Monitoring and Assessment Branch

NOAA National Centers for Coastal Ocean Science
Center for Coastal Monitoring and Assessment

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NOAA NCCOS Center for Coastal Monitoring and Assessment

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Monitoring & Assessment of Coastal Contaminants: Overview

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A synthesis from documents by several authors

Introduction

Background

Coastal contamination is a globally pervasive phenomenon. Even the most remote sites and endemic fauna in the Arctic have shown levels of certain contaminants that approach or exceed thresholds associated with adverse biological effects. However, the distribution of contaminants is not uniform; it is determined by local point sources, convergence of physical and biological transport pathways, food chains promoting selective uptake, transfer and bio-magnification, and accumulation in sediment. In sufficiently high concentrations, the contaminant-laden sediments pose serious health threats to coastal ecosystems, the sustainability of renewable resources, and human health. Within the sediment matrix, contaminants may be resuspended, transported, and redeposited in areas far from the original source. Under some circumstances, contaminants may be desorbed and released into water, making the bottom sediment not only a sink but also a source of contaminants far from their origin. Therefore, contaminants associated with sediments constitute major areas of emphasis in environmental research, monitoring and assessment programs, including the work led by the National Centers for Coastal Ocean Science (NCCOS)' Monitoring & Assessment (M&A) Branch.

In light of the generally low concentrations of contaminants present in natural waters and the analytical challenges for maintaining a routine monitoring program of this caliber, and further recognizing the importance of assessing impacts of contaminants on biota, the National Oceanic and Atmospheric Administration (NOAA)' National Ocean Service (NOS) established the National Mussel Watch Program (MWP). The MWP followed the pioneering work by Philip Butler in the 1960s at the Bureau of Commercial Fisheries Biological Laboratory at Gulf Breeze, Florida, in which pesticide residues were monitored in oysters and related to growth and other biological parameters. His work was later expanded to include a larger suite of contaminants and contaminant monitoring using bivalves in several coastal states. A chapter in this document is dedicated to the Long-term monitoring program aspects of the Branch and the role of the National Mussel Watch program.

The Monitoring & Assessment Branch originally focused on five major types of sediment contaminants which directly or indirectly cause a wide range of adverse biological effects in plants and animals, including people, through direct chemical toxicity, genotoxicity, physiological dysfunction, and behavioral abnormalities. These contaminants include:

- Bulk organics, including organic wastes from sewage treatment plants, oil and grease, other deoxygenating substances, and humic materials;
- Halogenated hydrocarbons or persistent organic contaminants such as DDTs and polychlorinated biphenyls (PCBs) that have accumulated in the environment long after discontinuation of their use;
- Polycyclic aromatic hydrocarbons (PAHs), contaminants associated with crude oil and distillate products, burning of fossil fuels, municipal and industrial effluents, and natural sources;
- Metals, such as copper, iron, zinc, lead and mercury, and metalloids such as arsenic and selenium;

Since, the M&A Branch has expanded its portfolio of contaminants to include a much larger suite of contaminants of emerging concern (CECs) such as pharmaceutical and personal care products (PPCPs), current use pesticides, flame retardants, new industrial chemicals, stain resistant compounds, and endocrine-disrupting chemicals, including perfluorinated compounds (PFCs), and flame retardants (polybrominated diphenyl ethers; PBDEs).

Understanding the impacts of contaminants on biological populations, communities and ecosystems is an essential component in the overall assessment of environmental contamination. To this end, the development and application of biomarkers and ecological indicators provide useful tools for determining cause and effect relationships between environmental stressors and biological responses. Over the past 20 years, the M&A Branch has led and/or sponsored studies to apply or further develop over 30 different biomarkers and ecological indicators as environmental assessment tools. M&A Branch staff routinely measures a broad suite of chemical contaminants across sediment, water and biological samples, additional contaminants such as dioxins and furans are measured on a site-specific basis. A chapter in this document focuses on Placed-Based Assessments and provides a suite of examples on how the M&A Branch has successfully applied this approach across a variety of ecosystem types and regional scales.

Coastal Monitoring & Assessment of Contaminants at the Federal Level

The task of assessing environmental impacts from coastal contamination is sufficiently complex that no single federal agency is responsible for addressing and resolving the issue. More than 10 different laws give the National Oceanic and Atmospheric Administration (NOAA), U.S. Environmental Protection Agency, the Army Corps of Engineers, and other federal and state agencies and tribal entities authority to address environmental contamination issues. As a coastal stewardship agency, Titles II and V of the National Oceanic and Atmospheric Administration Authorization Act of 1992, the Marine Protection, Research and Sanctuaries Act, the Coastal Zone Management Act, the Harmful Algal Bloom and Hypoxic Research and Control Act, and the Water Resources Development Act provide the M&A Branch with the mission objectives and research drivers necessary to implement a comprehensive contaminant monitoring and assessment program. As directed by Federal legislation and under institutional authorities of agencies, NOAA is addressing the problem of coastal contamination by:

- Identifying the spatial extent and severity of sediment contamination in U.S. coastal waters;
- Providing an appropriate degree of uniformity and quality control in coastal monitoring programs and ensuring flexibility in such programs to address region-specific needs;
- Developing technological tools, such as computer-based models, or scientific guidelines to assess current environmental conditions and forecast changes under different resource management scenarios; and,
- Providing and integrating data and assessments to support remediation strategies that will most effectively reduce the risk associated with coastal contamination.

Very few programs in the United States focus on contaminants, and fewer yet monitor coastal environments, therefore, the monitoring and assessment activities carried out by the Branch fill a unique niche in the nation's contaminant monitoring portfolio. Other nationwide projects include Air Toxics Monitoring Network (EPA), National Dioxin Air Monitoring Network (EPA), National Water Quality Assessment Program (USGS), and National Health and Nutritional Examination Survey (CDC). Together, these projects can offer a wealth of useful information for deriving a more cohesive and integrated view of pollution transport, severity and exposure. However, coordination among these programs is largely incidental, often leading to compilation rather than integration of data. Previous program recommendations have been put in place to improve existing environmental monitoring programs at the Federal level, these include:

- Interagency cooperation with more focused efforts for documenting environmental change and providing solutions to environmental problems and conflicts;
- Federal-state partnerships for more effective implementation of environmental policy and resource management strategies; and,
- Government-academia cooperation for integrating monitoring and assessment with research, and developing new procedures and technologies.

Recent technological advances, such as numerical and analytical models, biotechnologies, interactive graphics and Geographic Information Systems, and sophisticated environmental sensors, can be extremely useful not only for obtaining accurate and quality assured measurements, but also for elucidating complex coastal environmental features and processes on multiple time and space scales. The Branch continues to apply these advances on a myriad of projects regionally focused on the Great Lakes. A chapter in this document addresses these approaches in detail.

Historic Context for Monitoring & Assessment Programs

Coastal monitoring of contaminants and toxicity assessment programs are credited with providing uniform and comparable sets of data on marine pollution. The first such program in the United States evolved following recommendations of the National Academy of Sciences in 1975. The program collected and analyzed samples from 62 sites on the east and west coasts of the United States during the period 1976-78. The program was adapted in 1977 for use in water quality surveillance and monitoring efforts of the State of California. In recent years greater emphasis has been placed on assessment of sediment toxicity, in situ changes in benthic biological community structure, and occurrence of pollution indicator species. The French Mussel Watch program has maintained a network of sites since 1979 to describe the quality of the marine environment around its coast.

The use of mussels or other bivalves in assessing the extent of chemical contamination of coastal waters in other parts of the world has been endorsed as the International Mussel Watch (IMW) Program under the sponsorship of the Intergovernmental Oceanographic Commission, the United Nations Environmental Program's Ocean and Coastal Areas Program, and the U.S. National Oceanic and Atmospheric Administration. The initial phase of the IMW Program was concluded with the sampling at 76 sites in central and South America and the wider Caribbean followed by the sampling phase in the Asian-Pacific region. The IMW Program has been valuable in terms of capacity building in host countries, comparison of data between regions, and collective awareness of the condition of coastal resources.

Nationally, the National Oceanic and Atmospheric Administration (NOAA) established the Mussel Watch Project in 1986 in response to its legislative mandate under Section 202 of Title II of the Marine Protection, Research and Sanctuaries Act (MPRSA) (33 USC 1442), which called on the Secretary of Commerce to, among other activities, initiate a continuous monitoring program to assess the health of the marine environment including monitoring of contaminant levels in biota, sediment and the water column. The project was patterned after earlier environmental monitoring projects that utilized bivalve mollusks as sentinel organisms, starting with monitoring of pesticides in oysters in several bays in the Gulf of Mexico in the early 1960s. The concept was adapted for routine monitoring by the U.S. Environmental Protection Agency's Mussel Watch programs (1965-72, and 1976-78) and the California State Mussel Watch Program (since 1976). The NOAA Mussel Watch Project (now the National Mussel Watch Program) monitors chemical contaminants in resident bivalve mollusks (e.g., mussels and oysters) throughout the Nation's coastal waters, estuaries and the Great Lakes. The sampling sites are situated away from municipal outfalls, industrial effluents, and known "hot spots" of contamination.

In 1992, the overall approach and activities of NOAA's formerly National Status and Trends (NS&T) Program and today's Monitoring & Assessment Branch were essentially codified under provisions of the National Coastal Monitoring Act (Title V of the MPRSA), which was part of the NOAA Authorization Act of 1992 (PL 102-567). The Act called for a consistent, nationwide water quality monitoring program with an appropriate degree of uniformity of methods and analytical procedures (i.e., Mussel Watch), intensive studies to assess environmental conditions in selected waterbodies throughout the United States (i.e., Bioeffects Studies and Benthic Surveillance), development of uniform indicators of coastal ecosystem quality (i.e., biomarkers and ecological indices), and an environmental data management program to distribute coastal data and information products for use by local governments, federal agencies, and other interested parties (i.e., web-based NCCOS data portal presently under development).

Over the years, the Mussel Watch and Bioeffect Programs have remained the backbone of environmental monitoring in U.S. coastal waters. The programs have established benchmarks and context by which to gauge national to local-level spatial distribution, and temporal trends of chemical contamination, and provide information to coastal managers and stakeholders regarding the health of their managed areas. NCCOS scientists have written hundreds of technical reports, scientific journal articles and book chapters (Table 1) documenting the project's results and information products, provided scientific counsel and advice to coastal managers about the project's data, provided data to non-NOAA scientists, and discussed the project's rationale and scope at interagency and international meetings, scientific fora and with the public at large.

Relevance of the Monitoring & Assessment Branch and Mussel Watch Program

Pertinent Legislative Mandates

<u>*Title II of MPRSA of 1972*</u> (Comprehensive Research on Ocean Dumping)

Section 202 states that the Secretary of Commerce, in close consultation with appropriate Federal departments shall initiate a continuing program of research with respect to the possible long-range effects of pollution, overfishing, and man-induced changes of ocean ecosystems:

- A program to assess the health of the marine environment, including but not limited to the monitoring of bottom oxygen concentrations, contaminant levels in biota, sediments and the water column, disease in fish and shellfish, and changes in the types and abundance of indicator species (M&A Branch components);

- The development and assessment of scientific techniques to define and quantify the degradation of the marine environment (ecological indicators and biomarkers); and
- Development of methodologies, techniques, and equipment for disposal of waste materials to minimize degradation of the marine environment (EPA).

Title V of MPRSA (National Coastal Monitoring Act) part of NOAA Authorization Act of 1992 – essentially a codification of the M&A Branch and related programs.

- Establish a comprehensive national program for consistent monitoring of the Nation's coastal ecosystems (Mussel Watch);
- Establish long-term water quality assessment and monitoring programs for high priority coastal waters that will enhance the ability of Federal, State, and local authorities to develop and implement effective remedial programs for those waters (Sediment Toxicity Assessment and Benthic Surveillance);
- Establish a system for reviewing and evaluating the scientific, analytical and technological means that are available for monitoring the environmental quality of coastal ecosystems;
- Establish methods for identifying uniform indicators of coastal ecosystem quality (ecological indices and biomarkers);
- Provide for periodic, comprehensive reports to Congress concerning the quality of the Nation's coastal ecosystems;
- Establish a coastal environmental information program to distribute coastal monitoring information (NCCOS website);
- Provide state programs authorized under the Coastal Zone Management Act with information necessary to design land use plans and coastal regulations that will contribute to the protection of coastal ecosystems;
- Provide certain water pollution control programs authorized under the Federal Water Pollution Control Act with information necessary to design and implement effective coastal water pollution controls.

Coastal Zone Act Reauthorization Amendments of 1990
Section 6217 states that NOAA will be involved with state managers in dealing with the impacts of non-point source pollution on coastal water quality.

National Oceanic and Atmospheric Administration Authorization Act of 1992
Title II, Section 201(b) provides funding for NOAA's ocean and coastal programs under broad categories of "observations and assessment" in the National Ocean Service, including funding of programs under Title II of MPRSA.

Water Resources Development Act of 1992
Section 503 states that the Administrator of the U.S. Environmental Protection Agency, in consultation with the Administrator of the National Oceanic and Atmospheric Administration, shall conduct a comprehensive national survey of data regarding aquatic sediment quality in the United States. (Coastal Sediment Database, COSED). Section 503 also states that the EPA Administrator, in consultation with the NOAA Administrator, shall conduct a comprehensive and continuing program to assess sediment quality [the National Contaminated Sediment Assessment and Management Act]. The program conducted pursuant to this subsection shall at a minimum:

- Identify the location of pollutants in aquatic sediment;
- Identify the extent of pollutants in sediment and those sediments which are contaminated pursuant to Section 501 b – [PL 102-580 states sediment containing substances in excess of appropriate geo-chemical, toxicological or sediment quality criteria or measures, or otherwise determined to pose a threat to human health or the environment];
- Establish methods and protocols for monitoring the physical, chemical and biological effects of pollutants in aquatic sediment and of contaminated sediment;
- Develop a system for the management, storage, and dissemination of data concerning aquatic sediment quality;
- Identify those locations where pollutants in sediments may pose a threat to the quality of drinking water supplies, fisheries resources, and marine habitats;
- Establish a clearinghouse for information on technology, methods, and practices available for the remediation, decontamination, and control of sediment contamination. (Bioeffects Studies and Sediment Quality Guidelines).

Estuary Restoration Act (NCCOS Data Portal)
Section 2906 (Monitoring of Estuary Habitat Restoration Projects) mandates that the Under Secretary of Commerce shall:

- Develop and maintain an appropriate database of information concerning estuary habitat restoration projects including information on project techniques, project completion, monitoring data, and other relevant information;
- Develop standard data formats for monitoring projects, along with requirements for types of data collected and frequency of monitoring;
- Compile data from other sources and that meets the

quality control requirements and data standards;
- Use existing NOAA programs to create and maintain the database required under this section;
- Make the information collection and maintained under this section available to the public.
- Nutrients, which can lead to unwanted algal growth, oxygen depletion in bottom waters, loss of habitat and altered food chains or species succession.

Monitoring & Assessment Branch Structure

Branch Goal and Objectives

The National Centers for Coastal Ocean Science (NCCOS) serves as the research arm of the National Ocean Service, as such, the objectives of the Monitoring & Assessment Branch fall under the dual roles of advancing the state of science on chemical contaminant monitoring and assessments, while continuously providing national-level contaminant trends, and regional assessments data and information products. Across all services provided, the M&A Branch strives to meet rigorous quality standards and follow consistent field survey and analytical protocols to provide data quality standards that are transparent and repeatable.

Information products from the Monitoring & Assessment Branch, in conjunction with data and information from other agencies are routinely delivered in the form of NOAA Technical Reports, specialized documents, and peer reviewed publications (Table 1). Data is also distributed across several government data bases and archived for future uses in reliable data architecture systems. In addition, information products and data from the Branch support the development and key findings that define the condition of the Nation's coastal environment and ecosystems in biennial or special reports to Congress. Typically, a coastal condition report includes the following:
- an assessment of the status and health of the Nation's coastal ecosystems;
- an evaluation of environmental trends in coastal ecosystems;
- identification of sources of environmental degradation affecting coastal ecosystems;
- an assessment of the impact of government programs designed to abate the degradation of coastal ecosystems; and
- an evaluation of the adequacy of monitoring programs and identification of any additional program elements which may be needed.

In order to deliver these products and services, the Monitoring & Assessment Branch supports NCCOS as the leading body of chemical contaminants and toxicity monitoring and assessment subject matter experts for the National Ocean Service. The branch leads, coordinates and/or supports a myriad of projects focused on understanding biological effects from toxicity that are regionally specific in scope, and provide monitoring of contaminants to establish national context implications.

Since 1999, the Monitoring & Assessment Branch has been implementing a singularly focused goal. However, the objectives leading to meeting this goal are continuously updated by staff to reflect the ever changing landscape of coastal contaminant monitoring and assessment research and applications:

<u>Monitoring & Assessment Goal:</u>

To develop and implement a nationwide program of environmental monitoring, assessment and related research in order to describe the current status of, and to detect changes in, the environmental quality of our Nation's estuarine and coastal waters.

Items in **bold** below, reflect active objectives being carried out by the Branch today.

<u>Objective 1</u>

Develop and implement a national program for consistent monitoring to describe spatial distribution and temporal trends in the Nation's coastal waters, estuaries and the Great Lakes region.

Sentinel species (National Mussel Watch Program)

Sediment cores

Quality assurance / quality control

Integration of Contaminants of Emerging Concern (CEC) and Pharmaceutical and Personal Care Products (PPCP) to monitoring portfolios

Objective 2

Implement a comprehensive and continuing program of environmental assessment and related research in order to describe the nature and scales of biological effects associated with contaminants and other sources of environmental degradation.

Benthic Surveillance Project

Sediment Quality Triad

National scorecard of the spatial extent of sediment toxicity

Topical (e.g., radionuclides) or regional (e.g., Tampa Bay) assessments

Nutrient over-enrichment and hypoxia

National Coastal Condition Report

Objectives 3

Develop and improve diagnostic and predictive capabilities, including environmental indicators and biomarkers, to determine the biological effects of coastal contamination and other sources of environmental degradation.

Bivalve Health Indicators:
Metabolomics, DNA Damage

Land-use indicator studies; socio-economic assessments

Objective 4

Develop a data dissemination platform with a user-driven portal, to facilitate information synthesis and public outreach to strengthen the scientific understanding of the coastal environments and to promote informed decisions affecting coastal environments and ecosystems.

Establishment of Machine Learning and Artificial Intelligence tools for contaminant data mining

Monitoring & Assessment Branch Staff

Long-term implementation of the Branch's goal and its objectives requires a blend of staff with high technical skills in analytical chemistry, statistical and modeling experience, and data management acumen. The Branch is currently staffed by 8 Federal employees and 2 contract personnel (Table 2). While the majority of the staff is relatively senior, the distribution of work is assigned collegially and based on the expertise of the members, rather than along hierarchical lines. The Branch is organically organized by areas of interest and research expertise along the following groups: National Mussel Watch Program, Great Lakes Mussel Watch, regional bioeffect assessments (coral monitoring) group, new monitoring technologies and data management and integration groups (Figure 1). Branch members lead, or collaboratively support several of these groups regularly based on project needs, or provide guidance and expertise on an 'as needed' basis.

Coastal Contaminants Monitoring & Assessment Branch Users

Users of the Branch's data and information products are coastal states, regional environmental programs or organizations (for example, the Chesapeake Bay Program, Delaware River Basin Commission, Gulf of Maine Council, and Comprehensive Everglades Restoration Program). Occasionally, the program conducts studies in partnership with coastal states to fulfill the state's information needs, either as a cooperative study (e.g., State of Washington and Oregon Fish & Wildlife Programs) or under a Joint Project Agreement (e.g., Florida DEP study) (Figure 2).

There are numerous manifold and unanticipated users of the program's data and information products. For example, the program's data on polynuclear aromatic hydrocarbons are used nearly every time as benchmark to assess impacts following an oil spill in coastal waters. The data have also been used to evaluate the significance of toxic chemicals and other contaminants released by cruise ships in Alaskan waters, explain the high occurrence of cadmium in oysters shipped from British Columbia waters, assessing impact on wildlife resources from dumping of DDT off Palos Verdes, CA, and to describe mercury distribution in coastal waters of the Gulf of Mexico. Most recently, capitalizing on the long-term PAH datasets acquired by the Branch and the research capabilities of the Branch staff, a study resolved a standing litigation between a private company and the U.S. Government regarding the responsibility for containing a spill originated by a toppling oil-rig in the Mississippi Canyon area 20 of the Gulf of Mexico. Chemical analyses conclusively established that the source of the oil and gas entering the marine environment is active releases from multiple reservoirs near the toppled platform, rather than from contaminated sediments, thus establishing that the government was not liable for containing the spill.

As a matter of long-standing NOAA policy, the Branch is committed to achieving scientific excellence and ensuring the highest quality of science in its studies. This goal is attained not only by programmatic design, project formulation, data collection and analyses but also by interpretation and reporting of results in NOAA technical reports, scientific journals and dissemination of information products to the users. Acceptance of products by peers, such as publication in scientific and technical journals, as well as presentations and leadership roles at professional meetings or symposia are among the generally accepted criteria for scientific quality. Branch staff have had a long tradition of research publications and scientific leadership roles, and have offered expert scientific counsel to states, national organizations, international bodies, and the public at large.

The Mussel Watch Program and components of the Monitoring & Assessment Branch have been reviewed several times, first in 1990, then again in 1994 and followed by a comprehensive 2-phase review in 2004/2005 (these reports are available upon request). In 2013, and a result of a National Mussel Watch Stakeholder meeting, NCCOS redesigned the program to focus on a rotating regional model while still maintaining the program's requirements and drivers. The Branch and its projects have benefited greatly from previous reviews, which have helped redefine its objectives to more effectively meet the more comprehensive strategic goals and objectives of NOAA and the National Ocean Service.

Publications

Hundreds of publications have been produced as a result from the NS&T Program through today's Monitoring & Assessment Branch (Table 1). It is often difficult to identify publications that contain strictly Mussel Watch Program data, versus those containing data from the larger Monitoring & Assessment Branch, and as a result, citations from both have been assembled (Figure 3). In addition, while many of the publications were authored by NOAA personnel, many other authors have published papers on their own using data published by the Branch.

Outreach and Education

Monitoring & Assessment data has been used by universities as part of their curricula. The data are used to teach how to apply statistical methods to environmental data, and Mussel Watch Program results are used as examples of long-term coastal monitoring. Institutions include Texas A&M University, the University of Miami, Woods Hole Oceanographic Institution and the University of Washington.

In addition, UNESCO funded the preparation of a workbook on the use of standard and reference materials in the measurement of chlorinated hydrocarbon residues. The workbook was published as a UNESCO publication and a NOAA Technical Memorandum.

M&A Branch staff routinely hosts undergraduate and graduate level students affiliated with fellowships and NOAA Education Office sponsorships to expand and train the next generation of environmental scientists. Students have access to the expanded contaminant database and learn from the Branch scientists on how to utilize data mining tools to analyze large datasets and provide answers to questions particular to their research objectives.

New Horizons for the Monitoring & Assessment Branch

Long-term, nationwide environmental monitoring programs form a backbone for obtaining quality assured data of variables and parameters that are nationally significant, i.e., subject of Federal legislation and other mandates intended to improve environmental quality and conserve natural resources. In the case of coastal and marine pollution, data from such monitoring programs are used to characterize contaminant concentrations and trends, identify areas that need priority consideration for restoration or remediation, evaluate the effectiveness of pollution abatement programs, and support research objectives (e.g., long-range transport; sources, sinks and methods of sequestration in different environmental matrices; and environmental and human exposure trends).

While the Branch goal and its current objectives are technically sound, the capacity and set of capabilities to achieve them all is presently nominal, at best. A revised vision to achieve the Branch's goal is in the works, and it may include a smaller, robust set of objectives. While the Branch has been very effective to-date at executing both its contaminant research science and routine contaminant survey programs as two distinct efforts, a paradigm shift on the types of products demanded by customers, services requested by stakeholders and data integration desired by academic partners is growing, and the Branch is slowly but steadily rising to meet this shift. Other drivers for this renewed vision include changes in staff and slowly-eroding and unpredictable base budgets.

This new vision intends to better integrate and expand the collaborations between the National Mussel Watch contaminant concentration and bioeffects toxicity data, the innovative research aspects of the bivalve health projects and, the data mining and integration afforded by the incorporation of machine learning and artificial intelligence tools. Branch products and services resulting from the streamlining of research and monitoring fronts will be targeted to a reduced number of customers served primarily via curated data sets, completed (QA/QC) data compendiums, and a variety of publications distributed via the NCCOS website.

As part of this vision, the Branch is developing a detailed set of performance metrics that better reflect the impacts of products and services on the customers that receive them. These metrics will be focused on two general areas: delivering information products, and providing knowledge services. Depending on the type of products and services rendered by the branch, successful metrics will measure an increase in either the number of data downloads by academics and private-sector parties, or the number of services requested by stakeholders, such as coastal managers and regional environmental programs. The development of these metrics is only just starting and it is not ready for application in the near term. However, as the Branch adjusts its objectives, the metrics will follow.

The Branch is also developing a mid through long-range strategic plan to go alongside with an annual work plan (including performance metrics). It is expected that these plans will align with the, NCCOS Science Plan, which is also currently being updated for the next five-year cycle.

An NCCOS-wide review of scientific research, assessment and monitoring identified five new areas of research that pertain to long-term monitoring of toxic chemicals in the environment: (1) New classes of contaminants (e.g., contemporary use pesticide and pharmaceuticals), (2) New indicators, including biomarkers based on field observations, laboratory bioassays, and mesocosm experiments, (3) Endocrine disrupting chemicals (including screening assays and models), (4) Cumulative effect of contaminants, and (5) Linking coastal contamination with land development activities and formulating management strategies to reduce contaminant loading. The Branch has engaged in 4 of these new areas of research (1, 2, 3 & 4) and invested significant staff and funding resources to develop these research areas with successful results. It is with this same can-do attitude, that the Branch staff will take on its new vision when finalized.

Increased Collaboration

The Monitoring & Assessment Branch has a strong history of collaboration, both across NOAA (e.g. Coral Reef Conservation Program; Ocean Acidification Program – potential 2021 RFP) and intergovernmentally, including work with the US National Park Service (NPS), US Food and Drug Administration (FDA), Florida Department of Environmental Protection (FL DEP), Washington and Oregon Fish & Wildlife offices, and currently as part of the Great Lakes Restoration Initiative (GLRI), a consortia of Federal agencies that include: the EPA, USGS, USFW and the USACE. As NCCOS strives for a more effective role for its scientific projects and products in coastal resource management decisions, the M&A Branch will continue to focus on developing projects that support resource management decisions in coastal areas and NOAA-managed areas, and establishing joint projects with researchers both within and outside NOAA.

Summary

The Monitoring & Assessment Branch finds itself at a crossroads between maintaining and growing its marquee program, the world-class National Mussel Watch program, and continuing to advance its coastal monitoring and assessment research efforts. Coupled with a number of recent staff reductions and a flat and unpredictable budget picture, the Branch is now focusing on addressing the breadth and scope of each of the objectives, keeping its goal intact, and advancing the number of products and services delivered to a narrower but targeted set of users and stakeholders.

Integration and augmentation of Branch data sets with other data types to include: land use, socio economic and demographic classes, for example, to deliver management sought products; additionally, incorporation of artificial intelligence and machine learning tools to Branch data sets to bring up insights not ascertained with regular statistical methods, will continue to keep Branch monitoring & assessment data and research products fresh and relevant to NOAA users and stakeholders.

Tables and Appendices

Tables

Table 1. Impact and performance of Monitoring & Assessment Branch, and National Mussel Watch Journal Articles.

Bibliometric Indicator	Value
Total number of Mussel Watch articles	45
Total number citations received by Mussel Watch articles	1,862
Percentage of Mussel Watch articles cited	93.33%
Average number of citation per article	41.38
H-Index*	23
Percentage of Documents in Top 1%**	2.22%
Percentage of Documents in Top 10%**	31.11%

* An H-Index of 23 indicates that this group of 45 publications includes 23 articles that have each received 23 or more citations
** Papers in the top 1% and top 10% based on citations by category, year, and document type. 31.11% of Mussel Watch articles received more citations than 90% of other articles published in the same category and year.

Table 2. Monitoring & Assessment Branch Staff

Name	Position in Branch	Education	Affiliation
Felipe Arzayus	Branch Chief	M.S.	Federal
Dennis Apeti	Lead Scientist; Manager, National Mussel Watch Program	Ph.D.	Federal
Erik Davenport	Biologist, Statistician, Modeler	Ph.D.	Federal
Michael Edwards	Statistician, Geospatial Architect	Ph.D.	Federal
Annie Jacob	Chemist, Environmental Scientist	Ph.D.	Contract
Ed Johnson	Lead Scientist; Manager, Great Lakes Mussel Watch Program	Ph.D.	Federal
Kimani Kimbrough	Organic Chemist, Lead Data and Informatics team	Ph.D.	Federal
Tony Pait	Senior Scientist, Organic Chemist	Ph.D.	Federal
Mary Rider	Support Scientist, National Mussel Watch Program	M.S.	Contract
Rob Warner	Lead, Water Quality Platforms and Unmanned Systems team	M.S.	Federal
Dave Whitall	Lead Scientist, Environmental Chemistry	Ph.D.	Federal

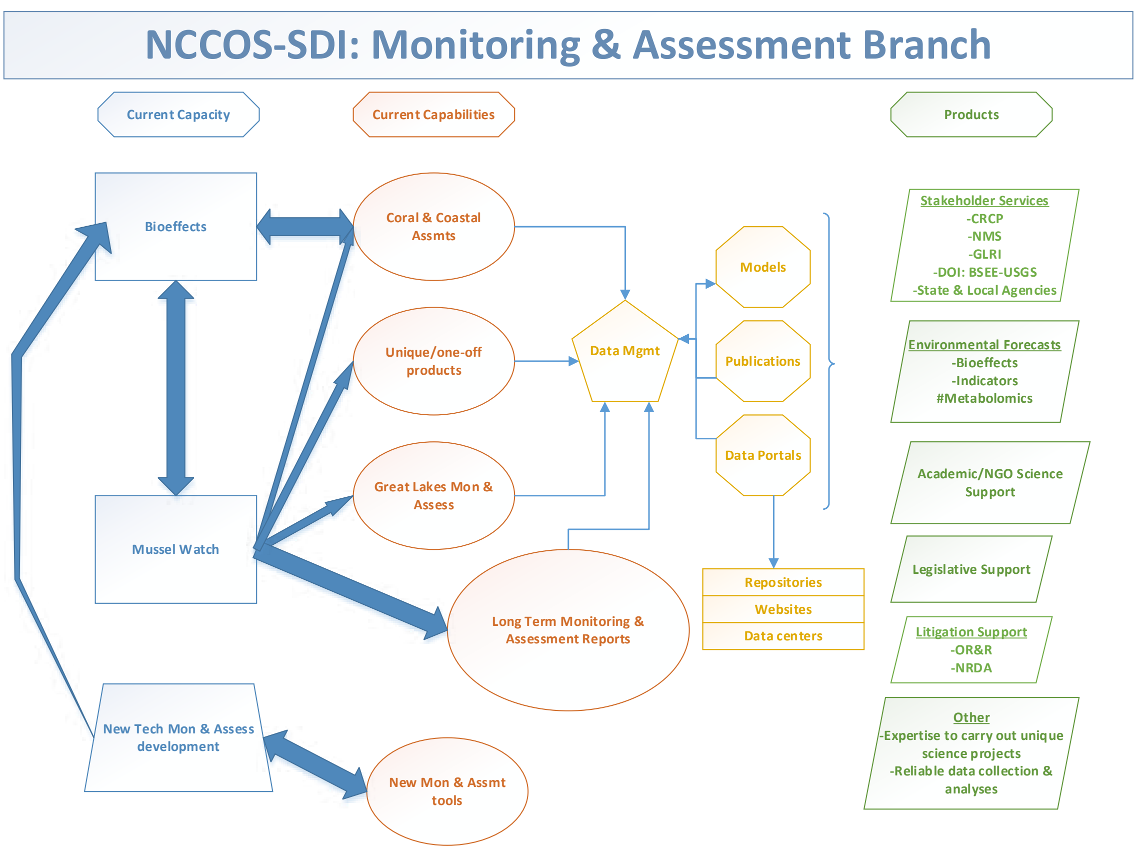
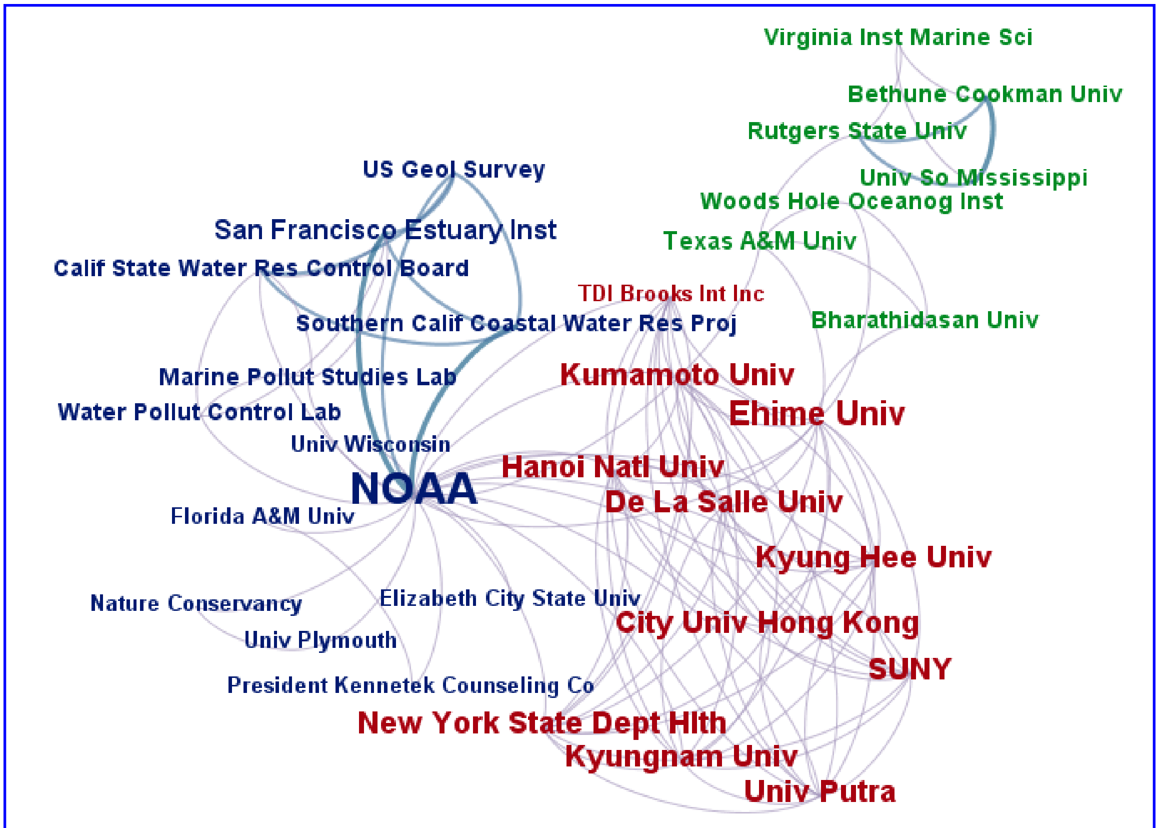


Figure 1. Monitoring & Assessment Branch work flow



Institutional Collaborations

Network map of 32 institutions who collaborated on two or more Mussel Watch articles published between 1990 and 2020. In the map, word size indicates the number of articles which two institutions collaborated on and names of institutions are colored based on the results of a community detection algorithm to indicate groups of institutions that tended to collaborate. Lines represent article on which the institutions collaborated, with line size and darkness indicating the number of articles produced by that collaboration.

Figure 2. Literature-based collaborative heat-map based on Monitoring & Assessment Branch publications.

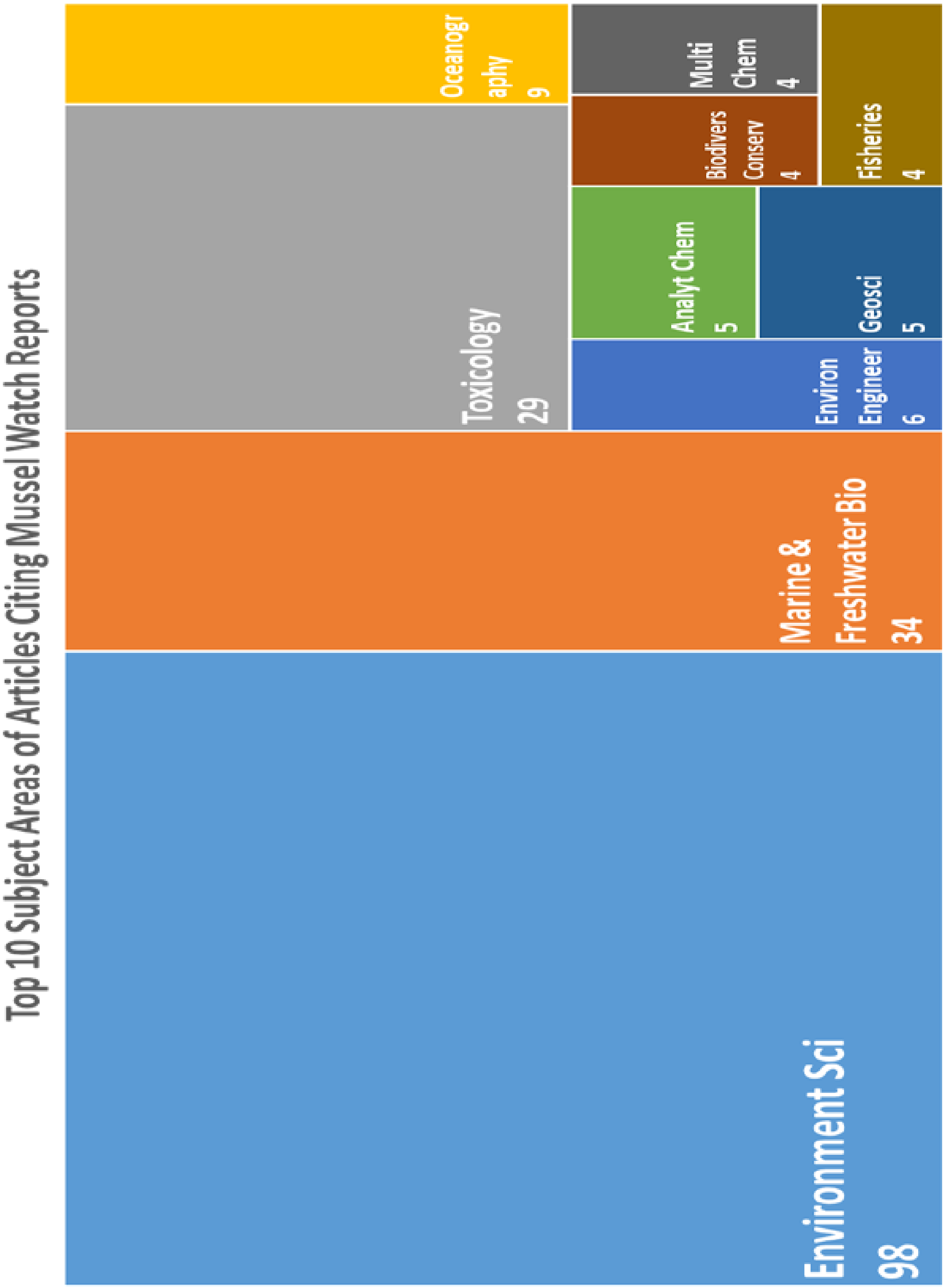


Figure 3. Top subject areas from M& A Branch and Mussel Watch publications. Areas are assigned by Web of Science based on the journal in which the article appeared. These subjects are not mutually exclusive and an article may be assigned to multiple subject areas.

Appendices

Appendix 1. Abbreviated staff curriculum vitae

Felipe Arzayus

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Professional and Academic Credentials
College of William & Mary, School of Marine Science, Master of Science, 2000

University of North Dakota; Biology, Bachelor of Science, 1995

University of North Dakota; Aeronautical Studies, Bachelor of Science, 1995

Additionally:
Society of Environmental Toxicology and Chemistry
American Fisheries Society
NOAA Diver
Commercial Pilot, single engine, land and sea

Relevant Activities
My primary focus is leading the Monitoring & Assessment Branch research directions and contaminant monitoring programs so that they stay relevant and scientifically up to date, venture into new and exciting contaminant research and monitoring fronts, and keep on delivering products and services to the users and stakeholders that can apply this information and knowledge for their own purposes.
My research interests are broad and diverse, and are centered on the links between contaminants, and ocean acidification, 'omics and more specifically population genetics. Toxicity effects, and ecosystem feedbacks. These relationships are not clearly understood and are often dismissed because of their complexity. However, as the number of chemicals being used in the manufacturing of goods increases severalfold annually, my goal is to develop a macro-suite of contaminant bio indicators for use by managers and stakeholders.

Selected Publications
Li-Qing Jiang, Wei-Jun Cai, Richard A. Feely, Yongchen Wang, Xianghui Guo, Felipe Arzayus, Xinping Hu, Feizhou Chen, Justin Hartmann, and Longjun Zhang. Carbonate saturation states on the continental shelf of the Southeastern United States. 2009, Geophysical Research Letters.

A. E. Strong, F. Arzayus, W. Skirving, and S. F. Heron. Identifying Coral Bleaching Remotely via Coral Reef Watch – Improved Integration and Implications for a Changing Climate. Coastal and Estuarine Studies, 2006.

Skirving, W. J., A. E. Strong, G. Liu, L. F. Arzayus, C. Liu, and J. Sapper, Extreme events and perturbations of coastal ecosystems, pp.11-25, Richardson, L. L., and E. F. LeDrew (eds), 2006, In Remote Sensing of Aquatic Coastal Ecosystem Processes, Springer Remote Sensing and Digital Processing series, Vol. 9, pp. 324, 2006.

Skirving W.J., Heron S.F., Steinberg C.R., Strong A.E., McLean C., Heron, M.L., Choukroun S.M., Arzayus L.F. & Bauman A.G. (2005) "Palau Modeling Final Report" National Oceanic and Atmospheric Administration and Australian Institute of Marine Science, 46pp.

Arzayus, L. F., and W. J. Skirving, Correlations between ENSO and Coral Reef Bleaching. 10th International Coral Reef Symposium. Okinawa, Japan, 2004.

Arzayus, L. F.; Strong, A. E.; Dahl, A. L.: The challenge of observing coral reefs: report from the coral sub-theme to the Integrated Global Observing Strategy (IGOS) partners. ASLO/TOS 2004 Ocean Research Conference. Honolulu, Hawaii.

Heron, S. F., G. Liu, L. F. Arzayus,W. J. Skirving, and A. E. Strong, A benefit from hurricanes, PORSEC 2004, Concepcion, Chile, 2004.

Skirving W.j., Heron S.F., Stweinberg C.R., Strong A.E., McLean C, Heron M.L., Choukroun S.M., Arzayuus L.F. & Bauman A.G. (2005) "Palau Modeling Final Report" National Oceanic and Atmospheric Administration and Australian Institute of Marine Science, 46pp

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Education Credentials

PhD. Environmental Sciences, Florida A&M University, 2005.

M.S. Environmental Chemistry, Florida A&M University, 2001.

B.S. Chemistry, Florida Atlantic University, 1997

M.S. Geology, University of Benin, 1992

B.S. Biological Sciences, University of Benin, 1991

Relevant Professional Activities
Lead scientist on the NOAA national Mussel Watch coastal pollution monitoring program, responsible including managing the program, implementing projects and executing budget. Offers more than 15 years of experience in estuarine and marine ecosystem health research, with particular emphasis on chemical contaminants monitoring and assessment. Extensive experience in project management, technical and scientific writing, and research project development. Experienced in fostering collaboration with scientists from academic, fed, state and tribal organizations including US-NPS, US-FDA, WAFW, Chugach and Snohomish tribes. Skills include analytical data processing, data review as per quality application programs, statistical analysis, technical report development and snorkel diving. Efficiency in Microsoft Applications, SAS, JMP, SigmaPlot statistical software, as well as in ArcGIS, and InDesign applications. Professional membership with Society of Environmental Toxicology and Chemistry (SETAC), National Organization of Black Chemists and Chemical Engineers (NOBCChE), and Coastal Estuarine Research Federation (CERF).

