

Advancing the Science of Water: AwwaRF and Disinfection By-products

The use of chlorine to disinfect drinking water has virtually eliminated waterborne diseases such as typhoid, cholera, and dysentery in developed countries. But research in the early 1970s showed that chlorine interacts with natural organic matter (NOM) present in drinking water supplies to form compounds known as disinfection by-products (DBPs). Some of these compounds have been linked to cancer in laboratory animals and other adverse health effects such as reproductive and developmental anomalies.

The discovery of DBPs spawned a new era in water treatment practice. Now, water suppliers must protect the public from the possible chronic effects of life-long exposure to DBPs as well as the acute health effects of waterborne disease. AwwaRF has enabled water suppliers to carry out this dual responsibility by funding critical research to advance our understanding of DBPs and providing essential data for the development of water quality regulations.

Fundamental contributions of AwwaRF's DBP research include:

- Documenting nationwide DBP occurrence,
- Identifying precursors and water quality characteristics affecting DBP formation,
- Determining the mechanisms of DBP formation,
- Creating models to predict DBP formation,
- Evaluating alternative disinfectants and their by-products,
- Developing analytical techniques to measure various DBP species,
- Optimizing treatment and control strategies,
- Estimating capital and operations costs associated with DBP control,
- Defining the DBP research agenda,
- Providing data used to establish federal standards for DBPs in drinking water, and
- Examining potential health effects associated with DBPs.

"Among AwwaRF's most groundbreaking contributions to DBP research," according to Alan Roberson, director of security and regulatory affairs for the American Water Works Association (AWWA), "were determining DBP formation mechanisms, identifying the range of DBP species being formed, and quantifying relative DBP concentrations in treated water."

"AwwaRF has funded DBP research at bench, pilot, and full scale, supplying information about what's going on in the treatment plant and the distribution system," said Stuart Krasner, principal environmental specialist in the water quality laboratory of Metropolitan Water District of Southern California. "AwwaRF studies on occurrence and human exposure have contributed to epidemiologic studies on cancer and reproductive risks associated with DBPs. And AwwaRF data were used in the DBP rule-making process to ensure these regulations were based on sound science."

Ascertaining THM Occurrence

In 1986 AwwaRF funded a nationwide survey documenting the occurrence of trihalomethanes (THMs), the first DBP species to be identified in drinking water (*AwwaRF Trihalomethane Survey*, Project 236, funded 1986, published in *Journal AWWA*, January 1988). This was the first THM survey conducted after the THM regulation was promulgated in 1979; earlier surveys had been conducted by James M. Symons and Alan A. Stevens at the US Environmental Protection Agency (USEPA). For the AwwaRF survey, 727 US water utilities provided data on THM concentrations in their finished water. The project, led by Michael J. McGuire, now vice-president of McGuire Malcolm Pirnie Environmental Consultants, estimated the costs associated with controlling THM formation and assessed the potential effects of more stringent THM standards.

Three Approaches to Controlling DBPs

AwwaRF research helped to define the three major approaches water suppliers use to protect the public from potential health effects posed by DBPs: (1) remove DBP precursors, (2) reduce the amount of disinfectant and/or change the point of application, and (3) switch from chlorine to alternative primary and/or secondary disinfectants.

Removing Precursors

A key study funded in 1990 characterized NOM in untreated water supplies and examined how NOM fractions could be removed during treatment (*Characterization of Natural Organic Matter and Its Relationship to Treatability*, Project 603, funded 1990, published 1993, order number 90631). This study, conducted by Doug Owen, Gary Amy, and Zaid Chowdhury, recommended source water parameters that utilities should measure in order to predict the effect of NOM on treatability. "Participants in the 1992–93 regulatory negotiations that led to promulgation of the Stage 1 Disinfectants/Disinfection By-products (D/DBP) Rule in 1998 used baseline data from this study to assess the treatability of DBPs in US water supplies," according to Owen, now a vice-president of Malcolm Pirnie, Inc.

