QUESTIONS REGARDING DISINFECTION BY-PRODUCTS
Updated August 2010

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 N-nitrosodimethylamine, 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: HEALTH EFFECTS

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^3. 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 21st 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 N-nitrosodimethylamine (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 detection limit of 2 ng/L but less than the CDPH Notification Level of 10 ng/L. NDMA has been 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.
Iodide 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.