

April 10, 2007

Andrew DeGraca, PE  
Water Quality Bureau Manager  
San Francisco Public Utilities Commission  
1657 Rollins Road  
Burlingame, CA 94010

Subject: *Opinion as to Probable Chloramine Speciation in San Francisco Public Utilities Drinking Water Distribution System*

Dear Mr. DeGraca:

Several concerns have been raised to the San Francisco Public Utilities Commission (SFPUC) that relate to the chemistry of chloramines which I feel I can confidently address based upon the fundamental chemistry that controls speciation. In formulating my opinion at the request of SFPUC staff, I have reviewed information supplied to me (see Appendix A).

### **Opinion**

Under the water quality and treatment conditions utilized by the SFPUC, it is my opinion that:

- a) monochloramine is the dominant species and likely constitutes more than 99% of the total measured disinfectant concentration,
- b) dichloramine is likely an undetectable species below a detection limit of approximately 0.01 mg/L Cl<sub>2</sub> and
- c) trichloramine is highly unlikely to occur except at exceedingly small and undetectable concentrations well below a detection limit of 0.01 mg/L Cl<sub>2</sub>.

Rationale for my opinion on speciation is presented below.

### **Credentials**

I currently serve as a professor of Civil and Environmental Engineering at the University of Iowa, a position I have held for the last 24 years. My research has focused on chloramine chemistry including reactions that control its formation and fate in distribution systems, as well as formation of some disinfection by-products. Currently I am conducting research on the occurrence of inorganic contaminants in distribution systems, and on the formation of disinfection by-products by novel reaction pathways. Appendix B lists my relevant publications.

## Rationale

Theoretically, under most water quality conditions, all forms for chloramines and free chlorine can co-exist even if at exceedingly small and unmeasurable concentrations. Practically, however, under typical water quality conditions such as maintained by the SFPUC (e.g., pH > 8.2 and Cl<sub>2</sub>:N weight ratio < 5), monochloramine (NH<sub>2</sub>Cl) will be the dominant form and should be the only measurable form. All other species [e.g., dichloramine (NHCl<sub>2</sub>), trichloramine (NCl<sub>3</sub>), and free chlorine, which is the sum of hypochlorous acid and hypochlorite ion (HOCl and OCl<sup>-</sup>)] will not be detected in chloraminated distribution system by currently approved analytical methods and are not of significance from a water supply point of view.

I do agree with the statements made by the SFPUC regarding chloramine speciation, and believe they did an excellent job at addressing customer concerns based on a firm understanding of the literature and the chemistry and toxicology of chloramines (see Attachment A).

### Some relevant chloramine chemistry

Monochloramine is made by addition of free chlorine and ammonia in water at a ratio such that there is a small excess of free ammonia while at the same time no significant amounts of other chloramines are formed. The primary variables are the ratio of total chlorine to total ammonia added (the added Cl<sub>2</sub>:N ratio) and the pH. While in principle it would appear that addition of one mole of chlorine per mole of ammonia (Cl<sub>2</sub>:N ratio of 1:1 by mole or 5:1 by weight) would be sufficient to produce a solution of only monochloramine, in practice, a small "excess" amount of free ammonia is added and utilities operate at a ratio of chlorine to ammonia less than 5:1 by weight. For example, operational target for Cl<sub>2</sub>:N ratio at SFPUC is 4.6:1 at the treatment facilities. This small excess of ammonia is required to minimize the chance of forming other chloramines such as dichloramine and trichloramine and "stabilizes" monochloramine which very slowly decays in a reaction involving the oxidation of "ammoniacal nitrogen" which can be written stoichiometrically as:



Reaction 1 actually involves a series of complex reactions and is accelerated by increasing the ratio of Cl<sub>2</sub>:N and decreasing pH. As the ratio of chlorine to ammonia increases, there is a tendency toward the formation of more chlorinated forms of amines. In practice, unless the pH of water is lowered to less than approximately 7.5 or the ratio of Cl<sub>2</sub>:N exceeds approximately 5 by weight or 1:1 by mole, measurable dichloramine will not exist. It is formed too slowly and is too reactive at SFPUC water quality conditions so that it would disappear as fast as it would form. Trichloramine can only form at measurable concentrations if significant concentrations of free chlorine are also present; a condition, which does not exist in chloraminated SFPUC distribution system. At such an unusual condition, monochloramine would no longer exist at measurable

concentrations. Furthermore, the ratio of  $\text{Cl}_2:\text{N}$  in the drinking water distribution system will decrease with time if ammonia is stable making dichloramine and trichloramine formation even more unlikely. This is a consequence of reaction 1 and other reactions in solution and with the deposits on pipe walls that lead to a reduction of monochloramine and formation of free ammonia.

In the practice of chloramination, if the targeted amount of chlorine at the correct  $\text{Cl}_2:\text{N}$  ratio is added (slightly less than 5:1 usually), then there are no processes that could lead to the sudden and unexpected formation of dichloramine or trichloramine except if the pH were suddenly greatly lowered below about 7.0 (Note: the minimum regulatory pH for corrosion control in SFPUC distribution system is 8.2 and typical pH range is near or above 9.0). As mentioned, the ratio of  $\text{Cl}_2:\text{N}$  in the water will decrease with time insuring that dichloramine or trichloramine should not form to significant values at or above the detection limit of currently approved wet chemistry methods of approximately 0.01 mg/L  $\text{Cl}_2$  for dichloramine and trichloramine. I would expect their concentrations to be much lower than this and therefore it would be difficult to demonstrate that they are actually present.