A second project, conducted by Owen and Scott Summers, studied the removal of DBP precursors by granular activated carbon (GAC) adsorption (*Removal of DBP Precursors by GAC Adsorption*, Project 816, funded 1992, published 1999, order number 90744). Evaluating GAC's ability to remove DBPs at six representative water utilities, Owen and

Summers provided optimization guidelines and cost estimates for utilities planning to implement this technology. "We used data from this study to construct the GAC treatment module in a water treatment plant simulation model designed to help utilities balance the need for disinfection and the need to control DBPs," said Owen. "The regulatory negotiators used this model to determine which technologies utilities would use to meet various regulatory options."

The study also established uniform formation conditions (UFCs) for estimating DBP formation potential in individual water supplies. By standardizing the chlorine dosage and water quality parameters used to predict DBP formation, UFCs allow more realistic assessments of the treatment challenges posed by DBPs.

A follow-up NOM characterization study evaluated various new technologies for isolating NOM and predicting its impact on DBP concentrations in treated water (*Characterization of Natural Organic Matter in Drinking Water*, Project 159, funded 1994, published 2000 order number 90780). Led by Steve Reiber and Mark M. Benjamin, this study examined simple approaches that could be carried out in a water utility laboratory as well as more complex NOM isolation methods.

Another technique for removing DBP precursors involves optimizing two traditional water treatment technologies—coagulation and lime softening. An AwwaRF study led by Stephen J. Randtke laid the groundwork for utilities to apply enhanced coagulation and enhanced softening to better remove total organic carbon (TOC) from source water supplies (*Removal of DBP Precursors by Enhanced Coagulation and Lime Softening*, Project 814, funded 1992, published 1999, order number 90783). This study assessed costs and the degree of DBP precursor removal as a function of source water characteristics, season, treatment technique, and treatment process optimization. Information from this study helped refine the requirements of the Stage 1 D/DBP Rule, according to Krasner. "There was controversy regarding how much TOC various utilities could remove. Utilities whose water supplies had high TOC concentrations and low alkalinity were generally able to remove more TOC than utilities whose supplies had low TOC concentrations and high alkalinity. Data from this study helped with development of a nationwide database out of which the enhanced coagulation requirements grew."

Modifying Disinfection Practices

A number of AwwaRF projects examined the feasibility of controlling DBPs by replacing chlorine with alternative means of disinfection. Early studies looked at the application of chloramines (disinfectant produced by mixing chlorine and ammonia), chlorine dioxide, and ozone and documented their by-products. Later projects studied the effectiveness of innovative treatment processes such as membrane filtration (which can remove microbes as well as organic and inorganic contaminants) and ultraviolet (UV) light (which by inactivating waterborne pathogens such as protozoa and viruses permits water suppliers to eliminate or lower the dosage of primary disinfectant in the treatment plant).

Optimizing the Use of Chloramines. "AwwaRF has had a continuing interest in chloramines," says McGuire. "Its research has helped utilities apply this technology, troubleshoot problems, and avoid pitfalls."

Early AwwaRF studies on chloramines were instrumental in helping utilities implement this alternative method of disinfection. A 1993 project led by Gregory J. Kirmeyer produced a chloramination optimization manual for water utilities (*Optimizing Chloramine Treatment*, Project 610, funded 1990, published 1993, order number 90620). The manual discussed the regulatory situation at the time, reviewed pertinent literature, presented case studies, and described the resources needed to optimize the chloramination process.

AwwaRF published an updated manual on best management practices for optimizing chloramination in 2004 (*Optimizing Chloramine Treatment, Second Edition*, Project 2760, funded 2001, published 2004, order number 90993). This second edition synthesized relevant research and practical information on the use of chloramines in water treatment. Focusing on implementation and operations, the current manual incorporates new water utility case studies and includes a CD.

