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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 (NOM) present in water supplies to form regulated and emerging disinfection byproducts (DBPs).

To minimize the formation of regulated DBPs and comply with regulations, water utilities have been moving away from chlorine to alternative disinfectants like chloramine or installing more advanced treatment processes, such as ozone or granular activated carbon (GAC) to remove DBP precursors. However, while reducing the formation of halogenated DBPs, alternative oxidants can 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 recent work focuses on emerging 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

Eleven DBPs 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 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.

To help utilities understand changes that might be necessary to mitigate DBP formation, in 2003, WRF published *Case Studies of Modified Treatment Practices for Disinfection Byproduct Control* (369). It features lessons learned from 10 drinking water utilities that have

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 reproductive effects in lab animals and suggested bladder cancer and reproductive effects in humans.
Description	The DBPRs require public water systems (PWSs) 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.

implemented treatment modifications, including ozonation, membranes, GAC, and chloramination.

In 2016, WRF published *Effect of Ozone Dissolution on Bromate Formation, Disinfection Credit, and Operating Cost* (4588), which included a case study at Halton Region (Ontario, Canada). It provides full-scale evidence regarding the difference between ozone dissolution using fine bubble diffusion versus sidestream injection with degas. Pilot-scale research helped 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.

Emerging 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 regulated DBPs, they generally form other emerging DBPs. In recent years, nitrogenous DBPs (N-DBPs) and I-DBPs have gained attention because of potential health risks.

N-nitrosamines are a group of chemicals suspected to be carcinogenic. The most frequently detected N-nitrosamine in drinking water is N-nitrosodimethylamine (NDMA). Although both chlorination and chloramination have been implicated 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).

WRF has published several projects that investigate NDMA occurrence, formation, and control. Published in 2005, *Alternative Methods for Analysis of NDMA and Other Nitrosamines in Water and Wastewater* (Reuse-01-01/1572) develops multiple methods for NDMA analysis and assesses how well these methods can 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* (2678) 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. 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 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 control the formation of HNMs, I-THMs, and THMs simultaneously.

Published in 2013, *Guidance on Complying with Stage 2 D/DBP Regulation* (4427) reviews the 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.

Published in 2019, *GAC Control of Regulated and Emerging DBPs of Health Concern* (4560) found that the use of GAC in combination with various disinfection strategies removed precursors for many types of carbonaceous and nitrogenous DBPs and can lower the overall DBP precursor load of a given water. This project also investigated how allowing GAC to remain in place beyond its useful adsorptive capacity, thereby becoming a biologically active GAC filter, impacts DBP management. The study indicated that biologically active GAC (BAC) without pre-ozonation provides mixed performance in overall reduction of regulated and unregulated DBP formation potential. The decision to convert GAC to BAC is one that should be made based on considerations other than DBP control.

Occurrence Survey of Bromide and Iodide in Water Supplies (4711), published in 2021, found that bromide levels are not increasing nationally and that bromide levels can have weekly or monthly variations in some water sources. Bromide concentrations were found to be higher in groundwaters than in surface waters. While most of the utilities sampled in this project had bromide present in their source waters, fewer utilities had iodide present. To remove bromide and iodide from source waters, the research team tested silver-impregnated adsorbents, silver-amended coagulation processes, and ion exchange processes. These technologies worked well for low conductivity and waters with low chloride.

DBPs and Recycled Water

Wastewater reclamation using secondary effluent is an effective way to reduce the demand on limited natural freshwater sources. High-quality recycled water takes advantage of reverse osmosis or ultrafiltration membranes to achieve this goal. One of the challenges common to membrane treatment is membrane fouling,

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.

which is an accumulation of materials on or within the membrane that reduces permeability. Fouling can be due to 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 treated water quality.

Published in 2015, R*egulated and Emerging Disinfection Byproducts During the Production of High-Quality Recycled Water* (Reuse-10-18/1687) 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 treatment alternative in potable reuse applications. However, the formation of potentially carcinogenic nitrosamines could be a barrier to the widespread use of ozone. Published in 2015, *Formation of Nitrosamines and Perfluoroalkyl Acids During Ozonation in Water Reuse Applications* (Reuse-11-08/1693) showed that control strategies, such as sufficient biological, physical, or chemical pretreatment of precursors (e.g., biological activated carbon and nanofiltration), can mitigate the formation of nitrosamines.

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. Published in 2019, *Application of Peracetic Acid for Municipal Wastewater Processes* (LIFT14T16/4805) documented existing knowledge around PAA for wastewater disinfection and other uses in wastewater treatment, and enhanced understanding of PAA effects on wastewater processes and aquatic life. The research gathered information from utilities implementing PAA from their testing or operations and identified key factors that were considered when utilities made the transition to PAA disinfection.

WHAT'S NEXT?

There is still more to learn about how advanced treatment processes might impact DBP formation, and WRF research is leading the way in this area. An ongoing project, *The Impact of Pre-Chlorination and GAC Treatment on DBP Formation and Overall Toxicity in Drinking Water* (5140), will investigate the impact of GAC with and without pre-chlorination on DBP formation and the resulting toxicity of drinking water using bioassays. Another project, *Impact of Bromate Control on Ozone Oxidation and Disinfection and Downstream Treatment in Potable Reuse* (5035) will review bromate formation mechanisms, chemical control techniques, design considerations, and upstream/downstream process considerations offering a holistic approach to bromate management in treatment plants.

Recent research shows that certain emerging DBPs are substantially more toxic than the currently regulated DBPs. WRF has a variety of ongoing projects to inform regulatory agencies, assist utilities in preparing for future regulations, and protect public health. *Precursors and Control of Halogenated Acetonitriles* (5053) will determine the sources and types of HAN precursors, identify precursor structures and formation pathways, and evaluate HAN degradation behavior to provide guidance on controlling HANs.

Future regulations may expand the currently regulated five haloacetic acids (HAA5) to nine (HAA9), which would include four additional brominated compounds. *Impact of a Haloacetic Acid MCL Revision on DBP Exposure and Health Risk Reduction* (5085) will assess the potential impacts of this expansion and develop materials to support clear, concise communication about the issues surrounding a move from an HAA5- to HAA9-based regulation. Another project, *Technologies and Approaches to Minimize Brominated and Iodinated DBPs in Distribution Systems* (5122) will develop creative and novel techniques and approaches to minimize the formation of currently unregulated brominated and iodinated DBPs in the distribution system, considering practical applicability and economic feasibility for existing treatment systems.