Connecting the Nation's Environmental Laboratories

Racine Health Department Laboratory Takes a Comprehensive Approach to Beach Health

By Julie Kinzelman, PhD, laboratory director, Racine Health Department

It's April in the Great Lakes: one day it's 60 degrees and the next it's snowing, but the laboratory is getting ready for the summer swimming season. Although only three months long (short in comparison to many of our east, west and Gulf coast counterparts), hundreds of thousands of visitors flock to Great Lakes coastal beaches each June, July and August. As the local health department laboratory for the City of Racine, Wisconsin, we have responsibility for monitoring water quality at our Lake Michigan beaches.

Surface waters have been monitored for decades as the first line of defense in public health protection. Routine recreational water quality monitoring helps prevent exposure during periods of greater waterborne disease risk. This was not always a standard practice. The Beaches Environmental Assessment and Coastal Health Act of 2000 (BEACH Act), an amendment to the Clean Water Act of 1972, was the first national legislation requiring the adoption of routine regulatory monitoring (based on a fecal indicator bacteria standard) and public notification programs.



Elias Munthali kayaks to sample and assess surface water quality at the Samuel Myers Park embayment in Racine, WI. Photo by Adrian Koski, City of Racine Health Department

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While a positive step, routine monitoring only partially prevents disease transmission. Culture-based laboratory tests require a minimum of 18 hours before results are received. The lag between sample collection and result receipt leads to retrospective or inappropriate public health action (i.e. posting beach advisory notifications after exposure has already occurred or prohibiting swimming when water quality is good).

Surface waters lie on the surface of the land and include streams, rivers, lakes, reservoirs and wetlands. Recreational water quality monitoring is typically conducted in surface waters where primary contact recreation occurs, such as swimming, bathing, surfing, water skiing, tubing and water play by children. These activities typically have a high degree of bodily contact with the water and immersion and ingestion is likely.

Coastal communities like Racine regard beaches and shorelines as amenities, contributing to economic development, quality of life and providing resiliency from adverse weather events. As such, we must strike a balance between preventing illness, maximizing utility and preserving the environment. The Health Department Laboratory has been an active participant in ensuring all of these objectives are met.

From an economic development perspective, **unnecessary beach closures lead to lost revenue**. One way to reduce them is to improve laboratory turnaround time. Since 2005, the Racine Health Department Laboratory

has partnered with EPA to validate rapid, lab-based assays for fecal indicator bacteria quantification (quantitative polymerase chain reaction or qPCR), **reducing turnaround time from 18 hours to less than three**. In May 2012, we became the first laboratory in the US to receive state and federal approval to regulate our beaches using molecular methods to quantify *Escherichia coli* (E. coli).

In December 2012, EPA released revised recreational water quality criteria for beaches, including criteria for regulatory decision-making using molecular methods, and guidance for those seeking to implement locally. For laboratories lacking molecular capability, EPA has also developed predictive model building software (Virtual Beach). Predictive models estimate fecal indicator bacteria levels based on measured environmental parameters such as wave height, rainfall, wind direction/speed, turbidity, water temperature and other conditions associated with poor water quality. The Racine Health Department Laboratory has developed a model that predicts both culture-based and molecular targets, an analytical solution that allows us to retain near real-time public notification while conserving costs.

Rapid testing has improved our ability to prevent exposure, but **real public health protection lies in pollutant source identification and mitigation**. Investigative monitoring approaches such as the EPA Beach Sanitary Survey tool creates a common protocol that communities can use to track and determine the relative contribution of a variety of potential contaminants. Data-based results can ultimately focus financial resources to the greatest effect.

Collection, analysis and use of beach sanitary survey data to guide restoration efforts has resulted in a significant reduction in water quality advisories at North Beach, Racine's main public beach. Water quality advisories have dropped from 62 advisories/closures out of a 94-day beach season in 2000 to less than 10 per season since 2005. This has led to the development of comprehensive restoration plans for

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Samuel Myers Park, a site posted as unsafe for human contact for 20 years. **Improved water quality translates into economic potential**. Since water quality improvements occurred at North Beach, usage has gone up from hundreds to tens of thousands per weekend day, with over 200,000 beach visitors in 2015 alone. This translates into over \$5 million in revenue annually.