AwwaRF-funded research at the University of Houston advanced our understanding of chloramination by-products. A 1998 study conducted by Symons and Gerald E. Speitel Jr. identified conditions that promote DBP formation during chloramination in a variety of water sources and developed analytical techniques to identify DBPs that were unknown at the time (*Factors Affecting DBP Formation During Chloramination*, Project 803, funded 1992, published 1998, order number 90728). A subsequent Speitel study contributed additional data on DBP formation, especially dihalogenated species, during chloramination and described practical strategies for minimizing formation (*Disinfection By-product Formation and Control During Chloramination*, Project 2677, funded 2000, published 2004, order number 91040F).

Evaluating Chlorine Dioxide. As utilities assessed the advisability of switching from chlorine to another primary disinfectant, they also relied on AwwaRF-funded studies of chlorine dioxide and its by-products. A 1992 symposium sponsored by AwwaRF, the Chemical Manufacturers Association, and USEPA considered the advantages and disadvantages of chlorine dioxide as a water treatment tool.

To evaluate whether the chlorine dioxide by-product chlorite could be effectively controlled, Robert C. Hoehn and his colleagues examined new methods for measuring chlorite and evaluated chlorite reduction technologies, including GAC and powdered activated carbon (PAC), and their estimated costs (*Sources, Occurrence, and Control of Chlorine Dioxide By-product Residuals in Drinking Water*, Project 611, funded 1990, published 1994, order number 90656). In addition to forming by-products, chlorine dioxide disinfection caused distribution system taste and odor problems in certain situations, imposing additional limitations on its use. Hoehn and Andrea Dietrich examined the causes of these problems as well as methods of controlling them (*Taste and*

Odor Problems Associated With Chlorine Dioxide, Project 405, funded 1988, published 1991, order number 90589).

Assessing Ozone and Its By-products. Another groundbreaking AwwaRF project was an early 1990s study of the DBPs found in ten North American utilities using ozone as an alternative oxidant and water supplies with wide-ranging quality characteristics. William H. Glaze served as principal investigator of this study (*Identification and Occurrence of Ozonation By-products in Drinking Water*, Project 510, funded 1989, published 1993, order number 90625).

"Although European water utilities had been using ozone for nearly a century, few studies of ozone by-products had been conducted before this one," Krasner observed. "At this time, interest in ozone was escalating in the United States because of new regulations for disinfection and DBPs and because of ozone's efficacy in controlling taste and odor problems. This study came at a pivotal time, when engineering knowledge was good but understanding of ozone's by-products was limited. This seminal study and successive ones established what ozone could do to control certain by-products and identified some of the trade-offs associated with its use."

According to Krasner, this was the first study in the world to measure drinking water concentrations of bromate (the only ozone by-product currently regulated in the United States) as well as the first to examine methods for bromate control. This research showed that concentrations of brominated organic by-products formed with ozone applied as a sole oxidant were low compared with concentrations of chlorinated DBPs. It also provided data on aldehydes (a class of ozonation by-products) and how to control them with biological filtration. "The study also helped establish which ozone by-products were of concern and which were not," Krasner said. "Some were inherently unstable or readily removable with biological filtration so they didn't reach consumers."

In 1991 AwwaRF and the French water utility Compagnie Generale des Eaux (now Viola Water) published a manual on ozone practice (*Ozone in Water Treatment: Application and Engineering*, Project 421, funded 1988, published 1991, order number L474LAFD, Lewis Publishers, 800.272.7737). The handbook described current applications of ozone technology in drinking water treatment in terms of purpose (e.g., control of DBPs or taste and odor problems), design, installation, and operation. Case studies and economic considerations were also included.

"AwwaRF's ozone research went a long way toward making ozone technology more widely known and more acceptable," said McGuire. "Besides supporting academic research, AwwaRF also supports case studies with immediate practical value. These studies give utilities the confidence to move forward with innovative technologies. Ozone is an example."

