What is in Our Drinking Water?

Identification of New Chemical Disinfection By-products (DBPs)

What is a DBP? A drinking water disinfection by-product (DBP) is formed when the chemical used for disinfecting the drinking water reacts with natural organic matter and/or bromide/iodide in the source water. Popular disinfectants include chlorine, ozone, chlorine dioxide, and chloramine. Source waters include rivers, lakes, streams, groundwater, and sometimes seawater. We have only known about DBPs since 1974, when chloroform was identified by Rook as a DBP resulting from the chlorination of tap water. Since then, hundreds of DBPs have been identified in drinking water.

So what? Millions of people in the U.S. are exposed to these drinking water DBPs every day. While it is vitally important to disinfect drinking water, as thousands of people died from waterborne illnesses before we started disinfection practices in the early 1900s, it is also important to minimize the chemical DBPs formed. Several DBPs have been linked to cancer in laboratory animals, and as a result, the U.S. EPA has some of these DBPs regulated. However, there are many more DBPs that have still not been identified and tested for toxicity or cancer effects. Currently, we have only identified about 50% of the total organic halide (TOX) that is measured in chlorinated drinking water. There is much less known about DBPs from the newer alternative disinfectants, such as ozone, chlorine dioxide, and chloramine, which are gaining in popularity in the U.S. Are these alternative disinfectants safer than chlorine? What kinds of by-products are formed? And, what about the unidentified chlorine DBPs that people are exposed to through their drinking water--both from drinking and showering/bathing? The objective of our research is to find out what these DBPs are--to thoroughly characterize the chemicals formed in drinking water treatment--and to ultimately minimize any harmful ones that are formed.

Our research approach

- Gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), and gas chromatography/infrared spectroscopy (GC/IR) techniques are used to identify the unknown by-products
- NIST and Wiley mass spectral databases are used first to identify any DBPs that happen to be present in these databases
- Because many DBPs are not in these databases, most of our work involves unconventional MS and IR techniques, as well as a great deal of scientific interpretation of the spectra
- High resolution MS provides empirical formula information for the unknown chemical (e.g., how many carbons, hydrogens, oxygens, nitrogens, etc. are in the chemical's structure)
- Chemical ionization MS provides molecular weight information when this is not provided in conventional electron ionization mass spectra
- IR spectroscopy provides functional group information (e.g., whether the oxygens are due to a carboxylic acid group, a ketone, an alcohol, or an aldehyde)
- LC/MS is used to identify compounds that cannot be extracted from water (the highly polar, hydrophilic ones), as well as the high molecular weight, nonvolatile DBPs. This is a major missing gap in our knowledge about DBPs--so far, most DBPs identified have been those that are easily extracted from water and are volatile enough to analyze by GC/MS
- Novel derivatization techniques are also applied to aid in the identification of highly polar DBPs

and fate & transport studies are conducted to better understand how certain priority DBPs are formed and ed in treatment and distribution systems

Currently

We completed an iodo-DBP occurrence study (published in the Nov. 15, 2008 issue of Environmental Science & Technology; ES&T 2008, 42 (22), 8330-8338) that involved the measurement of iodo-acid DBPs and iodo-THMs in drinking waters from 23 cities across the U.S. and Canada, and the study of their genotoxicity and cytotoxicity. We identified the iodo-acids for the first time as part of a large nationwide occurrence study of priority DBPs (mentioned below), and they are important because iodoacetic acid was found to be highly genotoxic (to mammalian cells), and it is more genotoxic than the regulated chloro/bromo-haloacetic acids (ES&T 2004, 38 (18): 4713-4722). This study helped to underscore the increased formation of iodo-DBPs with chloramination, which is an increasingly popular disinfectant used in the U.S.

The first phase of the study was also published (see special issue of Journal of Toxicology and Environmental Health, Part A, October 22, 2008 issue), where we combined chemical and toxicological characterization (with an emphasis on newer reproductive and developmental effects) of complex DBP mixtures. This study is called the Four Lab Study because it involves the collaboration of scientists from across EPA's research programs including Health and Environmental Effects, Exposure, Risk Management, and Environmental Assessment. The study serves to address potential health concerns that cannot be addressed directly by the toxicological study of individual DBPs or defined DBP mixtures, and in essence, provides toxicological information for the complete drinking water mixture: both the known DBPs, as well as the unidentified fraction of DBPs. Drinking water treated with chlorine or ozone-chlorine was concentrated by reverse osmosis to maintain a water matrix suitable for the animal studies. The next phase of this work is also nearing completion and included a larger battery of toxicological endpoints and focused on chlorinated drinking water.

