



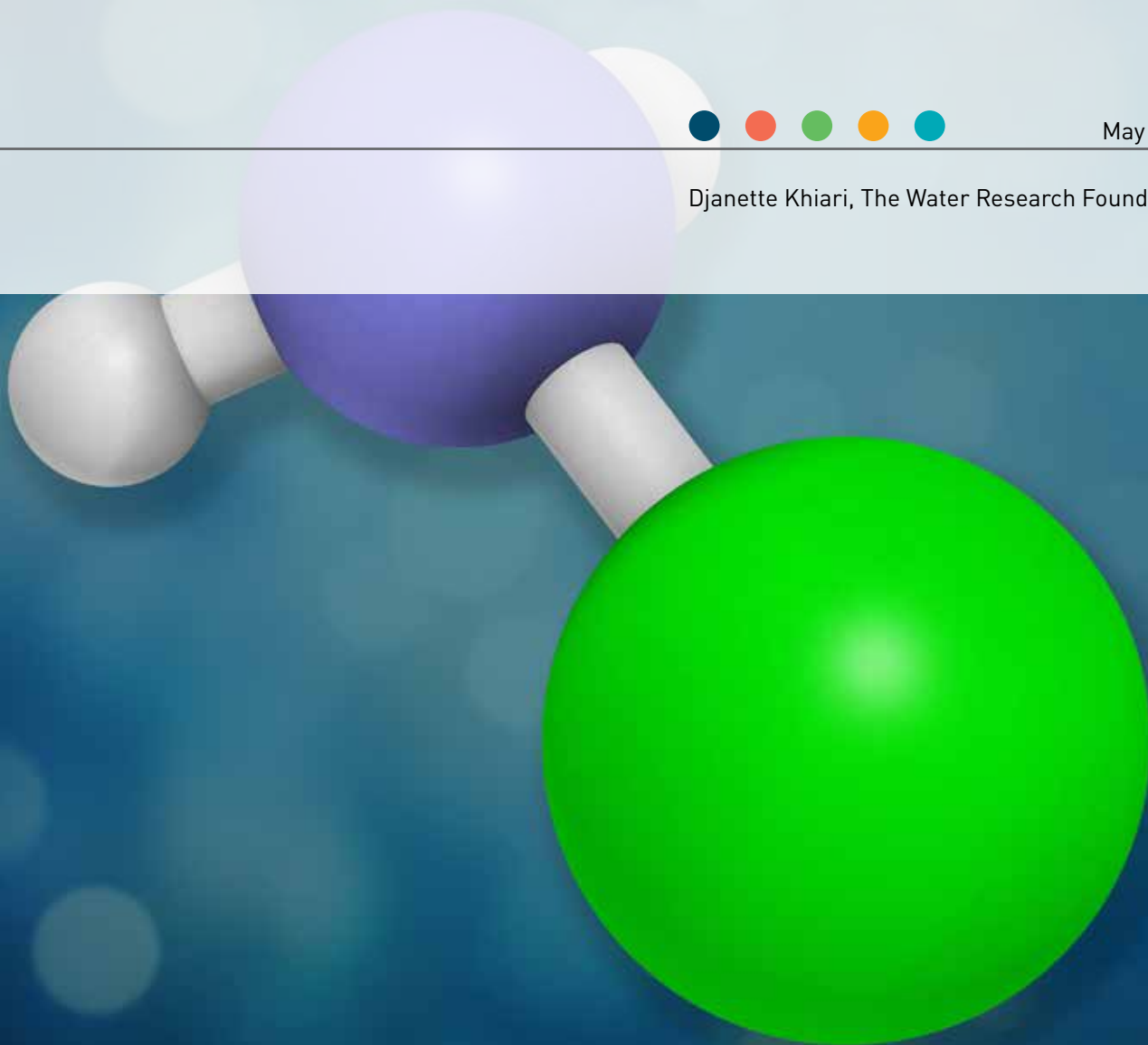
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The Role and Behavior of Chloramines in Drinking Water



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CHLORAMINATION HAS BEEN USED in drinking water treatment since the early 1900s, but its use has been low compared to that of chlorine. In recent years, many utilities implemented chloramine, primarily to comply with the U.S. Environmental Protection Agency's (EPA) Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules (D/DBPR). Chloramines are less reactive than chlorine and produce lower concentrations of trihalomethanes (THMs) and haloacetic acids (HAAs).