In addition to direct economic benefits, clean water and accessible recreational venues improves quality of life. In visioning exercises, all demographic groups have identified Racine's coastal beaches as a community asset. The lack of parking or user fees facilitate social equity and many remark that North Beach is the "melting pot" of Racine, a location enjoyed by all socio-economic backgrounds and ages. In 2016, it was voted as one of the top five freshwater beaches in the country by **USA Today**. Because the site is so well used, the Health Department, in cooperation with the Departments of Public Works, Community Development and Parks/Recreation/Cultural Services, has initiated the development of a master plan for the beach and surrounding neighborhood to ensure that it is used sustainably and remains a vital part of our community for future generations.



North Beach, Racine, WI. Photo by Monica Schmidt, City of Racine Health Department

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The final pillar of sustainability is environmental preservation. The laboratory is currently leading an effort to restore the long-neglected Samuel Myers Park. Long neglected, poor water quality and invasive species have resulted in degraded habitat. Comprehensive 2010-2012 beach sanitary surveys identified multiple pollution sources, including stormwater runoff and excessive numbers of nuisance shorebirds. Successful grant applications and donations are providing funding for the investigation, engineering plans, construction and remedial activities necessary to restore this important environmental corridor and migratory bird flyway, create public access and fortify the shoreline against extreme weather events.

The Racine Health Department Laboratory has taken a comprehensive approach to beach health, extending itself beyond traditional laboratory testing to environmental sciences, economics, urban planning and engineering. By partnering with the federal government on rapid method validation/implementation, investigating/remediating pollution sources, actualizing economic benefits, providing social equity, contributing to community development and ensuring environmental integrity, we have met the goals of protecting public health, maximizing utility and preserving our coastal resources.

New Mexico Scientific Laboratory Supports Air Quality Management Program

By Frank See, MS, air and metals section manager, New Mexico Scientific Laboratory

The New Mexico Environment Department and Bernalillo County air quality programs operate a network of monitors that continuously sample air throughout the state and its largest metropolitan area, Albuquerque. The New Mexico Scientific Laboratory, the state's sole public health, environmental and drug laboratory, supports this effort by measuring the particulate matter trapped on air sampling equipment filters in its gravimetric laboratory.

The air samplers are designed to trap particulate matter less than 10 microns (PM_{10}) and 2.5 microns ($PM_{2.5}$) in diameter. Small enough to be inhaled into the lungs, scientific studies have shown links between long-term

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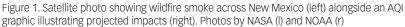




Figure 2. A late afternoon look at the western horizon during the height of the particulate matter plume passing through the Albuquerque area. Photo by Frank See

particulate matter exposure and chronic lung disease. Short-term particulate matter pollution exposure can increase respiratory symptoms such as coughing, wheezing and shortness of breath.

Particulate matter is comprised of different chemical components such as carbon, sulfates, nitrates and geological materials in soils. "Primary" particulates are directly emitted into the air and "secondary" particulates can form indirectly from fuel combustion emissions, industrial processes and forest fires. Size and origin can cause particulates to behave differently in the air and particulate composition can vary regionally and seasonally.

Citizens in New Mexico and the surrounding region are frequently subjected to particulates generated from regional forest fires, particularly during extended drought periods. For example, the 2011 Arizona Wallow Fire created a large plume of ash and soot that was transported by prevailing winds into the Rio Grande Valley Corridor (Figure 1). Citizens were alerted of the possible adverse impacts of the particulate matter plume traveling into the area by Air Quality Index (AQI) maps (Figure 1). Visually, the smoke caused periods of full sunshine to appear as dark as dusk (Figure 2). As evidenced by the dark coloration of filters collected during this time period, laboratory gravimetric samples show high amounts of ash and soot, particularly from 6/2 to 6/4, when the plume traveled up the Rio Grande Valley Corridor into the Albuquerque metropolitan area (Figure 3).

Gravimetric analysis is used to determine particulate matter mass by taking comparative filter measurements before and after a defined sampling period. The laboratory weighs filter media on a microbalance and then sends the filters out to be placed into the samplers (Figure 4). Over a twenty-four hour period, the air sampler passes a known volume of ambient air through the filter where the passes are sampled to determine passes.