Selected Publications
Apeti, D.A., Rider, M., Jones, S. and Wirth, E., 2020. An Assessment of Contaminants of Emerging Concern in the Gulf of Maine. NOAA Technical Memorandum NOS NCCOS. Silver Spring, MD (under review)

Rider, M., Apeti, D.A., Jacob, A., Kimbrough, K., Davenport, E., Bower, M., Coletti, H. and Esler, D., 2020. A Synthesis of Ten Years of Chemical Contaminants Monitoring in National Park Service - Southeast and Southwest Alaska Networks. A collaboration with the NOAA National Mussel Watch Program. NOAA Technical Memorandum NOS NCCOS x. Silver Spring, MD. (Under review).

Pisarski, E.C., E.F. Wirth, S.I. Hartwell, B.S. Shaddrix, D.R. Whitall, D.A. Apeti, M.H. Fulton, G. Baker. 2018. Assessment of Hydrocarbon Carryover Potential for Six Field Cleaning Protocols. NOAA Technical Memorandum NOS NCCOS 247. Silver Spring, MD. 36 pp.

Pait, A.S., W.M.C. Whitman, S.I. Hartwell, D.R. Whitall, and D.A. Apeti. 2018. Measurement of Turbidity, Suspended Sediments and Nutrients in Three Rivers that Drain to the Achang Preserve from the Manell Watershed, Guam. NOAA Technical Memorandum NOS NCCOS 268. Silver Spring, MD. 33 pp

Pait, A.S., A.L. Mason, S.I. Hartwell, and D.A. Apeti. 2019. An Assessment of Chemical Contaminants in the Waters Around Cocos Island, Guam Using Polyethylene Passive Water Samplers. NOAA Technical Memorandum NOS NCCOS 261. Silver Spring, MD. 43 pp

Pait, AS, S.I. Hartwell, D.A. Apeti, and A. Mason. 2018. An assessment of nutrients and sedimentation in the St. Thomas East End Reserves, US Virgin Islands, Journal of Environmental Monitoring and Assessment. 186(8):793-806

Hartwell, S.I., D.A. Apeti, and A.S. Pait. 2018. Benthic Habitat Contaminant Status and Sediment Toxicity in Bristol Bay, Alaska". Journal of Environmental Monitoring and Assessment (submission under review EMAS-D-18)

Greg Baker, Emily Pisarski, Ed Wirth, Dennis Apeti, Mike Fulton, Ian Hartwell, David Whitall, and Brian Shaddrix. 2018. Field Equipment Cleaning and Decontamination Assessment for Oil and Oil-related Contaminants in Sediments. NOAA, NCCOS Technical Memorandum (Under review)

Apeti, A.D., Wirth, E., Leight A.K., and Mason, A. 2018. National Status and Trends, Mussel Watch Program: An Assessment of Contaminants of Emerging Concern in Chesapeake Bay, MD and Charleston Harbor, SC. NOAA Technical Memorandum NOS/NCCOS. Silver Spring, Maryland (under review).

Pait, A.S., S.I. Hartwell, A.D. Apeti, A.L. Mason. 2017. An Analysis of Chemical Contaminants in Sediment and Fish Tissue from Cocos Lagoon, Guam. NOAA Technical Memorandum NOS/NCCOS. Silver Spring, MD. 73 pp.

Apeti, A.D. and S.I. Hartwell. 2016. Baseline Assessment of Organic Contaminant Concentrations in Surficial Sediment from Kachemak Bay, Alaska. Regional Studies in Marine RSMA, V.7:196-203.

Apeti, A.D. and S.I. Hartwell. 2015. Baseline assessment of heavy metal concentrations in surficial sediment from Kachemak Bay, Alaska. Journal of Env. Monit. and Assess. 187:4106

Hartwell, S I, D A. Apeti, A S. Pait 2016. Bioeffects Assessment in Kvichak and Nushagak Bay, Alaska: Database on Contaminants, Benthic Habitats, and Fish Histopathology.

S. Ian Hartwell, Dennis A. Apeti, Andrew L. Mason, and Anthony S. Pait, 2016: An assessment of tributyltin and metals in sediment cores in the St. Thomas East End Reserves". Journal of Environmental Monitoring and Assessment. (EMAS).

Pait, A.S., S.I. Hartwell, A.D. Apeti, A.L. Mason, R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, , F.R. Galdo Jr., and S.J. Pittman. 2016. Integrated Environmental Assessment of the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS NCCOS. Silver Spring, MD.

Apeti, D.A., Y. Kim, G.G. Lauenstein, E.N. Powell, J. Tull, and R. Warner. 2014. Parasites and Disease in Oysters and Mussels of the U.S. Coastal Waters. National Status and Trends, the Mussel Watch Monitoring Program. NOAA Technical Memorandum NOSS/NCCOS 182. Silver Spring, MD 51 pp.

Apeti, A.D. and S.I. Hartwell. 2015. Baseline Assessment of organic contaminant Concentrations in Surficial Sediment from Kachemak Bay, Alaska. Environmental Monitoring and Assessment.

Apeti, A.D. and S.I. Hartwell. 2014. Baseline Assessment of Heavy Metal Concentrations in Surficial Sediment from Kachemak Bay, Alaska. Environmental Monitoring and Assessment. 187(1):4106-4116

Apeti A.D., A.L. Mason, A.S. Pait, S.I. Hartwell, R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, F.R. Galdo Jr., and S.J. Pittman. 2014. An assessment of chemical contaminants body burden in Coral (Porites astreoides) and queen conch (Strombus gigas) from the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS NCCOS 177. Silver Spring, MD.

Pait, A.S., S.I. Hartwell, A.L. Mason, R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, A.D. Apeti, F.R. Galdo Jr., and S.J. Pittman. 2013. An assessment of chemical contaminants, toxicity and benthic infauna in sediments from the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS NCCOS 156. Silver Spring, MD.

Apeti, A.D., Lauenstein, G.G. and Evans, D.W. 2012. Recent status of mercury and methyl mercury in the coastal waters of the northern Gulf of Mexico using oysters and sediments from NOAA's Mussel Watch Program. Marine Pollution Bulletin, 64(11): 399-408

Apeti, A.D., Lauenstein, G.G, Christensen, J.D., Johnson, W.E. and Andrew Mason 2011. Assessment of Coastal Storm Impacts on Contamination Body Burdens of Oysters Collected from the Gulf of Mexico. Environmental Monitoring and Assessment, 181:399-418.

Apeti, A.D., Whitall, D.R., Pait, A.S., Lauenstein, G.G., Zitello, A.G, and Dieppa, A. 2011. Characterization of Land Based Sources of Pollution in Jobos Bay, Puerto Rico: Status of Heavy Metal Concentration in Bed Sediment. Environmental Monitoring and Assessment. 184(2):811-30 http://www.springerlink.com/content/31wg076188888023.

Mason, AL, Apeti, A.D., and Whitall D. 2011. National Centers for Coastal Ocean Science (NCCOS) Research Highlights in the Chesapeake Bay. NOAA Technical Memorandum NOS NCCOS 128, Silver Spring, MD

Apeti, A.D., Lauenstein, G.G, Christensen, J.D., Kimbrough, K., Johnson, W.E., Kennedy, M. and Grant, K.G. 2010. Historical assessment of coastal contamination in Birch Harbor, Maine based on the analysis of mussels collected in the 1940s and the Mussel Watch program. Maine Pollution Bulletin, 60: 732-742.

Hartwell, S.I., Apeti, A.D., Claflin, L.W., Johnson, W.E. and Kimbrough, K. 2009. Sediment Quality Triad Assessment in Kachemak Bay: Characterization of Soft Bottom Benthic Habitats and Contaminant Bioeffects Assessment. North Pacific Research Board Final Report 726, 138pp

Apeti, A.D. and G.G. Lauenstein. 2009. Cadmium distribution in coastal sediment and mollusks of the US. Marine

Pollution Bulletin, Vol. 58(7): 1016-1024.
Johnson, E., A.D. Apeti, S. Haynes and L. Robinson. 2008. Solute or heat transport in a flat duct. American Journal of Environmental Sciences, 4(6): 721-726

Kimbrough, K.L., W.E. Johnson, G.G. Gunnar, J.D. Christensen and D.A. Apeti. 2008. An assessment of two decades of contaminant monitoring in the Nation's coastal zone. NOAA Technical Memorandum, NOS/NCCOS. 105pp. Silver Spring, MD

Kimbrough, K.L., W.E. Johnson, G.G. Gunnar, J.D. Christensen and D.A. Apeti. 2009. An assessment of polybrominated diphenyl ethers (PBDEs) in sediment and bivalves of the U.S. coastal zone. NOAA Technical Memorandum, NOS/NCCOS, 78.76 pp. Silver Spring, Maryland

Apeti, A.D. and G.G. Lauenstein. 2006. Assessment of mirex concentrations along the southern shoreline of the Great Lakes, USA. Journal of Environmental Sciences, 2(3): 95-103.

Hartwell I.S., A.D. Apeti, and A. Mason. 2006. Characterization of chemical contamination. In: A biogeographic Assessment of the Stellwagen Bank National Marine Sanctuary. Silver Spring, MD. NOS NOAA Technical Memorandum 45.

Apeti, A.D., E. Johnson, and L. Robinson. 2005. Relationship between metal concentration and physico-chemical characteristics in surficial sediments from Apalachicola Bay, Florida. American Journal of Environmental Sciences, 1(3):179-186.

Apeti, A.D., E. Johnson, and L. Robinson. 2005. A model for bioaccumulation of Cd and Zn in the American oyster (Crassostrea virginica) from Apalachicola Bay, Florida. American Journal of Environmental Sciences. 1:239-248

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Professional and Academic Credentials

Morgan State University, Bio-Environmental Science, Doctor of Philosophy, 2015

Morgan State University, Biology; Master of Science, 2005
University of Maryland Eastern Shore, Environmental Science, Bachelor of Science, 1997

Relevant Activities

Research interests include the application of computational ecology and bioinformatics to develop mathematical models and analytical tools that quantify adverse impacts to aquatic organisms from chemical contaminants in the environment. Current research efforts focus on metabolomics and the identification and differentiation of metabolomes that are associated with various chemical and environmental stressors. A pilot-study to assess the consistency of the transcriptome and metabolome of mussels at sites in the Great Lakes with varying chemical mixture characterizations. The results of this study will be applied to the development of a model that characterizes the environmental health status and for biomonitoring.

Additionally, for the last 3 years, I've managed and developed algorithms that annually implement NOAA's Northern Gulf of Mexico Hypoxia and Western Lake Erie Harmful Algal Blooms (HABs) forecasts. These forecasts are used to monitor, assess, and inform the public about the annual severity of the hypoxia and HABs sizes.

Selected Publications

1. M. Edwards, A.P. Jacob, K.L. Kimbrough, E. Davenport, and W.E. Johnson. Assessment of contaminant concentrations in california mussels (Mytilus spp): Relationship to land use and outfalls. Marine Pollution Bulletin 81(2), 2014.

2. Suzanne Bricker, Joao Ferreira, Changbo Zhu, Julie Rose, Eve Gal- imany, Gary Wikfors, Camille Saurel, Robin Landeck-Miller, James Wands, Philip Trowbridge, Raymond Grizzle, Katharine Wellman, Robert Rheault, Jacob Steinberg, Annie Jacob, Erik Davenport, Suzanne Ayvazian, Marnita Chintala, and Mark Tedesco. The role of shellfish aquaculture in reduction of eutrophication in an urban estuary. Environmental Science and Technology 52(1), 2017.

3. Suzanne Bricker, Joao Ferreira, Changbo Zhu, Julie Rose, Eve Gal- imany, Gary Wikfors, Camille Saurel, Robin Landeck-Miller, James Wands, Philip Trowbridge, Raymond Grizzle, Katharine Wellman, Robert Rheault, Jacob Steinberg, Annie Jacob, Erik Davenport, Suzanne Ayvazian, Marnita Chintala, and Mark Tedesco. Bioextractive removal of nitrogen by oysters in great bay piscataqua river estuary, new hampshire, usa. Estuaries and Coast 43:23-38, 2020.

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Professional and Academic Credentials:

Morgan State University, Environmental Engineering, Doctor of Engineering, 2020

City College New York (CUNY), Geology/Earth System Sciences, Master of Arts, 2005

Medgar Evers College (CUNY), Environmental Science, Bachelor of Science, 2001

Relevant Activities:
Current area of research and interest includes the assessment and classification of emerging contaminants in coastal freshwater systems. Research efforts include examining the environmental pathways and distribution of various contaminants including pharmaceuticals and personal care products (PPCPs) and legacy/current-use pesticides (CUPs) and their relationship to a suite of environmental variables including land-use gradients and point/diffuse sources. Additional research and projects include studies incorporating machine learning, pattern recognition and multivariate techniques in understanding the distribution of PPCPs and current-use pesticides (CUPs) detected in a suite of indicator organisms (Dreissena spp and Corbicula fluminea) and Polar Organic Chemical Integrative Sampler (POCIS) in coastal freshwater environment and associated riverine systems currently monitored by the Great Lakes Mussel Watch Program. Experience and skills in data analysis and various geographical information system (GIS) platforms have been used to foster collaboration at an interagency level and also among academia. The above skills and collaborative efforts have resulted in other projects and work that assessed and identified various permitted facilities including wastewater systems within the United States coastal zone and various areas of interest that are susceptible to environmental degradation through a suite of remote sensing, machine learning and GIS platforms.

Selected Publications:

Edwards, M, A., Jacobs, A., Davenport, E., Kimbrough, K., Johnson, E., Hunter, J., and Kang, D. (Anticipated 2020). An Assessment and Characterization of Pharmaceuticals and Personal Care Products (PPCPs) along the Great Lakes Basin Coastal Zone: Relationship to Land-use and Point Sources (2020 - In Review)

Kimbrough, K., W.E. Johnson, A. Jacob, M. Edwards, and E. Davenport. (2018). Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern. NOAA Technical Memorandum NOS NCCOS 249. Silver Spring, MD. 66 pp. doi:10.25923/2jp9-pn57.

Edwards, M. A., Jacob, A., Kimbrough, K., Johnson, W., & Davenport, E. D. (2016). Great Lakes Mussel Watch Sites Land-use Characterization and Assessment. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 208, 138pp

Edwards, M., Jacob, A. P., Kimbrough, K. L., E. Davenport, E., & Johnson, W. E. (2014). Assessment of trace elements and legacy contaminant concentrations in California Mussels (Mytilus spp.): Relationship to land use and outfalls. Marine Pollution Bulletin. 81(2), 325–333.

K. Kimbrough, W. E. Johnson, A. Jacob, M. Edwards, E. Davenport, G. Lauenstein, T. Nalepa, M. Fulton and A. Pait. 2014. Mussel Watch Great Lakes Contaminant Monitoring and Assessment: Phase 1. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 180, 113 pp.

Pittman, S. J., D. S. Dorfman, S. D. Hile, C.F.G. Jeffrey, M. A. Edwards, and C. Caldow. 2013. Land-Sea Characterization of the St. Croix East End Marine Park, U.S. Virgin Islands. NOAA Technical Memorandum NOS NCCOS 170. Silver Spring, MD. 119 pp.

Bly, P.L., and Edwards, M, A. (2010). 'The Applicability of Geographic Information Systems (GIS) and Remote Sensing in Identifying Polybrominated Diphenyl Ethers (PBDEs) sources using NOAA National Status & Trends Mussel Watch Program Data', International Geoscience and Remote Sensing Symposium (IGARSS), 421 - 424, DOI: 10.1109/IGARSS.2010.5650007

Edwards, M, A., and Blake, R. (2009). "Characterization and Assessment of Endemic Ecosystems with the Aid of Remote Sensing Techniques and Transformations", (In 33rd International Symposium on Remote Sensing of Environment (ISRSE) conference preceeding, Stresa, Italy, 4-8 May 2009.).

Pirhalla D.E., V. Ransibrahmanakul, R. Clark, A. Desch, T. Wynne, and M. Edwards. 2009. An Oceanographic Characterization of the Olympic Coast National Marine Sanctuary and Pacific Northwest: Interpretive Summary of Ocean Climate and Regional Processes Through Satellite Remote Sensing. NOAA Technical Memorandum NOS NCCOS 90. Prepared by NCCOS's Coastal Oceanographic Assessments, Status and Trends Division in cooperation with the National Marine Sanctuary Program. Silver Spring, MD. 53 pp.

Edwards, M, A., Winslow, M., and Blake, R. (2007). Evaluating Endemic Ecosystem with the Aid of Optical Remote Sensing and Geographical Information Systems (GIS) Techniques, International Federation of Surveyors (FIG), 1-10. (In International Federation of Surveyors (FIG) Conference Proceedings, San José, Costa Rica, 12 – 15 November 2007).

Edwards, M, A., Winslow, M., and Blake, R. (2007). Assessing Pine Barrens Soil Moisture Regimes using Synthetic Aperture Radar (SAR) Techniques, International Geoscience and Remote Sensing Symposium (IGARSS), 1828-1831 (on IGARSS CD-ROM in International Geoscience and Remote Sensing Symposium (IGARSS) Conference Proceedings, Barcelona, Spain - 23-27 July 2007).

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Professional and Academic Credentials
Ohio State University, Major: Evolution, Ecology & Organismal Biology, Minor: Soil Chemistry, Doctor of Philosophy, 2008

Cochin University of Science and Technology, India, Marine Biology; Master of Science, 2002

Mahatma Gandhi University, India, Zoology, Bachelor of Science, 1999

Additionally:
Certified Associate in Project Management (CAPM), Project Management Institute, 2020.
Enrolled in National Environmental Policy Act (NEPA) Certificate Program (Utah State University/Shipley Group). Expected completion by 2021.
National Honor Society of Phi Kappa Phi for academic excellence, 2008
Robert H. Edgerley Environmental Toxicology Summer Fellowship, 2006
Professional Affiliation: Society of Environmental Toxicology and Chemistry

Relevant Activities
My areas of interest lie at the interface of applied ecology, environmental chemistry and ecotoxicology. Currently working as an Environmental Scientist for the Great Lakes Mussel Watch project since 2011. In this capacity, I primarily provide scientific support to all aspects of planning, designing and implementation of the Great Lakes contaminant monitoring program including proposal writings, field missions, data quality assurance, data analysis, technical report writing, presentation of findings at conferences and stakeholder engagement. I have also worked on projects related to Deepwater Horizon oil spill, nutrient bioextraction ecosystem services using bivalves, developing programmatic categorical exclusion document for Harmful Algal Bloom Program, summarization of 10 years of contaminant monitoring data from Alaska for National Mussel watch and assessment of oil-related contaminants at the former Taylor Energy MC-20 site. Prior to joining CSS Inc./NOAA, I worked as a contractor for the National Exposure Research Laboratory at Environmental Protection Agency and was involved in the proposal development to study the biodegradation of fullerenes.

SELECT PUBLICATIONS:

1. Bricker, S.B., Grizzle, R.E., Trowbridge, P. et al. Bioextractive Removal of Nitrogen by Oysters in Great Bay Piscataqua River Estuary, New Hampshire, USA. Estuaries and Coasts 43, 23–38 (2020). https://doi.org/10.1007/s12237-019-00661-8

2. Rider, M., Apeti, D.A., Jacob, A., Kimbrough, K., Davenport, E., Bower, M., Coletti, H. and Esler, D., 2020. A Synthesis of Ten Years of Chemical Contaminants Monitoring in National Park Service - Southeast and Southwest Alaska Networks. A collaboration with the NOAA National Mussel Watch Program. NOAA Technical Memorandum NOS NCCOS. Silver Spring, MD. (under review)

3. Mason, A.L., A.P. Jacob, M.M. Rider, M.A. Gaskins, S.I. Hartwell, and I.R. MacDonald. 2019. Chapter 7: An Assessment of Oil-related Chemical Contaminants in Sediment, Water, and Oil from the MC20 Site in the Northern Gulf of Mexico. pp. 79-105. In: A.L. Mason, J.C. Taylor, and I.R. MacDonald (eds.), An Integrated Assessment of Oil and Gas Release into the Marine Environment at the Former Taylor Energy MC20 Site. NOAA National Ocean Service, National Centers for Coastal Ocean Science. NOAA Technical Memorandum 260. Silver Spring, MD. 147 pp. doi: 10.25923/kykm-sn39

4. Kimbrough, K.L., A. Jacob, W. E. Johnson, M. Edwards and E. Davenport. 2018. Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 249, 66 pp.

5. Bricker, Suzanne B., et al. 2018. Role of Shellfish Aquaculture in the Reduction of Eutrophication in an Urban Estuary. Environmental Science and Technology, vol. 52 (1): 173-183.

6. Jaruga P, Coskun E, Kimbrough K, Jacob A, Johnson

WE, Dizdaroglu M. 2017. Biomarkers of oxidatively induced DNA damage in dreissenid mussels: A genotoxicity assessment tool for the Laurentian Great Lakes". Environmental Toxicology 32: 2144–2153. doi: 10.1002/tox.22427.

7. Edwards, M. A., A. P. Jacob, K. Kimbrough, W. Johnson, and E. D. Davenport. 2016. Great Lakes Mussel Watch Sites Land-use Characterization and Assessment. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 208, 138pp.

8. Bricker, S.B., J. Ferreira, C. Zhu, J. Rose, E. Galimany, G. Wikfors, C. Saurel, R. Landeck Miller, J. Wands, P. Trowbridge, R. Grizzle, K. Wellman, R. Rheault, J. Steinberg, A. Jacob, E. Davenport, S. Ayvazian, M. Chintala, and M. Tedesco. 2015. An Ecosystem Services Assessment using bioextraction technologies for removal of nitrogen and other substances in Long Island Sound and the Great Bay/Piscataqua Region Estuaries. NCCOS Coastal Ocean Program, Decision Analysis Series No. 194.

9. Jacob, A.P., D.A. Culver, R. P. Lanno and A. Voigt. 2015. Ecological impacts of fluridone and copper sulphate in catfish aquaculture ponds. Environmental Toxicology and Chemistry 35:1183-1194.

10. Kimbrough, K. L., W. E. Johnson, A. P. Jacob, M. Edwards, E. Davenport , G. G. Lauenstein, T. Nalepa, M. Fulton and A. Pait. 2014. Mussel Watch Great Lakes Contaminant Monitoring and Assessment: Phase 1. NOAA Technical Memorandum NOS NCCOS 180. 113 pp.

11. Edwards, M., A. P. Jacob., K. L. Kimbrough., W. E. Johnson, E.D. Davenport. 2014. Assessment of Trace Elements and Legacy Contaminant Concentrations in California Mussels (Mytilus spp): Relationship to Land Use and Outfalls. Marine Pollution Bulletin 81: 325 -333.

12. Apeti, D., D. Whitall, G. Lauenstein., T. McTigue, K. L. Kimbrough, A. P. Jacob and A. Mason. 2013. Assessing the Impacts of the Deepwater Horizon Oil Spill: The National Status and Trends Program Response. NOAA Technical Memorandum NOS NCCOS 167.

13. Kimbrough, K. L., W. E. Johnson, A. P. Jacob, and G. G. Lauenstein. 2013. Contaminant Concentrations in Dreissenid Mussels from the Laurentian Great Lakes: A Summary of Trends from the Mussel Watch Program. In T. F. Nalepa and D. W. Schloesser [eds] Quagga and Zebra Mussels: Biology, Impacts, and Control. 2nd Edition. CRC Press Boca Raton, FL

14. Kimbrough, K. L., W. E. Johnson, A. P. Jacob, G. G. Lauenstein, V. Serveiss and A. Antonette. 2013. Contaminant in Mussels. In Assessment of Progress Made Towards Restoring and Maintaining Great Lakes Water Quality Since 1987. International Joint Commission U.S and Canada.

15. Jacob, A.P., and Culver, D.A. 2010. Experimental evaluation of the impacts of reduced inorganic phosphorus fertilization rates on juvenile saugeye production. Aquaculture 304: 22-33.

W. Edward Johnson

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Professional and Academic Credentials
University of Maryland, Environmental Chemistry, Doctor of Philosophy, 1995

University of Maryland, Environmental Toxicology; Master of Science, 1986

Virginia Tech University, Fisheries, Forestry & Wildlife, Bachelor of Science, 1980

Additionally:
Society of Environmental Toxicology and Chemistry
NOAA Science Diver

Relevant Activities
Serve as the project manager and co-principle investigator and for the National Status and Trends Great Lakes Mussel Watch Program to assess chemicals of emerging concern and their effects on fish and wildlife. I manage the annual Great Lakes Restoration Initiative funding (~$450K per year since 2010) for NOAA's effort to monitor and assess of chemicals of emerging concern and their bioeffects. The sampling effort includes measurement of chemicals in water, sediment and biota (bivalves, fish, benthic infauna, and passive water samples). In addition, bivalve health metrics including metabolomics, transcriptomics, DNA damage, and cellular biomarkers, have been monitored to assess molecular level bioeffects. I coordinate the field efforts including boat and shore crews, diving operations, small boat support, and ship support (EPA's R/V Lake Guardian) for offshore deep-water collections. I am responsible for the field effort including state and federal permits/NEPA, sample chain of custody and coordination with contract laboratories (six).

Selected Publications
Kimbrough, K., W.E. Johnson, A. Jacob, M. Edwards, and E. Davenport. 2018. Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern. NOAA technical memorandum NOS NCCOS; 249. 67pp.

Jaruga P, Coskun E, Kimbrough K, Jacob A, Johnson WE, Dizdaroglu M. Biomarkers of oxidatively induced DNA damage in dreissenid mussels: A genotoxicity assessment tool for the Laurentian Great Lakes. 2017. Environmental Toxicology. 32:2144–2153. https://doi.org/10.1002/tox.22427

Edwards, M. A., A. Jacob, K. Kimbrough, W.E. Johnson, and E. D. Davenport. 2016. Great Lakes Mussel Watch Sites Land-use Characterization and Assessment. NOAA Technical Memorandum NOS NCCOS 208. 138pp.

Watanabe, M., Meyer, K.A., Jackson, T.M., Schock, T.B., Johnson, W.E., Beardan, D.W. 2015. Application of NMR-based metabolomics for environmental assessment in the Great Lakes using zebra mussel (Dreissena polymorpha). Metabolomics 11:1302-1315. https://doi.org/10.1007/s11306-015-0789-4

K. Kimbrough, W. E. Johnson, A. Jacob, M. Edwards, E. Davenport, G. Lauenstein, T. Nalepa, M. Fulton and A. Pait. 2014. Mussel Watch Great Lakes Contaminant Monitoring and Assessment: Phase 1. NOAA Technical Memorandum NOS NCCOS 180. 113 pp.

Johnson, W.E. Kimbrough, K.L., Lauenstein, G.G., and Christensen, J. 2009. Chemical Contamination Assessment of the Gulf of Mexico in Response to Hurricanes Katrina and Rita. Environ Monit Assess 150: 211. https://doi.org/10.1007/s10661-008-0676-9

Kimbrough, K. L., W. E. Johnson, G. G. Lauenstein, J. D. Christensen and D. A. Apeti. 2009. An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS94. 87 pp.

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Professional and Academic Credentials

Virginia Institute of Marine Science, School of Marine Science, College of William and Mary, Ph.D. in Marine Science, 2002

Hampton University, B.S. Marine and Environmental Science, 1995

Additionally:

Society of Environmental Toxicology and Chemistry
NCCOS representative to the NOS AI Working Group
Great Lakes Water Quality Agreement Annex 3 Representative

Relevant Activities

I serve as lead for the data management team where I work to automate QA, visualization, and statistical tasks for all MAB chemistry data. I support several MAB groups with a focus on the Great Lakes Restoration Initiative and the Social Science Contaminants of Emerging Concern (CEC) project. The focus of my scientific work is on polycyclic aromatic hydrocarbons (PAHs), machine learning and spatial analysis. Currently I am working on projects that mine spatial data that for all MAB sites to predict the distribution of pharmaceutical, pesticides, and PAHs nationally. Before moving on to the data management and machine learning I focused on developing summary reports for the Mussel Watch program, field work.

Selected Publications

Kimbrough, K., W.E. Johnson, A. Jacob, M. Edwards, and E. Davenport. 2018. Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern. NOAA technical memorandum NOS NCCOS; 249. 67pp.

Jaruga P, Coskun E, Kimbrough K, Jacob A, Johnson WE, Dizdaroglu M. Biomarkers of oxidatively induced DNA damage in dreissenid mussels: A genotoxicity assessment tool for the Laurentian Great Lakes. 2017. Environmental Toxicology. 32:2144–2153. https://doi.org/10.1002/tox.22427

Edwards, M. A., A. Jacob, K. Kimbrough, W.E. Johnson, and E. D. Davenport. 2016. Great Lakes Mussel Watch Sites Land-use Characterization and Assessment. NOAA Technical Memorandum NOS NCCOS 208. 138pp.

K. Kimbrough, W. E. Johnson, A. Jacob, M. Edwards, E. Davenport, G. Lauenstein, T. Nalepa, M. Fulton and A. Pait. 2014. Mussel Watch Great Lakes Contaminant Monitoring and Assessment: Phase 1. NOAA Technical Memorandum NOS NCCOS 180. 113 pp.

Edwards, M., Jacob, A. P., Kimbrough, K. L., E. Davenport, E., & Johnson, W. E. (2014). Assessment of trace elements and legacy contaminant concentrations in California Mussels (Mytilus spp.): Relationship to land use and outfalls. Marine Pollution Bulletin. 81(2), 325–333.

Johnson, W.E. Kimbrough, K.L., Lauenstein, G.G., and Christensen, J. 2009. Chemical Contamination Assessment of the Gulf of Mexico in Response to Hurricanes Katrina and Rita. Environ Monit Assess 150: 211. https://doi.org/10.1007/s10661-008-0676-9

Kimbrough, K. L., W. E. Johnson, G. G. Lauenstein, J. D. Christensen and D. A. Apeti. 2009. An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS94. 87 pp.

Kimbrough, K.L., W.E. Johnson, G.G. Gunnar, J.D. Christensen and D.A. Apeti. 2008. An assessment of two decades of contaminant monitoring in the Nation's coastal zone. NOAA Technical Memorandum, NOS/NCCOS. 105pp. Silver Spring, MD

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Professional and Academic Credentials

- Doctor of Philosophy, Marine-Estuarine Environmental Sciences Program, University of Maryland, 2001
- Master of Science, Marine-Estuarine Environmental Sciences Program, University of Maryland, 1987
- Bachelor of Science, Biological Sciences. 1980. St. Mary's College of Maryland

Relevant Activities

Conduct a variety of projects to assess the presence, fate and effects of chemical contaminants in marine and estuarine environments. Recent work has involved investigating the impacts of chemical contaminants in coral reef ecosystems in the Caribbean and in the Pacific. Working closely with partners in territories, states, and in other federal agencies to leverage knowledge and resources has been a key to the success of all these projects. Other work has included investigations on emerging contaminants of concern in the Chesapeake Bay and in coastal waters of California and South Korea, along with vertebrate endocrine disruption in the Chesapeake Bay and tributaries, and agricultural pesticide use and impacts in coastal areas of the US. Responsible for project management including planning, implementation, QA/QC and statistical analysis of data, along with publication and communication of results.

Selected Publications

Pait, A.S., W.M.C. Whitman, S.I. Hartwell, D.R. Whitall, and D.A. Apeti. 2019. Measurement of Turbidity, Suspended Sediments and Nutrients in Three Rivers that Drain to the Achang Preserve from the Manell Watershed, Guam. NOAA Technical Memorandum NOS NCCOS 268. Silver Spring, MD. 33 pp.

Pait, A.S., A.L. Mason, S.I. Hartwell, and D.A. Apeti. 2019. An Assessment of Chemical Contaminants in the Waters Around Cocos Island, Guam Using Polyethylene Passive Water Samplers. NOAA Technical Memorandum NOS NCCOS 261. Silver Spring, MD. 43 pp

Pait, A.S., S.I. Hartwell, D.A. Apeti, and A.L. Mason. 2017. An Analysis of Chemical Contaminants in Sediments and Fish from Cocos Lagoon, Guam. NOAA Technical Memorandum NOS NCCOS 235. Silver Spring, MD. 74 pp.

Hartwell, S.I., D.A. Apeti, A.L. Mason and A.S. Pait. 2016. An Assessment of Tributyltin and Metals in Sediment Cores from the St. Thomas East End Reserves. NOAA Technical Memorandum NOS NCCOS 217. Silver Spring, MD. 20 pp

Pait, A.S., S.I. Hartwell, L.J. Bauer, D.A. Apeti, and A.L. Mason. 2016. An Integrated Environmental Assessment of the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS NCCOS 202. Silver Spring, MD. 219 pp.

Apeti, D.A., A.L. Mason, S.I. Hartwell, A.S. Pait, L.J. Bauer, C.F.G. Jeffrey, A.M. Hoffman, F.R. Galdo Jr, and S.J. Pittman. 2014. An Assessment of Contaminant Body Burdens in the Coral (Porites astreoides) and Queen Conch (Strombus gigas) from the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS/NCCOS 177. Silver Spring, MD. 37pp.

Kimbrough, K., W. E. Johnson, A. Jacob, M. Edwards, E. Davenport, G. Lauenstein, T. Nalepa, M. Fulton and A. Pait. 2014. . Mussel Watch Great Lakes Contaminant Monitoring and Assessment: Phase 1. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 180, 113 pp.

Pait, A.S., F.R. Galdo Jr, S.I. Hartwell, A.L. Mason, D.A. Apeti, C.F.G. Jeffrey, A.M. Hoffman, and S.J. Pittman. 2014. An assessment of Nutrients, Sedimentation, and Total Suspended Solids (TSS) in the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS/NCCOS 184. Silver Spring, MD. 60pp.

Pait, A.S., S.I. Hartwell, A.L Mason, R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, D.A. Apeti, and S.J. Pittman. 2014. An assessment of chemical contaminants in sediments from the St. Thomas East End Reserves, St. Thomas, USVI. Environmental Monitoring and Assessment.186:4793–4806.

Pait, A.S., S.I. Hartwell, A.L. Mason, R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, D.A. Apeti, F.R. Galdo Jr., and S.J. Pittman. 2013. An Assessment of Chemical Contaminants, Toxicity and Benthic Infauna in Sediments from the St. Thomas East End Reserves (STEER). NOAA Technical

Memorandum NOS NCCOS 156. Silver Spring, MD. 70 pp.

Pait, A.S., S.I. Hartwell, A.L. Mason, F.R. Galdo, Jr., R.A. Warner, C.F.G. Jeffrey, A.M. Hoffman, D.A. Apeti, and S.J. Pittman. 2013. An Assessment of Chemical Contaminants Detected in Passive Water Samplers Deployed in the St. Thomas East End Reserves (STEER). NOAA Technical Memorandum NOS/NCCOS 157. Silver Spring, MD. 22 pp.
P
ait, A.S., D. R. Whitall, A. Dieppa, S. E. Newton, L. Brune, C. Caldow, A. L. Mason, D. A. Apeti, and J. D. Christensen (2012). Characterization of organic chemical contaminants in sediments from Jobos Bay, Puerto Rico. Environmental Monitoring and Assessment. 184: 5065-5075

Apeti, D.A., D. R. Whitall, A. S. Pait, A. Dieppa and A. G. Zitello. (2012). Characterization of land-based sources of pollution in Jobos Bay, Puerto Rico: status of heavy metal concentration in bed sediment. Environmental Monitoring and Assessment. 184:811–830.

Hartwell, S.I., M. J. Hameedi, and A. S. Pait. 2011. Empirical assessment of incorporating sediment quality triad data into a single index to distinguish dominant stressors between sites. Environmental Monitoring and Assessment (2011) 174:605–623.

Pait, A.S., C. F.G. Jeffrey, C. Caldow, D. R. Whitall, S. I. Hartwell, A. L. Mason, and J. D. Christensen. Chemical contamination in southwest Puerto Rico: a survey of contaminants in the coral Porites astreoides. Caribbean Journal of Science (2010) Vol 45, No. 2-3, pp191-203.

Pait, A.S., A. L. Mason, D. R. Whitall, J. D. Christensen, and S. I. Hartwell. 2010. Chapter 5: Assessment of Chemical Contaminants in Sediments and Corals in Vieques. pp101-150. In: Bauer and Kendall (eds.), An Ecological Characterization of the Marine Resources of Vieques, Puerto Rico Part II: Field Studies of Habitats, Nutrients, Contaminants, Fish, and Benthic Communities. NOAA Technical Memorandum NOS NCCOS 110. Silver Spring, MD. 174 pp.

Pait, A.S., and J.O. Nelson. 2009. A survey of indicators for reproductive endocrine disruption in Fundulus heteroclitus (killifish) at selected sites in the Chesapeake Bay. Marine Environmental Research. 68: 170-177.

Choi, M., H.B. Moon, J. Yu, S.S. Kim, A.S. Pait, and H.G. Choi. 2009. Nationwide monitoring of nonylphenolic compounds and coprostanol in sediments from Korean coastal waters. Marine Pollution Bulletin. 58: 1078 – 1095.

Pait, A.S., D.R. Whitall, C.F.G. Jeffrey, C. Caldow, A.L. Mason, G.G. Lauenstein, and J.D. Christensen. 2008. Chemical contamination in southwest Puerto Rico: an assessment of trace and major elements in nearshore sediments. Marine Pollution Bulletin. 56: 1949 – 1956.

Pait, A.S., D.R. Whitall, C.F.G. Jeffrey, C. Caldow, A.L. Mason, G.G. Lauenstein, and J.D. Christensen. 2008. Chemical contamination in southwest Puerto Rico: an assessment of organic contaminants in nearshore sediments. Marine Pollution Bulletin. 56: 580 - 606.

Pait, A.S., D.R. Whitall, C.F.G. Jeffrey, C. Caldow, J.D. Christensen, A.L. Mason and J. Ramirez. 2007. Contaminants and Coral Health in Southwest Puerto Rico: A Survey of Chemical Contaminants in Sediments. NOS NCCOS 52. Silver Spring, MD. NOAA/NOS/Center for Coastal Monitoring and Assessment. 116pp.

Pait, A.S., R.A. Warner, S.I. Hartwell, J.O. Nelson, P.A. Pacheco, and A.L. Mason. 2006. Human Use Pharmaceuticals in the Estuarine Environment: A Survey of the Chesapeake Bay, Biscayne Bay, and Gulf of the Farallones. NOS NCCOS 7. Silver Spring, MD. NOAA/NOS/Center for Coastal Monitoring and Assessment. 22pp.

Pait, A.S., T.P. O'Connor, and D. R. Whitall. 2004. Health of Galveston Bay for Human Use. National Coastal Condition Report, Chapter 9. 10pp.

Pait, A. S. and J.O. Nelson. 2003. Vitellogenesis in male Fundulus heteroclitus (killifish) induced by selected estrogenic compounds. Aquatic Toxicology. 64: 331-342.

Harmon, M., A.S. Pait, and M.J. Hameedi. 2003. Sediment Contamination, Toxicity, and Macroinvertebrate Infaunal Community in Galveston Bay. NOAA Technical Memorandum NOS NCCOS CCMA 122. 67pp.

Pait, A.S., and J.O. Nelson. Endocrine Disruption in Fish: An Assessment of Recent Research and Results. 2002. NOAA Technical Memorandum NOS NCCOS CCMA 149. 55pp.

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Professional and Academic Credentials:
Pierre and Marie Curie University, Oceanography and Marine Environments, Master, 2016
Sacred Heart University, Environmental Science and Management, Professional Master, 2014
Johns Hopkins University, Romance Languages, Psychology, Bachelor of Arts, 2009
Additionally:
Society of Environmental Toxicology and Chemistry (SETAC)

Relevant Activities:
Environmental scientist for the National Status and Trends (NS&T) Mussel Watch Program (MWP). Primary duties are to assist in the collection, management, analysis, and interpretation of environmental chemical and biological data by developing technical reports and publications, assessing coastal water quality status and trends, and assisting in the overall execution of coastal monitoring assessments and the national MWP. Additional responsibilities include performing the duties of the data manager for the national Mussel Watch team and improving the analytical and dating mining capabilities of the Monitoring and Assessment Branch through the development of large-scale spatial and statistical analyses of NS&T data. This is accomplished by means of Python and R language code for advanced data analysis and eventual use in predictive models. Responsibilities also include using InDesign software to increase the speed and efficiency with which technical reports can be produced and to improve the overall presentation and consistency of MWP data by creating template reports that can be easily populated and adjusted.
Since joining NOAA in 2018, work on specific projects includes:

- Analyzing the presence of legacy contaminants in the Chesapeake Bay, MD, and Charleston Harbor, SC,
- Creating a 10-year synthesis of legacy contaminant data in southern Alaska by combining the sampling data of the MWP, Southeast Alaska Network and Southwest Alaska network, and comparing it to the national historic data for relevance,
- Analyzing the presence of contaminants of emerging concern in the Gulf of Maine in cooperation with the Gulf of Maine Gulfwatch program,
- And supporting the high visibility MC-20 project including developing the Environmental Compliance document, writing the introduction for the official report, reviewing the chemistry chapter throughout its iterations, and providing other general support as needed such as creating meeting synthesis reports.

Selected Publications
Rider, M., Apeti, D.A., Jacob, A., Kimbrough, K., Davenport, E., Bower, M., Coletti, H. and Esler, D., 2020. A Synthesis of Ten Years of Chemical Contaminants Monitoring in National Park Service - Southeast and Southwest Alaska Networks. A collaboration with the NOAA National Mussel Watch Program. NOAA Technical Memorandum NOS NCCOS. Silver Spring, MD. (under review)

Apeti, D.A., **Rider, M.**, Jones, S. and Wirth, E., 2020. An Assessment of Contaminants of Emerging Concern in the Gulf of Maine. NOAA Technical Memorandum NOS NCCOS. Silver Spring, MD. (under review)

Mason, A.L., **Rider, M.M.,** MacDonald, I.R. and Taylor, J.C., 2019. Chapter 1: Introduction and Background Conditions at the Former Taylor Energy MC20 Site in September 2018. pp. 1-6. In: A.L. Mason, J.C. Taylor, and I.R. MacDonald (eds.), An Integrated Assessment of Oil and Gas Release into the Marine Environment at the Former Taylor Energy MC20 Site. NOAA National Ocean Service, National Centers for Coastal Ocean Science. NOAA Technical Memorandum 260. Silver Spring, MD. 147 pp. doi: 10.25923/kykm-sn39

Mason, A.L., Jacob, A.P., **Rider, M.M.,** Gaskins, M.A., Hartwell, S.I. and MacDonald, I.R., 2019. Chapter 7: An Assessment of Oil-related Chemical Contaminants in Sediment, Water, and Oil from the MC20 Site in the Northern Gulf of Mexico. pp. 79-106. In: A.L. Mason, J.C. Taylor, and I.R. MacDonald (eds.), An Integrated Assessment of Oil and Gas Release into the Marine Environment at the Former Taylor Energy MC20 Site. NOAA National Ocean Service, National Centers for Coastal Ocean Science. NOAA Technical Memorandum 260. Silver Spring, MD. 147 pp. doi: 10.25923/kykm-sn39

Mercader, M., **Rider, M.,** Cheminée, A., Pastor, J., Zawadzki, A., Mercière, A., Crec'hriou, R., Verdoit-Jarraya, M. and Lenfant, P., 2018. Spatial distribution of juvenile fish along an artificialized seascape, insights from common coastal species in the Northwestern Mediterranean Sea. Marine environmental research, 137, pp.60-72.

Cheminée, A., **Rider, M.,** Lenfant,P., Zawadzki, A., Mercière, A., Crec'hriou, R., Mercader, M., Saragoni, G., Neveu, R., Ternon, Q., Pastor, J., 2017. Shallow rocky nursery habitat for fish: Spatial variability of juvenile fishes among this poorly protected essential habitat. Marine Pollution Bulletin, Volume 119, Issue 1, 15 June 2017, Pages 245–254.

Mercader, M., Mercière, A., Saragoni, G., Cheminée, A., Crec'hriou, R., Pastor, J., **Rider, M.,** Dubas, R., Lecaillon, G., Boissery, P., Lenfant, P., 2017. Small artificial habitats to enhance the nursery function for juvenile fish in a large commercial port of the Mediterranean. Ecological Engineering, Volume 105, August 2017, Pages 78-86.

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Professional and Academic Credentials
Master of Science, Oceanography, College of Geoscience, Texas A&M University 1980

Bachelor of Science, Microbiology, College of Science, Texas A&M University 1975

Post-masters university education:

Remote Sensing Institute, College of Marine Studies, University of Delaware 1987

International Environmental Policy, School of International Affairs, Space Policy Institute, George Washington University. 1988

Relevant Activities
With a diverse educational background of microbiology, oceanography and remote sensing, I have been involved in a wide range of research topics. In NCCOS my research interests are related to water quality and technologies to facilitate those data acquisitions. Working on a multi-line NOAA team, we are using remote sensing assets to derive water quality related biogeochemical products. Primary users of the water quality products have been watershed managers in the Caribbean and Pacific. Other users are stakeholders who want methods to routinely monitor water quality in their areas of interest. These water quality products are used for such applications as to detect and map the extent of runoff plumes. The sediment plumes, can contain chemical contaminants and thus can assist where to sample for chemical analysis.