Sincerely,

A handwritten signature in black ink, appearing to read "Richard J. Valentine". The signature is cursive and somewhat stylized, with the first name "Richard" and last name "Valentine" clearly legible.

Richard Valentine, Ph.D.  
Professor  
Department of Environmental Engineering  
University of Iowa

## Appendix A. Information Reviewed

- 1) SFPUC operational water quality data for system entries for 2004 through 2006
- 2) SFPUC Memorandum to PUC: Review of Chloramine Concerns, dated Nov 8, 2006
- 3) “Notes on Chloramine in Drinking Water System” by Robert Helwing, dated Nov 14, 2006
- 4) SFPUC Response to “Notes on Chloramine in Drinking Water System” by Robert Helwing, Dec 5, 2006
- 5) “Chloramine in Our Water Supply” by Denise Johnson-Kula and Lillian Lieberman, Concerned Citizens Against Chloramine, dated Feb 21, 2005

## Appendix B. Relevant Publications

- Hartwig, E., and Valentine, R.L., "Bromoform Production in Tropical Open-Ocean Waters," Water Chlorination: Environmental Impact and Health Effects, Vol. 4, Book 1, 1982; R.L. Jolley et al, eds., Ann Arbor Science, pp. 311-330.
- Valentine, R.L. and Selleck, R.E., "Effect of Bromide and Nitrite on the Degradation of Monochloramine," Water Chlorination: Environmental Impact and Health Effects, Vol. 4, Book 1, 1982; R.L. Jolley et al, eds., Ann Arbor Science, pp. 125-137.
- Venkataramiah, A., Lakshmi, G., Best, C., Hartwig, E. and Valentine, R.L., "Effect of Chlorinated Discharges on Marine Animals," Water Chlorination: Environmental Impact and Health Effects, Vol 4, Book 2, 1982; R.L. Jolley, et al, eds., Ann Arbor Science, pp. 947-958.
- Valentine, R.L. and Jafvert, C., "Commentary on the Kinetics of Monobromamine Disproportionation - Dibromamine Formation in Aqueous Ammonia Solutions", Environmental Science and Technology, Vol. 19, No. 3, 1985, pp. 286-287.
- Valentine, R.L., "The Disappearance of Monochloramine in the Presence of Nitrite", Water Chlorination: Environmental Impact and Health Effects; 1985, R.L. Jolley, ed., Ann Arbor Science, pp. 975-984.
- Valentine, R.L., "Bromochloramine Oxidation of N,N-diethyl-p-phenylenediamine in the Presence of Monochloramine", Environ. Sci. and Technology, Vol. 20, No. 2, 1986, 166-170.
- Valentine, R.L., Brandt, K.I., Jafvert, C.T., "A Spectrophotometric Study of the Formation of an Unidentified Monochloramine Decomposition Product", Water Research, Vol. 20, No. 8, 1986, pp. 1067-1074.
- Jafvert, C.T., Valentine, R.L., "Dichloramine Decomposition in the Presence of Excess Ammonia", Water Research, Vol. 21, No. 8, August 1987, pp. 967-973.
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- Valentine, R.L. and Wilber, G., "Some Physical-Chemical Characteristics of an Unidentified Chloramine Decomposition Product", In Water Chlorination: Chemistry, Environmental Impact and Health Effects, Vol. 6, 1989.
- Jafvert, C. and Valentine, R.L., "A Reaction Scheme for Chlorination of Ammoniacal Water", Environmental Science and Technology, Vol. 26, No. 3, 1992, pp. 577-586.
- Leung, S.W. and Valentine, R. L. "An Unidentified Chloramine Decomposition Product, I: A Proposed Formation Mechanism", Water Research, Vol. 28, No. 6, 1994, pp.1475-1483 .
- Leung, S.W. and Valentine, R. L. "An Unidentified Chloramine Decomposition Product, II: Chemistry and Characteristics", Water Research, Vol. 28, No. 6, 1994, pp. 1485-1495.

- Chung M., Hao, Oliver J., and Valentine, Richard L. "Kinetics of Monochloramine Reactions with Nitrite", *Journal of Environmental Engineering (ASCE)*, Vol. 120, No. 4, 1994, (July/Aug.), pp. 859-874.
- Ozekin, Kenan; Valentine, Richard L., and Vikesland, Peter J. "Modeling Chloramine Decay in Natural Waters", *American Chemical Society (ACS) Symposium Series 649, Water Disinfection and Natural Organic Matter*, 1996, pp. 113-125.
- Vikesland, Peter J.; Valentine, Richard L. and Ozekin, Kenan. "Application of Product Studies in the Elucidation of Chloramine Reaction Pathways", *American Chemical Society (ACS) Symposium Series 649, Water Disinfection and Natural Organic Matter*, 1996, pp. 105-114.
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