Figure 3. Filters retrieved from air sampling equipment located in the Albuquerque area during the 2011 Arizona Wallow Fire. The filters are either labeled FB (field blank for reference) or by sample date (6/2-6/7). Photo by Erik Bacon



Figure 4. Air particle samplers located in the Albuquerque area. Photo by Albuquerque Department of Environmental Health

passes a known volume of ambient air through the filter where the particulates become entrapped (Figure 5). The filter is then returned to the gravimetric laboratory and reweighed (Figure 6). The difference in mass pre-





Figure 5. Air particle sampler interior showing the filter cassettes used to load and unload filters from the air flow mechanism. Photo by Albuquerque Department of Environmental Health



Figure 6. Staff member weighing filters at the balance table. Photo by Frank See

and post-sample is used to calculate the particulate mass in micrograms per unit volume of metric air (μ g/m3). The air samplers run continuously throughout the year and can be set up to collect either PM₁₀ or PM₂₅.

Air particulate sampler filters are made of Teflon® and 47 millimeters in diameter. When filters are returned to the laboratory, pre- and post-sample weight difference may be as small as 5 to 10 micrograms (µg) (1x10-6 gram). Special equipment and controlled environments are required to measure these minute differences. Filters are weighed after a twenty-four hour

Learn more about New Mexico Scientific Laboratory's environmental work during the 2016 APHL Annual Meeting and Tenth Government Environmental Laboratory Conference in Albuquerque, NM from June 6-9. On Thursday, June 9, attend the session "Coal Ash and Mine Spills: Environmental Laboratory Implications" from 9:00–10:30 am and tour the laboratory from 1:00 PM–3:30 pm. The scientific poster "New Mexico Scientific Laboratory Division Response to the Gold King Mine Spill, August 2015" can be viewed throughout the conference.

conditioning period to equilibrate with laboratory environment. Weighing rooms are constantly maintained at 20-23° Celsius and 30-40% relative humidity to help control electrostatic charge buildup on the filters. Polonium brushes and strips also aid in neutralizing static charge on the filters.

The gravimetric studies done by New Mexico Scientific Laboratory support EPA's routine ambient air monitoring program and analyses strictly adhere to EPA protocols. The particulate matter data are uploaded into regional and national databases to enable study of temporal and regional trends. The air quality models developed from this data help EPA, governmental agencies and other researchers better understand air pollutants and set appropriate policy to manage exposure and protect public health.

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2016 TNI Standard for Environmental Radiochemistry Laboratory Accreditation

By Bob Shannon, Quality Radioanalytical Support, LLC

Radiochemistry laboratories across the country routinely conduct measurements for radionuclides in a wide range of environmental matrices. While these measurements are used for many purposes, there is something common to them all: the need for "quality." Expectations in the area of quality, however, have evolved significantly over the past 30 years.

The need for laboratory certification or accreditation has moved beyond the EPA "go-to" certification for Safe Drinking Water Act (SDWA) compliance measurements. Although the SDWA program plays a vital role in ensuring national drinking water quality, the program's scope is relatively narrow and focuses primarily on a short list of naturally-occurring radionuclides in clean water. It also relies on a fixed list of approved methods, most of which have not been updated since the 1980s. Many of these methods would not rise to 2016 expectations for method performance documentation or quality requirements.

The National Environmental Laboratory Accreditation Program (NELAP) formed in the late 1990s to develop unified accreditation standards and facilitate cooperation among accrediting agencies of different states and governmental bodies. The accreditation program came into full swing as the National Environmental Laboratory Accreditation Conference (NELAC) standard was implemented in 12 states in 1999. The NELAC Institute (TNI) was formed in 2006 to establish a self-sufficient consensus standard development organization responsible for the TNI Standard. Fifteen years of improved assessment outcomes since the standard was first issued indicate that NELAP and the TNI standards development process have strengthened the overall quality and defensibility of radiochemical data.

Several years ago, the TNI Consensus Standards Development program added a committee of radiochemical experts drawn from various industry sectors across the country. They were tasked with preparing a revision of the 2009 TNI Standard–Quality Systems for Radiochemical Testing. This module underwent significant revision, successfully completed the last of four ballots in September 2015 and will be included in the 2016 revision of the TNI Standard.