Selected Publications
Hernandez, W.J., S. Ortiz-Rosa, R.A. Armstrong, E.E. Geiger, C.M. Eakin and R.A. Warner. 2020. Quantifying the effects of hurricanes Irma and Maria on coastal water quality in Puerto Rico using moderate resolution satellite sensors. Remote Sensing 2020,12:964-979. http://dx.doi.org/10.3390/rs12060964

Latham, W., D. Jochum, R.A. Warner. 2019. Advanced Coastal Monitor: Autonomy and Modularity in Marine Survey Vehicles. NOAA Emerging Technologies Conference, College Park, MD.

Jochum, D., W. Latham, C. Iturrino, C. Wah, R. Solis, H. Sierra Gil, E. Arzuaga, W. Hernandez, A. Strong, R.A. Warner. 2019. NOAA Applications Using Autonomous Vehicles and Other Emerging Technologies. NOAA Emerging Technologies Conference, College Park, MD.

Gieger, Erick F, William J. Hernandez, C. Mark Eakin, Menghua Wang, Jacqueline L. De La Cour, Gang Liu, Kyle V. Tirak, Scott F. Heron, William J. Skirving, Robert A. Warner, Alan E. Strong 2018. NOAA Coral Reef Watch Near Real-Time Satellite Ocean Color Tools for Land-based Sources of Pollution and Coral Reef Management. AGU/ASLO Ocean Sciences Meeting 2018.

Strong, Alan, Menghua Wang3, C. Mark Eakin1, Erick F. Geiger1,5, Robert A. Warner, William J. Skirving2,5, Gang Liu1,5, Scott F. Heron2,5, Kyle V. Tirak1,5, Michael Ondrusek3, William J. Hernandez5,6,7, Maria Cardona-Maldonado6, Roy A. Armstrong6,7, and Jacqueline L. De La Cour NEW VIIRS SATELLITE OCEAN COLOR PRODUCTS FOR MANAGEMENT OF LAND-BASED SOURCES OF POLLUTION OVER CORAL REEFS. International Coral Reef Symposium, June 19-24, 2016, Oahu, Hawai'i.

Kaplan, M., R.A. Armstrong, R.A. Warner. 2016. Four coral health projects in collaboration with NOAA's Educational Partnership Program. International Coral Reef Symposium, June 19-24, 2016, Oahu, Hawai'i.

Cardona, M.A., W.J. Hernandez, R.A. Armstrong, A.E. Strong, M. Wang, E. Gieger, M. Eakin, G. Piniak, R.A. Warner. 2016. Collaborative effort to develop a forecasting product that integrates water quality, physiological and optical properties to address the stress response of coral reef ecosystems. National Monitoring Conference (NWQMC) May 2-6, 2016. Tampa, Florida.

Hernandez, W.J., M.A. Cardona, R.A. Armstrong, A.E. Strong, M. Wang, E. Gieger, M. Eakin, G. Piniak, R.A. Warner. 2016. Development of water quality products derived from NOAA operational satellite sensor (VIIRS) data. National Monitoring Conference (NWQMC) May 2-6, 2016. Tampa, Florida.

Fan, C., R.A.Warner. 2014. Characterization of water reflectance spectra variability: implications for hyperspectral remote sensing in estuarine waters. Marine Science 4(1): 1-9.

DOI:10.5923/j.ms.20140401.01

Warner, R.A. and C. Fan. 2013. Optical spectra of phytoplankton cultures for remote sensing applications: focus on harmful algal blooms. International Journal of Environmental Science and Development, Vol. 4, No. 2,p.94-98 April 2013. IJESD 2013 Vol.4(2): 94-98 ISSN: 2010-0264 DOI: 10.7763/IJESD.2013.V4.312.

Wynne,T.T., R.P. Stumpf, M.C. Tomlinson, R.A. Warner, P.A. Tester, J. Dyble, G.L. Fahnenstiel. 2008. Relating spectral shape to cyanobacterial blooms in the Laurentian Great Lakes. International Journal of Remote Sensing Vol.29 (12):3665-3672.

Warner, J. X., J. M. Grossmann, D. A. Chu, K. Fuemmrich, and R. A. Warner, 2006, Airborne hyperspectral data collection with the UMBC VNIR sensor. Proceedings of the SPIE, Volume 6299, pp. 62990X, 10.1117/12.680996, 2006.

Kendall, M.S., C.R. Kruer, K.R. Buja, J.D. Christensen, E. Diaz, R.A. Warner, and M.E. Monaco. 2004. A characterization of the shallow-water coral reefs and associated habitats of Puerto Rico. Gulf and Caribbean Research 16(2):177-184.

Zaitzeff, J.B., E.J. D'Sa, C.S. Yentsch, J.L. Miller, R.G. Steward, R. Ives, and R. Warner. 2001. Rapid remote assessments of salinity contrasts in Florida Bay and bio-optical variability. In: Linkages between ecosystems in the south Florida hydroscape: The river of grass continues, J.W. Porter and K.G. Porter, eds., CRC press

Warner, R.A. and W.B. Campbell 1993. Chapter 10, "Ice Monitoring", In: Satellite Remote Sensing of the Oceanic Environment Ian S.F. Jones, Y. Sugimori, and R.W. Stewart (editors). Southwood Press pp. 528.

Oliver,J.D., R.A. Warner, and D.R. Cleland. 1983. Distribution of Vibrio vulnificus and other lactose-fermenting vibrios in the marine environment. Applied and Environmental Micro-biology. 45:985-998.

David R. Whitall

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Professional and Academic Credentials:
The University of North Carolina at Chapel Hill Ph D. in Environmental Sciences and Engineering 2000

The Pennsylvania State University. B.S. in Environmental Resource Management 1995

Relevant Activities:
Lead scientist on a variety of projects assessing the extent and magnitude of pollution in the environment including developing research projects, experimental/sampling designs, field work, data analysis, including statistical and spatial analysis techniques, and communication of interpretated data products (oral presentations, technical papers, web sites, press releases, one pagers) for a variety of audiences (technical, coastal managers, state and local governments, Congress, industry, tribes, general public). Specific areas of research interest include effects of nutrients, pesticides, heavy metals, PAHs, pharmaceuticals, and personal care products on estuarine, temperate near coastal and coral reef ecosystems. Collaborated with a variety of interagency (USEPA, USGS, USDA, USFWS), state, academic, territory and local partners.

Selected Publications:

Whitall, DR, SB Bricker, D Cox, J Baez, J Stamates, KL Gregg, FE Pagan. 2019. Southeast Florida Reef Tract Water Quality Assessment. NOAA Technical Memoradum NOS NCCOS 271. Silver Spring. 116 p

Mason, AL, DR Whitall. 2019. A Baseline Chemical Contaminants Assessment of Sediment from the Nu'uuli Pala Lagoon, American Samoa. NOAA Technical Memoradum NOS NCCOS 267. Silver Spring. 35 p

Pait, AS, W Whitman, SI Hartwell, DR Whitall, DA Apeti 2019. Measurement of Turbidity, Suspended Sediments and Nutrients in Three Rivers that Drain to the Achang Preserve from the Manell Watershed, Guam. NOAA Technical Memoradum NOS NCCOS 268. Silver Spring. 33 p

Whitall, D, M Curtis, A Mason, B Vargas-Angel. 2019. Excess Nutrients in Vatia Bay, American Samoa: Spatiotemporal Variability, Source Identification and Impact on Coral Reef Ecosystems. NOAA Technical Memoradum NOS NCCOS 266. Silver Spring. 112 p

Pisarski, E.C., E.F. Wirth, S.I. Hartwell, B.S. Shaddrix, D.R. Whitall, D.A. Apeti, M.H. Fulton, and G. Baker. 2018. Assessment of Hydrocarbon Carryover Potential for Six Field Cleaning Protocols. NOAA Technical Memorandum NOS NCCOS 247. Silver Spring, MD. 36 p.

Whitall, D. A. Ramos, D. Wehner, M. Fulton, A. Mason, E. Wirth, B. West, A. Pait, E. Pisarski, B. Shaddix, L. Reed. 2016. Contaminants in Queen Conch (Strombus gigas) in Vieques, Puerto Rico. Regional Studies in Marine Science 5: 80-86.

Whitall, D.R., A.L. Mason, M. Fulton, E. Wirth, D. Wehner, A. Ramos-Alvarez, A.S. Pait, B. West, E. Pisarski, B. Shaddrix, L. Reed. 2016. Contaminants in Marine Resources of Vieques, Puerto Rico. NOAA Technical Memorandum

Whitall, D, A. Mason, S. Johnson, R. Okano, J. Iguel. 2016. Chemical Contaminants in Corals (Pocillopora damicornis) in Tinian, CNMI. NCCOS Tech Memo.

Holst, S., A. Messina, T. Biggs, B. Vargas-Angel, D. Whitall. 2016. Baseline Assessment of Faga'alu Watershed: A Ridge to Reef Assessment in Support of Sediment Reduction Activities and Future Evaluation of Their Success. CRCP Tech Memo 23.

Whitall, D., A. Pait, S. Hartwell. 2015. Regional Studies in Marine Science 5:80-86.
Chemical Contaminants in Surficial Sediment in Coral and Fish Bays, St. John, U.S. Virgin Islands. Marine Environmental Research 112:1-8.

Whitall, D. and S. Holst. 2015. Pollution in Surface Sediments in Faga'alu Bay, Tutuila, American Samoa. NCCOS Tech Memo 201.

Kumar, N. D. Ramirez-Ortiz, H. Solo-Gabriele, J. Treaster, O. Carrasquillo, M. Toborek, S. Deo, J. Klaus, L. Bachus, D. Whitall, S. Daunert, J. Szapocznik. 2015. Environmental PCBs in Guánica Bay, Puerto Rico: implications for community health. Environmental Science and Pollution Research

23: 1-11.

Whitall, D., A Mason, A Pait, L Brune, M Fulton, E Wirth, L Vandiver. 2014. Organic and metal contamination in marine surface sediments of Guánica Bay, Puerto Rico Marine Pollution Bulletin 80: 293-301

I. McCarty, G. C. Hapeman. C. Rice, D. Hively, L. McConell, A. Sadeghi, M Lang, D Whitall, K. Bialek and P. Downey. 2014. Metolachlor metabolite (MESA) reveals agricultural nitrate-N fate and transport in Choptank River watershed. Science of the Total Environment 473: 473-482.

II. Potter, T.L., D.D Bosch, A. Dieppa, D. R. Whitall, T.C. Strickland. 2013. Atrazine fate and transport within the coastal zone in southeastern Puerto Rico. Marine Pollution Bulletin 67:36-44.

III. Whitall, D., A. Mason, A. Pait. 2012. Nutrient Dynamics in Coastal Lagoons and Marine Waters of Vieques, Puerto Rico. Tropical Conservation Science Vol.5 (4):495-509, 2012

Hively D, Hapeman CJ, McConnell LL, Fisher TR, Rice CP, McCarty GW, Sadeghi AM, Whitall DR, Downey PM, Niño de Guzmán GT, Bialek-Kalinski K, Lang MW, Gustafson AB, Sutton AJ, Sefton KA, Harman Fetcho JA. 2011. Relating nutrient and herbicide fate with landscape features and characteristics of 15 subwatersheds in the Choptank River watershed. Science of the Total Environment 409: 3866-78.

Whitall, D, Pait, A, Apeti, D, Dieppa, A, Newton, S, Brune, L, Caldow, C, Mason, A, and Christensen, J. 2011. Contaminants in Sediments and Coral Tissues of Jobos Bay. In: A Baseline Assessment of the Ecological Resources of Jobos Bay, Puerto Rico. Whitall, D.R., B.M. Costa, L.J. Bauer, A. Dieppa, and S.D. Hile (eds). NOAA Technical Memorandum NOS NCCOS 133. Silver Spring, MD. 188 pp.

Whitall, D, Dieppa, A and Potter, T. 2011. Spatial and Temporal Variability in the Water Column Nutrients and Pesticides of Jobos Bay. In: A Baseline Assessment of the Ecological Resources of Jobos Bay, Puerto Rico. Whitall, D.R., B.M. Costa, L.J. Bauer, A. Dieppa, and S.D. Hile (eds). NOAA Technical Memorandum NOS NCCOS 133. Silver Spring, MD. 188 pp.

Apeti, D, Whitall, D, Pait, A, Dieppa, A, Newton, S, Brune, L, Caldow, C, Mason, A, and Christensen, J. 2012. Characterization of Land Based Sources of Pollution in Jobos Bay, Puerto Rico: Status of Heavy Metal Concentration in Bed Sediment. Environmental Monitoring and Assessment 184(2):811-30

Pait, A, Whitall, D, Apeti, D, Dieppa, A, Newton, S, Brune, L, Caldow, C, Mason, A, and Christensen, J. 2012. Characterization of organic chemical contaminants in sediments from Jobos Bay, Puerto Rico. Environmental Monitoring and Assessment. 184(8):5065-75

Whitall, D, Hively, W, Leight, A.K., Hapeman, C, McConnell, L, Fisher T, Rice, C, Codling, E, McCarty, G, Sadeghi, A, Gustafson, A, Bialek, K. 2010. Pollutant fate and spatio-temporal variability in the choptank river estuary: Factors influencing water quality. Science of the Total Environment 408: 2096–2108

Whitall, D.R., A.L. Mason, A.S. Pait, V Ransibrahmanakul and J.D. Christensen. 2010. Characterization of Spatial and Temporal Nutrient Dynamics. pp. 151-168. In: Bauer and Kendall (eds.), An Ecological Characterization of the Marine Resources of Vieques, Puerto Rico Part II: Field Studies of Habitats, Nutrients, Contaminants, Fish, and Benthic Communities. NOAA Technical Memorandum NOS NCCOS 110. Silver Spring, MD. 174 pp.

Pait, A.S., Mason, A.L., Whitall,D.R., Christensen, J.D., and Hartwell, S.I. 2010. Assessment of Contaminants in Sediments and Corals in Vieques. In: Bauer and Kendall (eds.), An Ecological Characterization of the Marine Resources of Vieques, Puerto Rico Part II: Field Studies of Habitats, Nutrients, Contaminants, Fish, and Benthic Communities. NOAA Technical Memorandum NOS NCCOS 110. Silver Spring, MD. 174 pp.

Pait, A. Jeffrey, C, Caldow, C, Whitall, D, Hartwell, I, Mason, A, Christensen, J. 2010. Chemical contamination in southwest Puerto Rico: A survey of contaminants in the coral Porites astreoides. Caribbean Journal of Science 45: 191-203.

Pait, A.S., D.R. Whitall, C.F.G. Jeffrey, C. Caldow, A.L. Mason, J.D. Christensen. 2008.
Chemical contamination in southwest Puerto Rico: An assessment of organic contaminants in nearshore sediments. Marine Pollution Bulletin 56: 580-587.

Pait, A.S, D.R. Whitall, C.F.G. Jeffrey, C. Caldow, A.L. Mason, G.G. Lauenstein and J.D. Christensen.
2008. Chemical contamination in southwest Puerto Rico: An assessment of trace and major element in nearshore sedi-

ments. Marine Pollution Bulletin, 56: 1949-1956

McCarty G., L.L. McConnell, C.J. Hapeman, A. Sadeghi, C. Graff, W.D. Hively, M.W. Lang, T.R. Fisher, T. Jordan, C.P. Rice, E.E. Codling, D. Whitall, A. Lynn, J. Keppler, and M.L. Fogel. 2008. Water quality and conservation practice effects in the Choptank River watershed. Journal of Soil and Water Conservation 63: 463-474.

Zitello, A.G., D.R. Whitall, A. Dieppa, J.D. Christensen, M.E. Monaco and S.O. Rohmann. 2008. Characterizing Jobos Bay, Puerto Rico: A Watershed Modeling Analysis and Monitoring Plan. NOAA Technical Memorandum NOS NCCOS 76. 81 pp.

Whitall, D.R. 2008. Historical Nitrogen and Phosphorus Loadings to the Northern Gulf of Mexico NOS NCCOS 85. Silver Spring, MD. NOAA/NOS/Center for Coastal Monitoring and Assessment. 25 pp.

Pait, A.S., D.R. Whitall, C.F.G. Jeffrey, C. Caldow, A.L. Mason, J.D. Christensen, Mark E. Monaco, and J. Ramirez. 2007. An Assessment of Chemical Contaminants in the Marine Sediments of Southwest Puerto Rico. NOS NCCOS 52. Silver Spring, MD. NOAA/NOS/Center for Coastal Monitoring and Assessment. 116pp..

Whitall D, S Bricker, J.G. Ferreira, A. Nobre, T. Simas, M.C. Silva. 2007. Assessment of eutrophication in estuaries: pressure-state-response and source apportionment. Journal of Environmental Management 40:678–690.

O'Connor T and D. Whitall. 2007. Linking hypoxia to shrimp catch in the northern Gulf of Mexico. Marine Pollution Bulletin 54 460–463.

The National Mussel Watch Program: Long-term Contaminant Monitoring Program

Dennis Apeti

Overview

The National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program (MWP) is a contaminant monitoring program that monitors the status and trends of chemical contaminants and biological stressors in the nation's coastal waters. Since 1986, the Mussel Watch Program remains the longest running continuous contaminant-monitoring program of its kind in the United States. The program is sponsored by the National Center for Coastal Ocean Science (NCCOS), and utilizes a sentinel-based approach to monitoring, by collecting and analyzing sediment and bivalves (oysters and mussels) as surrogates for water pollution and bioaccumulation at a network of nearly 300 coastal sites including the Great Lakes, Alaska, Hawaii, and Puerto Rico. Contaminants monitored include a suite of organic and inorganic chemicals, such as pesticides (e.g. DDT), antifouling agents (e.g. butyltin), industrial contaminants (e.g. PCB), oil and fossil fuel related contaminants (e.g. PAH) and heavy metals (e.g. mercury). Recently, more than 280 contaminants of emerging concern (CEC) are being measured for long-term or place-based monitoring consideration; these include pharmaceuticals and personal care products, flame-retardants, current-use pesticides, surfactants, and stain repellant compounds. Along with other ancillary data, including sediment grain size and bivalve shell length and lipid content, the program has also historically measured biological indicators of water quality. The bacteria *Clostridium perfringens* is measured in sediment as an indicator of sewage waste, and from 1995 through 2009, the program had monitored histopathology stressors (diseases and parasites, and gonadal index) in mussels and oysters as indicators of bivalve health and water quality. Since its inception in 1986, the National Status &Trends (NS&T) Program's Mussel Watch Project has produced a wealth of data on the levels and distribution of chemical contaminants in coastal waters of the United States. The program's long-term monitoring data are georeferenced and served to the public via an NCCOS website data portal. The data provides a unique historic benchmark for assessing coastal health and ecosystem management efforts. Mussel Watch is able to assess the effects of environmental disasters such as the 2010 Deepwater Horizon oil spill, the 2001 World Trade Center collapse, and natural disasters such as the 2005 Hurricane Katrina. The data are utilized by such end-users as federal, state, and academic scientists for environmental modeling, risk assessments, spill response and damage assessments, and resource management. Thus, the MWP data have been the center-piece of hundreds of technical reports and peer reviewed publications, many of which are available at the NCCOS' product webpage.

Introduction

Coastal pollution is a major environmental concern in the US. Chemical contaminants from diverse “point’ and/or “non-point” sources continue to accumulate in coastal environment causing decreased water quality and creating, along with their metabolites, toxic stressors for living organisms. Contaminants, particularly those that are lipophilic, can be biomagnified in the coastal food chain by shellfish and fish with increasing concentrations in predatory wildlife and humans. Excessive levels of contaminants in the coastal areas, whether of natural or anthropogenic origin, can pose ecological and human-health risks. The presence of contaminants in coastal ecosystems can lead to loss of biodiversity through degraded habitats, biomagnification of contaminants in the coastal ecosystem, and human consumption of contaminated fish and wildlife. Thus, monitoring and characterizing coastal pollution is often viewed as an important goal of coastal resource management.

In response to concerns over the environmental quality of the nation's coastal and estuarine ecosystems, the federal government authorized the National Oceanic and Atmospheric Administration (NOAA) to create the National Mussel Watch Program (MWP). NOAA established Mussel Watch in response to a legislative mandate under Section 202 of Title II of the Marine Protection, Research and Sanctuaries Act (MPRSA) (33 USC 1442), which called on the Secretary of Commerce to, among other activities, initiate a continuous monitoring program “to assess the health of the marine environment, including monitoring of contaminant levels in biota, sediment and the water column.”

The MWP is managed by National Center for Coastal Ocean Science (NCCOS) as part of the National Status and Trends (NS&T) program managed by the Monitoring & Assessment Branch, which encompasses a Place-based Research component, previously known as the Bioeffects program that conducts more intense and in-depth studies of ecosystem and organism health as result of chemical stressor exposure. Recent funding constraints couple with the need to evolve in response to changing conditions and drivers have required NCCOS to re-examine the scope and scale of the MWP while still meeting its mandated requirements. Thus, in 2013, NCCOS undertook the task of re-designing the MWP to focus on a rotating regional model. However, the program’s long-term goals to “conduct nationwide environmental monitoring, assessment and related research in order to describe the current status of pollution and to detect changes in the environmental quality of our Nation’s estuarine and coastal waters by providing information, tools and knowledge to regional, federal, state and local resource managers to support management actions” still remain.

The program’s framework involves multifaceted activities designed to help achieve its mission. These include:

- The use of sentinel-based approach to monitoring, by collecting and analyzing sediment and bivalves (oysters and mussels) as surrogates for water pollution. Sample are collected from a network of nearly 300 established coastal sites including, the Great Lakes, Alaska, Hawaii, and Puerto Rico (Figure 1). Contaminants monitored include a suite of organic and inorganic chemicals, such as pesticides (e.g. DDT), antifouling agents (e.g. butyltin), industrial contaminants (e.g. PCB), oil and fossil fuel related contaminants (e.g. PAH) and heavy metals (e.g. mercury). Recently, more than 280 contaminants of emerging concern (CECs) are being measured for long-term or place-based monitoring consideration. These include pharmaceuticals and personal care products, flame-retardants, current-use pesticides, surfactants, and stain repellant compounds. Additionally, ancillary data such as bivalve lipid content and shell length, and sediment grain-size, TOC, along with the bacteria *Clostridium perfringens* concentration is measured in sediment as an indicator of sewage waste are routinely collected as part of the monitoring effort.
- The monitoring of histopathology stressors (diseases and parasites, and gonadal index) in mussels and oysters as indicators of bivalve

health and water quality from 1995 - 2010

- The specimen-banking program, which was run from 1986 - 2000 in collaboration with the National Institute of Standard and Technology (NIST).
- Special responses to natural and accidental disasters, including impacts assessments of the 2010 Deepwater Horizon oil spill, 2005 Hurricane Katrina, and the 2001 World Trade Center collapse.
- The program's long-term monitoring data are georeferenced and publicly available for download from the NCCOS' website data portal.

Mussel Watch is designed to provide coastal managers with a national context to assess local and regional environmental condition monitoring activities. Thus, the program's data provide a unique historic benchmark for assessing coastal health and ecosystem management efforts. The data are utilized by such end-users as federal, state, and academic scientists for environmental modeling, risk assessments, spill response and damage assessments, and resource management. Thus, the MWP data have been the subject of hundreds of technical reports and peer reviewed publications, many of which are available at the NCCOS' product webpage.

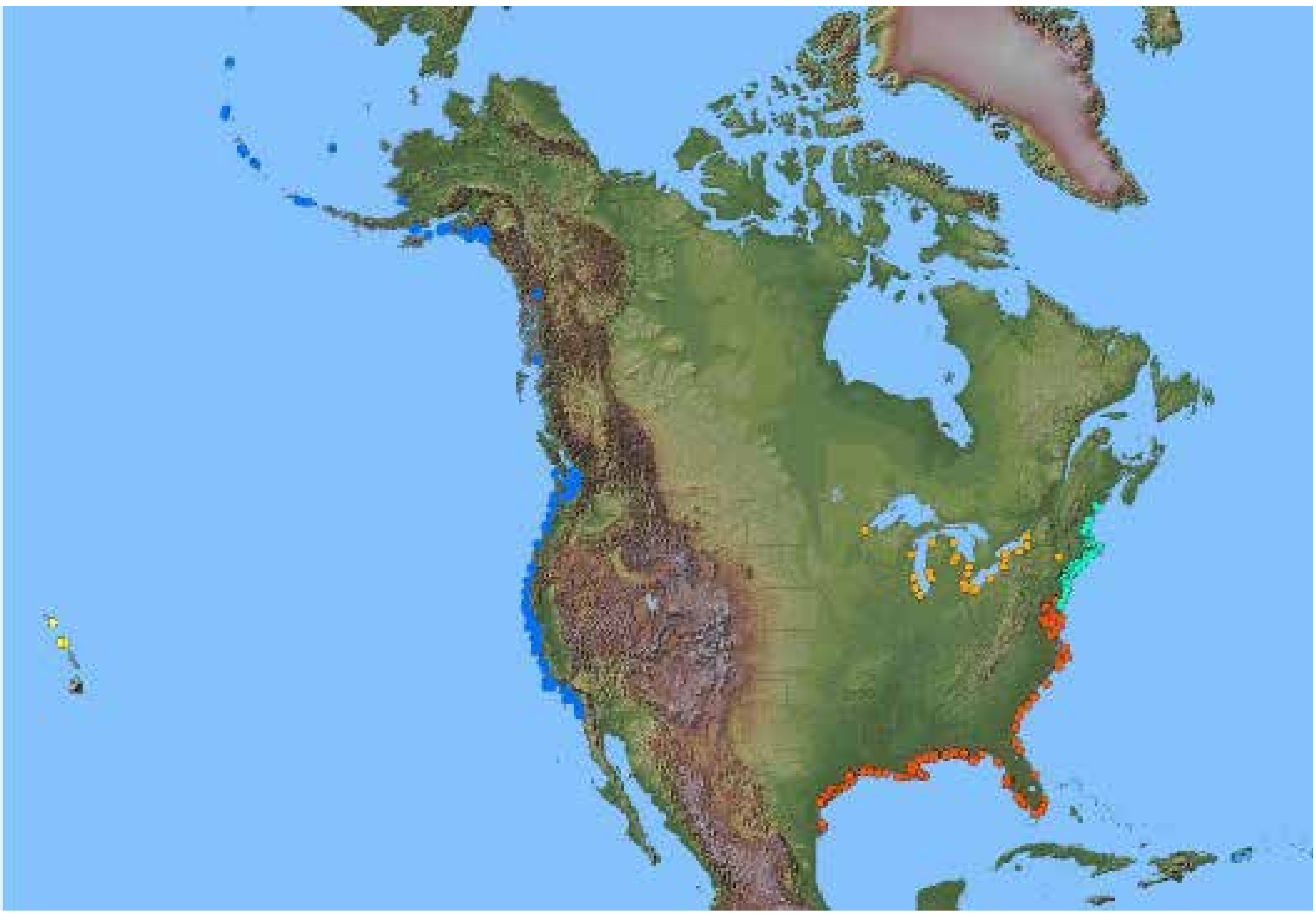


Figure 1. National network of traditional Mussel Watch contaminants monitoring sites. Different colors represent the different species of bivalves sampled (see Sentinel Species section below).

Mussel Watch Program: A Quality Assured Monitoring Approach

Site Selection

Coastal pollution is a major environmental concern iMussel Watch monitoring sites have been chosen by consultation with state coastal managers and academic professionals. To ensure consistency and data quality, the MWP monitoring sites are established following standard criteria (Apeti et a. 2012, Lauenstein et al. 1997 tm112). Sites must have sufficient populations of bivalves for repeated future sampling. An offshore subtidal bivalve collection site is defined as being a circle with a 400 m radius around the site center. Intertidal shoreline sites are defined as being 100 m in length along the shore or breakwater. A sediment site must be a sub-tidal (never exposed at lowest tides), low energy depositional area, hence, sediments may be collected within 2 km of the bivalve site center if depositional sediments cannot be found closer to the intertidal sites or within the 400 m radius of the bivalve site. Established sites are georeferenced and assigned a unique four-letter site code, with the first two letters refer to the site general location, while the second two letters refer to the exact specific location (e.g., BHDI for Boston Harbor, Deer Island).

In 1986, its inaugural year, Mussel Watch only sampled 145 sites, many of which coincided with the 1976-1978 EPA Mussel Watch sites. Over the years, the program has evolved and as of 2020, approximately 300 active monitoring sites have been established. Currently the program has sites located in every coastal region in the continental U.S., Alaska, Puerto Rico and Hawaii. Additionally 25 of the 29 NOAA National Estuarine Research Reserves (NERRs) have Mussel Watch sites located in, or in close proximity to, the reserves. These sites complement the existing NERRs System Wide Monitoring Program (SWMP), which monitors water quality data (water temperature, conductivity, salinity, percent saturation, dissolved oxygen concentration, water depth, pH and turbidity).

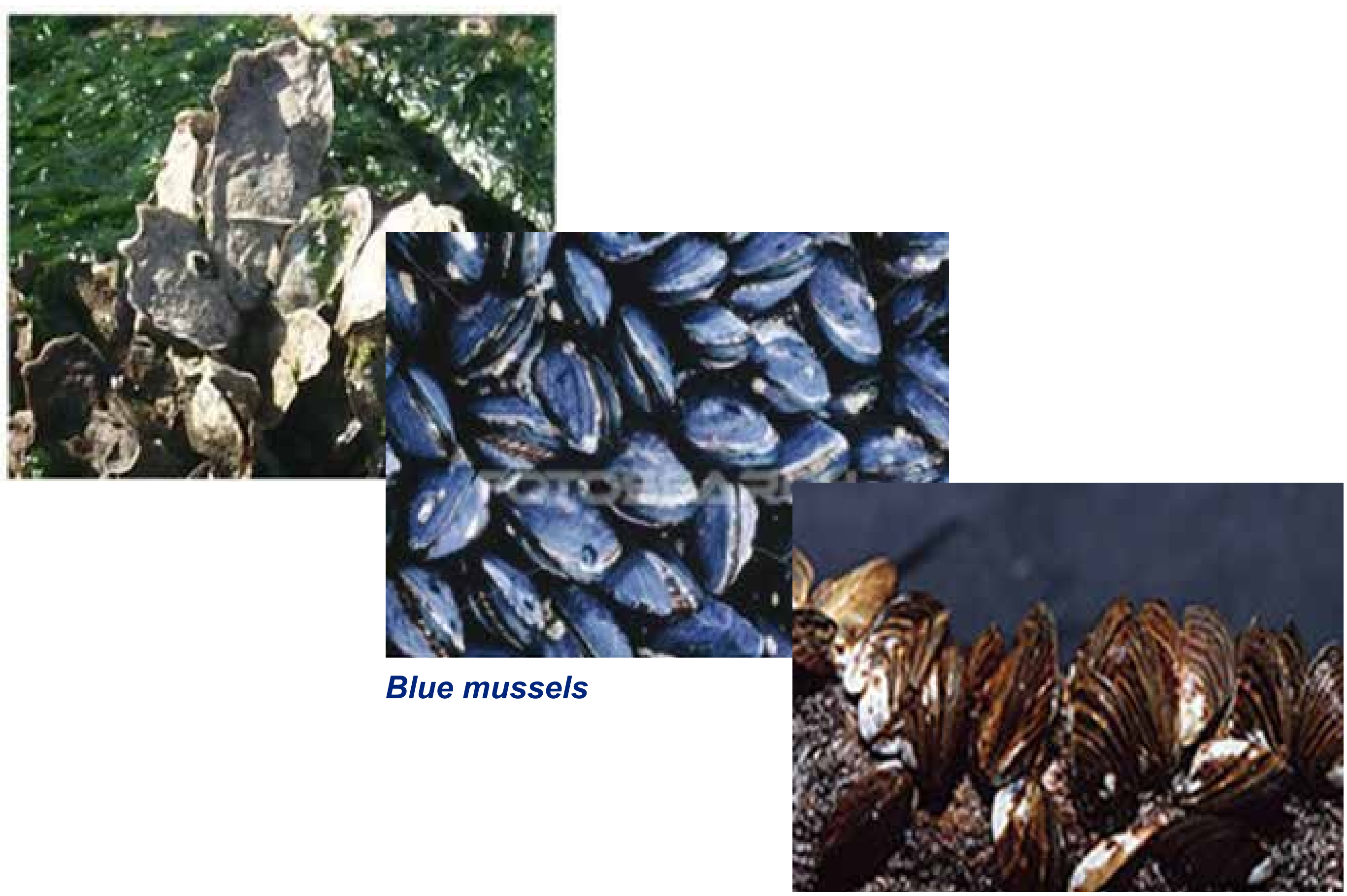
Sentinel Species

The MWP uses species of bivalve shellfish including mussels and oysters as sentinel bioindicator for coastal pollution. Bivalves filter-feed, and it has been demonstrated that an adult oyster can filter up to 6-10 L of water per day (Shumway, 1991) removing suspended particles (complex mixtures of various living microorganisms, detritus, and inorganic particles) from the water column. Through this natural and indiscriminate feeding mechanism, bivalves are continuously exposed to environmental contaminants in the water. Bivalves have minimal ability to metabolize many contaminants (Walker and Livingstone, 1992) in comparison to fish, thus they are able to survive in adverse environmental conditions, and bioaccumulate chemicals to factors 102 to 105 times that of the ambient water. For example, PAHs do not accumulate in fish, but reach easily measurable concentrations in bivalves (Hellou et al., 2000; Mearns et al., 1999; Oros and Ross, 2005). The limited metabolism of most toxic compounds coupled with their ubiquity and sessile life style identify bivalves as the most attractive biomonitors (Ambrose, 1999).

Bivalves are thus suitable for chemical monitoring, and have been used as indicators of contaminants throughout the United States and around the world (Hunt and Slone, 2010; Lauenstein and Daskalakis, 1998; O’Connor and Lauenstein, 2006; Ramu et al., 2007; Roach and Runcie, 1998; Stephenson and Leonard, 1994). Resident and transplanted mussels have been used to assess patterns in bioaccumulation in California waters for over four decades (Butler, 1973; Graham, 1972; Mearns et al., 1991).

Because Mussel Watch is nationwide, a number of different species of mussels and oysters are used as sentinel species depending on the location (Figure 2). The American oyster (*Crassostrea virginica*) is collected from Delaware Bay southward and throughout the Gulf of Mexico. The California mussel (*Mytilus californianus*) is collected from the California coast, the Mediterranean mussel (*M. galloprovincialis*) and the bay mussel (*M. trossulus*) along the Oregon and Washington coastline, and the blue mussel (*M. edulis*) along the northeastern coast from Maine to Cape May and Cape Halopen, NJ. The invasive zebra mussels (*Dreissena polymorpha*) and quagga mussels (*D. bugensis*) are collected in the Great Lakes, the Smooth-edged jewelbox (*Chama sinuosa*) from the Florida Keys, the Mangrove oyster (*C. rhizophorae*) from Puerto Rico and the tropical oyster (*Dendostrea sandvicensis*) from Hawaii.

Bay oysters



Blue mussels

Zebra mussels

Figure 2. Bivalve species used by the national Mussel Watch Program.

Quality Assured Field Collection

Since contaminant concentrations vary as a function of where samples are collected, it is essential to occupy the same site year after year in order to determine environmental trends. For sampling quality assurance, collection stand protocols have been developed (Apeti et al. 2012, Lauenstein and Cantillo 1993) tm71). Global Positioning System (GPS) and Geographic Information System (GIS) technologies are utilized to re-occupy established monitoring sites within a few meters. Photographic documentation of each site, and directions as to how to reach the site, are also important. Since field samples must be collected in a consistent manner, all field crews regardless of their level of scientific expertise are trained in the MWP field sampling protocols. Sampling is performed using gasoline-powered boats often equipped with a davit and pulley.

Bivalve Collection Methods Summary: Bivalves are collected at marine sites in the months of November-March with each site visited within three weeks of a prescribed target date. In the Great Lakes, collections are made in late August or early September. Using non-powder nitril glove, bivalves are collected by hand at low tide in intertidal zones by diving (SCUBA or snorkeling) or dredged at sites located in the subtidal zones (Figure 3). The preferred size ranges are 5-8 cm for mussels, 7-10 cm for *C. virginica*, 2.5-5 cm for *O. sandvicensis*, and 2-4 cm for *D. polymorpha* and *D. bugensis*. Debris are removed and the samples are then packed on ice and shipped to the laboratory. Composite chemistry samples are prepared by homogenizing the soft parts of 30 mussels or 20 oysters. The small size of Dreissena spp. requires that composite samples from the Great Lake sites consists of up to 100 or more individuals.

Sediment Collection Methods Summary: Sediments are collected using 1/25 m2, stainless steel Young-modified Van Veen grab samplers or a hand held box corers. The top two to three centimeter of the surface sediment is scooped from the grab sampler and retained for the chemical analyses. Multiple grabs are processed until sufficient sediments are collected. Any large debris encountered are removed, but otherwise the sample included resident organisms. Sediment samples are separated into two fractions for storage until analysis. One fraction is frozen and used in the chemical analysis, and the other is analyzed for the total organic carbon and percent moisture parameters. Samples are analyzed for organic analyses, trace element analyses, sediment grain size, total organic carbon and total inorganic carbon. Detailed MWP sample collection methods are provided in Apeti et al. (2012), and Lauenstein and Cantillo (1993).

Figure 3. Sample collection activities.

Quality Assured Analytical Methods

The quality of the analytical data generated by the NS&T Program is overseen by the performance-based Quality Assurance (QA) Project. The QA Project, in operation since 1985, assures that despite differences in the analytical methodologies used, data are comparable between all participating laboratories. The QA Project is designed to document sampling protocols, analytical procedures and laboratory performance (Cantillo and Lauenstein, 1998). Requirements include

- Analytical instruments calibrated by standard laboratory procedures.
- Laboratory analysis QA/QC, including assessment of procedural blanks, duplicates, matrix spikes, matrix spike duplicates and reference materials (e.g., SRMs, CRMs, laboratory reference standards) for each batch.
- Approximately 5% of all analyses should be QC analyses.
- Processing quality is considered acceptable with the following criteria: blanks were less than three times the minimum detection limit; accuracy, as determined by analysis of reference materials, was within 30% for organic analytes and within 20% for inorganic analytes; and precision, as determined by replicate analyses, was within 30% for organic analytes and within 20% for inorganic analytes.
- Reporting limit should be based on Method Detection Limits (MDLs). These values are based on the standard deviation of the signal from replicate analysis of real matrix samples containing, in principle, low levels of the analyte (CFR, 1990). The MDL is "x" times the standard deviation, where "x" is defined by the Student's t-distribution to cover 99% of the distribution of possible values (for 7 analyses, x = 3.5).

Legacy Organic and Trace Elements Analysis

The contaminants monitored were chosen through consultation with expert scientists from academia and government as many of the contaminants are listed as Environmental Protection Agency (EPA) Priority Pollutants. Table 1 illustrates the list of legacy organic and trace elements routinely monitored by the MWP. With adaptive changes and leveraging regional partnerships, the program has increased its scientific relevance and reputation, and has evolved to include nearly 280 chemical contaminants, including trace metals, legacy organic compounds most of which are banned in the 70's.

Samples are analyzed for organic contaminant and trace elements, and until 2010, gonadal index and histopathology were also analyzed. From 1986 through 1999, sample analyses were conducted by multiple laboratories including Battelle laboratory in Duxbury, MA, and GERG in College Station, TX. Since 2000, TDI-Brooks International has been the only laboratory doing the analyses. However, since 2015, trace metals measurement has been done in-house at the NCCOS Charleston chemistry laboratory. Detailed analytical methods of organic contaminants and trace elements are provided in Kimbrough et al. (2006 and 2007).

Table 1. List of legacy organic contaminants and trace metals routinely monitored as part of the NOAA Mussel Watch Program.

Contaminant Group	Contaminants
Metals	Silver (Ag), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Mercury (Hg), Manganese (Mn), Nickel (Ni), Selenium (Se), Tin (Sn), Zinc (Zn)
Butyltins	monobutyltin, dibutyltin, tributyltin, tetrabutyltin
Chlordanes	alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor, trans-nonachlor, heptachlor, Heptachlor-Epoxide
Chlorobenzenes	1,2,3,4-Tetrachlorobenzene, 1,2,4,5-Tetrachlorobenzene, Hexachlorobenzene, Pentachlorobenzene, Pentachloroanisole
Chlorpyrifos	Chlorpyrifos
Dichlorodiphenyltrichloroethane (DDTs)	ortho and para forms of parent 2,4'DDT and 4,4'DDT and metabolites 2,4'DDE; 4,4'DDE; 2,4'DDD; 4,4'DDD
Dieldrins	aldrin, dieldrin, endrin
Endolsulfans	Endosulfan I, Endosulfan II, Endosulfan sulfate
Hexachlorocyclohexanes (HCHs)	Alpha-Hexachlorocyclohexane, Beta-Hexachlorocyclohexane, Delta-Hexachlorocyclohexane, Gamma-Hexachlorocyclohexane
Mirex	Mirex
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene, C1-Naphthalenes, C2-Naphthalenes, C3-Naphthalenes, C4-Naphthalenes, Benzothiophene, C1-Benzothiophenes, C2-Benzothiophenes, C3-Benzothiophenes, Biphenyl, Acenaphthylene, Acenaphthene, Dibenzofuran, Fluorene, C1-Fluorenes, C2-Fluorenes, C3-Fluorenes, Anthracene, Phenanthrene, C1-Phenanthrenes/Anthracenes, C2-Phenanthrenes/Anthracenes, C3-Phenanthrenes/Anthracenes, C4-Phenanthrenes/Anthracenes, Dibenzothiophene, C1-Dibenzothiophenes, C2-Dibenzothiophenes, C3-Dibenzothiophenes, Fluoranthene, Pyrene, C1-Fluoranthenes/Pyrenes, C2-Fluoranthenes/Pyrenes, C3-Fluoranthenes/Pyrenes, Naphthobenzothiophene, C1-Naphthobenzothiophenes, C2-Naphthobenzothiophenes, C3-Naphthobenzothiophenes, Benz(a)anthracene, Chrysene/Triphenylene, C1-Chrysenes, C2-Chrysenes, C3-Chrysenes, C4-Chrysenes, Benzo(b)fluoranthene, Benzo(k,j)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-c,d) pyrene, Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene Individual Alkyl Isomers: 2-Methylnaphthalene, 1-Methylnaphthalene, 2,6-Dimethylnaphthalene, 1,6,7-Trimethylnaphthalene, 1-Methylphenanthrene, C29-Hopane, 18a-Oleanane, C30-Hopane
Polychlorinated biphenyls (PCBs)	PCB8/5, PCB18, PCB28, PCB29, PCB31, PCB44, PCB45, PCB49, PCB52, PCB56/60, PCB66, PCB70, PCB74/61, PCB87/115, PCB95, PCB99, PCB101/90, PCB105, PCB110/77, PCB118, PCB128, PCB138/160, PCB146, PCB149/123, PCB151, PCB153/132, PCB156/171/202, PCB158, PCB170/190, PCB174, PCB180, PCB183, PCB187, PCB194, PCB195/208, PCB199, PCB201/157/173, PCB206, PCB209

Analysis of Contaminants of Emerging Concern

Based on EPA recommendations as described in Ankley et al. (2008), classes of CECs to consider for monitoring should include: 1) Persistent organic pollutants (POPs) such as flame retardants, current use pesticides and industrial by-products, such as perfluorinated and phenolic compounds; 2) Pharmaceuticals and personal care products (PPCPs) such as prescription and/or illegal drugs, sunscreens, and synthetic musks; 3) Veterinary medicines such as antimicrobials, antibiotics, anti-fungals, and growth hormones for animals; 4) Endocrine-disrupting chemicals (EDCs) including synthetic estrogens and androgens as well as many other compounds capable of modulating normal hormonal functions and steroidal synthesis; and 5) Nanoparticles such as carbon nanotubes or nano-scale particulates of which little is known about either their environmental fate or effects. Through a series of pilot studies, the MWP has been assessing a suite of CEC compounds (Table 2) in diverse coastal regions for potential consideration for long-term monitoring. This list includes compounds that serve as flame retardants, dispersants such as of alkylphenols compounds (APs), pharmaceutical and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs) such as perfluorinated compound (PFAS), and current-use pesticides (CUPs).

