Project Profile Information Form

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Project Title: Chloramine Decomposition in Distribution System and Model Waters

Project Number: 937

Principal Investigators: Richard. L. Valentine, University of Iowa

Objectives:

(State the relevant objectives of the project; 75 words or less.)
This study was designed to contribute to a better understanding of the fate of chloramines in distribution systems. The project objectives were to: 1) characterize the influence of water quality parameters on chloramine decomposition rates; 2) evaluate and compare chloramine decomposition rates in distribution system water with rates determined in model systems; 3) characterize the nature of chloramine decomposition products; 4) perform mass and redox balances that include all known nitrogen-containing and chlorine-containing products, and; 5) develop mathematical relationships and models of use to describing the rate of chloramine loss in drinking water.

Background:

(Provide background information; 75 words or less.)
Chloramines, produced by a reaction between free chlorine and ammonia in a process called chloramination, have long been used to provide a disinfecting residual in distribution systems where it is difficult to maintain a free chlorine residual. More recently chloramines have been used to replace free chlorine because they are believed to produce fewer disinfection by-products (DBPs). The U.S. Environmental Protection Agency has promulgated a maximum contaminant level (MCL) of 4.0 mg/L as Cl₂. Although chloramines are generally believed to be less reactive than free chlorine, they are unstable, even in the absence of organic matter, and they disappear slowly. To meet DBP and disinfection objectives, it is desirable that the chloramine residual be a stable as possible. In spite of a long history of use, the fate of chloramines in distribution systems and the characteristics and processes that influence their stability are largely unknown.

Highlights:

(Provide “at a glance” the main findings of the research [minimum of three]; 100 words or less.)
This research developed both a sophisticated model that mechanistically describes monochloramine decay and a simplified model that can be used to determine the theoretical stability of monochloramine for a
given set of conditions. The sophisticated model makes it possible to have a good fundamental understanding of the reactions monochloramine undergoes as it decays. On the other hand, the simplified model makes it possible to do a quick calculation for a given water to determine what its monochloramine stability should be. The mass and redox balances are also valuable because they indicate that any unidentified product(s) formed by monochloramine decay consist of less than 15 percent of the initial chlorine and nitrogen, and it was also shown that NOM primarily acts as a reactant with monochloramine and did not have any significant catalytic abilities.

Approach:
(Describe the research approach for this project. May use subject subheads; 125 words or less.)

Chloramine decay experiments were performed by spiking aliquots of stock chloramine solution into laboratory-prepared water or water collected from the distribution systems of the five utility participants. Both kinetic and mass balance studies were performed under a variety of different conditions. Individual reactors were periodically opened and monochloramine concentrations were determined. Chlorine, nitrate and total ammonia were measured using ion chromatography. Modeling and model verification of the decomposition reactions were important aspects of this project. An existing model was tested to determine if it adequately describes the decomposition kinetics at low initial chloramine concentrations. The model was used to: 1) evaluate the effects of other parameters not accounted for such as ionic strength, temperature, etc. and; 2) compare results from experiments involving model laboratory waters with data from collected distribution system waters. Modeling goals also included developing a rationally based simple relationships that could be used as a guide in predicting chloramine decomposition kinetics.

Results/Findings:
(Describe the results/findings of the research. May use subject subheads; 200 words or less.)

As pH and ammonia concentrations decrease, the rate of monochloramine decay increases. The catalytic effect of bicarbonate on monochloramine decay was reevaluated and new rate constants that more accurately describe the kinetics were determined. Previous estimates of these rate constants indicated that bicarbonate did not have a large an effect on monochloramine decay as was shown here. The correspondence between model and measured monochloramine concentrations was good for all reaction conditions. In general, the monochloramine concentration predicted after a 7-day decay period is within 5 to 10 percent of the measured value. This model was also shown to have the capability to predict monochloramine decay in actual distribution system waters.

The presence of NOM had two effects. First there was an initial chlorine demand followed by an accelerated decay rate. Based on the chloramine decay model it is expected that concentrations of dissolved organic carbon (DOC) found in many waters may measurably increase the rate of
monochloramine decay. A comparison with results obtained with collected distribution system waters does, however, suggest that the NOM in treated waters is less reactive than either SRFA or AH.

Bromide at a level of 0.1 mg/L did not significantly affect monochloramine decay. Increasing the levels to 0.5 mg/L and above measurably accelerated monochloramine decay. After the kinetic model was modified for bromide oxidation, results in predicted values were in good agreement with those measured at pH 7.5 and above. The model did a poor job at pH 6.5, suggesting the model formulation was incomplete.

Measuring the formation of monochloramine decay products and comparing them to the observed monochloramine decay illuminated a great deal about the pathways by which monochloramine decays. It was observed that the reduced product (chloride) formation is essentially unaffected by changing the initial monochloramine concentration or by the presence of absence of NOM. It did appear that changes in pH affect the amount of chloride produced for a given level of monochloramine decay. As the pH increases the amount of chloride recovered decreases.

Nitrite formation occurs in drinking water sources when conditions arise that promotes biological nitrification of excess added ammonia. Its oxidation kinetics are important from the standpoint of a sink for monochloramine and as a substance generally thought less desirable than its oxidation product, nitrate. The model could adequately predict the oxidation of nitrite.

A simplified second-order decay model was formulated and adequately described monochloramine decay kinetics under a number of different conditions. A single decay coefficient was developed and may be used to describe chloramine stability for a wide variety of conditions.

**Impact:**

(Describe the relevant impacts that the research results may have on the water industry. Use general subheads such as recommendations or benefits. Subheads more specific to the project may also be used, such as treatment, analytical development, regulatory implications, and so forth; 100 words or less.)

This study will help water utilities gain a better understanding about monochloramine decay in the following ways.

1. A monochloramine decay model was developed for use under conditions that closely approximate those of waters leaving the drinking water treatment plant.
2. The influence of nitrite, bromide, and NOM on monochloramine decay were studied and modeled.
3. Except in one case, water with a light NOM concentration, the model predicted decay in actual treated waters to within 10 to 15 percent of experimental values.
4. It was found that when monochloramine autodecomposes in the absences of NOM, the primary nitrogen containing products are ammonia, nitrogen gas, and nitrate, with ammonia and nitrogen gas being predominant. When NOM is present, the decay product speciatation changes and ammonia becomes the predominant product.
5. In a simplified second-order decay model, a single decay coefficient was developed and may be used to describe chloramine stability for a wide variety of conditions.
**Participating Utilities** (if applicable; maximum of five): University of Iowa, Iowa City; Cedar Rapids, Iowa; Belle Glade Water Utility, Florida; Minneapolis Water Utility, Minnesota; Metropolitan Water District of Southern California.