Bridges

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Connecting the Nation's Environmental Laboratories

US EPA's New Comprehensive Environmental Sampling & Analytical Methods (ESAM) Program

By Amelia McCall, public affairs specialist; Erin Silvestri, MPH, biologist; Emily Snyder, PhD, acting division director; Kathy Hall, MBA, health physicist; Sarah Taft, PhD, associate division director, US EPA National Homeland Security Research Center, Threat and Consequence Assessment Division

When an environmental catastrophe occurs, whether from an intentional contamination incident such as a terrorist attack or an unintentional incident such as an industrial spill, emergency responders and decision-makers need fast and accurate data for response, remediation and recovery options. Accurate measurements and fast laboratory analysis are critical in an incident aftermath because responders need to determine the contaminant type and extent to make informed decisions.

To help address this need and to support the US Environmental Protection Agency (US EPA) Environmental Response Laboratory Network (including the Water Laboratory Alliance), US EPA's Homeland Security Research Program (HSRP) developed the *Standardized Analytical Methods for Environmental Restoration following Homeland Security Events* (SAM) in 2004. The SAM was developed with input from experts across federal, state and local agencies, universities and municipalities, and was intended to be a compendium of analytical methods for use during environmental response activities. SAM is unique in that it identifies a single selected method for each analyte/sample type. Using the same set of methods permits sample load sharing between laboratories, increases analysis speed, improves data comparability and simplifies potential outsourcing for analytical support.

Over time, additional resources have been added to the SAM website, such as the Sample Collection Information Document, which provides information for sample collection (e.g., sample volume, container types, preservation and shipping), and other companion documents that support rapid screening, preliminary sample analysis and sample disposal. SAM also included full documentation of publicly-available laboratory methods and links to technical contacts and key collaborators. Since implementation of the original SAM document, additional priority analytes and matrices have been added over the many

2004	2017
Chemicals / Matrices	
82 / 4	145 / 5
Pathogens / Matrices	
27 / 3	33 / 5
Radiochemicals /Matrices	
N/A	36 / 10
Biotoxins / Matrices	
N/A	17 / 5

Figure 1: A comparison of methods in the original SAM document (2004) and the current version (2017).

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The Association of Public Health Laboratories (APHL) works to strengthen laboratory systems serving the public's health in the US and globally. APHL's member laboratories protect the public's health by monitoring and detecting infectious and foodborne diseases, environmental contaminants, terrorist agents, genetic disorders in newborns and other diverse health threats.

Funders

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document revisions. The current version, updated in 2017, is called *Selected Analytical Methods for Environmental Remediation and Recovery*.

Sponge wipe sampling is used to test surfaces for contaminants that may be present after a disaster. Sampling procedures such as these can be found in the Sample Collection Information Document. Photo: US EPA

Since 2004, it has become clear that during a response, it is critical for sampling and analysis personnel and decision-makers to have timely access to a more complete set of resources that support environmental characterization. To address this, HSRP expanded the SAM program and associated companions into one all-encompassing initiative: the Environmental Sampling & Analytical Methods (ESAM) program. ESAM—a one-stop resource for sampling and analysis needs before, during and after an environmental contamination—is a collection of field- and laboratory-ready documents and web-based tools for responders, laboratories and decision-makers. As a comprehensive program, ESAM helps coordinate field and laboratory response to chemical, radiochemical, biotoxin or pathogen contamination. ESAM provides the single best-available sample collection, handling, processing and analysis method to improve data evaluation and validation. Most importantly, when a single method is used, those using the data can feel confident about its integrity, more easily interpret what it means, communicate the data and make decisions based upon it. In its final embodiment, ESAM will also provide resources to develop sampling strategies and to interpret and manage data.

The ESAM website is currently broken up into several components (Figure 2):

- **Sample Collection and Handling:** Includes the SCID query tool (for searches based on analyte, sample type and parameters that display in the results) and links to HSRP-developed sample collection protocols and procedures. It will eventually include information related to sampling strategy development.
- **Sample Processing and Analysis:** Includes the SAM query tool (for searches based on analyte, sample type and parameters that display in the results) and HSRP and HSRP partner-developed sampling processing and analytical protocols and methods.
- The **Sample Results Interpretation** and **Data Management** sections are still under development.

Figure 2: Diagram of ESAM program components.

All these components work together to support decisions for environmental remediation and recovery. Having these resources in one location cuts down on time needed to search for the needed resources during an actual contamination incident.

The ESAM webpage will be updated as new methods and resources become available. Laboratory and sampling personnel, who may be responsible for sample collection or analysis following an environmental contamination event, should review and become familiar with the resources available there. This review improves the nation's preparedness and facilitates resource feedback. We welcome laboratory feedback on the ESAM website, method improvements and gaps for future method research. Please send feedback to Kathy Hall at Hall.Kathy@epa.gov.

Actualizing the Benefits of Shoreline Restoration in Racine, WI

By Julie Kinzelman, PhD, laboratory director, City of Racine Public Health Department Laboratory

Coastal and inland ecosystems are constantly challenged as adjacent land becomes increasingly urbanized. Removing natural buffering systems, such as wetlands, can have adverse impacts on coastal and human health by altering natural chemical (carbon, nitrogen, phosphorous and sulfur) cycles. For example, influxes of phosphorous, a common lawn fertilizer constituent, can result in the propagation of green plants (which are often non-native species), eutrophication and algal blooms. Increased population density associated with urban centers also increases pollution delivery to the nearshore environment through storm water discharge and sewage releases. As a result, water quality impairments are affecting urban beaches throughout the Great Lakes and limiting public access to recreational waters. In addition to increasing the likelihood of waterborne disease outbreaks, beach closures impact recreation, economics and the perceived value of coastal water resources.

Breakwater supplement (to reduce overtopping from Lake Michigan during large storms), constructed wetlands and a variety of native vegetation transformed the landscape at Samuel Myers Park. Photo: Julie Kinzelman

Regulatory monitoring provides public health protection, but more intensive scientific studies are necessary to detect contamination sources. Given sufficient quality and quantity, expanded monitoring data can help identify and develop cost-effective remediation measures. The City of Racine Public Health Department Laboratory has embraced this course of action, employing beach sanitary surveys to identify pollution sources and develop sustainable solutions and best practices to restore beneficial uses to coastal municipal parks, while protecting public health in the context of water recreation. The restoration of Samuel Myers Park is one such example.