The Radiochemistry Expert Committee's revisions have focused attention on areas where radiochemistry differs from conventional areas such as inorganic and organic chemistry. Key concepts unique to radiochemical measurements, including uncertainty and detection, are defined in the revised standard. While the standard recognizes that laboratories must still use EPA-approved reference methods when performing drinking water compliance measurements, the reality is that environmental radiochemistry labs rely heavily on more modern laboratory-developed and laboratory-modified methods. These methods often incorporate state-of-the-art chemical separation techniques and produce robust, high-quality results in a wide variety of matrices (beyond clean water), while minimizing processing time, costs and hazardous and mixed wastes.

The revision ensures that validated performance will be documented for all methods (reference and otherwise). It addresses the estimation and reporting of uncertainties and detection statistics, and differentiates between requirements unique to the SDWA (i.e., uncertainty based on "counting statistics), and that used for most other measurements (total or combined uncertainty). Quality control practices have been updated and are now less prescriptive, more universal and more effective. While the changes may require some laboratories to update



certain systems, for the most part, they reflect practices already in place at many environmental radiochemistry laboratories across the country.

With the revision process complete, the committee is now preparing standard implementation tools, including guidance documents and an optional assessment checklist. Training is also being developed for laboratories, accrediting bodies and assessors, and will be presented at regular conferences and as webinars. The first training session was a live webinar at the January TNI meeting in Tulsa, Oklahoma. See the TNI website for more information on training and tools as these become available.

The Radiochemistry Expert Committee welcomes persons interested in becoming involved in the process to participate as associate members of the committee. The committee meets at 1 PM ET on the third Wednesday of each month. Interested parties may contact Bob Shannon at BobShannon@boreal.org, or Ilona Taunton at ilona. taunton@nelac-institute.org.

State Lab Partnerships as a Path Forward for Radiochemists?

By Andrew W. Nelson, PhD, MPH, Forbes Group postdoctoral scholar, Department of Chemistry, University of Iowa, Iowa City, IA; and Dustin May, radiochemistry department director, State Hygienic Laboratory at the University of Iowa, Coralville IA and PhD student, Schultz Group, Interdisciplinary Human Toxicology, University of Iowa, Iowa City, IA

As described in the National Research Council article, Assuring a Future U.S.-Based Nuclear and Radiochemistry Expertise, and frequently discussed in radiochemistry conferences, it is common knowledge in the radiochemistry field that a shortage of trained practitioners is coming. As in any field, when our mentors retire, incredibly valuable resources are lost. The concern in the radiochemical field is that we are losing these resources without a strong core of young, highly-trained professionals to replace them. Efforts are underway nationally to reduce the shortage of young radiochemists, including the expansion or creation of graduate radiochemistry programs. Graduate academic training programs are a necessary component of training a highly-skilled workforce; however, academia may lack applied, real-world training that is essential to a public health safety net.

We would like to suggest, from our own experience, an alternative way to expand the depth and breadth of our younger generation of radiochemists. The following discussion highlights a collaborative approach between a federal agency, a consulting firm, a state public health laboratory, and a radiochemistry graduate program, and characterizes the successes, challenges, and lessons learned during the project from the trainee perspective.



Andrew Nelson analyzes Marcellus Shale produced fluids for uranium, thorium and polonium at the IA SHL. Photo by Pat Blake

Project Description

Between 2000 and 2010, new drilling and hydraulic fracturing (fracking) techniques revolutionized the way natural gas is extracted on dry land in the United States. These extraction techniques raised numerous environmental pollution and health concerns, including the potential release of and exposure to naturally-occurring radioactive materials (NORM). In 2011, state and federal scientists reported that complex liquid wastes from the Marcellus Shale, which primarily underlies West Virginia, Ohio, Pennsylvania and New York, contained, in some cases, radium (Ra) isotopes. When these reports first emerged, there were no validated radiochemical methods for NORM (including Ra) quantitation in fracking wastes.



In 2013, under contract to the EPA, Environmental Management Support, Inc. (EMS) was tasked to develop and validate a method to screen for gross alpha and beta radioactivity from Naturally Occurring Radioactive Materials (NORM) in flowback and produced water from hydraulic fracturing. EMS worked together with researchers at the University of Iowa (UIowa) and practitioners at State Hygienic Laboratory (SHL) at UIowa to develop the laboratory components of this new method. All laboratory work was performed at the SHL, a National Environmental Laboratory Accreditation Program (NELAP) accredited laboratory that maintained all of the radiochemisty equipment needed for the project. The goal of this project was two-pronged: first to develop a simple method that could be easily and routinely applied to hydraulic fracturing liquid wastes, and second to train us (Andrew and Dustin) on the ins and outs of radiochemical method development.

