It is safe to use chloraminated water in cleaning an open wound because virtually no water can enter the bloodstream that way (Kirmeyer et al., 2004). In dialysis patients, blood may come into direct contact (via a semi-permeable membrane) with between 90 and 190 liters of water in a single session. Even if a person soaked a bleeding wound in one liter of water at the typical concentration of 2 mg/L for several hours the wound would be exposed only to the 2 milligrams of chloramine in the liter. Not all of that would be absorbed into the bloodstream via the wound, and even if it were, it would still not be enough to make any difference in the usual level of hemoglobin that is available to carry oxygen in the bloodstream.

### Q: Can chloramine and ammonia bioaccumulate in the body?

A: Chloramine and ammonia do not bioaccumulate in the body. Chloramine is broken down quickly in the digestive system and eliminated through the urine. The breakdown product ammonia is converted to urea in the urea cycle. All proteins that people ingest are broken down into ammonia and converted to urea in the same way. These products do not bioaccumulate. Chloramine is not a persistent chemical and is neutralized rapidly by common drinks (e.g., tea, coffee, juices) or foods (e.g., chicken stock).

### Q: Is ammonia toxic and/or digestible?

A: Ammonia, in the concentrations used for drinking water disinfection, is not toxic. Ammonia is not of direct importance for health in the concentrations to be expected in drinking-water. (WHO, 2003) Whether it comes from the breakdown of chloramine or the breakdown of proteins in foods like hamburger or tofu, ammonia is transformed to urea in the urea cycle. Ammonia does not bioaccumulate. About 99% of metabolically produced ammonia is absorbed from the gastrointestinal tract and transported to the liver, where it is incorporated into urea as part of the urea cycle. Urea formed in the liver is absorbed by the blood, transferred to the kidney, and excreted in urine (WHO, 2003)

Many foods contain ammonia, and the exposure via drinking water is a small fraction of that in other foods. Water typically contains about 2 mg/L chloramine and less than 1 mg/L ammonia, typically 0.5 mg/L NH<sub>3</sub>-N, so ingesting 1 liter of water results in ingestion of less than 1 mg NH<sub>3</sub>. By comparison, a one-ounce serving of cheddar cheese contains about 31 mg NH<sub>3</sub> (derived from Rudman et al., 1973). The estimated daily ammonia intake through food and drinking-water is 18 mg, by inhalation less than 1 mg, and through cigarette smoking (20 cigarettes per day) also less than 1 mg. In contrast, 4000 mg of ammonia per day are produced endogenously in the human intestine. Ammonia is a key metabolite in mammals. It has an essential role in acid–base regulation and the biosynthesis of purines, pyrimidines, and non-essential amino acids. It is formed in the body by the deamination of amino acids in the liver, as a metabolite in nerve excitation and muscular activity, and in the gastrointestinal tract by the enzymatic breakdown of food components with the assistance of bacterial flora (WHO, 2003).

## SPECIFIC HEALTH CONDITIONS

# Q: What types of evidence are taken into account when evaluating the toxicity of drinking water disinfectants?

A: Three different kinds of evidence are available with regard to the potential adverse effects of disinfectants in drinking water: (1) information from animal testing; (2) information from feeding studies in humans; and (3) information from epidemiologic studies. The Integrated Risk Information System (IRIS) provides a summary of the USEPA's risk assessment of chloramine. The summary includes information on oral toxicity, chronic exposure and carcinogenicity of chloramine, based on human and animal studies. IRIS was updated with a comprehensive literature review in 2005, which determined that no new information is available to reconsider the conclusions made regarding reference doses or possible carcinogenicity (USEPA, 1992).

# Q: What is the evidence that drinking or bathing in chloraminated water does not cause health problems? Why haven't there been long-term studies of the health effects of chloraminated water?

A: The Integrated Risk Information System (IRIS) provides a summary of the USEPA's risk assessment of chloramine. The summary includes information on oral toxicity, chronic exposure and carcinogenicity of chloramine, based on human and animal studies. The oral reference dose for chloramine of 0.1 mg/kg/day is based principally on the National Toxicology Program studies in rats and mice that were published in 1992. (US DHHS, 1992) The rat studies found "no clinical changes attributable to consumption of chloraminated water" and "no non-neoplastic lesions after the 2-year treatment with chloraminated water." The mouse studies had similar results (USEPA, 1992). One study in humans found no acute effects on lipid and thyroid metabolism associated with ingestion of chloraminated water at 2 mg/L concentration (Wones et al., 1993). EPA evaluated monochloramine primarily through an analysis of human health and animal data. EPA's monochloramine standard is set at a level where no human health effects are expected to occur. (USEPA, 2009)

Both chlorination and chloramination result in the formation of disinfection byproducts, although fewer halogenated by-products are formed with chloramine. Some studies have looked at the relationships between different health outcomes and the use of chloraminated water compared to water that is not chloraminated. One study (Zierler et al., 1988) showed that people who consumed water disinfected with chloramine had lower risk of bladder cancer compared to people who consumed chlorinated water. This result is likely due to the fact that chloraminated water has fewer disinfection byproducts than chlorinated water. In 1993, McGeehin and colleagues published a study finding that the longer people were exposed to chloraminated surface water, the lower their risk of bladder cancer. The study also found that the risk of bladder cancer among those exposed to chloraminated water (McGeehin et al., 1993), More recently a large study did not find an association between disinfection byproduct exposure and pregnancy loss in three study sites, two of which used chloramination (Savitz et al., 2005).

Another study by Zierler et al (1986) found a slightly increased mortality due to pneumonia and influenza in cities that use chloramine versus those that use chlorine. In the 20 years since this study was published, these results have never been replicated, pointing to the likelihood of alternative explanations for these findings, which are well discussed in the manuscript (e.g. that

differences in reporting or recording deaths could have led to these results, or that other differences such as smoking, occupational exposures, or other environmental differences could have explained the finding). A recent study of *Legionella* showed that chloramine has a beneficial effect in that it virtually eliminated the presence of *Legionella* species in San Francisco (Flannery et al 2006). Harms and Owen (2004) received a number of inquiries on the following topics prior to chloramine conversion at a large water utility in Florida: contact lenses, immune deficiencies, allergies, dermal absorption of chlorine and chloramine, ulcers and digestive disorders. A review of literature and inquiries to national experts found no indication that chloramine was related to or had any impacts on these topics. Harms and Owen (2004) conducted a survey of chloramination practice among 63 utilities nationwide (out of 111 utilities contacted): 17 respondents listed medical issues as a potential concern but identified none as a problem in practice, disinfection efficiency was identified by 15 respondents as a potential concern but none in practice.

Q: Can drinking or bathing in chloraminated water cause chronic or acute health conditions, including buildup of fluid in lungs, pulmonary edema, death, blood in stool, pain, heart failure, blue-baby syndrome, weight loss, weight gain, hair loss, depression or oral lesions?

A: Presently, there is no evidence in the medical literature that links chloraminated drinking or bathing water to any of these health conditions. Lack of evidence does not necessarily imply that chloramine is not related to any of these conditions, however the likelihood of a relationship to these health conditions is minimal, principally because there is also no evidence that exposure to chloramine from drinking or bathing water is occurring in a way that people are not able to deal with physiologically.

For example, when drinking water is ingested, chloramine gets broken down. The chloride is eliminated through the urine, and the ammonia is transformed to urea in the urea cycle. There is also no evidence that chloramine would be absorbed to the bloodstream through the skin, as such, there have been no published studies on the absorption of chloramine through the skin, in either animals or humans (USEPA, 1994). There is no evidence that chloramine volatilizes in the shower. There is always the possibility that individuals have specific hypersensitivities to chemicals in their environment, however there is no evidence that any of these alleged health effects occur on the population level. People with individual health problems may wish to discuss treatment alternatives with their doctors. Chloramination is not a new technology. Chloramine has been used as a drinking water disinfectant for over 90 years (chlorine for 100 years). SFPUC staff is committed to tracking research and publications regarding chlorine, chloramine and other disinfectants and their potential health effects.

The concerns of chloramine being a respiratory irritant may be based on a concern that one can be exposed to dichloramine and trichloramine in their shower or bath, however these chloramine species do not form in the shower, bath or drinking water (see Dr. Richard Valentine's opinion of chloramine chemistry at sfwater.org).

The conditions to form dichloramine are: pH range of 4 to 6 (at 5:1 - 7.6:1 chlorine to ammonia weight ratios) or pH range 7 to 8 (at a 10:1 weight ratio) (Kirmeyer et al, 2004). The conditions to form tri-chloramine are at pH < 4.4 at weight ratios greater than 7.6:1 (Kirmeyer et al, 2004). The conditions to form either dichloramine or trichloramine do not exist in the SFPUC distribution system. SFPUC maintains slightly alkaline water pH in the distribution system for corrosion control (the target is 8.6 to 9.4 depending on the water source), and a minimum of 8.2 is required by the California Department of Public Health (CDPH). The pH is stable in the system and does not drift

appreciably in spite of low alkalinity and low mineral content of SFPUC waters. SFPUC provides rigorous quality control to maintain a target chlorine to ammonia-nitrogen weight ratio of 4.5 - 4.9:1 at the point of chloramine (monochloramine) formation. This ratio may decrease slightly in the distribution system as chloramine demand is exerted during water transmission and storage.

Both dichloramine and trichloramine are short lived and even if trace amounts were formed, any of these chloramine species would not persist to impact customers. Dichloramine and trichloramine will not form as long as proper pH of the water is maintained above the range of their formation, and as long as minimum free ammonia is present to maintain chlorine to ammonia weight ratio less than 5:1.

Some water systems monitored for mono-, di-, and tri-chloramine; however, these monitoring programs were discontinued because di- and tri-chloramine were never found. Water quality labs at water utilities typically do not speciate chloramine but measure total chlorine.

Studies describing the fate of chloramine in ambient air do not exist. In the air phase, it would be expected that chloramine would dissipate due to advection and dilution and would be subject to reaction, although no information has been located characterizing reactions for chloramine in a gaseous state. Various studies indicate that chloramines are thermodynamically unstable and susceptible to photolysis. Monochloramine and dichloramine are very water soluble and are thus susceptible to removal from the atmosphere by rain (Environment Canada, 2001). Inorganic chloramine fate is governed largely by water-phase processes (Environment Canada, 2001).

#### Q: Does chloramine cause asthma?

A: There is no evidence that chloraminated drinking water causes or exacerbates asthma symptoms. Monochloramine does not enter the air easily and therefore would be difficult to inhale. Breathing problems associated with trichloramine and indoor swimming pools have been reported. (USEPA, 2009) While some studies have found links between nitrogen trichloride (trichloramine) and asthma symptoms, no studies have demonstrated an association between exposure to chloramine in public drinking water supplies and asthma symptoms. This is because trichloramine cannot exist in SFPUC chloraminated drinking water in the absence of free chlorine.

Many different environmental conditions are responsible for asthma and its incidence is increasing worldwide, particularly in developing countries (where chloramine is not typically used). Factors including second hand tobacco smoke, air pollutants, occupational exposures, microbes, dietary factors, and allergens such as dust mites, cockroaches, and cat dander may contribute to worsening existing asthma conditions (Eder *et al.*, 2006).

#### Q: Does chloramine cause dry skin, skin rashes?

A: The San Francisco Department of Public Health (SFDPH) literature review in 2004 indicated that skin rashes have not been associated with exposure to chloramine. An updated review in 2007 confirmed that no additional evidence of any association between chloramine and skin complaints has been published in the peer-reviewed medical literature. Approximately 10% to 12% of the population experiences dermatitis on a given day. Dermatitis may be caused by any number of inherited and environmental factors, including: soap, detergents and any prolonged wet work, strong chemical cleaning products including concentrated oxidants and disinfectants (e.g., chlorine bleach), paints, solvents, glues and resins, citrus fruits and vegetable juices, including tomato, onion and garlic, acids and alkalis, abrasive dust from stones, bricks, cement, sand or soil, nickel which may be found in jewelry, cutlery and coins, perfume and fragrances in toiletries and skin care

products, plants, particularly chrysanthemums, primula and grass, rubber (latex), which can be found in some protective gloves, the adhesive used in sticking plasters, metal primers and leather, molds, and pharmaceutical products.

A review of the San Francisco Public Utilities (SFPUC) water quality customer complaints database for the time period 2002 - 2007 has not revealed any increased trends in customer complaints regarding water quality or general health due to chloramine. The SFPUC Water Quality Division (WQD) typically receives and responds (with on-site inspector follow-up) to approximately one customer complaint per day on average from the San Francisco Water System; this call volume did not change in the time period 2002 – 2006 in any water quality category. One exception was dirty water complaints, which decreased after chloramine conversion due to improved water quality maintenance practices implemented for chloramine conversion.

The customer complaints/inquiries at other utilities that converted to chloramine in recent years were that "skin feels dry or scalp itches more". These utilities felt that customers had made an association between a known change and an unrelated condition. Calls with similar complaints lasted for a couple of months. The response to known changes in water treatment procedures has been studied and documented (Lamberg et al., 1997; Lyons et al., 1999).

Skin complaints associated with municipal drinking water are not uncommon; however there is no evidence of a link between any specific water quality parameter and such complaints (du Peloux Menage & Greaves, 1995; Bircher, 1990). An investigation by the San Francisco Department of Public Health of 17 people in the SFPUC service area, mostly from suburban areas served by agencies purchasing water from SFPUC, who had skin irritations and symptoms of dermatitis found that it was unlikely that the symptoms were due to any common cause, including exposure to the chloraminated drinking water (Weintraub et al, 2006). EPA believes that water disinfected with monochloramine that meets regulatory standards has no known or anticipated adverse health effects, including skin problems. (USEPA, 2009)

# Q: If chloramine is not a cause of skin irritation symptoms reported by people, what other reasons might explain why some people experience fewer symptoms when they shower or bathe with water that has not been chloraminated?

A: When people reduce the frequency or change the location that they bathe, or when they bathe using bottled water, they are not just changing the quality of the water they are using. They are also changing many other things that may have been responsible for symptoms that they may believe were related only to the water. For example, the temperature of the water may be different, the types of cleaning products that are used in each location may differ, the types of soaps and lotions that the person is using may have changed, the length of time spent in the shower or bath may have been reduced, or other environmental allergens that were present in one location may not be present in the other. The American Academy of Dermatology recommends reducing the duration, temperature and frequency of baths and showers to help people who experience dry skin, itchiness, and other problems with their skin (American Academy of Dermatology, 2006).

#### Q: Is chloramine a carcinogen?

A: The USEPA has not classified chloramine as to its carcinogenicity because there is inadequate human data and equivocal evidence of carcinogenicity from animal bioassays (USEPA, 1992).

USEPA imposes maximum residual disinfectant levels for chlorine and chloramine at 4 mg/L and for chlorine dioxide at 0.8 mg/L based on 12-month averages. None of the disinfectants are carcinogenic. The toxicological effects of disinfectants (e.g., chlorine and chloramine) are nonspecific and occur at concentrations well above the suggested use levels. More specific effects appear to be associated with hypochlorite solutions, chlorine dioxide, and iodine with respect to effects on thyroid function. Only in the case of iodine does this seem to limit its long-term use in the disinfection of municipal drinking water (Bull et al., 2001). EPA believes that water disinfected with monochloramine that meets regulatory standards poses no known or anticipated adverse health effects, including cancer. (USEPA, 2009)

# Q: Is there evidence of a link between chloramine in drinking water and the occurrence of Acanthamoeba Keratitis?

A: Acanthamoeba Keratitis is a waterborne ameba commonly found in the environment that may cause eye infection. Most people will be exposed to Acanthamoeba during their lifetime and will not get sick. Although an early investigation of increased acanthamoeba keratitis rates in Illinois hypothesized that there may be a link to the type of disinfectant used in municipal drinking water, no data supporting this hypothesis have been presented in the initial or subsequent publications. The CDC addressed this more completely in a comprehensive case-control study, which concluded that water disinfection type was not an important risk factor in this outbreak (Vernai et al, 2009).

#### Q: Is there any association between chloramine and heart failure?

A: Chloramine is not associated with heart failure. Chloramine has a different molecular structure from, for example, phenylpropanolamine, which has been linked to heart problems.

# Q: What are the impacts on dialysis patients and can chloramine contribute to kidney failure?

A: Chloramine ingestion does not contribute to kidney failure. Both chlorine and chloramine can harm kidney dialysis patients during the dialysis process if they are not removed from the water prior to dialysis treatment. This is because between 90 and 190 liters of water is used in the kidney dialysis treatment process, and this water comes into direct contact (via a semi-permeable membrane) with the patient's bloodstream. To protect patients during the dialysis process, chloramine, like chlorine, is removed from tap water at treatment facilities before dialysis treatment takes place (Amato 2005). Prior to the SFPUC conversion to chloramine in 2004, the California Department of Public Health inspected and certified all hospitals and dialysis patient care facilities in the SFPUC service area to insure that all facilities had made the necessary changes to their water treatment systems. Home dialysis patients receive care and direction through a certified hemodialysis care facility. There are very few home dialysis patients throughout the SFPUC service area and all of those were contacted through their care facility. Kidney dialysis patients can safely drink chlorinated and chloraminated water (USEPA, 2009) as residual disinfectants are broken down in the digestive process. For the standard methods used in kidney dialysis systems, see http://www.aami.org/publications/standards/dialysis.html. The Transpacific Renal Network can be found at: ESRD Network #17 Home Page

#### Q: Can chloramine cause gastric lesions?

A: There is no evidence that chloramine ingested in drinking water causes gastric lesions. This concern is likely due to a misunderstanding of scientific articles that investigate the role of monochloramine produced by cells in cancer associated with *helicobacter pylori* infection (see, for example, lishi et al., 1997). The relevance of this research to drinking water or other exogenous exposures is not known.

#### Q: What is the interaction between chloramine and acid reflux?

A: Chloraminated water will not affect acid reflux. According to the Society of Thoracic Surgeons, gastro esophageal reflux disease, commonly referred to as acid reflux, can be aggravated by certain foods and drinks. This disease is thought to be caused by a deficiency in the stomach valve allowing the contents of the stomach to be released into the esophagus, where irritation occurs (Ferguson, 2000).

# Q: Is chloraminated tap water safe for people with disease such as AIDS, cancer, kidney dialysis, diabetes, hepatitis, or lupus?

A: Chloraminated water is safe for people with suppressed immune systems or other diseases. A comprehensive search of the medical literature does not reveal any studies showing that people with chronic diseases, including those with compromised immune systems and those who are taking medications, have any special problems metabolizing chloramines.

# Q: Why does the CDC recommend that people with compromised immune systems boil their drinking water?

A: Neither chlorine, nor chloramine can destroy certain protozoans like *Cryptosporidium*. Therefore some people who have compromised immune systems may wish to use bottled water or to boil their water to make sure that they are not exposed to pathogens that might be present in the water despite the use of these disinfectants. In 2006, the USEPA promulgated a new Federal regulation, the Long Term 2 Enhanced Surface Water Treatment Rule, to specifically regulate the removal or disinfection of *Cryptosporidium* (USEPA, 2006b). The SFPUC is in the planning phase to comply with this requirement by year 2011.

#### Q: Are there any known interactions between chloramine and medications?

A: When drugs are tested in clinical trials most investigators do not specify that water other than tap water be used. Enough cities already use chloramine that it is quite likely that the efficacy of some drugs is already based on how they act in persons drinking chloraminated water. Chloramine interaction with pharmaceuticals has not been specifically studied

# Q: What is the general sensitivity to ammonia? Is there any damage from ammonia and upsets to the pH balance of the body?

A: The ammonia is predominantly bound in chloramine with a slight excess of so called "free ammonia" and will not produce adverse effects from exposure by washing. Ammonia is released during the digestion of chloramine in the digestive system.

#### Q: Are people with urea cycle disorder able to drink chloraminated water?

A: People with urea cycle disorder are not able to metabolize ammonia, therefore it is certainly possible that people with this condition could benefit by drinking non-chloraminated water if they are reducing their ammonia intake in other ways as well. Since ammonia-containing foods are common, people with these disorders would probably achieve greater reductions by avoiding foods with higher ammonia contributions first. Ingesting 1 liter of water results in ingestion of less than 1 mg NH3 (typically less than 0.5 mg/L NH3). By comparison, a one-ounce serving of cheddar cheese contains about 31 mg NH3 (derived from Rudman et al, 1973). We have been unable to identify any medical literature that suggests drinking chloraminated water is an important exposure pathway for people with urea cycle disorder. Boiling water for 20 minutes will remove chloramine and ammonia.

#### Q: Is it safe for babies to drink chloraminated water?

A: Yes.

#### PLUMBING

Q: What is the compliance with lead regulation in the SFPUC system?

A: SFPUC has been in compliance with the Action Level for lead (15 ug/L), including several samplings after chloramine conversion in 2004, 2005, 2006 and 2009 in the Regional and San Francisco Water Systems. These results indicate no negative impact of chloramine on lead levels.

Lead in drinking water is regulated by the Lead and Copper Rule (LCR), a Federal and State drinking water standard (USEPA, 1991) that specifies an Action Level of 15 ug/L for lead in drinking water systems, measured at customers' taps. If lead concentrations exceed an action level of 15 ug/L in more than 10% of customer taps sampled, the system must undertake a number of additional actions to control corrosion. If the action level for lead is exceeded, the system must also inform the public about steps to protect health. Additionally, lead service lines under control of the system may need to be replaced. The Action Level refers to a concentration measured at the tap rather than in municipal water supply system because lead in drinking water is derived principally from household plumbing, especially in systems like the SFPUC that do not have any lead service lines or distribution pipes. The leaching of lead in the distribution system is greater if the water is slightly acidic.

The SFPUC corrosion control treatment consists of maintaining slightly alkaline water pH (above neutral) throughout the distribution system. This practice is typical for water systems serving low mineral content high quality water from mountain supplies. In addition, SFPUC has conducted an active program in the last 25 years focused on reducing the potential for lead to appear in the drinking water at the consumer's tap: (1) in the 1980s all lead service lines in the San Francisco Water System were removed including lead whips (goosenecks) connecting the service lines to the mains, (2) in 1994 SFPUC initiated a "Lead Test for a Fee" program for the customers, (3) in 1998 SFPUC began free lead-in-water tests for Women, Infants & Children (WIC) program participants, (4) since 2000 SFPUC has provided lead-free faucets to childcare centers and schools, (5) in 2001 SFPUC started providing lead-free faucets to City residents via annual sales at street fairs, (6) in 2002 SFPUC initiated a 20-year-long 8% lead water meter replacement program. SFPUC has monitored for lead numerous times as part of LCR compliance and has been in compliance with the Action Level for lead (15 ug/L), including several samplings after chloramine conversion in 2004, 2005, 2006 and 2009 in the Regional and San Francisco Water Systems. These results are a testimony to SFPUC's efforts in lead control over the last two decades. They also indicate no negative impact of chloramine on lead levels. The results obtained at SFPUC were documented by Wilczak et al. (2010). The studies of Giammar et al. (2010) and Boyd et al. (2010) confirmed that monochloramine would have no impact on the release of either lead or copper due to chloramine conversion under water chemistry conditions of SFPUC system.

Customers in the City of San Francisco interested in measuring lead levels in their homes may request a sampling kit and analysis for a small fee by calling 877-737-8297. The results of this "Lead Test for a Fee" sampling program for the customers in San Francisco (conducted at customers' residences at their request) indicate no impact of chloramine on lead levels.

# Q: What is the potential impact of the disinfectants on the release of lead from pipes and plumbing?

A: Reiber (1993) found that neither lead nor lead solders were substantially influenced by the presence of chlorine or chloramine at pH levels common to distribution systems. The increased corrosion of lead and increase in lead levels in the distribution systems as a result of chloramination have not been observed in the industry in the past. Instances of increased lead levels in the tap at a utility in Washington DC, and at several utilities in North Carolina and Virginia were recently attributed to chloramination because they coincided with a change to chloramine disinfectant in the distribution system at these utilities. The conclusions of subsequent technical investigations, which revealed other causes of lead leaching; are summarized below. Current USEPA information on lead corrosion is summarized at

#### http://www.epa.gov/ORD/NRMRL/wswrd/cr/corr res lead.html

In 2002, the utility serving Washington DC reported high levels of lead at the customer taps after conversion to chloramine (Edwards and Dudi, 2004). Until recently it has been assumed that the primary oxidation state of lead on the corroded surface of lead pipe is divalent Pb[II], typically in the form of lead oxide, lead carbonate or lead hydroxy-carbonate (Crittenden et al., 2005).

The tetravalent state of lead Pb[IV] on the other hand, is much less soluble than Pb[II]. Until recently, it was assumed that Pb[IV] plays an insignificant role in controlling lead solubility, however analysis of the surface scale of lead pipe harvested from a number of water utilities across the U.S. suggests the presence of tetravalent lead is more common than once thought (Schock et al., 2005). After elevated lead levels occurred in Washington D.C., testing of the water profile from the taps of several homes showing high lead levels suggested that the highest lead levels were coming from lead service lines. Subsequent work analyzing the scales on the surface of lead pipes from Washington D.C. before and after chloramination have shown that Pb[IV] is the dominant form during the presence of high levels of chlorine and it gradually reverts to more soluble Pb[II] after exposure to chloramine. The presence of these two different minerals also showed a strong correlation with the levels of lead found in the system (Schock and Giani, 2004).