Prior to restoration, Samuel Myers Park was primarily comprised of non-native Phragmites and other invasive plant species. The legacy boat launch (lower right) was unusable and the flat topography resulted in the accumulation of storm water runoff on land. Photo: City of Racine Public Health Laboratory

Samuel Myers Park is located along the shores of Lake Michigan in Racine, WI. Initially comprised of a turf grass area and boat launch, the park's waterfront has gradually changed over the decades due to the accumulation of sediment transported via alongshore currents affected by hydrological changes. Sediment has decreased the adjacent embayment's water depth, distancing the boat launch from the water's edge. Successive accretion periods also resulted in shoreline sediment accumulation, allowing the formation of wetlands. However, wetland function was impaired because they were primarily comprised of non-native, invasive species, and storm water accumulated along the shoreline due to low elevations. Surface water quality was unsupportive of recreational uses and a swimming prohibition, implemented by the health department, had been in place for over a decade.

In 2009, a four-year intensive monitoring program began to identify pollution sources. Poor water quality at Sam Myers Park was found to be associated with shoreline sources of *E. coli* including high amounts of submerged algae, a significant fecal burden in foreshore sediments, and wildlife (primarily geese and seagulls). Environmental variables such as turbidity, northern alongshore currents, southern winds, and 24-hour rainfall served as indicators of, or delivery mechanisms for, the transfer of bacteria to the nearshore water.

Once pollution sources were identified, engineering plans were developed, a wetland delineation was performed and state/federal permits were secured. More frequent and intense storms required incorporation of design elements that could absorb the force and accommodate the volume of event-associated water, such as raising the height of the existing breakwater and constructing wetlands and rain gardens. As part of the restoration process, five acres of invasive species were removed and replaced with 40,000 native plants, forbs and trees. Native species are well adapted to this environment and, due to their root structure, are good storm water infiltrators that work in tandem with the natural and constructed features.

Year	Sample Depth (ft)	n	*E. coli* (Most Probable Number/100 ml)	Advisories/ Season	% of Beach Season
2015	3	14	178.5	6	42.9
2016	3	8	108.5	1	12.5
2017	3	13	41	1	7.7

Table 1. Water quality has improved substantially since restoration began in 2014, with only one water quality advisory occurring in 2017.

Since construction began in November 2014, the restoration process has resulted in reduced nutrient loading, improved surface water quality (Table 1), the return of fish/amphibians/reptiles and increased migratory bird diversity. Improved wetland function has been aided by the development of successive coastal ecosystems (e.g., upland, dry prairie, interdunal/constructed wetlands, dunes and coastal wetlands), preventing direct storm water runoff from reaching the shoreline. The taller breakwater and improved hydrologic connectivity between the wetland features have proven protective through successive storm events.

Samuel Myers Park is now the second-best birding hotspot in Racine, with 38 new species seen since 2014, and a frequent destination for Audubon Society local chapter members. In 2017, it was designated as a Monarch Waystation due to its three butterfly gardens and variety of milkweed species. Nearshore water quality has improved, resulting in the removal of the swim ban and creation of an offshore/"boater's" beach, which provides an opportunity for water recreation within the shallow embayment while protecting the critical native habitat along the shoreline.

One of three butterfly gardens at Samuel Myers Park. Photo: Julie Kinzelman

Unique in the Milwaukee-Chicago corridor, this park now serves as a recreation destination and an outdoor education venue for local schools and universities. Total funding from research to implementation was approximately $1.07 million from 23 different sources, including US EPA Great Lakes Restoration Initiative, Fund for Lake Michigan, WI Coastal Management Program, US Forest Service, foundations and local environmental groups.

Conducting on-the-ground restoration is not a common laboratory activity, but through collaboration and decision-making informed by monitoring data, this became a feasible project. Specifically, the laboratory data guided the development of the engineering controls at the outset and proved they were functioning as

anticipated after construction occurred. Other laboratories looking to undertake this type of project would need to be prepared to work outside of their discipline.

The Racine Public Health Department Laboratory will continue to conduct annual wetland mitigation assessments, manage invasive species and increase the tree canopy/native plant communities at Samuel Myers Park over the next four years. There are several new laboratory collaborations with the City of Racine on the horizon, as well. One will be with the Storm Water Utility to design plans to naturalize or create storm water retention features in other parks. Another will assist the Forestry Department in managing the plant communities at Olsen Prairie, a 23-acre nature area located in the southeastern portion of the City that includes hiking trails, wetlands and a woodland area.

The Samuel Myers Park restoration project is an excellent example of a public health-initiated, science-driven restoration effort designed to improve coastal habitat, increase resiliency and enhance utility in a highly-urbanized population center. Please contact Julie Kinzelman for more information.

Agricultural Water Testing and the FSMA Produce Safety Rule

By Don Stoeckel, regional extension associate, and Betsy Bihn, director, Cornell University, Produce Safety Alliance; Phil Tocco, educator, Marissa Schuh, educator, and Ben Phillips, educator, Michigan State University Extension; and Kaiping Deng, research assistant professor, Illinois Institute of Technology, Sprout Safety Alliance

In 2011, the Food Safety Modernization Act (FSMA) updated US food safety regulatory standards and for the first time included regulations governing the production of fresh produce (e.g., fruits, vegetables, herbs, nuts, mushrooms, sprouts). The US Food and Drug Administration creates the FSMA rules and oversees enforcement, often in collaboration with states. The purpose of this article is to describe:[1]

- Specific agricultural water testing requirements from the FSMA Produce Safety Rule,
- How these requirements might impact analysis requests to water testing laboratories, and
- How agricultural water testing may be different from the testing needs of more traditional laboratory clients such as drinking water utilities, wastewater utilities, water districts, and public beach managers.

Many of the words and numbers associated with agricultural water are similar to ambient and drinking water analysis but some specific FSMA Produce Safety Rule requirements are different, such as sampling frequency and situational acceptability of leaving in-line devices in place when sampling.

Which types of water need to be tested?

The FSMA Produce Safety Rule regulatory requirements are limited to agricultural water that contacts covered produce (see Key Definitions) during activities like irrigation, foliar pesticide application, washing, application of ice; or associated food contact surfaces (e.g., boxes, tables, workers' hands).

Microbial quality standards are different for agricultural water prior to harvest (production water) versus during or after harvest (postharvest water). Sprouts, despite being a produce crop, have their own subpart within the FSMA Produce Safety Rule and sprout-specific requirements are highlighted throughout this document.

When is agricultural water testing required?

