THE Water Research FOUNDATION

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Disinfection Byproducts

THE CHALLENGE

The use of oxidants to disinfect water has virtually eliminated waterborne diseases like typhoid, cholera, and dysentery in developed countries. However, research has shown that chlorine interacts with natural organic matter present in water supplies to form regulated and non-regulated disinfection byproducts (DBPs).

To minimize the formation of regulated DBPs and comply with existing regulations, water utilities have increasingly been moving away from chlorine to alternative disinfectants like chloramine, or installing more advanced and costly treatment processes, such as ozone or granular activated carbon (GAC) to remove DBP 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 halonitromethanes [HNMs], and chloramines producing N-nitrosodimethylamine [NDMA] and iodinated DBPs [I-DBPs]).

THE RESEARCH

WRF has been funding research on DBPs for over 30 years. Early studies focused on general occurrence and public health implications of regulated DBPs, while more recent work focuses on control strategies for emerging non-regulated DBPs. WRF research has also explored the presence of DBP precursors in wastewater and subsequent formation of DBPs during production of recycled water. WRF has partnered on this body of research with the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the Centers for Disease Control and Prevention (CDC), the National Science Foundation (NSF), UK Drinking Water Inspectorate, and the German Water Centre (TZW).

Regulated DBPs

Although hundreds of DBPs have been identified in drinking water, only 11 are currently regulated in the United States: four trihalomethanes (THMs), five haloacetic acids (HAAs), bromate, and chlorite. In 1998, EPA released Stage 1 of the Disinfection Byproducts Rule to help reduce exposure to byproducts generated during drinking water treatment. The Stage 2 Disinfectant/Disinfection Byproduct (D/DBP) Rule, released in 2006, maintains existing maximum contaminant levels (MCLs) of 80 μg/L for total THMs and 60 μg/L for the sum of five HAAs from the Stage 1 D/DBPR, but focuses on a locational running annual average instead of a system-wide annual average, resulting in effectively stricter limits for many utilities of all sizes.

In partnership with EPA, in 1998 WRF published *Factors Affecting Disinfection Byproduct Formation During Chloramination* (803). The project identifies water chemistry and mixing conditions that promote the formation of DBPs during chloramination to provide insight into the expected behavior of full-scale plants based on pilot testing. The report addresses DBP formation in water sources from a wide variety of geographic locations and develops analytical techniques for identifying DBPs that were unknown at the time.

OVERVIEW OF EPA RULES

Title/ Release Date	• Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 DBPR) December 16, 1998 • Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) January 4, 2006
Purpose	Improve public health protection by reducing exposure to disinfection byproducts. Some disinfectants and disinfection byproducts have been shown to cause cancer and reporductive effects in lab animals and suggested bladder cancer and reproductive effects in humans.
Description	The DBPRs require public water systems (PWS) to: • Comply with established maximum contaminant levels (MCLs) and operational evaluation levels (OELs) for DBPs and maximum residual disinfection levels (MRDLs) for disinfectant residuals. • Conduct an initial evaluation of their distribution system. In addition, PWSs using conventional filtration are required to remove specific percentages of organic material that may react to form DBPs through the implementation of a treatment technique.
Utilities Covered	The DBPRs apply to all sizes of community water systems and nontransient noncommunity water systems that add a disinfectant other than ultraviolet light or deliver disinfected water, and transient noncommunity water systems that add chlorine dioxide.

Source: Adapted from EPA 2019. *Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide.* EPA 816-F-10-080.

In the late 1990s, a regulatory impact analysis estimated that up to 70% of large surface water systems would need to make at least some treatment modifications to comply with the D/DBP Rule. In 2003, WRF published *Case Studies of Modified Treatment Practices for Disinfection Byproduct Control* (369), which features lessons learned from 10 diverse drinking water utilities that have implemented such treatment modifications. The case studies offer a wealth of information on various DBP control strategies, including ozonation, membranes, granular activated carbon, and chloramination.