The experience in Washington D.C. makes it clear that circumstances can occur where the switch from chlorine to chloramine may result in elevated lead levels. But this occurrence is clearly more the exception than the rule. The special conditions applicable in Washington D.C. are the following: (1) Washington D.C. had a great deal of lead pipe, lead service lines and, in some cases, lead plumbing in homes, (2) During the years immediately prior to the change, Washington

D.C. maintained rather high chlorine residuals, ranging from 2.5 to 4 mg/L. SFPUC's situation is different for the following reasons: (1) LCR sampling conducted before and after the switch to chloramine in SFPUC system showed lead levels below the Action Level requirement in the rule,

(2) Unlike Washington D.C., the SFPUC system has no known lead services or homes with lead plumbing, (3) SFPUC has never practiced the unusually high levels of chlorine residual in Washington D.C. before the change of disinfectant to chloramine. The lead corrosion control strategy and the results obtained at SFPUC were documented by Wilczak et al. (2010). Recent USEPA (2007) report confirms these general findings and states that a combination of factors – not a single source or a single causative event – contributed to the problematic release of lead in water at consumers' taps in the Washington DC (DCWASA) system. The primary source of lead release was attributed to the presence of lead service lines (LSLs) in the DCWASA service area.

A change to chloramine as a distribution system disinfectant at a utility in North Carolina was attributed in the media to increased lead levels. Follow-up investigation by Triantafyllidou and

Edwards (2006) at three utilities in Virginia and North Carolina, all of which had recently switched to chloramine, determined that a change in coagulant – an inorganic salt used to remove organic matter from the water – was in fact responsible in all three cases for increased lead leaching (Triantafyllidou and Edwards, 2006). Field data demonstrated that changes in coagulants containing sulfate to those containing chloride increased the chloride to sulfate ratio in treated waters and caused lead release from the solder and brass. Lead solder particles trapped in the drinking water tap aerator were a key source of lead. Lead levels decreased upon changing back to coagulants containing sulfate in all cases and the utilities continue to use chloramine. Triantafyllidou and Edwards (2006) suggested that lead leaching could be most sensitive to coagulant type when treating waters with relatively low chloride and sulfate, since potential changes may be most significant in these situations.

A recent study by Sharp et al (2007) evaluated lead and copper leaching to determine the possible impacts of New York City switching distribution system disinfectants from free chlorine to chloramine. The results from the first phase of studies indicate that the application of chloramine prepared with a chlorine to nitrogen ratio of 3:1 and a pH that ensures complete monochloramine formation will not result in increased lead and copper leaching compared to that of the current New York City drinking water. The studies of Giammar et al. (2010) and Boyd et al. (2010) confirmed that monochloramine would have no impact on the release of either lead or copper due to chloramine conversion under water chemistry conditions of SFPUC system.

# Q: What practices are recommended by the USEPA to reduce potential lead exposure from household plumbing?

A: <u>The USEPA (http://water.epa.gov/drink/info/lead/index.cfm) recommends the following routine</u> practices to reduce possible exposure to lead in the tap water. (1) Flush pipes before drinking, and only use cold water for consumption. The more time water has been sitting in a home's pipes, the more lead it may contain. Anytime the water in a particular faucet has not been used for six hours or longer, "flush" cold-water pipes by running the water until it becomes as cold as it can get. This could take as little as five to thirty seconds if there has been recent water use such as showering or toilet flushing. Otherwise, it could take two minutes or longer. (2) Use only water from the coldwater tap for drinking, cooking, and especially for making baby formula. Hot water is likely to contain higher levels of lead. The two actions recommended by USEPA should be effective in reducing lead levels because most of the lead in household water usually comes from the plumbing in the house, not from the local water supply. The USEPA also recommends removing the screen and aerator at the end of a faucet and cleaning it of debris on a regular basis. The small screen at the end of a faucet can trap sediments that may contain lead solder particles released from customer plumbing. This practice, along with flushing of the drinking water tap (until water gets cold), will minimize exposure to lead.

# Q: What practices are recommended by the USEPA to reduce potential lead exposure from plumbing in schools and childcare centers?

A: The USEPA (<u>http://www.epa.gov/safewater/consumer/leadinschools.html</u>) recommends the following routine practices to help reduce exposure to lead in drinking water in schools and child care centers:

Clean debris from accessible screens (aerators) frequently. Clean and inspect periodically. Thoroughly flush holding tanks to remove sediment.

Use only cold water for food and beverage preparation in kitchens.

Placard bathroom sinks with notices that water should not be consumed. Use pictures if there are small children using the bathroom.

#### Q: What is the compliance with copper regulation in the SFPUC system?

A: SFPUC has always been in compliance with the Action Level for copper (1.3 mg/L), including several samplings after chloramine conversion in 2004, 2005, 2006 and 2009 in the Regional and San Francisco Water Systems. There is no impact of chloramine on copper corrosion in SFPUC system.

Copper in drinking water is regulated by the Lead and Copper Rule, a Federal and State drinking water standard (USEPA, 1991) that specifies an Action Level of 1.3 mg/L for copper in drinking water systems, measured at customers' taps. If copper concentrations exceed an action level of

1.3 mg/L in more than 10% of customer taps sampled, the system must undertake a number of additional actions to control corrosion. The Action Level refers to a concentration measured at the tap rather than in municipal water supply system because much of the copper in drinking water is derived from household plumbing. The leaching of copper in the home distribution system is greater if the water is slightly acidic.

The SFPUC copper corrosion control treatment consists of maintaining slightly alkaline water pH (above neutral) throughout the distribution system. This practice is typical for water systems serving low mineral content, high quality water from mountain supplies. The study of Boyd et al. (2010) confirmed that monochloramine would have no impact on the release of copper due to chloramine conversion under water chemistry conditions of SFPUC system.

#### Q: What are the factors that may influence copper corrosion in a drinking water system?

A: Numerous factors may contribute to copper corrosion including water quality, presence of biofilms, pipe manufacturing process, and the design and installation methods of piping systems. The major water quality factors include pH, alkalinity, sulfates, chlorides, dissolved solids, dissolved oxygen, temperature, and the presence or absence of disinfectants such as chlorine and chloramine (Kirmeyer et al., 2004). The single most important factor for uniform corrosion of copper tubing appears to be pH. Copper corrosion is sensitive to pH, especially at pH levels below 6, and at pH 8 and above, copper corrosion is near its minimum achievable level (Reiber, 1993). Operationally, there are no reports of accelerated copper failure in chloraminated systems (Reiber, 1993). Little information has been reported in the literature about the effect of chloramine on copper or iron. Some authors reported that chloramine was less corrosive than free chlorine towards iron; an increase in red water complaints was reported following the use of chlorine residual instead of chloramine (Health Canada, 2009). A recent study by Boyd et al. (2010) confirmed that

monochloramine would have no impact on the release of copper due to chloramine conversion under water chemistry conditions of SFPUC system.

Reiber (1993) exposed metals in the laboratory to varying levels of pH, chlorine, chloramine and ammonia. Both chlorine and chloramine accelerated the corrosion of copper and its alloys at pH 6 but caused minimal corrosion at pH 8. The corrosion was greatest for brass, followed by copper and then bronze. The presence of chlorine or chloramine did not lead to pitting type corrosion on copper or copper alloy surfaces. The presence of ammonium ions at less than 10 mg/L produced no discernible increase in corrosion rates. In equal concentrations, chlorine was slightly more corrosive than chloramine on copper and its alloys. If significantly higher levels of chloramine are required compared to chlorine, chloramine could result in a higher copper corrosion rate, especially at lower pH values. Corrosion phenomena are relatively complex and new information has been developed in recent years since the implementation of the USEPA Lead and Copper Rule in 1991 (USEPA, 1991). Recent USEPA information on copper corrosion is summarized at http://www.epa.gov/ORD/NRMRL/wswrd/cr/corr res copper.html

#### Q: What is the potential impact of the disinfectants on pitting corrosion of copper pipes?

A: Copper corrosion is categorized as either uniform or localized based on visual inspection (Edwards et al., 1994). High uniform corrosion rates are typically associated with waters of low pH and low alkalinity; corrective treatment involves raising pH or increasing bicarbonate. If uniform corrosion rates are excessive, unacceptable levels of copper corrosion by-products may be introduced into drinking waters, which in turn, may lead to consumer complaints of green or blue water caused by copper-containing particles in water. Perforation of the pipe wall and associated failure are rare under uniform corrosion (Edwards et al, 1994).

Copper pitting corrosion remains poorly understood despite a number of reports released in recent years (USEPA, 2006c). There have been cases of copper pitting reported in waters having high pH, low alkalinity, and significant levels of sulfate and chloride. In some of those cases, aluminum, silica, total organic carbon, and other materials have been suggested as the cause of pitting. Also, the role of orthophosphate as a corrosion inhibitor and reducer of the pitting tendency of water has shown some promise. Presence of the high levels of chloride appears to be a main factor for the development of pitting copper corrosion in low alkalinity, high pH waters. Practical experience indicates that pitting copper corrosion may or may not occur in systems disinfected with chlorine, chloramine or chlorine dioxide (Lytle, 2006). Sulfate and chloride were deemed important in the pitting process based on their presence in the corrosion regions (Lytle et al., 2005).

Localized corrosion of copper or "pitting" corrosion is complex, and resulting pinhole leaks are still poorly understood and remediation strategies are not completely developed. Pitting copper corrosion by chloramine is an unproven research hypothesis. Side by side experiments showed pitting corrosion of copper with chlorine but not chloramine. Few studies attempting to demonstrate pitting corrosion of copper in the lab have been done with chlorine and the evidence seems to point out that high levels of aluminum were necessary to start copper pitting corrosion with chlorine in these tests – this is a preliminary finding based on a limited number of laboratory tests (Marshall et al., 2003; Marshall and Edwards, 2005). The experiments on copper pipe corrosion were conducted by Marshall et al. (2003) with chlorine at doses up to 4.8 mg/L Cl<sub>2</sub> and aluminum at 2 mg/L Al. If the aluminum was present, copper corroded as fast at pH 9 as it did at pH 6 without aluminum. The presence of chlorine and aluminum seemed to initiate pitting corrosion of copper. Marshall and Edwards (2005) conducted follow-up laboratory experiments on copper pipes using potable water containing aluminum (2 mg/L Al) and high chlorine residual (4 mg/L Cl<sub>2</sub>). Pinhole

leaks and severe pitting was observed in the presence of chlorine and aluminum at pH 9.2, whereas no pitting was observed in the absence of aluminum. This research is the first to reproduce copper pitting in the laboratory and to suggest water quality parameters that may influence this process. The levels of aluminum in SFPUC treated waters are more than 20 times lower than amount used in experiments to simulate pitting copper corrosion. Also, the presence of disinfectant residual is essential to prevent microbially induced pitting corrosion.

Chlorine has been observed to both increase and decrease the corrosion of copper. Chlorine residual of 2 mg/L Cl<sub>2</sub> decreased the copper corrosion rate in a water at pH 9.3, leading to the conclusion that a chlorine residual might prevent the unusual "blue water" or soft water pitting problems (Boulay and Edwards, 2001). The presence of organic matter increased copper corrosion by-product release. In another study, a chlorine dose of 0.7 mg/L Cl<sub>2</sub> increased copper by-product release at pH 9.5 but the effects were small. Moreover, chlorine is known to stop other copper corrosion problems in soft waters such as pitting corrosion (Boulay and Edwards, 2001).

#### Q: What is the occurrence of copper pitting corrosion?

A: Localized copper corrosion often appears nearly at random in a distribution system. For example, in new housing developments some homes may have severe localized corrosion whereas others are unaffected, or corrosion may appear isolated to specific floors of tall buildings. Pitting corrosion may be troublesome because of unacceptable metal release or because of the perforation of the pipe wall. Three distinct types of pitting are commonly recognized, encompassing cold, hot, and soft waters (Edwards et al., 1994). Cold water pitting is the most common cause of copper pipe failures. Hot water pitting failures usually take some years to occur, in contrast to coldwater pitting in which failures may occur in just a few months.

Soft water pitting was previously thought to be very rare. Waters supporting soft water pitting are cold, of low conductivity, of low alkalinity, and of relatively high pH. Chloride, sulfate and nitrate may play a role in copper pitting corrosion. Natural organic matter (NOM) seems to prevent or in some cases increase certain copper corrosion within distribution systems. Increased corrosion by-product release and pitting attack may be possible subsequent to NOM removal (Edwards et al., 1994).

Pitting corrosion of copper pipes in hot and cold water can result from microbial influenced corrosion (MIC) and has been observed world wide (Germany, England, Sweden, Saudi Arabia). High numbers of bacteria were associated with the pits, however the presence of bacteria did not always result in pitting and the range of bacterial species was quite variable. A combination of factors appears to contribute to the biocorrosion of copper pipe: soft waters with low pH, high suspended solids and assimilable organic carbon (AOC) content, long-term periods of stagnation of water in the pipe, which produces widely fluctuating oxygen concentrations; low to nonexistent levels of chlorine; maintenance of water temperatures that promote rapid growth and activity of naturally occurring bacteria that form biofilm on the pipe wall (Bremer et al., 2001).

#### Q: What is the impact of disinfectants on rubber parts?

A: Certain older natural rubber products and their derivatives used in household appliances (e.g., toilet flapper valves, hot water heater plastic dip tubes) deteriorate faster in the presence of chloramine than with chlorine. Replacing these with alternative synthetic materials available in plumbing and hardware stores eliminates this issue.

Reiber (1993) conducted a series of experiments on the deterioration of various materials under conditions of very high chlorine and chloramine concentrations to simulate material corrosion under accelerated conditions. Concentrated solutions of chloraminated waters (300 mg/L) were more aggressive to elastomer compounds (especially natural rubbers and their derivatives) than equivalent concentrations of chlorine. Elastomeric failure was unrelated to excess ammonia (Reiber, 1993). Consistent with the results of Reiber's experiments, 23% of utilities surveyed by Kirmeyer et al. (2004) experienced an increase in degradation of certain rubber materials after implementation of chloramine. Synthetic polymers or hard rubbers specifically developed for chemical resistance such as silicon and fluorocarbon-based elastomers are resistant to deterioration from chloramine (Reiber, 1993; Kirmeyer et al., 2004). Replacement of rubber plumbing components with chloramine resistant materials such as: high quality rubber (synthetic polymer) parts, flexible copper tubing, or tubing made of corrugated stainless flex, takes care of this temporary inconvenience. These effects are generally experienced within the first six months to a year after change of disinfectant to chloramine.

Although earlier reports (Reiber, 1993) suggested that some elastomers, primarily nitriles, styrene butadiene, natural rubbers, neoprenes, and ethylene-propylene are susceptible to chloramine, these tests were conducted based on exposure of the large surface area of the materials to the test solutions at very high concentrations of 300 mg/L of the disinfectant. Bonds (2004) tested similar materials as pipe gaskets and did not observe visual degradation after exposure to 110 mg/L chloramine for one year. It was concluded that exposure tests of sheet materials were not relevant to pipe gaskets (Bonds, 2004). To put these results in perspective, typical levels of either chlorine or chloramine in drinking water distribution systems range from 1 to 2 mg/L. AWWA Research Foundation has recently published a report on elastomer performance with reference to disinfection (Rockaway et al, 2007). Each elastomer formulation has a unique reaction when exposed to free chlorine or chloramine; some have been observed to resist degradation, while others degrade rapidly. To predict the long-term performance of commonly found elastomers, accelerated aging tests were conducted at combinations of three temperatures (23, 45, and 70 C) and three disinfectant concentrations (1, 30, and 60 mg/L) for natural rubber; neoprene rubber; ethylene propylene diene monomer, peroxide-cured (EPDM-P); styrene butadiene rubber (SBR); ethylene propylene diene monomer, sulfur-cured (EPDM-S); and nitrile rubber. Elastomer degradation was characterized by mass change, volume change, breaking stress, breaking strain, and hardness, Relatively, EPDM(P) and EPDM(S) were found to be least susceptible to chloramine degradation followed by nitrile rubber, SBR, natural rubber, and neoprene rubber. This was confirmed by Nagisetti et al. (2010).

Least Sensitive	Sensitive	Acutely Sensitive
EPDM(P), EPDM(S)	Nitrile Rubber, SBR, Natural Rubber	Neoprene Rubber

#### Sensitivity of elastomers to degradation in chloraminated water

EPDM(P)----Ethylene propylene diene monomer, peroxide-cured, EPDM(S)----Ethylene propylene diene monomer, sulfurcured, SBR-styrene butadiene rubber

#### Q: What is the potential impact of the disinfectants on plastic piping?

A: There are no known reports of any impacts of drinking water disinfectants at concentrations present in the municipal drinking water distribution systems on plastic or polyvinyl chloride (PVC) pipes. PVC pipes are resistant to almost all types of corrosion – both chemical and electrochemical. Because PVC is a nonconductor, galvanic and electrochemical effects are nonexistent in PVC piping systems. PVC pipe cannot be damaged by aggressive waters or corrosive soils. PVC pressure pipe is resistant to chlorine and chloramine, nearly totally resistant to microorganisms, but subject to ultraviolet (UV) degradation, unless specifically formulated (AWWA, 2002). The performance of PVC pipe is significantly related to its operating temperature.

PVC pipe is rated for performance properties at a temperature of 73.4 F (23 C). Most municipal water systems operate at temperatures at or below 23 C. As the operating temperature decreases, the pipe's stiffness and tensile strength increase but PVC pipe loses impact strength and becomes less ductile (AWWA, 2002). Plumbers contacted in San Francisco have not seen any increase in pipe breaks in the recent years. PVC piping experiencing more leaks than metal piping can often be attributed to installation issues, for example pipes installed on slopes may have increased risk of breaks and leaks than metal pipes.

Research has documented that pipe materials, such as polyethylene, polybutylene, PVC, asbestos cement, and elastomers, such as those used in jointing gaskets, may be subject to permeation by lower molecular weight organic solvents and petroleum products (AWWA, 2002; AWWA, 2006d). There are no PVC pipes in San Francisco drinking water distribution system.

#### ANIMALS AND ENVIRONMENT

#### Q: What are the impacts of chlorine and chloramine on fish and aquatic organisms?

# A: Fish and other aquatic organisms are very sensitive to both chlorine and chloramine and may die if exposed to these oxidants. Concentrations of chloramine as low as 0.07 mg/L have been shown to be lethal to coho salmon in 96 hour studies.

Chloramine does not bioaccumulate or transfer up the food chain (Environment Canada, 2002). For fish-owners, the challenge with chloramine is twofold: it does not dissipate rapidly so letting the water sit for a day or two will not make it safe for fish, and the "chlorine neutralizers" are not effective for chloramine (Harms and Owen, 2004). The ammonia in the chloraminated water may be harmful to fish under certain conditions. Chloramine neutralizing chemicals are available in pet stores. Utilities dechlorinate water when discharging large volumes of chloraminated or chlorinated water to the environment.

The mechanism responsible for the toxicity of chloramine to fish differs somewhat from chlorine toxicity. Chlorine does not readily pass the permeable gill epithelium compared with chloramine. Chlorine destroys the cells of the gills by oxidation, causing an impairment of normal gaseous exchange. Affected fish exhibit labored respiration due to an inability to utilize available dissolved oxygen in the water. Chloramine crosses the gill epithelium with an insignificant amount of cellular damage as compared with chlorine. Once the chloramine has entered the bloodstream it chemically binds to iron in hemoglobin in red blood cells causing an inability of the cells to bind oxygen (Environment Canada, 2001; Kirmeyer et al., 2004). The toxicity of chloramine to aquatic organisms is dependent on biological species, chloramine compounds, presence of chlorine and organic chloramines, pH, temperature, exposure duration and life stage of the biological species (Environment Canada, 2001).

Two methods can be used to remove chloramine from water to be used in aquariums or ornamental fish ponds: addition of specific agents, which will remove chloramine and ammonia, or use of granular activated carbon (GAC) filter. A home test kit may be purchased to test the aquarium water for total chlorine and ammonia. Most pet stores sell dechlorinating agents and recommend their use. It may take more dechlorinating agent and more time to remove chloramine than chlorine. Ammonia can be toxic to fish, although all fish produce some ammonia as a natural by-product. Commercial products are available at pet stores to remove excess ammonia. Biological filters, natural zeolites and pH control methods are also effective in reducing the toxic effects of ammonia. Ammonia removal is especially important at high pH, because at a higher pH, ammonia is more toxic to fish. Chloramine can also be removed by using a GAC filter. It is important to allow the appropriate amount of contact time for chloramine removal using that method (Kirmeyer et al., 2004).

#### Q: What are the effects of ammonia on fish?

A: Ammonia is not toxic below pH 7, since ammonia is in the ionized ammonium ion form NH<sub>4</sub>.

For example in water with a pH of 6.9 and at a temperature of 24 C, 99.58% of the ammonia is in the non-toxic ammonium ion form and 0.42% as potentially toxic unionized ammonia. However, at the same temperature but at a pH of 8, such as in marine aquarium, the percentage of ionized ammonia is 90.51%, and the unionized form 9.49% (Kirmeyer et al., 2004).

Ammonia can be toxic to fish above pH 7, although all fish produce some ammonia as natural byproduct. Ammonia is also released when chloramine is chemically removed. Although ammonia levels may be tolerable in individual tanks or ponds, commercial products are available at pet supply stores to remove excess ammonia. Also, biological filters, natural zeolites and pH control methods are effective in reducing the effects of ammonia (Kirmeyer et al 2004). In established aquaria and pond systems with properly functioning biological filter beds, the nitrifying bacteria will remove the ammonia produced during dechloramination in a fairly short period of time. Therefore it may not be necessary to use zeolites under such conditions. However, they should be used whenever setting up new aquariums, when the water is alkaline, and where there is insufficient biological filtration. It is also important to note that zeolites can only be used for the removal of ammonia in fresh water. In salt water, zeolites are unable to function properly due to the high concentration of sodium chloride.

# **Q:** Will chloramine dissipate when watering the lawns and how will runoff impact environment?

A: Watering lawns releases low volumes of water and disinfectant and is considered an incidental discharge. Chloramine will dissipate as a result of lawn watering because chloramine will be neutralized by the soil particles (this process is termed "chloramine demand"). The small amount of chloramine should not have any effect on plants of any type. Based on the available evidence, adverse effects on soil microorganisms and associated soil processes from inorganic chloramine are considered unlikely (Environment Canada, 2001).

Incidental discharges should not pose a direct risk to fish. Most of the water that is used for landscape irrigation percolates into the ground. As this water gradually runs off landscaping, soil or pavement, the "chloramine demand" consumes the residual chlorine or chloramine, effectively neutralizing any residual before it enters the storm sewer or bay. There will be no effect on estuarine or marine organisms. Before water leaves any Bay Area wastewater treatment plant, the chlorine or chloramine are neutralized. This applies to combined sewer overflows as well.

A high volume direct discharge of chloraminated water to the environment can result from pipeline breaks or flushing fire hydrants. As with chlorinated water, this needs to be avoided because chlorine residual in the chloraminated water may pose a direct acute health risk to fish in creeks and streams. Water companies use dechlorinating agents to remove chloramine from the water during high volume discharges and while flushing fire hydrants.

#### Q: What are the impacts of chloramine on pets?

A: Chloramine is safe for all mammals and birds and most reptiles. Chloramine is not expected to cause any health problems for dogs or cats. Some people have been worried because trichloramine has been associated with a disorder called "canine hysteria" in dogs. However, this disorder is associated with trichloramine, not monochloramine; trichloramine is not present in the SFPUC chloraminated drinking water.

Harms and Owen (2004) interviewed several veterinarians in a local chloraminated system about impacts to pets and no issues or concerns were identified. With the exception of one reptile group (turtles) and amphibians, no known adverse effects are reported in the literature for exposure to or consumption of chloraminated water. Turtles and amphibians spend a significant amount of time in water and, based on recommendations of a local zoological garden, it was recommended that both

chlorine and chloramine be removed from their water. No adverse impacts on any pets have been reported to the utility.

#### Q: If cows drink chloraminated water will chloramine be in their milk?

A: No, chloramine does not enter cows' milk. Monochloramine is broken down in the digestive process and it is "not expected to enter the systemic circulation" (Hankin 2001). Additionally, it is rare for cows to be supplied with treated drinking water. Most livestock drink untreated well water or water from streams, not tap water. Even if they were exposed to monochloramine, chloramine would be broken down in their digestive process.

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#### ACRONYMS

µg/L	microgram per liter
AOC	assimilable organic carbon
AWWA	American Water Works Association
BAWSCA	Bay Area Water Supply and Conservation Agency
CCLHO	California Conference of Local Health Officers
CDC	Centers for Disease Control and Prevention
CDPH	California Department of Public Health
DBP	disinfection by-products
D/DBPR	Disinfectants/Disinfection By-products Rule
FDA	Food and Drug Administration
GAC	granular activated carbon
HAAs	haloacetic acids
HPC	heterotrophic plate count
ICR	Information Collection Rule
IRIS	Integrated Risk Information System
LCR	Lead and Copper Rule
MCL	maximum contaminant level
mg/L	milligrams per liter
MIC	microbial influenced corrosion
MRDL	maximum residual disinfectant level
MSDS	Material Safety Data Sheet
MWDSC	Metropolitan Water District of Southern California
NDMA	N-nitrosodimethylamine
ng/L	nanograms per liter
NOM	natural organic matter
NSF	NSF International
OSHA	Occupational Safety and Health Administration
POUD	point-of-use devices
PVC	polyvinyl chloride
RO	
SDWA	reverse osmosis
-	Safe Drinking Water Act
SFDPH	San Francisco Department of Public Health
SFPUC	San Francisco Public Utilities Commission Surface Water Treatment Rule
SWTR	
TCR	Total Coliform Rule
THMs	trihalomethanes
TOC	total organic carbon
TOX	Total Organic Halides
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
WHO	World Health Organization
WIC	Women, Infants & Children
WQD	Water Quality Division



Rajiv Bhatia, MD, MPH, Director of EH

# Memorandum

To: Andrew DeGraca, P.E.

From: June M. Weintraub, Sc.D.