FSMA Produce Safety Rule water compliance dates are staggered according to farm business size and different compliance

[1] These suggestions are not a comprehensive overview of the FSMA Produce Safety Rule's water quality requirements. Find more information online about the FDA's FSMA Final Rule on Produce Safety, the FDA Produce Safety Network, the Produce Safety Alliance, the Sprout Safety Alliance and produce safety education teams, such as the one at Michigan State University.

dates apply to sprouts (January 26, 2017 for the largest sprout growers). FDA issued a proposed rule[2] that extends agricultural-water-related compliance dates for covered produce farms (other than sprouts) until at least January 26, 2022. The largest produce farms—those with over $500,000 average annual produce sales— have the earliest compliance dates. Dates for small farms ($250,000-$500,000) and very small farms ($25,000-$250,000) are one or two years later, where size is based on average annual produce sales. Farms with <$25,000[3] average annual produce sales are not covered. Despite the expected extension of compliance dates for most water requirements, farmers are encouraged to begin sampling now, and many farmers are already sampling their water to meet buyer requirements.

What are the sampling and quality requirements?

Different sampling and quality requirements apply to different agricultural water uses. Please note that agricultural water requirements (for covered produce other than sprouts) are under FDA review, so they may change prior to the current compliance dates. The water quality requirements for sprout production, on the other hand, are final as described below. Produce growers will only test for generic *E. coli* but sprout growers also have a requirement to test spent sprout irrigation water, from every batch produced, for pathogens.

Below are summaries[4] of sampling and quality requirements for different uses of agricultural water. Results may be colony forming units (CFU) or most probable number (MPN) depending on the method used:

Production water for covered produce other than sprouts: Untreated surface water must have a rolling 4-year, 20-or-more-sample data set (≥5 samples per year) with a geometric mean (GM) generic *E. coli* concentration of ≤126 CFU/100 mL and statistical threshold value (STV) of ≤410 CFU/100 mL after an initial 20-or-more-sample data set collected over 2 to 4 years.

For untreated ground water, the same values apply but they are based on a rolling 4-year, 4-or-more-sample data set after an initial 1-year, 4-or-more-sample data set.

Calculators are available to assist with calculating the GM and STV values and understanding the results for surface water and

Key Definitions* FSMA Produce Safety Rule (21 CFR Part 112)

Agricultural Water: "Water used in covered activities on covered produce where water is intended to, or is likely to, contact covered produce or food contact surfaces, including water used in growing activities … and in harvesting, packing, and holding activities …"

Covered Activity: Activity covered by the FSMA Produce Safety Rule requirements. This includes "Growing, harvesting, packing, or holding covered produce on a farm" as well as "… manufacturing/ processing … to the extent that such activities are within the meaning of 'farm' as defined in this chapter …"

Covered Produce: Produce covered by the FSMA Produce Safety Rule requirements. "Produce that is subject to the requirements of this part … refers to the harvestable or harvested part of the crop" including fresh fruits, vegetables, herbs, nuts, mushrooms, and sprouts grown on farms.

Produce: "Any fruit or vegetable (including mixes of intact fruits and vegetables) and includes mushrooms, sprouts (irrespective of seed source), peanuts, tree nuts, and herbs … Produce does not include food grains meaning the small, hard fruits or seeds of arable crops … for use as meal, flour, baked goods, cereals and oils …"

Spent Sprout Irrigation Water: "Water that has been used in the growing of sprouts."

**Abridged as indicated. Refer to the Code of Federal Regulations Title 21, Part 112.3 for full definitions.*

[2] Not final as of article publication.

[3] Three-year rolling average indexed for inflation to 2011. Current inflation-adjusted values are published by FDA in March each year.

[4] These are generalized descriptions of the FSMA Product Safety Rule's requirements. Training courses by the Produce Safety Alliance and the Sprout Safety Alliance are good resources for understanding the complexities of the water quality requirements and other topics in this article.

ground water data sets. The GM and STV values are collectively referred to as the microbial water quality profile (MWQP) in the FSMA Produce Safety Rule.

Production water for sprouts; postharvest water for all covered produce, food contact surfaces and handwashing:

Untreated ground water for sprout production and postharvest uses for all covered produce must have no detectable generic *E. coli* in 100 mL of water. Four or more samples are required during the initial year, with a rolling four-year data set of at least one sample per year thereafter.

Untreated surface water may not be used for these purposes (e.g., sprout production, hand washing, top icing, field packing, packing house sanitation).

Municipal water does not need to be tested by the farm, but a copy of test results or current certificates of compliance must be obtained from the provider for farm records.

Spent sprout irrigation water:

Spent sprout irrigation water from each batch must have no detectable *E. coli* O157:H7, *Salmonella* spp., or any other pathogens "reasonably necessary to minimize the risk of serious adverse health consequences or death from use of, or exposure to, sprouts."

What methods are acceptable under the FSMA Produce Safety Rule?

The FSMA Produce Safety Rule has a specific set of methods requirements. In all cases, regulatory monitoring may be done using a cited method or a method that is "at least equivalent … in accuracy, precision, and sensitivity" to the cited method. For generic *E. coli*, the cited method is EPA 2009, Method 1603 (modified mTEC). See Table 1 for acceptable equivalent test methodologies outlined by the FDA. For *E. coli* O157:H7 and *Salmonella* spp. the cited method is FDA 2005 "Testing Methodologies for *E. coli* O157:H7 and *Salmonella* species in Spent Sprout Irrigation Water (or Sprouts)." The authors recommend that farmers or their representatives who request water testing should prioritize methods that are acceptable under the FSMA Produce Safety Rule.

What are the sampling and handling requirements?

Under the FSMA Produce Safety Rule, agricultural water samples must be aseptically collected and tested. Other

	Membrane Filtration Methods (quantitative)	
Production or Postharvest Water	**Cited Method in FDA Fact Sheet**	**Shorthand Method Name**
	EPA Method 1603	Modified mTEC agar
	EPA Method 1103.1, Standard Methods 9213 D, ASTM method D5392-93	mTEC agar
	EPA Method 1604	MI agar
	Standard Methods 9222 B followed by 9222 G	m-Endo followed by NA-MUG agar
	Hach method 10029	m-ColiBlue 24 ampules
	Most Probable Number Methods (quantitative)	
	Product/Medium Named in FDA Fact Sheet	**Method Notes**
	IDEXX Colilert test kit, only if using Quanti-Tray/2000	There are several formats for Colilert, be sure the lab uses the FDA-named quantitative format. One reference protocol for this product is Standard Methods 9223B
	IDEXX Colilert-18 test kit, only if using Quanti-Tray/2000	
	Presence/Absence Methods (in 100 mL)	
Postharvest Water Only	**Product/Medium Named in FDA Fact Sheet**	**Manufacturer/Source**
	TECTATM EC/TC medium and instrument	Veolia Water Technologies
	Modified Colitag, ATP D05-0035	CPI International
	IDEXX Colilert test kit	IDEXX Laboratories, Inc.
	IDEXX Colilert-18 test kit	IDEXX Laboratories, Inc.
	IDEXX Colisure test kit	IDEXX Laboratories, Inc.
	E*Colite Bag or Vial test	Charm Sciences
	Readycult Coliforms 100	EMD Millipore, catalog 101298

Table 1. Acceptable FSMA Produce Safety Rule agricultural water testing methods for generic *E. coli*, as found in the FDA fact sheet on equivalent testing methodologies.

requirements (e.g., hold temperature, hold time) are indicated by reference to EPA Method 1603, the FDA sprout water testing methodology, or any equivalent methodology used. If the farm representative is collecting the sample, they may ask for guidance about aseptic collection technique and handling requirements.