In the late 1980s, AwwaRF helped fund a \$20 million oxidation demonstration project at the Metropolitan Water District of Southern California to test ozone and PEROXONE (ozone mixed with hydrogen peroxide) processes (*Demonstration-Scale Evaluation of*

Ozone and PEROXONE, Project 525, funded 1989, published 2000, order number 90790). The demonstration project, led by Jill Gramith (now Wicke), was undertaken to confirm the results of an earlier pilot-scale study that evaluated these two oxidants and analyzed their capital and operations costs.

According to McGuire, Metropolitan's Jensen plant is currently the largest ozone facility in the United States. "The utility will finish two more ozone facilities by 2012, making this the most extensive use of ozone at any single utility in the world," said McGuire. "These plants were a direct outgrowth of AwwaRF's early ozone work."

Though McGuire notes that the problem of bromate formation has slowed down application of ozone in certain areas, he credits AwwaRF with also funding bromate control studies. Investigations of bromate formation and control included those led by Amy (*Survey of Bromide in Drinking Water and Impacts on DBP Formation*, Project 825, funded 1992, published 1995, order number 90662; *Formation and Control of Brominated Ozone By-products*, Project 830, funded 1992, published 1997, order number 90714; and *Strategies to Control Bromate and Bromide*, Project 156, funded 1994, published 1999, order number 90751) and Issam Najm (*Bromate Formation and Control During Ozonation of Low Bromide Waters*, Project 493, funded 1997, published 2001, order number 90866).

Documenting Utility Experience With Case Studies

A 1990 AwwaRF report presented real-world data from a group of case studies describing how various water utilities were controlling THMs by modifying their disinfection practices. These case studies were assembled by Dennis George (*Case Studies of Modified Disinfection Practices for Trihalomethane Control*, Project 201, funded 1986, published 1990, order number 90574).

A second collection of case studies, published in 2003, documented the experiences of ten utilities that had implemented treatment modifications to comply with the Stage 1 D/DBP Rule and the Enhanced Surface Water Treatment Rule (*Case Studies of Modified Treatment Practices for Disinfection By-Product Control*, Project 369, funded 1996, published 2003, order number 90946F). Describing the use of chloramines, chlorine dioxide, ozone, enhanced coagulation, GAC, and membrane filtration to control DBPs and pathogenic microorganisms, the report also detailed the costs of these treatment processes as well as lessons learned during their implementation. "These case studies provided baseline data for the regulatory negotiators who were finalizing the Stage 2 D/DBP Rule," said Owen.

"The case studies were intended to benefit all utilities," said Krasner, the project's principal investigator, "but one of the utilities that benefited was the one in charge of putting together the report." Two of these case studies were accounts of facilities that had implemented chlorine dioxide disinfection. "Because the case studies focused on what worked and what didn't," Krasner said, "they streamlined our utility's subsequent research on potential alternative disinfectants. Using information from these two case

studies, we were able to study chlorine dioxide thoroughly in about a year and a half. Without this information, the investigation would have taken us many years."

Defining the DBP Research Agenda

In addition to funding specific research to help utilities minimize DBP precursors, change disinfection protocols, or implement alternative treatment processes, AwwaRF has made other significant contributions in the area of DBPs. Information from two workshops co-sponsored by AwwaRF and USEPA has defined the agenda for DBP research since 1993, and AwwaRF data have helped regulators determine a number of federal standards related to controlling DBPs and microbes in drinking water.

A two-day workshop in Miami in 1993 brought together 40 drinking water experts from water utilities, consulting firms, academia, the regulatory community, and nonprofit advocacy organizations to identify research needs related to risk assessment, drinking water contaminants, health effects associated with DBPs, and competing risks (*Drinking Water and Health in the Year 2000*, Project 643, funded 1990, published 1993, order number 90636). McGuire and William D. Bellamy conducted the workshop.