Date: November 8 2007

Re: Summary of Monochloramine Abstract Review November 2006-November 2007

Throughout the year, we monitor the literature relevant to monochloramine using PubMed, the bibliographic index of peer-reviewed health, scientific and chemistry journals. PubMed is maintained by the National Center for Biotechnology Information (NCBI) at the National Library of Medicine (NLM), located at the U.S. National Institutes of Health (NIH). The following is a summary of relevant abstracts of new peer-reviewed publications listed in the database between November 2006 and present. As of November 8, 2007 a total of 58 results are returned with the search criteria:

(chloramine OR monochloramine) AND 2006/11:2008/01[dp] NOT taurine NOT chloramine-T

Of the 58 total, 24 were not sufficiently relevant as to not warrant inclusion in this summary (titles of those not summarized are listed on the last pages). A summary of the abstracts of the remaining 34 publications follows. Abstracts fall into the following categories:

- I. Studies on NDMA and other chloramine DBPs (12 abstracts)
- II. Studies related to lead, copper or other pipe material issues (3 abstracts)
- III. Manuscripts relevant to microbiology and efficacy of chloramine (6 abstracts)
- IV. Taste and odor (5 abstracts)
- V. Swimming pools (5 abstracts)
- VI. Studies of molecular level monochloramine in the GI system (3 abstracts)

## I. Studies on NDMA and other chloramine DBPs

# 1. Richardson SD, Plewa MJ, Wagner ED, Schoeny R, Demarini DM.

Mutat Res. 2007 Sep 12; [Epub ahead of print]

Occurrence, genotoxicity, and carcinogenicity of emerging disinfection by-products in drinking water: A review and roadmap for research.

This 65-page review describes 600 identified disinfection byproducts and the potential interactions among them in drinking water. The authors describe categories of DBPs, identify

data gaps, and describe the emerging role of dermal/inhalation exposure to provide guidance for drinking water and public health research.

# 2. Chen Z, Valentine RL.

Environ Sci Technol. 2007 Sep 1;41(17):6059-65.

Formation of N-nitrosodimethylamine (NDMA) from humic substances in natural water. Civil & Environmental Engineering, 4105 Seamans Center for the Engineering Arts and Sciences, The University of Iowa, Iowa City, Iowa 52242-1527, USA.

Investigated N-nitrosodimethylamine (NDMA) formation in chloraminated Iowa River water to determine the contribution of various natural organic matter humic fractions to the NDMA formation potential (NDMA FP) in this drinking water source.

## 3. Fristachi A, Rice G.

J Water Health. 2007 Sep;5(3):341-55.

Estimation of the total daily oral intake of NDMA attributable to drinking water. Oak Ridge Institute for Science and Education assigned to US Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Cincinnati, OH 45268, USA. afristac@jhsph.edu

The goal of this study was to estimate NDMA concentrations from exogenous (i.e., drinking water and food) and endogenous (i.e., formed in the human body) sources, calculate average daily doses for ingestion route exposures and estimate the proportional oral intake (POI) of NDMA attributable to the consumption of drinking water relative to other ingestion sources of NDMA. The models created suggest that drinking water consumption is most likely a minor source of NDMA exposure.

# 4. Lee W, Westerhoff P, Croué JP.

Environ Sci Technol. 2007 Aug 1;41(15):5485-90.

Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, Nnitrosodimethylamine, and trichloronitromethane.

HDR Engineering, Inc., 3200 East Camelback Road, Suite 350, Phoenix, Arizona 85018, USA. wontae.lee@hdrinc.com

This study investigated whether levels of dissolved organic nitrogen contribute to formation of nitrogen-containing disinfection byproducts in waters disinfected with free chlorine or monochloramine. The results support the hypothesis that dissolved organic nitrogen promotes the formation of N-DBPs.

## 5. Kim J, Clevenger TE.

J Hazard Mater. 2007 Jun 25;145(1-2):270-6. Epub 2006 Nov 18. Prediction of N-nitrosodimethylamine (NDMA) formation as a disinfection by-product. Department of Environmental Education, Mokpo National University, Muan-gun, Chungkyemyon, Chonnam 534-729, Republic of Korea. jongokim@mokpo.ac.kr This study investigated the possibility of a statistical model application for the prediction of Nnitrosodimethylamine (NDMA) formation.

# 6. Hua G, Reckhow DA.

Environ Sci Technol. 2007 May 1;41(9):3309-15.

Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size.

Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA. ghua@jonesemunds.com

This study examined disinfection byproduct formation from five different water sources during chlorination and chloramination and determined how the chemical properties such as molecular weight or hydrophilic characteristics of DBP precursors were related to the class of DBP formed.

# 7. Hua G, Reckhow DA.

Water Res. 2007 Apr;41(8):1667-78. Epub 2007 Mar 13.

Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, MA 01003, USA.

This manuscript presents the results of an investigation of disinfection byproduct formation in seven different natural waters treated in the laboratory under five oxidation scenarios (chlorine, chloramine, both with and without preozonation, and chlorine dioxide). The manuscript describes how different disinfection scenarios result in increased or decreased disinfection byproduct formation.

# 8. Yang X, Shang C, Westerhoff P.

Water Res. 2007 Mar;41(6):1193-200. Epub 2007 Jan 30.

Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination.

Department of Civil Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

This study presents detailed effects of contact time, monochloramine doses, monochloramine application modes, pH, temperature and bromide ion concentrations on formation of disinfection by-products (DBPs) using model solutions containing Suwannee River natural organic matter.

## 9. Joo SH, Mitch WA.

Environ Sci Technol. 2007 Feb 15;41(4):1288-96.

Nitrile, aldehyde, and halonitroalkane formation during chlorination/chloramination of primary amines.

Department of Chemical Engineering, Yale University, Mason Lab 313b, 9 Hillhouse Avenue, New Haven, Connecticut 06520, USA.

This manuscript presents results indicating that chloramination reduces nitrile concentrations compared to chlorination but may increase the formation of aldehydes and halonitroalkanes at high oxidant doses.

# 10. Charrois JW, Hrudey SE.

Water Res. 2007 Feb;41(3):674-82. Epub 2006 Sep 15. Breakpoint chlorination and free-chlorine contact time: implications for drinking water Nnitrosodimethylamine concentrations. Department of Public Health Sciences, University of Alberta, 10-102 Clinical Sciences Building,

Edmonton, Alta., Canada T6G 2G3. charrois@arc.ab.ca

This manuscript presents NDMA formation results from two full-scale chloraminating water treatment plants in Alberta between 2003 and 2005 and from bench-scale chloramination/breakpoint experiments. Distribution system NDMA concentrations varied and tended to increase with increasing distribution residence time. Bench-scale disinfection experiments resulted in peak NDMA production near the theoretical monochloramine maximum in the sub-breakpoint region of the disinfection curve.

# 11. Muellner MG, Wagner ED, McCalla K, Richardson SD, Woo YT, Plewa MJ.

Environ Sci Technol. 2007 Jan 15;41(2):645-51.

Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic? College of Agricultural, Consumer and Environmental Sciences, Department of Crop Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA.

The authors analyzed 7 haloacetonitriles (HANs) to determine cytotoxic potency, concluding that "...As a chemical class, the HANs are more toxic than regulated carbon-based DBPs, such as the haloacetic acids. The toxicity of N-DBPs may become a health concern because of the increased use of alternative disinfectants, such as chloramines, which may enhance the formation of N-DBPs, including HANs."

# 12. Chen Z, Valentine RL.

Environ Sci Technol. 2006 Dec 1;40(23):7290-7. Modeling the formation of N-nitrosodimethylamine (NDMA) from the reaction of natural organic matter (NOM) with monochloramine.

Civil and Environmental Engineering, 4105 Seamans Center for the Engineering Arts and Sciences, The University of Iowa, Iowa City, Iowa 52242-1527, USA.

This paper presents a kinetic model to validate proposed reactions and predict NDMA formation in chloraminated water during the time frame of 1-5 days. The model may be used as a tool in developing strategies to minimize NDMA formation.

II. Studies related to lead, copper or other pipe material issues

# 1. Maas RP, Patch SC, Christian AM, Coplan MJ.

Neurotoxicology. 2007 Sep;28(5):1023-31. Epub 2007 Jun 30.

Effects of fluoridation and disinfection agent combinations on lead leaching from leaded-brass parts.

Environmental Quality Institute, The University of North Carolina-Asheville, One University Heights, Asheville, NC 28804, United States.

This commentary by anti-fluoride researchers includes results from an investigation of the effects on water-borne lead from combinations of chlorine or chloramines with fluosilicic acid or sodium fluoride after a 16-hour stagnation period.

# 2. Rajasekharan VV, Clark BN, Boonsalee S, Switzer JA.

Environ Sci Technol. 2007 Jun 15;41(12):4252-7.

Electrochemistry of free chlorine and monochloramine and its relevance to the presence of Pb in drinking water.

Department of Chemistry and Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65409-117, USA.

The study found that monochloramine is not capable of producing a passivating PbO2 layer on Pb, and could lead to elevated levels of dissolved Pb in drinking water.

# 3. Miranda ML, Kim D, Hull AP, Paul CJ, Galeano MA.

Changes in blood lead levels associated with use of chloramines in water treatment systems. Environ Health Perspect. 2007 Feb;115(2):221-5. Epub 2006 Nov 7.

This study found a relationship between children's blood lead levels and living in the City of Goldsboro North Carolina after 2000, when the city started using chloramine for residual disinfection. The data and analysis do not support the strong conclusions and a letter to the editor of Environmental Health Perspectives commenting on flaws in the study was subsequently published. A principal weakness which the authors were not able to respond to is that the authors failed to consider that Hurricane Floyd was a plausible alternative explanation of their findings of increased blood lead levels in the city of Goldsboro North Carolina after 2000. The letter and the authors' response was published online September 10 2007 at <a href="http://www.ehponline.org/docs/2007/10453/letter.html">http://www.ehponline.org/docs/2007/10453/letter.html</a> and will appear in the print version of this peer reviewed journal in due course.

III. Manuscripts relevant to microbiology and efficacy of chloramine

## 1. Rose LJ, Rice EW, Hodges L, Peterson A, Arduino MJ.

Appl Environ Microbiol. 2007 May;73(10):3437-9. Epub 2007 Mar 30. Monochloramine inactivation of bacterial select agents. Centers for Disease Control and Prevention, 1600 Clifton Rd. N.E., MS C-16, Atlanta, GA 30033, USA. lrose@cdc.gov

Seven species of bacterial select agents were tested for susceptibility to monochloramine. Under test conditions, the monochloramine routinely maintained in potable water would reduce six of

the species by 2 orders of magnitude within 4.2 h. Bacillus anthracis spores would require up to 3.5 days for the same inactivation with monochloramine.

## 2. Srinivasan S, Harrington GW.

Water Res. 2007 May;41(10):2127-38. Epub 2007 Apr 3. Biostability analysis for drinking water distribution systems. Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI 53705, USA. soumyas@cae.wisc.edu

This paper presents a standardized algorithm for generating biostability curves, a graphical approach for studying the two competing effects that determine bacterial regrowth in a distribution system: inactivation due to the presence of a disinfectant, and growth due to the presence of a substrate.

## 3. Rodríguez E, Sordo A, Metcalf JS, Acero JL.

Water Res. 2007 May;41(9):2048-56. Epub 2007 Mar 13.

Kinetics of the oxidation of cylindrospermopsin and anatoxin-a with chlorine, monochloramine and permanganate.

Departamento de Ingenieria Quimica y Energetica, Universidad de Extremadura, 06071 Badajoz, Spain.

This study reported details of the reactions of cyanobacteria with chlorine, monochloramine and potassium permanganate, including the influence of pH and temperature. Cyanobacteria produce toxins that may contaminate drinking water sources.

## 4. Chen C, Zhang XJ, He WJ, Han HD.

Biomed Environ Sci. 2007 Apr;20(2):119-25.

Simultaneous control of microorganisms and disinfection by-products by sequential chlorination. Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China. chen\_water@tsinghua.edu.cn

This manuscript presents the results of pilot tests in China for a disinfection process in which short-term free chlorine and chloramine are sequentially added. The pilot tests found that TTHM and THAA5 formation was lower than with free chlorination, concluding that the process allows simultaneous control of microbes and DBPs in an effective and economic way.

## 5. Debiemme-Chouvy C, Haskouri S, Folcher G, Cachet H.

Langmuir. 2007 Mar 27;23(7):3873-9. Epub 2007 Feb 21.

An original route to immobilize an organic biocide onto a transparent tin dioxide electrode. Laboratoire Interfaces et Systèmes Electrochimiques, UPR 15 du CNRS, UPMC, Case Courrier 133, 4 place Jussieu, 75252 Paris Cedex, France. debiemme@ccr.jussieu.fr

This manuscript reports the results of an experiment to use electrochemical techniques to prevent biofilm growth on surfaces immersed in water.

#### 6. King BJ, Monis PT.

Parasitology. 2007 Mar;134(Pt 3):309-23. Epub 2006 Nov 13. Critical processes affecting Cryptosporidium oocyst survival in the environment. The Co-operative Research Centre for Water Quality and Treatment, Australian Water Quality Centre, SA Water Corporation, Salisbury, South Australia 5108, Australia.

This paper reviews the critical processes involved in the inactivation or removal of cryptosporidium oocysts and considers how these processes will respond in the context of climate change.

#### IV. Taste and odor

## 1. Heim TH, Dietrich AM.

Water Res. 2007 Feb;41(4):757-64. Epub 2007 Jan 16. Sensory aspects and water quality impacts of chlorinated and chloraminated drinking water in contact with HDPE and cPVC pipe.

Charles E. Via Department of Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, 418 Durham Hall, Blacksburg, VA 24061-0246, USA.

This manuscript presents results of an investigation of odor, organic chemical release, trihalomethane (THM) formation, free chlorine demand and monochloramine demand for water exposed to HDPE and cPVC pipes.

## 2. Wiesenthal KE, McGuire MJ, Suffet IH.

Water Sci Technol. 2007;55(5):293-300.

Characteristics of salt taste and free chlorine or chloramine in drinking water. Department of Environmental Health and Science, School of Public Health, University of California at Los Angeles, Los Angeles, CA 90095-1772, USA. kwiesent@ucla.edu

This manuscript is a discussion of technical and methodological issues in using the flavour profile analysis (FPA) taste panel method., finding that dechlorinated tap water may be the best background water to use for a particular drinking water evaluation of chlorine and chloramine thresholds.

## 3. McGuire MJ, Loveland J, Means EG, Garvey J.

Water Sci Technol. 2007;55(5):275-82.

Use of flavour profile and consumer panels to determine differences between local water supplies and desalinated seawater.

McGuire Malcolm Pirnie, 1919 Santa Monica Blvd., Suite 200, Santa Monica, CA 90404, USA. <u>mmcguire@pirnie.com</u>

The study reports the results of a flavour profile analysis panel and consumer evaluation sessions. One of the relevant findings was that consumer perception of the taste and odour of desalinated seawater or blends with Colorado River water and State project water was not affected by type or concentration of disinfectant used.

## 4. Heim TH, Dietrich AM.

Water Sci Technol. 2007;55(5):161-8. Sensory aspects of drinking water in contact with epoxy lined copper pipe. Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, 418 Durham Hall, Blacksburg, VA, 24061-0246, USA. heimt@vt.edu

This investigation examined the effects on odour, TOC, THM formation and disinfectant demand in water exposed to epoxy-lined copper pipes used for home plumbing. A study conducted at a full scale installation at an apartment demonstrated that after installation and regular use, the epoxy lining did not yield detectable differences in water quality.

#### 5. Durand ML, Dietrich AM.

Water Sci Technol. 2007;55(5):153-60.

Contributions of silane cross-linked PEX pipe to chemical/solvent odours in drinking water. Civil and Environmental Engineering, Virginia Polytechnic Institute and State University, 418 Durham Hall, Blacksburg, VA, 24061-0246, USA. mdurand@vt.edu

This investigation examined taste and odor of a commonly used plastic plumbing pipe, silanecross-linked polyethylene (PEX-b according to European standards) after exposure of new PEX pipe to chlorine, monochloramine or no disinfectant, finding that odours were described if chlorine or monochloramine were present.

#### V. Swimming pools

Five new manuscripts relevant to swimming pool chloramine levels were published in the time period. These support the relationship between swimming pool maintenance, swimming pool trichloramine exposures, and adverse health effects. These studies are not relevant to drinking water exposures.

#### 1. Li J, Blatchley ER 3rd.

Environ Sci Technol. 2007 Oct 1;41(19):6732-9.Links

Volatile disinfection byproduct formation resulting from chlorination of organic-nitrogen precursors in swimming pools.

School of Civil Engineering, Purdue University, West Lafayette, Indiana 47907-2051, USA.

This study examined volatile DBP formation resulting from the chlorination of four model compounds (creatinine, urea, L-histidine, and L-arginine) finding that volatile DBP formation in swimming pools is not limited to inorganic chloramines and haloforms.

## 2. Centers for Disease Control and Prevention (CDC).

Ocular and respiratory illness associated with an indoor swimming pool--Nebraska, 2006. MMWR Morb Mortal Wkly Rep. 2007 Sep 14;56(36):929-32.

This manuscript reports the investigation of an outbreak of respiratory illness that was likely the result of exposure to toxic levels of chloramines that had accumulated in the air in the enclosed space above the swimming pool, and highlights the potential health risks from chemical exposure

at improperly maintained pools and the need for properly trained pool operators to maintain water quality.

#### 3: Kaydos-Daniels SC, Beach MJ, Shwe T, Magri J, Bixler D.

Health effects associated with indoor swimming pools: A suspected toxic chloramine exposure. Public Health. 2007 Sep 7

This manuscript presents the results of an investigation of an outbreak among children who attended a party at a hotel pool. The investigation found that the pool operator lacked formal training in pool maintenance and underscored the need for regular pool maintenance, improved air quality, education and certification for all operators of public and semipublic pools, and education about healthy swimming practices.

# 4. Bowen AB, Kile JC, Otto C, Kazerouni N, Austin C, Blount BC, Wong HN, Beach MJ, Fry AM.

Outbreaks of short-incubation ocular and respiratory illness following exposure to indoor swimming pools.

Environ Health Perspect. 2007 Feb;115(2):267-71. Epub 2006 Nov 28.

This investigation of outbreaks of ocular and respiratory symptoms associated with chlorinated indoor swimming pools at two hotels concluded that indoor pool areas were associated with illness and that improved staff training, pool maintenance, and pool area ventilation could prevent future outbreaks.

**5. Jacobs JH, Spaan S, van Rooy GB, Meliefste C, Zaat VA, Rooyackers JM, Heederik D.** Exposure to trichloramine and respiratory symptoms in indoor swimming pool workers. Eur Respir J. 2007 Apr;29(4):690-8. Epub 2006 Nov 15.

The association between swimming pool characteristics and activities of employees and respiratory symptoms in employees was studied in the Netherlands, finding an excess risk for respiratory symptoms indicative of asthma in swimming pool employees. The study concluded that aggravation of existing respiratory disease or interactions between irritants and allergen exposures are the most likely explanations for the observed associations.

## VI. Studies of molecular level monochloramine in the GI system

Three manuscripts report results of research on the molecular and cellular level monochloramine. The relevance of this research to drinking water or other exogenous exposures is not known.

# 1. Carlson RM, Vavricka SR, Eloranta JJ, Musch MW, Arvans DL, Kles KA, Walsh-Reitz MM, Kullak-Ublick GA, Chang EB.

Am J Physiol Gastrointest Liver Physiol. 2007 Apr;292(4):G1070-8. Epub 2006 Dec 21. fMLP induces Hsp27 expression, attenuates NF-kappaB activation, and confers intestinal epithelial cell protection.

Martin Boyer Laboratories, The University of Chicago Inflammatory Bowel Disease Research Center, Chicago, IL, USA.

This study examined some mechanisms of intestinal homeostasis, including the role of certain proteins in cellular changes caused by cellular monochloramine.

### 2. Walsh BM, Naik HB, Dubach JM, Beshire M, Wieland AM, Soybel DI.

Am J Physiol Cell Physiol. 2007 Feb 7; [Epub ahead of print]

Thiol-Oxidant Monochloramine Mobilizes Intracellular Ca2+ in Parietal Cells of Rabbit Gastric Glands.

Surgery, Brigham and Women's Hospital, Boston, Massachusetts, United States.

This manuscript presents results indicating that under certain conditions, cellular monochloramine may act not as an irritant but as an agent that activates intracellular signaling pathways.

## 3. Winterbourn CC, Hampton MB, Livesey JH, Kettle AJ.

J Biol Chem. 2006 Dec 29;281(52):39860-9. Epub 2006 Oct 30. Modeling the reactions of superoxide and myeloperoxidase in the neutrophil phagosome: implications for microbial killing.

Department of Pathology, Christchurch School of Medicine and Health Sciences, P. O. Box 4345, Christchurch, New Zealand. christine.winterbourn@chmeds.ac.nz

This manuscript describes a kinetic model to examine the fate of superoxide and its interactions with myeloperoxidase to assess what oxidative mechanisms are likely to operate in the narrow confines of the phagosome, where chloramine products may be effectors of antimicrobial activity.

#### Alphabetical list of author groups of 34 manuscripts summarized above:

Bowen AB, Kile JC, Otto C, Kazerouni N, Austin C, Blount BC, Wong HN, Beach MJ, Fry AM. Carlson RM, Vavricka SR, Eloranta JJ, Musch MW, Arvans DL, Kles KA, Walsh-Reitz MM, Kullak-Ublick GA, Chang EB. Centers for Disease Control and Prevention (CDC). Charrois JW, Hrudey SE. Chen C, Zhang XJ, He WJ, Han HD. Chen Z, Valentine RL. Chen Z, Valentine RL. Debiemme-Chouvy C, Haskouri S, Folcher G, Cachet H. Durand ML, Dietrich AM. Fristachi A, Rice G. Heim TH, Dietrich AM. Heim TH, Dietrich AM. Hua G, Reckhow DA. Hua G, Reckhow DA. Jacobs JH, Spaan S, van Rooy GB, Meliefste C, Zaat VA, Rooyackers JM, Heederik D. Joo SH, Mitch WA. Kaydos-Daniels SC, Beach MJ, Shwe T, Magri J, Bixler D. Kim J, Clevenger TE. King BJ, Monis PT. Lee W, Westerhoff P, Croué JP. Li J, Blatchley ER 3rd. Maas RP, Patch SC, Christian AM, Coplan MJ. McGuire MJ, Loveland J, Means EG, Garvey J. Miranda ML, Kim D, Hull AP, Paul CJ, Galeano MA. Muellner MG, Wagner ED, McCalla K, Richardson SD, Woo YT, Plewa MJ. Rajasekharan VV, Clark BN, Boonsalee S, Switzer JA. Richardson SD, Plewa MJ, Wagner ED, Schoeny R, Demarini DM. Rodríguez E, Sordo A, Metcalf JS, Acero JL. Rose LJ, Rice EW, Hodges L, Peterson A, Arduino MJ. Srinivasan S, Harrington GW. Walsh BM, Naik HB, Dubach JM, Beshire M, Wieland AM, Soybel DI. Wiesenthal KE, McGuire MJ, Suffet IH. Winterbourn CC, Hampton MB, Livesey JH, Kettle AJ.

Yang X, Shang C, Westerhoff P.

#### Titles and authors of 24 manuscripts returned by search but not summarized:

- Alipour M, Omri A, Smith MG, Suntres ZE. Prophylactic effect of liposomal N-acetylcysteine against LPS-induced liver injuries. J Endotoxin Res. 2007;13(5):297-304.
- Bedner M, Maccrehan WA. Reactions of the amine-containing drugs fluoxetine and metoprolol during chlorination and dechlorination processes used in wastewater treatment. Chemosphere. 2006 Dec;65(11):2130-7. Epub 2006 Jul 25.
- Bew SP, Hughes DL, Palmer NJ, Savic V, Soapi KM, Wilson MA. Stereoselective synthesis of N-alkylaziridines from N-chloroamines. Chem Commun (Camb). 2006 Nov 4;(41):4338-40. Epub 2006 Sep 5.
- Calvo P, Crugeiras J, Rios A, Rios MA. Nucleophilic substitution reactions of N-chloramines: evidence for a change in mechanism with increasing nucleophile reactivity. J Org Chem. 2007 Apr 27;72(9):3171-8. Epub 2007 Mar 31.
- Chen MY, Li WM, Xu D, Chen WB. [Experimental study for the targeting therapy of mouse lung carcinoma treated by anti-hnRNPB1 monoclonal antibody with 131I] Sichuan Da Xue Xue Bao Yi Xue Ban. 2007 Sep;38(5):766-9. Chinese.
- Cooper WJ, Jones AC, Whitehead RF, Zika RG. Sunlight-induced photochemical decay of oxidants in natural waters: implications in ballast water treatment. Environ Sci Technol. 2007 May 15;41(10):3728-33.
- Deng YJ, Lou SF, Xu YZ. [Experimental study of 131I-labeled granulocyte macrophage colonystimulating factor in SCID mouse-acute myeloid leukemia model] Zhonghua Xue Ye Xue Za Zhi. 2007 Jan;28(1):33-6. Chinese.
- Droschl HH, Wendl B. Comparison of bond strength using various fixation methods. World J Orthod. 2007 Summer;8(2):153-6.
- Hillier RJ, Kumar N. Tonometer disinfection practice in the United Kingdom: A national survey. Eye. 2007 Apr 20; [Epub ahead of print]
- Kawai Y, Kiyokawa H, Kimura Y, Kato Y, Tsuchiya K, Terao J. Hypochlorous acid-derived modification of phospholipids: characterization of aminophospholipids as regulatory molecules for lipid peroxidation. Biochemistry. 2006 Nov 28;45(47):14201-11.
- Kunakbaeva AF, Karazhas NV, Zigangirova NA, Rybalkina TN, Galstian GM, Osmanov EA, Petrosov VV, Bosh'ian RE, Savitskaia NV, Feklisova LV, Iuditskii MV. [Detection of Pneumocystis carinii DNA in air and washes from medical equipment in hospitals] Zh Mikrobiol Epidemiol Immunobiol. 2006 Nov-Dec;(7):100-3. Russian.
- Laggner H, Muellner MK, Schreier S, Sturm B, Hermann M, Exner M, Gmeiner BM, Kapiotis S. Hydrogen sulphide: a novel physiological inhibitor of LDL atherogenic modification by HOC1. Free Radic Res. 2007 Jul;41(7):741-7.
- Lee W, Westerhoff P, Yang X, Shang C. Comparison of colorimetric and membrane introduction mass spectrometry techniques for chloramine analysis. Water Res. 2007 Jul;41(14):3097-102. Epub 2007 May 7. Erratum in: Water Res. 2007 Oct;41(18):4271.