In 2016, WRF published *Effect of Ozone Dissolution on Bromate Formation, Disinfection Credit, and Operating Cost* (4588), which investigates the effect of different ozone dissolution systems on disinfection credit and bromate formation. A case study at Halton Region (Ontario, Canada) provides full-scale evidence regarding the difference between ozone dissolution using fine bubble diffusion versus side stream injection with degas. Pilot-scale research investigated several research gaps to help utilities, design engineers, and manufacturers better understand the impact of different types of ozone dissolution systems on bromate formation and calculating disinfection credits for viruses. The application of these results provides utilities with cost information needed to make decisions regarding which method of ozone mass transfer is appropriate.

Non-Regulated DBPs

Since the early 2000s, as knowledge of regulated DBPs increased, many U.S. drinking water utilities changed disinfectants to comply with stricter standards for regulated THMs and HAAs. Although alternative disinfectants may minimize the formation of these regulated DBPs, they generally form other non-regulated DBPs that may have adverse health effects. In recent years, nitrogenous DBPs (N-DBPs) and I-DBPs have gained attention because of potential health risks.

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 early 2000s, it was suspected that chlorination and chloramination may contribute to NDMA formation in drinking water. In the last several years, WRF has published several projects that investigate NDMA occurrence and formation, as well as control strategies to prevent NDMA formation while minimizing unintended consequences. Published in 2005, *Alternative Methods for Analysis of NDMA and Other Nitrosamines in Water and Wastewater* (Reuse-01-01) develops multiple methods for NDMA analysis, and where applicable, assesses how well these methods are able to detect other nitrosamines. Although low-level detection limits are important considerations for developing these methods, the project also evaluates the performance of multiple methods when applied to a variety of water matrices.

Published in 2006, *Factors Affecting the Formation of NDMA in Water and Occurrence* (01-ECO-2CO) describes NDMA formation mechanisms in drinking water and the role played by chlorination and chloramination. It also examines the role of various water and wastewater treatment processes on NDMA formation. The study involved three distinct, but related, tasks aimed at improving the understanding of the NDMA formation: mechanistic reaction studies, an occurrence survey, and study of treatment process influences. Another study dealing with control of NDMA, *Controlling the Formation of Nitrosamines During Water Treatment* (4370), offers improved strategies to minimize nitrosamine formation during drinking water treatment and provides treatment guidance for utilities.

Because seasonal variations and climatic events can impact the occurrence of NDMA precursors in water sources, WRF took a closer look at these impacts in *Seasonal Changes in NDMA Formation Potential and its Removal During Water Treatment* (4444). The study examines these cyclical impacts and explores the removal of the NDMA precursors by conventional treatment processes currently optimized for THM and HAA control. The project also examines the formation of NDMA in distribution systems, as well as the effectiveness of an integrated pre-oxidation strategy for NDMA control during seasonal variations.

Two emerging classes of DBPs, halonitromethanes (HNMs) and iodo-trihalomethanes (I-THMs), are not currently regulated but have been observed in drinking water systems. The 2011 WRF project *Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water* (4063) examines the conditions and precursors involved in HNM and I-THM formation. Overall, this study finds that ozonation followed by chloramination or chloramination alone may be a reasonable treatment to control the formation of HNMs, I-THMs, and THMs simultaneously.

Published in 2013, *Guidance on Complying with Stage 2 D/DBP Regulation* (4427) is a practical, relevant, and comprehensive guidance document that includes a review of available knowledge on DBP control, focusing mainly on TTHMs and HAA5. The research identifies DBP minimization strategies along with estimated costs and other decision criteria relevant to utilities. The project also features a decision support tool, called the Stage 2 D/DBP Calculator, which helps utilities work through the decision process and provides specific options based on system characteristics.

DBPs and Recycled Water

Wastewater reclamation using secondary effluent is recognized as one of the most effective ways to reduce the demand on limited natural freshwater sources. High-quality recycled

SOLUTIONS IN THE FIELD: El Paso Water

El Paso Water has used ozone to disinfect and oxidize taste-and-odor compounds at the Jonathan W. Rogers water treatment plant since it was built in 1993. The plant's source water, the Rio Grande River, is consistently high in bromide. Although ozone is a highly effective disinfectant and successfully reduces tastes and odors, it also reacts with bromide to form bromate, a DBP regulated by the Safe Drinking Water Act. As a result, the plant found itself at various times close to the point of exceeding the bromate maximum contaminant level (MCL).