Communicating with farms about sampling, handling, and analysis requirements

Laboratory representatives should keep the FSMA Produce Safety Rule requirements in mind when making recommendations about on-farm sampling, sample handling, and testing methodology. Specifically, the current language (subject to revision as FDA re-evaluates water-related requirements) is "the samples of agricultural water must be representative of your use of the water and must be collected as close in time as practicable to, but prior to, harvest." Many farms have questions about timing and location of sample collection. Until formal guidance is issued and compliance dates come into effect, the following recommendations from the authors may be useful:

Timing

Some farms grow multiple crops with different harvest timeframes making it difficult to determine when to sample close to harvest. Until compliance, we recommend that farmers (other than sprouts) sample each surface water source three times during the season, prior to and during water use, to establish a baseline understanding of quality. Ground water generally is sampled once, preferably during the growing season.

Location

We currently recommend that farmers sample at the source, as close to the intake pipe or wellhead as possible, or from the distribution system. Some farms use inline devices such as sand filters to improve water quality. In such cases, they can sample after the device and do not necessarily need to remove the device even when sampling from a location in the water distribution system where water quality is affected by the device.

Conclusion

Keep in mind that the FSMA Produce Safety Rule agricultural water quality requirements for covered produce crops (other than sprouts) are being re-evaluated, including compliance dates and testing strategies. For laboratories that work with farms, the Produce Safety Alliance maintains a fact sheet that summarizes current status.

We appreciate your attention to this introduction of water characterized as agricultural water, and welcome feedback and questions that you may have after reviewing this article. For more information, contact Don Stoeckel.

Pasadena Becomes Home to California's Newest Reference Laboratory

By Mui Koltunov, PhD, chief, Environmental Chemistry Laboratory-Pasadena

The California Department of Toxic Substances Control (DTSC), Environmental Chemistry Laboratory (ECL) has two laboratories that are strategically placed in northern and southern California to support the mission of DTSC. The northern California laboratory is located at the Aquatic Park of Berkeley, a hub of academic, biotech and pharmaceutical research and innovation.

The southern California laboratory has a new facility in Pasadena to replace its archaic laboratory that had been located in downtown Los Angeles for the past 30 years. The 13,000 square-foot facility houses state-of-the-art analytical instruments and equipment to develop methodologies to identify and quantitate regulated and emerging chemicals of concern for the State of California.

Pasadena ECL's new Organic Instrumentation Laboratory (photo taken before fully occupied or functional). Photo: Ament Commercial Photography

ECL coordinates closely with its departmental programs to enforce California's hazardous waste laws and regulations. The following are some examples of ECL's projects:

Toxic Metals in Jewelry

ECL collaborated with DTSC's Office of Criminal Investigations (OCI) to confirm toxic lead and cadmium levels in jewelry sold by retail stores in Oakland and wholesale suppliers in downtown Los Angeles. The Department removed or confiscated hundreds of different styles of toxic jewelry, such as hair accessories, necklaces, pendants and bracelets. ECL measured parts of children's jewelry that contained up to 96% lead, which exceeds the regulatory limits of 0.02% – 0.06%, depending on the jewelry material. Up to 99% cadmium was found in parts of children's jewelry, which exceeds the 0.03% regulatory limit. The efforts of ECL and OCI resulted in penalties as high as $1.6 million against these stores and suppliers for selling toxic products.

Name	Environmental Chemistry Laboratory, Pasadena (ECL-Pasadena)
Location	757 S. Raymond Ave., Suite 105, Pasadena, CA 91105
Population Served	39.78 million Californians
Funding Source	California special and general funds
Matrices	Solid wastes, water, indoor air, soil gas and products
Instrumentation	• GC-FID: Gas chromatography – Flame Ionization Detector • GC-μECD: Gas chromatography – micro-Electron Capture Detector • GC-MS: Gas chromatography – Single Quadrupole Mass Spectrometer • GC-MS-MS: Gas chromatography – Triple Quadrupole Mass Spectrometer • GC-QTOF: Gas chromatography – Quadrupole Time of Flight • ICP-OES: Inductively Coupled Plasma – Optical Emission Spectroscopy • ICP-MS-MS: Inductively Coupled Plasma – Triple Quadrupole Mass Spectrometer • LC-MS-MS: Liquid Chromatography – Triple Quadrupole Mass Spectrometer • LC-TOF: Liquid chromatography – Time of Flight Mass Spectrometer • FIMS: Flow Injection Mercury System • DMA: Direct Mercury Analyzer
Number of Staff	15

People vs. Comcast

ECL coordinated with OCI, the Alameda County District Attorney's Office Environmental Protection Division and the California Highway Patrol to perform all analytical testing of samples collected from Comcast facilities during waste inspections. ECL analytical data supported the allegations against Comcast for illegal hazardous waste management, resulting in a settlement of $25.95 million. As part of the settlement, ECL received $1.6 million to enhance its analytical capability, OCI received $400,000 in equipment and DTSC received $200,000 in reimbursement costs.

Senate Bill (SB) 1249 – Enactment of Metal Shredding Facilities Law

The Metal Shredding Facilities Law requires DTSC to evaluate the risks posed by metal shredding facilities and the management of metal shredder aggregates. ECL participated in the Treatability Study to evaluate the process effectiveness for treating and managing metal shredder aggregates. ECL analyzed 575 samples through more than 3300 analyses to measure the concentration of metals and polychlorinated biphenyls (PCBs) that could potentially leach into the environment from these processes. The results indicated that the process used to treat metal shredder aggregates was ineffective at preventing metals from leaching into the environment above the regulatory limits. Alternative management standards need to be explored or the facilities and their hazardous wastes must be subject to full hazardous waste management requirements.

"Toxic Crusaders" STEM Outreach Event

ECL also conducts outreach activities to help educate and inform our stakeholders about the work we do. In collaboration with APHL, ECL recently held a four-hour STEM event for 32 students from local Los Angeles County middle schools prior to the 2018 APHL Annual Meeting in Pasadena. The students had a chance to conduct an investigation of a hypothetical spill at their local playground. Students collected environmental samples at a mock contamination site, characterized sample corrosivity and measured toxic chemical concentration using Inductively Coupled Plasma – Optical Emission Spectroscopy and Ultraviolet – Visible Spectrophotometer. According to student and volunteer feedback, the STEM event was a great success—many reported a desire to participate in future Toxic Crusaders events.