- Meseguer-Lloret S, Molins-Legua C, Verdu-Andres J, Campins-Falco P. Chemiluminescent method for detection of eutrophication sources by estimation of organic amino nitrogen and ammonium in water. Anal Chem. 2006 Nov 1;78(21):7504-10.
- Nagy P, Ashby MT. Kinetics and mechanism of the oxidation of the glutathione dimer by hypochlorous Acid and catalytic reduction of the chloroamine product by glutathione reductase. Chem Res Toxicol. 2007 Jan;20(1):79-87.
- Pattison DI, Hawkins CL, Davies MJ. Hypochlorous acid-mediated protein oxidation: how important are chloramine transfer reactions and protein tertiary structure? Biochemistry. 2007 Aug 28;46(34):9853-64. Epub 2007 Aug 3.
- Raftery MJ. Detection and characterization of N-alpha-chloramines by electrospray tandem mass spectrometry. Anal Biochem. 2007 Jul 15;366(2):218-27. Epub 2007 Apr 14.
- Roshchupkin DI, Murina MA, Kravchenko NN, Sergienko VI. [Initial selectivity of the antiplatelet covalent action of biogenic chloramines on platelet-rich plasma] Biofizika. 2007 May-Jun;52(3):527-33. Russian.
- Watts MJ, Linden KG. Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. Water Res. 2007 Jul;41(13):2871-8. Epub 2007 May 11.
- Williams GJ, Sheikh B, Holden RB, Kouretas TJ, Nelson KL. The impact of increased loading rate on granular media, rapid depth filtration of wastewater. Water Res. 2007 Nov;41(19):4535-45. Epub 2007 Jun 15.
- Xu SZ, Wang CX, Zhao W, Chu JF, Liu WD, Li M. [Correlation between matrix metalloproteinases activities and myocardial injury in neonatal rats after asphyxia] Zhonghua Er Ke Za Zhi. 2007 Feb;45(2):134-7. Chinese.
- Yeh E, Blasiak LC, Koglin A, Drennan CL, Walsh CT. Chlorination by a long-lived intermediate in the mechanism of flavin-dependent halogenases. Biochemistry. 2007 Feb 6;46(5):1284-92.
- Zhai H, Parvez M, Back TG. A highly stereoselective synthesis of (-)-(ent)-julifloridine from the cyclization of an alanine-derived chloroamine with an acetylenic sulfone. J Org Chem. 2007 May 11;72(10):3853-8. Epub 2007 Apr 17.
- Zhitkov MIu, Chechina GN, Vinnichenko IuA, Rudenko OE, Kulazhenko TV, Serebriakov LE. [Comparative study of injuring action of the preparations used for chemical-mechanic removal of carious dentine] Stomatologiia (Mosk). 2007;86(2):9-11. Russian.



## Memorandum

To: Andrew DeGraca, P.E.

From: June M. Weintraub, Sc.D.

Date: October 14, 2008

Re: Summary of Monochloramine Abstract Review November 2007-October 2008

Throughout the year, we monitor the literature relevant to monochloramine using PubMed, the bibliographic index of peer-reviewed health, scientific and chemistry journals. PubMed is maintained by the National Center for Biotechnology Information (NCBI) at the National Library of Medicine (NLM), located at the U.S. National Institutes of Health (NIH). The following is a summary of relevant abstracts of new peer-reviewed publications that had been entered into the database between November 9, 2007 and October 10, 2008. A total of 44 results were returned with the search criteria:

(chloramine OR monochloramine) AND 2007/11/09:2008/10/10[edat] NOT taurine NOT chloramine-T

Of the 44 total, 17 were not sufficiently relevant, and these are listed at the end of this memo, but not described in detail. A summary of the abstracts of the remaining 27 publications follows. **Our abstract review did not reveal any new evidence that warrants reconsideration of our support for the use chloramine, and SFDPH continues to support the use of chloramine for secondary disinfection in the SFPUC water system**. Abstracts fall into the following categories:

- I. Studies on NDMA and other chloramine DBPs (8 abstracts)
- II. Manuscripts relevant to microbiology and efficacy of chloramine (11 abstracts)
- III. Nitrification (2 abstracts)
- IV. Chloramine chemistry (3 abstracts)
- V. Chloramine analysis (3 abstracts)
- VI. Not relevant (17 abstracts)

In contrast to our 2007 search, there were no studies specific to swimming pools or specific to corrosion or pipe materials.

### I. Studies on NDMA and other chloramine DBPs (8 abstracts)

**1.** Chen WH, Young TM.

NDMA formation during chlorination and chloramination of aqueous diuron solutions. Environ Sci Technol. 2008 Feb 15;42(4):1072-7.

This manuscript presented the results of a study of NDMA formation in waters contaminated with the phenylurea herbicide diuron, finding that in the presence of diuron, NDMA formation was lowest using Hypochlorite, higher with monochloramine, and highest with dichloramine.

## 2. Chen Z, Valentine RL.

The influence of the pre-oxidation of natural organic matter on the formation of Nnitrosodimethylamine (NDMA).

Environ Sci Technol. 2008 Jul 15;42(14):5062-7.

The authors report the results of experiments investigating the effect of preoxidation with free chlorine, permanganate, hydrogen peroxide, ozone and simulated sunlight on subsequent formation of NDMA after monochloramination, finding that NDMA formation was reduced by preoxidation.

Note: SFPUC practices preoxidation at all primary treatment facilities: Hetch Hetchy (at Tesla) chlorine, at HTWTP ozone and chlorine, at SVWTP chlorine.

## **3.** Duirk SE, Valentine RL.

Bromide oxidation and formation of dihaloacetic acids in chloraminated water. Environ Sci Technol. 2007 Oct 15;41(20):7047-53.

The authors describe a model developed that demonstrates the effect of bromide on monochloramine loss and the formation of bromine and chlorine containing dihaloacetic acids in the presence of natural organic matter (NOM). The rate of NOM oxidation by active bromine species was faster than monochloramine autodecomposition catalyzed by bromide. Bromine and chlorine were incorporated into DHAAs in proportion to the amount of NOM oxidized by each halogen.

# 4. Mitch WA, Schreiber IM.

Degradation of tertiary alkylamines during chlorination/chloramination: implications for formation of aldehydes, nitriles, halonitroalkanes, and nitrosamines.

Environ Sci Technol. 2008 Jul 1;42(13):4811-7.

The authors the degradation of model tertiary alkylamines during chlorination and chloramination, finding that during either chlorination or chloramination tertiary alkylamines degrade nearly instantaneously to form aldehydes and secondary alkylamines; the degradation rate is slower with chloramination, yielding lower concentrations of aldehydes. They also found that trichloronitromethane was formed at very low yields during chlorination, and not at all during chloramination; monochloronitromethane and dichloronitromethane were never detected. The authors also reported low nitrile yields by the reaction between chloramines and aldehydes.

# 5. Onstad GD, Weinberg HS, Krasner SW.

Occurrence of halogenated furanones in U.S. drinking waters. Environ Sci Technol. 2008 May 1;42(9):3341-8. This study compared formation of the disinfection byproduct MX in 3 pairs of drinking water treatment plants. Each pair had the same source water and different treatment schemes. Among the study findings were that MX-analogues had higher occurrence in waters disinfected with free chlorine compared to monochloramine.

6. Walsh ME, Gagnon GA, Alam Z, Andrews RC.

Biostability and disinfectant by-product formation in drinking water blended with UF-treated filter backwash water.

Water Res. 2008 Apr;42(8-9):2135-45. Epub 2007 Nov 24.

This study is relevant for utilities that use already disinfected water to backwash their filters, then recycle the backwash filter water through the treatment process. The study examined the effect of blending 10% filter backwash water on DBP formation, finding that, in general, creation of trihalomethanes or haloacetic acids after blending was not different regardless of whether the filtered backwash water was treated with chlorine, chlorine dioxide or monochloramine. However, because the chlorinated filter backwash water had higher preformed THM and HAA concentration, blending resulted in higher finished water THM and HAA concentrations that could exceed regulatory limits.

7. Yang X, Shang C, Lee W, Westerhoff P, Fan C.

Correlations between organic matter properties and DBP formation during chloramination. Water Res. 2008 Apr;42(8-9):2329-39. Epub 2008 Jan 4.

The authors performed experiments to develop and propose a reaction model that relates chloramine concentrations, organic matter levels and formation of disinfection byproducts. The experiments revealed linear relationships between organic matter fractions and formation of dichloroacetic acid, chloroform, dichloracetonitrile, and total organic halogen, but no linear relationship was observed for formation of cyanogen chloride or chlorpicrin.

8. Zhao YY, Boyd JM, Woodbeck M, Andrews RC, Qin F, Hrudey SE, Li XF.

Formation of N-nitrosamines from eleven disinfection treatments of seven different surface waters.

Environ Sci Technol. 2008 Jul 1;42(13):4857-62.

The authors performed experiments using seven source waters with TOC ranging from 2-24 mg/L and NDMA ranging from 0-53 ng/L. The source waters were treated with 11 different disinfection treatment schemes to evaluate formation of nine N-nitrosamines. These disinfection treatments were chlorine (OCl-), chloramine (NH2Cl), chlorine dioxide (ClO2), ozone (O3), ultraviolet (UV), advanced oxidation processes (AOP) alone and in combinations. NDMA concentrations in the disinfected water samples ranged form 0-118 ng/L. "N-nitrosodiethylamine (NDEA), N-nitrosomorpholine (NMor), and N-nitrosodiphenylamine (NDPhA) were also identified in some of the disinfected water samples. NDPhA (0.2-0.6 ng x L(-1)) was formed after disinfection with OCl-, NH2Cl, O3, and MPUV/OCl-. NMEA was produced with OCl- and MPUV/OCl-, and NMor formation was associated with O3. In addition, UVtreatment alone degraded NDMA; however, UV/ OCl- and AOP/OCl- treatments produced higher amounts of NDMA compared to UV and AOP alone, respectively. These results suggest that UV degradation or AOP oxidation treatment may provide a source of NDMA precursors. This study demonstrates that environmental concentrations and mixtures of unknown nitrosamine precursors in source waters can form NDMA and other nitrosamines."

### **II.** Manuscripts relevant to microbiology and efficacy of chloramine (11 abstracts)

1. Alleron L, Merlet N, Lacombe C, Frère J.

Long-Term Survival of Legionella pneumophila in the Viable But Nonculturable State After Monochloramine Treatment.

Curr Microbiol. 2008 Oct 7. [Epub ahead of print]

The authors report an experiment where monochloramine treatment in concentrations ranging from 0.25 mg/L to 10 mg/L were applied to biofilm containing *L. pneumophila*. They found that some L. pneumophila remained in a "Viable but Non Culturable" (VBNC) state with membrane integrity and esterase activity; some of the cells were resuscitated when amoeba were introduced, however no resuscitation was observed in any sample treated with monochloramine doses greater than or equal to 1 mg/L.

2. Cole KD, Gaigalas A, Almeida JL.

Process monitoring the inactivation of ricin and model proteins by disinfectants using fluorescence and biological activity.

Biotechnol Prog. 2008 May-Jun;24(3):784-91. Epub 2008 Apr 4.

This manuscript focus was on the use of fluorescence to determine inactivation of ricin in the environment. Fluorescence revealed that monochloramine required higher concentrations and more time to reveal significant changes in fluorescence, compared to sodium hypochlorite.

3. Farooq S, Hashmi I, Qazi IA, Qaiser S, Rasheed S.

Monitoring of Coliforms and chlorine residual in water distribution network of Rawalpindi, Pakistan.

Environ Monit Assess. 2008 May;140(1-3):339-47. Epub 2007 Nov 8.

This study looked at microbiology of water in distribution systems in Pakistan, where water treatment and maintenance of residuals in the distribution are inadequate. The study is not clear what treatment schemes were in place at the eight plants that they sampled, so the study is not specifically relevant to monochloramine.

4. Jurgens DJ, Sattar SA, Mah TF.

Chloraminated drinking water does not generate bacterial resistance to antibiotics in Pseudomonas aeruginosa biofilms.

Lett Appl Microbiol. 2008 May;46(5):562-7.

This study treated biofilm with 0.5 mg/l and 1.0 mg/l chloramine for 15 or 21 days, finding that fewer antibiotic resistant isolates of *Pseudomonas aeruginosa* were formed with chloramine compared to water with no disinfectant concentration.

5. Keegan A, Daminato D, Saint CP, Monis PT.

Effect of water treatment processes on Cryptosporidium infectivity.

Water Res. 2008 Mar;42(6-7):1805-11. Epub 2007 Nov 17.

This manuscript reported the results of an experiment that found that treatment schemes that included aluminum sulphate, dissolved air flotation, and chlorine or chloramine did not affect the infectivity (as measured by cell culture and PCR techniques) of Cryptosporidium oocysts.

6. Murphy HM, Payne SJ, Gagnon GA.

Sequential UV- and chlorine-based disinfection to mitigate Escherichia coli in drinking water

biofilms.

Water Res. 2008 Apr;42(8-9):2083-92. Epub 2008 Jan 4.

This manuscript reported an experiment where different combinations of UV and chlorine dioxide, monochloramine, or chlorine were tested for their efficacy against E. coli in either polycarbonate or cast iron reactors. The purpose was to determine the magnitude of additional disinfection achieved by adding UV to traditional disinfection regimes. The study found that all three disinfectants removed E. coli effectively. The addition of UV to chlorine resulted in a longer persistence of E. coli; with lower concentrations of ClO2, E. coli reappeared in the cast iron reactors only, which the authors hypothesized could be attributed to the oxidation of iron by chlorite. Adding UV to monochloramine resulted in decrease of E. Coli levels to below detection in the reactors, however E. coli was detected in the biofilm of the cast-iron reactor at both higher and lower NH2Cl concentrations.

7. Sanderson SS, Stewart PS.

Evidence of bacterial adaptation to monochloramine in Pseudomonas aeruginosa biofilms and evaluation of biocide action model.

Biotechnol Bioeng. 1997 Oct 20;56(2):201-9.

This 1997 manuscript appeared in our search because it was entered into the PubMed database in 2008. The authors tested a mathematical model to predict microbial biofilm Pseudomonas concentrations in the presence of different concentrations of monochloramine.

8. Sirikanchana K, Shisler JL, Mariñas BJ.

Effect of exposure to UV-C irradiation and monochloramine on adenovirus serotype 2 early protein expression and DNA replication.

Appl Environ Microbiol. 2008 Jun;74(12):3774-82. Epub 2008 Apr 18.

This manuscript reports a comparison between UV-C irradiation and monochloramine treatment on two steps of the adenovirus life cycle, with a goal of elucidating the mechanism by which these two disinfectants control adenovirus. The authors found that UV-C and monochloramine had the same efficacy to minimize E1A protein synthesis but UV was more effective than monochloramine at reducing genomic DNA levels.

9. Sirikanchana K, Shisler JL, Mariñas BJ.

Inactivation kinetics of adenovirus serotype 2 with monochloramine.

Water Res. 2008 Mar;42(6-7):1467-74. Epub 2007 Oct 23.

This paper presented results of an experiment to determine how quickly monochloramine inactivation of adenovirus occurs under differing pH, temperature, initial monochloramine concentration, and ammonia nitrogen-to-chlorine molar ratios. The authors reported that inactivation of adenovirus serotype 2 with monochloramine decreased with increasing pH.

10. Zhang XJ, Chen C, Wang Y.

Synergetic inactivation of microorganisms in drinking water by short-term free chlorination and subsequent monochloramination.

Biomed Environ Sci. 2007 Oct;20(5):373-80.

The authors report results of experiments to test effect on indicator microorganisms when free chlorine is applied for less than 15 minutes followed by monochlorame. Inactivation of Escherichia coli, Staphylococcus aureus, Candida albicans, and spores of Bacillus subtilis was

more efficient with sequential process than free chlorine alone. The efficacy was influenced by ammonia addition time, temperature and pH.

11. Westrick JA.

Cyanobacterial toxin removal in drinking water treatment processes and recreational waters. Adv Exp Med Biol. 2008;619:275-90.

This review article discusses the effect of disinfection decisionmaking on algal toxins concentrations. The manuscript includes discussion of microcystin LR and several microcystin variants, as well as anatoxin-a, saxitoxins, and cyclindrospermopsin.

## III. Nitrification (2 abstracts)

**1.** Sathasivan A, Fisher I, Tam T.

Onset of severe nitrification in mildly nitrifying chloraminated bulk waters and its relation to biostability.

Water Res. 2008 Aug;42(14):3623-32. Epub 2008 Jun 21.

The authors investigated occurrence of nitrogenous compounds and total chlorine in bulk water samples to identify parameters that would provide early warning of severe nitrification. They found that in samples with total ammoniacal nitrogen in the range 0.25 and 0.35mg-N/L, severe nitrification was triggered when chloramine residuals dropped below the range of 0.2-0.65mg/L. Nitrite levels in winter were not good indicators of nitrifying status.

2. Zhang Y, Griffin A, Edwards M.

Nitrification in premise plumbing: role of phosphate, pH and pipe corrosion.

Environ Sci Technol. 2008 Jun 15;42(12):4280-4.

In bench experiments, the authors found the following, as reported in their abstract: "Nitrification in PVC premise plumbing is a weak function of pH over the range 6.5--8.5 and is insensitive to phosphate concentrations 5--1000 ppb. Lead pipe enhanced nitrification relative to PVC, consistent with expectations that nitrifiers could benefit from ammonia recycled from nitrate via lead corrosion. Relatively new copper pipe (< 1.5-years-old) did not allow nitrifiers to establish, but nitrifiers gradually colonized over a period of months in brass pipes when copper concentrations were reduced by pH adjustment or orthophosphate. Nitrifiers were inhibited by trace copper, but not by lead levels up to 8000 ppb. In some systems using chloramines, brass in plastic plumbing systems might be more susceptible to lead/copper leaching, and accelerated dezincification, due to lower pH values resulting from nitrification."

# IV. Chloramine chemistry (3 abstracts)

1. Chen JL, Shi HC, Xu LL.

Effect of pH for the electrochemical oxidation products and oxidation pathways of ammonia Huan Jing Ke Xue. 2008 Aug;29(8):2277-81. Chinese.

This manuscript is in Chinese and is relevant to wastewater; however the English abstract indicates one of the findings was that trichloramine formation can be avoided as long as pH is maintained above 5.

2. Kochany J, Lipczynska-Kochany E.

Catalytic destruction of chloramine to nitrogen using chlorination and activated carbon--case study.

Water Environ Res. 2008 Apr;80(4):339-45.

The paper describes a novel method of removing monochloramine from water that minimizes production of ammonia. The authors found that ammonia production is minimized at an optimal chlorine-to-ammonia ration of 7:1 followed by treatment with catalytic activated carbon at temperatures ranging from 5 to 20 degrees C.

**3.** Shang F, Uber JG, Rossman LA.

Modeling reaction and transport of multiple species in water distribution systems. Environ Sci Technol. 2008 Feb 1;42(3):808-14.

This manuscript describes a framework for modeling chemicals in drinking water distribution systems using novel numerical methods and mathematical functions.

### V. Chloramine analysis (3 abstracts)

These manuscripts investigate methods for detecting chloramine in laboratory settings.

1. Amiri F, Andrews S.

Development of a size exclusion chromatography-electrochemical detection method for the analysis of total organic and inorganic chloramines. J Chromatogr Sci. 2008 Aug;46(7):591-5.

- 2. Senthilmohan ST, Kettle AJ, McEwan MJ, Dummer J, Edwards SJ, Wilson PF, Epton MJ. Detection of monobromamine, monochloramine and dichloramine using selected ion flow tube mass spectrometry and their relevance as breath markers. Rapid Commun Mass Spectrom. 2008;22(5):677-81.
- **3.** Tao H, Chen ZL, Li X, Yang YL, Li GB. Salicylate-spectrophotometric determination of inorganic monochloramine. Anal Chim Acta. 2008 May 19;615(2):184-90. Epub 2008 Apr 9.

# VI. Not relevant (17 abstracts)

### Biochemical studies of molecular level monochloramine

Twelve manuscripts report results of research on the molecular and cellular level monochloramine. The relevance of this research to drinking water or other exogenous exposures is not known.

 Kang JI Jr, Neidigh JW. Hypochlorous acid damages histone proteins forming 3-chlorotyrosine and 3,5dichlorotyrosine. Chem Res Toxicol. 2008 May;21(5):1028-38. Epub 2008 May 2.

- **2.** Marsche G, Furtmüller PG, Obinger C, Sattler W, Malle E. Hypochlorite-modified high-density lipoprotein acts as a sink for myeloperoxidase in vitro. Cardiovasc Res. 2008 Jul 1;79(1):187-94. Epub 2008 Feb 23.
- **3.** Mitsopoulos P, Omri A, Alipour M, Vermeulen N, Smith MG, Suntres ZE. Effectiveness of liposomal-N-acetylcysteine against LPS-induced lung injuries in rodents. Int J Pharm. 2008 Nov 3;363(1-2):106-11. Epub 2008 Jul 23.
- 4. Ogino T, Ozaki M, Hosako M, Omori M, Okada S, Matsukawa A. Activation of c-Jun N-terminal kinase is essential for oxidative stress-induced Jurkat cell apoptosis by monochloramine. Leuk Res. 2008 Aug 19. [Epub ahead of print]
- **5.** Prinz G, Diener M. Characterization of ryanodine receptors in rat colonic epithelium. Acta Physiol (Oxf). 2008 Jun;193(2):151-62. Epub 2007 Nov 15.
- Rawal GK, Kumar A, Tawar U, Vankar YD. New method for chloroamidation of olefins. Application in the synthesis of N-glycopeptides and anticancer agents. Org Lett. 2007 Dec 6;9(25):5171-4. Epub 2007 Nov 10.
- 7. Richter G, Schober C, Süss R, Fuchs B, Müller M, Schiller J. The reaction between phosphatidylethanolamines and HOCl investigated by TLC: fading of the dye primuline is induced by dichloramines. J Chromatogr B Analyt Technol Biomed Life Sci. 2008 May 15;867(2):233-7. Epub 2008 Apr 15.
- Richter G, Schober C, Süss R, Fuchs B, Birkemeyer C, Schiller J. Comparison of the positive and negative ion electrospray ionization and matrix-assisted laser desorption ionization-time-of-flight mass spectra of the reaction products of phosphatidylethanolamines and hypochlorous acid. Anal Biochem. 2008 May 1;376(1):157-9. Epub 2008 Jan 31.
- **9.** Robaszkiewicz A, Bartosz G, Soszyński M. Effect of N-chloroamino acids on the erythrocyte. Free Radic Res. 2008 Jan;42(1):30-9.

10. Skaff O, Pattison DI, Davies MJ. The vinyl ether linkages of plasmalogens are favored targets for myeloperoxidase-derived oxidants: a kinetic study. Biochemistry. 2008 Aug 5;47(31):8237-45. Epub 2008 Jul 8.

**11.** Stief TW, Richter A, Maisch B, Renz H. Monitoring of Functional Plasminogen in Blood of Patients Receiving Fibrinolytics. Clin Appl Thromb Hemost. 2007 Dec 26. [Epub ahead of print] **12.** Wojtecka-Lukasik E, Grzybowska-Kowalczyk A, Maslinska D, Szukiewicz D, Schunack W, No Abstract

Effect of histamine chloramine on luminol-dependent chemiluminescence of granulocytes. Inflamm Res. 2008;57 Suppl 1:S19-20. No abstract available.

#### Other not relevant

In addition to the twelve manuscripts describing molecular level monochloramine, five manuscripts appeared in our search that either are not relevant to drinking water (Bendall 2008; Bussadori et al., 2008; Kibadi 2008; Minakata et al., 2008), or that appear to erroneously have been categorized by the keyword chloramine (Sharma 2008).

#### 13. Bendall JG.

Semicarbazide is non-specific as a marker metabolite to reveal nitrofurazone abuse as it can form under Hofmann conditions.

Food Addit Contam. 2008 Jun 12:1-10. [Epub ahead of print]

### 14. Bussadori SK, Guedes CC, Hermida Bruno ML, Ram D.

Chemo-mechanical removal of caries in an adolescent patient using a papain gel: case report. J Clin Pediatr Dent. 2008 Spring;32(3):177-80.

### 15. Kibadi K.

[Mycobacterium ulcerans infection treated by Rifater, pyrazynamide, Myambutol, and surgery: a case report with a 6-year follow-up] Med Mal Infect. 2008 Mar;38(3):156-8. Epub 2008 Feb 20. French.

### 16. Minakata S, Tsuruoka R, Nagamachi T, Komatsu M.

The ionic introduction of an N1 unit to C60 and a unique rearrangement of aziridinofullerene. Chem Commun (Camb). 2008 Jan 21;(3):323-5.

### 17. Sharma RN, Goel S.

Chlorinated drinking water, cancers and adverse health outcomes in Gangtok, Sikkim, India. J Environ Sci Eng. 2007 Oct;49(4):247-54.