In considering how to control bromate formation, El Paso Water pilot tested an additional treatment step documented in the WRF report, *Use of Chlorine Dioxide and Ozone for Control of Disinfection Byproducts* (2742). Based on the report's recommendations, they added a chlorine-dioxide feed following the sedimentation ponds, prior to ozonation.

For El Paso Water, adding chlorine dioxide prior to ozonation provided benefits by ensuring compliance with the bromate MCL. The additional chemical treatment is an added expense; thus, the utility doesn't measure the benefits of its solution in monetary terms. Rather, it gauges success in terms of improved decision-making and increased protection of public health.

water takes advantage of reverse osmosis or ultrafiltration membranes to achieve this goal. One of the challenges common to membrane treatment is membrane fouling, which is an accumulation of materials on or within the membrane that reduces membrane permeability. Fouling can be due to natural organic matter (NOM), certain polymers, chemical impurities, or biofouling. Protecting the membranes from biofouling requires use of disinfectants that react with organic matter in the water to produce DBPs, compromising the quality of treated water destined to supplement a drinking water supply.

Published in 2015, *Regulated and Emerging Disinfection Byproducts During the Production of High-Quality Recycled Water* (Reuse-10-18) provides utilities with insight into water quality issues associated with use of membranes for advanced water treatment. The research evaluates DBP occurrence in full-scale advanced water treatment plants and their formation and speciation during the disinfection of secondary effluent. The research found that DBPs were formed during the disinfection of secondary effluent and not all were rejected well by the membranes. Because DBP formation cannot be entirely prevented, membrane operation should carefully balance the risks and benefits of meeting the original treatment objectives.

The ability of ozone treatment to mitigate human and environmental impacts associated with pathogens and trace organic contaminants makes it a promising and trending treatment alternative in water reuse applications, particularly potable reuse. However, the formation of potentially carcinogenic nitrosamines could be a barrier to the widespread use of ozone. Therefore, an evaluation of their occurrence, factors affecting formation, and potential mitigation strategies is warranted. Published in 2015, *Formation of Nitrosamines and Perfluoroalkyl Acids During Ozonation in Water Reuse Applications* (Reuse-11-08) assesses the formation of nitrosamines (e.g., NDMA) upon ozonation of treated wastewaters, evaluates the factors responsible for the formation of these ozone byproducts, and recommends potential mitigation strategies. The research shows that control strategies, such as sufficient biological, physical, or chemical pretreatment of precursors (e.g., biological activated carbon and nanofiltration), can be applied to mitigate the formation of nitrosamines.

LIFT

The Leaders Innovation Forum for Technology (LIFT) helps move water technologies to the field quickly and efficiently. LIFT Focus Groups bring together experts and professionals to study priority topics. LIFT's Disinfection Focus Group is a forum for utilities to come together to discuss the latest challenges and technologies around disinfection, and finding treatment strategies to minimize the formation of DBPs is a priority.

WHAT'S NEXT?

New research shows that certain non-regulated DBPs are substantially (orders of magnitude) more toxic than the currently regulated DBPs. In 2017, WRF initiated a Research Priority Area to address these concerns. The research area, Non-Regulated Disinfection Byproducts in Drinking, Recycled, and Desalinated Water: Occurrence, Toxicological Relevance, and Control Strategies is working to develop information that will inform regulatory agencies, assist utilities in preparing for future regulations, and protect public health.

Chlorination became the standard for disinfecting treated wastewater in the 20th century. However, governments in North America have reduced limits for chlorine residuals and DBPs to reduce environmental and public-health impacts. Today, about a quarter of all municipal wastewater treatment plants use UV disinfection; and while there is interest in ozone for wastewater, technical challenges and high capital costs have stunted this market. Peroxyacetic acid or peracetic acid (PAA) is gaining interest for wastewater disinfection due to its ability to inactivate microbes at costs competitive to other mature disinfection technologies, with secondary benefits of a chemical oxidant. An ongoing project, *Design and Implementation of Peracetic Acid for Municipal Water and Wastewater Related Processes* (4805) will document existing knowledge around PAA for wastewater disinfection and other uses in wastewater treatment, as well as enhance understanding of PAA effects on wastewater processes and aquatic life. The research will gather targeted information from utilities implementing PAA from their testing or operations and identify key factors that were considered when utilities made the transition to PAA disinfection.