A "Toxic Crusader" collects contaminated samples at a hypothetical spill site. Photo: ECL-Pasadena

Future Collaborations

ECL welcomes the opportunity to collaborate with other local, state, federal and international entities to develop new methodologies and technologies for emerging contaminants. If interested, please contact Mui Koltunov.

National Atmospheric Deposition Program Moves to Wisconsin State Lab of Hygiene

By Janet Klawitter, public affairs manager, Wisconsin State Laboratory of Hygiene

The Wisconsin State Laboratory of Hygiene (WSLH) at the University of Wisconsin–Madison (UW) is the new Central Analytical Laboratory (CAL) and Program Office (PO) for the National Atmospheric Deposition Program (NADP).

NADP serves public and environmental health, science, education and agriculture by monitoring North America's precipitation and atmosphere for a range of chemicals and uses that data to determine time and space trends for concentration and deposition.

NADP data have been used for decades to understand and solve real-world problems impacting people and the planet, including helping to facilitate cleaner water, healthier air quality, more productive fisheries, smarter environmental planning, improved air quality and climate forecasting, stronger roads and buildings, and responsible environmental stewardship.

"NADP is the international gold standard for long-term, high-quality air pollutant monitoring and has been in operation for 40 years (since 1978). The program aligns quite well with the WSLH's mission," said WSLH Director and UW Civil and Environmental Engineering Professor Jamie Schauer, NADP principal investigator. "NADP coming to the WSLH will facilitate partnerships that will ultimately strengthen the program and the impact of the NADP products. As a part of UW-Madison, the WSLH is closely integrated with university research efforts and bridges the connection with academic research and public health surveillance and monitoring. We believe the NADP program will benefit from expanded interactions with academic research and public health networks, including public health laboratories."

More than 300 monitoring sites in North America participate in NADP's five networks:

- **National Trends Network (NTN):** Provides a long-term record of the acids, nutrients, and base cations in US precipitation
- **Mercury Deposition Network (MDN):** Provides data on the geographic distributions and trends of mercury in precipitation
- **Atmospheric Integrated Research Monitoring Network (AIRMoN):** Reports measurements of acids, bases, and nutrients for studying and modeling atmospheric processes
- **Atmospheric Mercury Network (AMNet):** Reports atmospheric mercury concentrations for determination of mercury dry deposition
- **Ammonia Monitoring Network (AMoN):** Reports atmospheric ammonia concentrations to determine ammonia dry deposition

As the CAL and PO, the WSLH provides pre-analytic services, analytic testing and post-analytic results and data analysis.

NADP is a cooperative effort between many different groups—federal, state tribal and local governmental agencies, educational institutions, private companies and non-governmental agencies—which provide funding, scientific and technical support. Funding comes from monitoring site participants and the following primary federal agencies:

- National Park Service
- US Geological Survey
- National Oceanic & Atmospheric Administration
- Bureau of Land Management
- US Environmental Protection Agency
- US Dept. of Agriculture Forest Service
- Agricultural Research Service

April Grant prepares NTN samples for ammonium and orthophosphate analysis using flow injection analysis. NTN is the only network providing a long-term record of precipitation chemistry across the US. Photo: Jan Klawitter

The NADP at the WSLH measures pH, conductance, calcium, magnesium, sodium, potassium, sulfate, nitrate, bromide, chloride, ammonium, ambient ammonia gas, and gaseous oxidized, particulate-bound, and elemental gaseous mercury. Elemental and methyl mercury measurements in precipitation samples are performed by Eurofins Frontier Global Sciences, Inc., in Seattle.

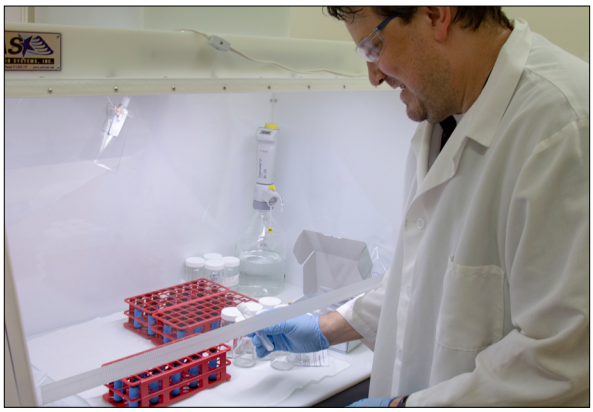
All data are made publicly available on the NADP website and through printed reports. The PO also works with NADP committees on network operations, science, education, and outreach activities.

"NADP has played a key role in providing long-term monitoring data to assess policies aimed at reducing air pollution and ecological impacts of atmospheric deposition," Schauer explains. "The program includes monitoring networks for programs including acid rain, mercury, and reactive nitrogen. Policy implementation for acid rain mitigation is relatively mature and the evolution of these policies is reflective in NADP monitoring data. Programs for regulating mercury and reactive nitrogen deposition are less mature and NADP monitoring will be critical in future years to assess control program efficacy."

"The WSLH and other public health laboratories have not been directly involved with NADP before this, but NADP works with many of our partner agencies including state, tribal, and local environmental control agencies," Schauer said. "NADP coming to the WSLH provides an opportunity to better connect public health laboratories to air quality networks that are critical to protecting human health and ecosystem health. We look forward to working with other research entities and public health laboratories to be on the forefront of environmental monitoring."

The NADP CAL and PO had been housed at the University of Illinois at Urbana-Champaign.

Part of the University of Wisconsin-Madison since its founding in 1903, the WSLH provides public, environmental, and occupational health laboratory and consultation expertise to a wide variety of national, state and local partners. For more information about the NADP at WSLH and possible participation opportunities, please contact NADP Program Coordinator Michael Olson.



Jesse Wouters prepares AMoN samplers for shipment. AMoN is the only network providing a consistent, long-term record of ammonia gas concentrations across the US. Photo: Jan Klawitter

Removing Ammonia and Other Inorganic Contaminants from Drinking Water

by Michaela Burns, ORAU student contractor, US EPA, Office of Research and Development, Science Communications

Many United States drinking water sources are contaminated with excessive ammonia levels due to naturally-occurring processes like the nitrogen cycle and human-caused stressors like agricultural runoff. Though ammonia does not pose a direct health concern to humans, nitrification (the conversion of ammonia to nitrite and nitrate by bacteria) of ammonia in a drinking water distribution system can be a serious problem. Nitrification in the distribution system leads to issues such as pipe corrosion, water taste and odor changes, elevated nitrate and nitrite levels and potentially poor water treatment performance. The US Environmental Protection Agency (US EPA) is providing information and treatment approaches to communities to help them reduce inorganic contaminants like ammonia in their water supplies.