This study appears to have been erroneously categorized with the keyword chloramine. The manuscript reports a cross sectional study of the relationship between cancer and gastrointestinal and infectious diseases and exposure to chlorinated and non chlorinated drinking water in India. It is not clear what drinking water treatment was received by the "non chlorinated" group. Since the abstract does not mention chloramine, it appears this manuscript may have erroneously been categorized by the keyword chloramine.



City and County of San Francisco DEPARTMENT OF PUBLIC HEALTH ENVIRONMENTAL HEALTH SECTION

#### Memorandum

To: Andrew DeGraca, P.E.

From: June M. Weintraub, Sc.D.

Date: February 3, 2009

Re: Addendum to 2008 Summary of Monochloramine Abstract Review October 2008-February 2009

As you know, throughout the year, we monitor the literature relevant to monochloramine using PubMed, the bibliographic index of peer-reviewed health, scientific and chemistry journals. PubMed is maintained by the National Center for Biotechnology Information (NCBI) at the National Library of Medicine (NLM), located at the U.S. National Institutes of Health (NIH).

Annually, we provide to you a formal summary of the abstracts. This addendum covers the part of the year since we last provided a summary, and covers the period October 11, 2008 – February 3, 2009. A total of 16 results were returned with the search criteria:

(chloramine OR monochloramine) AND 2008/10/11:2009/02/03[edat] NOT taurine NOT chloramine-T

In this time period, the studies of most critical interest were relevant to the chemistry and potential health effects of lead in the presence of monochloramine.<sup>\*</sup> These results are useful and interesting to utilities that have lead service lines or lead pipe in their distribution systems; the SFPUC system does not have lead service lines or lead piping in the distribution system, and has consistently complied with all regulations for presence of lead.

This addendum to our abstract review did not reveal any new evidence that warrants reconsideration of our support for the use chloramine, and SFDPH continues to support the use of chloramine for secondary disinfection in the SFPUC water system. A brief summary of each of the 16 abstracts follows.

<sup>&</sup>lt;sup>\*</sup> Note that a recent study published in Environmental Science and Technology described the relationship between blood lead levels and drinking water lead in Washington DC. This manuscript has not yet been entered into the PubMed database, and does not appear in these results, however we reviewed this manuscript upon its release. The citation is Edwards M; Triantafyllidou S, and Best D. Elevated Blood Lead in Young Children Due to Lead-Contaminated Drinking Water: Washington, DC, 2001–2004. Environ. Sci. Technol. DOI: 10.1021/es802789w Publication Date (Web): January 27, 2009

**1.** Lin YP, Valentine RL.

Release of Pb(II) from monochloramine-mediated reduction of lead oxide (PbO2). Environ Sci Technol. 2008 Dec 15;42(24):9137-43.

This interesting manuscript describes experiments on the release of soluble lead from the reduction of lead oxide scales by monochloramine. The relevance of this work to SFPUC has been discussed and put into context for SFPUC by the senior author, Dr. Richard Valentine, who concluded in a letter to SFPUC that "...the lead levels in SFPUC system are well below regulatory limits and not impacted by this hypothesized process."

2. Tsuruoka R, Nagamachi T, Murakami Y, Komatsu M, Minakata S.

Aziridination of C(60) with Simple Amides and Catalytic Rearrangement of the Aziridinofullerenes to Azafulleroids.

J Org Chem. 2009 Jan 22. [Epub ahead of print]

This study is not relevant—it describes a study that included chloramine B.

**3.** Shao J, Fang X, He Y, Jin Q.

Emergency membrane contactor based absorption system for ammonia leaks in water treatment plants.

J Environ Sci (China). 2008;20(10):1189-94.

This manuscript describes a pilot study of an membrane absorption system for responding to ammonia leaks in the water treatment plant storage room.

4. de Oliveira RM, de los Santos CA, Antonello I, d'Avila D.

Warning: an anemia outbreak due to chloramine exposure in a clean hemodialysis unit--an issue to be revisited.

Ren Fail. 2009;31(1):81-3.

This manuscript describes a 2004 incident in Brazil in which treatment failure led to incomplete removal of chloramine in a dialysis unit.

5. Kohler JE, Mathew J, Tai K, Blass AL, Kelly E, Soybel DI.
Monochloramine Impairs Caspase-3 Through Thiol Oxidation and Zn(2+) Release.
J Surg Res. 2008 Jun 27. [Epub ahead of print]
This manuscript describes a hypothesis of the mechanism of action of intracellular monochloramine, which is not relevant to drinking water exposure to monochloramine.

6. Fisher I, Sathasivan A, Chuo P, Kastl G.

Effects of stratification on chloramine decay in distribution system service reservoirs. Water Res. 2008 Dec 24. [Epub ahead of print]

This Australian study describes the use of the microbial decay factor (F(m)) method, to predict the loss of chloramine residual and inform prevention of nitrification.

**7.** Inactivation of Nitrosomonas europaea and pathogenic Escherichia coli by chlorine and monochloramine.

Chauret C, Smith C, Baribeau H.

J Water Health. 2008 Sep;6(3):315-22.

This study measured the chlorine and monochloramine inactivation kinetics of Nitrosomonas europaea, concluding that the CT values present in distribution systems are likely to be sufficient to control suspended cells of both N. europaea and E. Coli.

8. Re: "Water disinfection by-products and pre labor rupture of membranes".

Heitz A, Kristiana I.

Am J Epidemiol. 2009 Jan 1;169(1):122-3; discussion 123. Epub 2008 Nov 24.

This correspondence commented on a manuscript that described an association between nitrate and pre labor rupture of membranes. The correspondence focused on the fraction of total nitrogen represented by nitrate in the Australian water system that was the setting for the original study.

### 9. Brown SM.

Comment on "Nitrification in premise plumbing: role of phosphate, pH, and pipe corrosion". Environ Sci Technol. 2008 Nov 1;42(21):8170; author reply 8171.

This letter to the editor commented on a study of nitrification in premise plumbing (described in our 2008 annual abstract review). The correspondence noted the unrealistic conditions of the experiment reported in the original manuscript.

10. Luh J, Tong N, Raskin L, Mariñas BJ.

Inactivation of Mycobacterium avium with monochloramine.

Environ Sci Technol. 2008 Nov 1;42(21):8051-6.

This manuscript described the results of batch experiments inactivation kinetics of *Mycobacterium avium* in the presence of monochloramine at 5-30 degrees C, pH 6-10, and 0.30-42.3 mg Cl2/ L, finding inactivation efficiency varies broadly depending on these variables.

11. Fu J, Qu J, Liu R, Zhao X, Qiang Z.

The influence of Cu(II) on the decay of monochloramine.

Chemosphere. 2009 Jan;74(2):181-6. Epub 2008 Nov 14.

This paper described experiments undertaken by researchers in China to understand the decomposition rate of monochloramine in the presence of Cu(II) at differing pH. The purpose of the paper was to inform monochloramine dose where Cu(II) exists.

**12.** Stone ME, Scott JW, Schultz ST, Berry DL, Wilcoxon M, Piwoni M, Panno B, Bordson G. Comparison of chlorine and chloramine in the release of mercury from dental amalgam. Sci Total Environ. 2009 Jan 1:407(2):770-5. Epub 2008 Oct 30.

This study reported results of an experiment that found that changing from chlorine to chloramine disinfection at water treatment plants would not be expected to produce substantial increases in dissolved mercury levels in dental-unit wastewater.

**13.** Hashmi I, Farooq S, Qaiser S.

Chlorination and water quality monitoring within a public drinking water supply in Rawalpindi Cantt (Westridge and Tench) area, Pakistan.

Environ Monit Assess. 2008 Oct 30. [Epub ahead of print]

This study of drinking water quality in Pakistan supports the importance of maintaining disinfectant residual in the distribution system.

14. Iwao Y, Nakajou K, Nagai R, Kitamura K, Anraku M, Maruyama T, Otagiri M.

CD36 is one of important receptors promoting renal tubular injury by advanced oxidation protein products.

Am J Physiol Renal Physiol. 2008 Dec;295(6):F1871-80. Epub 2008 Oct 29.

This study is not relevant—the chloramine reference is to the use of a chloramine solution in preparing the experimental materials.

15. Emmert GL, Coutant DE, Sweetin DL, Gordon G, Bubnis B.

Studies of selectivity in the amaranth method for chlorine dioxide.

Talanta. 2000 Apr 28;51(5):879-88.

This older manuscript appears because it was only recently entered into the PubMed database. The manuscript describes a technique for measuring disinfectant in water.

16. Morrow JB, Almeida JL, Fitzgerald LA, Cole KD.

Association and decontamination of Bacillus spores in a simulated drinking water system. Water Res. 2008 Dec;42(20):5011-21. Epub 2008 Sep 30.

This manuscript describes the disinfectant susceptibility of Bacillus anthracis Sterne (BA) and Bacillus thuringiensis (BT) spores in biofilm on PVC and copper pipe materials.



City and County of San Francisco DEPARTMENT OF PUBLIC HEALTH ENVIRONMENTAL HEALTH SECTION Gavin Newsom, Mayor Mitchell H. Katz, MD, Director of Health Rajiv Bhatia, MD, MPH, Director of EH

#### Memorandum

To: Andrew DeGraca, P.E.

From: June M. Weintraub, Sc.D.

Date: August 19, 2010

Re: Summary of Monochloramine Abstract Review February 2009-July 2010

1. M. ti

Throughout the year, we monitor the literature relevant to monochloramine using PubMed, the bibliographic index of peer-reviewed health, scientific and chemistry journals. PubMed is maintained by the National Center for Biotechnology Information (NCBI) at the National Library of Medicine (NLM), located at the U.S. National Institutes of Health (NIH). The following is a summary of relevant abstracts of new peer-reviewed publications that had been entered into the database between February 4, 2009 and July 15, 2010. A total of 93 results were returned with the search criteria:

(chloramine OR monochloramine) AND 2009/02/04:2010/07/15[edat] NOT taurine NOT chloramine-T

Of the 93 total, 33 were not relevant, and these are listed at the end of this memo. We reviewed the abstracts of the remaining 60 publications, and categorized them as follows:

- I. Studies on Chloramine Disinfection By-products (20 abstracts)
- II. Manuscripts relevant to efficacy of chloramine (16 abstracts)
- III. Lead and/or Nitrification (6 abstracts)
- IV. Chloramine chemistry (8 abstracts)
- V. Dialysis (2 abstracts)
- VI. Chloramine analysis (2 abstracts)
- VII. Swimming Pools (6 abstracts)
- VIII. Not relevant (33 abstracts)

Our abstract review did not reveal any new evidence that warrants reconsideration of our support for the use chloramine, and SFDPH continues to support the use of chloramine for secondary disinfection in the SFPUC water system.

#### I. <u>Studies on Chloramine Disinfection By-products (20 abstracts)</u>

These studies investigated the formation of disinfection by-products in drinking water disinfected with chloramine. Some studies looked at formation potential of waters that used different types of disinfection schemes, other studies examined disinfection byproduct precursors, and others investigated methods for disinfection byproduct control.

- **1.** Bougeard CM, Goslan EH, Jefferson B, Parsons SA. Comparison of the disinfection byproduct formation potential of treated waters exposed to chlorine and monochloramine. Water Res. 2010 Feb;44(3):729-40. Epub 2009 Nov 10. PubMed PMID: 19910014.
- **2.** Bull RJ, Rice G, Teuschler L, Feder P. Chemical measures of similarity among disinfection by-product mixtures. J Toxicol Environ Health A. 2009;72(7):482-93. PubMed PMID: 19267309.
- **3.** Chen B, Westerhoff P. Predicting disinfection by-product formation potential in water. Water Res. 2010 Jul;44(13):3755-3762. Epub 2010 Apr 28. PubMed PMID: 20605186.
- **4.** Dotson A, Westerhoff P, Krasner SW. Nitrogen enriched dissolved organic matter (DOM) isolates and their affinity to form emerging disinfection by-products. Water Sci Technol. 2009;60(1):135-43. PubMed PMID: 19587411.
- **5.** Fu J, Qu J, Liu R, Qiang Z, Liu H, Zhao X. Cu(II)-catalyzed THM formation during water chlorination and monochloramination: a comparison study. J Hazard Mater. 2009 Oct 15;170(1):58-65. Epub 2009 May 9. PubMed PMID: 19520506.
- **6.** Goslan EH, Krasner SW, Bower M, Rocks SA, Holmes P, Levy LS, Parsons SA. A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland. Water Res. 2009 Oct;43(18):4698-706. Epub 2009 Jul 26. PubMed PMID: 19665750.
- 7. Hayes-Larson EL, Mitch WA. Influence of the method of reagent addition on dichloroacetonitrile formation during chloramination. Environ Sci Technol. 2010 Jan 15;44(2):700-6. PubMed PMID: 20000677.
- **8.** Hu J, Song H, Karanfil T. Comparative analysis of halonitromethane and trihalomethane formation and speciation in drinking water: the effects of disinfectants, pH, bromide, and nitrite. Environ Sci Technol. 2010 Jan 15;44(2):794-9. PubMed PMID: 20000680.
- **9.** Kemper JM, Walse SS, Mitch WA. Quaternary amines as nitrosamine precursors: a role for consumer products? Environ Sci Technol. 2010 Feb 15;44(4):1224-31. PubMed PMID: 20085252.
- **10.** Kemper JM, Westerhoff P, Dotson A, Mitch WA. Nitrosamine, dimethylnitramine, and chloropicrin formation during strong base anion-exchange treatment. Environ Sci Technol. 2009 Jan 15;43(2):466-72. PubMed PMID: 19238981.

- **11.** Krasner SW, Westerhoff P, Chen B, Rittmann BE, Amy G. Occurrence of disinfection byproducts in United States wastewater treatment plant effluents. Environ Sci Technol. 2009 Nov 1;43(21):8320-5. PubMed PMID: 19924963.
- **12.** Krasner SW. The formation and control of emerging disinfection by-products of health concern. Philos Transact A Math Phys Eng Sci. 2009 Oct 13;367(1904):4077-95. Review. PubMed PMID: 19736234.
- **13.** Kristiana I, Gallard H, Joll C, Croué JP. The formation of halogen-specific TOX from chlorination and chloramination of natural organic matter isolates. Water Res. 2009 Sep;43(17):4177-86. Epub 2009 Jun 27. PubMed PMID: 19616274.
- **14.** Li Y, Zhang X, Shang C. Effect of reductive property of activated carbon on total organic halogen analysis. Environ Sci Technol. 2010 Mar 15;44(6):2105-11. PubMed PMID: 20158207.
- **15.** Liu J, Chen C, Zhang XJ, Wang Y. [Use of two-points-short-term free chlorine plus chloramines disinfection process in conventional treatments of water supply]. Huan Jing Ke Xue. 2008 Dec;29(12):3368-71. Chinese. PubMed PMID: 19256369.
- **16.** Liu J, Chen C, Zhang XJ. [Disinfection by-products reduction of combined disinfection by chlorine and monochloramines in distribution system]. Huan Jing Ke Xue. 2009 Sep 15;30(9):2538-42. Chinese. PubMed PMID: 19927800.
- **17.** : Liu Q, Zhang LP, Liu WJ, Nie XB, Zhang SX, Zhang S. [Genotoxicity of drinking water during chlorine and chloramine disinfection and the influence of disinfection conditions using the umu-test]. Huan Jing Ke Xue. 2010 Jan;31(1):93-8. Chinese. PubMed PMID: 20329522.
- **18.** Park SH, Wei S, Mizaikoff B, Taylor AE, Favero C, Huang CH. Degradation of aminebased water treatment polymers during chloramination as N-nitrosodimethylamine (NDMA) precursors. Environ Sci Technol. 2009 Mar 1;43(5):1360-6. PubMed PMID: 19350904.
- **19.** Yang X, Fan C, Shang C, Zhao Q.Nitrogenous disinfection byproducts formation and nitrogen origin exploration during chloramination of nitrogenous organic compounds. Water Res. 2010 May;44(9):2691-702. Epub 2010 Feb 1.
- **20.** Zhou WJ, Boyd JM, Qin F, Hrudey SE, Li XF. Formation of N-nitrosodiphenylamine and two new N-containing disinfection byproducts from chloramination of water containing diphenylamine. Environ Sci Technol. 2009 Nov 1;43(21):8443-8. PubMed PMID: 19924982.

### II. <u>Manuscripts relevant to efficacy of chloramine (16 abstracts)</u>

Sixteen studies examined the efficacy of chloramine disinfection, including investigations of conditions that improve chloramine effectiveness, ability to inactivate microbial contaminants, and chemical reactions in the presence of chloramine.

- 1. Amiri F, Mesquita MM, Andrews SA. Disinfection effectiveness of organic chloramines, investigating the effect of pH. Water Res. 2010 Feb;44(3):845-53. Epub 2009 Sep 8. PubMed PMID: 19945732.
- **2.** Berry D, Xi C, Raskin L. Effect of growth conditions on inactivation of Escherichia coli with monochloramine. Environ Sci Technol. 2009 Feb 1;43(3):884-9. PubMed PMID: 19245031.
- **3.** Chamberlain EF, Wang C, Shi H, Adams CD, Ma Y. Oxidative removal and kinetics of fipronil in various oxidation systems for drinking water treatment. J Agric Food Chem. 2010 Jun 9;58(11):6895-9. PubMed PMID: 20455564.
- 4. Cheng X, Shi H, Adams CD, Timmons T, Ma Y. Effects of oxidative and physical treatments on inactivation of Cylindrospermopsis raciborskii and removal of cylindrospermopsin. Water Sci Technol. 2009;60(3):689-97. PubMed PMID: 19657164.
- **5.** Cromeans TL, Kahler AM, Hill VR. Inactivation of adenoviruses, enteroviruses, and murine norovirus in water by free chlorine and monochloramine. Appl Environ Microbiol. 2010 Feb;76(4):1028-33. Epub 2009 Dec 18. PubMed PMID: 20023080; PubMed Central PMCID: PMC2820971.
- Duirk SE, Desetto LM, Davis GM, Lindell C, Cornelison CT. Chloramination of organophosphorus pesticides found in drinking water sources. Water Res. 2010 Feb;44(3):761-8. Epub 2009 Oct 21. PubMed PMID: 19900689.

This study developed a to elucidate degradation pathways and parameterize critical reaction parameters for the reaction of chloramine with organophosphorous pesticides.

7. Fang W, Hu J, Ong SL. Effects of phosphorus on biofilm disinfections in model drinking water distribution systems. J Water Health. 2010 Sep;8(3):446-54. Epub 2009 Dec 4. PubMed PMID: 20375474

This study found that monochloramine performed better for biofilm removal compared to free chlorine in the presence of phosphate-based corrosion inhibitors.

- **8.** Lee J, Deininger RA. Real-time determination of the efficacy of residual disinfection to limit wastewater contamination in a water distribution system using filtration-based luminescence. Water Environ Res. 2010 May;82(5):475-8. PubMed PMID: 20480769.
- **9.** Lee W, Westerhoff P. Formation of organic chloramines during water disinfection: chlorination versus chloramination. Water Res. 2009 May;43(8):2233-9. Epub 2009 Feb 20. PubMed PMID: 19269665.
- **10.** Lénès D, Deboosere N, Ménard-Szczebara F, Jossent J, Alexandre V, Machinal C, Vialette M. Assessment of the removal and inactivation of influenza viruses H5N1 and H1N1 by drinking water treatment. Water Res. 2010 Apr;44(8):2473-86. Epub 2010 Jan 25. PubMed PMID: 20149404.

- **11.** : Liu J, Chen C, Zhang XJ, Zhang CQ. [Reaction of free chlorine transforms into chloramines in microorganism inactivation experiment]. Huan Jing Ke Xue. 2008 Nov;29(11):3054-8. Chinese. PubMed PMID: 19186801.
- **12.** Mena KD, Gerba CP. Risk assessment of Pseudomonas aeruginosa in water. Rev Environ Contam Toxicol. 2009;201:71-115. Review. PubMed PMID: 19484589.
- O'Connell HA, Rose LJ, Shams A, Bradley M, Arduino MJ, Rice EW. Variability of Burkholderia pseudomallei strain sensitivities to chlorine disinfection. Appl Environ Microbiol. 2009 Aug;75(16):5405-9. Epub 2009 Jun 19. PubMed PMID: 19542324; PubMed Central PMCID: PMC2725453.
- **14.** Votava M, Slitrová B. [Comparison of susceptibility of spores of Bacillus subtilis and Czech strains of Clostridium difficile to disinfectants]. Epidemiol Mikrobiol Imunol. 2009 Feb;58(1):36-42. Czech. PubMed PMID: 19358452.
- **15.** Zhang M, Cui FY, Liu DM, He WJ, Han HD. [Removing efficiency study on Cyclops cooperating with water treatment process by alternative oxidants]. Huan Jing Ke Xue. 2009 Dec;30(12):3568-72. Chinese. PubMed PMID: 20187388.
- **16.** : Zhou LL, Zhang YJ, Li X, Li GB. [Effect of chloramines disinfection for biofilm formation control on copper and stainless steel pipe materials]. Huan Jing Ke Xue. 2008 Dec;29(12):3372-5. Chinese. PubMed PMID: 19256370.

# III. Lead and/or Nitrification (6 abstracts)

Six studies looked at how chloramine may affect the release of lead from pipe materials. An emerging area of research is the impact of nitrification and ammonia oxidizing bacteria on lead levels.

- **1.** Bai XH, Cai YL, Zhou BH, Zhi XH. [Effect of ammonia-oxidizing bacteria (AOB) on chloraminated disinfection attenuation in drinking water distribution system]. Huan Jing Ke Xue. 2009 Jun 15;30(6):1649-52. Chinese. PubMed PMID: 19662845.
- **2.** Lin YP, Valentine RL. Reduction of lead oxide (PbO2) and release of Pb(II) in mixtures of natural organic matter, free chlorine and monochloramine. Environ Sci Technol. 2009 May 15;43(10):3872-7. PubMed PMID: 19544901.
- **3.** Lytle DA, Schock MR, Scheckel K. The inhibition of Pb(IV) oxide formation in chlorinated water by orthophosphate. Environ Sci Technol. 2009 Sep 1;43(17):6624-31. PubMed PMID: 19764227.
- 4. Wahman DG, Wulfeck-Kleier KA, Pressman JG. Monochloramine disinfection kinetics of Nitrosomonas europaea by propidium monoazide quantitative PCR and Live/dead BacLight methods. Appl Environ Microbiol. 2009 Sep;75(17):5555-62. Epub 2009 Jun 26. PubMed PMID: 19561179; PubMed Central PMCID: PMC2737938.

- **5.** Zhang Y, Griffin A, Rahman M, Camper A, Baribeau H, Edwards M. Lead contamination of potable water due to nitrification. Environ Sci Technol. 2009 Mar 15;43(6):1890-5. PubMed PMID: 19368188.
- **6.** Zhang Y, Griffin A, Rahman M, Camper A, Baribeau H, Edwards M. Lead contamination of potable water due to nitrification. Environ Sci Technol. 2009 Mar 15;43(6):1890-5. PubMed PMID: 19368188.

### IV. <u>Chloramine chemistry (8 abstracts)</u>

Eight abstracts that were reviewed described chemical reactions in chloraminated waters and/or degradation and decomposition of chloramine in disinfected waters. Many of these are also relevant to disinfection by-product formation and control.

- 1. De Laat J, Boudiaf N, Dossier-Berne F. Effect of dissolved oxygen on the photodecomposition of monochloramine and dichloramine in aqueous solution by UV irradiation at 253.7 nm. Water Res. 2010 May;44(10):3261-9. Epub 2010 Mar 15. PubMed PMID: 20362321.
- **2.** Fu J, Qu J, Liu R, Qiang Z, Zhao X, Liu H. Mechanism of Cu(II)-catalyzed monochloramine decomposition in aqueous solution. Sci Total Environ. 2009 Jun 15;407(13):4105-9. Epub 2009 Apr 5. PubMed PMID: 19345982
- **3.** Katano H, Uematsu K, Tatsumi H, Tsukatani T. Decomposition of free chlorine with tertiary ammonium. Anal Sci. 2010;26(3):349-53. PubMed PMID: 20215685.
- **4.** Li J, Blatchley ER 3rd. UV photodegradation of inorganic chloramines. Environ Sci Technol. 2009 Jan 1;43(1):60-5. PubMed PMID: 19209585.
- **5.** Liu SG, Zhu ZL, Han C, Qiu YL, Zhao JF. [Kinetics of monochloramine decay in disinfection of drinking water]. Huan Jing Ke Xue. 2009 Sep 15;30(9):2543-9. Chinese. PubMed PMID: 19927801.
- 6. Mincher BJ, Mezyk SP, Cooper WJ, Cole SK, Fox RV, Gardinali PR. Free-radical chemistry of disinfection byproducts. 3. Degradation mechanisms of chloronitromethane, bromonitromethane, and dichloronitromethane. J Phys Chem A. 2010 Jan 14;114(1):117-25. PubMed PMID: 20055512.
- 7. Rayson MS, Altarawneh M, Mackie JC, Kennedy EM, Dlugogorski BZ. Theoretical study of the ammonia-hypochlorous acid reaction mechanism. J Phys Chem A. 2010 Feb 25;114(7):2597-606. PubMed PMID: 20112901.
- **8.** Sathasivan A, Bal Krishna K, Fisher I. Development and application of a method for quantifying factors affecting chloramine decay in service reservoirs. Water Res. 2010 Jun 12. [Epub ahead of print] PubMed PMID: 20621323.

## V. <u>Dialysis (2 abstracts)</u>

Two abstracts described studies specific to dialysis applications. Residual disinfectants, particulates, organics, ions and remaining microorganisms must be removed prior to use in hemodialysis units, and some research continues to inform improvements in removal methods and ensure protection of dialysis patients from adverse effects.