Our earlier nationwide DBP occurrence study was published in ES&T in the Dec. 1, 2006 issue (ES&T, 2006, 40, 7175-7185), and can also be found in its full 400+ page report at EPA/600/R-02/068. This large study involved the sampling of drinking waters across the U.S. (disinfected with the different disinfectants and with different water quality, including elevated levels of bromide in the source water). A group of >50 DBPs that resulted from a prioritization of >500 DBPs in the literature for predicted adverse health effects was quantified in these drinking waters. Fate and transport studies were also conducted in the drinking water distribution systems to determine whether these DBPs changed in concentration or were transformed in the distribution systems. In addition to obtaining important quantitative information on these new DBPs (to help in prioritizing health effects testing), important new discoveries were made regarding the use of alternative disinfectants. While the use of alternative disinfectants lowered the levels of the four regulated trihalomethanes and five haloacetic acids (as compared to chlorine), many of the other prioritized DBPs were formed at higher levels with these alternative disinfectants. For example, the highest levels of iodinated DBPs were found in chloraminated drinking water, the highest levels of halonitromethanes were found in pre-ozonated drinking water, and dihaloaldehydes were highest at a plant using chloramines and ozone.

Our new work includes investigating other potential sources of iodine in the formation of iodo-DBPs and investigating the influence of the length of free chlorine contact time (before ammonia addition to form chloramines) on their formation. In other research, a toxicity-based identification approach (using mammalian cell and medaka fish assays) is being used to focus identification efforts on the most toxic drinking water fractions, with an emphasis on obtaining new information on high molecular weight DBPs (which are believed to make up approximately 50% of the halogenated DBPs produced).

Recent results

- A recent iodo-DBP occurrence study (ES&T 2008, 42 (22), 8330-8338) has provided the first quantitative occurrence data for highly genotoxic iodo-acid DBPs and information on their formation (along with iodo-THMs) in chloraminated drinking water, along with the first toxicity data for iodo-THMs and iodo-acids (beyond the first work on iodoacetic acid)

- The first phase of the Four Lab Study (Environ. Toxicol. Health, Pt. A, 2008, 71, 1125-1132 and following papers in this issue) reports results from an integrated chemical/toxicological research study to investigate the toxicological effects of complex DBP mixtures

- A Nationwide DBP Occurrence Study (ES&T 2006 40:7175-7185) provided important new quantitative information on ...ed DBPs that have the potential to cause adverse health effects based on a structure-activity analysis (Woo et al., 2002); several of these DBPs have concentrations similar to some that are already regulated
- The use of alternative disinfectants can produce higher levels of these DBPs, as compared to chlorine
- Collaborations are ongoing with health effects researchers to study selected DBPs for potential adverse health effects

Gordon Research Conference on DBPs

The second Gordon Research Conference on drinking water DBPs was held August 9-14, 2009, at Mount Holyoke College in South Hadley, Massachusetts. Like the first one initiated in 2006 (where scientists from 22 countries came), this conference brought together scientists from different disciplines: chemists, toxicologists, epidemiologists, engineers, clinicians, human exposure scientists, risk assessors, and regulators to address the issues with drinking water DBPs. Ben Blount from the Centers for Disease Control and Prevention (CDC) was the Chair of the 2009 conference, and Manolis Kogevinas from Centre for Research in Environmental Epidemiology (CREAL) and the Municipal Institute of Medical Research (IMIM-Hospital del Mar) in Barcelona, Spain will be the next chair of the upcoming 2012 conference Contact Susan Richardson (richardson.susan@epa.gov) or Manolis Kogevinas (kogevinas@creal.cat) for more information.

Useful publications

LaKind, J. S., S. D. Richardson, B. C. Blount. 2010. The good, the bad, and the volatile – Can we have both healthy pools and healthy people? *Environ. Sci. Technol*., in press.

Richardson, S. D. 2009. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem*., 81(12): 4645-4677. (Invited biennial review article).