US EPA's research is crucial to supporting small drinking water systems on this issue. Small drinking water systems—those that serve 10,000 or fewer people—make up 97% of the 151,119 public drinking water systems in the United States. While many of these small systems provide safe, reliable drinking water to their customers, some small systems face many challenges maintaining sustainable service. These challenges include high operator turnover, aging infrastructure and lack of financial resources.

One successful example of US EPA's support of small systems is the study conducted in the small community of Palo, Iowa. Like other small systems in the Midwest, Palo is greatly impacted by ammonia in their drinking water source. Before 2008, Palo did not have a centralized water treatment or drinking water distribution center. Following extensive 2008

regional flooding, plans were made to build the infrastructure necessary to supply the community with potable drinking water. Crucially, the community needed a treatment system that could address high ammonia and iron levels in the source water. The Iowa Department of Natural Resources (IA DNR) requested US EPA assistance to address their water quality concerns. As a result, US EPA's Office of Research and Development, with support from US EPA's Region 7 and the IA DNR, conducted a pilot study to evaluate the ability of an innovative biological treatment to remove ammonia from Palo's source water.

The pilot treatment process was based on an US EPA-patented approach to reduce elevated ammonia and iron levels in source water. The treatment approach relies on naturally-present bacteria to convert ammonia (NH_3) to nitrite (NO_2) and then nitrate (NO_3) in the presence of oxygen. If the ammonia levels are lower than nitrate's maximum contaminant level (10 milligram of nitrogen/liter) in source water then this biological treatment can be effective and simple. This treatment approach can benefit consumers by producing more biologically-stable water, avoiding nitrification in the distribution system, and maintaining chlorine presence, which can be an important safeguard against microbial contamination.

The pilot biological water treatment system used to evaluate ammonia removal in Palo. Photo: US EPA

From March 2011 to April 2012, a pilot-scale treatment plant was installed and studied in Palo, IA. The pilot study was deemed a success in April 2012 because it achieved the goal of completely oxidizing the source water ammonia to nitrate. After its pilot success, the IA DNR approved treatment plans and the city of Palo built a full-scale treatment system based on the pilot system design.

US EPA has replicated the study success in towns across the country, even building on the initial US EPA-patented biological treatment approach. A big part of that success can be attributed to the Cooperative Research and Development Agreement (CRADA) US EPA has with AdEdge Water Technologies, LLC. The CRADA is to develop a full-scale biological treatment system called "NoMonia" based on the treatment approach used in Palo, IA.

One example is in Gilbert, IA, where US EPA researchers collaborated with the IA DNR and AdEdge to evaluate the ability of biological treatment to effectively reduce ammonia, iron, manganese and arsenic from source water. Like in the Palo, IA, project, the treatment depends on naturally-occurring bacteria to convert ammonia to nitrate. In addition, biological activity plays a role in the oxidation and removal of arsenic iron, and manganese. By the study's end, the source water's ammonia completely oxidized to nitrate and the arsenic and manganese was removed through anthracite silica sand filtration. The study, conducted from 2016 – 2017, will help in the design and installation of a full-scale water treatment plant that addresses customer needs in Gilbert, IA.

Similar research was shared at US EPA's 15th Annual Drinking Water Workshop: Small Systems Challenges and Solutions where APHL hosted a breakout group discussion of analytics and laboratory issues. The workshop was held from August 28-30 and provided in-depth information and training on various solutions and strategies to address small drinking water systems challenges. US EPA hosts this workshop in cooperation with the Association of State Drinking Water

The pilot biological water treatment system used to evaluate ammonia, arsenic, iron and manganese removal in Gilbert. Photo: US EPA

Administrators for state personnel responsible for drinking water regulation compliance and treatment technologies permitting. However, others—such as systems owners and operators, local and tribal government personnel and academics—may also be interested in the research. This conference is yet another example of US EPA's commitment to supporting small drinking water systems.

Multi-Residue Pesticide Screen by GC/MS in Maine

by Vera A. Maheu, chemist II, State of Maine Health & Environmental Testing Laboratory

Background

The State of Maine Health & Environmental Testing Laboratory (HETL) receives several requests each year for pesticide analysis. These requests generally come from people looking to purchase property that was once a farm or orchard and are concerned about what has been used on the property by previous owners. In the past, HETL has only been able to offer:

- EPA 8081 Gas Chromatography-Electron Capture Detector (GC-ECD) method for soils and water,
- EPA 8270 Gas Chromatography/Mass Spectrometry(GC/MS) method analysis for soils and water, and
- Regulated drinking water compounds for well water testing.

These lists were limited to mostly the EPA-banned, chlorinated pesticides. Other EPA methods allow other pesticide class testing (e.g., EPA 8141 for organophosphorus pesticides), but each method is generally limited to a specific class.

Because many pesticides (in various classes) are thermally-labile and will break down at typical GC inlet temperatures, most pesticide residue analysis is performed by High Performance Liquid Chromatography-Mass Spectrometry/Mass Spectrometry (HPLC-MS/MS). HPLC-MS/MS is able to analyze several pesticide classes at once, but the price makes it out of reach for many environmental laboratories.

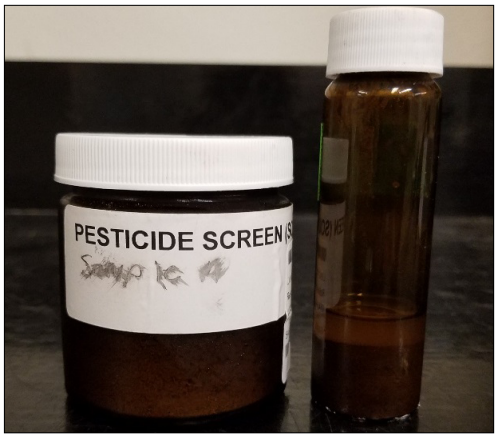
To better serve the public, HETL developed an in-house pesticide screening method using an Agilent 7890B Gas Chromatograph/5977A Mass Selective Detector with a 7693 autosampler. The GC is equipped with a Multi-Mode Inlet (MMI), allowing for a temperature-programmable injection. It should be noted that this pesticide screen is qualitative only, due to high costs of the pesticide standards.