A second workshop, also involving a broad range of stakeholders and also led by McGuire, convened in Vail, Colorado, in 2001 (*Assessment of Microbial and Disinfection Byproduct Research Needs*, Project 2803, funded 2001, completed 2002, report available only to AwwaRF subscribers). Participants in this workshop identified the research needed to answer questions that arose during and after the 1999–2000 regulatory negotiation process through which the Stage 2 D/DBP Rule and the Long Term 2 Enhanced Surface Water Treatment Rule were developed.

Providing Sound Science for Regulations

In addition to observing that AwwaRF research has facilitated the application of several innovative treatment technologies, Roberson emphasizes the role of AwwaRF data in shaping several water quality regulations promulgated between 1998 and 2006. These regulations—including two D/DBP Rules and three Surface Water Treatment Rules—resulted from provisions in the 1996 Safe Drinking Water Act (SDWA) Amendments requiring USEPA to develop regulations to help water suppliers control the health risks posed by microbial pathogens and DBPs.

"I've worked with the regulatory negotiation process since 1993," Roberson says. "AwwaRF has always been represented at the table—not as an organization but through its investigators." Krasner concurs: "If you look at the proposal for the Stage 1 D/DBP Rule, the references read like a who's who of AwwaRF investigators."

In accordance with a provision of the Stage 1 Rule, AwwaRF and USEPA formed a Microbial/DBP (M/DBP) Research Council through which the two organizations co-sponsored research to fill data gaps before the Stage 2 D/DBP Rule was promulgated in

2006. This arrangement, according to Krasner, allowed USEPA "to take advantage of AwwaRF's ability to fund and oversee good research."

Another method USEPA used to support decision-making for the Stage 2 Rule was requiring large water utilities to report monitoring and treatment data under a short-term regulation called the Information Collection Rule (ICR). Under this rule, 500 treatment plants representing 296 utilities conducted ICR monitoring from July 1997 through December 1998.

Roberson cites an M/DBP Research Council project that he considers especially useful—publication of the book *ICR Data Analysis* (Project 2799, funded 2001, published 2002, order number 90947). A compilation of reports analyzing various subsets of ICR data, the book is intended to help utilities and members of the scientific community make sense of the massive amount of data collected under this rule. Roberson characterizes the book as "a valuable reference that otherwise wouldn't have been disseminated outside the Beltway."

Quantifying Health Effects

Recent M/DBP Research Council studies in epidemiology have provided a more balanced perspective on what's known and not known about the effects of THMs (particularly bromodichloromethane) and other DBPs such as haloacetic acids on reproduction and fetal development (*Drinking Water Disinfection By-products and Pregnancy Outcome*, Project 2579, funded 1998, published 2005, order number 91088F). According to Krasner, these studies, which were conducted by David Savitz, have "helped us understand the limits of previous epidemiologic research, and they prevented regulators from overemphasizing this unresolved issue in the Stage 2 D/DBP Rule." The Savitz studies found no strong association between pregnancy loss and THMs or haloacetic acids.

Controlling DBPs with Innovative Treatment Technologies

For detailed information about AwwaRF-sponsored research on controlling DBPs with membrane filtration and UV disinfection, see the section of this document on Innovative Technologies.

Conclusion

AwwaRF-funded research has significantly advanced our knowledge of DBPs and the technologies used to control them. According to Krasner, "AwwaRF's pilot- and full-scale tests have allowed these technologies to move from bench-scale investigations to full application. Because AwwaRF requires utility partners in its studies, most of the full-scale DBP tests were conducted at drinking water facilities, and even the university studies were conducted with real water supplies.

"AwwaRF has also facilitated the application of these findings through presentations and publications, in addition to other forms of technology transfer. The information hasn't stayed locked up in some ivory tower; it's been presented to utilities across the country," Krasner continued.

"The AwwaRF projects my utility has been involved with have allowed us to leverage what we've done in our own facilities, not only by bringing in funding but also by bringing in other researchers such as university people and consultants. We've also closely followed the projects our utility wasn't involved with. I don't think there's a single AwwaRF-funded DBP study whose information we haven't used in some way," Krasner concluded.