Among the diverse group of alkylphenols, nonylphenol ethoxylates (NPEOs), metabolites of commercial dispersants, and their environmental degradation products nonylphenols (NPs) were included in the EPA New Use Rules list of 15 toxic AP compounds (EPA 2014a). The MWP measures two NPEO and two NP compounds (Table 2) for which analytical methods are well established. The analyses were conducted by the NCCOS' chemistry laboratory in Charleston, SC based on published methods by Petrovic et al. (2002) and Loyo-Rosales et al. (2003). The PPCPs analyzed are grouped by analytical methods identified as HormoneNEG, HormonePOS, PPCP-I, PPCP-III, PPCP-IV, PPCP-V and PPCP-VI (Table 2). The analyses were conducted by the NCCOS' chemistry laboratory in Charleston, SC. Sample extraction, clean-up and quantitation procedures were based on modified EPA method 1694 (EPA 2007) and methods described in Klosterhaus et al. (2013) and Apeti et al (2018). TDI-Brooks International Inc. following procedures used by the NOAA NS&T Program (Kimbrough et al. 2007) analyzes brominated flame retardants (BFRs) as PBDE and PBBs primarily used in firefighting materials. However, measurements of alternate flame retardants compounds (MLA-070 REV.02.03 method), current-use-pesticides (MLA-035 REV.07.04), perfluro-alkyl substances (PFAS) (MLA-043 REV.08.06) all which are in Table 2, are conducted by AXYS Analytical Services Ltd. AXYS' analytical methods are proprietary and confidential. Hence, only method names are mentioned, but their contact information (AXYS Analytical Services Ltd, 2045 Mills Road W., Sidney, BC, Canada, V8L 5X2. Tel. (250) 655-5800, fax (250) 655-5811) are provided for further references.

Table 2. List of contaminants of emerging concern (CECs) being measured by the Mussel Watch Program as part of the pilot studies.

Contaminant Group	Contaminants
Alkylphenol Compounds (APs)	4-NP, 4-n-OP, NP1EO, NP2EO
Alternative Flame Retardants (AFRs)	alpha-HBCD, beta-HBCD, gamma-HBCD, BTBPE, TBB, TBPH, TCEP, TCPP, TDCPP
Current-Use Pesticides (CUPs)	Ametryn, Atrazine, Azinphos-Methyl, Captan, Chlorothalonil, Chlorpyrifos, Chlorpyrifos-Methyl, Chlorpyrifos-Oxon, Cyanazine, Cypermethrin, Dacthal, Desethylatrazine, Diazinon, Diazi-non-Oxon, Dimethoate, Disulfoton, Disulfoton Sulfone, Ethion, Fenitrothion, Fonofos, Hexa-zinone, Malathion, Methoxychlor, Metribuzin, Parathion-Ethyl, Parathion-Methyl, Permethrin, Perthane, Phosmet, Pirimiphos-Methyl, Quintozene, Simazine, Tecnazene
Perfluoro-alkyl Substances (PFAS)	PFBS, PFDA, PFDODA, PFDS, PFHPA, PFHXA, PFHXS, PFNA, PFOA, PFOS, PFOSA, PFUNDA
Pharmaceuticals and Personal Care Products (PPCPs)	10-hydroxy-amitriptyline, 17a-DihydroEquilin, 17a-estradiol, 17a-Ethynyl estradiol, 17B-estradi-ol, 2-Hydroxy-ibuprofen, Acetaminophen, Albuterol, Allyl Trenbolone, Alprazolam, Amitriptyline, Amlodipine, Amphetamine, Androstenedione, Androsterone, Atenolol, Atorvastatin, Azithromy-cin, Benzoylecgonine, Benztropine, Betamethasone, Bisphenol-A, Busulfan, Caffeine, Car-badox, Carbamazepine, Cimetidine, Ciprofloxacin, Citalopram, Clarithromycin, Clinafloxacin, Clonidine, Clotrimazole, Cloxacillin, Cocaine, Codeine, Cotinine, DEET, Dehydronifedipine, Desogestrel, Diazepam, Diethylstilbestrol, Digoxigenin, Digoxin, Diltiazem, Diphenhydramine, Enalapril, Enrofloxacin, Equilenin, Equilin, Erythromycin, Estriol, Estrone, Etoposide, Flume-quine, Fluocinonide, Fluoxetine, Fluticasone propionate, Furosemide, Gemfibrozil, Glipizide, Glyburide, Hydrochlorothiazide, Hydrocodone, Hydrocortisone, Ibuprofen, Lomefloxacin, Meprobamate, Mestranol, Metformin, Methylprednisolone, Metprolol, Miconazole, N-Desmeth-yldiltiazem, Naproxen, Norfloxacin, Norfluoxetine, Norgestimate, Norgestrel, Norverapamil, Ofloxacin, Ormetoprim, Oxacillin, Oxolinic Acid, Oxycodone, Paraxanthine, Paroxetine, Peni-cillin G, Penicillin V, Prednisolone, Prednisone, Progesterone, Promethazine, Propoxyphene, Propranolol, Ranitidine, Roxithromycin, Sarafloxacin, Sertraline, Simvastatin, Sulfachloro-pyridazine, Sulfadiazine, Sulfadimethoxine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfanilamide, Sulfathiazole, Testosterone, Theophylline, Thiabendazole, Triamterene, Triclocarban, Triclosan, Trimethoprim, Tylosin, Valsartan, Venlafaxine, Verapamil, Warfarin
Polybrominated Flame Retardants (BFRs)	Polybrominated Biphenyls (PBBs): PBB 1, PBB 2, PBB 3, PBB 4, PBB 7, PBB 9, PBB 10, PBB 15, PBB 18, PBB 26, PBB 30, PBB 31, PBB 49, PBB 52, PBB 53, PBB 77, PBB 80, PBB 103, PBB 155 Polybrominated Diphenyl Ethers (PBDEs): PBDE-1, PBDE-2, PBDE-3, PBDE-7, PBDE-8, PBDE-10, PBDE-11, PBDE-12, PBDE-13, PBDE-15, PBDE-17, PBDE-25, PBDE-28, PBDE-30, PBDE-32, PBDE-33, PBDE-35, PBDE-37, PBDE-47, PBDE-66, PBDE-71/49, PBDE-75, PBDE-77, PBDE-85, PBDE-99, PBDE-100, PBDE-116, PBDE-118, PBDE-119, PBDE-126, PBDE-138, PBDE-153, PBDE-154, PBDE-155, PBDE-166, PBDE-181, PBDE-183, PBDE-190, PBDE-194, PBDE-195, PBDE-196, PBDE-197, PBDE-198/199/203/200, PBDE-201, PBDE-202, PBDE-204, PBDE-205, PBDE-206, PBDE-207, PBDE-208, PBDE-209

Ancillary measurements

Along with the regular monitoring parameters, Mussel Watch routinely collects ancillary data (Table 3), including sediment grain size and bivalve shell length and lipid content. The program has also historically measured biological indicators of water quality, such as the bacteria *Clostridium perfringens*, which is measured in sediment as an indicator of sewage waste. From 1995 through 2009, the program monitored histopathology stressors (diseases and parasites, and gonadal index) in mussels and oysters as indicators of bivalve health and water quality. Ancillary methods are described in MacDonald et al. (2006), while histopathology and gonadal index techniques are provided in Kim et al. (2006).

Table 3. Ancillary measurement routinely collected by the MWP.

Matrix	Parameter measured
Tissue	shell length; shell volume lipid content; wet tissue weight; dry tissue weight
Sediment	grain size (% silt; % mud; % sand) total organic carbon (TOC) wet sediment weight; dry sediment weight sewage marker (*Clostridium perfringens*)
Water	salinity dissolved oxygen (DO) temperature depth

Data Management

A primary product of the national Mussel Watch Program is the data. The MWP monitoring data along with datasets from Place-based projects are subjected to a rigorous QA/QC process before any types of data processing and analysis. All processed data are georeferenced and archived as part of the NOAA National Status and Trends database. These data are publically served via NOAA data-portal such as the National Centers for Environmental Information (NCEI) and the Office of Response and Restoration's (OR&R) Data Integration Visualization Exploration and Reporting (DIVER). These searchable portals cover data from 1986 – 2012, however, the more recent data information are serviced on demand. Metadata files are prepared to provide information on the MWP dataset including, sampling events, laboratory procedures, and description of the different parameters measured. However, generally, the Mussel Watch chemistry data are tagged to a chemical group as described in Tables 1 and 2. Group names include: phenols (e.g., Alkylphenols, Alkylphenol ethoxylates, nonylphenols), Butyltins (e.g., Tri, di, and mono butyltin), Carbon (Organic carbon, inorganic carbon) Chlordanes Dichloridiphenyltrichloroethanes (DDTs and metabolites) Dieldrines Endosulfans, Polychlorinated biphenyls (PCBs), Polychlorinated dibenzofurans, Energetics, sediment Grain size, Polycyclic aromatic hydrocarbons (PAHs), Perfluoro compounds, Pesticides of current use, Petroleum Hydrocarbons, Polybrominated biphenyls, Polybrominated biphenyl ethers (PBDEs), Sewage markers, and Trace Metals. In addition, percent wet and dry weight data are entered into the Ancillary group, and quantitative and semi-quantitative bivalve histopathology and gonadal index data are entered into a Histopathology group.

More detailed information about NS&T and Mussel Watch data management as well as future approaches to data analysis for added values are discussed in the data management chapter further in this document.

Mussel Watch Program Monitoring

Historic Monitoring Collection Frequency

From 1986 until 1992, the program conducted site triplicate sampling (3 composite samples per site) with bivalve being collected annually and sediment every ten years except at newly established sites. Thereafter and until 2012 due to budget constraints, composited triplicate samples with biennial collection was enacted. In this design, bivalves were collected, biennially with half of the sites collected in even years and the other half in odd years. Sample composite sediments are still collected every ten year. While reducing the number of samples collected and doing away with site specific variability, this design managed to maintain with minor impacts the long-term data trend that the program is built up to provide.

Mussel Watch Program: Current Approach

Rotating Regional Model

The current aim of the national MWP is to provide actionable information to stakeholders and the scientific community while improving its monitoring approach. However, recent funding constraints have required NOAA to re-examine the scope and scale of the MWP while still meeting its mandated requirements to monitor the coastal environment. A fundamental challenge faced by any long-term environmental monitoring program is how (or whether) to evolve in response to changing conditions and drivers. The necessity to respond to emerging environmental concerns such as new contaminants, coupled with the increasingly different data needs of state partners/clients, prompted NCCOS to undertake the task of re-designing the MWP program. Beginning in 2013, NCCOS began assessing the feasibility of a rotating regional monitoring approach while consideration of the following technical adjustments:

1. Improvement of the survey design. Bivalve samples are pooled at a site and may be representative, but lack of statistical replication at a site level in the fixed site design has meant statistical power can only be achieved by pooling sites—but variability in site characteristics (inter- vs. subtidal, grain size profile, changes in land use since the sites were established) confounds data interpretation. Moving to a stratified random design would also help (and there are hybrid survey models that use a mixture of fixed and stratified sites). Changes to the survey design could also allow for newer/different statistical techniques.

2. Placing a greater emphasis on monitoring the most relevant contaminants—whatever they may be. That could mean focusing on CECs that accumulate in bivalves, using caged organisms to allow us to sample locations without sufficient sentinel organisms *in situ*, or move towards different matrices/passive samplers instead of or in addition to bivalves.

3. Increase emphasis on organismal and/or ecosystem health through bioeffects (bioassays, biomarkers and “omics”)—that is, better balance the “so what” with the “why” questions. It might be considerably cheaper to do a smaller group of core contaminants and screen for effects for contaminants generally by using biological metrics. This may also be more easily integrate the effects of mixtures, as contaminants may rarely occur alone.

Pilot Study Framework

Because of the specific challenges caused by the regional diversity of coastal zones around the US and host of resident bivalve species used by the MWP as sentinel organisms, multi-year pilot studies were envisioned in order to build a capacity focused on a more robust regional monitoring model that factors in local stakeholders participation. The scopes of the studies are sub-regional in nature, balancing short-term flexibility in study design against the cost of broad CEC surveys. The objectives included assessment of the feasibility and applicability of applying a regional approach to a national monitoring program, and how 'regionally-focused' information can be utilized to inform a national status of toxicity and contaminant trends in a way that meets statistical standards of robustness and reliability in the data.

The framework of the pilot study included a seven-year plan that would evaluate:

1. CEC bioaccumulation in each of the major Mussel watch sentinel species group (oysters, blue mussels, zebra mussels) and regions (NE, Mid-Atlantic, SE, Gulf of Mexico, SW, NW, and the Great Lakes) in order to explore statistical means to account for regional variabilities in the data.
2. Differential accumulation of CEC in different environmental matrices such as tissue and sediment.
3. Organismal and/or ecosystem health through bioeffects (bioassays, biomarkers and "omics")—that is to better balance the "so what?" with the "why?"
4. Different survey designs including multi-matrix (co-located sediment and bivalves) assessment, caged-bivalves, retrospective analyses and land-use consideration.
5. Regional capacity building by forging and strengthening collaboration with local stakeholders in order to leverage data and resources.

Pilot Study Activities

To inform the planning of pilot studies an initial broad scan CEC analyses was conducted with a retrospective analysis of dreissenid (zebra/quagga) mussels collected under the Great Lakes Restoration Initiative (Kimbrough et al. 2018).

Year 1: In 2015, Mussel Watch collaborated with NCCOS's Ecotoxicology Branch in Charleston to conduct two case studies to assess the magnitude and concentration of CECs in oysters (*C. virginica*) and sediment.

- A survey in Charleston Harbor, SC, which looked at wild oysters, collected from a combination of traditional Mussel Watch sites and new-targeted sites in a range of land use types.
- A survey in the Chesapeake Bay, MD, which utilized a combination of traditional Mussel Watch sites and caged oyster deployments to target land use and wastewater outfalls.

Year 2: In 2016, a survey of CEC in wild blue mussels (*M. edulis*) was conducted in collaboration with the Gulf of Maine GulfWatch program, an international consortium of agencies from MA, ME, NH in the US and Nova Scotia and Brunswick provinces in Canada. This study assessed a regional capacity building with GulfWatch scientists trained to collect the samples from both the traditional Mussel Watch sites in the region and GulfWatch sites.

Year 3: In 2017, a survey in the Gulf of Mexico was based on the collection of oyster (*C. virginica*) using contractual services.

Year 4: In 2018, MWP collaborated with the Southern California Coastal Water Research Project (SCCWRP) to assess the magnitude and distribution of CEC in California blue mussels (*M. californianus*) and surficial sediment. Additionally, a special CEC bioeffects study using bioanalytical screening tools was planned. This effort leveraged SCCWRP for sample collection.

Year 5: In 2019, MWP collaborated with the Oregon (ORFW) and Washington (WAFW) Departments of Fish and Wildlife to conduct two case studies.

- In Oregon, ORFW scientists collected wild mussels (*M. galloprovincialis*) from traditional Mussel Watch sites.
- In Washington, the survey consisted of deployment of caged-mussels at both traditional Mussel Watch sites and WAFW T-BiOS program sites.

Year 6: Mussel Watch is collaborating with NCCOS's Ecotoxicology Branch in Charleston, and NOAA Atlantic Oceanographic and Meteorological Laboratory, Ocean Chemistry & Ecosystem Division for its 2020 pilot study in the Southeast Atlantic (NC – FL). This study will assess the magnitude and distribution of CECs in sediment and wild oysters from traditional MW sites. Additional samples will be collected to assess sediment quality in the NOAA's Biscayne Bay Habitat Focus Area.

Year 7: The last pilot study will be conducted in 2021. This study will assess the magnitude and distribution of CECs in sediment and wild bivalves (oyster and blue mussels) in the mid-Atlantic sub-region from New York to Delaware.

Mussel Watch Special Projects

Historic Projects

Often Mussel Watch collaborates with state and federal agencies to respond to impacts assessment from unforeseen natural and accidental disasters. These special assessments are more relevant with the national and annual monitoring approach. Examples of these special collection events include the following: Exxon Valdez response in 1989, Pribilof Island oil spill 2000, World Trade Center Collapse 2001, Athos island oil spill 2004, Hurricane Katrina 2005, Cosco Busan 2007, Deepwater Horizon oil spill 2010 (Figure 4).

WTC collapse 2001

Exxon Valdez 1989

DWH oil spill 2010

Athos I, Delaware R. oil spill 2004

Hurrican Katrina & Rita

Figure 4. Selected natural and accidental events studied by the Mussel Watch Program.

Current Project: Great Lakes Mussel Watch

Great Lakes Mussel Watch supports the Great Lakes Restoration Initiative (GLRI) and is one of the many ongoing projects by Mussel Watch. This project uses both historical data from Mussel Watch as well as increasingly more temporally and spatially prioritized data to better identify remediation efforts at Great Lake Areas of Concern (AOC). The project design include a more intensive samplings and effect-based assessments (Figure 5) leading to a better characterization of ecosystem and bivalve health. The chapter on new approaches for monitoring and assessments provides more detail, but overall the study design includes:

- Place-based Intensive Assessments
- Caged Mussel Deployments (5-10 weeks)
- Multi-matrix – POCIS, PEDs, Hester Dendy & Data loggers
- Mussel Chemistry and Mussel Health

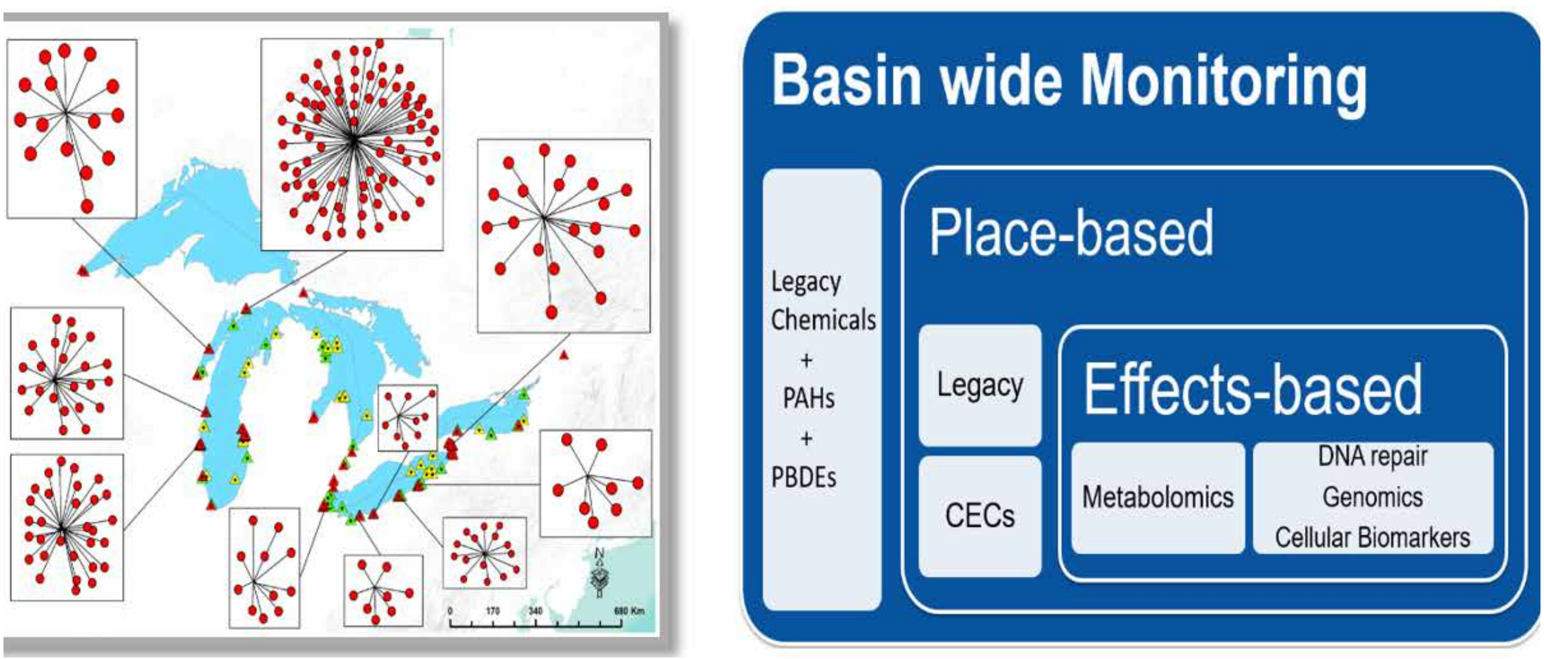
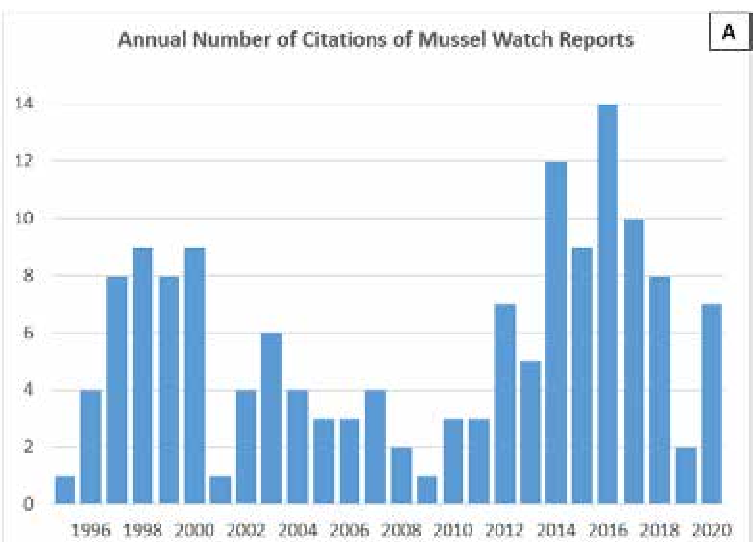


Figure 5. Mussel Watch Great Lakes project characteristic study design: intensive sampling and health-based assessment.

Relevant Mussel Watch Program Data Products

Since its inception in 1986, the NS&T Program's Mussel Watch Project has produced a wealth of data on the levels and distribution of chemical contaminants in coastal waters of the United States. The MWP provides unique data that is vital to evaluating the health of the nation's estuarine and coastal waters, particularly describing the levels of chemical contamination. The program's long-term data supports the assessment of potential impacts of unforeseen events such as oil spills and hurricanes, as well as evaluating the effectiveness of regulations that ban toxic chemicals or support legislation such as the Clean Air and Clean Water Acts. Federal, state and local resource managers, as well as university scholars, have used the data to make informed decisions Figure 6). These data have been used to produce scientific papers and reports on the regional distribution of contaminants; comparison of local conditions, including "hot spots" and restoration targets with ambient concentrations nationwide; temporal trends for specific contaminants. Hundreds of scientific journal articles and technical reports are based on Mussel Watch data. Figures 7a and 7b illustrates selected technical reports and international journal publications using the MW data.



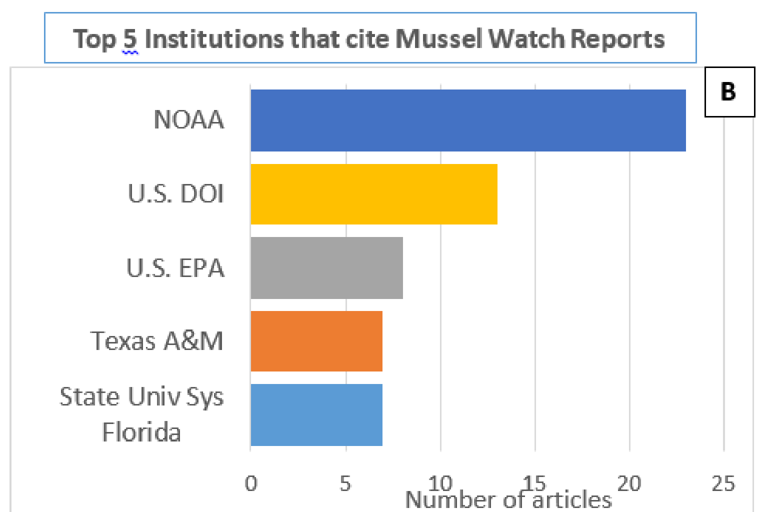
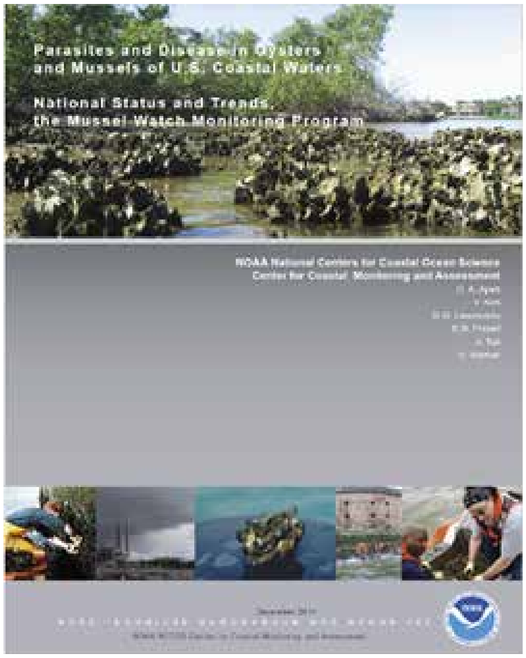


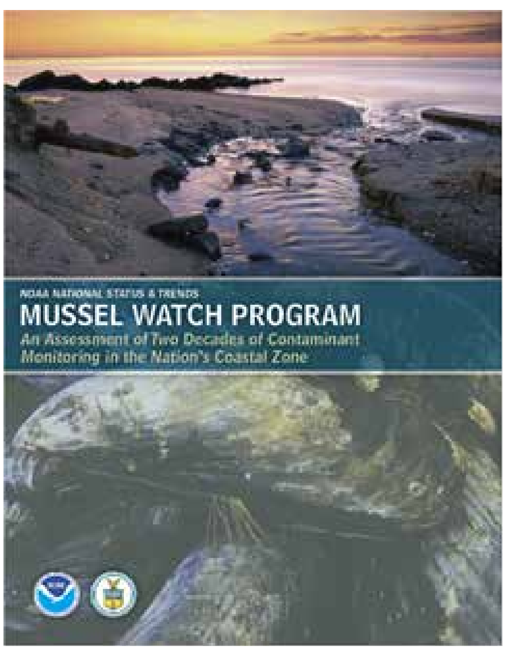
Figure 6. Impact of NS&T Program/Mussel Watch reports and publications."A" depicts annual numbers of cited NS&T Mussel Watch reports since 1994 based on a 'Web of Science" data summary. "B" illustrates how different institution utilize NS&T Mussel Watch reports and information.

Selected Historic Monitoring Data Summaries

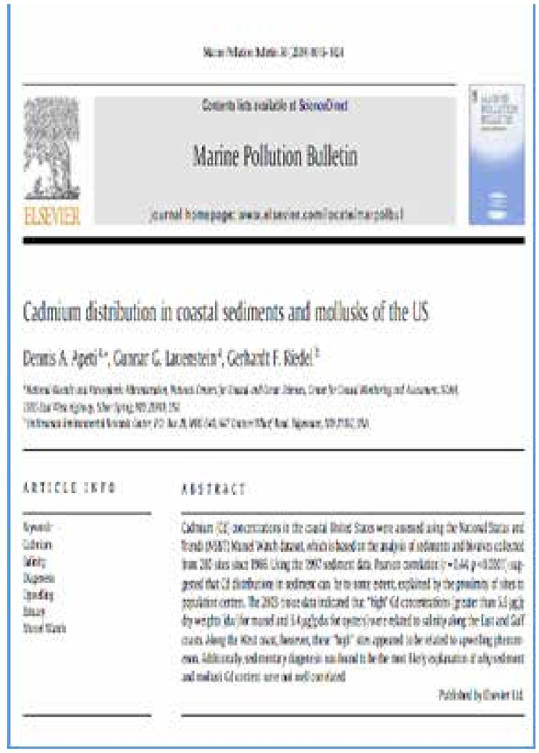
The following reports provide a summary of cases where Mussel Watch data received prominence in either elucidating a particular environmental issue or providing a useful context for national coastal condition assessment.



Assessed the occurrence and distribution of parasites and diseases in oysters and mussels of the U.S. coastal waters based on the Mussel Watch monitoring data. (Apeti et al. 2014)



Utilized the historic Mussel Watch data (two decades of data) to assess long-term trends of coastal contamination in the U.S. Location specific conditions were evaluated in the regional and national context. (Kimbrough et al. 2008)


Contents lists available at ScienceDirect

Marine Pollution Bulletin

Cadmium distribution in coastal sediments and mollusks of the US

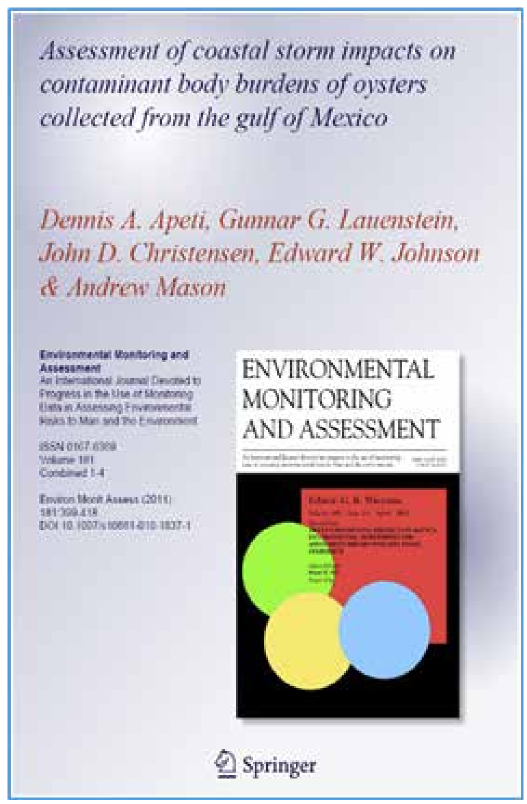
Dennis A. Apeti, Gunnar G. Lauenstein, Gerhardt F. Riedel

ARTICLE INFO

ABSTRACT

Published by Elsevier Ltd.

The magnitude and distribution of cadmium, a heavy and toxic metal in the U.S. coastal waters were assessed using the Mussel Watch sediment and bivalves concentration data. (Apeti et al. 2009)



The long-term Mussel Watch monitoring data and mined historic storm data were used to investigate influence of coastal storm on contaminants body burden of oysters in the Gulf of Mexico. (Apeti 2011)

Figure 7a. Selected technical reports and international journal publications based on NS&T Mussel Watch long-term data.

Selected Research/Special Projects

The Mussel Watch data and derived parameters are usually used in assessing impact – and in some case, assessing injury to federal trust resources – resulting from oil spills in U.S. coastal waters, most commonly in the aftermath of the Deepwater Horizon oil spill (2010). Other examples include the , Pribilof Island oil spill 2000, World Trade Center Collapse 2001, Athos island oil spill 2004, Hurricane Katrina 2005, Cosco Busan 2007, Deepwater Horizon oil spill 2010Chalk Point pipeline rupture in 2000 (near Patuxent River, Chesapeake Bay), the New Carissa oil spill off Oregon in 1999 and the North Cape Oil spill off Rhode Island in 1996.

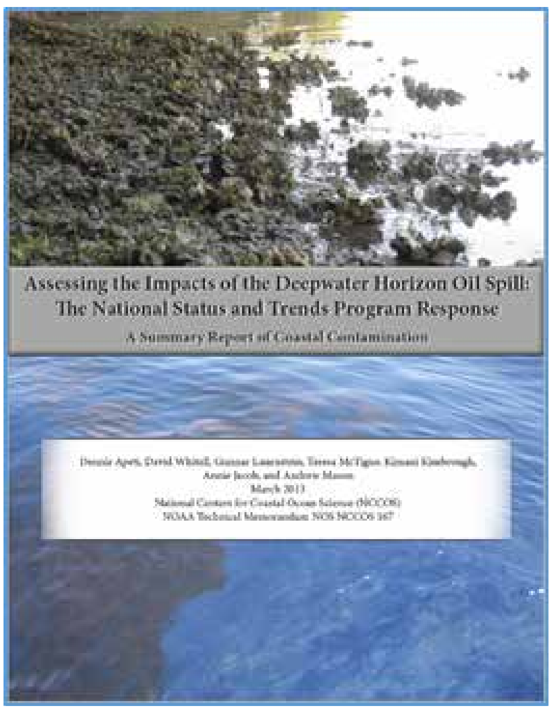
Springer Link

Chemical contamination assessment of Gulf of Mexico oysters in response to hurricanes Katrina and Rita

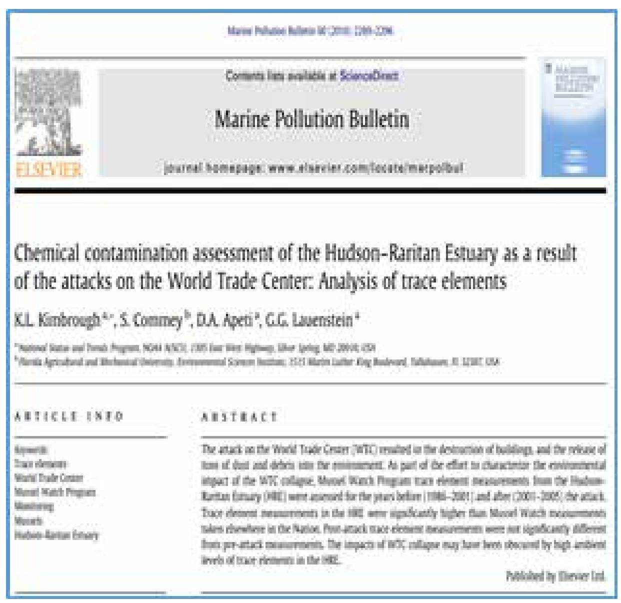
Abstract

Hurricane Katrina made landfall on August 29, 2005 and caused widespread devastation along the central Gulf Coast states. Less than a month later Hurricane Rita followed a similar track slightly west of Katrina's. A coordinated multi agency response followed to collect water, sediment and tissue samples for a variety of chemical, biological and toxicological indicators. The National Oceanic and Atmospheric Administration's National Status and Trends Program (NS&T) participated in this effort by measuring chemical contamination in sediment and oyster tissue as part of the Mussel Watch Program, a long-term monitoring program to assess spatial and temporal trends in a wide range of coastal pollutants. This paper describes results for contaminants measured in oyster tissue collected between September 29 and October 10, 2005 and discusses the results in the context of Mussel Watch and its 20 year record of chemical contamination in the region and the nation. In general, levels of metals in oyster tissue were higher than pre- hurricane levels while organic contaminants were at or near record lows. No contaminant reported here exceeded the FDA action level for food safety.

Chemical Contamination Assessment of Gulf of Mexico Oysters in Response to Hurricanes Karina and Rita (Johnson et al. 2009)



Assessing the Impacts of the Deepwater Horizon Oil Spill: The National Status and Trends Program Response (Apeti et al. 2013)



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Marine Pollution Bulletin

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Chemical contamination assessment of the Hudson-Raritan Estuary as a result of the attacks on the World Trade Center: Analysis of trace elements

K.L. Kimbrough, S. Commey, D.A. Apeti, G.G. Lauenstein

ARTICLE INFO

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ABSTRACT

The attack on the World Trade Center (WTC) resulted in the destruction of buildings, and the release of tons of dust and debris into the environment. As part of the effort to characterize the environmental impact of the WTC collapse, Mussel Watch Program trace element measurements from the Hudson-Raritan Estuary (HRE) were assessed for the years before (1986–2001) and after (2001–2005) the attack. Trace element measurements in the HRE were significantly higher than Mussel Watch measurements taken elsewhere in the Nation. Post-attack trace element measurements were not significantly different from pre-attack measurements. The impacts of WTC collapse may have been obscured by high ambient levels of trace elements in the HRE.

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Chemical Contamination Assessment of the Hudson-Raritan Estuary as a result of the Attacks on the World Trade Center: Analysis of trace elements (Kimbrough et al. 2010)

Figure 7b. Selected technical reports and international journal publications based on NS&T Mussel Watch data from special assessments.

Selected Pilot Study Result Summaries

The following reports provide a summary of cases where Mussel Watch data received prominence in either elucidating a particular environmental issue, or providing a useful context for national coastal condition assessment.

An Assessment of Contaminants of Emerging Concern in Chesapeake Bay, MD and Charleston Harbor, SC

Dennis Apeti, Ed Wirth, Andrew K. Leight, Andrew Mason, and Emily Pisarski - NOAA Technical Memorandum NOS NCCOS 240

In 2015, the National Status and Trends (NS&T) Mussel Watch Program collaborated with NCCOS's Ecotoxicology Branch to study the magnitude and distribution of contaminants of emerging concern (CEC) in shellfish and sediment from different coastal embayment in the Chesapeake Bay, MD and Charleston Harbor, SC. In the Chesapeake Bay, the project benefited from the expertise of NCCOS' Cooperative Oxford Laboratory, Maryland Department of Natural Resources (MD-DNR) scientists, and a network of citizen groups such as Marylanders Grow Oysters (MGO) and River Keepers. In South Carolina, scientists from NCCOS' Charleston and Hollings Marine Laboratories took the lead in conducting a field reconnaissance effort to identify appropriate survey sites. In each study, NCCOS scientists were able to respond to the regional needs, as determined by local and state stakeholders engagement, by tailoring each local study to maximize its effectiveness in meeting both NCCOS and stakeholders science goals.

Study Objectives

1) assess the distribution of flame retardants, chemicals that enhance stain-resistance, current-used pesticides (CUPs) and contemporary contaminants, pharmaceutical and personal care products (PPCPs), and other chemicals associated with human activity that may bioaccumulate in bivalve (oyster, mussel) tissue and sediment; 2) assess possible links between land-use types and the prevalence and magnitude of CECs in bivalve tissue and sediment; and 3) identify candidate CECs for long-term contaminant monitoring. In the Chesapeake Bay, the project benefited from the expertise of NCCOS' Cooperative Oxford Laboratory, Maryland Department of Natural Resources (MD-DNR) scientists, and a network of citizen groups such as Marylanders Grow Oysters (MGO) and River Keepers. In South Carolina, scientists from NCCOS' Charleston and Hollings Marine Laboratories took the lead in conducting a field reconnaissance effort to identify appropriate survey sites.

Study design

The Chesapeake Bay component of this study was designed to survey four tributaries (the Choptank, Patapsco, Rhode, and Severn Rivers), which were selected based on their differing land-uses (urban and industrial, undeveloped, low-development). Due to the lack of abundant shellfish beds in most of these rivers, oysters were deployed in cages. After two months deployment, the oysters were collected and measured for contaminants of emerging concern (CECs). In order to test the relative importance of monitoring CECs at existing Mussel Watch sites, samples of oyster tissue and sediments were also collected at five long-term Mussel Watch sites (Figure 8a).

South Carolina sampling sites included 15 traditional Mussel Watch sites and 15 targeted sites strategically selected in diverse land-use areas in Charleston Harbor (Figure 8b).

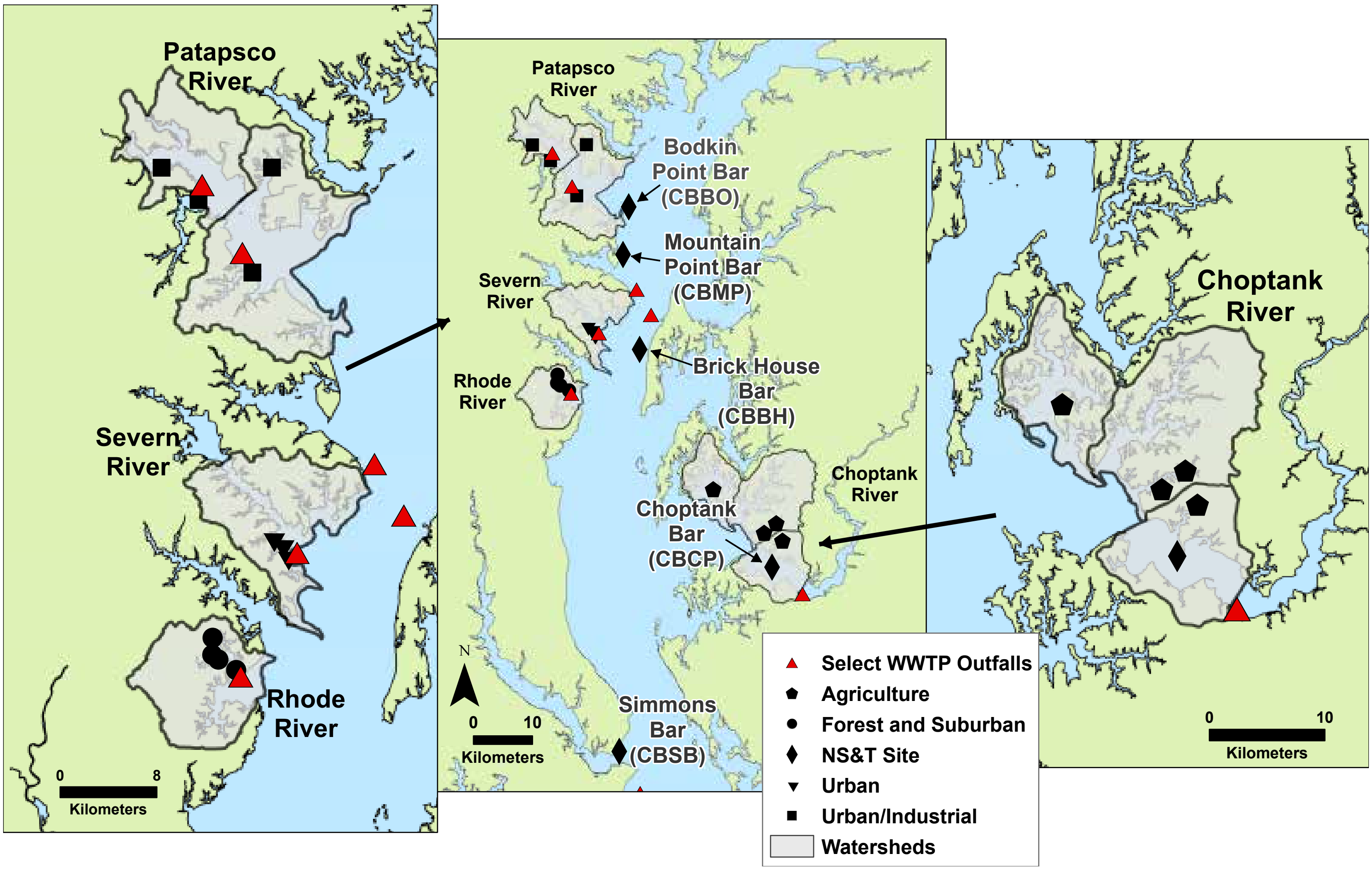

Figure 8a. General locations for the assessment of contaminants of emerging concern in Chesapeake Bay, Maryland. The central panel shows the entire sampling extent, with side panels showing the tributaries at a smaller scale. All black station markers, except for the diamonds, show the locations of deployed oysters. The black diamonds show the locations of sediment and oyster collections from existing oyster beds. Wastewater treatment plants (WWTP) in relatively close proximity to sampling locations are shown by the pink triangles.