Weisel, C. P., S. D. Richardson, B. Nemery, G. Aggazzotti, E. Baraldi, E. R. Blatchley, III, B. C. Blount, K-H. Carlsen, P. A. Eggleston, F. H. Frimmel, M. Goodman, G. Gordon, S. A. Grinshpun, D. Heederik, M. Kogenvinas, J. S. LaKind, M. J. Nieuwenhuijsen, F. C. Piper, S. A. Sattar. 2009. Childhood Asthma and Environmental Exposures at Swimming Pools: State of the Science and Research Recommendations. *Environ. Health Perspect.*, 117 (4): 500-507.

Richardson, S. D. 2009. Disinfection By-Products and Drinking Water Treatment. In *Drinking Water – Sources, Sanitation and Safeguarding*. Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning: Stockholm Sweden. (Invited book chapter for World Water Week book).

Richardson, S. D., C. Rav-Acha, and G. D. Simpson. 2009. Chlorine Dioxide Chemistry, Reactions, and Disinfection By-Products. In *State of the Science of Chlorine Dioxide in Drinking Water,* Water Research Foundation and Fondazione AMGA: Denver, CO. (Invited book chapter).

Richardson, S. D., F. Fasano, J. J. Ellington, F. G. Crumley, K. M. Buettner, J. J. Evans, B. C. Blount, L. K. Silva, T. J. Waite, G. W. Luther, A. B. McKague, R. J. Miltner, E. D. Wagner, and M. J. Plewa. 2008. Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in Drinking Water. *Environ. Sci. Technol*., 42 (22): 8330-8338.

Plewa, M. J., M. G. Muellner, S. D. Richardson, F. Fasano, K. M. Buettner, Y.-T. Woo, A. B. McKague, and E. D. Wagner. 2008. Occurrence, Synthesis, and Genotoxicity of Haloacetamides: An Emerging Class of Nitrogenous Drinking Water Disinfection Byproducts. *Environ. Sci. Technol.*, 42 (3), 955-961.

Richardson, S. D., A. D. Thruston, Jr., S. W. Krasner, H. S. Weinberg, R. J. Miltner, M. G. Narotsky, and J. E. Simmons. 2008. Integrated Disinfection Byproducts Mixtures Research: Comprehensive Characterization of Water Concentrates Prepared from Chlorinated and Ozonated/Postchlorinated Drinking Water. *J. Toxicol. Environ. Health*, Pt. A, 71: 1165-1186.

Simmons, J. E., S. D. Richardson, T. F. Speth, R. J. Miltner, G. Rice, K. M. Schenck, E. S. Hunter, III, and L. K. Teuschler. 2008. [illegible]es Underlying the Four-Lab Study: Integrated Disinfection Byproducts Mixtures Research. *J. Toxicol. Environ. Health*, Pt. A, 71: 1125-1132.

Miltner, R. J., T. F. Speth, S. D. Richardson, S. W. Krasner, H. S. Weinberg, and J. E. Simmons. 2008. Integrated Disinfection Byproducts Mixtures Research: Disinfection of Drinking Waters by Chlorination and Ozonation/Postchlorination Treatment Scenarios. *J. Toxicol. Environ. Health*, Pt. A, 71: 1133-1148.

Speth, T. F., R. J. Miltner, S. D. Richardson, and J. E. Simmons. 2008. Integrated Disinfection Byproducts Mixtures Research: Concentration by Reverse Osmosis Membrane Techniques of Disinfection Byproducts from Water Disinfected by Chlorination and Ozonation/Postchlorination. *J. Toxicol. Environ. Health*, Pt. A, 71: 1149-1164.

Rice, G., L. K. Teuschler, S. D. Richardson, T. F. Speth, and J. E. Simmons. 2008. Integrated Disinfection Byproducts Mixtures Research: Assessing Reproductive and Developmental Risks Posed by Complex Disinfection Byproduct Mixtures. *J. Toxicol. Environ. Health*, Pt. A, 71: 1222-1234.

Richardson. S. D. 2008. Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. *Anal. Chem*., 80(12): 4373-4402.

Richardson, S. D., M. J. Plewa, E. D. Wagner, R. Schoeny, and D. M. DeMarini. Occurrence, Genotoxicity, and Carcinogenicity of Emerging Disinfection By-Products in Drinking Water: A Review and Roadmap for Research. 2007. *Mutat. Res*., 636: 178-242.