Challenges

At the onset, this project seemed fraught with challenges, including a deadline of less than four months. Marcellus Shale liquid wastes are exceptionally complex, with total dissolved solids (TDS) exceeding 250,000 milligrams per liter (thousands of times saltier than drinking water). As young radiochemists, our knowledge of chemical approaches to simplify the liquid waste matrix were quite limited, and every approach we tried backfired. Luckily, we had numerous advisors, including highly-experienced EMS consultants, Mr. Bob Shannon and Dr. Bob Litman. Mr. Shannon and Dr. Litman were invaluable resources and routinely provided insights into how they solved problems with other challenging samples they encountered over their careers. The industry/consultant perspective provided realistic deadlines and steady workflow maintenance—concepts with which academics sometimes struggle. Their input was complimented by Dr.



Marinea Mehrhoff, Dustin May and Andrew Nelson work at a liquid scintillation counter at the IA SHL. Photo by Pat Blake

Michael K. Schultz, a UIowa academic advisor deeply invested in pushing the technological limits of the field. To round out the help, we had hands-on assistance from Ms. Marinea Mehrhoff, a retired SHL Radiochemistry Division supervisor with over 30 years of practical laboratory analysis experience. Theoretical chemistry described in scientific reports is not always as easy to implement as authors might have the reader believe, and Ms. Mehrhoff knew dozens of techniques to turn ideas into results. Without her, the project would have certainly been over budget and behind schedule. The four-month turnaround time was unusually short for a graduate student project, where success is often measured in product novelty rather than speed, and the aid of these experienced scientists enabled us to complete the project within the allotted time.

Successes

All in all, this project was a huge success, especially for us, the trainees. We were able to experience and contribute to a project that ultimately led to an EPA radiochemical method. Follow-up work directly resulted in four peer-reviewed journal articles, one of which won an award for the "Best Letter of the Year" from the American Chemical Society in 2014 and was selected as an "Editor's Choice" open-access article (1–3). Project publicity also led to presentations at national conferences including the Association of Public Health Laboratories (2013), the Radiobioassay Radiochemical Measurements Conference (2013, 2014, 2015), the American Chemical Society (2014), the American Society for Testing and Materials (2014, 2015), and the National Environmental Monitoring Conference (2014). Project results provided the foundation for Andrew's PhD dissertation and encouraged Dustin to pursue a PhD.

Public health laboratories are a tremendous resource of knowledge and expertise—this project helped to strengthen ties between the University and the SHL, which has allowed us to pursue important and practical research that we would not otherwise be able to perform as pure academics. Likewise, this project has allowed



the SHL Radiochemistry Department to become more involved in research and development instead of simply providing fee-for-service analytical work.

Public health laboratories have a great deal to offer academia, especially in terms of quality assurance, accreditation, and a wealth of practical, hands-on experience. Although this project could have been completed at a contract laboratory, potentially at a lower cost, we believe the partnership between academia, industry, and a public health laboratory allowed more room for scientific discovery and the development of radiochemical expertise.

The partnerships developed in this project have paved the way for similar research relationships between UIowa, SHL, and others, that we hope will broaden our understanding of the natural world. This project was just the beginning of our careers and collaboration with generous, patient and knowledgeable mentors provided us strong foundations upon which to build.

In conclusion, we encourage academia, industry and public health laboratories to collaborate and to include younger radiochemists as key players in the discovery process. Please know that many young radiochemists are eager to learn and appreciative of opportunities to expand our experiences and our skills.

References

- 1. Nelson AW, Johns AJ, Eitrheim ES, Knight AW, Basile M, Bettis III EA, et al. Partitioning of naturally-occurring radionuclides (NORM) in Marcellus Shale produced fluids influenced by chemical matrix. Environ Sci Process Impacts [Internet]. The Royal Society of Chemistry; 2016;-. Available from: http://dx.doi.org/10.1039/C5EM00540J
- 2. Nelson AW, Eitrheim ES, Knight AW, May D, Mehrhoff MA, Shannon R, Litman R, Burnett WC, Forbes TZ, Schultz MK. 2015. Understanding the radioactive ingrowth and decay of naturally occurring radioactive materials in the environment: an analysis of produced fluids from the Marcellus Shale. Environ Health Perspect 123:689–696; http://dx.doi.org.proxy.lib.uiowa.edu/10.1289/ehp.1408855
- 3. Nelson AW, Knight AW, May D, Eitrheim ES, Schultz MK. Naturally-Occurring Radioactive Materials (NORM) Associated with Unconventional Drilling for Shale Gas. In: ACS Symposium Series [Internet]. 2015 [cited 2015 Dec 29]. p. 89–128. Available from: http://pubs.acs.org.proxy.lib.uiowa.edu/doi/abs/10.1021/bk-2015-1216.ch004