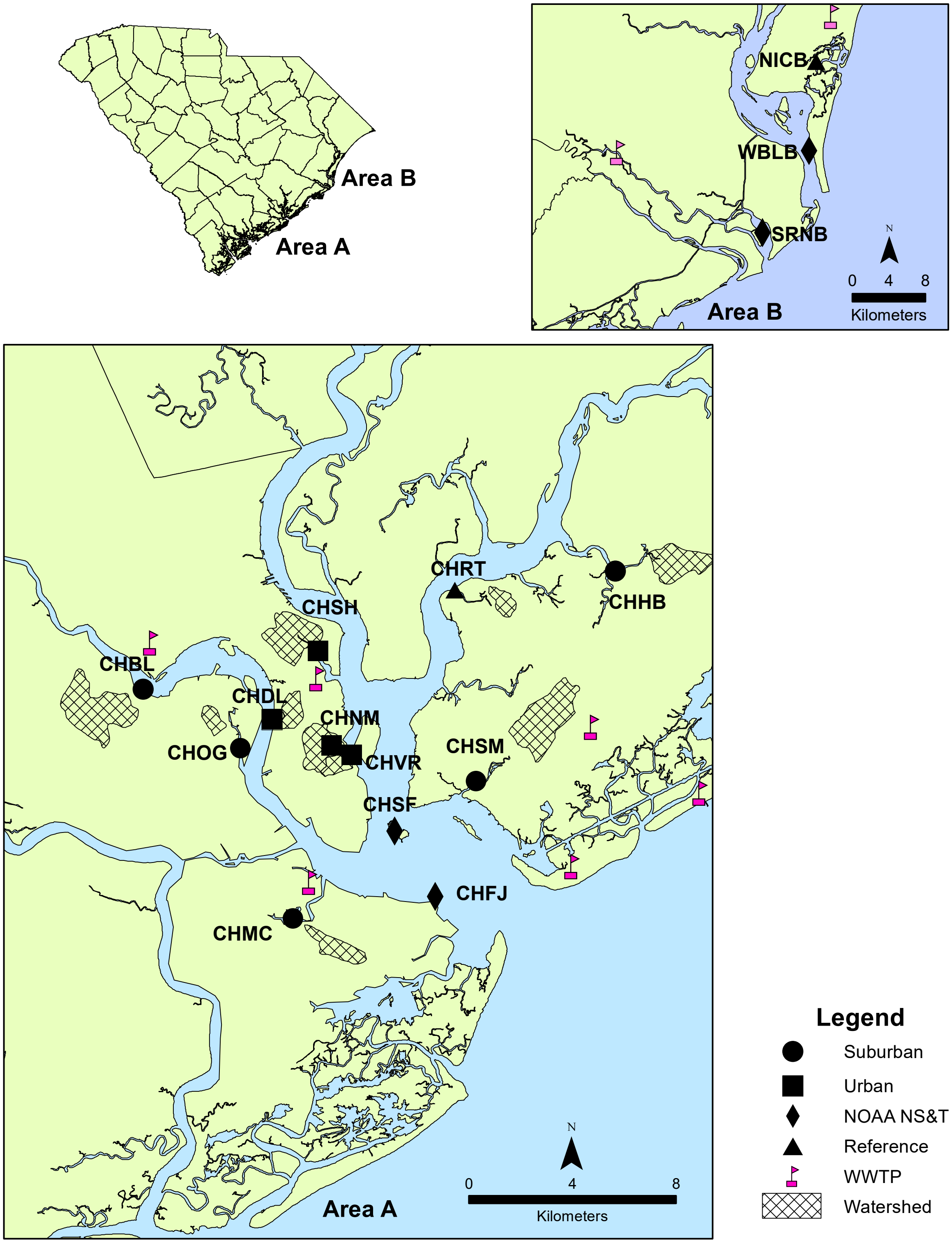

Figure 8b. General locations of the assessment of the contaminants of emerging concern in Charleston Harbor area in South Carolina. Land-use identified stations (Urban, Suburban and Reference) are located in tidal creeks that directly drain the identified watershed. Wastewater treatment plants (WWTP) in relatively close proximity to sampling locations are shown by the pink triangles.

Table 4. Survey site names and sample matrix collected at each site in the Chesapeake Bay and Charleston Harbor study areas.

	Site description		Sample matrix	
Site	**General location**	**Specific location**	**Oyster**	**Sediment**
CBBH	Chesapeake Bay	Brick House	wild oyster	sediment
CBBO	Chesapeake Bay	Bodkin Point	wild oyster	sediment
CBCP	Chesapeake Bay	Choptank River	wild oyster	sediment
CBCT	Chesapeake Bay	Choptank River	caged oyster	
CBMP	Chesapeake Bay	Mountain Point	wild oyster	sediment
CBPT	Chesapeake Bay	Patapsco River	caged oyster	
CBRD	Chesapeake Bay	Rhode River	caged oyster	
CBSB	Chesapeake Bay	Simon Bar	wild oyster	sediment
CBSV	Chesapeake Bay	Severn River	caged oyster	
CHBL	Charleston Harbor	Bull Creek	wild oyster	sediment
CHDL	Charleston Harbor	Diesel Creek	wild oyster	sediment
CHFJ	Charleston Harbor	Fort Johnson	wild oyster	sediment
CHHB	Charleston Harbor	Horlbeck Creek	wild oyster	sediment
CHMC	Charleston Harbor	Metcalf Creek	wild oyster	sediment
CHNM	Charleston Harbor	New Market Creek	wild oyster	sediment
CHOG	Charleston Harbor	Orange Grove Creek	wild oyster	sediment
CHRT	Charleston Harbor	Rathall Creek	wild oyster	sediment
CHSF	Charleston Harbor	Shutes Folly	wild oyster	sediment
CHSH	Charleston Harbor	Shipyard Creek	wild oyster	sediment
CHSM	Charleston Harbor	Shem Creek	wild oyster	sediment
CHVR	Charleston Harbor	Vardell Creek	wild oyster	sediment
NICB	North Inlet	Clam Bank	wild oyster	sediment
SRNB	Santee River	North Bay	wild oyster	sediment
WBLB	Winyah Bay	Lower Bay	wild oyster	sediment

Findings

Results indicated that CECs are being accumulated at various degrees in coastal resources and the environment (Table 5). Classes of CECs most frequently detected in oyster tissues and sediments from both study areas were the perfluorinated compounds (PFAS) (Figures 9a and b), the flame retardants (polybrominated diphenyl ethers; PBDEs), and current use pesticides. In the Chesapeake Bay, at least one PFAS and PBDE flame retardant was detected in all sediment samples. In Chesapeake Bay sediment samples, PFAS and PBDEs were detected in 40% and 21%, respectively, of all measurements (considering both numbers of compounds and numbers of samples). In contrast, alternative (non-brominated) flame retardants had the lowest frequency of detection of all CEC classes. The highest concentrations of CECs detected in Maryland oyster tissues were found to be associated with the pharmaceuticals prednisone (144,000 pg/g wet mass), hydrocortisone (47400 pg/g wet mass), and acetaminophen (23,300 pg/g wet mass). However, PPCPs were detected far less frequently than PBDEs and PFAS in Maryland tissue and sediment. At least one CEC was detected at each South Carolina station for both sediment and oysters samples. In Charleston Harbor samples, CEC detection frequencies followed a similar overall pattern as in Chesapeake Bay. Perfluorinated compounds (PFAS) were the most frequently detected CECs, at 16.7% and 11.1% in sediments and oysters respectively. The flame retardants (PBDEs) were also often detected in both sediments and oysters in South Carolina samples. The highest concentrations reported in Charleston Harbor sediments, however, were for current use pesticides, specifically the pyrethroid insecticides permethrin (6,890 ng/g dry mass) and cypermethrin (1,590 ng/g dry mass).

Table 5. Detection frequencies of CEC classes in both the MD and SC studies. Percentages represent the number of detections divided by the number of compounds multiplied by the number of samples collected.

CEC Class	Detection Frequency (%)			
	Sediment		Oyster	
	MD	SC	MD	SC
PFC	40	16.7	6.3	11.1
PPCP	0.5	1.1	2.5	1.3
AP	0	8.3	2.5	0
PBDE	21.1	12	11.5	8.1
AFR	1.4	1.2	1.6	0.2
MRES	10	3.3	5.7	2.6

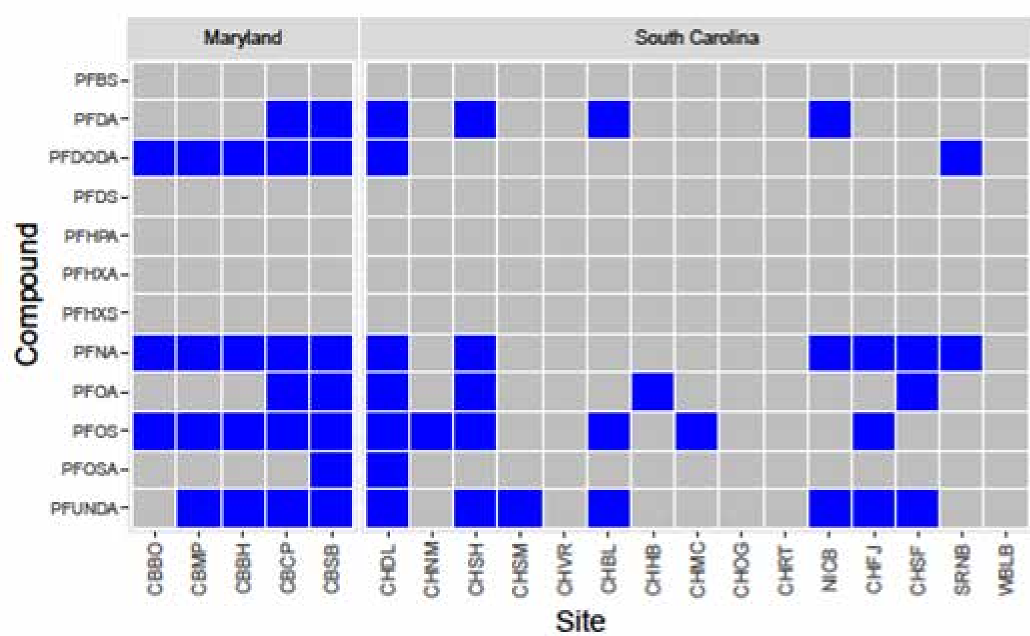

Figure 9a. Distribution map showing presence ( ) and absence ( )) of PFC compounds measured in sediment. Site acronyms (x axis) are defined in Table 4; compound abbreviations (y axis) are defined in Table 2.

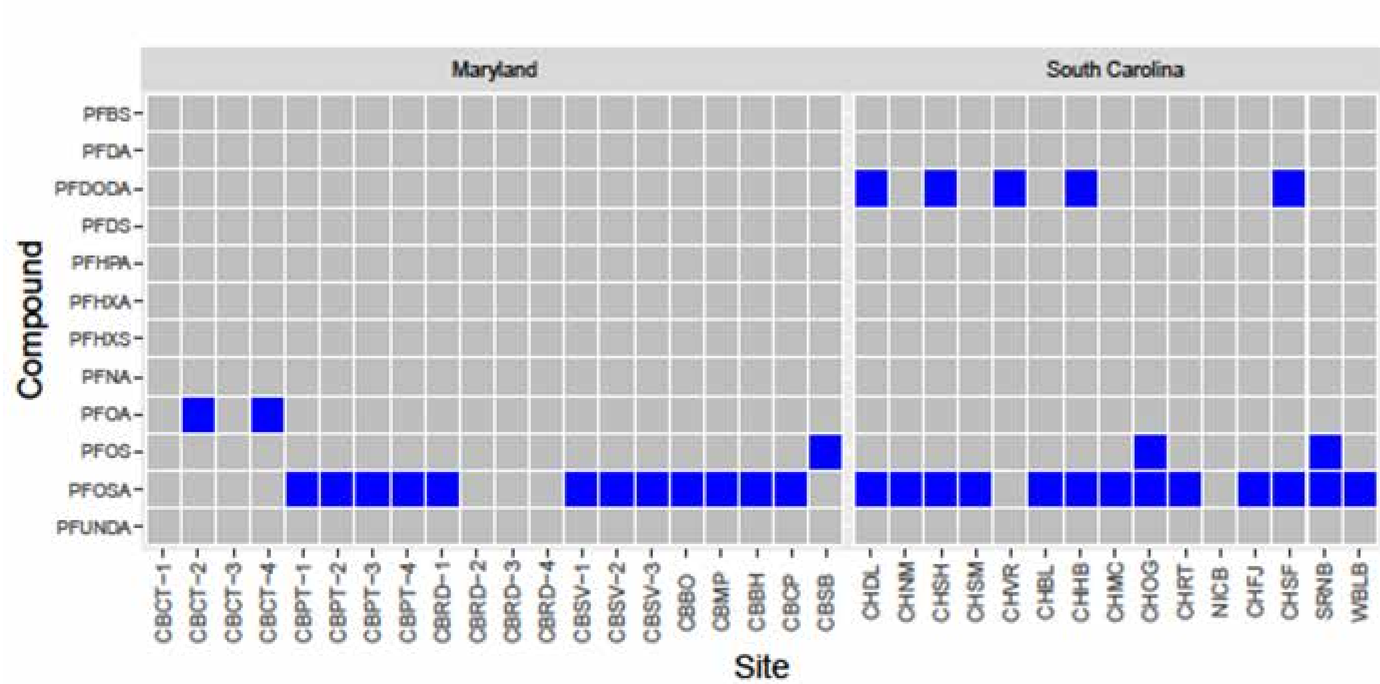

Figure 9b. Distribution map showing presence ( ) and absence ( ) of PFC compounds measured in oyster tissue from the MD and SC study areas. Site acronyms (x-axis) are defined in Table 4; compound abbreviations (y-axis) are defined in Table 2.

Study Summary

Overall detection frequencies were generally quite low (<50%; Table 5). There was no specific trend between MD and SC detection frequencies. In sediments, the frequency of detecting PFCs, PBDEs and MRES were higher in Chesapeake sites while detection frequencies were higher in SC for PPCPs, APs, and AFRs. The highest class specific detection frequency was from sites in MD for the PFCs (40%). In oyster tissues, detection frequencies for all CEC classes were higher in MD than frequencies found in SC tissues except for the PFAS. The highest detection frequency found in oysters was 11.5% for PBDEs in MD samples.

Spatial distribution of some CEC chemicals appeared to be associated with land use categories in the watershed adjacent to the survey sites. Although further study is required to confirm this association, in general, the number of reported concentrations at urban sites was elevated compared to the suburban sites in both study areas. The same relative numbers were observed between suburban and undeveloped (or Reference) sites. In each study, NCCOS scientists were able to respond to the regional needs, as determined by local and state stakeholders engagement, by tailoring each local study to maximize its effectiveness in meeting both NCCOS and stakeholders science goals.

Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern

Kimani Kimbrough, Ed Johnson, Annie Jacob, Michael Edwards and Erik Davenport - NOAA Technical Memorandum NOS NCCOS

In the Great Lakes, Mussel Watch initiated contaminant monitoring in 1992 after the invasion and proliferation of Ponto-Caspian mussels in the region. Beginning in 2010, MWP expanded its monitoring activities in the Great Lakes under the Great Lakes Restoration Initiative (GLRI), Action Plan I (2010-2014), Focus Area "Toxic Substances and Areas of Concern". MWP added sites in all the U.S. Areas of Concern (AOC) and data from the basin-wide assessment conducted in 2009-2010 is summarized in Kimbrough et al., 2014. AOCs were a target for work because of their importance to the GLRI initiative. Under GLRI, MWP also initiated the use of caged mussels to conduct place-based contamination assessments in the Manistique River, Milwaukee Estuary, and Niagara River. Caged mussels were typically deployed for approximately four weeks and strategically located in areas with known or suspected pollution.

The data presented here are from multiple studies including the Maumee and Ottawa Rivers, Niagara River and select tributaries, Milwaukee Estuary, Ashtabula River, Cuyahoga River, Presque Isle Bay, and Black River. The location and number of samples are given in Figure 8. All samples included in this report were collected between June 2013 and June 2015. Because some sites were sampled multiple times, letters have been added to the site names to indicate temporal variations in sampling. Samples are a combination of *in situ* mussels collected from outer harbor stone breakwaters and caged mussels deployed in rivers.

All samples were measured for Pharmaceuticals and Personal Care Products (PPCPs). Pesticides were measured in samples from the Maumee and Ottawa Rivers, because they come from a watershed with a high percentage of planted cropland, and are of local interest. A subset of samples were measured for phenols (octylphenol, nonylphenol, nonylphenol ethoxylates), and hexabromocyclododecane (HBCDD) based on stakeholder interest.

Study Objectives

The primary objective of this two-year study was to determine the frequency and magnitude of current use pesticides in mussel tissue. However, other CECs were also monitored to provide a broad characterization of CECs in mussels.

Study design

Mussel reference site(s) were established in the lake nearshore zones or connecting channels. To increase the likelihood of finding CECs, samples from rivers and harbors were selected preferentially over samples collected from relatively less polluted nearshore lake sites.Divers harvested *in situ* mussels from established populations in the open lake, nearshore lake zone, or outer harbor breakwaters. Locations with 1-2 sites (Figure 10) and harvest/reference sites used *in situ* mussels for chemical analyses. At the Niagara, Maumee and Milwaukee locations *in situ* mussels from harvest sites were relocated in cages. All samples included in this report were collected between June 2013 and June 2015. Sample analysis occurred between June 2015 and March 2016.

Findings

Results are summarized and characterized by analytical method.

Pharmaceuticals and personal care products were analyzed at all sites. Pharmaceuticals are inherently bioactive and many are chronically or acutely toxic with some being identified as endocrine disruptors. The pharmaceuticals have human and veterinarian uses making both

wastewater treatment plants and concentrated animal feeding lots potential sources. Of the 141 compounds analyzed, 45 compounds (32%) were detected in dreissenid mussels (Table 6). The highest mean concentrations found were for Iopamidol, Sertraline and 2-Hydroxy-ibuprofen. Sertraline was the only compound detected at all sites. PPCP concentrations ranged four orders of

Figure 10. Great Lakes Mussel Watch CEC study locations. Size and color of circles designate the number of sites at each location. The Niagara, Maumee and Milwaukee Rivers have relatively more sites in addition to multiple time periods for some sites. Locations with 1-2 sites are a part of our screening effort and are not meant to characterize the entire location.

magnitude for those compounds that were detected (0.06 - 269 ng/g wet) (Figure 11).

A total of 74 current-used pesticides and metabolites (CUPs) were measured in samples from the Maumee and Ottawa River study. Of the CUPs, 32 (44%) contaminants were detected in dreissenid mussels. Trifluralin was the only CUP detected at all sites. Concentrations for CUPs ranged about three orders of magnitude for those compounds that were detected (0.02 - 48.3 ng/g wet).

Hexabromocyclododecane is mainly used as a flame retardant in polystyrene foam, textiles, and electronic equipment. Commercial HBCDD products are a mixture of mainly three isomers (alpha, beta, and gamma), which are measured in this study. HBCDD is toxic to some aquatic organisms and may have recruitment consequences for some species (Desjardins et al., 2004).. Of the 3 compounds analyzed, 2 were detected in dreissenid mussels.

The alpha-HBCDD was the dominant isomer found in mussel tissue followed by gamma. The beta-HBCDD was not detected in mussel tissue.

Alkylphenols have a wide variety of commercial and industrial applications ranging from additives in oil to laundry detergents. They degrade slowly in aquatic systems making them persistent in addition to being bioaccumulative. All four compounds measured by this method were detected in dreissenid mussels (Table 7). Three of the four compounds measured were detected at all sites. One or more of all four compounds analyzed were detected at one or more of the reference sites (Milwaukee 5, Niagara 9 and Niagara 1).

Table 6. Summary of compound concentrations in ng/g wet weight. Concentrations below 3 x detection limit were changed to zero. * List is not comprehensive and represents some of the most common usages of each compound.

			Concentration (ng/g wet weight)		
Compound	Usage*		maximum	mean	median
2-Hydroxy-ibuprofen	Pharmaceutical	Anti-inflammatory	269	9.41	0.00
Iopamidol	Pharmaceutical	Contrast agent	261	19.27	0.00
Sertraline	Pharmaceutical	Antidepressant	61.7	12.42	7.25
Triclocarban	Pharmaceutical	Antibacterial	46.2	6.55	4.09
Ciprofloxacin	Pharmaceutical	Antibiotic	44.5	1.02	0.00
DEET	Personal Care	Insect repellent	23.75	1.18	0.00
Azithromycin	Pharmaceutical	Antibiotic	6.59	0.81	0.00
Etoposide	Pharmaceutical	Cancer	6.1	0.78	0.00
Citalopram	Pharmaceutical	Antidepressant	5.48	0.93	0.68
Fluoxetine	Pharmaceutical	Antidepressant	5.45	0.15	0.00
Amitriptyline	Pharmaceutical	Antidepressant	5.12	1.01	0.72
Diphenhydramine	Pharmaceutical	Antihistamine	4.33	0.58	0.00
Triamterene	Pharmaceutical	Blood pressure/Diuretic	3.62	0.09	0.00
Propranolol	Pharmaceutical	Blood pressure/Chest pain	3.11	0.16	0.00
Diltiazem	Pharmaceutical	Blood pressure/Chest pain	0.702	0.02	0.00
Venlafaxine	Pharmaceutical	Antidepressant	0.662	0.01	0.00
Verapamil	Pharmaceutical	Antihypertensive	0.654	0.06	0.00
10-Hydroxy-amitriptyline	Pharmaceutical	Metabolite of Amitriptyline	0.401	0.01	0.00
Cocaine	Recreational drug	Stimulant	0.311	0.01	0.00

Table 7. Summary of alkylphenol compound concentrations in ng/g wet weight. Concentrations below 3 x detection limit were changed to zero.

			Concentration (ng/g wet weight)		
COMPOUND	Usage		maximum	mean	median
NP1EO	Industrial	Alkylphenols	206	68.75	54.65
NP2EO	Industrial	Alkylphenols	53	17.14	10.12
4-NP	Industrial	Alkylphenols	395	89.19	59.82
4n-OP	Industrial	Alkylphenols	4.19	0.25	0.00

Study Summary

Our results indicate that some CECs are accumulated in mussel tissue at concentrations that can be measured by current analytical methods. CEC detections occurred at all sites and the frequency of detection was greater at sites located in river/harbor areas with known contaminant sources such as runoff of agrochemical and wastewater treatment outfalls. Some CECs were detected in references sites distant from known sources of pollution suggesting persistence and/or transport offshore.

These results support the use of biomonitoring of CECs. However, when chemicals are not detected in mussel tissue, it does not necessarily mean that they are not present in the water column. The next steps are to include water sampling along with mussel sampling in order to confirm waterborne exposure of CECs to biota. Concurrent with this effort of water and bivalve CEC monitoring should be the inclusion of bivalve health indicators, techniques utilizing omics and biomarker assays that measure biological response to environmental stressors that help link CEC exposure to biological effects.

These results serve as an initial assessment to characterize various suites of CECs that had the highest probability of being detected in tissue, and to identify what methods could be used in the future.

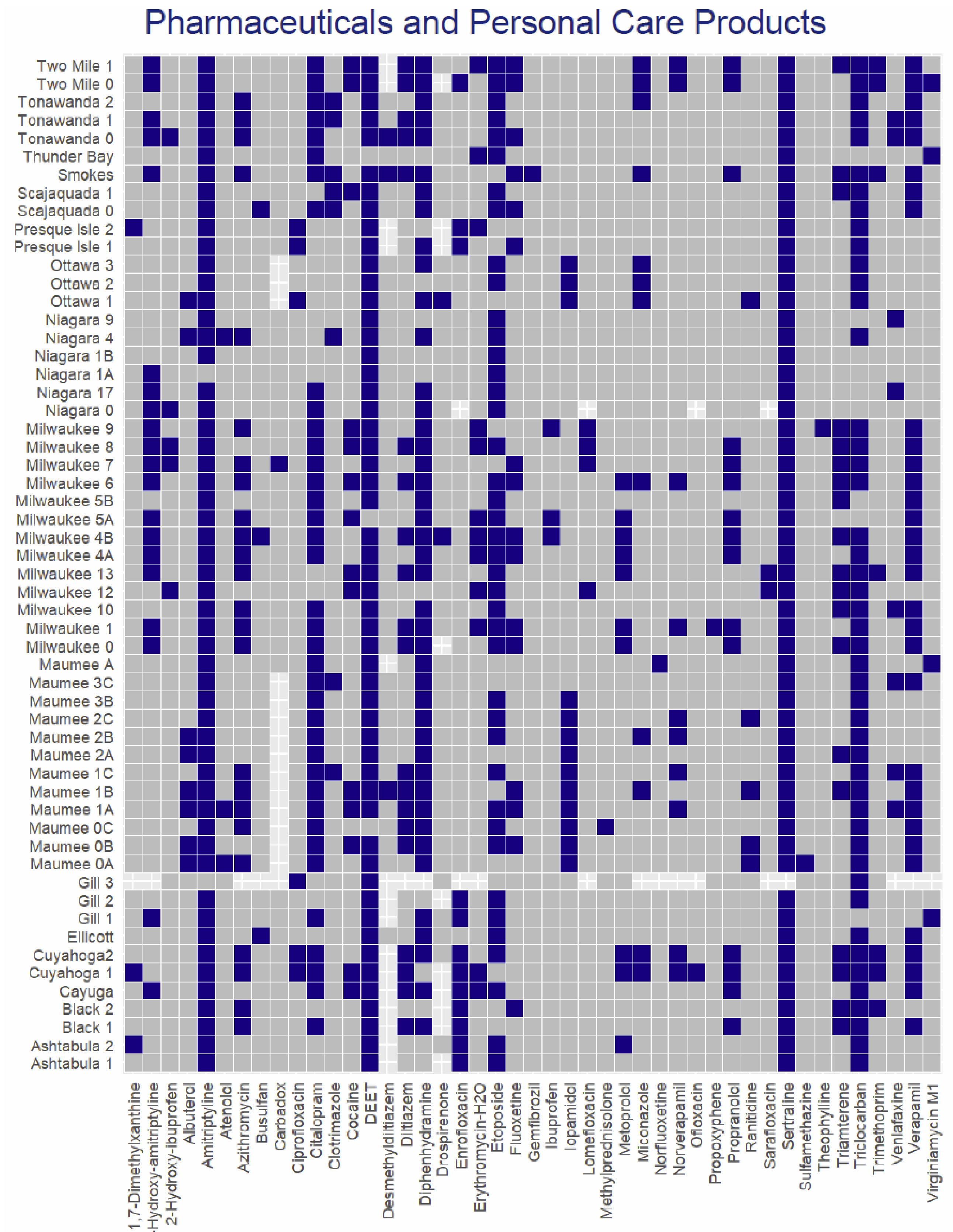

Figure 11. Presence ( ) and absence ( ) of each compound found in mussel tissue at various locations. Maumee sites ending in A, B, and C represent samples collected in May, June and July of 2015 respectively. Milwaukee sites ending in A and B represent samples collected in June and July of 2013 respectively. Niagara sites ending in A and B represent samples collected in June and July of 2014 respectively. Analytes that were not quantifiable (NQ) are designated by white lines in the box.

Magnitude and Distribution of Contaminants of Emerging Concern in the Gulf of Maine

Dennis Apeti, Mary Rider, Stephen Jones, and Ed Wirth - NOAA Technical Memorandum NOS NCCOS

The Gulf of Maine extends from Cape Sable, Nova Scotia, through New Brunswick, Maine, and New Hampshire to Cape Cod, Massachusetts, and includes the Bay of Fundy and Georges Bank. The immense upwelling of nutrients and the combined productivity of seaweed, salt marsh grasses, and phytoplankton make it one of the world's most productive ecosystems supporting a vast array of organisms, including some of great commercial importance.

In collaboration with the Gulf of Maine Gulfwatch Program, an international consortium of agencies from MA, ME, NH in the US and Nova Scotia and Brunswick provinces in Canada, the NS&T Mussel Watch Program conducted an assessment of contaminants of emerging concern (CECs) in the Gulf of Maine's coastal waters in 2016. Like the national MWP, the Gulfwatch monitoring program utilizes a sentinel-based monitoring approach by collecting and analyzing bivalves as surrogates for coastal water pollution. A total of 52 composited blue mussel tissue samples were analyzed for this study, from a combined 41 monitoring sites located across the four jurisdictions of the Gulfwatch program. The mussel samples were measured for a total of 249 individual CEC compounds, including 4 alkylphenol compounds (APs), 9 alternative flame retardants (AFRs), 33 current-use pesticides (CUPs), 12 perfluorinated compounds (PFCs), 121 pharmaceutical and personal care products (PPCPs), and 70 polybrominated flame retardants (BFRs) such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). The results indicated that CECs are present at various degrees in coastal waters of the Gulf of Maine. APs had the highest detection frequency at 10%, followed by PBDEs (7.1%) and PFAS (3.8%). The maximum concentrations of PBDE found across the study area were recorded for the congener PBDE-209 found at 1.04 ng/g ww and 0.96 ng/g ww at the Merrimac River (MAME) and Cohassett (MACO) sites respectively in MA. The congeners PBDE-71/49 was measured at 0.76 ng/g ww at the Stroudwater-Fore Portland Harbor (MEPH) site in ME. It is important to note that bioaccumulation of the CEC contaminants in mussels are typically compound dependent, with a small subset of contaminants representing the majority of detections within each class. Moreover, the distribution and magnitude of the CEC contaminants also depend on location and land-use types in watersheds adjacent to the monitoring location. The most pervasive PFAS in blue mussels was perfluorooctane sulfonamide (PFOSA), which was found in all Gulf of Maine jurisdictions except NS in Canada. A maximum concentration of 5.46 ng/g ww was recorded for PFOSA at the MEPH in Maine.

Pilot studies, such as this Gulf of Maine CEC assessment, not only provide needed data and information for the national MWP, but also address crucial CEC monitoring data gaps for the Gulfwatch program and support water quality data required by coastal resources managers as they develop effective long-term policies protecting services provided by the coastal environment within this region.

Study Objectives

1) Assess the presence and distribution of flame retardants, chemicals that enhance stain-resistance, current-use pesticides, PPCPs, and other chemicals associated with human activity that may bioaccumulate in the Gulf of Maine

2) Evaluate possible links between land-use types and the prevalence and magnitude of CECs in bivalve tissue

3) Conduct inter-jurisdiction comparisons of the CEC results in the Gulf of Maine and weigh the results of this study against previous studies

4) Make the data electronically available to coastal resource managers in the Gulf of Maine region

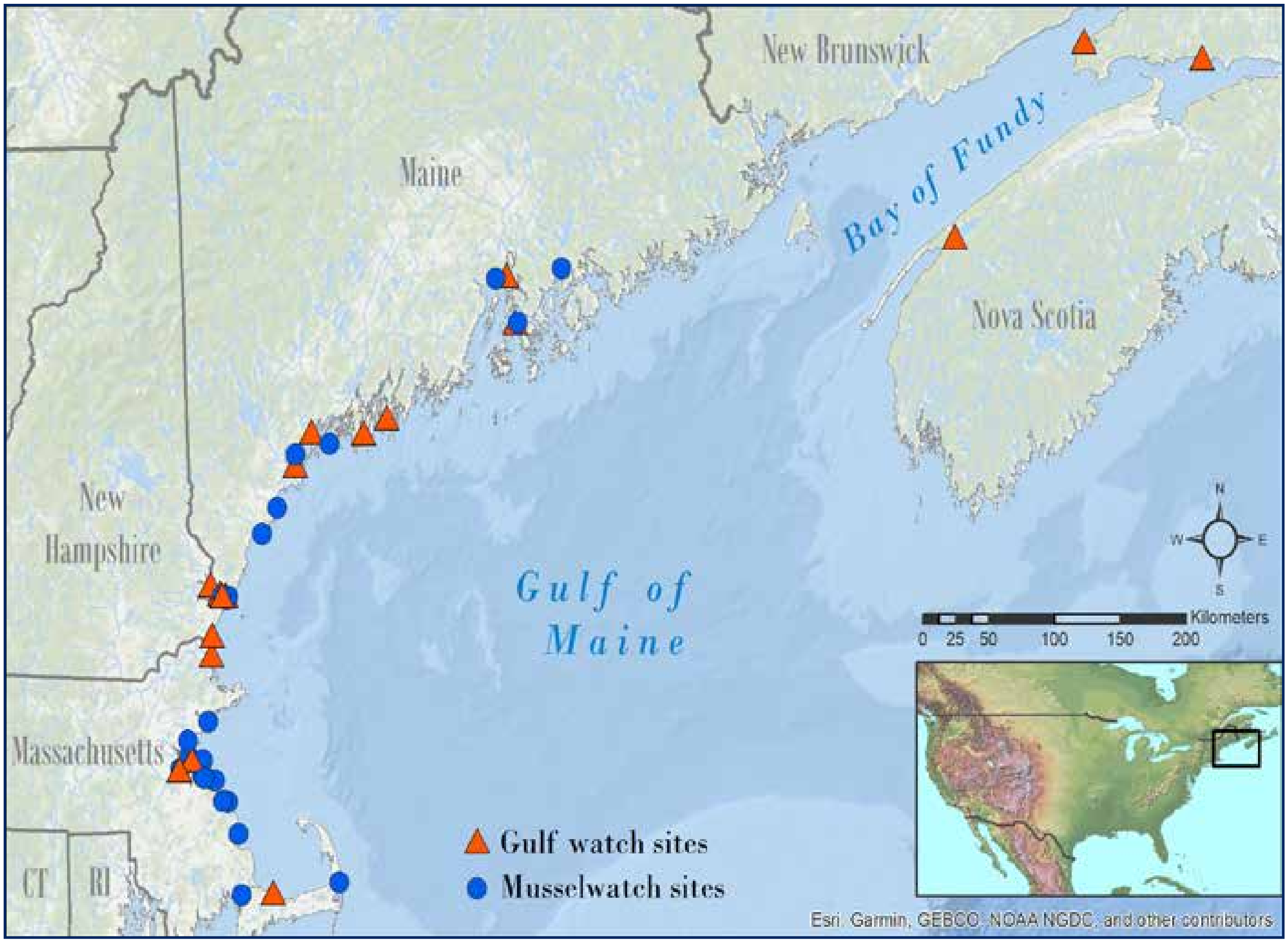

Figure 12. Combined Mussel Watch Program and Gulfwatch selected sites for 2015/2016 survey.

Study design

The study was designed within the framework of the MWP regional monitoring approach, which balances short-term flexibility in study design against the cost of broad CEC surveys and combines traditional Mussel Watch sites with those of the Gulfwatch Program. The MWP has 23 historic monitoring sites in the Gulf of Maine, while the Gulfwatch Program has a network of 46 core monitoring sites distributed in the five jurisdictions of Nova Scotia, New Brunswick, Massachusetts, New Hampshire and Maine (Figure 12). The sampling design included selections of both MWP and Gulfwatch established monitoring sites. Site selection was conducted in collaboration with resources managers in the region that are part of the Gulf of Maine Council on Marine Environment and it involved a strategic mixture of sites that met both programs' monitoring needs. The Gulfwatch program, following modified standard protocols utilized by the national MWP and the Gulfwatch Program (Apeti et al., 2012), conducted the collection. A total of 52 samples were analyzed including 37 composited samples collected in 2016 and 15 frozen samples previously collected by the Gulfwatch Program in 2015 (Figure 12).

The monitoring sites in both programs were not randomly selected nor designed to target specific pollution sources. The sites were selected in locations with an abundant population of bivalves to allow repetitive sampling and to convey information about the degree of chemical contamination in the general area. However, the spatial distribution of the monitoring sites in diverse waterbodies, tributaries and embayment, sometimes allows the possibility of grouping them into watersheds and conducting land-use assessment.

Findings

The following provide a succinct summary of the findings of each class of CEC.

The magnitude of AP contaminants, used in detergents and surfactants in industrial processes, varied in mussel tissue across the Gulf of Maine. The AP contaminants 4-nonylphenol mono-ethoxylate (NP1E0), 4-nonylphenol di-ethoxylate (NP2E0), and 4-n-octylphenol (4-n-OP) were detected. NP1EO was the most frequently detected (Table 8) with a maximum concentration of 16.5 ng/g ww recorded at the South Mill Pond (NHSM) site in NH. Jurisdiction specific assessments indicated that APs were more prevalent in NH and ME than MA. AP contaminants were not de-tected in NS, Canada.

AFR contaminants, which are primarily used in household consumer products such as upholstery, polystyrene and textiles, were only detected in the mussel tissue from MA and ME (Table 8). The TBB and TBPH contaminants were detected. A maximum concentration of 3.27 ng/g ww for the TBB was recorded in the MADI site in MA, while the TBPH was found at 0.73 ng/g ww at the MEKN site in ME.

CUPs include pesticides and their associated degradation products. The current-use pesticides are typically designed to be more water-soluble than the legacy organochlorine pesticides and often do not readily bioaccumulate in organisms. The results indicated that CUP contaminants were not present in the Gulf of Maine. However, these contaminants have been measured in oysters (Apeti et al. 2018) and freshwater invasive dreissenid mussels (Kimbrough et al., 2018) at low concentrations relative to detection limit values. This indicates that CUPs can potentially bioaccumulate in coastal organisms, but accumulation magnitude may depend on location and land-use types.

PFAS are industrial chemicals related to surface protection/coatings and fire fighting foam. PFAS contaminants were detected at different locations across the Gulf of Maine (Table 8) including the most toxic perfluorooctane sulfonate (PFOS)(Li, 2008). The most pervasive PFAS in blue mussels was perfluorooctane sulfonamide (PFOSA), which was found in all Gulf of Maine jurisdictions except NS in Canada. A maximum concentration of 5.46 ng/g ww was recorded for PFOSA at the MEPH in Maine, and perfluorooctane sulfonate (PFOS) found at the MANR site in MA had a con-centration of 0.60 ng/g ww.

Environmental PPCPs include a wide spectrum of therapeutic and consumer-use compounds such as prescription and over-the-counter medications, hormones, synthetic fragrances, disinfectants, insect repellants, and antimicrobial agents. PPCP contaminants most frequently detected were the insect repellant DEET, the antidepressant drug sertraline, and the antihistamine drug diphenhydramine. A similar pattern was observed by Kimbrough et al. (2018) with DEET, sertraline, and diphenhydramine being among the most commonly detected PPCPs in the Great lakes. It is worth noting that some PPCPs were found at relatively elevated concentration compared to the others. These include meprobamate, a sedative drug used for insomnia and psychiatric anxiety, and caffeine found at the concentrations of 59.44 and 57.72 ng/g ww respectively at the MABI and SHFP sites in MA. Metprolol and propranolol, which are both used to treat angina and hypertension, were detected respectively at 46.65 and 42.57 ng/g ww in mussel tissues from the sites MERY in ME and NHDP in NH. PPCP contaminants were indiscriminately found in every jurisdiction in the Gulf of Maine including NS in Canada, however, they were found at higher frequency and elevated concentration in harbor areas and near wastewater treat-ment plants and outfalls.

BFRs, such as PBDEs and PBBs, are toxic firefighting materials with 209 possible unique congeners each. In this study a combined 70 congeners were measured. In contrast to the PBB congeners, which were not detected in any mussel sample, several PBDE congeners were found at various concentrations throughout the Gulf of Maine including all three of the NS sites in Canada. The most frequently detected PBDEs in the Gulf of Maine were congeners PBDE-47 (at 80.5% of the sites), PBDE-99 (63.4%), PBDE-71/49 (58.5%), PBDE-119 (53.66%) and PBDE-77 (48.8%). The maximum

Table 8. Summary of Gulf-wide number of detects measured at each site ranked by Jurisdictions and Detectection frequency (%).

Jurisdiction	Site	Total number of compounds analyzed	Total number of compounds detected	Detection frequency (%)	AP Total	AFR Total	CUP Total	PFAS Total	PPCP Total	PBB Total	PBDE Total
MA	MANR	249	17	6.8	1	0	0	2	6	0	7
MA	MAME	249	15	6.0	1	0	0	1	4	0	9
MA	BHDB	248	10	4.0	0	0	0	0	5	0	5
MA	BHDI	249	10	4.0	1	1	0	0	5	0	3
MA	MAPR	249	9	3.6	0	0	0	0	4	0	5
MA	MADI	249	9	3.6	0	1	0	1	3	0	4
MA	MABI	239	8	3.3	0	NA	0	1	2	0	5
MA	DBCI	248	8	3.2	0	1	0	0	1	0	6
MA	MAWR	248	8	3.2	0	0	0	1	1	0	6
MA	SHFP	248	7	2.8	0	0	0	0	4	0	3
MA	BHHB	249	7	2.8	0	1	0	0	2	0	4
MA	MACO	248	6	2.4	0	0	0	1	1	0	4
MA	MAMF	248	5	2.0	0	0	0	0	1	0	4
MA	MASN	249	4	1.6	0	0	0	0	1	0	3
MA	BBCC	249	3	1.2	0	0	0	1	2	0	0
MA	MBNR	249	3	1.2	0	0	0	0	2	0	1
MA	CCNH	248	2	0.8	0	0	0	1	1	0	0
MA Total		**4216**	**130**	**3.1**	**3**	**4**	**0**	**9**	**45**	**0**	**69**
ME	MECC	249	11	4.4	1	0	0	1	5	0	4
ME	MEPR	249	10	4.0	2	1	0	0	4	0	3
ME	MEKN	249	10	4.0	1	2	0	1	4	0	2
ME	MEBB	249	10	4.0	0	0	0	2	3	0	5
ME	MEPH	249	8	3.2	1	0	0	1	3	0	3
ME	MESA	249	7	2.8	0	0	0	0	4	0	3
ME	MERY	249	7	2.8	0	0	0	0	3	0	4
ME	MEFP	249	7	2.8	0	0	0	0	2	0	5
ME	MSPP	248	5	2.0	0	0	0	0	3	0	2
ME	PBSI	249	5	2.0	0	0	0	0	2	0	3
ME	MEPI	249	5	2.0	0	0	0	0	1	0	4
ME	CAKP	249	3	1.2	1	0	0	0	1	0	1
ME	PBPI	249	3	1.2	0	0	0	0	3	0	0
ME	MEUR	249	2	0.8	0	0	0	0	2	0	0
ME Total		**3485**	**93**	**2.7**	**6**	**3**	**0**	**5**	**40**	**0**	**39**
NH	NHHS	249	13	5.2	2	0	0	0	5	0	6
NH	NHNM	240	11	4.6	1	NA	0	1	4	0	5
NH	NHSM	249	11	4.4	2	0	0	1	5	0	3
NH	NHDP	249	11	4.4	1	0	0	0	5	0	5
NH	NHNC	248	10	4.0	1	0	0	1	3	0	5
NH	NHPI	248	8	3.2	0	0	0	0	4	0	4
NH	NHLH	248	6	2.4	0	0	0	1	1	0	4
NH Total		**1731**	**70**	**4**	**7**	**0**	**0**	**4**	**27**	**0**	**32**
NS	NSFI	70	4	5.7	NA	NA	NA	NA	NA	0	4
NS	NSAR	248	4	1.6	0	0	0	0	0	0	4
NS	NSDI	248	3	1.2	0	0	0	0	1	0	2
NS Total		**566**	**11**	**1.9**	**0**	**0**	**0**	**0**	**1**	**0**	**10**

concentrations found across the study area were recorded for the congener PBDE-209 found at 1.04 ng/g ww and 0.96 ng/g ww at the Merrimac River (MAME) and Cohassett (MACO) sites respectively in MA. The congeners PBDE-71/49 was measured at 0.76 ng/g ww at the Stroudwater-Fore Portland Harbor (MEPH) site in ME, and the congener PBDE-77 was detected at a concentration of 0.67 ng/g ww in mussel sample from the Hampton Seabrook Estuary (NHHS) site in NH.

Study Summary

The results indicated that CECs are present at various degrees in coastal waters of the Gulf of Maine and they are being accumulated at various concentrations in coastal resources. Mussel samples from all 41 monitoring sites exhibited the presence of at least two CEC compounds highlighting the ubiquity of these contaminants in the coastal zone throughout the four Gulf of Maine jurisdictions (Table 8). APs had the highest detection frequency at 10%, followed by PBDEs (7.1%) and PFC (3.8%) (Table 9). It is important to note that the presence and magnitude, hence bioaccumulation of the CEC contaminants in organisms such as mussels are typically compound dependent, with a small subset of contaminants representing the majority of detections within each class. Moreover, the distribution and magnitude of the CEC contaminants also depend on location and land-use types in watersheds adjacent to the monitoring location. Based on our land-use assessment, CEC contaminants were detected in areas with developed, undeveloped and open-water land-uses however many of the highest detection frequencies were located in developed areas including Boston, MA, Portsmouth, NH, and Portland, ME. Additionally, a GIS visual assessment indicated that sites with high detection frequencies and elevated concentrations of CECs were influenced either by wastewater treatment plants or by combined sewer outfalls.

The study leveraged resources from both programs where the Gulfwatch Program provided all the fieldwork and the MWP assumed the analytical analyses and data management. In addition to filling CEC data gaps in the region, this study strengthened federal and state collaboration in monitoring and protecting coastal ecosystems in the Gulf of Maine. Results from this study support the Gulf of Maine Council on the Marine Environment and the Gulfwatch program's mission to provide "…high quality and relevant data to allow for characterization of the condition of ecosystems in the Gulf of Maine for enhancing marine resource management and protecting public health" (GOMC, 1991a).

Table 9. Summary of Gulf-wide detection frequency for each class of CEC assessed in the Gulf of Maine.