In drinking water treatment, chloramines are primarily used as a secondary disinfectant to provide a residual in the distribution system. The three forms of inorganic chloramines are mono-, di-, and tri-chloramine. Chloramines are a class of disinfectants formed by the reaction of chlorine and ammonia. The ratio at which chlorine and ammonia are fed determines the species of chloramine produced. Monochloramine is the preferred species, as it is more effective and less likely to cause taste-and-odor problems.

In addition to minimizing the formation potential of THMs and HAAs, chloramines are more stable than chlorine and therefore last longer in the distribution system. Chloramine stability is advantageous in distribution systems with long detention times. Chloramination can be a complex process and improper operations can sometimes result in unintended consequences including nitrification, formation of non-regulated DBPs, and deleterious effects on some elastomeric materials used in the distribution system. Since chloramine use has been increasing, water professionals need to understand the various aspects of chloramination with the goal to better manage and operate their systems and minimize unintended consequences.

Since the mid-1980s, The Water Research Foundation (WRF) has

funded more than 70 research projects on the optimization of chloramination while considering chloramine-related issues, such as key factors to consider when making the switch to chloramines, prevention and mitigation of nitrification events, minimization of disinfection by-products, and lead and copper release related to chloramine use. What follows is a summary of the relevant chloramine-related WRF reports. For an overview of chloramine use in water treatment and a discussion of the concerns associated with chloramine use, refer to the archived WRF webcast, "[Talking About Chloramines: A Discussion of the Concerns and Questions Regarding Water Treatment](#)." This webcast is available for on-demand viewing on the WRF website.

Switching to Chloramines

ALTHOUGH THE ECONOMIC ANALYSIS for the Stage 2 D/DBP Rule produced by the EPA estimated that more than 50% of surface water systems would use chloramines as a secondary disinfectant, the switch to chloramination has been somewhat slower than expected. The 2004 AWWA secondary disinfection practices survey found that 29% of community water systems currently use chloramines for secondary disinfection and that another 3% are converting to chloramine use (Seidel et al. 2005).

Switching to chloramines is certainly not easy and requires extensive planning and a thorough understanding of source water characteristics and system operations. Utilities considering such a switch need to consider issues ranging from public perception to compatibility of chloramines with the distribution system. [Optimizing Chloramine Treatment: Second Edition](#) (2760), an update to an earlier report, is a manual on the use of chloramines and the role

they play in water quality improvements for drinking water utilities. Using documented information from 68 utilities that use chloramines, the report identifies critical parameters for controlling chloramination and spells out a chloramination optimization strategy.

[A Guide for the Implementation and Use of Chloramines](#) (2847) summarizes the current state of knowledge regarding chloramine use and synthesizes the information into step-by-step procedures for using chloramines in a water system.

Finally, [Long-Term Effects of Disinfection Changes on Water Quality](#) (2940) documents the long-term effects of disinfectant changes on distribution system conditions, including changes in microbial community, chemical composition, and aesthetic characteristics. The report contains issue papers on microbial quality, chemical quality (DBPs, corrosion, metal release, and particle characteristics), and aesthetic quality impacts associated with disinfectant changes.

Nitrification

TWO-THIRDS OF THE MEDIUM AND large systems in the United States using chloramination experience nitrification episodes to some degree. Nitrification can significantly alter water quality and can result in violations of coliform, loss of disinfectant residual, as well as overall increased microbial growth in the affected areas. Therefore, utilities using chloramines are concerned about nitrification events that occur when chloramines decay in the distribution system. The use of chloramines can cause biological instability and promote the growth of nitrifying bacteria. When chloramines decompose, ammonia is released and can be oxidized to nitrite and nitrate. This process, known as nitrification, is believed to be facilitated by ammonia-oxidizing

bacteria (AOB), which use the ammonia as an energy source. These bacteria are commonly found in drinking water systems, and nitrification occurs when conditions allow their numbers to rise. Although AOB seem to be implicated in most nitrification events, new information from WRF and others indicates that other bacteria may also play a critical role. Other factors that could play a role in nitrification include:

- Water quality factors
 - pH
 - Temperature
 - Chloramine residual
 - Ammonia concentration
 - Chlorine-to-ammonia ratio
 - Concentrations of organic compounds
- Distribution system factors
 - Detention time
 - Reservoir design and operation
 - Sediment
 - Tuberculation in piping
 - Biofilm
 - Absence of sunlight

Understanding chloramine decay and nitrification events is clearly a critical issue in the effective use of this disinfectant, and WRF has conducted considerable research on this topic and will continue this work in the future.

In a WRF study of chloramine decomposition, [Chloramine Decomposition in Distribution System and Model Waters](#) (937), researcher Richard Valentine of the University of Iowa and his colleagues described the influence of water quality parameters on chloramine decomposition rates, compared decay rates in actual distribution systems with rates in model systems, and characterized chloramine decomposition products. The research team found that the rate of monochloramine decay increased as pH and ammonia concentrations decreased. Valentine and his team also produced two models

of chloramine loss in drinking water. The more sophisticated model elucidates the reactions monochloramine undergoes as it decays. The simplified model can be used to determine the theoretical stability of monochloramine in a given finished water supply.

In the report, [Ammonia from Chloramine Decay: Effects on Distribution System Nitrification](#) (553), Greg Harrington of the University of Wisconsin and his colleagues studied the influence of ammonia release on the growth of AOB and evaluated treatment methods to reduce the frequency of nitrification in distribution systems. Harrington and his team also produced a model that simulates the water quality effects associated with chloramine decay and nitrification.

The focus of the WRF project, [Characterizing the Microbial Community Responsible for Nitrification](#) (4165), was to validate a high-throughput microarray and evaluate the microbial communities present in pilot-scale and full-scale water treatment systems that are capable of contributing to nitrification events. A comprehensive analysis consisting of 112 drinking water samples including source water, filter effluent, and chloraminated distribution systems at both pilot- and full-scale was conducted to evaluate the presence of different microorganisms associated with nitrification. For this purpose, a high-throughput microarray was designed, validated, and used to analyze different drinking water samples. The microarray was capable of identifying targeted microorganisms using the 16S rRNA gene, the subunit A of the ammonia monooxygenase (*amoA*) gene for ammonia-oxidizing bacteria (AOB), and the *amoA* gene for ammonia-oxidizing archaea (AOA). This project successfully demonstrated the ability of microarray technology to detect the presence or

absence of a wide variety of microorganisms in a timely and robust manner. If microarray technology can be cost-effectively implemented by drinking water utilities, this technology can help utilities overcome several operational concerns. Of particular interest for this study was nitrification in chloraminated distribution systems.

Disinfection Byproducts

CHLORINE-BASED DISINFECTANTS like chlorine and chloramine can react with organic matter of natural and anthropogenic origin to form regulated and non-regulated DBPs, albeit with different species and concentrations. Chloramine is a weaker oxidant than chlorine and it generally forms less halogenated byproducts than chlorine. In general, the total organic halogen (TOX) and regulated DBPs (THMs and HAAs) concentrations formed during chloramination are lower than the TOX/regulation DBPs produced during chlorination (Khiari et al. 1996).

To minimize the formation of these regulated DBPs and comply with existing regulations, water utilities have increasingly been switching to alternative disinfectants, such as chloramine, or installing more advanced and costly treatment processes, such as ozone or granular activated carbon (GAC) to remove precursors. However, while reducing the formation of halogenated DBPs, alternative oxidants have been shown to favor the formation of other DBPs (e.g., ozone-producing bromate and forming more halonitromethanes [HNMs], chloramines producing N-nitrosodimethylamine [NDMA], and in certain circumstances iodinated DBPs [I-DBPs]).

It is important to remember that the formation of DBPs is water matrix-specific. One must always consider the risk trade-offs associated with various treatment scenarios. Utilities must use

a battery of tests to select the most appropriate treatment while successfully minimizing unintended consequences and protecting public health.