Methodology

System operating parameters were taken from an Agilent application note (see references), with minor modifications:

- Column: Agilent HP-5MS, 30 m x 0.25 mm x 0.25 um
- Carrier Gas: Helium
- Inlet: Programmable Temperature Vaporizing (PTV) operated in Solvent Vent Mode
- Oven Temperature Program: 70° C (2 min), 25° C/min to 150° C, 3° C/min to 200° C, 8° C/min to 280° C (12 min). Total run time: 43.9 min
- PTV Program: 70° C (1.03 min), 600° C/min to 325° C
- Injection Volume: 50 µl
- Liner: Dimpled liner
- MSD Mode: Full Scan/SIM (Selective Ion Monitoring) simultaneous,
  or SIM only
- Solvent Delay: 3 min
- Source: Electron Impact (EI), 70 eV
- Source, Quad, Transfer Line Temp: 230, 150, 280 °C
- Scan Range: 50-550 u (atomic mass units)

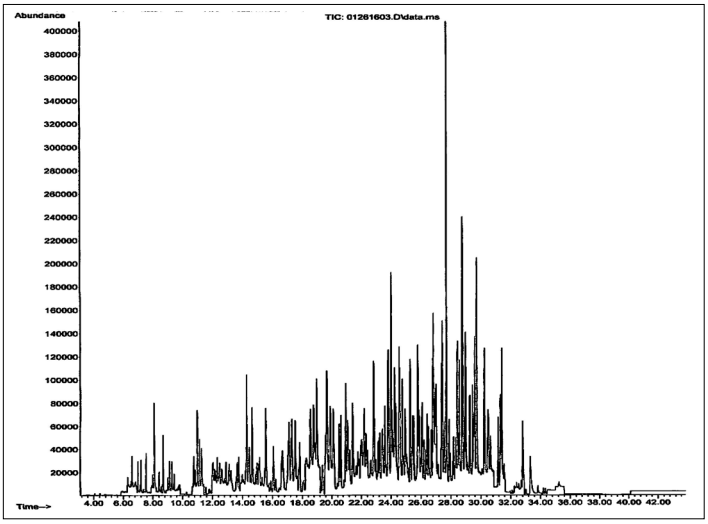
Pesticide standards were purchased as mixes from several suppliers, and each was diluted in acetonitrile to an appropriate analysis level (1.0 µg/ml for most compounds, a concentration assumed to be high enough above the signal-to-noise ratio to produce a decent size peak). Acetonitrile was chosen for the solvent to mimic the Quechers pesticide residue method typically performed by HPLC-MS/MS and to avoid solubility issues. Each mix was analyzed separately using a standard 1 µl injection/splitless method to determine retention time and obtain full-scan spectra for each compound. Most peaks were easily identified by performing a library search. Online and literature research was required to find the spectra of some compounds to scan for the appropriate ions in the chromatogram, and thus locate the peak.



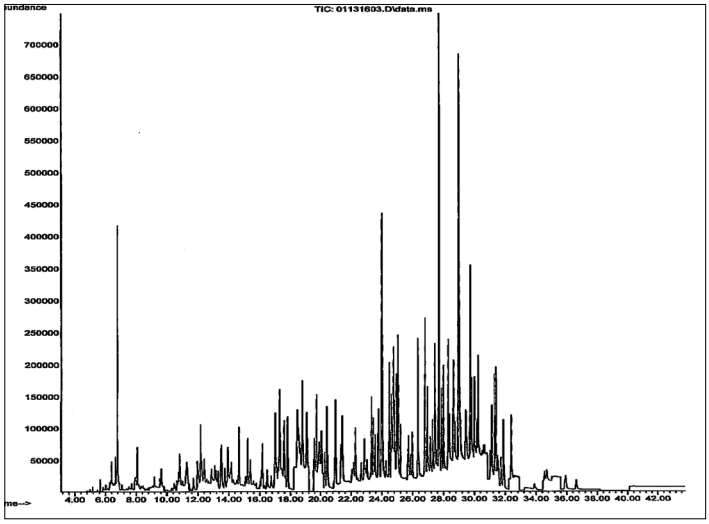
Typical soil sample and extract. Amber glass used to prevent photodegradation. Photo: Vera Maheu

Triphenylphosphate (from the Quechers method) was selected as the internal standard, and the method was Retention Time Locked to this compound. A method database was created for over 350 pesticides, and the Agilent Chemstation software's Auto SIM option was used to generate a SIM report. This report automatically groups compounds into SIM segments, based on factors such as switching time required between SIM groups when operating in Full Scan/SIM modes simultaneously, dwell time of the ions in the SIM group, etc. The software will also list the quantitation and qualifier ions that were user-assigned during method database creation. This acquisition method required the use of 50 SIM groups, but up to 100 SIM groups with 60 ions each can be created for a single data acquisition method. The SIM report can then be used to fill in the SIM Segment tables in the GC/MS data acquisition method. It should be noted that this is a very time-consuming process. Due to the number of compounds in the database, and the time required by the instrument to switch between Full Scan/SIM, some SIM segments had a significantly larger number of compounds. For these segments, some qualifier ions needed to be eliminated to stay within the 60 ion/segment limit.

Once the SIM segments were populated, the GC inlet was reconfigured for a large-volume injection (50 µl) using the Solvent Vent mode. The standard tower for the 7693 autosampler can accommodate a 100 µl syringe and can inject up to 50 µl. A dimpled liner is used for the Solvent Vent mode; the PTV inlet allows for a cool injection onto the liner, followed by a very fast temperature ramp (see operating parameters above), thus preventing breakdown of the thermally-labile pesticides in the inlet. Typical EPA methods require a much higher inlet temperature with no temperature ramp, but this



204 Pesticide "GC Mix," 5 ng/ml.



203 Pesticide "LC Mix," 5 ng/ml.

method mimics the lower HPLC-MS/MS temperatures. The Agilent software guides the user through the steps to create the injection parameters. The solvent used and the boiling point of the first eluting compound, as well as the injection volume, must be entered, and the injection speed is automatically calculated for the solvent to be properly vented. This particular method resulted in a 1.03 minute injection time.

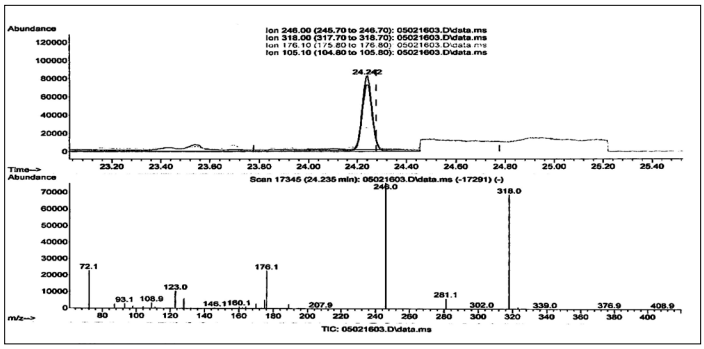
To evaluate the instrument detection limits for the various compounds, standards were prepared at 0.5-100 ng/ml (congeners 0.05-10 ng/ml) and analyzed in SIM-only mode. Most compounds were identifiable at the lowest concentration level evaluated—even the congeners at 0.05 ng/ml—while some compounds were grossly overloaded at the 100 ng/ml level. A wide variety of pesticide classes were evaluated, including organochlorine, organonitrogen, organophosphorus, pyrethroids, neonicotinoids, nitrogen-phosphorus, fungicides and carbamates. Overall, peak shapes were quite good, with some fronting or tailing observed on a few compounds.