- 1. James R. Dechlorination by ultraviolet radiation: a suitable alternative to activated carbon in dialysis water systems? J Ren Care. 2009 Dec;35(4):205-10. PubMed PMID: 19909414. This manuscript investigated methods for removing chlorine products for dialysis applications.
- **2.** Junglee NA, Rahman SU, Wild M, Wilms A, Hirst S, Jibani M, Seale JR. When pure is not so pure: Chloramine-related hemolytic anemia in home hemodialysis patients. Hemodial Int. 2010 Jul 5. [Epub ahead of print] PubMed PMID: 20618875.

# VI. <u>Chloramine analysis (2 abstracts)</u>

These manuscripts investigate methods for detecting chloramine in laboratory settings.

- 1. Hu WP, Langford VS, McEwan MJ, Milligan DB, Storer MK, Dummer J, Epton MJ. Monitoring chloramines and bromamines in a humid environment using selected ion flow tube mass spectrometry. Rapid Commun Mass Spectrom. 2010 Jun;24(12):1744-8. PubMed PMID: 20499318.
- **2.** Weinberg HS. Modern approaches to the analysis of disinfection by-products in drinking water. Philos Transact A Math Phys Eng Sci. 2009 Oct 13;367(1904):4097-118. Review. PubMed PMID: 19736235.

### VII. <u>Swimming Pools (6 abstracts)</u>

Six new manuscripts relevant to swimming pool chloramine levels were published in the time period. These support the relationship between swimming pool maintenance, swimming pool trichloramine exposures, and adverse health effects. These studies are not relevant to drinking water exposures.

- 1. Cimetiere N, De Laat J. Henry's law constant of N,N-dichloromethylamine: application to the contamination of the atmosphere of indoor swimming pools. Chemosphere. 2009 Oct;77(4):465-70. Epub 2009 Aug 22. PubMed PMID: 19700184.
- 2. Dang B, Chen L, Mueller C, Dunn KH, Almaguer D, Roberts JL, Otto CS. Ocular and respiratory symptoms among lifeguards at a hotel indoor waterpark resort. J Occup Environ Med. 2010 Feb;52(2):207-13. PubMed PMID: 20134344.

- **3.** Demange V, Bohadana A, Massin N, Wild P. Exhaled nitric oxide and airway hyperresponsiveness in workers: a preliminary study in lifeguards. BMC Pulm Med. 2009 Dec 31;9:53. PubMed PMID: 20043846; PubMed Central PMCID: PMC2805603.
- **4.** Vandyshev AB, Kulikov VA, Nikishin SN, Akramov RL. [Water decontamination in the swimming pools: standardization and practice]. Gig Sanit. 2010 Jan-Feb;(1):89-94. Russian. PubMed PMID: 20373723.
- **5.** Weaver WA, Li J, Wen Y, Johnston J, Blatchley MR, Blatchley ER 3rd. Volatile disinfection by-product analysis from chlorinated indoor swimming pools. Water Res. 2009 Jul;43(13):3308-18. Epub 2009 May 3. PubMed PMID: 19501873.
- **6.** Weisel CP, Richardson SD, Nemery B, Aggazzotti G, Baraldi E, Blatchley ER 3rd, Blount BC, Carlsen KH, Eggleston PA, Frimmel FH, Goodman M, Gordon G, Grinshpun SA, Heederik D, Kogevinas M, LaKind JS, Nieuwenhuijsen MJ, Piper FC, Sattar SA. Childhood asthma and environmental exposures at swimming pools: state of the science and research recommendations. Environ Health Perspect. 2009 Apr;117(4):500-7. Epub 2008 Sep 30. Review. PubMed PMID: 19440486; PubMed Central PMCID: PMC2679591.

# VIII. <u>Not relevant (33 abstracts)</u>

## Biochemical studies of molecular level monochloramine

Seventeen manuscripts report results of research on the molecular and cellular level monochloramine. The relevance of this research to drinking water or other exogenous exposures is not known.

- 1. Dhiman M, Estrada-Franco JG, Pando JM, Ramirez-Aguilar FJ, Spratt H, Vazquez-Corzo S, Perez-Molina G, Gallegos-Sandoval R, Moreno R, Garg NJ. Increased myeloperoxidase activity and protein nitration are indicators of inflammation in patients with Chagas' disease. Clin Vaccine Immunol. 2009 May;16(5):660-6. Epub 2009 Mar 18. PubMed PMID: 19297613; PubMed Central PMCID: PMC2681587.
- **2.** Flemmig J, Spalteholz H, Schubert K, Meier S, Arnhold J. Modification of phosphatidylserine by hypochlorous acid. Chem Phys Lipids. 2009 Sep;161(1):44-50. Epub 2009 Jul 3. PubMed PMID: 19577554.
- **3.** : Flemmig J, Arnhold J. Interaction of hypochlorous acid and myeloperoxidase with phosphatidylserine in the presence of ammonium ions. J Inorg Biochem. 2010 Jul;104(7):759-64. Epub 2010 Mar 25. PubMed PMID: 20400181.
- **4.** Jaskolla T, Fuchs B, Karas M, Schiller J. The new matrix 4-chloro-alpha-cyanocinnamic acid allows the detection of phosphatidylethanolamine chloramines by MALDI-TOF mass spectrometry. J Am Soc Mass Spectrom. 2009 May;20(5):867-74. Epub 2009 Jan 15. PubMed PMID: 19201617.

- 5. Kohler JE, Blass AL, Liu J, Tai K, Soybel DI. Antioxidant pre-treatment prevents omeprazole-induced toxicity in an in vitro model of infectious gastritis. Free Radic Biol Med. 2010 Jun 8. [Epub ahead of print] PubMed PMID: 20554018.
- **6.** Kohler JE, Dubach JM, Naik HB, Tai K, Blass AL, Soybel DI. Monochloramine-induced toxicity and dysregulation of intracellular Zn2+ in parietal cells of rabbit gastric glands. Am J Physiol Gastrointest Liver Physiol. 2010 Jul;299(1):G170-8. Epub 2010 Apr 29. PubMed PMID: 20430873.
- 7. Kunes JP, Cordero-Koning KS, Lee LH, Lynch SM. Vitamin C attenuates hypochloritemediated loss of paraoxonase-1 activity from human plasma. Nutr Res. 2009 Feb;29(2):114-22. PubMed PMID: 19285602.
- **8.** Murina MA, Roshchupkin DI, Petrova AO, Sergienko VI. [Amino acid chloramines and chlorimines as antiplatelet agents: reactive properties and mechanism of action]. Vestn Ross Akad Med Nauk. 2009;(10):43-9. Russian. PubMed PMID: 20000105.
- **9.** Pattison DI, Hawkins CL, Davies MJ. What are the plasma targets of the oxidant hypochlorous acid? A kinetic modeling approach. Chem Res Toxicol. 2009 May;22(5):807-17. PubMed PMID: 19326902.
- **10.** Peskin AV, Turner R, Maghzal GJ, Winterbourn CC, Kettle AJ. Oxidation of methionine to dehydromethionine by reactive halogen species generated by neutrophils. Biochemistry. 2009 Oct 27;48(42):10175-82. PubMed PMID: 19775156.
- **11.** Prokopowicz ZM, Arce F, Biedroń R, Chiang CL, Ciszek M, Katz DR, Nowakowska M, Zapotoczny S, Marcinkiewicz J, Chain BM. Hypochlorous acid: a natural adjuvant that facilitates antigen processing, cross-priming, and the induction of adaptive immunity. J Immunol. 2010 Jan 15;184(2):824-35. Epub 2009 Dec 16. PubMed PMID: 20018624
- Sakuma S, Miyoshi E, Sadatoku N, Fujita J, Negoro M, Arakawa Y, Fujimoto Y. Monochloramine produces reactive oxygen species in liver by converting xanthine dehydrogenase into xanthine oxidase. Toxicol Appl Pharmacol. 2009 Sep 15;239(3):268-72. Epub 2009 Jun 12. PubMed PMID: 19527742
- **13.** Sharaev PN, Sakhabutdinov EP, Lekomtseva OI, Koshikova SV. [A technique for determination of free and peptide-bound hydroxyproline in blood serum]. Klin Lab Diagn. 2009 Jan;(1):7-9. Russian. PubMed PMID: 19253691.
- **14.** Stacey MM, Peskin AV, Vissers MC, Winterbourn CC. Chloramines and hypochlorous acid oxidize erythrocyte peroxiredoxin 2. Free Radic Biol Med. 2009 Nov 15;47(10):1468-76. Epub 2009 Aug 27. PubMed PMID: 19716412.
- **15.** Szuchman-Sapir AJ, Pattison DI, Davies MJ, Witting PK. Site-specific hypochlorous acidinduced oxidation of recombinant human myoglobin affects specific amino acid residues and the rate of cytochrome b5-mediated heme reduction. Free Radic Biol Med. 2010 Jan 1;48(1):35-46. Epub 2009 Oct 2. PubMed PMID: 19800968.

- 16. Tachikawa M, Amano K, Nishiyama K, Urano A, Kato K, Yamanaka K. Methylamine dichloramine may play a role in the process of colorectal disease through architectural and oxidative changes in crypts in mice. Life Sci. 2009 Jun 19;84(25-26):923-8. Epub 2009 Apr 21. PubMed PMID: 19389412.
- **17.** Wojtecka-Lukasik E, Rzodkiewicz P, Maslinska D, Szukiewicz D, Schunack W, Maslinski S. Histamine chloramine modifies casein-induced inflammation. Inflamm Res. 2009 Apr;58 Suppl 1:20-1. PubMed PMID: 19271131.

### Other not relevant

In addition to the 17 manuscripts describing molecular level monochloramine, 16 manuscripts appeared in our search that were not relevant to drinking water.

- **18.** Barker TJ, Jarvo ER. Umpolung amination: nickel-catalyzed coupling reactions of N,N-dialkyl-N-chloroamines with diorganozinc reagents. J Am Chem Soc. 2009 Nov 4;131(43):15598-9. PubMed PMID: 19824677.
- **19.** Bendall JG. Semicarbazide is non-specific as a marker metabolite to reveal nitrofurazone abuse as it can form under Hofmann conditions. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2009 Jan;26(1):47-56. PubMed PMID: 19680870.
- **20.** Cimetiere N, Dossier-Berne F, De Laat J. Effect of some parameters on the formation of chloroform during chloramination of aqueous solutions of resorcinol. Water Res. 2010 Jun 12. [Epub ahead of print] PubMed PMID: 20591462.
- **21.** Cimetiere N, Dossier-Berne F, De Laat J. Monochloramination of resorcinol: mechanism and kinetic modeling. Environ Sci Technol. 2009 Dec 15;43(24):9380-5. PubMed PMID: 20000532
- Francavilla C, Low E, Nair S, Kim B, Shiau TP, Debabov D, Celeri C, Alvarez N, Houchin A, Xu P, Najafi R, Jain R. Quaternary ammonium N,N-dichloroamines as topical, antimicrobial agents. Bioorg Med Chem Lett. 2009 May 15;19(10):2731-4. Epub 2009 Mar 28. PubMed PMID: 19362467.
- **23.** Gopal A, Coventry J, Wan J, Roginski H, Ajlouni S. Alternative disinfection techniques to extend the shelf life of minimally processed iceberg lettuce. Food Microbiol. 2010 Apr;27(2):210-9. Epub 2009 Oct 13. PubMed PMID: 20141938.
- 24. Hatakeyama T, Yoshimoto Y, Ghorai SK, Nakamura M. Transition-metal-free electrophilic amination between aryl Grignard reagents and N-chloroamines. Org Lett. 2010 Apr 2;12(7):1516-9. PubMed PMID: 20222741.
- **25.** Kawano T, Hirano K, Satoh T, Miura M. A new entry of amination reagents for heteroaromatic C-H bonds: copper-catalyzed direct amination of azoles with chloroamines at room temperature. J Am Chem Soc. 2010 May 26;132(20):6900-1. PMID: 20438076.

- **26.** Kuttappan-Nair V, Samson-Thibault F, Wagner JR. Generation of 2'-deoxyadenosine N6aminyl radicals from the photolysis of phenylhydrazone derivatives. Chem Res Toxicol. 2010 Jan;23(1):48-54. PubMed PMID: 20000474
- **27.** Naumann M, Sterzenbach G, Rosentritt M, Beuer F, Frankenberger R. In vitro performance of self-adhesive resin cements for post-and-core build-ups: Influence of chewing simulation or 1-year storage in 0.5% chloramine solution. Acta Biomater. 2010 May 31. [Epub ahead of print] PubMed PMID: 20621613.
- **28.** Patil S, Harnisch F, Schröder U. Toxicity Response of Electroactive Microbial Biofilms-A Decisive Feature for Potential Biosensor and Power Source Applications. Chemphyschem. 2010 Jul 6. [Epub ahead of print] PubMed PMID: 20607711.
- **29.** Podzelinska K, Latimer R, Bhattacharya A, Vining LC, Zechel DL, Jia Z. Chloramphenicol biosynthesis: the structure of CmlS, a flavin-dependent halogenase showing a covalent flavin-aspartate bond. J Mol Biol. 2010 Mar 19;397(1):316-31. Epub 2010 Jan 18. PubMed PMID: 20080101.
- **30.** Roshchupkin DI, Murina MA, Petrova AO, Sergienko VI. [The relatioship between decomposition of amino acid chloramines and their structures]. Biomed Khim. 2009 Jul-Aug;55(4):510-8. Russian. PubMed PMID: 20000128.
- **31.** Whelligan DK, Thomson DW, Taylor D, Hoelder S. Two-step synthesis of aza- and diazaindoles from chloroamino-N-heterocycles using ethoxyvinylborolane. J Org Chem. 2010 Jan 1;75(1):11-5. PubMed PMID: 19950955.
- **32.** Yadav AK, Bracher A, Doran SF, Leustik M, Squadrito GL, Postlethwait EM, Matalon S. Mechanisms and modification of chlorine-induced lung injury in animals. Proc Am Thorac Soc. 2010 Jul;7(4):278-83. PubMed PMID: 20601632.
- **33.** Yuan W, Wang Y, Heinecke JW, Fu X. Hypochlorous acid converts the gamma-glutamyl group of glutathione disulfide to 5-hydroxybutyrolactam, a potential marker for neutrophil activation. J Biol Chem. 2009 Sep 25;284(39):26908-17. Epub 2009 Jul 7. PubMed PMID: 19584048; PubMed Central PMCID: PMC2785378.



Edwin M. Lee Mayor	To:	Andrew DeGraca, P.E.
Barbara Garcia MPA	From:	June M. Weintraub, Sc.D.
Director of Health Rajiv Bhatia MD, MPH	Date:	June 10, 2013
Director of Environmental Health	Re:	Summary of Monochloramine Abstract Review July 2010-June 2013

We routinely monitor the literature relevant to monochloramine using PubMed, the bibliographic index of peer-reviewed health, scientific and chemistry journals. PubMed is maintained by the National Center for Biotechnology Information (NCBI) at the National Library of Medicine (NLM), located at the U.S. National Institutes of Health (NIH). The following is a summary of relevant abstracts of new peer-reviewed publications that were entered into the database in the time since our last formal update to the SFPUC. Between July 15, 2010 and June 6, 2013, a total of 157 results in English were returned with the search criteria:

(chloramine OR monochloramine) AND 2010/07/15:2013/06/06[edat] NOT taurine NOT chloramine-T NOT chloramine B

Of the 157 total, 46 were not relevant, and these are listed at the end of this memo. We reviewed the abstracts of the remaining 111 publications; of these, we also reviewed many complete manuscripts. We categorized them as follows:

- I. Studies on Chloramine Disinfection By-products and Kinetics of Chemical Reactions (55 abstracts)
- II. Manuscripts relevant to chloramine disinfectant efficacy (29 abstracts)
- III. Lead and Corrosion Control (8 abstracts)
- IV. Dialysis (2 abstracts)
- V. Miscellaneous (7 abstracts)
- VI. Swimming Pools (11 abstracts)
- VII. Not relevant (46 abstracts)



Our abstract review did not reveal any new evidence that warrants reconsideration of our support for the use chloramine, and SFDPH continues to support the use of chloramine for secondary disinfection in the SFPUC water system.

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## I. <u>Studies on Chloramine Disinfection By-products and Kinetics of Chemical</u> <u>Reactions (55 abstracts)</u>

Studies included in this category include those that investigated the formation of disinfection byproducts in drinking water disinfected with chloramine; also included are some wastewater studies that were relevant to drinking water in the context of indirect potable reuse. Some studies looked at formation potential of waters that used different types of disinfection schemes, other studies examined disinfection byproduct precursors, and others investigated methods for disinfection byproduct control. Formation and control of nitrosamines continues to be a major and evolving area of research. A novel area of research is the investigation of the role of pharmaceuticals, personal care products and other organic contaminants as precursors to NDMA formation. General studies reporting chemical reactions in chloraminated waters, and degradation and decomposition of chloramine in disinfected waters are also included in this category.

Bull RJ, Reckhow DA, Li X, Humpage AR, Joll C, Hrudey SE. Potential carcinogenic hazards of non-regulated disinfection by-products: haloquinones, halo-cyclopentene and cyclohexene derivatives, N-halamines, halonitriles, and heterocyclic amines. Toxicology. 2011 Aug 15;286(1-3):1-19. doi: 10.1016/j.tox.2011.05.004. Epub 2011 May 14. Review. PubMed PMID: 21605618.

Calvo P, Crugeiras J, Ríos A. Acid-catalysed chlorine transfer from N-chloramines to iodide ion: experimental evidence for a predicted change in mechanism. Org Biomol Chem. 2010 Sep 21;8(18):4137-42. doi: 10.1039/c004976j. Epub 2010 Jul 22. PubMed PMID: 20664852.

Chamberlain E, Shi H, Wang T, Ma Y, Fulmer A, Adams C. Comprehensive screening study of pesticide degradation via oxidation and hydrolysis. J Agric Food Chem. 2012 Jan 11;60(1):354-63. doi: 10.1021/jf2033158. Epub 2011 Dec 28. PubMed PMID: 22141915.

Chang H, Chen C, Wang G. Characteristics of C-, N-DBPs formation from nitrogen-enriched dissolved organic matter in raw water and treated wastewater effluent. Water Res. 2013 May 15;47(8):2729-41. doi: 10.1016/j.watres.2013.02.033. Epub 2013 Mar 13. PubMed PMID: 23535379.

Chang H, Chen C, Wang G. Identification of potential nitrogenous organic precursors for C-, N-DBPs and characterization of their DBPs formation. Water Res. 2011 Jun;45(12):3753-64. doi: 10.1016/j.watres.2011.04.027. Epub 2011 Apr 22. PubMed PMID: 21555141.

Chang HH, Wang GS. Correlations between surrogate nitrogenous organic precursors and C-, N-DBP formation. Water Sci Technol. 2011;64(12):2395-403. doi: 10.2166/wst.2011.823. PubMed PMID: 22170833.

Chuang YH, Lin AY, Wang XH, Tung HH. The contribution of dissolved organic nitrogen and chloramines to nitrogenous disinfection byproduct formation from natural organic matter. Water Res. 2013 Mar 1;47(3):1308-16. doi: 10.1016/j.watres.2012.11.046. Epub 2012 Dec 17. PubMed PMID: 23286987.

Dai N, Mitch WA. Relative importance of N-nitrosodimethylamine compared to total Nnitrosamines in drinking waters. Environ Sci Technol. 2013 Apr 16;47(8):3648-56. doi: 10.1021/es305225b. Epub 2013 Apr 2. PubMed PMID: 23505971. Duirk SE, Lindell C, Cornelison CC, Kormos J, Ternes TA, Attene-Ramos M, Osiol J, Wagner ED, Plewa MJ, Richardson SD. Formation of toxic iodinated disinfection by-products from compounds used in medical imaging. Environ Sci Technol. 2011 Aug 15;45(16):6845-54. doi: 10.1021/es200983f. Epub 2011 Jul 15. PubMed PMID: 21761849.

Fang J, Yang X, Ma J, Shang C, Zhao Q. Characterization of algal organic matter and formation of DBPs from chlor(am)ination. Water Res. 2010 Dec;44(20):5897-906. doi: 10.1016/j.watres.2010.07.009. Epub 2010 Jul 13. PubMed PMID: 20797758.

Farré MJ, Radjenovic J, Gernjak W. Assessment of degradation byproducts and NDMA formation potential during UV and UV/H2O2 treatment of doxylamine in the presence of monochloramine. Environ Sci Technol. 2012 Dec 4;46(23):12904-12. doi: 10.1021/es302883n. Epub 2012 Nov 14. PubMed PMID: 23134233.

Farré MJ, Döderer K, Hearn L, Poussade Y, Keller J, Gernjak W. Understanding the operational parameters affecting NDMA formation at Advanced Water Treatment Plants. J Hazard Mater. 2011 Jan 30;185(2-3):1575-81. doi: 10.1016/j.jhazmat.2010.10.090. Epub 2010 Nov 3. PubMed PMID: 21115221.

Flowers RC, Singer PC. Anion Exchange Resins as Sources of Nitrosamines and Nitrosamine Precursors. Environ Sci Technol. 2013 May 7. [Epub ahead of print] PubMed PMID: 23647449.

Hatt JW, Lamy C, Germain E, Tupper M, Judd SJ. NDMA formation in secondary wastewater effluent. Chemosphere. 2013 Mar;91(1):83-7. doi: 10.1016/j.chemosphere.2012.11.003. Epub 2012 Dec 1. PubMed PMID: 23211329.

Hong H, Xiong Y, Ruan M, Liao F, Lin H, Liang Y. Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine. Sci Total Environ. 2013 Feb 1;444:196-204. doi: 10.1016/j.scitotenv.2012.11.086. Epub 2012 Dec 25. PubMed PMID: 23271145.

Hua G, Reckhow DA. Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. Water Res. 2012 Sep 1;46(13):4208-16. doi:10.1016/j.watres.2012.05.031. Epub 2012 May 23. PubMed PMID: 22687526.

Huang H, Wu QY, Hu HY, Mitch WA. Dichloroacetonitrile and dichloroacetamide can form independently during chlorination and chloramination of drinking waters, model organic matters, and wastewater effluents. Environ Sci Technol. 2012 Oct 2;46(19):10624-31. doi: 10.1021/es3025808. Epub 2012 Sep 14. PubMed PMID:22950789.

Huy NV, Murakami M, Sakai H, Oguma K, Kosaka K, Asami M, Takizawa S. Occurrence and formation potential of N-nitrosodimethylamine in ground water and river water in Tokyo. Water Res. 2011 May;45(11):3369-77. doi:10.1016/j.watres.2011.03.053. Epub 2011 Apr 5. PubMed PMID: 21514620.

Jones DB, Song H, Karanfil T. The effects of selected preoxidation strategies on I-THM formation and speciation. Water Res. 2012 Nov 1;46(17):5491-8. doi: 10.1016/j.watres.2012.07.018. Epub 2012 Jul 24. PubMed PMID: 22889665.

Jones DB, Saglam A, Song H, Karanfil T. The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation. Water Res. 2012 Jan 1;46(1):11-20. doi: 10.1016/j.watres.2011.10.005. Epub 2011 Oct 20. PubMed PMID: 22078225.

Jones DB, Saglam A, Triger A, Song H, Karanfil T. I-THM formation and speciation: preformed monochloramine versus prechlorination followed by ammonia addition. Environ Sci Technol. 2011 Dec 15;45(24):10429-37. doi:10.1021/es202745t. Epub 2011 Nov 29. PubMed PMID: 22050596.

Kristiana I, Tan J, Joll CA, Heitz A, von Gunten U, Charrois JW. Formation of N-nitrosamines from chlorination and chloramination of molecular weight fractions of natural organic matter. Water Res. 2013 Feb 1;47(2):535-46. doi: 10.1016/j.watres.2012.10.014. Epub 2012 Oct 23. PubMed PMID: 23164216.

Laingam S, Froscio SM, Bull RJ, Humpage AR. In vitro toxicity and genotoxicity assessment of disinfection by-products, organic N-chloramines. Environ Mol Mutagen. 2012 Mar;53(2):83-93. PubMed PMID: 22403827.

Le Roux J, Gallard H, Croué JP. Formation of NDMA and halogenated DBPs by chloramination of tertiary amines: the influence of bromide ion. Environ Sci Technol. 2012 Feb 7;46(3):1581-9. doi: 10.1021/es203785s. Epub 2012 Jan 20. PubMed PMID: 22214364.

Le Roux J, Gallard H, Croué JP. Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation. Water Res. 2011 May;45(10):3164-74. doi: 10.1016/j.watres.2011.03.035. Epub 2011 Mar 26. PubMed PMID: 21496861.

Liu W, Zhang Z, Yang X, Xu Y, Liang Y. Effects of UV irradiation and UV/chlorine coexposure on natural organic matter in water. Sci Total Environ. 2012 Jan 1;414:576-84. doi: 10.1016/j.scitotenv.2011.11.031. Epub 2011 Dec 3. PubMed PMID: 22142648.

Luh J, Mariñas BJ. Bromide ion effect on N-nitrosodimethylamine formation by monochloramine. Environ Sci Technol. 2012 May 1;46(9):5085-92. doi:10.1021/es300077x. Epub 2012 Apr 10. PubMed PMID: 22432896.

Luo Q, Wang D, Wang Z. Occurrences of nitrosamines in chlorinated and chloraminated drinking water in three representative cities, China. Sci Total Environ. 2012 Oct 15;437:219-25. doi: 10.1016/j.scitotenv.2012.08.023. Epub 2012 Aug 30. PubMed PMID: 22940482.

Lyon BA, Dotson AD, Linden KG, Weinberg HS. The effect of inorganic precursors on disinfection byproduct formation during UV-chlorine/chloramine drinking water treatment. Water Res. 2012 Oct 1;46(15):4653-64. doi:10.1016/j.watres.2012.06.011. Epub 2012 Jun 18. PubMed PMID: 22763290.