N-Nitrosamines

N-NITROSAMINES ARE A LARGE group of chemicals suspected to be carcinogenic. The most frequently detected *N*-nitrosamine in drinking water is *N*-nitrosodimethylamine (NDMA). NDMA is classified as a probable human carcinogen, based on animal studies. Although both chlorination and chloramination have been implicated in reaction mechanisms that result in NDMA formation, it is a DBP preferentially formed by chloramines. Sources of NDMA precursors include treated wastewater and certain polymers used in drinking water treatment (e.g., polyDADMAC, polyamine).

In the last several years, WRF has funded several projects that investigate NDMA occurrence, formation, and control strategies to prevent NDMA formation while minimizing unintended consequences. One of the most recent studies dealing with control of NDMA was [Controlling the Formation of Nitrosamines During Water Treatment](#) (4370), which developed improved strategies for minimizing nitrosamine formation during drinking water treatment and provided treatment guidance for utilities.

The research showed that pre-oxidation effectively destroyed watershed-derived precursors in the following order: ozone > chlorine > MPUV > LPUV > permanganate. Ozone was often effective at low exposure/contact time (CT). At higher exposure (e.g., longer free chlorine contact times), chlorine was more effective than at low exposure. Chlorine was more effective in the pH range of 8 to 9 and in warmer water. Ozone and MPUV were more effective at higher pH

levels. Polyamine-derived precursors were also destroyed by various pre-oxidants. In pre-oxidation testing of water with a very high dose (6.0 mg/L as the active ingredient) of polyDADMAC, NDMA formation potential (FP) increased. However, in waters with low polyDADMAC doses (≤ 0.8 mg/L as the active ingredient), as used at full-scale plants, NDMA formation did not appear to be exacerbated, as was observed in the bench-scale testing of the very high polyDADMAC dose.

Powdered activated carbon (PAC) and granular activated carbon (GAC) removed watershed-derived precursors. Low doses of PAC (e.g., ~5–10 mg/L) were often effective. GAC was able to remove NDMA FP better than that of the bulk TOC. PAC removed, in limited tests, polyamine-derived precursors, but did not remove polyDADMAC-derived precursors. GAC did not appear to be effective at removing polyDADMAC-derived precursors. Thus, polymer management and the use of alternative polymers must also be considered.

Halonitromethanes

THE IMPACT OF OXIDATION/disinfection, operating conditions, and water quality parameters on the formation of halonitromethanes (HNMs) in drinking water and wastewater effluents was investigated in [Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water](#) (4063).

The results of the study showed that among the five disinfection scenarios tested, the order of HNM formation in molar concentrations and yields on a dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) basis was in the order of ozonation-chlorination >> chlorination \geq ozonation-chloramination >> chloramination.

Ozonation/chlorination significantly enhanced HNM formation as compared to chlorine alone, while chloramination (using preformed monochloramine), alone or after ozonation, produced the fewest HNMs. Similar to drinking water treatment, HNM formation was greatly reduced by applying preformed monochloramine rather than chlorine (Cl₂), especially after pre-ozonation.

In addition to the disinfectant type, factors affecting the formation and speciation of DBPs in drinking water include DOC nature and characteristics, pH, bromide (Br⁻) concentration, and other water quality parameters. In this study, HNM formation was at appreciable levels for certain conditions under uniform formation conditions (UFC) (e.g., up to 25 μ g/L for Br⁻/DOC ratio of 100 and pH=8). The results indicated that the major precursors of THMs and HNMs were different in nature and reactivity, as the treated water exhibited significantly lower THM formation than raw water, while HNM concentrations formed in the raw and treated waters were comparable at ambient conditions. However, some similarities were noted regarding the formation of these two classes of DBPs. For both THMs and HNMs, formation increased with pH (6 to 8), and treated waters had higher amounts of brominated THM and HNM species as compared to the raw waters due to the removal of DOC, but not Br⁻, during conventional treatment.