Compound Class	Number of Detects	Number of Possible Detects	Detection Frequency (%)
AP	16	160	10.0
AFR	7	342	2.0
CUP	0	1308	0.0
PFAS	18	480	3.8
PPCP	113	4838	2.3
PBB	0	779	0.0
PBDE	150	2091	7.2

Screening and Identification of CECs in the southern California Bight

2018 Bight Program Special Study

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Background

Assessing impacts of chemicals of emerging concern (CECs) on aquatic ecosystem health is challenging due to their occurrence and potential for deleterious effects at exceedingly low concentrations, an ever-changing universe of CECs found in receiving waters, and a lack of standardized monitoring and assessment methods. Moreover, current chemical-specific monitoring does little to address unmonitored and/or unknown substances (e.g. drug metabolites, disinfection by-products) or the impacts of CEC mixtures. To address these challenges, a panel of experts convened by the State Water Board in 2012 recommended development and standardization of monitoring technologies that address CECs. High-throughput cell assays that provide an integrative measure of CECs acting via a common mode of action, offer a more efficient way to screen for both known and unknown chemicals that can be linked to a toxic effect. Non-targeted chemical analysis has also emerged as a means for identifying previously unknown CECs in complex mixtures, such as treated wastewater effluent and stormwater runoff. Coupling bioanalytical screening tools ("bioscreening") with non-targeted analysis will enhance current monitoring by broadening the chemical universe under investigation while improving our ability to identify and prioritize CECs that are most likely to impact aquatic ecosystem health.

The Southern California Bight Regional Monitoring Program ("Bight") is a cooperative effort among dozens of water quality agencies from Pt. Conception in Santa Barbara County to the International Border with Mexico. Performed every 5 years, Bight analyzes more than 300 sediment samples, collected from inshore and offshore habitats, using a weight of evidence assessment approach. In addition, numerous special studies are spawned during each Bight cycle, e.g. assessment of contaminants in marine life at various trophic levels. Because of the numerous physical, chemical and biological parameters measured by Bight participants on any given sample, the Bight Program serves as an excellent test bed for emerging approaches, such as bioscreening for and non-targeted analysis of CECs. Planning of special studies for Bight'18 will commence in September 2017.

The goal of this Bight'18 special study is to evaluate the utility of bioscreening and non-targeted analysis in enhancing current monitoring methods for CECs that occur in coastal and marine environments. Specifically, our objectives are to 1) determine the range of bioscreening responses in Bight sediments representing different habitats and for tissues of marine life at various trophic levels; 2) identify CECs responsible for detectable bioscreening responses; and 3) investigate the potential for bioaccumulation and trophic transfer of CECs in the marine environment. This evaluation will be aided by collection of core Bight measurements, including occurrence of more than 200 individual (known) contaminants, sediment toxicity and *in situ* benthic community analysis provided by Bight participants

Conclusions

To date, the National Status and Trends, Mussel Watch Program remains the longest running continuous contaminant-monitoring program of its kind in the United States. The importance of its national and yearly approaches to monitoring with high quality data is very relevant to federal, state and local coastal resource managers. In response to programmatic challenges, NCCOS undertook the task of re-designing the MWP to focus on a rotating regional model. Pilot studies were initiated to evaluate the feasibility of the regional monitoring approach.

Following a planned framework, the pilot studies were set to be regional in nature, balancing short-term flexibility in study design against the cost of broad CEC surveys. We collaborated with various stakeholders, tried various sampling approaches including caged-bivalves, and tested multiple bivalve species and sediment samples for contaminants of emerging concern (CECs) and bivalve health metrics. The followings highlights major outcomes from the pilot studies this far.

1. Data from past efforts in the Great Lakes, Charleston Harbor, Chesapeake Bay, and Gulf of Maine have been published, while those from the most recent assessments are being examined. The results showed evidence of CECs being accumulating at various degrees in coastal waters and they can be measured using the Mussel Watch approach. However, It is important to note that the accumulation and detection of CEC in coastal water are compound, matrix dependent. Additional information is needed to fully identify candidate CECs for long-term monitoring.

2. The studies showed CEC chemicals appeared to be associated with land-use categories in the watershed, and that caged-bivalve could be a great tool to assess CEC bioaccumulation and organism health at target locations devoid of natural reefs. However, we realized that the approach is time and resource consuming, hence very difficult to implement in a sustainable fashion.

3. The pilot studies evidently benefits regional capacity building of the MWP by forging and strengthening collaboration with local stakeholders. However, we found that level of engagement differs from region to the other. Hence, local support to help leverage resources is not sustainable and should be dealt with carefully when it is to be included in the long-term plan of the regional monitoring model. In addition to working with local stakeholders, the program's in-house collaboration with the NCCOS' Ecotoxicology Branch (collection and analysis) looks more reliable.

4. Overall, the results of the different pilot studies provided enough ground information on cost saving approaches through stakeholders interaction. The regional approach would help the program respond to local end-users specific data need and help fill local data gaps strengthen, however, the program would lose its national perspective, the unique long-term data trends and the ability to provide relevant baseline data to help assess impacts of unforeseen events such as oil spill and hurricanes.

The aim of the Mussel Watch monitoring program is to continue to improve its approaches and provide actionable information to stakeholders and the scientific community. Thus, for future efforts, the program is considering:

1. Incorporation of innovative scientific tools and technologies, such as omics

2. Increased linkages with new and existing data sets to expand uses of monitoring & assessment data and information

    a. Land cover/uses; socio, econ and demographic information

    b. Impervious surface areas; industrial, military zones, retirement communities

3. Increased collaboration and integration with NOAA response programs such OR&R

References

Ambrose R.B., 1999. Partition coefficients for metals in surface water, soil, and waste. US EPA Office of Solid Waste Washington, DC.

Apeti, D.A., Y. Kim, G. Lauenstein, J. Tull, and R. Warner. 2014. Occurrence of Parasites and Diseases in Oysters and Mussels of the U.S. Coastal Waters. National Status and Trends, the Mussel Watch monitoring program. NOAA Technical Memorandum NOSS/NCCOS 182. Silver Spring, MD 51 pp

Apeti, D.A., W.E. Johnson, G.G.Lauenstein and K. Kimbrough. 2012. National Status and Trends, Mussel Watch Program: Sampling Methods. NOAA Technical Memorandum NOS NCCOS Silver Spring, MD.

Apeti, D.A., G.G. Lauenstein, and G.F. Riedel. 2009. Cadmium Distribution in Coastal Sediments and Molusks of the US. Marine Pollution Bulletin 58:1016-1024

Apeti, A.D., Lauenstein, G.G. and Evans, D.W. 2012. Recent status of mercury and methyl mercury in the coastal waters of the northern Gulf of Mexico using oysters and sediments from NOAA's Mussel Watch Program. Marine Pollution Bulletin, 64(11): 399-408

Apeti, A.D., Lauenstein, G.G, Christensen, J.D., Johnson, W.E. and Andrew Mason 2011. Assessment of Coastal Storm Impacts on Contamination Body Burdens of Oysters Collected from the Gulf of Mexico. Environmental Monitoring and Assessment, 181:399-418

Kimbrough, K.L., G.G. Lauenstein, and W.E. Johnson. 2007. Organic Contaminant Analytical Methods of the National Status and Trends Program: Update 2000-2006, NOAA Technical Memoranda, NOS NCCOS 30. 22 Apr. 2008 http://www.ccma.nos.noaa.gov/publications/organicsmethods.pdf.

Kimbrough, K.L., and G.G. Lauenstein. 2007. Major and Trace Element Analytical Methods of the National Status and Trends Program: 2000-2006, NOAA Technical Memorandum, NOS NCCOS 29. 22Apr 2008. http://www.ccma.nos.noaa.gov/publications/nsandtmethods.pdf.

Kimbrough, K., W. E. Johnson, A. Jacob, M. Edwards and E. Davenport. 2018. Great Lakes Mussel Watch: Assessment of Contaminants of Emerging Concern. NOAA Technical Memorandum NOS NCCOS 249. Silver Spring, MD. 66 pp.

McDonald, S. J., D. S. Frank, J. A. Ramirez, B. Wang, and J. M. Brooks. 2006. Ancillary Methods of the National Status and Trends Program: Update 2000-2006, NOAA Technical Memorandum, NOS NCCOS 28. 22Apr. 2008. http://www.ccma.nos.noaa.gov/documents/ancillarymethodsnsandt.pdf.

Kimbrough, K.L.; Johnson, W.E., Lauenstein G.G., Christensen, J.D. and Apeti, A.D. 2008. Assessment of Two decades of Contaminant Monitoring in the Nation's Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 74. 105pp.

Kimbrough, K.L., W.E. Johnson, G.G. Gunnar, J.D. Christensen and D.A. Apeti. 2009. An assessment of polybrominated diphenyl ethers (PBDEs) in sediment and bivalves of the U.S. coastal zone. NOAA Technical Memorandum, NOS/NCCOS, 78.76 pp. Silver Spring, Maryland

Kim, Y., K.A. Ashton-Alcox, and E.N. Powell. 2006. Histological Techniques for Marine Bivalve Molluscs: Update, NOAA Technical Memorandum, NOS NCCOS 27. 22 Apr. 2008 http://www.ccma.nos.noaa.gov/publications/histopathtechmemofinal.pdf.

Cantillo, A. Y. and G. G. Lauenstein. 1998. Performance-based Quality Assurance - The NOAA National Status and Trends Program Experience. In: U.S. EPA Proceedings of the NWQMC National Conference - Monitoring: Critical Foundations to Protect Our Waters. Washington, DC. pp. III63-III73.

Lauenstein, G. G., A. Y. Cantillo, S. Kokkinakis, J. Jobling, and R.Fay. 1997. Mussel Watch Project Site Descriptions, through 1997. NOAA Technical Memorandum NOS ORCA 112, Silver Spring, MD.

O'Connor, T. P. and G. G. Lauenstein. 2006. Trends in Chemical Concentrations in Mussels and Oysters Collected along the U.S. Coast: Update to 2003. Marine Environmental Research 62:261-285.

Li, M.H., 2008. Toxicty of Perfluooctane Sulfonate and Perfluorooctanoic Acid to Plants and Aquatic Invertebrates. Environmental Toxicology. Published online 6 May 2008 in Wiley InterScience (www. interscience.wiley.com). DOI 10.1002/tox.20396

Apeti, D.A., Wirth, E., Leight, A.K., Mason, A. and Pisaski, E., 2018. An Assessment of Contaminants of Emerging Concern in Chesapeake Bay, MD and Charleston Harbor, SC. NOAA Technical Memorandum NOS NCCOS 240. Silver Spring, MD. 104pp. doi:10.25923/p4nc- 7m71

GOMC (Gulf of Maine Council), 1991a. Gulf of Maine Environmental Qualty Monitoring Program: An Initial Plan. The Gulf of Maine Council on the Marine Environment. 51pp.

Desjardins, D., Mac Gregor, J. A., Krueger, H. O. 2004. Hexabromocyclododecane (HBCD): A 72-hour toxicity test with the marine diatom (Skeletonema costatum). Final Report. Wildlife International, Ltd., Easton, Maryland, USA pp 66.

EPA (Environmental Protection Agency), 2014. Certain Nonylphenols and Nonylphenol Ethoxylates; Significant New Use Rule 190, Envi-ronmental Protection Agency, Federal Register. 59186-59195pp.

Loyo-Rosales, J.E., Schmitz-Afonso, I., Rice, C.P. and Torrents, A., 2003. Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/

EPA (Environmental Protection Agency), 2007. Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/ MS. EPA-821-R-08-002, U.S. Environmental Protection Agency; Office of Water; Office of Science and Technology. 72pp.

Klosterhaus, S.L., Grace, R., Hamilton, M.C. and Yee, D., 2013. Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary. Environment International 54:92-99.

Petrovic, M., Eljarrat, E., López de Alda, M.J. and Barceló, D., 2002. Recent advances in the mass spec-trometric analysis related to endocrine disrupting compounds in aquatic environmental samples. Journal of Chromatography A 974:23-51.

Loyo-Rosales, J.E., Schmitz-Afonso, I., Rice, C.P. and Torrents, A., 2003. Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/Tandem Mass Spectrometry. Analytical Chemistry 75:4811-4817.

Place Based Assessments: Case Studies to Illustrate Tools, Partners and Data Users

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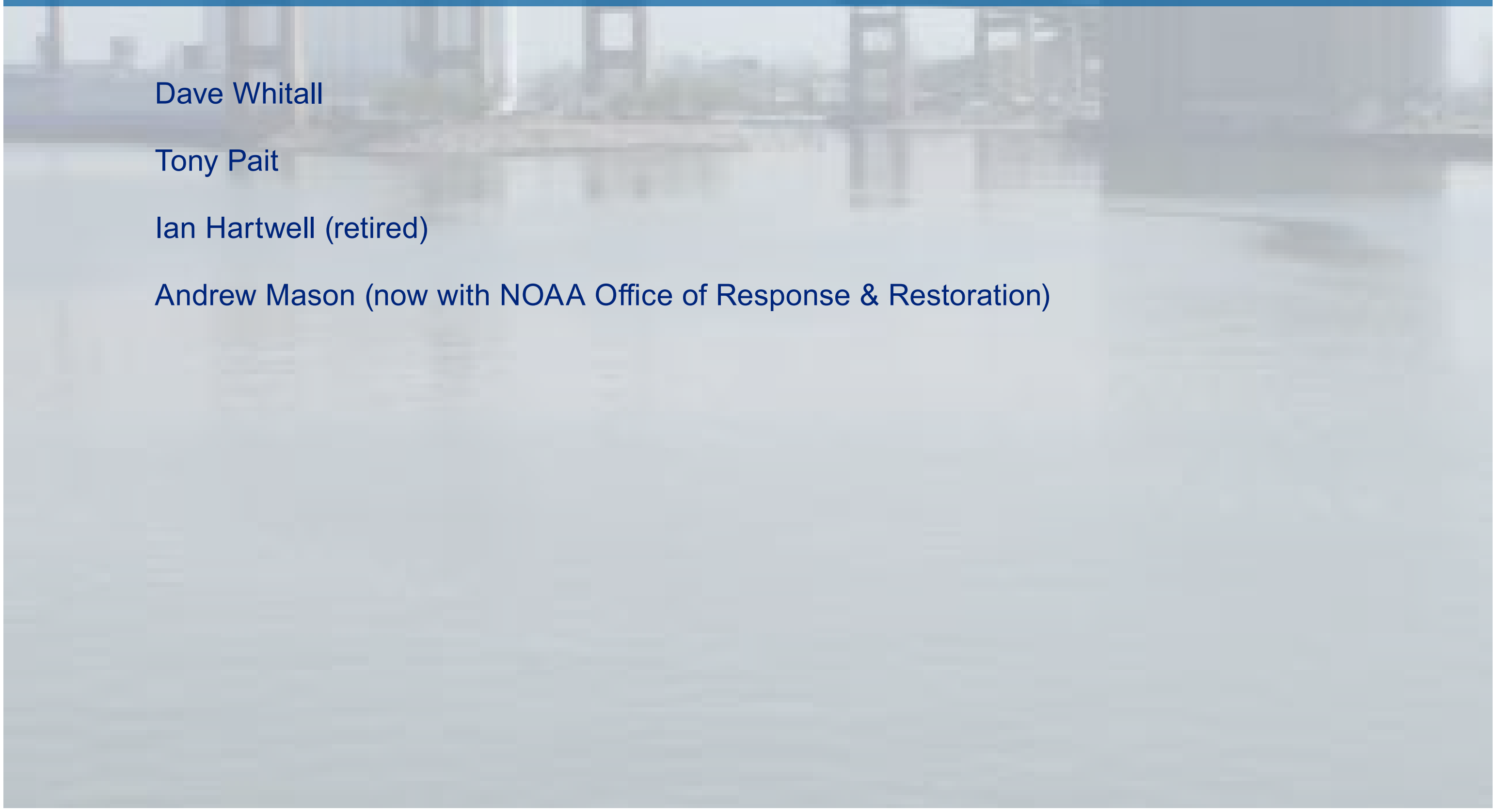


Abstract

While the Mussel Watch National Monitoring Program is the backbone of the National Status and Trends (NS&T) Program, there are some research questions, and underlying coastal management needs, that its design is not suitable to address. These types of questions are investigated through the Monitoring and Assessment Branch's (MAB) place based assessments. These shorter term (usually one to five years) research projects utilize a variety of scientific tools, including the Sediment Quality Triad, quantification of toxic contaminants in tissues and sediments, nutrient biogeochemistry and the use of in situ (passive or active) water samplers to address hydrophilic toxics. The tools allow MAB scientists to tackle site specific research needs for clients within the National Ocean Service (NOS), NOAA, other federal agencies and/or states and territories. The approach, both in terms of tools used and study design, is individually tailored to the specific site and the research needs therein. Place based assessments have historically occurred in geographies such as NOAA managed areas, non-NOAA Marine Protected Areas (MPAs), designated special management or priority areas, or places in which an adverse environmental event (e.g. oil spill) has occurred. The results from place based assessments can be used by coastal managers to determine pollutant threats to a resource and consider appropriate actions, to evaluate the efficacy of implemented management practices (e.g. before and after assessments) or as a baseline of current conditions against which to measure future change to a system (e.g. due to changes in land use practices). Here, we present five case studies from the past three years which demonstrate the breadth of MAB's place based assessments both in terms of the variety of research tools used, as well as the different geographies in which this research has occurred.

Introduction

Place based assessments make up an important component of the MAB portfolio, complementing the National Mussel Watch Program. The designs of these place based research studies are individually crafted to address the science and management needs of the coastal managers (local, state/territory/tribal, federal) in that place. MAB has a variety of assessment tools in its toolbox, but not all methodologies will be relevant to the research questions for a specific assessment. Rather than a "one size fits all" approach, each assessment is uniquely engineered with the most effective set of assessment tools available.

MAB scientists work closely with the clients to understand their data needs, often involving them in the study design, and sometimes the research itself (e.g. field work and publications). These projects are purposefully highly collaborative and often leverage not only external expertise, but also existing or planned work by partners (e.g. the Southern California Coastal Water Research Project's recurring "Bight" assessments). Recruiting local experts to participate in these assessments is a fundamental philosophy of MAB's approach. This local knowledge of a system greatly enhances the effectiveness of both study design and execution. Furthermore, by involving clients in the planning and execution of the project, this not only ensures that they are satisfied with the project's direction and progress, but also gives them a personal investment in project success.

Examples of places in which these assessments have occurred include NOAA managed areas (National Estuarine Research Reserves and National Marine Sanctuaries), non-NOAA MPAs (e.g. marine units of National Parks), designated special management or priority areas (e.g. NOAA Habitat Focus Areas, EPA Areas of Concern (AOCs), territorial Coral Reef Priority Watersheds) or places in which an adverse environmental event (e.g. oil spill) has occurred. Often times, MAB is approached for technical assistance by the clients who have specific data needs; this speaks to the demonstrated success of previous assessments and MAB's scientific reputation with the national community of coastal managers. Most commonly, funding for these place based assessments is external to NCCOS (e.g. NOAA Coral Reef Conservation Program) and sometimes external to NOAA (e.g. USEPA), with in-kind contributions being provided by both NCCOS (FTE time) and local partners (e.g. boat time and other logistical support).

Details regarding assessment methodologies are described in detail in the individual case studies, but are summarized here. Site selection can be approached from a stratified random design perspective (useful for characterizing large areas and statistically comparing those areas) or a targeted approach (useful for assessing specific points of interest). The sampling approach chosen depends on the research questions and management needs of that particular place. In some cases, a hybrid design using both random and targeted sites is used, but care must be taken when statistically comparing those two site types.

Toxic contaminants, in the form of trace and heavy metals, organochlorine pesticides (e.g. DDT, chlordane), PCBs, PAHs, organotins, current use pesticides (e.g. atrazine), personal care products and pharmaceuticals can be quantified in multiple matrices: sediments, water or tissues. The type of organisms considered for tissue analysis depends on the research questions (e.g. ecologically significant species, representative/commonly occurring species, species important for subsistence fishing, the home range of the species, etc.), but have included both finfish and shellfish (oysters, mussels, clams, conch, lobsters). In sediments, surface samples (top 2 to 3 cm) are usually collected in order to capture recent conditions, although some projects have utilized sediment cores to look at historical pollution levels. Some hydrophilic pollutants do not readily accumulate in tissues or sediment, so water chemistry must be considered if those pollutants are of interest in a given study. Unlike sediments or tissues, which integrate contaminant concentrations over time, water concentrations are ephemeral and can change rapidly with tides, currents and runoff events. Sampling via grab sample at one time point may not be very informative in that it is hard to evaluate how representative that sample might be. Additionally, for many waterborne contaminants, very large volumes of water might be needed in order to obtain analytically detectable levels. The sampling and transport of large volumes of water may be logistically prohibitive at certain field sites. In order to address both the temporal and volume concerns, a variety of in situ integrative water samplers have been used in place based assessments. These include passive samplers, such as Polar Organic Chemistry Integrated Samplers (POCIS), and Polyethelyne Devices (PEDs), as well as active samplers such as Continuous Low-level Ambient Monitoring (CLAM) devices. The passive samplers are relatively inexpensive, but must be deployed for relatively long periods of time (e.g. 30 days) which may not be suitable for the conditions of a given site (due to biofouling, risk of damage/vandalism, or field logistics). The CLAM devices are more expensive but are deployed for much shorter periods of time (24 hours). These devices actively pump known amounts of water across specialized filters (C18 and HLB). Because the volume of water is measured, an actual time integrated water concentration can be calculated. For the passive samplers, ambient concentrations can only be estimated based on the mass collected on the membrane and analyte specific equilibrium constants.

In systems where eutrophication is a concern, water column sampling for nutrients (and related compounds) is undertaken. Unlike contaminant sampling, which is usually done over a short period of time, nutrient sampling is usually a recurring (e.g. monthly) sampling design over a period of multiple years in order to adequately assess the temporal variability within a system. Analytes typically measured when quantifying nutrients are nitrate, nitrite, ammonium, urea, total nitrogen, orthophosphate and total phosphorus. Silica concentrations are useful when considering diatom productivity, but also as a tracer for freshwater inputs, as crustal erosion is a primary source of silica in marine environments. In addition to the nutrients themselves, MAB scientists have utilized compounds that are specific to human diets in order to differentiate between sources of nutrients in the marine environment. Sucralose (an artificial sweetener) and caffeine do not break down in the human gut or wastewater treatment and are persistent in the environment, making them useful compounds to help coastal managers identify sources of nutrients to a system.

The sediment quality triad (SQT) approach is used as an assessment tool to evaluate the extent of sediment degradation due to contaminants. This approach is based on multiple lines of evidence formulated from three components: sediment chemistry, sediment toxicity testing using relevant marine organisms, and the status of the benthic infaunal community. This approach does not provide a cause-and-effect relationship between individual chemicals and biological effects, but it does provide an assessment of sediment quality that is useful for describing degradation. The use of multiple lines of evidence provides a stronger assessment of condition than any singular (e.g sediment chemistry only) metric.

When possible, chemistry data is analyzed in conjunction with biological endpoint data. This may take the form of ecosystem level metrics of health (e.g. benthic infauna community richness, or coral species diversity) or metrics of health at the individual organism level. Recently, “omics” have been employed in place based studies in the Great Lakes to quantify biological impacts. These techniques are discussed in the subsequent chapter entitled “New Approaches for Monitoring and Assessment.”

Field sampling and analytical chemistry methods are standardized across projects so that data can be readily compared across the program. Analytical chemistry is primarily conducted at a NOAA contract laboratory (TDI Brooks, College Station, TX), although that laboratory sub-contracts some analyses to other laboratories (e.g. contaminants of emerging concern via SGS Axys, Geochemical Environmental Research Group (GERG) for nutrients, and Texas A&M for trace elements). For some projects, components of analytical chemistry have been done at the NCCOS Charleston lab. When appropriate, interlaboratory comparisons have been conducted to ensure data quality/comparability.

Products from these assessments take many forms. A primary product is the data itself, which is served to the public via repositories within NOAA such as the National Centers for Environmental Information (NCEI) and the Office of Response and Restoration's (OR&R) Data Integration Visualization Exploration and Reporting (DIVER). The data undergoes a rigorous QA/QC process prior to being shared. Each assessment also includes some form of interpreted data product. This often takes the form of a technical memorandum or journal article. These reports analyze, synthesize and interpret the data produced to yield a written assessment that puts the results into context and helps the reader understand the significance of the data. Data is frequently analyzed statistically as well as spatially visualized using Geographic Information System (GIS) software. MAB scientists also engage in a variety of outreach activities to publicize, disseminate and explain the findings of these assessments. Mechanisms for this include scientific presentations at conferences, seminars within NOAA (or at other state/federal agencies, or academia), presentations directly to coastal managers, and less technical written materials (i.e. "one pagers") that can be distributed to coastal managers or the public. Projects are also publicized via the NCCOS website, social media and through a variety of official NOAA processes (e.g. press releases, internal and external email announcements, etc.)

Examples of how place based assessments can be used by coastal managers include: identification of previously unknown pollution threats to ecosystem health, evaluation of the effectiveness of best management practices (i.e. comparing a "before" assessment to "after") or as a baseline of current conditions against which to measure future change to a system (e.g. due to changes in land use practices or climate change). In the following text, five case studies from the past three years are presented which highlight the various ways in which our scientific tools and expertise are applied to specific research questions in a variety of geographies.

Case Study #1: Over-enrichment of nutrients and source tracking in a coral reef ecosystem (Vatia, American Samoa)

Why Was This Study Done?

Vatia Bay has been designated as a priority management area by the territory of American Samoa. There have been local concerns about the impacts of land based sources of pollution and water quality on the coral reef ecosystems of Vatia Bay (NOAA CRCP 2012), based on qualitative observations that coral health in the Bay has declined and benthic algal cover has increased.

Coral reefs have the potential to be adversely affected by a variety of water quality problems, including toxics, sedimentation and over enrichment of nutrients. Nutrients (particularly nitrogen and phosphorus) are critical to ecosystem primary productivity, but excess amounts can lead to macroalgal and benthic algal blooms, which can overgrow or outcompete the corals (Kuffner et al. 2006; Hughes and Tanner 2000; D'Angelo and Wiedenmann 2014). Additionally, excess nutrients can directly affect corals by reducing calcification and photosynthesis rates (Marubini and Davis, 1996), and by lowering fertilization success (Harrison and Ward, 2001).

Like any pollutant, effective management of nutrients requires accurate source identification. This can be problematic because the number of potential sources is large. Chemical fertilizers (both agricultural and non-agricultural uses), industrial sources, animal waste, and human waste can all contribute both nitrogen and phosphorus to the coastal environment (Galloway et al., 2003).

Discussions between American Samoa's Coral Reef Advisory Group (CRAG) and NOAA led to the implementation of a research project to answer the following questions:

1. Are nutrient levels elevated in the Bay?
2. Are nutrient levels correlated with coral health?
3. What are the sources of nutrients to the Bay?

Where was the Study Site?

Vatia Bay is located on the north shore of the island of Tutuila, the largest and most populous island of the U.S. territory of American Samoa (Figure 1). American Samoa's reefs are considered to be among the most pristine in the United States (Birkeland et al. 2008). These reefs host approximately 950 species of fish, 240 species of algae, 330 species of coral and many other species of invertebrates (Birkeland et al. 2008).

At its widest point, Vatia Bay, which is roughly horseshoe shaped, is approximately 750 meters wide and 1 kilometer long, with the opening to the ocean oriented to the northeast. The Bay has a

Figure 1. Location of Vatia Bay, American Samoa.

diurnal tidal range of 0.85 m (Storlazzi et al 2017). The benthic habitat of the Bay is a mixture of hard bottom (live coral, coral rubble, pavement), crustose coralline algae (CCA), fleshy macroalgae, and turf algae, with small patches of sand (Vargas-Angel and Schumacher 2018). Previous work has quantified a biological gradient, with the inner Bay, which is most likely to be impacted by land based pollution, having worse coral reef conditions than the outer Bay (Vargas-Angel and Schumacher 2018).

There are three perennial streams, as well as some intermittent streams, that bring freshwater inflows from the surrounding watershed into the Bay. Additionally, groundwater may play a significant role in the freshwater influxes to the Bay (Shuler et al, 2019). The land adjacent to the Bay consists of the small village of Vatia (6.5 km2 in area), the entirety of which is very close to the coast because of the extremely steep slopes that typify the island. The village is made up 116 housing units and 640 residents (US Census, 2010), with minimal crop agriculture and no businesses or industries. After considering the land uses in the watershed, and literature values for nutrient flux (see modeling work contained in Castro et al. 2001), it was hypothesized that human waste and waste from the relatively small piggeries are likely to be the dominant sources of nutrients to the Bay. Discriminating between human and animal sources of waste is an important data need for coastal managers.

Who was involved?

The primary clients for this work were CRAG, American Samoa Environmental Protection Agency (ASEPA) and NOAA's Coral Reef Conservation Program (CRCP). Funding was provided by CRCP and NCCOS. NCCOS staff participating in the project were Dave Whitall, Andrew Mason and Greg Piniak. The project was conducted in close cooperation with a number of local partners including: CRAG, ASEPA, the National Park of American Samoa, and American Samoa Community College. This included significant effort by local partners in collecting field samples. Non-NCCOS NOAA partners included: National Marine Fisheries Services Pacific Islands Fisheries Science Center and CRCP. Including the clients in the planning and execution of the project served to increase their buy-in and investment in the project and its results.

What did we do?

Sixteen sites were randomly selected within four operationally articulated sampling strata (Inner Bay, Central Bay, North Bay, South Bay; see Figure 2). Additionally, one targeted site was selected near the mouth of the largest stream entering the Bay (just upstream from the largest bridge in the village). Details about each site, including latitude and longitude are shown in Table 1. During each sampling trip, water was collected both from the

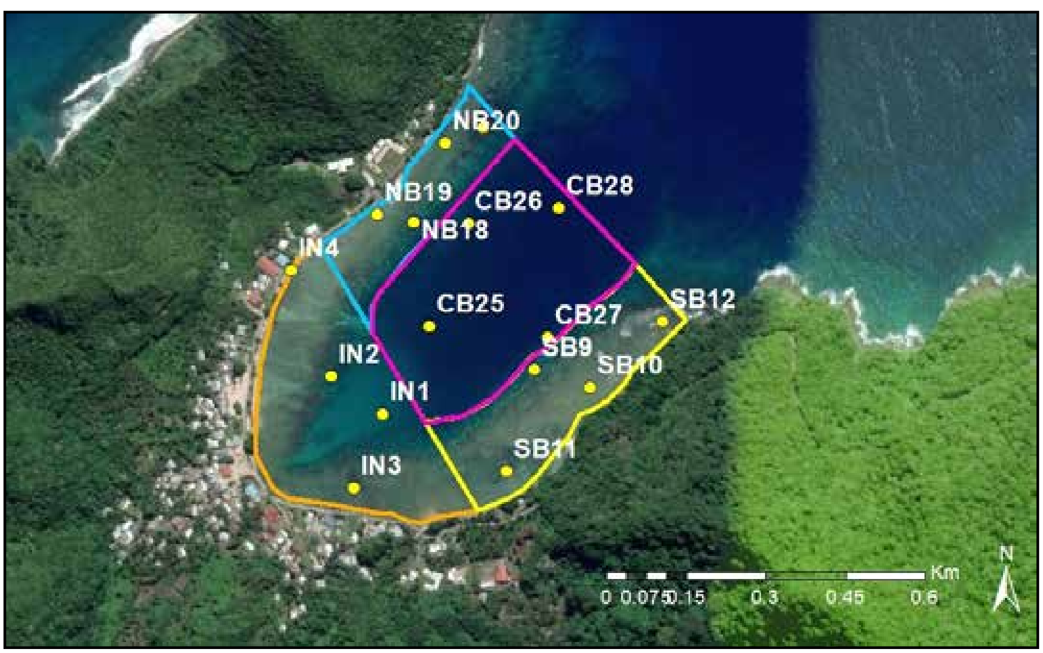


Figure 2. Vatia Bay sampling site locations. The colored polygons represent sampling strata (yellow= south bay; orange = inner bay; purple = central bay; blue = north bay).

Table 1: Details on each site, including lat/long, approximate depth, strata and site notes. Surface and bottom water samples were collected at each site unless otherwise noted.

Site	Depth(m)	Latitude	Longitude	Strata	Notes
CB25	7 m	-14.2479	-170.6724	Central	
CB26	7 m	-14.2462	-170.6717	Central	
CB27	5 m	-14.2481	-170.6703	Central	
CB28	7 m	-14.2459	-170.6701	Central	
IN1	3 m	-14.2494	-170.6732	Inner	
IN2	3 m	-14.2488	-170.6741	Inner	
IN3	<1 m	-14.2507	-170.6737	Inner	surface sample only
IN4	<1 m	-14.2470	-170.6748	Inner	surface sample only
NB17	>10 m	-14.2445	-170.6714	North	surface sample only
NB18	3 m	-14.2462	-170.6726	North	
NB19	<1 m	-14.2460	-170.6733	North	surface sample only
NB20	<1 m	-14.2448	-170.6721	North	surface sample only
SB10	<1 m	-14.2490	-170.6696	South	surface sample only
SB11	<1 m	-14.2504	-170.6710	South	surface sample only
SB12	1.5 m	-14.2478	-170.6683	South	
SB9	6 m	-14.2487	-170.6706	South	
Stream	<1 m	-14.2506	-170.6754	Stream	targeted site at bridge

From 2015 to 2017, each of these sites was visited monthly to collect grab samples. In 2018, sampling efforts focused on capturing precipitation events, so the sampling was conducted at less regular intervals (i.e. not every month). A total of 27 sampling trips were conducted. Samples were analyzed for: nitrate, nitrite, ammonium, urea, total nitrogen (TN), orthophosphate, total phosphorus (TP) and silica.

In order to determine if human waste was entering the Bay, two environmentally persistent chemicals (caffeine and sucralose) found only in human diets were quantified. In recent years, researchers have been measuring caffeine and sucralose in the environment as chemical proxies (or tracers) for human waste (Mead et al. 2009; Knee et al. 2010). During some sampling months (eight total), extra sample volume was collected (into amber glass vials) for analysis of caffeine and sucralose. These were sampled concurrently with the nutrient samples at the same sites.

Additional details regarding field and laboratory methods can be found in Whitall et al (2019).

surface (0.1 m below surface) and bottom (via Niskin bottle, just above bottom); exceptions to this were very shallow sites and one site (NB17) which consistently had high wave energy, making deploying the Niskin bottle from the sea kayak unsafe. At these sites only surface water was sampled.

Key Findings and Data Utility

When comparing the data from this study to water quality standards for the territory of American Samoa (USEPA 2013), it is clear that nutrient levels are elevated in this system. For embayments such as Vatia Bay, there are nutrient criteria for TP and TN, specifically that the median cannot exceed 0.02 mg/L and 0.15 mg/L respectively. Median values of TP and TN measured in this study on the reefs (i.e. bottom water, Table 2) indicate that all sites are in exceedance of these water quality standards for TN, and all sites except for SB11 (bottom) exceed the standard for TP. Based on these water quality standards, in combination with observed benthic prevalence of algae, we conclude that Vatia Bay is under nutrient stress.

Previous work by NOAA's Pacific Islands Fisheries Science Center characterized benthic habitat (cover type and coral species) and metrics of coral health (adult and juvenile coral colony density, colony partial mortality (old and recent), and condition (disease and bleaching) for total scleractinians) at Vatia Bay in 2015 (Vargas-Angel and Schumacher 2018). This study concluded that there were three levels of impact:

1. Inner Bay (very poor reef condition) where the benthic community was characterized by very low coral cover, and dominated by fleshy macroalgae;
2. Middle Bay (fair to moderate reef condition) where the reef community was dominated by plating/branching corals (Porites rus) intermingled with patches of sediment and calcifying macroalgae
3. Outer Bay (fair to good condition) where the benthos was characterized by robust coral reef development; community consisted of diverse assemblage of corals with low levels of macroalgae and only minor damage observed.

Table 2: Median bottom water values for Vatia Bay. Territorial water quality standards are 0.15 mg N/L total N and 0.02 mg P/L total P. All sites exceeded the standard for TN and only one site (SB11) did not exceed the standard for TP (highlighted in bold italics).

Site Name	Median TN (mg N/L)	Median TP (mg P/L)
CB25	0.261	0.030
CB26	0.247	0.032
CB27	0.224	0.028
CB28	0.225	0.029
IN1	0.242	0.030
IN2	0.261	0.031
NB18	0.245	0.028
SB11	0.386	0.019
SB9	0.202	0.024

Qualitatively this biological assessment mirrors the water quality data, i.e. degraded conditions closer to the stream mouth. While it is likely that the corals in Vatia Bay are subjected to multiple stressors, the spatial overlap between water quality issues and degraded habitat strongly suggests that water quality plays a role in reef health. Additional discussions relating biological condition to water quality data can be found in Whitall et al. (2019).

Both tracers of human waste (caffeine and sucralose) were detected in the Bay. Sucralose was detected in 51% of samples analyzed (97 out of 192) and caffeine was detected in 82% of the samples analyzed (157 out of 192). Concentrations of these tracers ranged from below limits of detection to 370 and 343 ng/L for sucralose and caffeine, respectively.

This definitively shows that human waste is entering the Bay. Additionally, the tracers are significantly correlated with some nutrient analytes (Table 3), suggesting that not only is human waste entering the Bay, but it may be a primary driver of excess nutrients.

Additional results from and discussion of these data can be found in Whitall et al. (2019).

The data presented in this study are critical to coastal managers in making decisions about remediation activities and best management practices. Proposed strategies to reduce pollution include improving on-site sewage disposal systems, and preventing future degradation through watershed and land-use planning. Environmental data, such as the dataset presented here, serve as a baseline of current conditions, which are needed to determine the efficacy of management efforts, i.e. measuring change over time. These data can be utilized by coastal managers to best prioritize management strategies in a way to maximize success in decreasing stressors on coral reef ecosystems.

Data Availability

This work was published as NCCOS Technical Memorandum #266. It can be accessed online here:

https://repository.library.noaa.gov/view/noaa/22423

The full citation is:

Whitall, D, M Curtis, A Mason, B Vargas-Angel. 2019. Excess Nutrients in Vatia Bay, American Samoa: Spatiotemporal Variability, Source Identification and Impact on Coral Reef Ecosystems. NOAA Technical Memorandum NOS NCCOS 266. Silver Spring. 69 pages. doi:10.25923/j8cp-x570

The data has been archived at NOAA's National Centers for Environmental Information and is can be accessed here:

https://data.nodc.noaa.gov/cgi-bin/iso?id=gov.noaa.nodc:0208020

Table 3: Spearman correlation coefficients for tracers (caffeine and sucralose) vs water quality concentrations by stratum. Only pairings with a statistically significant positive relationship are shown.

Strata	Variable	by Variable	Spearman ρ	Prob>|ρ|
South	Sucralose	Urea	0.549	0.000
North	Sucralose	Urea	0.470	0.003
North	Sucralose	Silica	0.393	0.016
Central	Sucralose	Orthophosphate	0.382	0.002
Central	Caffeine	Urea	0.354	0.004
Inner	Caffeine	Sucralose	0.343	0.020
Inner	Sucralose	Orthophosphate	0.335	0.023
Inner	Sucralose	Urea	0.327	0.027
Inner	Caffeine	Orthophosphate	0.293	0.048
Central	Caffeine	Ammonium	0.282	0.024
Central	Sucralose	Urea	0.263	0.036
Central	Caffeine	Nitrite	0.248	0.049

Case Study #2: Characterization of Benthic Habitats and Contaminant Assessment in Kenai Peninsula Fjords and Bays (Alaska)

Why Was This Study Done?

Contaminants, particularly those that are lipophilic, can biomagnify in the coastal food chain with increasing concentrations in predatory wildlife and humans. Thus, characterizing and delineating areas of sediment contamination and toxicity are viewed as important goals of coastal resource management. This is particularly important in Alaska, where subsistence food contamination is an emerging health concern, especially in rural areas where large amounts of these foods are consumed as a primary source of protein (Wolfe 1996). Partially due to its extremely large coastline, Alaska lacks adequate data to provide baseline information necessary to assess contaminant status. More environmental monitoring and research is needed to assess not only areas of known pollution impact, but also the whole Alaskan coastal region.

With no known current industrial point sources of contamination, current sources of pollution on the Kenai Peninsula may include wastewater discharge, marine activities associated with commercial and recreational fishing, commercial shipping, fuel tank leaks, storm water runoff, and long-range atmospheric transport. Historically, seafood canning operations and the mining and export of coal and minerals in the region have generated shoreline and watershed contaminant inputs in the region. Additionally, natural sources of pollution, particularly trace elements, may be associated with river runoff.

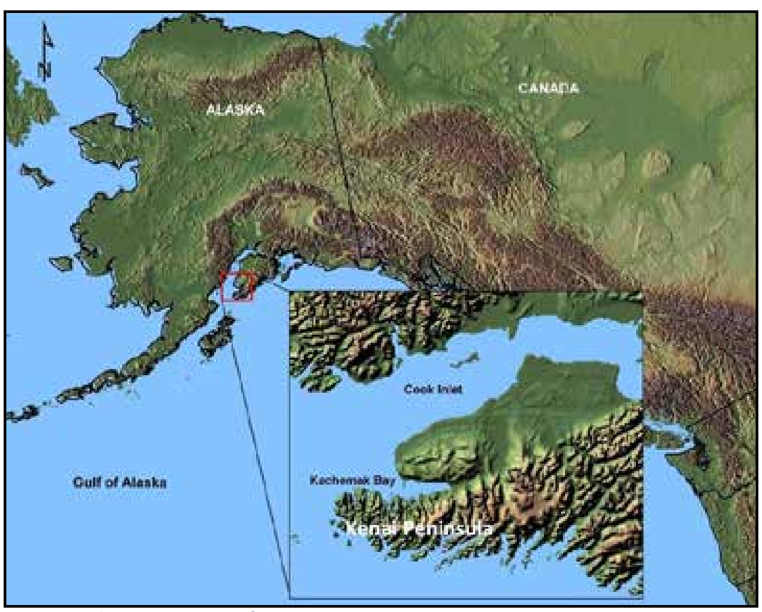


Figure 3. Location of Kenai Peninsula

The goal of this project was to assess chemistry, benthic community, and sediment toxicity in the embayments on the south side of Kachemak Bay and bays on the Kenai Peninsula, including an abandoned mining site. Clients for this work included: the North Pacific Research Board, the Cook Inlet Regional Citizens Advisory Council (CIRCAC) and the Alaska Department of Environmental Conservation (ADEC).

Where was the Study Site?

Kachemak Bay is a 64 km long glacial fjord on the east side of lower Cook Inlet located in south central Alaska. At the mouth between Anchor Point in the north and Point Pogibshi to the south, Kachemak Bay is nearly 40 km wide, but narrows to 10-11 km at Homer spit (Figure 3). The north shore of Kachemak Bay is characterized by extensive tidal flats below sandy bluffs with numerous coal seams. The south shore is bounded by the Kenai Peninsula, which has numerous smaller fjords and embayments cut into steep terrain that rises to glaciated valleys and uplifted mountain peaks. Inner Kachemak Bay has a relatively flat bottom and averages 46 m in depth.

The relatively flat watershed to the north lies in the Kenai Lowlands of the Cook Inlet Basin. In contrast, the south side on the Kenai Peninsula is characterized by steep mountains that rise 1,000-2,000 m. Runoff from the northern rivers is from spring and fall precipitation and spring snowmelt. Glacial meltwater carries a large sediment load of clay and silt, and this is what gives them their color and opacity. As glaciers melt in the summer, the freshwater drains into the Bay, altering salinity and possibly the circulation patterns. Glaciers can also cause flooding and large mudslides when ice dams that hold back lakes fail and release huge amounts of silt and water downstream.

The semi-diurnal tidal range in the inner bay is as high as 6 m. The tide and wind fuel the mixing of masses of fresh and saline waters in the inner bay that creates two counterclockwise tidal gyres that tend to deposit sediment in the northern portion of the bay (Burbank 1977). The Bay contains diverse habitats, such as exposed tidal flats, kelp beds, marshes and eelgrass beds, and a relatively deep zone in the middle of the bay. In addition to these habitats, the brackish and low current water makes the inner bay an excellent spawning ground and for several marine organisms (KBNERR 2001).

A nutrient rich estuarine environment sustains diverse marine wildlife of important economic value, such as shrimp, Dungeness crab, cockles, blue mussels, and clams (KBNERR 2001). The Bay supports significant subsistence and commercial fishery resources and it is considered as one of the most productive bays in the U.S., although stocks have been reported to be declining in recent years (Szarzi et al. 2007, ADF&G 1998). Commercial harvests of herring, coonstripe shrimp, and king, Dungeness, and Tanner crabs have been closed due to depressed stock (ADF&G 1998). Other studies point to impacts of natural changes and anthropogenic activities that cause pollution as the overriding causes of the depressed stock (Exxon Valdez Oil Spill Trustee Council 2002).

Who was involved?

Ian Hartwell (retired) was the principle NCCOS scientist on the project. Partners included the Alaska Department of Environmental Conservation and the University of Alaska Fairanks. NOAA's Kachemak Bay National Estuarine Research Reserve and NCCOS Kasitsna Bay Lab provided essential logistical support.