McKay G, Sjelin B, Chagnon M, Ishida KP, Mezyk SP. Kinetic study of the reactions between chloramine disinfectants and hydrogen peroxide: Temperature dependence and reaction mechanism. Chemosphere. 2013 Apr 17. pii: S0045-6535(13)00475-X. doi: 0.1016/j.chemosphere.2013.03.045. [Epub ahead of print]. PubMed PMID: 23601896.

Neale PA, Antony A, Bartkow ME, Farré MJ, Heitz A, Kristiana I, Tang JY, Escher BI. Bioanalytical assessment of the formation of disinfection byproducts in a drinking water

treatment plant. Environ Sci Technol. 2012 Sep 18;46(18):10317-25. doi: 10.1021/es302126t. Epub 2012 Aug 24. PubMed PMID: 22873573.

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Potera C. Nontoxic medical imaging agents form toxic DBPs. Environ Health Perspect. 2011 Dec;119(12):A511. doi: 10.1289/ehp.119-a511. PubMed PMID: 22134135; PubMed Central PMCID: PMC3261997.

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Shen R, Andrews SA. Demonstration of 20 pharmaceuticals and personal care products (PPCPs) as nitrosamine precursors during chloramine disinfection. Water Res. 2011 Jan;45(2):944-52. doi: 10.1016/j.watres.2010.09.036. Epub 2010 Oct 13. PubMed PMID: 20950838.

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Wan Y, Jia A, Zhu Z, Hu J. Transformation of tetracycline during chloramination: kinetics, products and pathways. Chemosphere. 2013 Jan;90(4):1427-34. doi: 10.1016/j.chemosphere.2012.09.001. Epub 2012 Sep 29. PubMed PMID: 23031248.

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Wert EC, Rosario-Ortiz FL. Intracellular Organic Matter from Cyanobacteria as a Precursor for Carbonaceous and Nitrogenous Disinfection Byproducts. Environ Sci Technol. 2013 Jun 4. [Epub ahead of print] PubMed PMID: 23675656.

Xu B, Qin C, Hu CY, Lin YL, Xia SJ, Xu Q, Mwakagenda SA, Bi XY, Gao NY. Degradation kinetics and N-Nitrosodimethylamine formation during monochloramination of chlortoluron. Sci Total Environ. 2012 Feb 15;417-418:241-7. doi: 10.1016/j.scitotenv.2011.12.056. Epub 2012 Jan 23. PubMed PMID: 22273262.

Yang X, Peng J, Chen B, Guo W, Liang Y, Liu W, Liu L. Effects of ozone and ozone/peroxide pretreatments on disinfection byproduct formation during subsequent chlorination and chloramination. J Hazard Mater. 2012 Nov 15;239-240:348-54. doi:10.1016/j.jhazmat.2012.09.006. Epub 2012 Sep 11. PubMed PMID: 23009791.

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Yang X, Shen Q, Guo W, Peng J, Liang Y. Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination. Chemosphere. 2012 Jun;88(1):25-32. doi:10.1016/j.chemosphere.2012.02.035. Epub 2012 Mar 15. PubMed PMID: 22425029.

Zhang H, Liu H, Zhao X, Qu J, Fan M. Formation of disinfection by-products in the chlorination of ammonia-containing effluents: significance of Cl2/N ratios and the DOM fractions. J Hazard Mater. 2011 Jun 15;190(1-3):645-51. doi:10.1016/j.jhazmat.2011.03.098. Epub 2011 Apr 6. PubMed PMID: 21514725.

Zhao Y, Anichina J, Lu X, Bull RJ, Krasner SW, Hrudey SE, Li XF. Occurrence and formation of chloro- and bromo-benzoquinones during drinking water disinfection. Water Res. 2012 Sep 15;46(14):4351-60. doi:10.1016/j.watres.2012.05.032. Epub 2012 Jun 2. PubMed PMID: 22739498.

Zhou W, Lou L, Zhu L, Li Z, Zhu L. Formation and cytotoxicity of a new disinfection byproduct (DBP) phenazine by chloramination of water containing diphenylamine. J Environ Sci (China). 2012;24(7):1217-24. PubMed PMID: 23513442.

# II. <u>Manuscripts relevant to chloramine disinfectant efficacy (29 abstracts)</u>

Twenty-nine abstracts described the efficacy of chloramine disinfection. These studies include investigations of conditions that improve chloramine effectiveness, enumeration of the presence of infectious agents in chloraminated waters, ability to inactivate microbial contaminants, ability to penetrate biofilm, and comparisons with other disinfection treatment processes. Many of these studies are also relevant to disinfection by-product formation and control. Studies that specifically investigated lead are listed separately in Section III.

Armbruster CR, Forster TS, Donlan RM, O'Connell HA, Shams AM, Williams MM. A biofilm model developed to investigate survival and disinfection of Mycobacterium mucogenicum in potable water. Biofouling. 2012;28(10):1129-39. doi: 10.1080/08927014.2012.735231. PubMed PMID: 23082863.

Bal Krishna KC, Sathasivan A, Chandra Sarker D. Evidence of soluble microbial products accelerating chloramine decay in nitrifying bulk water samples. Water Res. 2012 Sep 1;46(13):3977-88. doi: 10.1016/j.watres.2012.05.026. Epub 2012 May 26. PubMed PMID: 22695354.

Berry D, Holder D, Xi C, Raskin L. Comparative transcriptomics of the response of Escherichia coli to the disinfectant monochloramine and to growth conditions inducing monochloramine resistance. Water Res. 2010 Sep;44(17):4924-31. doi: 10.1016/j.watres.2010.07.026. Epub 2010 Jul 27. PubMed PMID: 20692677.

Berry D, Horn M, Xi C, Raskin L. Mycobacterium avium infections of Acanthamoeba strains: host strain variability, grazing-acquired infections, and altered dynamics of inactivation with monochloramine. Appl Environ Microbiol. 2010 Oct;76(19):6685-8. doi: 10.1128/AEM.00644-10. Epub 2010 Aug 13. PubMed PMID:20709834; PubMed Central PMCID: PMC2950453.

Chen YQ, Chen C, Zhang XJ, Zheng Q, Liu YY. Inactivation of resistant Mycobacteria mucogenicum in water: chlorine resistance and mechanism analysis. Biomed Environ Sci. 2012 Apr;25(2):230-7. PubMed PMID: 22998832.

Chien SH, Chowdhury I, Hsieh MK, Li H, Dzombak DA, Vidic RD. Control of biological growth in recirculating cooling systems using treated secondary effluent as makeup water with monochloramine. Water Res. 2012 Dec 1;46(19):6508-18. doi: 10.1016/j.watres.2012.09.027. Epub 2012 Sep 26. PubMed PMID: 23063442.

Chowdhury S. Heterotrophic bacteria in drinking water distribution system: a review. Environ Monit Assess. 2012 Oct;184(10):6087-137. doi: 10.1007/s10661-011-2407-x. Epub 2011 Nov 11. Review. PubMed PMID: 22076103.

Dupuy M, Mazoua S, Berne F, Bodet C, Garrec N, Herbelin P, Ménard-Szczebara F, Oberti S, Rodier MH, Soreau S, Wallet F, Héchard Y. Efficiency of water disinfectants against Legionella pneumophila and Acanthamoeba. Water Res. 2011 Jan;45(3):1087-94. doi: 10.1016/j.watres.2010.10.025. Epub 2010 Oct 28. PubMed PMID: 21093012.

Gomez-Alvarez V, Revetta RP, Santo Domingo JW. Metagenomic analyses of drinking water receiving different disinfection treatments. Appl Environ Microbiol. 2012 Sep;78(17):6095-102. doi: 10.1128/AEM.01018-12. Epub 2012 Jun 22. PubMed PMID: 22729545; PubMed Central PMCID: PMC3416622.

Ho L, Kayal N, Trolio R, Newcombe G. Determining the fate of Microcystis aeruginosa cells and microcystin toxins following chloramination. Water Sci Technol. 2010;62(2):442-50. doi: 10.2166/wst.2010.448. PubMed PMID: 20651451.

Hwang C, Ling F, Andersen GL, LeChevallier MW, Liu WT. Microbial community dynamics of an urban drinking water distribution system subjected to phases of chloramination and chlorination treatments. Appl Environ Microbiol. 2012 Nov;78(22):7856-65. doi: 10.1128/AEM.01892-12. Epub 2012 Aug 31. PubMed PMID:22941076; PubMed Central PMCID: PMC3485970.

Jakubek D, Le Brun M, Leblon G, Dubow M, Binet M. The impact of monochloramine on the diversity and dynamics of Legionella pneumophila subpopulations in a nuclear power plant cooling circuit. FEMS Microbiol Ecol. 2013 Mar 27. doi: 10.1111/1574-6941.12121. [Epub ahead of print] PubMed PMID: 23530621.

Kahler AM, Cromeans TL, Roberts JM, Hill VR. Source water quality effects on monochloramine inactivation of adenovirus, coxsackievirus, echovirus, and murine norovirus. Water Res. 2011 Feb;45(4):1745-51. doi: 10.1016/j.watres.2010.11.026. Epub 2010 Nov 24. PubMed PMID: 21145573.

Lee WH, Wahman DG, Bishop PL, Pressman JG. Free chlorine and monochloramine application to nitrifying biofilm: comparison of biofilm penetration, activity, and viability. Environ Sci Technol. 2011 Feb 15;45(4):1412-9. doi:10.1021/es1035305. Epub 2011 Jan 12. PubMed PMID: 21226531.

Lin YE, Stout JE, Yu VL. Controlling Legionella in hospital drinking water: an evidence-based review of disinfection methods. Infect Control Hosp Epidemiol. 2011 Feb;32(2):166-73. doi: 10.1086/657934. Review. PubMed PMID: 21460472.

Lin YE, Stout JE, Yu VL. Prevention of hospital-acquired legionellosis. Curr Opin Infect Dis. 2011 Aug;24(4):350-6. doi: 10.1097/QCO.0b013e3283486c6e. Review. PubMed PMID: 21666459.

Ling F, Liu WT. Impact of chloramination on the development of laboratory-grown biofilms fed with filter-pretreated groundwater. Microbes Environ. 2013;28(1):50-7. Epub 2012 Oct 31. PubMed PMID: 23124766.

Marchesi I, Cencetti S, Marchegiano P, Frezza G, Borella P, Bargellini A. Control of Legionella contamination in a hospital water distribution system by monochloramine. Am J Infect Control.

2012 Apr;40(3):279-81. doi: 10.1016/j.ajic.2011.03.008. Epub 2011 Jul 8. PubMed PMID: 21741121.

Marchesi I, Marchegiano P, Bargellini A, Cencetti S, Frezza G, Miselli M, Borella P. Effectiveness of different methods to control legionella in the water supply: ten-year experience in an Italian university hospital. J Hosp Infect. 2011 Jan;77(1):47-51. doi: 10.1016/j.jhin.2010.09.012. Epub 2010 Dec 4. PubMed PMID: 21131100.

Mogoa E, Bodet C, Morel F, Rodier MH, Legube B, Héchard Y. Cellular response of the amoeba Acanthamoeba castellanii to chlorine, chlorine dioxide, and monochloramine treatments. Appl Environ Microbiol. 2011 Jul;77(14):4974-80. doi: 10.1128/AEM.00234-11. Epub 2011 May 20. PubMed PMID: 21602398; PubMed Central PMCID: PMC3147406.

Nguyen C, Elfland C, Edwards M. Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth. Water Res. 2012 Mar 1;46(3):611-21. doi: 10.1016/j.watres.2011.11.006. Epub 2011 Nov 15. PubMed PMID: 22153355.

Pressman JG, Lee WH, Bishop PL, Wahman DG. Effect of free ammonia concentration on monochloramine penetration within a nitrifying biofilm and its effect on activity, viability, and recovery. Water Res. 2012 Mar 1;46(3):882-94. doi: 10.1016/j.watres.2011.11.071. Epub 2011 Dec 7. PubMed PMID: 22192761.

Ramseier MK, von Gunten U, Freihofer P, Hammes F. Kinetics of membrane damage to high (HNA) and low (LNA) nucleic acid bacterial clusters in drinking water by ozone, chlorine, chlorine dioxide, monochloramine, ferrate(VI), and permanganate. Water Res. 2011 Jan;45(3):1490-500. doi:10.1016/j.watres.2010.11.016. Epub 2010 Nov 18. PubMed PMID: 21146846.

Shin GA, Lee JK. Inactivation of human adenovirus by sequential disinfection with an alternative ultraviolet technology and monochloramine. Can J Microbiol. 2010 Jul;56(7):606-9. doi: 10.1139/w10-047. PubMed PMID: 20651860.

Wang H, Masters S, Hong Y, Stallings J, Falkinham JO 3rd, Edwards MA, Pruden A. Effect of disinfectant, water age, and pipe material on occurrence and persistence of Legionella, mycobacteria, Pseudomonas aeruginosa, and two amoebas. Environ Sci Technol. 2012 Nov 6;46(21):11566-74. doi: 10.1021/es303212a. Epub 2012 Oct 25. PubMed PMID: 23046164.

Wert EC, Dong MM, Rosario-Ortiz FL. Using digital flow cytometry to assess the degradation of three cyanobacteria species after oxidation processes. Water Res. 2013 Jul 1;47(11):3752-61. doi: 10.1016/j.watres.2013.04.038. Epub 2013 May 1. PubMed PMID: 23726712.

Xue Z, Hessler CM, Panmanee W, Hassett DJ, Seo Y. Pseudomonas aeruginosa inactivation mechanism is affected by capsular extracellular polymeric substances reactivity with chlorine and monochloramine. FEMS Microbiol Ecol. 2013 Jan;83(1):101-11. doi: 10.1111/j.1574-6941.2012.01453.x. Epub 2012 Aug 8. PubMed PMID: 22809489.

Yang J, LeChevallier MW, Teunis PF, Xu M. Managing risks from virus intrusion into water distribution systems due to pressure transients. J Water Health. 2011 Jun;9(2):291-305. PubMed PMID: 21942194.

Zeng DN, Fan ZY, Chi L, Wang X, Qu WD, Quan ZX. Analysis of the bacterial communities associated with different drinking water treatment processes. World J Microbiol Biotechnol. 2013 Mar 21. [Epub ahead of print]. PubMed PMID: 23515963.

### III. Lead and Corrosion Control (8 abstracts)

The impact of chloramine on the design and efficacy of corrosion control is an area that is of particular interest to researchers due to concerns about the potential for lead leaching from piping materials as well as the concern about the integrity of plumbing systems. The impact of nitrification and ammonia oxidizing bacteria on lead levels continues to be an area of developing research. Other potential mechanisms of lead release in the presence of chloramine are also being actively investigated by a number of researchers. Of note are the two wastewater studies by Hsieh et al, which found that corrosivity of wastewater in the presence of chloramine was lower than in the presence chlorine; this finding is different from several other studies.

Arnold RB Jr, Edwards M. Potential reversal and the effects of flow pattern on galvanic corrosion of lead. Environ Sci Technol. 2012 Oct 16;46(20):10941-7. doi: 10.1021/es3017396. Epub 2012 Oct 3. PubMed PMID: 22900550.

Edwards MA. Hundreds of partial pipe replacements conducted in Washington, DC before July 2004. Environ Res. 2011 Aug;111(6):888; author reply 889. doi:10.1016/j.envres.2011.05.009. Epub 2011 Jul 6. PubMed PMID: 21737070.

Hsieh MK, Chien SH, Li H, Monnell JD, Dzombak DA, Vidic RD. Corrosion control when using passively treated abandoned mine drainage as alternative makeup water for cooling systems. Water Environ Res. 2011 Sep;83(9):807-14. PubMed PMID: 22073728.

Hsieh MK, Li H, Chien SH, Monnell JD, Chowdhury I, Dzombak DA, Vidic RD. Corrosion control when using secondary treated municipal wastewater as alternative makeup water for cooling tower systems. Water Environ Res. 2010 Dec;82(12):2346-56. PubMed PMID: 21214028.

Ng DQ, Strathmann TJ, Lin YP. Role of orthophosphate as a corrosion inhibitor in chloraminated solutions containing tetravalent lead corrosion product PbO2. Environ Sci Technol. 2012 Oct 16;46(20):11062-9. doi: 10.1021/es302220t. Epub 2012 Sep 27. PubMed PMID: 22958199.

Sedlak DL, von Gunten U. Chemistry. The chlorine dilemma. Science. 2011 Jan 7;331(6013):42-3. doi: 10.1126/science.1196397. PubMed PMID: 21212347.

Wang H, Hu C, Hu X, Yang M, Qu J. Effects of disinfectant and biofilm on the corrosion of cast iron pipes in a reclaimed water distribution system. Water Res. 2012 Mar 15;46(4):1070-8. doi: 10.1016/j.watres.2011.12.001. Epub 2011 Dec 20. PubMed PMID: 22209261.

Xie Y, Wang Y, Giammar DE. Impact of chlorine disinfectants on dissolution of the lead corrosion product PbO2. Environ Sci Technol. 2010 Sep 15;44(18):7082-8. doi: 10.1021/es1016763. PubMed PMID: 20715864.

### IV. <u>Dialysis (2 abstracts)</u>

Two abstracts described a study specific to dialysis. Residual disinfectants, particulates, organics, ions and remaining microorganisms must be removed prior to use in hemodialysis units. The 2012 study by Braimoh and colleagues characterized hemodialysis water in Nigeria, finding that treated hemodialysis water at six centers in Lagos, Nigeria did not meet Association for the Advancement of Medical Instrumentation (AAMI) guidelines for most of the parameters tested. In particular calcium, sodium, magnesium and nitrate were moderately or markedly elevated, whereas levels of chloramines, fluoride, aluminum, zinc and sulfate were mildly elevated. The study by Smith et al reported the efficacy of reverse osmosis for chloramine removal in dialysis processes.

Braimoh RW, Mabayoje MO, Amira CO, Coker H. Quality of hemodialysis water in a resourcepoor country: the Nigerian example. Hemodial Int. 2012 Oct;16(4):532-8. doi: 10.1111/j.1542-4758.2012.00682.x. 2012 Apr 27.

Smith MP, Marr FE, Kanagasundaram NS. Chloramine reduction by reverse osmosis membranes. Hemodial Int. 2012 Jan;16(1):120-1. doi: 10.1111/j.1542-4758.2011.00590.x. PubMed PMID: 22099739.

### V. <u>Miscellaneous (7 abstracts)</u>

A few abstracts were difficult to categorize. These are included here with a brief summary for those whose titles do not help explain their relevance.

Bele C, Kumar Y, Walker T, Poussade Y, Zavlanos V. Operating boundaries of full-scale advanced water reuse treatment plants: many lessons learned from pilot plant experience. Water Sci Technol. 2010;62(7):1560-6. doi:10.2166/wst.2010.437. PubMed PMID: 20935373. This manuscript reports the results of a pilot study in Australia for secondary treatment of waste water for indirect potable reuse.

Guo TL, Germolec DR, Collins BJ, Luebke RW, Auttachoat W, Smith MJ, White KL. Immunotoxicological profile of chloramine in female B6C3F1 mice when administered in the drinking water for 28 days. J Immunotoxicol. 2011 Oct-Dec;8(4):381-8. doi: 10.3109/1547691X.2011.622317. Epub 2011 Oct 21. PubMed PMID: 22017662. This manuscript reports the first toxicological rodent feeding studies that we are aware of being completed since Dunnick's 1993 work, which found that "In contrast to the results with the trihalomethanes, administration of chlorine or chloramine did not cause a clear carcinogenic response in rats or mice after long-term exposure." (Assessment of the carcinogenic potential of chlorinated water: experimental studies of chlorine, chloramine, and trihalomethanes. Dunnick JK, Melnick RL. J Natl Cancer Inst. 1993 May 19;85(10):817-22.). The new study by Guo et al was published in 2011 and found that "chloramine produced no toxicological and immunotoxic effects in female B(6)C(3)F(1) mice when administered for 28 days in the drinking water at concentrations ranging from 2-200 ppm."

Mawhinney DB, Young RB, Vanderford BJ, Borch T, Snyder SA. Artificial sweetener sucralose in U.S. drinking water systems. Environ Sci Technol. 2011 Oct 15;45(20):8716-22. doi: 10.1021/es202404c. Epub 2011 Sep 26. PubMed PMID:21879743.

This study found that neither chlorine nor chloramine disinfection of wastewater transformed sucralose.

Ngwenya N, Ncube EJ, Parsons J. Recent advances in drinking water disinfection: successes and challenges. Rev Environ Contam Toxicol. 2013;222:111-70. PubMed PMID: 22990947. This 60 page review published in early 2013 provides a comprehensive look at research, practice and regulation of drinking water disinfection.

Sorlini S, Gialdini F. Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine. Water Res. 2010 Nov;44(19):5653-9. doi: 10.1016/j.watres.2010.06.032. Epub 2010 Jun 19. PubMed PMID: 20638704.

Wahman DG, Schrantz KA, Pressman JG. Determination of the effects of medium composition on the monochloramine disinfection kinetics of Nitrosomonas europaea by the propidium monoazide quantitative PCR and Live/Dead BacLight methods. Appl Environ Microbiol. 2010 Dec;76(24):8277-80. doi: 10.1128/AEM.01631-10. Epub 2010 Oct 15. PubMed PMID: 20952645; PubMed Central PMCID: PMC3008258.

This was a research methods paper that concluded there are differences in disinfection kinetics depending on the medium composition and recommended development of a standard medium for evaluating disinfection kinetics in drinking water.

Wu Q, Shi H, Adams CD, Timmons T, Ma Y. Oxidative removal of selected endocrinedisruptors and pharmaceuticals in drinking water treatment systems, and identification of degradation products of triclosan. Sci Total Environ. 2012 Nov 15;439:18-25. doi: 10.1016/j.scitotenv.2012.08.090. Epub 2012 Oct 9. PubMed PMID: 23059968.

### VI. <u>Swimming Pools (11 abstracts)</u>

Eleven new manuscripts relevant to swimming pool chloramine levels were published in the time period. These support the relationship between swimming pool maintenance, swimming pool trichloramine exposures, and adverse health effects. These studies are usually not relevant to drinking water exposures, however some of the chemical reactions discussed could be analogous to certain drinking water treatment processes.

Catto C, Sabrina S, Ginette CT, Manuel R, Robert T. Occurrence and spatial and temporal variations of disinfection by-products in the water and air of two indoor swimming pools. Int J Environ Res Public Health. 2012 Aug;9(8):2562-86. doi: 10.3390/ijerph9082562. Epub 2012 Jul 25. PubMed PMID: 23066383; PubMed Central PMCID: PMC3447573.

De Laat J, Feng W, Freyfer DA, Dossier-Berne F. Concentration levels of urea in swimming pool water and reactivity of chlorine with urea. Water Res. 2011 Jan;45(3):1139-46. doi: 10.1016/j.watres.2010.11.005. Epub 2010 Nov 10. PubMed PMID: 21115186.

Florentin A, Hautemanière A, Hartemann P. Health effects of disinfection by-products in chlorinated swimming pools. Int J Hyg Environ Health. 2011 Nov;214(6):461-9. doi: 10.1016/j.ijheh.2011.07.012. Epub 2011 Sep 1. Review. PubMed PMID: 21885333.

Hansen KM, Zortea R, Piketty A, Vega SR, Andersen HR. Photolytic removal of DBPs by medium pressure UV in swimming pool water. Sci Total Environ. 2013 Jan 15;443:850-6. doi: 10.1016/j.scitotenv.2012.11.064. Epub 2012 Dec 14. PubMed PMID: 23247288.

Richardson SD, DeMarini DM, Kogevinas M, Fernandez P, Marco E, Lourencetti C, Ballesté C, Heederik D, Meliefste K, McKague AB, Marcos R, Font-Ribera L, Grimalt JO, Villanueva CM. What's in the pool? A comprehensive identification of disinfection by-products and assessment of mutagenicity of chlorinated and brominated swimming pool water. Environ Health Perspect. 2010 Nov;118(11):1523-30. doi: 10.1289/ehp.1001965. PubMed PMID: 20833605; PubMed Central PMCID: PMC2974688.

Romberg K, Bjermer L, Tufvesson E. Exercise but not mannitol provocation increases urinary Clara cell protein (CC16) in elite swimmers. Respir Med. 2011 Jan;105(1):31-6. doi: 10.1016/j.rmed.2010.07.012. Epub 2010 Aug 8. PubMed PMID: 20696561.

Romberg K, Tufvesson E, Bjermer L. Asthma is more prevalent in elite swimming adolescents despite better mental and physical health. Scand J Med Sci Sports. 2012 Jun;22(3):362-71. doi: 10.1111/j.1600-0838.2010.01177.x. Epub 2010 Aug 30. PubMed PMID: 20807384.

Simard S, Tardif R, Rodriguez MJ. Variability of chlorination by-product occurrence in water of indoor and outdoor swimming pools. Water Res. 2013 Apr 1;47(5):1763-72. doi: 10.1016/j.watres.2012.12.024. Epub 2013 Jan 3. PubMed PMID: 23351434.

Soltermann F, Lee M, Canonica S, von Gunten U. Enhanced N-nitrosamine formation in pool water by UV irradiation of chlorinated secondary amines in the presence of monochloramine. Water Res. 2013 Jan 1;47(1):79-90. doi: 10.1016/j.watres.2012.09.034. Epub 2012 Sep 26. PubMed PMID: 23098367.

Weng S, Li J, Blatchley ER 3rd. Effects of UV 254 irradiation on residual chlorine and DBPs in chlorination of model organic-N precursors in swimming pools. Water Res. 2012 May 15;46(8):2674-82. doi: 10.1016/j.watres.2012.02.017. Epub 2012 Mar 1. PubMed PMID: 22425148.

Weng SC, Blatchley ER. UV-Induced Effects on Chloramine and Cyanogen Chloride Formation from Chlorination of Amino Acids. Environ Sci Technol. 2013 Apr 6. [Epub ahead of print] PubMed PMID: 23560482.