Iodinated DBPs (I-DBPs)

I-DBPS SUCH AS IODINATED THMS (I-THMs) and iodoacids are formed when iodine-containing water is disinfected with chlorine or chloramine. Research shows that the formation of I-DBPs is favored during chloramination, especially when chlorine or ozone is used as a pre-oxidant in the treatment process. When water contains multiple iodinated

precursors, complete oxidation is prevented, which creates a favorable environment for the formation of these I-DBPs. One I-DBP, tentatively identified as iodobutanol, has been found in finished waters from treatment plants located on coasts that can be impacted by saltwater intrusion, which is iodide- and bromide-rich (Weinberg et al. 2002).

Iodinated THMs

IN ADDITION TO THE formation of HNMs, [Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water](#) (4063) investigated the formation of iodinated THMs (I-THMs). The project investigated the importance of pH, the effect of contact time and dose of prechlorination, and the role of chloramination strategy (chlorine added before ammonia vs. preformed monochloramine (NH₂Cl) and the role of natural organic matter (NOM) characteristics.

When preformed chloramine is used, I-THM formation and speciation depended on a combination of Br⁻/I⁻ ratio and concentrations, natural organic matter (NOM) characteristics, and I⁻/DOC ratios. Generally, I-THM formation decreased as pH increased for a Br/I mass ratio of approximately 10. However, when the concentrations of Br⁻ and I⁻ were elevated, there was significant I-THM formation at higher pH due to iodoform formation. The formation of iodoform was rarely observed at lower and more typical Br⁻ and I⁻ levels.

I-THM yields did not depend on the NH₂Cl /I⁻ ratio, as increasing NH₂Cl concentrations from the UFC dose of approximately 2.4 mg/L to 5.0 mg/L (as Cl₂) did not have an appreciable effect on I-THM yields.

Prechlorination (HOCl contact time) prior to ammonia addition did not always result in lower ITHM concentrations as compared to preformed monochloramine. Prechlorination sometimes increased I-THM formation

as compared to preformed monochloramine under some circumstances. For prechlorination, the Cl₂/DOC ratio and/or the Cl₂/I⁻ ratio were critical to control both the extent of THM and I-THM formation as well as the ratio of THM to I-THM in a water sample. However, the critical Cl₂/DOC ratio to control both the concentrations of THM and I-THM appears to be water specific.

Iodine incorporation (ηI) dominated over bromine incorporation (ηBr) for preformed NH₂Cl, while the reverse trend was observed for prechlorination followed by ammonia addition.

Hydrazine

HYDRAZINE IS A POTENT carcinogen and is classified by the EPA as a probable human carcinogen with a 10⁻⁶ risk level of 10 ng/L in drinking water. While it is well-known that hydrazine is manufactured by the reaction between monochloramine and ammonia, the following two projects were the first to investigate its formation in drinking water.

[Formation of Hydrazine as a Chloramine By-Product](#) (2997) investigated the formation of hydrazine during chloramination. The study showed hydrazine formation was below detection when free ammonia concentration was less than 0.2 mg/L. The research team developed a computer simulation model to evaluate the impact of water quality parameters on hydrazine formation. Results from the model agreed with laboratory results. The model predicted that at pH < 9.5 and free ammonia less than 0.5 mg/L, hydrazine formation would be of no significant concern in chloraminated water.

A follow-up study, [Quantifying Hydrazine in Chloraminated Water](#) (4141), confirmed that the formation of hydrazine in natural water matrices is highly dependent on pH and ammonia concentration. At a pH of 9.9 and free ammonia < 0.2 mg/L as N, hydrazine concentrations were below 10 ng/L.

At a pH near 11.0 and free ammonia of 0.5 to 0.7 mg/L as N, hydrazine concentrations were as high as 100 ng/L.

Lead and Copper Release

RECENT LITERATURE INDICATES that when some water systems switch to chloramines, there is a concurring increase of lead in drinking water, perhaps because chloramines can cause lead to leach from pipes, fixtures, and solder. To investigate this phenomenon, WRF has funded several projects. [Effect of Changing Disinfectants on Distribution System Lead and Copper Release](#) (3107) examines the effect of changing disinfectants (from free chlorine to chloramines and vice versa) on metals' leaching rates and leaching levels from lead, brass, and copper distribution system components. The first phase of the project is a literature review, while the second phase includes the results of laboratory, pipe loop, and field studies.