Muellner, M. G., E. D. Wagner, K. McCalla, S. D. Richardson, Y.-T. Wood, and M. J. Plewa. 2007. Haloacetonitriles vs. Regulated Haloacetic Acids: Are Nitrogen Containing DBPs More Toxic? *Environ. Sci. Technol.,* 41 (2): 645-651.

Zwiener, C., S. D. Richardson, D. M. DeMarini, T. Grummt, T. Glauner, and F. H. Frimmel. 2007. Drowining in Disinfection By-Products? Swimming Pool Water Quality Reconsidered. *Environ. Sci. Technol*., 41 (2): 363-372.

Plewa, M. J., M. G. Muellner, S. D. Richardson, F. Fasano, K. M. Buettner, Y.-T. Woo, A. B. McKague, and E. D. Wagner. 2007. Occurrence, Synthesis, and Mammalian Cell Cytotoxicity and Genotoxicity of Haloacetamides: An Emerging Class of Nitrogenous Drinking Water Disinfection By-Product. *Environ. Sci. Technol.*, 42 (3): 955-961.

Richardson, S. D. Water Analysis: Emerging Contaminants and Current Issues. 2007. *Anal. Chem*., 79(12): 4295-4324.

Krasner, S. W., H. S. Weinberg, S. D. Richardson, S. Pastor, R. Chinn, M. J. Sclimenti, G. Onstad, and A. D. Thruston, Jr. 2006. The Occurrence of a New Generation of Disinfection Byproducts. *Environ. Sci. Technol.*, 40 (23): 7175-7185.

Richardson. S. D. Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. 2006. *Anal. Chem*., 78 (12): 4021-4046.

Richardson, S. D., and T. Ternes. 2005. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem*., 77(12): 3807-3838.

Cemeli, E., E. D. Wagner, D. Anderson, S. D. Richardson, and M. J. Plewa. 2006. Modulation of the Cytotoxicity and Genotoxicity of the Drinking Water DBP Iodoacetic Acid by Suppressors of Oxidative Stress. *Environ. Sci. Technol*., 40 (6): 1878-1883.

Vincenti, M., S. Biazzi, N. Ghiglione, M. C. Valsania, and S. D. Richardson. 2005. Comparison of Highly- Fluorinated Chloroformates as Direct Aqueous Sample Derivatizing Agents for Hydrophilic Analytes and Drinking Water Disinfection By-Products. *J. Am. Soc. Mass Spectrom*., 16 (6): 803-813.

Plewa, M. J., E. D. Wagner, S. D. Richardson, A. D. Thruston, Jr., Y.-T. Woo, and A. B. McKague. 2004. Chemical and Biological Characterization of Newly Discovered Iodoacid Drinking Water Disinfection Byproducts. *Environ. Sci. Technol*., 38(18): 4713-4722.

Zwiener, C., and S. D. Richardson. 2005. Drinking Water Disinfection By-Product Analysis by LC/MS and LC/MS/MS. *Trends Anal. Chem*., 24(7): 613-621. (Invited review article for special thematic issue on Liquid Chromatography-Tandem Mass Spectrometry).

Plewa, M. J., E. D. Wagner, P. Jazwierska, S. D. Richardson, P. H. Chen, and A. B. McKague. 2004. Halonitromethane Drinking Water Disinfection Byproducts: Chemical Characterization and Mammalian Cell Cytotoxicity and Genotoxicity. *Environ. Sci. Technol*., 38(1): 62-68.

Kundu, B., S. D. Richardson, P. D. Swartz, P. P. Matthews, A. M. Richard, and D. M. DeMarini. 2004. Mutagenicity in Salmonella of Halonitrometanes: A Recently Recognized Class of Disinfection By-Product in Drinking Water. *Mutat. Res*., 562: 39-65.

Kundu, B., S. D. Richardson, C. A. Granville, D. T. Shaughnessy, N. M. Hanley, P. D. Swartz, A. M. Richard, and D. M. DeMarini. 2004. Comparative Mutagenicity of Halomethanes and Halonitromethanes in Salmonella TA100: Structure-Activity Analysis and Mutation Spectra. *Mutat. Res*., 554: 335-350.

Richardson, S. D. 2004. Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. *Anal. Chem*., 76(12): 3337-3364.

Simmons, J. E., L. K. Teuschler, C. Gennings, T. F. Speth, S. D. Richardson, R. J. Miltner, M. G. Narotsky, K. D. Schenck, E. S. Hunter, III, R. C. Hertzberg, III, and G. Rice. 2004. Component-Based and Whole-Mixture Techniques for Addressing the Toxicity of Drinking Water Disinfection Byproducts Mixtures. *J. Toxicol. Environ. Health*, 67: 741-754.