### VII. <u>Not relevant (45 abstracts)</u>

Several manuscripts report results of research on the molecular and cellular level monochloramine; the relevance of this research to drinking water or other exogenous exposures is not known. Manuscripts specific to wastewater treatment are included in this section if they were determined to be irrelevant to drinking water applications. In addition, several other manuscripts appeared in our search that are not relevant to drinking water.

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Converting to Monochloramine
 for Residual Disinfection of
 Drinking Water
 A Local Public Health Department Perspective

June M. Weintraub, Sc.D. San Francisco Department of Public Health

Presentation to Federal State Toxicology and Risk Analysis Committee (FSTRAC) October 29, 2008 Arlington, VA

## • • Outline

- Background
- Converting to chloramine
- Responding to unanticipated health questions
- Recommendations for further national-level studies

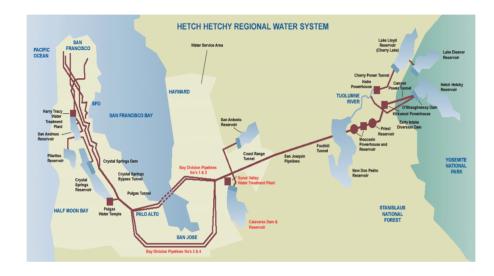
## SFDPH-SFPUC Collaboration History

Category	pre 1990	1990-1994	1995-199	9 pos	st 2000
Cross Connection Program	Ordinance Passed	Cross Connection Control Program			
Lead	Lead service line replacement project	Drinking water lead testing and Lead-free faucet programs			
Filtration Waiver and <i>Cryptosporidium</i>				Case Control Study (published 2002) <i>Cryptosporidium</i> Detection Action Plan	
Fluoride			S	ystemwid	de Fluoridation
Disinfection			THM and sponta abortion study s		Chloramine conversion

Water Security

### **EPA WSI**

# Background: San Francisco Water System



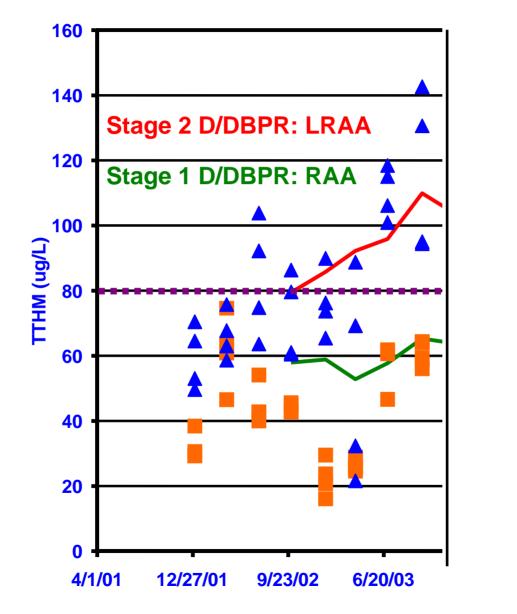
- SFPUC supplies water to 2.4 million customers in the Bay Area
- Unfiltered Hetch Hetchy Reservoir water (> 80%)
- Filtered local Bay Area reservoirs water (< 20%)

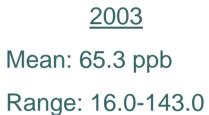
# Background: Disinfection By-products Regulations

### • Maximum Contaminant Levels (MCLs)

- Total Trihalomethanes: 0.080 mg/l
- Five Haloacetic acids (HAA5): 0.060 mg/l
- Stage I Disinfection By-products Rule
  - Compliance calculated by Running Annual Average
- Stage II Disinfection By-products Rule
  - Compliance calculated by Locational Running Average

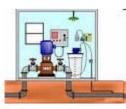
### **TTHM Levels With Free Chlorine**





# Background: Complying with Stage 2 DBP Rule

- Planning work identified chloramine as the best option to comply with more stringent DBP regulations
  - Eliminate DBP peaks
  - Lower DBP averages
  - Better control of DBPs in drought years for imported water
- Chloramine would also offer better disinfection residual management
  - Used 17 chlorine booster stations in San Francisco

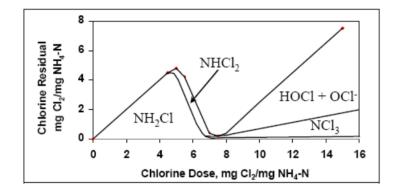


# Background: Chloramine Chemistry

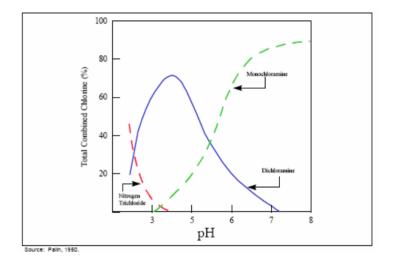
- Monochloramine is produced by adding ammonia to chlorinated water  $NH_3 + HOCI \rightarrow NH_2CI + H_2O$  monochloramine
- Depending on pH and Cl<sub>2</sub>:N ratio, as well as temperature and contact time, other species of chloramine may be produced:

 $NH_2CI + HOCI \rightarrow NHCI_2 + H_2O$  dichloramine  $NHCI_2 + HOCI \rightarrow NCI_3 + H_2O$  nitrogen trichloride

# Background: Chloramine Chemistry



Breakpoint Chlorination Curve at pH 6.5-8.5



## Chloramine species formation at differing pH

Figures source: Chapter 6, EPA Guidance Manual Alternative Disinfectants and Oxidants. April 1999

## Background: History of Chloramine Use

- Used for more than 90 years
- SFPUC used chloramine from 1935 to 1944 and again beginning in February 2004
- SFPUC was the last water utility in the Bay Area to switch to chloramine

North America		Bay Area		
City/System	Year Started	City/System	Year Started	
Ottawa, Canada	1917	Contra Costa WD	1981	
Denver, CO	1917	Santa Clara WD	1984	
Portland, OR	1924	Alameda County WD	1985-1997	
St. Louis, MO	1934	Marin MWD	1995	
Boston, MA	1944	East Bay MUD	1998	
Indianapolis, IN	1954			
Dallas, TX	1959	Chloramine is used internationally, for example, in the U.K., Australia, Israel, and Finland		
Milwaukee, WI	1964			

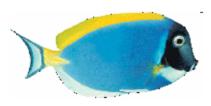
# February 2004 Chloramine Conversion

SFPUC outreach included:

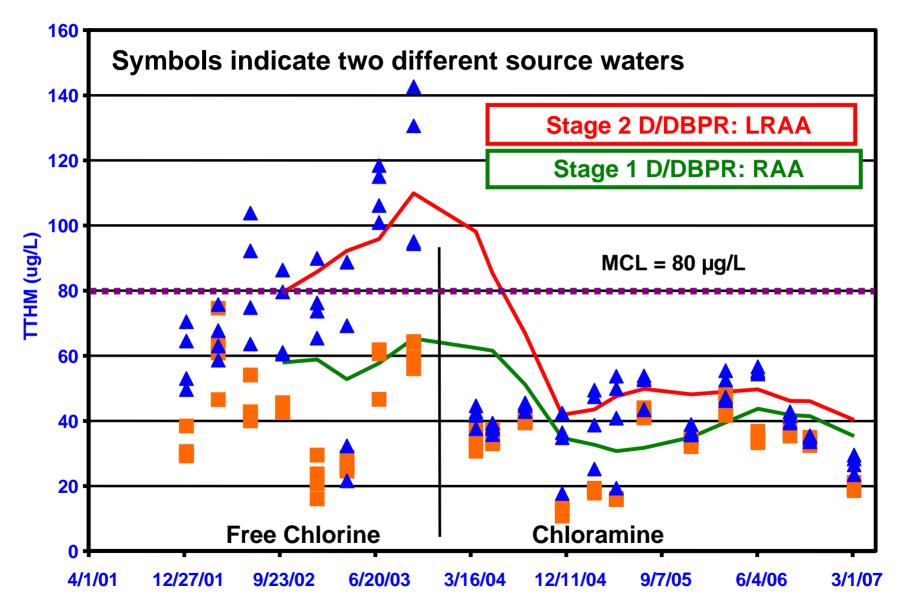
- Print Media
- Neighborhood Meetings
- Bill Inserts
- Fact sheets for website

SFDPH worked with SFPUC to anticipate and respond to concerns and questions

- Fish and aquarium owners
- Dialysis providers and patients
- Outreach to industrial users
- Nitrosodimethylamine (NDMA) fact sheet
- Collaborative research with CDC, CEIP on Legionella



TTHM Levels With Free Chlorine and After Conversion to Chloramine



# Responding to Unanticipated Health Questions



- April 2004: First phone call about skin rash
- June 2004: Began collaborating with California Conference of Local Health Officers
- August 2004: First version of detailed Q&A posted on sfwater.org

# Responding to Unanticipated Health Questions: Inhalation

- Monochloramine is highly soluble and loss to evaporation is minimal
- Di- and trichloramine cannot be present in SFPUC tap water due to pH and Cl<sub>2</sub>:N ratio control
- Concerns may be based on interpretation of chemistry and health data available on the Internet for concentrated chemicals and for swimming pools
  - Swimming pools have a higher load of ammonia from urine and sweat. Trichloramine inhalation may be an issue in improperly operated swimming pools



## Responding to Unanticipated Health Questions: Lead

- Elevated lead levels found in Washington DC in 2004:
  - More than 23,000 lead service lines
  - Non-optimized corrosion control strategy
  - Other site-specific issues



- Non-issue for SFPUC: meet compliance for lead and copper for both chloramine and free chlorine:
  - All lead service lines removed in 1980s
  - Consistent high pH>9.0 corrosion control strategy



- Several lead reduction/monitoring programs implemented
- Accelerated compliance sampling initiated

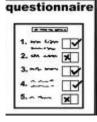
# Responding to Unanticipated Health Questions: Skin Rash

- No published medical literature
- No skin studies in IRIS
- Formal observational study designs challenging because no variation in exposure and high underlying prevalence of skin rash
- Decided to investigate as an outbreak/case series

# Responding to Unanticipated Health Questions: Skin Rash

**Case Investigation Goals** 

- Identify common features among respondents' descriptions of skin problem start date, appearance, and symptoms;
- Explore other exposures or explanations of the dermatitis complaints
- Determine need for further study



# Responding to Unanticipated Health Questions: Skin Rash

- Questionnaire administered by telephone to convenience sample of 17 respondents
- No consistent pattern of skin appearance or symptoms.
- Produced fact sheet urging respondents who continue to experience skin problems to visit a physician for follow up.
- Published findings in BMC journal Environmental Health



## Continuing Activities



SFDPH & SFPUC maintain a close collaboration:

- Stay apprised of and communicate emerging public health research relevant to chloramine
- Provide expertise to SFPUC Commissioners, advisory boards, management, and administration.
- Coordinate activities with other local health departments in the SFPUC service area
- Assist other jurisdictions with questions and strategies for responding to health questions relevant to chloramine.
- Work with legislators to ensure introduced legislation is sensible and factual.

CALIFORNIA LEGISLATURE-2007-08 REGULAR SESSION

House Resolution

No. 33

Introduced by Assembly Member Ruskin

July 14, 2008

House Resolution No. 33-Relative to drinking water treated with chloramine.

WHEREAS, Disinfection of public water supplies has been

2 considered by the Centers for Disease Control and Prevention as

3 one of the most significant public health accomplishments of all 4 time; and

5 WHEREAS, Water agencies have used chlorine or chloramine 6 as a residual disinfectant for over 90 years; and

7 WHEREAS, All disinfectants can react with natural organic 8 matter to form potentially harmful disinfection byproducts; and

9 WHEREAS, Chloramine forms lower levels of the regulated 10 disinfection byproducts than chlorine; and

11 WHEREAS, The California Conference of Local Health Officers

12 has reviewed current information and evidence regarding the

13 efficacy and safety of chloramine and concluded that chloramine

14 adequately protects the public health by controlling exposure to 15 waterborne organisms; and

16 WHEREAS, Some people are extremely concerned about the

17 use of chloramine as a drinking water disinfectant and the

18 unregulated disinfection byproducts that the use may produce; and

19 WHEREAS, Drinking water treated with chloramine is not 20 known to cause significant adverse human health effects; and

21 WHEREAS, Human health studies that focus on the symptoms

22 that some people attribute to chloramine exposure have not been

23 undertaken; and

HR 33

WHEREAS, Some disinfection byproducts of chloramine are not regulated by the United States Environmental Protection Agency; now, therefore, be it

4 Resolved by the Assembly of the State of California, That the 5 Assembly requests the State Department of Public Health to review 6 these public health concerns relating to the use of chloramine as 7 a drinking water disinfectant and to conduct studies, particularly

8 human health studies, as appropriate, to provide necessary public

9 health information to further clarify the human health effects of

10 chloramine; and be it further

11 Resolved, That the Chief Clerk of the Assembly transmit copies

12 of this resolution to the author for appropriate distribution.

13

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## Recommendations for Further National Level Studies

- Confirm results of SFPUC benchtop studies:
  - chloramine levels in foods and beverages prepared with water.
  - chloramine loss, conversion and volatilization in showers, baths, and dishwashers.
  - efficacy of filters and ascorbic acid for chloramine removal
- Continued research on DBPs and DBP mixtures formation, occurrence, and health effects
- Any health studies should:
  - Compare Chlorine vs. Chloramine
  - Done at National Level





<u>Miranda ML, Kim D, Hull AP, Paul CJ, Galeano MA. 2007. Changes in blood lead levels associated with use of chloramines in water treatment systems. Environ Health Perspect 115:221-5.</u>

### Background: Chloramine and Disinfection By-products

In the late 1970s and early 1980s it was discovered that chlorine reacts with naturally occurring organic matter to form trihalomethanes (THMs), haloacetic acids (HAAs), and other disinfection by-products (DBPs). Subsequent research showed that exposure to THMs over a lifetime may statistically increase the rates of some cancers. To protect public health, the U.S. Environmental Protection Agency (U.S. EPA) began regulating four THMs in 1979. Because chloramine reduces the formation of these potentially carcinogenic DBPs, many drinking water utilities have switched to chloramine for residual disinfection of their water supplies to reduce the formation of THMs and HAAs and to comply with U.S. EPA regulations.

### Background: Chloramine and Lead

There have been reported instances of increased drinking water lead levels after utilities switched to chloramine for distribution system disinfection. Most notably, in 2002 the utility serving Washington, DC reported high levels of lead at the customer taps after conversion to chloramine (Edwards and Dudi, 2004). It is clear that circumstances can occur where the switch from chlorine to chloramine may result in elevated drinking water lead levels, however such circumstances are more the exception than the rule. Water systems that have a great deal of lead pipe, lead service lines and/or lead plumbing in homes and that do not practice careful corrosion control may be susceptible to lead contamination, regardless of the type of disinfectant used (U.S. EPA 2007).

### Description of the study by Miranda et al

### Study design and Base Population

In 2000, the drinking water provider in Goldsboro North Carolina, Goldsboro Water Systems (GWS) switched to chloramine for residual disinfection of the drinking water. Although sampling conducted before and after the switch to chloramine showed that drinking water lead levels were below the Action Level requirement in the EPA's Lead and Copper Rule researchers interested in the potential link between chloramine and children's blood lead levels initiated an investigation of that association in this population.

The study by Miranda et al is a cross-sectional study that relied on ecological assignment of drinking water exposures based on residence location and on census-level exposures for housing age and other risk factors for lead exposure. The study base was all children under age six in Wayne County. In 2000, there were 9,530 children under age 6 living in Wayne County. With a birth rate of approximately 1,600 per year, the total population under age 6 in the five-year period covered by the study is approximately 15,900 children (assuming 9,500 in year 1999, and 1,600 new children each year for 2000, 2001, 2002 and 2003).

### Exposure

Exposure to chloraminated drinking water was determined based on place of residence and date. Children who lived in Goldsboro between March 2000 and December 2003 were considered to be exposed to chloraminated drinking water. The unexposed population included: (1) those who lived in Goldsboro between January 1999 and February 2000; (2) those who lived in some other part of Wayne County between 1999 and 2003

### Outcome

The outcome was blood lead levels, as determined from the North Carolina Childhood Lead Poisoning Prevention Program. Between 1999 and 2003, 18,284 records for 11,556 children were available. Of these 7,270 records were included. For children who were screened more than once, the authors selected the highest level at the earliest screening date.

This fact sheet was created in December 2007 by the San Francisco Department of Public Health Environmental Health Section in partnership with the San Francisco Public Utilities Commission. For more information, contact June.Weintraub@sfdph.org, or visit http://www.sfhealthequity.org/water

### Other exposures

Age of housing was determined from linked tax parcel data for each child. Percent African-American race and median income level for the census tract that the child lived in were determined from the U.S. census. Season of year (winter/spring/summer/fall) was also assessed.

### **Results and comments**

### 1. There were 7,270 records included in the analysis.

*Comment:* The authors do not state how many children the 7,270 records represent; assuming approximately 1.58 records per child (based on the overall ratio of 18,284/11,556), there were approximately 4,595 children included in the study. If the total base population is approximately 15,900 children under age six in Wayne County between the years 1999 and 2003, this means that approximately 71% of the eligible children were not included in the study. This high missingness could lead to considerable bias if more of the missing children who were exposed to chloramine had lower blood lead levels than those who were included in the study. For example, if a higher proportion of the missing children were from Seymour Johnson Air Force Base, which is annexed to the city of Goldsboro and which receives water from the Goldsboro Water System, this could have overestimated the effect of switching to chloramine if the missing children had lower blood lead levels. It has been shown that children residing on military bases tend to have lower lead exposures, regardless of the housing stock (Stroop et al. 2002).

The way that this bias could operate is shown in the following hypothetical two-by-two tables:

Theoretical study biased by missingness, assumes 3.5% of children exposed to chloramine have high blood lead levels, and 2.2% of others have high blood lead levels:

	High blood lead	Low blood lead	Total children (0.632*records)
Exposed to chloramine	57	1,558	1,615
Not exposed to chloramine	66	2,914	2,980
			4,595
Crude odds ratio			1.61

**Theoretical unbiased study** includes all 15,900 children, assumes 2.2% of all children have high blood lead levels, equivalent to 98.3% of missing children exposed to chloramine had low blood lead levels, and 97.8% of missing children not exposed to chloramine had low blood lead levels:

	High blood lead	Low blood lead	Total children (all records)
Exposed to chloramine	123	5,465	5,588
Not exposed to chloramine	227	10,085	10,312
			15,900
Crude odds ratio			1.00

### 2. A total of 2,555 records were from children who resided in the city of Goldsboro after March 2000. 651 records were from children who resided in the city of Goldsboro between January 1999 and February 2000. The remaining 4,064 records were from children who resided in other areas of Wayne County.

*Comment*: To the extent that children do not move in and out of the city of Goldsboro on a routine basis, the assignment of exposures based on place of residence is without bias. However, the method of exposure assignment is such that any external event coincidental with the switch to chloramine for residual drinking water disinfection could provide an alternative explanation for any findings. This is why the authors should have considered the possible impact of Hurricane Floyd. The September 1999 hurricane left many homeless; flooding, demolition and construction activities could well have been initiated around the same time as the switch to chloramine. Because of the older

housing stock and greater density of housing in the city of Goldsboro, these demolition and construction are likely to have affected children's blood lead levels to a greater extent in Goldsboro compared to the rest of Wayne County. Indeed the raw blood lead level data shows an increase county-wide in the year 2000, supporting an effect of the hurricane. Additionally, consideration of the effects of Hurricane Floyd provides a more biologically plausible explanation of interaction between calendar date and housing age.

### 3. The authors reported mean blood lead levels of 4.93 $\mu$ g/dL for children included in the study who resided in Goldsboro after March 2000 compared with mean blood lead level of 4.19 $\mu$ g/dL for all others in the study.

*Comment:* The authors do not report any information on blood lead testing in North Carolina such as detection limits or type of blood lead test. In North Carolina, all blood lead levels below the detection limit of 1  $\mu$ g/dL are reported as "1" in the state database (Miranda et al, 2007). The strategy of using the highest blood lead level assumes a false positive rate of zero. This may not be a reasonable assumption. A recent study of test results in Maine found 73% of capillary screening tests with results >10  $\mu$ g/dL were false positives when compared to venous confirmatory tests (Anderson et al., 2007)

Between 1999 and 2002, the geometric mean blood lead level among children aged 1–5 years in the U.S. was 1.9  $\mu$ g/dL (CDC 2005).

### 4. No information is given on differences in water chemistry such as pH or corrosivity, nor the presence of lead in the distribution systems or service lines.

*Comment*: These characteristics are important to determine the likelihood of lead leaching, regardless of the type of residual disinfectant used. In fact, the water serving Wayne County is heterogeneous. While the city of Goldsboro is served by surface water sources, the rest of Wayne County is served by seven smaller sanitary districts which rely on groundwater. Further, among the groundwater sources there is considerable variability in the water quality. Wayne Water Districts, comprised of five of the sanitary districts, had 39 wells in 2006, about half of which receive no treatment, with the remaining treated for iron removal, fluoride, chlorine and phosphate. The pH for Wayne Water Districts water ranges from 6.5-7.5, whereas Goldsboro Water usually maintains pH above 8.0.

All public drinking water providers are required to test for lead to show compliance with the Lead and Copper Rule. None of the water providers included in this study was out of compliance. Compliance sampling by Goldsboro Water System reported 90<sup>th</sup> percentile level in 1999 was 3 ppb, in 2000 the 90<sup>th</sup> percentile level was less than detection limit, in 2003 it was 6 ppb and in 2006 it was 3 ppb. Wayne Water Districts compliance sampling reported 90<sup>th</sup> percentile levels of less than the detection limit in 1999 and 5 ppb in 2003.

### 5. Tax parcel data indicated 15.6% of Wayne County Housing stock is built before 1925.

The tax parcel data differs markedly from that reported in the 2000 U.S. census, which reported just 7.6% built before 1939 (U.S. Census Bureau, 2000). In addition, the authors failed to consider differences in type of housing. According to the census, mobile homes represent a much higher percentage of housing stock outside of Goldsboro than within. Studies have shown that people living in mobile homes tend to have lower lead levels, regardless of housing age. Additionally, the authors failed to consider rental status differences. Studies have shown that children who live in rental housing are at higher risk of lead exposure, compared to those who live in owner-occupied housing (Lanphear et al., 2005)

UNITS IN STRUCTURE	Goldsboro		Wayne County, excluding Goldsboro	
	Number	Percent	Number	Percent
1-unit, detached	8,830	53.7%	18,691	60.5%
1-unit, attached	1,873	11.4%	121	0.4%
2 units	1,276	7.8%	262	0.8%
3 or more units	3,633	22.1%	572	1.9%
Mobile home	826	5.0%	11,213	36.3%
Boat, RV. van, etc	-	-	16	0.1%
Total	16,438	100%	30,875	100%
Renter-occupied	8409	51.2%	6,228	20.2%

#### U.S. Census Bureau Housing Characteristics in Wayne County

(Table source: U.S. Census Bureau, 2000)

#### 6. The authors stratified housing age into 25 year categories.

Comment: Stratifying housing age by 25 year categories may have led to misclassification. In 1988 the Consumer Product Safety Commission began enforcing the Federal Hazardous Substances Act restricting the use of lead solder in plumbing (CPSC 1988). The cutoffs used by Miranda et al. combine the years 1976-1988 together with newer housing stock which would not have lead solder in the plumbing, which may have biased their findings.

7. The authors found a statistically significant interaction between housing age and living in Goldsboro after March, 2000. They had investigated interaction because they "... expected that the effect of chloramines on blood lead levels would be less important and eventually unimportant as we moved into newer and newer housing stock."

According to EPA, the opposite of the authors' theory would be true: "Lead levels decrease as a building ages. This is because, as time passes, mineral deposits form a coating on the inside of the pipes (if the water is not corrosive). This coating insulates the water from the solder," (U.S. EPA 1993). In a published response to this comment, Miranda et al explained their theory of interaction between newer housing and lower lead levels with chloraminated water further, stating that "... an increase in the corrosivity of treated water after a switch to chloramines may expose lead that was shielded by mineral deposits." To test this hypothesis of interaction, a lag should have been incorporated into the exposure assignment, as any deterioration of mineral deposits would take some time, depending on the corrosivity of the water. Although no information is given on the corrosivity of the water served by GWS, the pH is maintained above 8.0, and maintaining slightly alkaline water pH (above neutral) throughout the distribution system is a standard component of corrosion control practice, because below pH 8.0 lead solubility increases (Crittenden et al, 2005). In the absence of evidence of the corrosivity of GWS water, the theory of interaction put forth by Miranda et al is not supported.

#### **Conclusion**

The analysis conducted by Miranda and colleagues is interesting and additional studies with individual level exposure measurements should be conducted. However their study does not provide a basis for recommending a broad alteration of blood lead screening strategies, nor does it provide any proof that elevated blood lead levels are related to drinking water in Goldsboro, North Carolina. The effects of Hurricane Floyd may have resulted in higher lead levels throughout the county coincidental with the timing of the GWS switch to chloramine disinfection.

States need to ensure that blood lead screening strategies are inclusive, especially of low income children who are at greatest risk of undetected elevations in blood lead levels. In accordance with the U.S. Preventive Services Task Force recommendations, (U.S. PSTF 2007) a prudent approach to prevent lead exposure via drinking water is that municipalities ensure careful corrosion control and remove lead service lines and distribution pipes, regardless of the method of residual disinfectant used.

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### Note:

This fact sheet is a technical summary and critique of research reported in the journal Environmental Health Perspectives. The original manuscript and accompanying correspondence are:

Miranda ML, Kim D, Hull AP, Paul CJ, Galeano MA. 2007. Changes in blood lead levels associated with use of chloramines in water treatment systems. Environ Health Perspect 115:221-5.

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