The study showed that for new (unpassivated) lead-bearing materials (lead and bronze), lead concentrations were affected primarily by background water quality conditions. In contrast, for new copper-bearing materials, copper concentrations were affected by the presence of disinfectant (free chlorine or chloramines), but the observed effects were transient. The research showed the presence of phosphate inhibitor reduced lead leaching by exerting a stabilizing influence on lead and copper solubility during chloramine conversion. For lead plumbing materials that are passivated and likely to have developed scales that are rich in lead oxide, changes in disinfectant—that is, conversion to chloramines or some other low oxidation-reduction potential (ORP) conditions—are likely to cause a notable increase of lead leaching.

[The Role of Free Chlorine, Chloramines, and Natural Organic Matter in the Release of Lead into Drinking Water](#)

[3172] investigated whether natural organic matter (NOM), free chlorine, and chloramines can act synergistically to either inhibit or accelerate the release of lead into drinking water. The study showed that lead oxide is relatively unstable in water. It is reduced to Pb(II) by water, but only very slowly at near neutral pH values. It is also reduced by NOM quite readily. The reductive capacity of the NOM, however, is reduced if it is pre-oxidized by free chlorine, consistent with a destruction of reductive NOM functionalities. However, if free chlorine were present with NOM, no apparent reduction of lead oxide occurs, presumably because it would oxidize any released Pb(III) back to lead oxide.

Monochloramine, generally considered an oxidant, was found to reduce lead oxide. The amount of Pb(III) formed was linearly related to the amount of monochloramine that decomposed via auto-oxidation. This suggests that the reaction mechanism involved a reaction of intermediates produced from the auto-decomposition of monochloramine, acting as potent reductants of lead oxide. Because NOM was also slowly oxidized by monochloramine, the effect of mixtures of monochloramine and NOM led to more complex behavior as each component did not act synergistically or independently. Studies also showed that lead oxide could oxidize iodide and lead to the formation of iodoform in the presence of NOM, a DBP formation mechanism that does not involve a disinfectant.

Elastomeric Material Degradation

ELASTOMERIC MATERIALS HAVE been widely used for components in drinking water distribution systems. Their use has ranged from rubber gaskets to valves, hydrants, and fittings, and they have proven to be equally adaptable to a wide variety of piping materials, including cast iron, ductile iron, steel, copper,

and PVC. In general, elastomers have performed well in the water distribution system; however, with the switch from chlorine to chloramines, an increase of elastomer failures has been noted. Reported problems associated with elastomer failure include increased leaks and line losses, increased maintenance and repair, budget planning difficulties, and customer dissatisfaction.

The goal of [Performance of Elastomeric Components in Contact with Potable Water](#) (2932), was to identify the factors that contribute to elastomer degradation and provide a quantitative method for predicting the performance and life expectancy of in-service elastomer components. Upon completion of the research study, life-cycle degradation curves were developed for generic formulations of several elastomers. For each material, a unique degradation curve was identified for surface hardness, elongation, and swell (weight and volume change). These degradation curves will help utilities specify appropriate materials with critical failure modes. In addition, the degradation curves will help utilities assess the long-term performance of elastomeric materials already within their system.

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- *A Guide for the Implementation and Use of Chloramines* (2847)
- *Performance of Elastomeric Components in Contact with Potable Water* (2932)
- *Long-Term Effects of Disinfection Changes on Water Quality* (2940)
- *Chloramine Decomposition in Distribution System and Model Waters* (937)
- *Ammonia from Chloramine Decay: Effects on Distribution System Nitrification* (553)
- *Effect of Changing Disinfectants on Distribution System Lead and Copper Release* (3107)
- *The Role of Free Chlorine, Chloramines, and Natural Organic Matter in the Release of Lead into Drinking Water* (3172)
- *Formation of Hydrazine as a Chloramine By-Product* (2997)
- *Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water* (4063)
- *Quantifying Hydrazine in Chloraminated Water* (4141)
- *Characterizing the Microbial Community Responsible for Nitrification* (4165)
- *Controlling the Formation of Nitrosamines During Water Treatment* (4370)



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