What did we do?

This study used the Sediment Quality Triad framework to assess the environmental status of the region. This method uses a preponderance of evidence approach and considers three quantitative components: sediment chemistry, sediment toxicity and benthic infaunal diversity/distribution. A stratified random sampling design was used to select sampling sites (see Figure 4). Fish and blue mussels were also collected for contaminant analysis at selected sites.

Surface sediments (top 2-3 cm) were collected at each site according to NS&T protocols (Apeti et al. 2012). Analytical chemistry was performed under NOAA contract by TDI Brooks (College Station, TX). Fish were collected via hook and line and kept frozen. Fish tissue analyses for metals was performed at the Alaska Department of Health Laboratory. Blue mussels were collected by hand via NS&T protocols and analyzed at TDI Brooks. A broad suite of sediment contaminants were analyzed at each station, including 51 PAHs, 25 aliphatics from C10-C34 plus pristane and phytane, 30 chlorinated pesticides, including DDT and its metabolites, 15 major and trace elements, and 54 polychlorinated biphenyls (PCBs). Other parameters included grain size analysis, total organic/inorganic carbon (TOC/TIC), and percent solids. Butyltins were analyzed in sediments collected in Seldovia Harbor.

Benthos samples were analyzed at a NOAA contract laboratory. Samples were quantified visually under dissecting microscope into major taxonomic groups (e.g. Polychaeta, Mollusca, and Arthropoda). The macroinvertebrates were then identified to the lowest practical identification level, which in most cases was to species level unless the specimen is a juvenile, damaged, or otherwise unidentifiable. The number of individuals of each taxon, excluding fragments was recorded. Abundance was calculated as the total number of individuals per square meter; taxa richness as the total number of taxa represented at a given site; and taxa diversity was calculated with the Shannon-Weiner Index.

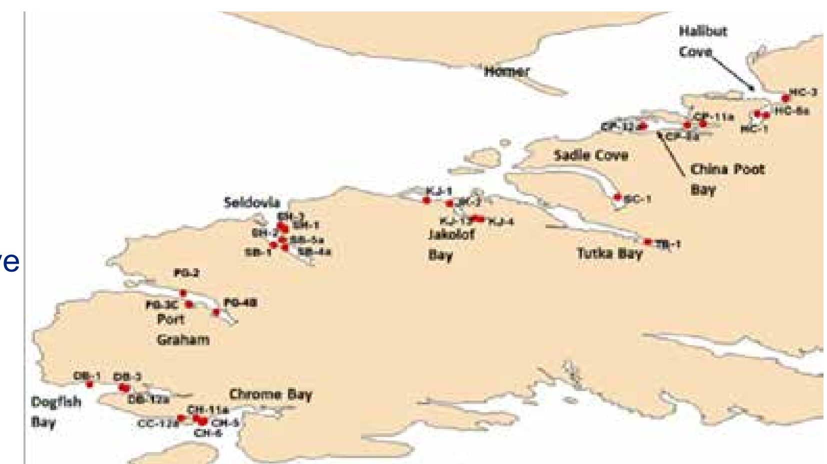


Figure 4. Sampling Sites

Sediment toxicity was assessed using amphipod mortality bioassays. These were carried out on the sediment samples collected at Chrome Bay only. All methods are based on standard techniques promulgated by ASTM (2004). The organisms are widely utilized test species with known ranges of sensitivity and their presence or absence in a particular habitat is not relevant because they are tested under standardized conditions. The amphipod Eohaustorius estuarius is found in shallow subtidal water along the Pacific coast. E. estuarius is a free burrowing deposit feeder found in medium-fine sand with some organic content. The tests were performed in accordance with a standard guide for conducting 10-day static sediment toxicity tests with amphipods (ASTM 2004), and additional guidance developed for testing four different amphipod species (U.S. EPA 1994). Briefly, amphipods were exposed to test and control sediments for 10 days under static conditions. The bioassays included 5 replicates, with 20 animals per replicate. The endpoints were mortality and failure to rebury.

Key Findings and Data Utility

Sediment concentrations of chromium and nickel were extremely high in Chrome Bay (Figure 5). Concentrations were several times higher than observed values seen throughout other locations in south-central Alaska. Other elemental concentrations varied between and within bays, with several locations exceeding sediment quality guidelines indicating possible toxicity. Concentrations of chlorinated pesticides, PAHs and PCBs were uniformly low, with the exception of Seldovia Harbor, where total DDT and PCBs exceeded sediment quality guidelines. Characteristics of the PAH compounds present indicate large contributions of pyrogenic sources (burned fuel and/or other organic matter). Body burdens of three species of fish captured in Chrome Bay did not exhibit elevated concentrations of metals relative to other studies in Kachemak Bay or the Alaska Dept. of Environmental Conservation, Fish Monitoring Program. Despite the very high concentrations of Cr and Ni in the sediments, the metals do not appear to be bioavailable to resident biota.

Whole sediment amphipod toxicity bioassays were conducted with sediments from Chrome Bay. No sample exhibited significant mortality or sub-lethal effects. Infaunal assemblages were highly variable. More than 280 taxa were enumerated throughout the study area. Sadie Cove lacked a variety of benthic species, with only 4 taxa and 15 organisms. This is likely due to hypoxic stress resulting from water circulation being impeded by glacial moraines.

These data will be used to the state of Alaska for coastal management purposes. These data shows some hotspots for PAHs, DDT and metals that would be useful to consider from both an ecological and human health (subsidence fishing) perspective. Since Kachemak Bay lies between Cook Inlet and Prince William Sound oil operations traffic, its deep water anchorage is being proposed as one of several repair sites and safe refuges for distressed and disabled vessels (ADEC 2006). The risk of using the Bay as shelter for vessels would be pollution from oil leaks and release of other hazardous substance that can impact marine resources. The Bay was impacted by the Exxon Valdez Oil Spill (EVOS) of 1989. Fourteen days after the spill, the oil slick travelled westward then northward through the Kennedy Entrance to cover part of the lower Cook Inlet and Kenai Peninsula (www.evostc.state.ak.us/History/PWSmap.cfm). Kachemak Bay, being

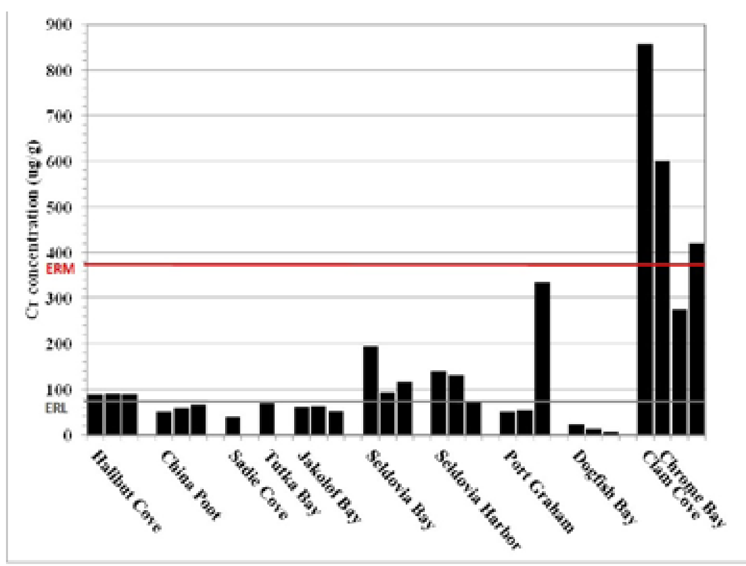


Figure 5. Sediment chromium concentrations (µg/g).

further removed from the spill epicenter in Prince William Sound, suffered relatively minimal ecological damages (Kuletz 1994), which nevertheless injured marine and coastal resources. It is anticipated that results of this study will serve as baseline data for unforeseen events and future reference.

Data Availability (where to find manuscript, where to find data)

This work is published as a NOAA Tech Memo and can be accessed via the link below

https://coastalscience.noaa.gov/data_reports/characterization-benthic-habitats-contaminant-assessment-kenai-peninsula-fjords-bays/

Different components of this work are also published as the following journal articles:

Hartwell, S. Ian, Doug Dasher, and Terri Lomax. "Characterization of metal/metalloid concentrations in fjords and bays on the Kenai Peninsula, Alaska." Environmental monitoring and assessment 191.5 (2019): 264.

Hartwell, S. Ian, Doug Dasher, and Terri Lomax. "Characterization of organic contaminants in fjords and bays on the Kenai Peninsula Alaska." Environmental monitoring and assessment 191.7 (2019): 427.

Case Study #3: An Integrated Assessment of Oil and Gas Release into the Marine Environment at the Former Taylor Energy MC20 Site (Gulf of Mexico)

Why Was This Study Done?

In 2004, the Taylor Energy Company's (TEC) Mississippi Canyon 20 (MC20) oil and gas drilling platform was toppled during Hurricane Ivan, a category 3 storm at the time. Severe wave action attributed to the storm triggered a subsea mudslide that toppled the TEC's Saratoga oil production platform A at Mississippi Canyon Block 20. The superstructure, also known as the jacket, came to rest on the ocean floor approximately 210 meters southeast of the original location. The collector bundle containing the original 28 well pipes was also dragged in the direction of the collapsed jacket, breaking and becoming buried by deposited sediment at the northwest corner of the final resting place of the structure (Figure 6).

After the collapse of the drilling platform and prior to the US Coast Guard's installation of a containment system in early 2019, the MC20 site was associated with persistent plumes of oil and gas and surface oil slicks. These slicks were visible on the ocean surface from ships and by aerial and satellite remote sensing and had been used as a means of measuring the output of hydrocarbons from the site. However, it was determined that these estimates needed to be compared to collections and measurements from within the water column, along with sediment collection for chemical analysis. Additionally, because vigorous and persistent gas plumes were observed at the site, we assessed the flux of hydrocarbon gas at the surface and into the atmosphere.

At the request of the Department of the Interior's Bureau of Safety and Environmental Enforcement (BSEE), NOAA's National Centers for Coastal Ocean Science (NCCOS), in cooperation with NOAA's Office of Response and Restoration, surveyed the MC20 site in September 2018 to determine the source, composition, and extent of the oil and gas discharge.

The Gulf of Mexico supports a highly diverse ecosystem and represents an important resource for commercial and recreational fishermen, tourism, and the oil and gas industry. When oil-related chemicals are released into the marine environment they can bioaccumulate in aquatic organisms. Many individual oil-related chemical compounds are toxic, with some being likely carcinogens.

The primary client for this work is the US Department of Interior's Bureau of Safety and Environmental Enforcement (BSEE) which also provided the funding. These data are being used as part of litigation against Taylor Energy for environmental damages, and will be used as part of the Natural Resource Damage Assessment (NRDA) at the MC20 site once litigation and final remediation of the site is completed.

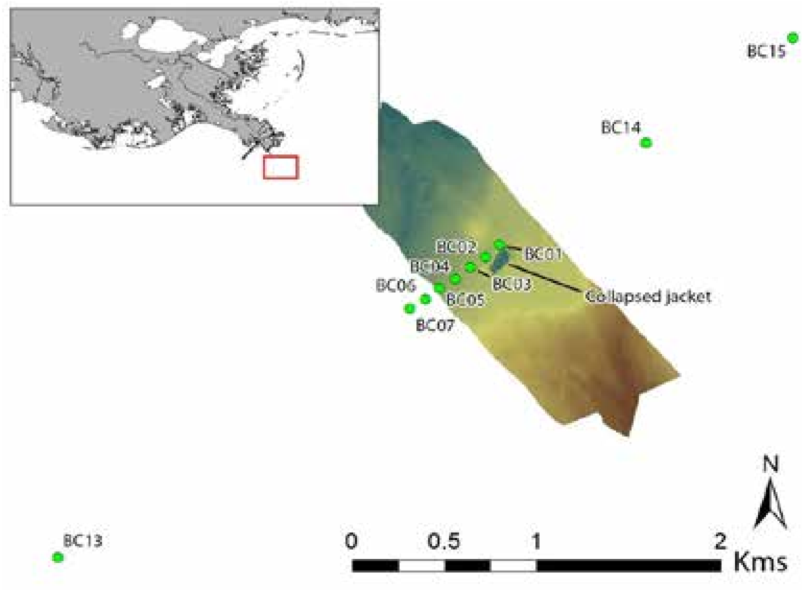


Figure 6. Location of MC20 study site and sampling sites.

Where was the Study Site?

The former TEC MC20 platform site is located in the northern Gulf of Mexico about 16 km southeast of the mouth of the South Pass of the Mississippi River. The fixed, 8-pile structure was installed in 1984 at a depth of 146 m and had 28 connected oil and gas wells reaching reservoirs as deep as 3.35 km. The study site included a transect of sediment samples up to 3 km away from the identified release point, located at the northwest corner of the toppled jacket structure. An erosional pit, excavated through ongoing release of oil and gas, sits at the center of the study site. Additional samples were collected from within the water column and from surface waters within the same 3 km boundary.

Who was involved?

The primary NCCOS scientists involved with the project were Andrew Mason (now with OR&R) and Chris Taylor (Marine Spatial Ecology Division). Partners included, NOAA's Office of Response and Restoration, Florida State University, Florida International University, and TDI Brooks International.

What did we do?

NCCOS scientists and partners conducted a series of integrated surveys from September 1–7, 2018 at the former Taylor Energy MC20 site. These surveys included surface and subsurface acoustic measurements; mid-water column oil, gas, and water collections; surface water sample collections; mid-water column video bubble collections; surface methane collections; and marine sediment collections. We also collected ancillary physical water column data, including ocean current profiles, and conductivity, temperature, and depth. Detailed methodology for each of these techniques is detailed in Mason et al. 2019. This case study will focus the work that MAB led, specifically the PAH chemistry.

Separate sampling strategies were developed for each individual matrix (water, gas, oil, and sediment) in accordance with establish National Status and Trends (NS&T) program protocols. For surficial sediment collection efforts, a targeted transect

Table 4. Site locations of the sediment samples.

Site	Date	Latitude	Longitude	Depth (m)	Distance from release (m)
BC01	9/7/18 5:29	N28 56.2560	W088 58.1714	135.42	27.9
BC02	9/7/18 4:58	N28 56.2176	W088 58.2181	134.55	99.8
BC03	9/7/18 4:27	N28 56.1842	W088 58.2685	134.13	203.2
BC04	9/7/18 4:04	N28 56.1477	W088 58.3158	133.92	304.4
BC05	9/7/18 3:44	N28 56.1174	W088 58.3690	132.34	406.9
BC06	9/7/18 3:15	N28 56.0843	W088 58.4159	131.86	505.7
BC07	9/7/18 2:54	N28 56.0524	W088 58.4664	128.66	604.8
BC13	9/6/18 4:02	N28 55.2625	W088 59.6240	133.69	2,990.2
BC14	9/7/18 6:08	N28 56.5811	W088 57.6889	129.57	995.9
BC15	9/7/18 6:47	N28 56.9134	W088 57.2063	133.73	2,006.8

design was selected to allow for the characterization of oil-related chemical contamination as it relates to distance from the northwest corner of the downed jacket. Ten samples were collected for chemical analysis. Samples were collected starting at a reference site 2,990.2 m (BC13) from the northwest corner of the jacket along a heading of approximately 60°. Distance between sampling locations were targeted at 100 m intervals until approximately 1 km distance from the northwest corner of the jacket was reached (Figure 6). Two additional targeted reference sites were collected on the opposite side of the collapsed jacket on a heading of 60° at 1 and 2 km. Sediment samples were collected using a 27 L box corer from September 5 through 7, 2018.

Prior to each sampling effort the box core sampling device and attached weights and frame were cleaned using soap/water and scrub brushes. Additionally, the interior of the box core was cleaned using alcohol wipes prior to deployment following methods developed by Pisarski et al. (2018). Chemistry samples were collected from the top 5 cm of collected sediment using a pre-cleaned stainless steel scoop. Sediment grain size samples were also collected from the top 5 cm of the box core. Samples were placed into certified pre-cleaned 250 mL iChem glass jars, sealed, labelled, and immediately frozen (-40° C). Grain size samples were placed into Whirl-pakTM samples bags, labelled, and immediately refrigerated (~3° C).

Surface water samples were collected from within visible surface sheen near where oil was observed to be reaching the ocean surface using a stainless steel bucket lowered over the side of the ship. The bucket was thoroughly pre-cleaned using soap and water then wiped down using alcohol wipes following methods developed by Pisarski et al. (2018). Once on deck, certified pre-cleaned 1 L amber jars were filled from the sample bucket surface water until full. Sample jars were sealed, labelled, and immediately refrigerated (~3° C).

Subsurface water, oil, and gas samples were all collected via specialized equipment attached to the bubblometer chamber described in Mason et al. 2019. All gas samples were labelled and frozen (-40° C) immediately after being collected.

Collection of the oil and water mixture were stored in certified pre-cleaned iChem 250 mL jar. The jars containing sample were immediately sealed, labelled, and refrigerated at ~3° C. Once these samples reached the laboratory the oil fraction was separated from the water fraction to allow for individual analysis. Due to budget constraints, more samples were collected than were analyzed. A total of six individual oil and water mixture were collected; only one was analyzed.

In between ROV deployments, an individual cylinder and its related fittings and valves were rinsed twice with Dichloromethane solvent to remove any residual contamination from the previous sampling effort. All related fittings and the bubblometer chamber, inverted funnel, and sample collection graduated cylinder were also rigorously cleaned with a combination of soap, water, scrub brushes, and alcohol wipes (Pisarski et al. 2018) between sample deployment efforts.

All samples were cataloged and Chain-of-Custody (CoC) maintained throughout the sample collection and delivery process to the laboratory. Samples were hand carried in signed and sealed coolers on blue ice and arrived at the laboratory in good condition.

Physical characteristics of the water column including temperature, salinity, and dissolved oxygen were all measured as part of each ROV dive. A Seabird SBE 19 Plus conductivity, temperature, depth (CTD) probe was mounted on the ROV sled and recorded data every 0.25 seconds.

All laboratory analysis were performed using protocols from the NS&T Program by TDI-Brooks International or its subcontractor GeoMark Research, which provided additional biomarker analysis for sediment and oil samples. GeoMark Research did not report concentrations of individual biomarkers but determined diagnostic ratios among them allowing for comparisons to one another and to a large proprietary database of Gulf of Mexico crude oils. The 64 polycyclic aromatic hydrocarbons (PAHs), sulfur-containing aromatics, as well as decalins and 27 individual alkyl-PAH isomers and selected terpanes and triaromatic steroids were analyzed using gas chromatography/mass spectrometry in selected ion monitoring mode. The 37 saturated hydrocarbons were analyzed by gas chromatography/flame ionization detection. Additional detailed descriptions of NS&T protocols, including quality assurance/quality control (QA/QC) used for these analysis can be found in Kimbrough et. al. (2006).

NOAA numerical sediment quality guidelines (SQG) developed by Long and Morgan (1990) and Long et al. (1995), known as Effects Range-Median (ERM), and Effects Range-Low (ERL), each express statistically derived contamination levels above which toxic effects can be expected. These toxic effects are described as occurring at least 50% frequency (ERM) or less than 10% (ERL) where effects are rarely expected. The ratio of the ERM value to the sediment concentration for each chemical, or sum of chemicals such as total PAHs, is called the ERM quotient or ERMq (Long et al., 1998). This quotient expresses how close measured concentrations are to the established ERM level on a zero to one scale. A quotient of one or greater means the concentrations are at or above the ERM. This also normalizes the ERMs for different chemicals to a common scale. By averaging the mean ERMq of contaminants it is possible to express a measure of contamination across the entirety of all analytes. Previous studies by Hyland et al. (1999) suggest that mean ERMq values of 0.1 in southeast US coastal waters represent a threshold above which degradation in benthic communities start appearing. The mean quotient of the ERMs and contaminant concentrations have been calculated on a site by site basis.

Key Findings and Data Utility

Total Polycyclic Aromatic Hydrocarbons (PAH), Total Petroleum Hydrocarbons (TPH), biomarker Hydrocarbons (HC), and total n-alkanes in sediments all rapidly decrease as distance from the northwest corner of the collapsed jacket and the identified release point increases. The highest concentrations of total PAHs, TPHs, HCs, and total n-alkanes were also consistently at concentrations at least an order of magnitude higher at the perimeter of the erosional pit than in the surrounding area. Beyond 500 m there is no measurable level of MC20 oil in the sediments. TPH in sediments has an inverse relationship to distance from the release point (TPH increases and distance decreases; logNormal distribution - $F > 0.0283$).

Concentrations of oil in sediments at MC20 are higher than those measured by MMS (Continental Shelf Associates, Inc., 2006) adjacent to other Gulf of Mexico drill sites, likely owing to the excess of oil released due to both the original accident and the ongoing release, greater proximity to other sources on the shelf (compared to MMS study sites), and greater proximity to Mississippi River effluent's influence on shelf sediments. The concentrations of total PAHs in sediments around the MC20 site are also an order of magnitude higher than all but one of the sediment sites measured by NOAA's Mussel Watch Program along the nearby Louisiana coastline. Full characterization of the distribution of oil related contaminants in sediments at the MC20 site will require future sampling efforts.

Looking at the percent weight of total for saturated hydrocarbons, the MC20 oil along with WAT01, WAT08A, and WAT11A we observe a progressive loss of n-alkanes in the n-C9 through n-C14 range and a resultant increase (as a percent of the total) in the degradation resistant acyclic isoprenoids pristane and phytane (Figure 7). This loss is indicative of weathering from evaporation, and photolysis. The variability among water column oil (WAT05) and water column water (WAT01) indicates that the oil being released from the seafloor is not homogeneously weathered and may potentially vary in the short-term. This heterogeneity in weathering is also accompanied by heterogeneity in the specific biomarkers of the emanating oil. Taken together, this collective heterogeneity is evidence that there is more than one leaking oil well with multiple oils entering the marine environment at depth and commingling to various degrees under different physical ocean current and surface conditions. Adding to the conclusion of ongoing release from multiple leaking wells at the MC20 site is the data from two original wells (three reservoirs sampled

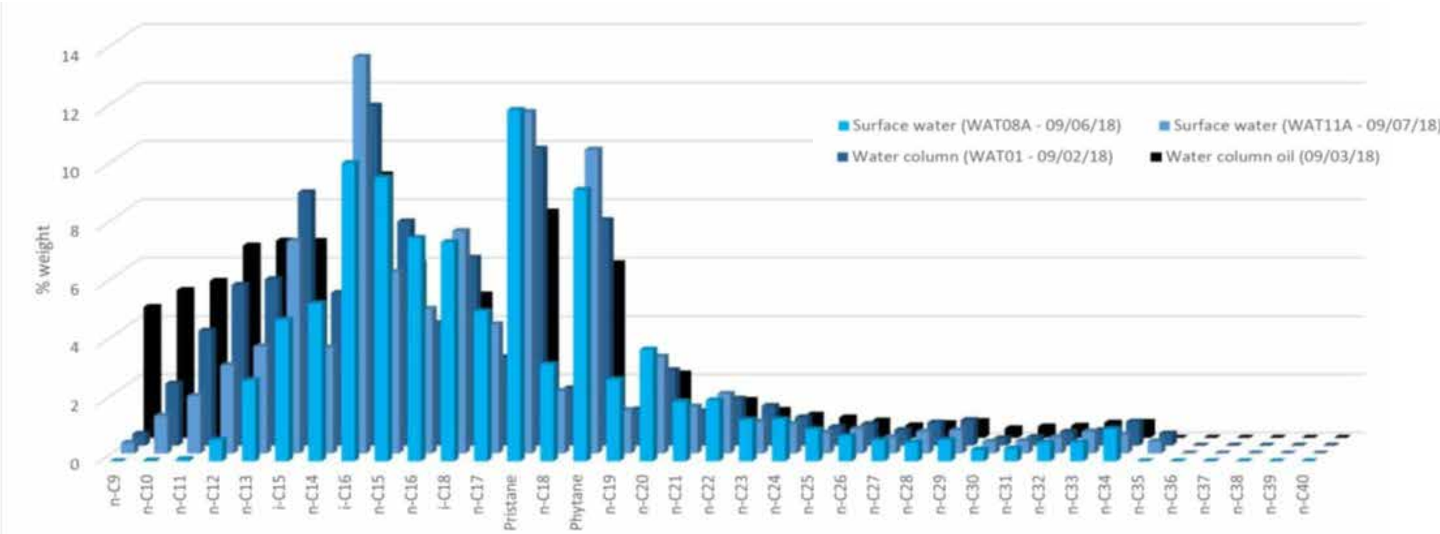


Figure 7. Comparison of subsurface collected oil, subsurface collected water, and surface water by percent weight of total n-alkanes.

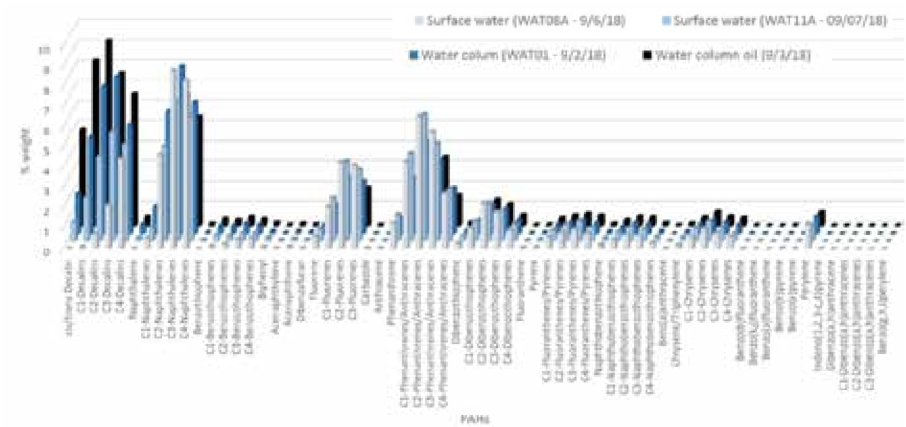


Figure 8. Comparison of subsurface collected oil, subsurface collected water, and surface water by percent weight of total Polycyclic Aromatic Hydrocarbons (PAHs) including decalins.

at the time of well exploration) analyzed by GERG in 1985. The fact that oil from the GERG sample labelled Well #9 is degraded in the reservoir along with the variability between the oils from Wells #9 and #2 all help to explain why we continue to see heterogeneous degraded oil continuing to be released into the marine environment. It is therefore not surprising that subtle heterogeneities are observed in this and other datasets.

Similar results were observed in the lighter Low Molecular Weight (LMW) PAHs, especially in the decalins and naphthalene, where we observe progressive losses and a resultant increase (as a percent of the total) in the relatively heavier LMW PAHs including fluorenes and phenanthrene/ anthracenes (Figure 8) due to evaporation at the surface. Subtleties between surface water samples and mid-water column collected oil again point toward heterogeneities in the multiple MC20 oils being released from the ocean floor.

By comparing TPH, saturated hydrocarbons, and PAH data for all three matrices (MC20 subsurface oil, erosional pit sediment (BC01), subsurface water (WAT01), and surface water (WAT11A)) we can further try to understand the source and fate of the oil entering the environment. The severely degraded nature of the saturated hydrocarbons in sediments within and proximal to the erosional pit precludes them from being the primary source of the mildly degraded MC20 oil collected and measured in the water column. The similarity between the subsurface collected MC20 oil, subsurface collected water, and surface water samples also point towards a primary source other than the sediment. The oil escaping the seafloor from the identified release point(s) is less weathered than oil residues in the surrounding sediments.

With the location of the erosional pit residing above the terminal end of the damaged conductor bundle, along with the finding that oil in the water column is only mildly degraded as compared to the heavily degraded sediment oils (Figure 9), we conclude that oil continues to be actively released into the marine environment. Because the conductor bundle terminus is buried under approximately 20 m of deposited sediment from the original mud slide, any released oil and gas must travel through that sediment before reaching the ocean floor. That distance would most likely include channelization and varying residence times for oil as different fractions partition into the adjacent sediment, are resuspended by upward motion of both oil and gas, or pass through relatively unimpeded. The fact that we find relatively little long chain n-alkanes as a percent of total weight in the subsurface collected oil, subsurface water, and surface water and find those fractions in the sediments points toward rapid partitioning out of the heavier fractions once the water column is reached, if not partially before, and precipitation of these fractions onto the nearby ocean floor sediments. Additionally, biodegradation of oil as it passes through the top 1-2 m of sediment is possible (Wenger and Isaksen, 2002) and could further explain some of the mild degradation of mid-water column collected MC20 oil.

The simplest explanation for the degradation observed in mid-water column oil at the MC20 site comes from the original 1985 oil data analyzed by GERG for what was labelled Well #9, where the oil in the reservoir is degraded. While we cannot say whether any of the oil collected mid-water column for this study is from either of the wells sampled by GERG in 1985, the fact that at least one of the

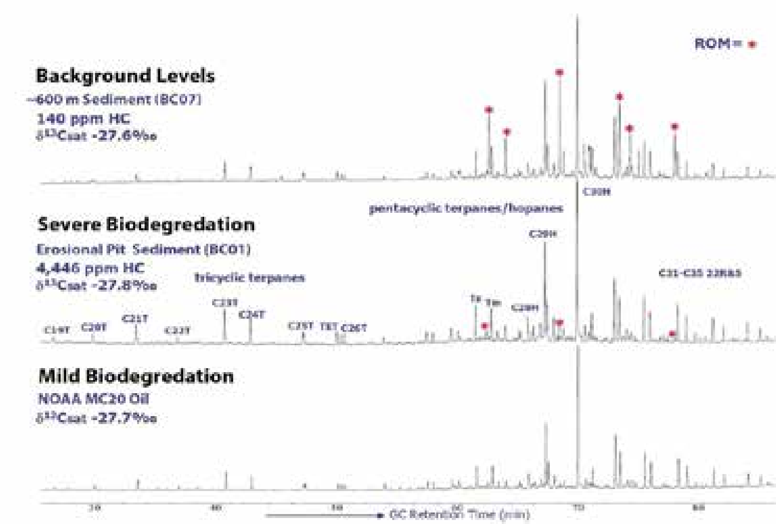


Figure 9. Saturated petroleum biomarker comparison between NOAA MC20 sediments (BC01 and BC07) and oil (subsurface collected via ROV). ROM = Recent Organic Material.

reservoirs at MC20 contained in-reservoir degraded oil points toward the possibility that other wells at MC20 may also have exhibited similar properties.

Taken together, results from this analysis of oil related compounds in the water column, sediments, and surface slick all point toward continued release of MC20 oil from multiple Pliocene oil reservoirs.

Overall, this assessment advanced NCCOS's ability to measure oil flow rates, using a new, innovative application of acoustic technology, and the creation of a new device to estimate the flow rate of oil being released from the wells. Further research could add to our understanding of this system, including:

- Full sediment chemistry survey to determine extent and distribution of oil related contaminants in the area (expand on single transect from 2018)
- Sediment toxicity analysis and benthic infaunal community analysis (indicator of effects of oil on biota)
- ROV mounted mid water column sampling for microbial community analysis

After all well intervention and remediation actions were completed (2011) and prior to September of 2018, the USCG had been provided multiple estimates about the amount of oil being released at the MC20 site, ranging from roughly 3-5 gallons per day up to over 900 barrels of oil per day. This lack of consensus between studies commissioned by the Responsible Party (RP) and independent entities (e.g. SkyTruth) had prevented USCG from ordering containment at the site. The results from our study, both from the initial gas chemistry and ROV video, all pointed toward a significant, reservoir sourced ongoing release of both oil and gas at the site. These initial results were presented to the Federal partners involved in the response at the end of September 2018 (including the DOJ, BSEE, USCG, and NOAA's OR&R), and while we presented no conclusions on the amount of oil being released at that briefing, the video and acoustic backscatter provided enough visual evidence of significant release, and the initial gas chemistry results of reservoir sourced gas, provided the USCG enough additional evidence for the Federal On Scene Coordinator (FOSC) to issue an order for containment a few days after our initial mission report.

Data Availability (where to find manuscript, where to find data)

This work was published as NCCOS Technical Memorandum #260 which can be accessed here:

https://repository.library.noaa.gov/view/noaa/20612

The full reference is:

Mason, A.L., J.C. Taylor, and I.R. MacDonald (eds.). 2019. An Integrated Assessment of Oil and Gas Release into the Marine Environment at the Former Taylor Energy MC20 Site. NOAA National Ocean Service, National Centers for Coastal Ocean Science. NOAA Technical Memorandum 260. Silver Spring, MD. 147 pp. doi: 10.25923/kykm-sn39

Case Study #4: Cocos Island, Guam: Passive water sampling to inform restoration efforts

Why Was This Study Done?

Previous studies on and around Cocos Island (Guam) found elevated levels of several contaminant classes including polychlorinated biphenyls (PCBs) in the soils, and in marine fish (Environet, 2005; Element Environmental, 2008, 2013, 2014). The likely source of these chemicals was the US Coast Guard LORAN navigation station which operated on the island from 1944 to 1963. Over the years, typhoons caused significant damage to the station, and there are also anecdotal reports of some equipment, including electrical transformers, being dumped into the lagoon or buried on the island.

In 2006, a fish consumption advisory was put in place for all of Cocos Lagoon (Guam EPA, 2006). The advisory recommended that the community limit or avoid the consumption of fish caught in and around Cocos Lagoon. That advisory remains in place. In 2014, local resource managers reached out to MAB to request a survey of chemical contaminants present in Cocos Lagoon, including the area around Cocos Island. In May 2015, scientists from the Guam Environmental Protection Agency (Guam EPA) and NOAA's NCCOS, with funding from NOAA's Coral Reef Conservation Program (CRCP), conducted a project to characterize chemical contaminants in sediments and fish throughout Cocos Lagoon.

Results from the 2015 project indicated low levels of chemical contaminants in sediments. However, a number of fish collected from around Cocos Island had highly elevated levels of PCBs, along with the banned organochlorine insecticide DDT (dichlorodiphenyltrichloroethane) (Hartwell et al., 2017). Almost all of the fish collected from around Cocos Island had concentrations of PCBs and DDT above subsistence and even recreational fisher screening values established by the US Environmental Protection Agency (USEPA, 2000), indicating a potential public health concern, and the need for more intensive site-specific monitoring and/or further evaluation of the human health risk from the presence of these chemical contaminants in fish.

Sediments typically serve as a reservoir for chemical contaminants that accumulate in aquatic organisms, however, sediments may not be the only source or medium through which contaminants are accumulating in the fish in the waters around Cocos Island. Sediments collected during the May 2015 project were composed primarily of sand, and contained only low levels of PCBs and DDT. Sandy sediment generally have a lower affinity for accumulating organic contaminants.

A possibility discussed by project partners was that dissolved (i.e., in the water column) concentrations of contaminants, perhaps transported by groundwater or subsurface water from Cocos Island into nearshore waters, could be a source for their direct uptake in fish. These discussions led to the current project, funded by NOAA's CRCP, in which passive water samplers were deployed in the nearshore waters around Cocos Island. The goal was to assess whether PCBs and perhaps DDT were being transported in the dissolved phase, either as a result of surface water runoff that might occur after a rainfall event, or through some type of groundwater input from Cocos Island, that could subsequently be taken up by fish and other marine organisms from the water column.

Where was the Study Site?

Located in the western Pacific Ocean and the most southerly and largest (both in area and population) member of the Mariana Islands, Guam has a land area of approximately 550 square kilometers, and a maximum altitude of 405 meters (Emery, 1962). At the southern tip of Guam is Cocos Lagoon (Figure 10), an atoll-like coral reef lagoon, which is triangular in shape. It is approximately 8.9 km long on the south side, and 4.4 km at its widest point and is separated from the open ocean by a series of fringing reefs and barrier islands, of which Cocos Island is the largest (Figure 11). Cocos Lagoon is an important area for subsistence fishing, and a popular area for recreational activities including fishing, boating and diving. The lagoon is fairly shallow, with an average depth of approximately 2 meters.

Figure 11. Cocos lagoon map.

Who was involved?

Figure 10. Cocos Lagoon location map.

NCCOS partnered closely with Guam EPA, USEPA and the US Coast Guard for project planning and implementation. Additionally, NOAA's Pacific Islands Fisheries Science Center provided logistical support in sample transport from Guam to the laboratory. Funding was provided by NOAA's Coral Reef Conservation Program and NCCOS. NCCOS personnel involved in the project included: Tony Pait, Andrew Mason (now with OR&R), Ian Hartwell (retired) and Dennis Apeti.

What did we do?

Because many organic chemical contaminants have a low solubility in water, traditional grab sampling often requires very large volumes of water in order to collect detectable quantities. In recent years, passive (in situ) water samplers have gained widespread use as an alternative for detecting chemical contaminants in the aquatic environment. Passive water samplers work by allowing chemicals to accumulate on a specialized material over a period of time. This material is then extracted in the laboratory for chemical analysis. In addition to allowing for the detection of low levels of contaminants, passive samplers also integrate the sample over time. This avoids a common problem with traditional grab samples, which do not capture short term (e.g. tidal) fluctuations in water concentrations. A variety of passive waters samplers exist including, SPMDs, or semi-permeable membrane devices, and POCIS (Polar Organic Chemical Integrated Sampler, Alvarez 2010).

More recently, polymers including silicone, polyoxymethylene, and polyethylene have been used (Lohmann, 2012) by attaching a polymer sheet to some of type of rigid frame and then suspended in water and/or sediment. One advantage of using these polyethylene devices (PEDs) is cost. The polyethylene used in passive water samplers is relatively inexpensive, and is frequently constructed of the same material sold as plastic drop cloths in hardware stores (Burgess, 2012). The PEDs deployed around Cocos Island were provided by project partners at the USEPA.

Conversations with project partners, including Guam EPA, USEPA, and USCG, resulted in the identification of 26 sites around Cocos Island (Figure 12). The USCG requested two sites be established just below the high water mark as well, along the beach close to the site of the former LORAN station. The PEDs at Sites 9-1 and 9-2 were buried in the sand and the location of these can also be seen in Figure 12. Prior to deployment the PED devices were kept frozen. Once on site, PEDS were anchored to rebar. Two PEDs were deployed at each site. Water depths where the PEDs were deployed ranged from 0.3 to 2.4 meters. The insertion of the PEDs into the sediment at three sites (9-1, 9-2, and 4-3 #035), was done in order to assess the movement of subsurface or groundwater adjacent to Cocos Island (Site 9-1 and 9-2) or further out (Site 4-3 #035), possibly carrying dissolved chemical contaminants.

The retrieval of the PEDs was done by Guam EPA. The retrieval occurred between 27 and 30 October 2017. Wearing nitrile gloves, each PED was cut out of the frame, any biofouling was wiped off, and then the PED was placed into a corresponding labeled jar. The jars were then placed in a cooler on ice while in the field, and then placed in a freezer at Guam EPA. The PEDs that had been deployed at site 8-2 were not found during retrieval. More information on field methodology is available in Pait et al. 2019.

PEDs were extracted and analyzed at the NCCOS contract laboratory (TDI Brooks, College Station, TX). Organic analyses were conducted using gas chromatography/mass spectrometry or gas chromatography/electron capture. Detailed descriptions of NOAA's National Status and Trends (NS&T) protocols, including quality assurance/quality control (QA/QC) used in the analysis of the organic contaminants, can be found in Kimbrough et al. (2006).

The PEDs were analyzed for a suite of 171 organic contaminants by TDI-Brooks, using protocols established by the NS&T Program. The PEDs were analyzed for hydrocarbons, organochlorine pesticides, and for PCBs. No metals were analyzed, as the PEDs are not efficient at accumulating metals.

Key Findings and Data Utility

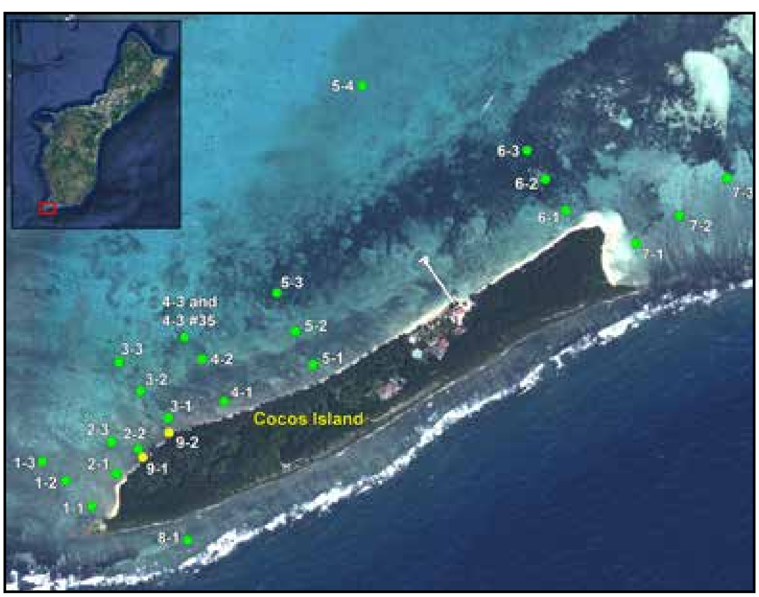
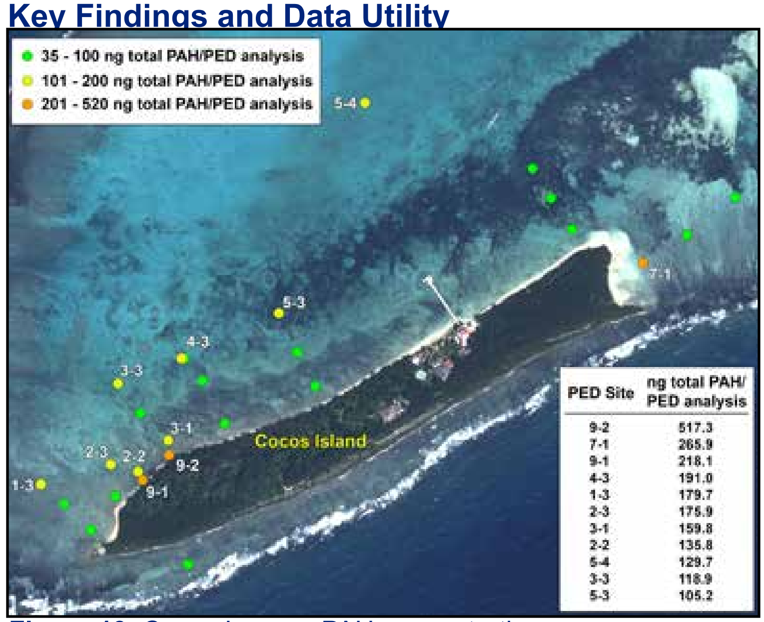


Figure 12. Cocos lagoon site map.



PED Site	ng total PAH/ PED analysis
9-2	517.3
7-1	265.9
9-1	218.1
4-3	191.0
1-3	179.7
2-3	175.9
3-1	159.8
2-2	135.8
5-4	129.7
3-3	118.9
5-3	105.2

Figure 13. Cocos Lagoon PAH concentrations.

PAHs were the most commonly identified contaminant on the PEDs in Cocos Lagoon (Figure 13). This is likely due to boat traffic in the area. The distribution of total DDT and total PCBs was limited spatially. Total DDT was only detected at a few very nearshore areas. Total PCBs were even more spatially limited with only three sites having total PCB detections. Two of these, however, were on the PEDs buried in the sand near the former LORAN station. These results are somewhat surprising in that the fish analyzed by Hartwell et al. (2017) found to have elevated levels of total DDT and total PCBs, were collected near the former LORAN station site and feed on invertebrates and algae in nearshore waters. It is possible that accumulation of DDT and PCBs through the food chain, or exposure/uptake through sediment porewater explains the relatively high levels in fish without observing similarly high levels in the sediment or water.

From the current work and the recent investigation by Hartwell et al. (2017), it appears that contaminants like DDT and PCBs are still present in the nearshore waters around Cocos Island, including fish. Previous remediation work included the removal of approximately 380 cubic yards of soil from the island in 2007. Additional work to try to pinpoint where the remaining contaminants are coming from may be useful. One possibility that has been discussed among project partners is the installation of piezometers (i.e., shallow wells) around the former location of the LORAN station, followed by installation of PEDs, to assess if the contaminants may be concentrated in one part of the former site. It may also be useful to place piezometers, perhaps in an array towards the water, to see if a gradient of dissolved concentrations of contaminants is present, and if so, if the higher concentrations are limited to a particular area that may be related to past land use activities or groundwater/subsurface flow, or if it is more diffuse, covering a larger area. This type of information would be important to resource managers in deciding how to follow up with any restoration activities such as the removal of additional soil from the island, to ultimately reduce the amount of contaminants like PCBs and DDT going into Cocos Lagoon.