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Public Health Laboratories Respond to New and Emerging Environmental Threats: Fungicide & Algal Toxin Testing in Iowa and Rhode Island

By Henry Leibouitz, PhD, chief environmental laboratory scientist, Rhode Island State Health Laboratories; John Vargo, PhD, program manager, State Hygienic Laboratory at the University of Iowa; and Michael Wichman, PhD, environmental health associate director, State Hygienic Laboratory at the University of Iowa

This is the first article in a series on new and emerging environmental contaminants. If your laboratory has developed or implemented new/emerging contaminant analytical methods that could be shared to help other laboratories, please contact sarah.wright@aphl.org.

Fungicides

On September 25, 2007, soybean rust was found in a field in Dallas County, Iowa and fungicides were applied throughout the state to combat the disease. To monitor streams and rivers for these fungicides, the Iowa Department of Natural Resources requested the State Hygienic Laboratory at the University of Iowa (IA SHL) develop a method for fungicides approved for application in Iowa.

Due in part to the availability of liquid chromatography-tandem mass spectrometry (LC-MS/MS) technology from the Laboratory Response Network for Chemical Threats (LRN-C) program, IA SHL chemists developed, validated and implemented a highly specific and very sensitive LC/MS/MS method to determine several fungicides. IA SHL can now detect most triazole, strobilurin and chlorinated fungicides listed in Table I at very low concentrations* in



Terry Cain, IA SHL environmental laboratory supervisor, works at a Gas Chromatograph/Mass Spectrometer analytical system to test environmental samples. Photo by Pat Blake

a wide variety of samples, including drinking water and surface water, soil, vegetation and food products.

Table I: IA SHL Chlorinated Fungicide Method Analytes

Azoxystrobin	Metconazole	Tebuconazole
Chlorothalonil	Myclobutanil	Tetraconazole
Cyproconazole	Propiconazole	Trifloxystrobin
Fluoxastrobin	Pyraclostrobin	

*Reporting Limit: 20 ng/L (parts per trillion) in water samples

The availability of this new method proved to be fortuitous when an F5 tornado devastated much of Parkersburg, Iowa on May 25, 2008, including an agricultural chemical storage facility. Fungicides from the facility spilled into a local stream and the IA SHL analyzed numerous stream samples to determine the extent of the spill. The method is still in use today. Recently, more widespread aerial fungicide applications on corn and soybeans have been associated with fish kills in streams throughout Iowa.

Harmful Algal Bloom (HAB) Toxins

Cyanotoxin contamination produced by blue-green algae (more appropriately called cyanobacteria) has occurred during active blooms in public surface water supplies. Last year this public health concern

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resulted in EPA issuing drinking water health advisories for the cyanobacterial toxins microcystins and cylindrospermopsins.

Cyanotoxins have been found to constitute an increasing health risk typically from mid-spring to mid-autumn in warm, nutrient-rich water bodies. Toxins may affect the liver, nervous system and/or the gastrointestinal system. Exposure can occur by ingestion or inhalation of aerosolized toxins or dermal contact through activities such as swimming or fishing. EPA set the drinking water advisory limit for children six years old or less to 0.3 μg/L for total microcystins and 0.7 μg/L for cylindrospermopsin. The drinking water advisory limit for school-age children to adults is 1.6 µg/L for total microcystins and 3.0 µg/L for cylindrospermopsin. EPA is also considering the inclusion of select drinking water toxins in their Fourth Unregulated Contaminant Monitoring Rule. The

World Health Organization has recommended a maximum total microcystins exposure limit of 1 µg/L in finished drinking water.