Richardson, S.D., J. E. Simmons, and G. Rice. 2002. DBPs: The Next Generation. *Environ. Sci. Technol*., *36*(9): 198A-205A.

Woo, Y.-T., D. Lai, J. L. McLain, M. K. Manibusan, and V. Dellarco. 2002. *Environ. Health Perspect*., 110 (Suppl. 1): 75-87.

Richardson, S. D., A. D. Thruston, Jr., C. Rav-Acha, L. Groisman, I. Popilevsky, V. Glezer, A. B. McKague, M. J. Plewa, and E. D. Wagner. 2003. Tribromopyrrole and Other DBPs Produced by the Disinfection of Drinking Water Rich in Bromide. *Environ. Sci. Technol*., 37(17): 3782-3793.

Richardson, S. D. 2003. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem*., 75(12): 2831-2857.

Richardson, S. D. 2003. Disinfection By-Products and Other Emerging Contaminants in Drinking Water. *Trends Anal. Chem*., 22 (10):666-684.

Weinberg, H. S., S. W. Krasner, S. D. Richardson, and A. D. Thruston, Jr. The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study. EPA/600/R02/068. U.S. Environmental Protection Agency, National Exposure Research Laboratory, Athens, GA. 2002.

Chen, P. H., S. D. Richardson, S. W. Krasner, G. Majetich, and G. L. Glish. 2002. Hydrogen Abstraction and Decomposition of Tribromonitromethane and Other Trihalo Compounds by GC/MS. *Environ. Sci. Technol*., 36(15): 3362-3371.

Simmons, J. E., S. D. Richardson, T. F. Speth, R. J. Miltner, G. Rice, K. M. Schenck, E. S. Hunter, III, and L. K. Teuschler. 2002. Development of a Research Strategy for Integrated Technology-Based Toxicological and Chemical Evaluation of Complex Mixtures of Drinking Water Disinfection Byproducts. *Environ. Health Perspect.*, 110(Supp. 6): 1013-1024.

Arbuckle, T. E., S. E. Hrudey, S. W. Krasner, J. R. Nuckols, S. D. Richardson, P. Singer, P. Mendola, L. Dodds, C. Weisel, D. L. Ashley, K. L. Froese, R. A. Pegram, I. R. Schultz, J. Reif, A. M. Bachand, F. M. Benoit, M. Lynberg, C. Poole, and K. Waller. 2002. Assessing Exposure in Epidemiologic Studies to Disinfection By-products in Drinking Water: Report from an International Workshop. *Environ. Health Perspect*., 110 (Supp. 1): 53-60.

Richardson, S. D., T. V. Caughran, T. Poiger, Y. Guo, and F. G. Crumley. 2000. Application of DNPH Derivatization with LC/MS to the Identification of Polar Carbonyl Disinfection By-products in Drinking Water. *Ozone Sci. Engin*., 22: 653-675.

Richardson, S. D., A. D. Thruston, Jr., T. V. Caughran, P. H. Chen, T. W. Collette, T. L. Floyd, K. M. Schenck, B. W. Lykins, Jr., G.-R. Sun, and G. Majetich. 1999. Identification of New Ozone Disinfection By-products in Drinking Water. *Environ. Sci. Technol*., 33: 3368-3377.

D., A. D. Thruston, Jr., T. V. Caughran, P. H. Chen, T. W. Collette, T. L. Floyd, K. M. Schenck, B. W. Lykins, Jr., G. Majetich. 1999. Identification of New Drinking Water Disinfection By-products Formed in the Presence of Bromide. *Environ. Sci. Technol.*, 33: 3378-3383.

Richardson, S. D., A. D. Thruston, Jr., T. V. Caughran, P. H. Chen, T. W. Collette, K. M. Schenck, B. W. Lykins, Jr., C. Rav-Acha, and V. Glezer. 2000. Identification of New Drinking Water Disinfection By-products from Ozone, Chlorine Dioxide, Chloramine, and Chlorine. *Water Air Soil Pollut*., 123: 95-102.

*For more information, contact Susan Richardson (richardson.susan@epa.gov)

WCMS
Last updated on 8/13/2015