To extract pesticides from soils, the "shake and shoot" method is used in order to reduce solvent use and save time compared to published EPA methods. Extract 10 g with 10 ml of acetonitrile. An aliquot of the extract is subjected to a graphitized carbon black cleanup before analysis by GC/MS.

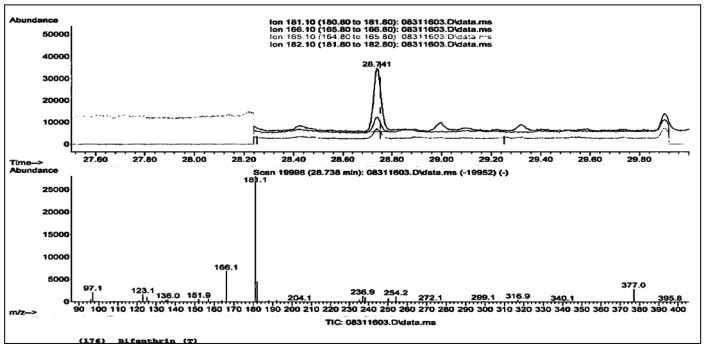
Lessons Learned

Setting up a Full Scan/SIM method for over 350 compounds is incredibly cumbersome, and requires limitations on the number of ions used to identify a compound.

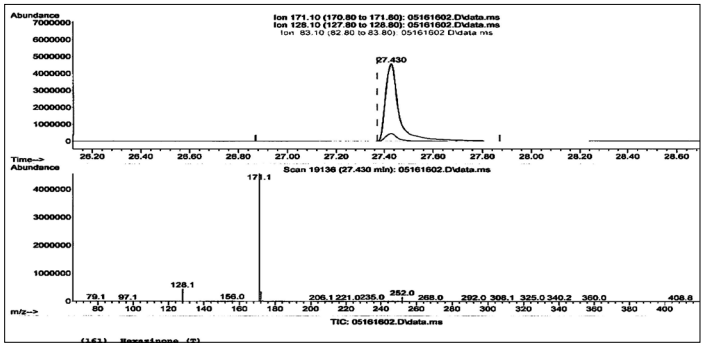
The Retention Time Locking is a valuable tool, but it's not perfect—care must be taken to ensure that compounds near the beginning or end of a SIM segment are not lost when the column is clipped and the method is re-locked, which can cause slight changes in retention times. To avoid this, a compound's quant ion can be added to the SIM segment immediately before or after (assuming the 60 ion limit has not already been reached) so it does not get lost. Peak integration and quantitation across SIM segments was possible using this technique. As stated previously, the temperature-programmable inlet allows for many thermally-labile pesticides to be analyzed by GC/MS rather than by HPLC-MS/MS. However, it takes quite a bit of time



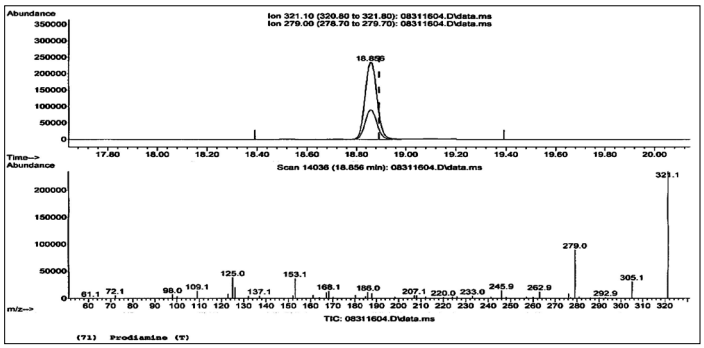
p,p'-DDE extracted from soil, a breakdown product of p,p'-DDT.



Bifenthrin, a pyrethroid insecticide used on corn.



Hexazinone (Velpar), a broad spectrum herbicide used extensively on blueberry fields in Maine.



Prodiamine, a pre-emergent herbicide used on crabgrass.

for the inlet to cool between runs. Sample particulates must be removed carefully to prevent clogging of the dimpled liner and Multi-Mode Inlet components. If the Multi-Mode Inlet is not functioning properly, compounds can migrate onto the column before the start of the temperature program and desorption from the liner. This can result in more than one peak per compound, separated by several minutes, and may not be noticeable if running in SIM only, as the appropriate quant ion may not be in the SIM segment corresponding to the extra peaks. A loss of response will be seen, but the true problem will only be realized when running Full Scan.

When collecting data in Full Scan/SIM simultaneously, the Agilent software will quantitate based on Full Scan data. SIM-only acquisition must be used to quantitate from the SIM data.

Options for Future Method Development

The Agilent software allows for unique multiplier voltages for each SIM segment. This could be a useful option for compounds that give a low response due to their chemical structure, such as Rotenone—a broad-spectrum insecticide, pesticide and piscicide (fish killer).

Summary

With the technology built into today's standard GC/MS systems, a wide variety of pesticide classes can be analyzed, even those once considered to be applicable only to HPLC-MS/MS analysis. Full Scan/SIM simultaneous data collection, decreased noise, improved sensitivity, source inertness, temperature programmable inlets, large volume injections, and fast computing are now commonplace. The cost of a Multi-Mode Inlet option is significantly less expensive than an HPLC-MS/MS system. Environmental laboratory personnel can easily switch between typical EPA-method analytical setups and a multi-residue pesticide screen just by swapping syringes and liners. Samples are extracted quickly, with minimal solvent, and require no concentration steps. This can be a cost-effective way to offer a new service. Again, it should be emphasized that this is a qualitative-only screen, and certainly does not meet the quality control rigors of an EPA-approved method, but it has given clients valuable information they can use when deciding to purchase a piece of property.

Please contact Vera Maheu with questions.

Reference

Screening for 926 Pesticides and Endocrine Disruptors by GC/MS with Deconvolution Reporting Software and a New Pesticide Library, Agilent Technologies Application Note. April 18, 2006. 5989-5076EN.

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

The APHL MRC is a vital instrument for the environmental laboratory community to remain knowledgeable in meeting today's challenges. Please send feedback to memberresources@aphl.org.