IA SHL routinely screens water samples for microcystin toxins using the rapid test enzyme-linked immunosorbent assay (ELISA). Free and total toxins can be detected in water using freeze/thaw cycles to rupture the cyanobacterial cells. In the near future, IA SHL plans to implement an LC-MS/MS procedure to determine specific microcystin toxins, as well as nodularins, anatoxin-A and cylindrospermopsin.

The Rhode Island State Health Laboratories (RI SHL) maintains both ELISA and LC/MS/MS testing for microcystins, cylindrospermopsin and other cyanotoxins including nodularins and anatoxin-a. During the 2014 active bloom season, RI SHL conducted weekly testing of raw and finished water samples collected from all 10 surface water supplies in Rhode Island. Microcystin was detected in one raw water sample but not



Unbranched filamentous cyanobacteria collected from a 2015 bloom in RI identified as Anabaena sp., which can produce multiple toxins, including microcystins and anatoxin. Anatoxin-a was detected in this sample with a concentration of 2.1 µg/L. Photo by RI SHL

in the associated finished water sample. In 2015, RI SHL began developing the capability to count cyanobacteria units (colonies, filaments, cells) per milliliter of water to provide additional cyanotoxin concentration and cyanobacteria data to consider when making public health advisories.

Currently the RI SHL is considering a third approach for microcystin analysis developed by Green Water Laboratories, FL and published in Toxicon (Toxicon 104 (2015) 91 -101). Using LC-MS/MS, the method chemically oxidizes microcystins so they can be detected equally regardless of variant. The formation of 2-methyl-3-methoxy-4phenylbutyric acid (MMPB) from microcystin oxidation allows for the determination of total microcystins in water samples. This method alleviates the need to maintain stocks of individual microcystin variants, many of which are not commercially attainable.

EPA has published two guidance methods for the determination of cyanotoxin in drinking water. EPA Method 544 is for the extraction and analysis of microcystin variants and nodularin by LC-MS/MS. EPA Method 545 is for the analysis of cylindrospermopsin and anatoxin-a by direct injection analysis by LC-MS/MS.



Pond and reservoir samples collected in 2014 for algal toxin analysis at RI SHL. Photo by RI SHL



For public health laboratories interested in adding cyanotoxin testing to their services, the following three approaches are currently considered appropriate:

- ELISA A useful screening tool for the detection of all microcystins (ADDA Kit) with a low detection limit. This assay is prone to matrix interference and confirmatory analysis (e.g., LC-MS/MS) is recommended for any positive samples.
- LC-MS/(MS) A powerful and highly-specific technique used in confirmatory analysis to accurately identify and quantify specific microcystin and nodularin variants. Either a scan or tandem mass spectrometry (MS/MS) can be conducted on a suite of microcystins, including those that are commercially attainable: [DAsp3]MC-RR, MC-RR, MC-YR, MC-LR, [DAsp3]MC-LR, , MC-WR, MC-HilR, MC-LY, MC-LA, MC-LF, MC-LW and nodularin.
- MMPB LC-MS/MS Chemical oxidation of microcystins produces 2-methyl-3-methoxy-4-phenylbutyric acid (MMPB). MMPB can be detected equally regardless of the variant. MMPB analysis allows for the determination of total microcystins, bound and unbound, in water samples, although this technique may not be suitable for heavily-chlorinated water samples.

For more information on emerging contaminants, attend the "What's In Our Water and How Do We Know?" roundtable session on Wednesday, June 8 from 8:00–8:45 am at the 2016 APHL Annual Meeting and 10th Government Environmental Laboratory Conference in Albuquerque, NM.

Contribute to the Member Resource Center

The APHL Member Resource Center (MRC) provides an extensive range of resource materials designed to provide technical assistance within the public health and environmental laboratory sector. Created by and for the APHL member community, the MRC provides a virtual clearinghouse of documents designed to exchange practices, communications, protocols, state newsletters and more. The MRC assists APHL members in accessing timely, peer-contributed, public and environmental health information—rapidly and easily. These resources are not necessarily endorsed by APHL.

Examples of MRC resources include:

- Promising laboratory practices
- Media relations procedures
- Laboratory newsletters
- Human relations processes
- Lab testing protocols and guidelines
- Local fact sheets
- Energy management practices.

The APHL MRC is a vital instrument for the environmental laboratory community to remain knowledgeable in meeting today's challenges. For more information and to submit a resource visit http://www.aphl.org/MRC/. Send feedback to memberresources@aphl.org.