Data Availability (where to find manuscript, where to find data)

This work was published as NCCOS Technical Memorandum #261 which can be accessed here:

https://repository.library.noaa.gov/view/noaa/17261

The full citation is:

Pait, A.S., A.L. Mason, S.I. Hartwell, and D.A. Apeti. 2019. An Assessment of Chemical Contaminants in the Waters Around Cocos Island, Guam Using Polyethylene Passive Water Samplers. NOAA Technical Memorandum NOS NCCOS 261. Silver Spring, MD. 43 pp. doi:10.25923/0bvz-p335

The data has been archived at NOAA's National Centers for Environmental Information and is can be accessed here:

https://data.nodc.noaa.gov/cgi-bin/iso?id=gov.noaa.nodc:0184259

Case Study #5: Novel In Situ Sampling Technology to Quantify Land Based Stressors in the National Marine Sanctuary of American Samoa

Why Was This Study Done?

There is currently minimal data describing the level of contamination in Fagatele Bay, a unit of the National Marine Sanctuary of American Samoa. Resource managers have significant concerns about the potential inputs of contaminants from a landfill in close proximity to the Bay. Leachate from the landfill may include both organic (e.g. PCBs, personal care products) and inorganic (e.g. heavy metals) pollutants, and could reach the Bay through groundwater or surface runoff. There is also potential for other sources of land-based sources of pollution (LBSP, such as pesticides) being transported to the Bay.

The treatment of solid waste is a serious problem on most islands because leakage of toxic substances due to inappropriate waste disposal can negatively impact the environment. It had not been previously quantified if the landfill above Fagatele Bay reduces the water quality in the Bay through leakage of pollutants. The National Marine Sanctuary of American Samoa requested that NCCOS take on this important research question, i.e. what contaminants are present in Fagatele Bay? This assessment is important for two reasons: 1) to assess the extent to which pollution in the Bay is a problem; and 2) to serve as baseline to evaluate the effectiveness of future watershed management activities which might be designed to improve coral reef ecosystem health by LBSP.

Figure 14. Fagatele Bay location map.

Where Was the Study Site?

Fagatele Bay is located on the south shore of the island of Tutuila, the largest and most populous island of the U.S. territory of American Samoa (Figure 14). It is part of the NOAA managed National Marine Sanctuary of American Samoa. American Samoa's reefs are considered to be among the most pristine in the United States (Birkeland et al. 2008). These reefs host approximately 950 species of fish, 240 species of algae, 330 species of coral

Table 5a: Analytes quantified on CLAM filters. Note: not all of these compounds were detected. Please see Table 6.

Aldrin	HCH, gamma	PCB 6	PCB 76/70	PCB 134/133
alpha-Endosulphan	Heptachlor Epoxide	PCB 8/5	PCB 66/80	PCB 165/131
Atrazine	Hexazinone	PCB 14	PCB 55	PCB 142/146/161
beta-Endosulphan	Linuron	PCB 11	PCB 56	PCB 153/168
Chlordane, oxy-	Malathion	PCB 12	PCB 60	PCB 132
Desethylatrazine	Methoxychlor	PCB 13	PCB 79	PCB 141
Endrin Ketone	Metolachlor	PCB 15	PCB 78	PCB 137
HCH, beta	Metribuzin	PCB 19	PCB 81	PCB 130
Heptachlor	Nonachlor, cis-	PCB 30	PCB 77	PCB 138/164/163
Hexachlorobenzene	Nonachlor, trans-	PCB 18	PCB 104	PCB 160/158
Mirex	Octachlorostyrene	PCB 17	PCB 96/103	PCB 129
Simazine	Parathion-Ethyl	PCB 27	PCB 100	PCB 166
2,4'-DDD	Parathion-Methyl	PCB 24	PCB 94	PCB 159
2,4'-DDE	Pendimethalin	PCB 16/32	PCB 102/98	PCB 162
2,4'-DDT	Permethrin	PCB 34	PCB 121/93/95	PCB 128/167
4,4'-DDD	Perthane	PCB 23	PCB 88	PCB 156
4,4'-DDE	Phorate	PCB 29	PCB 91	PCB 157
4,4'-DDT	Phosmet	PCB 26	PCB 92	PCB 169
Alachlor	Pirimiphos-Methyl	PCB 25	PCB 101/84/90	PCB 188
Ametryn	Quintozene	PCB 28/31	PCB 89/113	PCB 184
Azinphos-Methyl	Tebuconazol	PCB 21/20/33	PCB 99	PCB 179
Butralin	Tecnazene	PCB 22	PCB 119	PCB 176
Butylate	Terbufos	PCB 36	PCB 112	PCB 186/178
Captan	Triallate	PCB 39	PCB 120/83	PCB 175
Chlordane, alpha (cis)	Trifluralin	PCB 38	PCB 97/125/86	PCB 187/182
Chlordane, gamma (trans)	Endrin Aldehyde	PCB 35	PCB 116/117	PCB 183

and many other species of invertebrates (Birkeland et al. 2008). Fagatele Bay's reefs are considered to be in very good condition due to its relatively remote location (NMSP 2007). The Bay is roughly horseshoe shaped and is approximately 0.6 km wide at its widest point. The Bay's opening to the ocean faces the south-southwest. There is very little development in the watershed, with a handful of residences scattered across the landscape. The main potential source of pollution is the solid waste landfill, which is the only landfill on the island, and is unlined.

Who was Involved? (NCCOS staff and partners)

NCCOS partnered closely in study design and execution with the National Marine Sanctuary of American Samoa. Sanctuary staff participated in field work alongside NCCOS personnel. CRCP provided dive support, and additional logistical support was provided by American Samoa Community College and NOAA's Pacific Islands Fisheries Science Center. NCCOS staff involved were Dave Whitall (PI), Andrew Mason, Laura Webster and Cheryl Woodley. Dr. Michael Martinez-Colon (Florida A&M University) also collaborated on the project.

Table 5a continued: Analytes quantified on CLAM filters. Note: not all of these compounds were detected. Please see Table 6.

Chlorothalonil	Heptachlor-Epoxide	PCB 37	PCB 111/115/87	PCB 185
Chlorpyriphos	Oxychlordane	PCB 54	PCB 109	PCB 174
Chlorpyriphos-Methyl	Alpha-Chlordane	PCB 50	PCB 85	PCB 181
Chlorpyriphos-Oxon	Gamma-Chlordane	PCB 53	PCB 110	PCB 177
Cyanazine	Trans-Nonachlor	PCB 51	PCB 82	PCB 171
Cypermethrin	Cis-Nonachlor	PCB 45	PCB 124	PCB 173
Dacthal	Alpha-HCH	PCB 46/69/73	PCB 106/107	PCB 192/172
Diazinon	Beta-HCH	PCB 52	PCB 123	PCB 180/193
Diazinon-Oxon	Delta-HCH	PCB 43	PCB 118/108	PCB 191
Dieldrin	Gamma-HCH	PCB 49	PCB 114/122	PCB 170/190
Dimethenamid	DDMU	PCB 48/75/47	PCB 105/127	PCB 189
Dimethoate	1,2,3,4-Tetrachloro-benzene	PCB 65	PCB 126	PCB 202
Disulfoton	1,2,4,5-Tetrachloro-benzene	PCB 62	PCB 155	PCB 201
Disulfoton Sulfone	Pentachloroanisole	PCB 44	PCB 150	PCB 204
Endosulphan Sul-phate	Pentachlorobenzene	PCB 59	PCB 152	PCB 197
Endrin	Endosulfan II	PCB 42	PCB 148/145	PCB 200
Ethalfluralin	Endosulfan I	PCB 72	PCB 136/154	PCB 198
Ethion	Endosulfan Sulfate	PCB 71	PCB 151	PCB 199
Fenitrothion	Chlorpyrifos	PCB 68/41/64	PCB 135	PCB 203/196
Flufenacet	PCB 1	PCB 40/57	PCB 144	PCB 195
Flutriafol	PCB 2	PCB 67	PCB 147	PCB 194
Fonofos	PCB 3	PCB 58	PCB 149/139	PCB 205
HCH, alpha	PCB 4/10	PCB 63	PCB 140	PCB 208
HCH, delta	PCB 7/9	PCB 61/74	PCB 143	PCB 207

Table 5b: Analytes quantified on CLAM filters. Note: not all of these compounds were detected. Please see Table 6.

PCB 206	C1-Chrysenes	Norfloxacin	Trenbolone acetate
PCB 209	C2-Chrysenes	Norgestimate	Valsartan
cis/trans Decalin	C3-Chrysenes	Ofloxacin	Verapamil
C1-Decalins	C4-Chrysenes	Ormetoprim	Cocaine
C2-Decalins	Benzo(b)fluoranthene	Oxacillin	DEET
C3-Decalins	Benzo(k,j)fluoranthene	Oxolinic Acid	Prednisolone
C4-Decalins	Benzo(a)fluoranthene	Penicillin G	Diatrizoic acid
Naphthalene	Benzo(e)pyrene	Penicillin V	Iopamidol
C1-Naphthalenes	Benzo(a)pyrene	Roxithromycin	Citalopram
C2-Naphthalenes	Perylene	Sarafloxacin	Tamoxifen
C3-Naphthalenes	Indeno(1,2,3-c,d)pyrene	Sulfachloropyridazine	Cyclophosphamide
C4-Naphthalenes	Dibenzo(a,h)anthracene	Sulfadiazine	Venlafaxine
Benzothiophene	C1-Dibenzo(a,h)anthracenes	Sulfadimethoxine	Amsacrine
C1-Benzothiophenes	C2-Dibenzo(a,h)anthracenes	Sulfamerazine	Azathioprine
C2-Benzothiophenes	C3-Dibenzo(a,h)anthracenes	Sulfamethazine	Busulfan
C3-Benzothiophenes	Benzo(g,h,i)perylene	Sulfamethizole	Clotrimazole
C4-Benzothiophenes	Bisphenol A	Sulfamethoxazole	Colchicine
Biphenyl	Furosemide	Sulfanilamide	Daunorubicin
Acenaphthylene	Gemfibrozil	Sulfathiazole	Doxorubicin
Acenaphthene	Glipizide	Thiabendazole	Drospirenone
Dibenzofuran	Glyburide	Trimethoprim	Etoposide
Fluorene	Hydrochlorothiazide	Tylosin	Medroxyprogesterone Acetate
C1-Fluorenes	2-Hydroxy-ibuprofen	Virginiamycin M1	Metronidazole
C2-Fluorenes	Ibuprofen	1,7-Dimethylxanthine	Moxifloxacin
C3-Fluorenes	Naproxen	Alprazolam	Oxazepam
Carbazole	Triclocarban	Amitriptyline	Rosuvastatin
Anthracene	Triclosan	Amlodipine	Teniposide
Phenanthrene	Warfarin	Benzoylecgonine	Zidovudine
C1-Phenanthrenes/Anthracenes	Acetaminophen	Benztropine	Melphalan
C2-Phenanthrenes/Anthracenes	Azithromycin	Betamethasone	Albuterol
C3-Phenanthrenes/Anthracenes	Caffeine	Desmethyldiltiazem	Atenolol
C4-Phenanthrenes/Anthracenes	Carbadox	Diazepam	Atorvastatin

What Did We Do?

Although sediments typically serve as a reservoir for chemical contaminants that can accumulate in aquatic organisms, very sandy sediments (such as those found in Fagatele Bay) are poor integrators of most pollutants. Furthermore, some water soluble compounds (e.g. current use pesticides, personal care products) do not accumulate in sediments due to their hydrophilic nature. Collecting grab samples of water also has its limitations, including difficulty in quantifying low (but environmentally relevant) concentrations, and temporal variability due to tides, currents and precipitation. As such, in situ water samplers can allow the concentrations of chemicals in the water column to be determined in a time integrated manner that will best answer the relevant research questions.

To assess the potential impact of the adjacent landfill on Fagatele Bay, an array of in situ water samplers known as Continuous Low-level Aquatic Monitoring (CLAMs) were deployed. The CLAMs pump a known volume of water across specialized membranes (HLB and C18) which trap the contaminants for subsequent analysis in the laboratory. The sites were selected in a targeted manner in order to roughly follow the shoreline of the Bay (Figure 15) so as to maximize the likelihood of capturing the groundwater signal coming from land. The CLAMs were deployed for 24 hours at a time in order to integrate the temporal variability in the system and not "miss" key events. In April 2019, CLAM units were deployed on the bottom (attached to rebar that had been driven into the pavement) at eight reef sites within the Bay. Each filter type (HLB vs C18) was deployed twice (two 24 hours periods) at each site and the like filters were composited for analysis so that there was one concentration value per site generated. Each value represented an integrated concentration value reflecting between 68 and 245 liters of water over that 48 hour period. CLAM filters were analyzed for over 400 organic contaminants (Table 5). Additionally, at each CLAMs site where there was

Table 5b continued: Analytes quantified on CLAM filters. Note: not all of these compounds were detected. Please see Table 6.

Dibenzothiophene	Carbamazepine	Fluocinonide	Cimetidine
C1-Dibenzothiophenes	Cefotaxime	Fluticasone propionate	Clonidine
C2-Dibenzothiophenes	Ciprofloxacin	Hydrocortisone	Codeine
C3-Dibenzothiophenes	Clarithromycin	10-hydroxy-amitriptyline	Enalapril
C4-Dibenzothiophenes	Clinafloxacin	Meprobamate	Hydrocodone
Fluoranthene	Cloxacillin	Methylprednisolone	Metformin
Pyrene	Dehydronifedipine	Metoprolol	Oxycodone
C1-Fluoranthenes/Pyrenes	Diphenhydramine	Norfluoxetine	Ranitidine
C2-Fluoranthenes/Pyrenes	Diltiazem	Norverapamil	Triamterene
C3-Fluoranthenes/Pyrenes	Digoxin	Paroxetine	Amphetamine
C4-Fluoranthenes/Pyrenes	Digoxigenin	Prednisone	Cotinine
Naphthobenzothiophene	Enrofloxacin	Promethazine	
C1-Naphthobenzothiophenes	Erythromycin-H2O	Propoxyphene	
C2-Naphthobenzothiophenes	Flumequine	Propranolol	
C3-Naphthobenzothiophenes	Fluoxetine	Sertraline	
C4-Naphthobenzothiophenes	Lincomycin	Simvastatin	
Benz(a)anthracene	Lomefloxacin	Theophylline	
Chrysene/Triphenylene	Miconazole	Trenbolone	

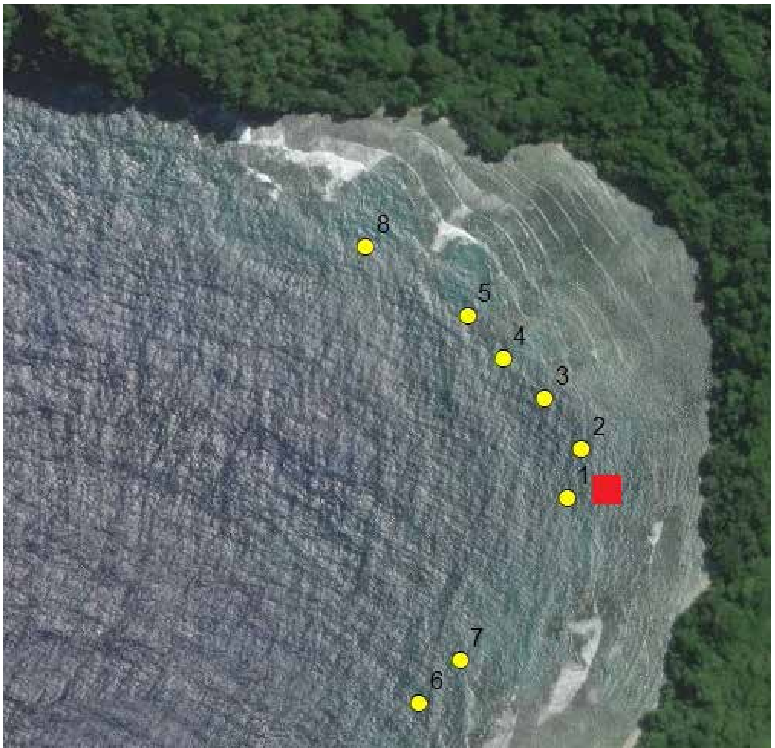


Figure 15. Fagatele Bay site map. Red square denotes a temperature anomaly at which additional water samples were collected.

sediment (sand) a small amount of material was collected for metals analysis because C18 and HLB filters do not capture metals. Grab samples for water column nutrient analysis were also collected at each site. Chemistry analyses were conducted under contract at TDI Brooks (College Station, TX) and SGS AXYS (Vancouver) laboratories. Additional water was collected for sea urchin toxicity analysis, and additional sediment for foraminifera diversity quantification. These two methods provide an assessment of biological impacts of potential pollutants in the Bay.

Key Findings and Data Utility

As of the publication of this briefing book, only a subset of the laboratory analyses of the field samples from this study have been completed. Preliminary data shows that the CLAM units were successful at sampling a variety of contaminants, especially current use pesticides, personal care products and pharmaceuticals, in very low (picogram per liter) concentrations. Table Z shows the contaminants which were detected and their maximum concentrations in the Bay. Many of these analytes do not have environmental guidelines/ threshold above which ecological harm is expected, but for those that have existing criteria (e.g. LC50s), concentrations observed in Fagatele are much lower than levels of concern. Even though these may be low concentrations, these data show that even in a relatively remote "pristine" system, a variety of waterborne contaminants have the potential to adversely affect ecosystem health.

These data will be used by the National Marine Sanctuary as part of the Sanctuary Assessment process. There are no other land based sources of pollution data available for the Fagatele Bay unit of the Sanctuary, so these data are critical to understanding the system.

Table 6a: Maximum observed concentrations for organic analytes detected via CLAM sampling in Fagatele Bay. Units are ng/L.

Analytes	Concentration
Aldrin	0.0005
alpha-Endosulphan	0.0094
Amphetamine	0.0993
Atrazine	0.0229
beta-Endosulphan	0.0044
Chlordane, oxy-	0.0082
Cocaine	0.0292
Cotinine	0.0107
DEET	0.1077
Desethylatrazine	0.0040
Endrin Ketone	0.0431
HCH, beta	0.0020
Heptachlor	0.0002
Hexachlorobenzene	0.0215
Mirex	0.0003
Prednisolone	0.4037
Simazine	0.0085

Data Availability

Once finalized the data will be served via NOAA's NCEI. The final interpreted data product, a technical memorandum, will be housed via NOAA's publications repository.

Table 6b: Maximum observed concentrations for organic analytes (hydrocarbons) detected via CLAM sampling in Fagatele Bay. Units are ng/L.

Compound	Max (ng/L)
cis/trans Decalin	5.78
C1-Decalins	2.49
C2-Decalins	2.52
C2-Fluorenes	14.49
C3-Fluorenes	21.40
Carbazole	2.05
C1-Phenanthrenes/ Anthracenes	17.11
C1-Dibenzothiophenes	40.33
C2-Dibenzothiophenes	14.33
C3-Dibenzothiophenes	21.71
C2-Naphthobenzothiophenes	47.89
Perylene	51.28
Benzo(g,h,i)perylene	7.48

Table 6c: Maximum observed concentrations for trace elements detected in the sediment in Fagatele Bay. Units are ug/L.

Analyte	Conc (ug/L)
Ag	0.0185
Al	4910
As	4.62
Cd	0.0185
Cr	55
Cu	6.4
Fe	8540
Hg	0.0043
Mn	144
Ni	69.6
Pb	0.994
Sb	0.0762
Se	0.139
Si	14500
Sn	0.212
Zn	11.6

Discussion and Conclusions

These case studies illustrate the breadth of both methodologies and geographies involved with the Monitoring and Assessment Branch's place based assessments. MAB, and its precursor organizations, has a 20+ year record of producing excellent environmental data that is useful to coastal managers. These data have been extensively published in the peer review journal literature, as well as via NOAA Technical Memoranda. End users of these types of data frequently seek out MAB for technical assistance which speaks to not only the utility of these types of data, but also to the reputation of MAB within the marine science community. In addition to the historical techniques which have been extensively utilized throughout the program history, MAB scientists are always working to incorporate new methods (e.g. "omics", dietary tracers, active in situ water samplers) to better address the data needs of coastal managers.

References

ADEC. 2006. Places of Refuge for the Cook Inlet Subarea. Alaska Dept. of Environmental Conservation, Division of Spill Prevention and Response. http://www.adec.state.ak.us/spar/perp/cookinletpor/index.htm

ADF&G. 1998. Final Environmental Impact Statement/Final Management Plan. Kachemak Bay National Estuarine Research Reserve. Online at www.habitat.adfg.state.ak.us.

Alvarez, D.A., 2010, Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies: U.S. Geological Survey, Techniques and Methods 1–D4, 28 p.

Apeti, D.A., W.E. Johnson, K.L. Kimbrough, and G.G. Lauenstein. 2012. National Status and Trends Mussel Watch Program: Sampling Methods 2012 Update. NOAA Technical Memorandum NOS NCCOS 134. Silver Spring, MD. 39 pp.

ASTM. 2004. Standard test method for measuring the toxicity of sediment-associated contaminants with estuarine and marine invertebrates. ASTM Standard Method No. EI 367-03e I. In: 2004 Annual Book of ASTM Standards, volume 11.05, Biological effects and environmental fate; biotechnology; pesticides. ASTM International, West Conshohocken, PA.

Birkeland C, Craig P, Fenner D, Smith L, Kiene W, Riegl B. 2008. Geologic setting and ecological functioning of coral reefs in American Samoa Coral Reefs of the USA. Springer, pp 741-765.

Burbank, D.C. 1977. Circulation studies in Kachemak Bay and lower Cook Inlet, Volume III of Environmental Studies of Kachemak Bay and lower Cook Inlet, Trasky et al. (eds.) Marine/Coastal Habitat Management Report, Alaska Department of Fish and Game. Anchorage, AK.

Burgess, R. M. 2012. Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-11/115.

Castro, M, Driscoll, C, Jordan, T, Reay, W, Boyton,W, Seitzinger, S, Styles, R, Cable, J. 2001. Contribution of atmospheric deposition to the total nitrogen loads to thirty-four estuaries on the Atlantic and Gulf Coasts of the United States. In: Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective, Volume 57, Valigura, R, Alexander, R, Castro, M, Meyers, T, Paerl, H, Stacey, P, Turner, E (editors).

Continental Shelf Associates, Inc. 2006. Effects of Oil and Gas Exploration and Development at Selected Continental Slope Sites in the Gulf of Mexico. Volume II: Technical Report. U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 2006-045. 636 pp.

D'Angelo, C, and Wiedenmann, J. 2014. Impacts of nutrient enrichment on coral reefs: New perspectives and implications for coastal management and reef survival. Current Opinion in Environmental Sustainability 7:82–93.

Element Environmental. 2008. Report: Follow-On Site Investigation Former LORAN Station Cocos Island, Cocos Island, Guam. Prepared for the US Coast Guard. Contract No. HSCG86-08-C-6XA607. 115pp.

Element Environmental. 2013. Final Report: Follow-On Environmental Site Investigation Former LORAN Station Cocos Island, Cocos Island, Guam. Prepared for the US Coast Guard. Contract No. HSCG86-12-N-PXA008. 242 pp.

Element Environmental. 2014. Final Report: Follow-On Environmental Site Investigation Former LORAN Station Cocos Island, Cocos Island, Guam. Prepared for the US Coast Guard. Contract No. HSCG86-14-N-PXA003. 289pp.

Emery, K.O. 1962. Marine Geology of Guam. Geological Survey Professional Paper 403-B. United States Department of the Interior, Geological Survey. 85pp.

Environet. 2005. Project Report: Environmental Investigation Former LORAN Station Cocos Island, Guam. Prepared for the US Coast Guard. 110pp.

Exxon Valdez Oil Spill Trustee council. 2002. Update on injured resources and services. Exxon Valdez Oil Spill Restoration Plan. Anchorage, Alaska.

Galloway J, Aber, J, Erisman, J, Seitzinger, S, Howarth, R, Cowling, E, Cosby B. 2003. The nitrogen cascade. BioScience 53: 341–356.

Guam Environmental Protection Agency (Guam EPA). 2006. Guam EPA, Public Health issue fish consumption advisory for Cocos Lagoon; preliminary results indicate PCBs in fish tissue. Accessed at: http://www.guamagentorange.info/yahoo_site_admin/assets/docs/EPA_Warning_Fish.153185612.pdf.

Harrison, P, Ward, S. 2001. Elevated levels of nitrogen and phosphorus reduce fertilisation success of gametes from scleractinian reef corals. Marine Biology 39:1057-1068.

Hartwell, S.I., D.A. Apeti, A.S. Pait, A.L. Mason, and C. Robinson. 2017. An Analysis of Chemical Contaminants in Sediments and Fish from Cocos Lagoon, Guam. NOAA Technical Memorandum NOS NCCOS 235. Silver Spring, MD. 74 pp.

Hughes T, Tanner J. 2000. Recruitment failure, life histories, and long-term decline of Caribbean corals. Ecology 81: 2250-2263.

Kachemak Bay National Estuarine Research Reserve (KBNERR). 2001. Kachemak Bay Ecological Characterization. CD-ROM. NOAA/CSC/20017-CD. Charleston, SC.

Kimbrough, K. L., G. G. Lauenstein and W. E. Johnson (Eds). 2006. Organic contaminant analytical methods of the National Status and Trends Program: Update 2000-2006. NOAA Technical Memorandum NOS NCCOS 30. 137pp.

Knee, K, Gossett, R, Boehm A, Paytan, A. 2010. Caffeine and agricultural pesticide concentrations in surface water and groundwater on the north shore of Kauai (Hawaii, USA) Marine Pollution Bulletin 60:1376–1382.

Kuffner I, Walters L, Becerro M, Paul V, Ritson-Williams R, Beach K. 2006. Inhibition of coral recruitment by macroalgae and cyanobacteria. Marine Ecology Progress Series 323: 107-117.

Lohmann, R. 2012. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. Environmental Science and Technology.. 46: 606-618.

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environment and Management 19:81-97.

Long, E.R., and L.G. Morgan. 1990. The Potential for Biological Effects of Sediment-Sorbed Contaminants Tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52, Seattle WA 175pp.

Marubini, F, Davies, P. 1996. Nitrate increases zooxanthellae population density and reduces skeletogenesis in corals. Marine Biology 127: 319-328.

Mason, A.L., A.P. Jacob, M.M. Rider, M.A. Gaskins, S.I. Hartwell, and I.R. MacDonald. 2019. Chapter 8: An Oil-related Chemical Contaminants Assessment of the Sediment, Water, and Oil Collected from the MC20 Site in the Northern Gulf of Mexico. In: An Integrated Survey of Oil and Gas Release to the Marine Environment at the Former Taylor Energy MC20 Site. NOAA Technical Memorandum NOS NCCOS 260. 147 pp.

Mead, R., Morgan, J, Brooks, G, Avery Jr.,R, Kieber,J, Kirk, A, Skrabal, S, Willey, J. 2009. Occurrence of the artificial sweetener sucralose in coastal and marine waters of the United States Marine Chemistry 116:13-17.

National Marine Sanctuary Program. 2007. Fagatele Bay National Marine Sanctuary Condition Report 2007. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National

Marine Sanctuary Program, Silver Spring, MD. 39 pp.

NOAA CRCP 2012. American Samoa's Coral Reef Management Priorities. https://www.coris.noaa.gov/activities/management_priorities/amsam_mngmnt.pdf

Pait, A.S., A.L. Mason, S.I. Hartwell, and D.A. Apeti. 2019. An Assessment of Chemical Contaminants in the Waters Around Cocos Island, Guam Using Polyethylene Passive Water Samplers. NOAA Technical Memorandum NOS NCCOS 261. Silver Spring, MD. 43 pp. doi:10.25923/0bvz-p335

Pisarski, E.C., E.F. Wirth, S.I. Hartwell, B.S. Shaddrix, D.R. Whitall, D.A. Apeti, M.H. Fulton, G. Baker. (2018) Assessment of Hydrocarbon Carryover Potential for Six Field Cleaning Protocols. NOAA Technical Memorandum NOS NCCOS 247. Silver Spring, MD. 36 pp

Shuler, C, Amato, D, Gibson, V, Baker, L, Olguin, A, Dulai, H, Smith, C, Alegado, R. 2019. Assessment of Terrigenous Nutrient Loading to Coastal Ecosystems along a Human Land-Use. Hydrology 6:18.

Storlazzi C, Cheriton O, Rosenberger K, Logan J, Clark T. 2017, Coastal circulation and water-column properties in the National Park of American Samoa, February–July 2015: U.S. Geological Survey Open-File Report 2017–1060, 104 p., https://doi.org/10.3133/ofr20171060.

Szarzi, N.J. C.M. Kerkvliet, C.E. Stock and M.D. Booz. 2007. Recreational Fisheries in the Lower Cook Inlet Management Area, 2005-2007, with updates for 2004. Alaska Department of Fish and Game, Division of Sport Fish and Commercial Fish, Fishery Management Report No. 07-55, Anchorage Alaska.

US Environmental Protection Agency (USEPA). 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1 - Fish Sampling and Analysis, Third Edition. 485pp.

U.S. Environmental Protection Agency (EPA). 1994. Methods for assessing the toxicity of sediment associated contaminants with estuarine and marine amphipods, EPA-600/R-94/025. Office of Research and Development, U.S. EPA, Narragansett, RI.

USEPA. American Samoa Water Quality Standards. 2013 Revision Administrative Rule No. 001-2013.

US Census. 2010. Island Area: American Samoa, Population Counts for Places (Villages). https://www.census.gov/population/www/cen2010/island_area/as.html

Vargas-Angel, B., Schumacher, B. 2018. Baseline Surveys for Coral Reef Community Structure and Demographics in Vatia and Faga'alu Bay, American Samoa NOAA Pacific Islands Fisheries Science Center, PIFSC Special Publication, SP-18-002, 38 pp.

Whitall, D, M Curtis, A Mason, B Vargas-Angel. 2019. Excess Nutrients in Vatia Bay, American Samoa: Spatiotemporal Variability, Source Identification and Impact on Coral Reef Ecosystems. NOAA Technical Memorandum NOS NCCOS 266. Silver Spring. 69 pages. doi:10.25923/j8cp-x570

New Approaches for Monitoring and Assessment

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Abstract

Activities of NOAA's National Status and Trends Program were essentially codified under provisions of the National Coastal Monitoring Act (Title V of the MPRSA), which was part of the NOAA Authorization Act of 1992 (PL 102-567). The Act called for a consistent, nationwide water quality monitoring program with an appropriate degree of uniformity of methods and analytical procedures, development of uniform indicators of coastal ecosystem quality (i.e., biomarkers and ecological indices), and an environmental data management program. Finding the right balance (cost/benefit) of chemical contaminant monitoring and biomarkers of ecosystem health is critical to the Programs survival. Bivalve health metrics were applied in the Great Lakes basin using dreissenid mussels as the model. Each metric helped to characterize sites across the Great Lakes and its tributaries and the relative stress on in situ and caged bivalves. The preliminary results support the general concept that health metrics may be a more informative to coastal resource managers and more affordable to the National Status and Trends Program.

Introduction

The National Status and Trends Program (NS&T) is perhaps most recognized for its chemical contaminant monitoring of bivalve and fish tissue, and sediment, however the program has also historically evaluated many bio-effects indicators. The effort and was initially supported by the NOAA Coastal Ocean Program, with the objective of developing and transferring techniques and technologies to states and other entities for environmental (sediment) quality assessment. Some of the biomarkers and other indicators have been investigated and used by the Program are listed in Table 1 (Hameedi, 2005), some of which were found useful with bivalves in field monitoring and assessment programs.

In this chapter, we will highlight three bio-effects indicators that have been routinely applied across the Laurentian Great Lakes since 2016. Among them are two newer techniques not previously used by NS&T including metabolomics and metabolites of DNA damage. In February of 2020, NOAA released a set of final strategies to dramatically expand the agency's application of three emerging science and technology focus areas — NOAA Unmanned Systems, Artificial Intelligence and 'Omics — that will guide transformative advancements in the quality and timeliness of NOAA science, products and services (NOAA 2020a, b, c). The overarching 'Omics Strategy goal is to apply 'omics science to advance NOAA mission by building the necessary expertise in 'omics related computational science (bioinformatics). Bioinformatics combines biology, computer science, information engineering, mathematics, and statistics to analyze and interpret 'omics data.

Table 1. Examples of Biomarkers Studied under the NOAA National Status and Trends Program (Hameedi, 2005).

Cellular Integrity and Cytogenetic Damage

Lysosomal destabilization

DNA adducts

DNA strand breakage

Stress Proteins/Detoxification Response

Phase I enzymes (CYP1A, BPH)

Phase II enzymes (GST)

Multi-xenobiotic resistance proteins (MXRs)

Stress proteins (hsp70, hsp76, chaperonin)

Metallothioneins

Antioxidants

Impaired Reproduction

Gonadotropins

Steroids (plasma estradiol, testosterone)

Vitellogenin

Impaired Immune System

Hemocyte numbers and types

Killing index/phagocytic index

Serum lysozymes

Wellness and Condition

Darwinian "fitness parameters"

Atrophied organs and connective tissue

Parasitic infection

Disease and abnormalities

Lesions and tumors

While monitoring the presence of contaminants in the environment is useful it does not alone inform on actual adverse effects on biota. Nor does the measurement of contaminants in tissues always translate into adverse effects since bioaccumulation reflects the net effects of various physico-chemical factors that affect bioavailability. Moreover, organisms may respond by sequestering or detoxifying the chemicals. Therefore, sensitive reliable biomarkers can determine if significant contaminant exposures that have exceeded detoxification or compensatory mechanisms leading to adverse effects on physiological and biochemical responses.

As the equivalent of Mytilus in the marine environment, dreissenid mussels have been used as a bio-indicator species in freshwater ecosystems (Binelli et al. 2015). The National Mussel Watch Program began annual contaminant biomonitoring in the Great Lakes in 1992 using dreissenids following their introduction from ballast water of trans-Atlantic ships in the mid- 1980s and widespread distribution. Due to their sessile nature and filter feeding strategy, both marine and freshwater mussels are commonly used as indicator species in global biomonitoring programs, including in the Adriatic Sea (Bajt et al. 2019), the Greek coastline (Tsangaris et al. 2010), the Sydney Estuary (Markich and Jeffree 2019), and Lake Mead, Nevada (Bai and Acharya 2019).

This chapter summarizes bivalve health metrics that have been systematically applied using dreissenid mussels at sites across the Laurentian Great Lakes since 2016 while monitoring body burdens of contaminants as part of NOAA's Mussel Watch contribution to the Great Lakes Restoration Initiative (GLRI, Table 2). Here we use the name Great Lakes Mussel Watch (GLMW) to distinguish the monitoring approaches applied under the GLRI from those used by NOAA's national Mussel Watch Program.

Approach

The work described herein is part of a larger effort of five federal partners that includes NOAA, USEPA, USFWS, USACE, and the USGS. Here we

Table 2.

Indicator	Matrix	Institution/Laboratory
chemicals of emerging concern	bivalves	SGS AXYS Analytical
Halogenated organics & PAHs	bivalves	TDI Brooks, International, Inc.
chemicals of emerging concern	POCIS	SGS AXYS Analytical
PAHs	SPMD	SGS AXYS Analytical
targeted metabolomics	bivalves	SGS AXYS Analytical
untargeted metabolomics	bivalves	National Institute of Standards and Technology
DNA damage	bivalves	National Institute of Standards and Technology
lipid Peroxidation (LPx)	bivalves	University of North Carolina - Charlotte
glutathione (GSH)	bivalves	University of North Carolina - Charlotte
acetylcholinesterase (AChE)	bivalves	University of North Carolina - Charlotte
biomass, length, dry wt.	bivalves	NOAA/Great Lakes Environment Research Lab.

provide a brief description to add context to NOAA's contribution to the larger multi-federal effort and partnership.

The USEPA Region-5, Great Lakes National Program Office provides the coordination for the execution of the Great Lakes Restoration Initiative (GLRI). Funding for the GLRI is approximately $300 million per year since 2010, of which approximately $5 million per year has gone to support contaminant monitoring and bio-effects of chemicals of emerging concern and other priority chemicals. Of the $5 million, Great Lakes Mussel Watch (GLMW) has received, on average, about $450,000 per year since 2010.

In 2015, under the direction of EPA's project manager, five federal partners (EPA/ORD, NOAA, USGS, FWS, and USACE) began working collaboratively to address chemicals of emerging concern (CECs) and their effects on fish and wildlife. These five partners, collectively referred to as the CEC Team developed a strategic plan to address the GLRI, Action Plan II, Focus Area 1, Objective 1.2 Chemicals of Emerging Concern and Their Effects on Fish and Wildlife. The strategic plan defines guiding factors for new and coordinated work for the duration of Action Plan II (2015-2019) and applies a triad approach of monitoring and assessment consisting of 1) basin-wide Surveillance, 2) Integrated Assessment Case-Studies (IACS), and 3) Priority Contaminant Mixtures (Figure 1).

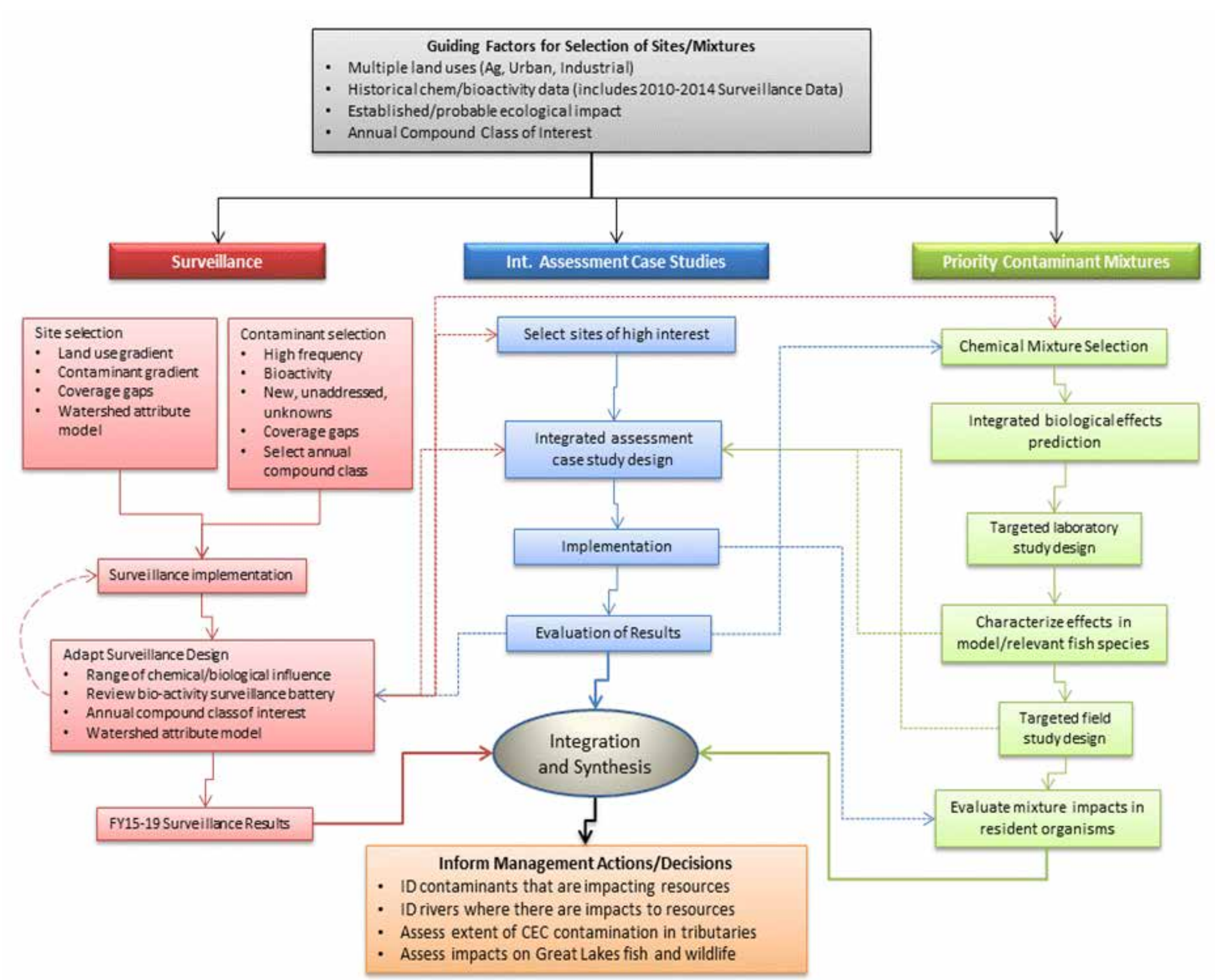


Figure 1. From the Strategic Plan of the CEC Team under Action Plan II of the Great Lakes Restoration Initiative.

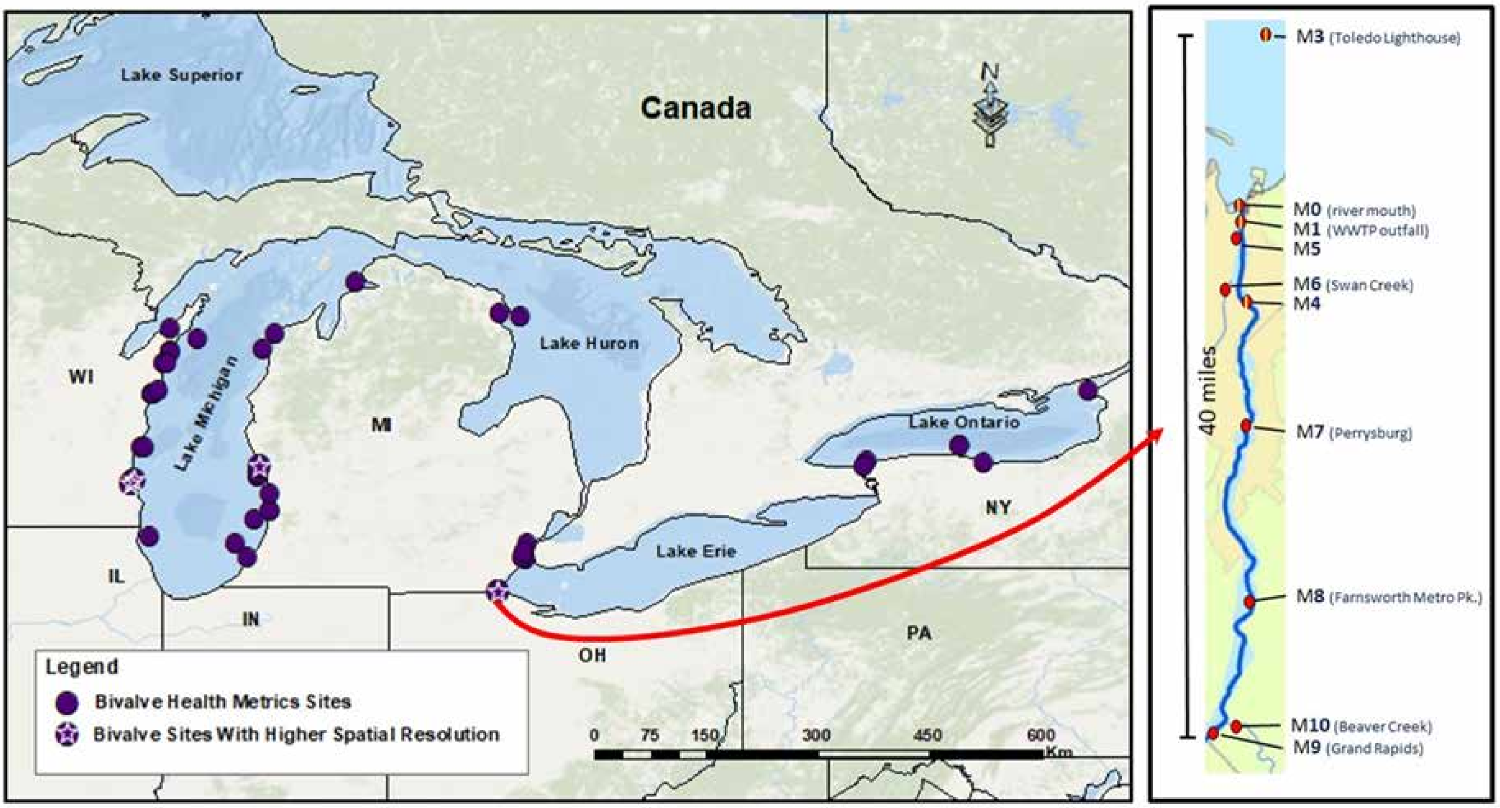


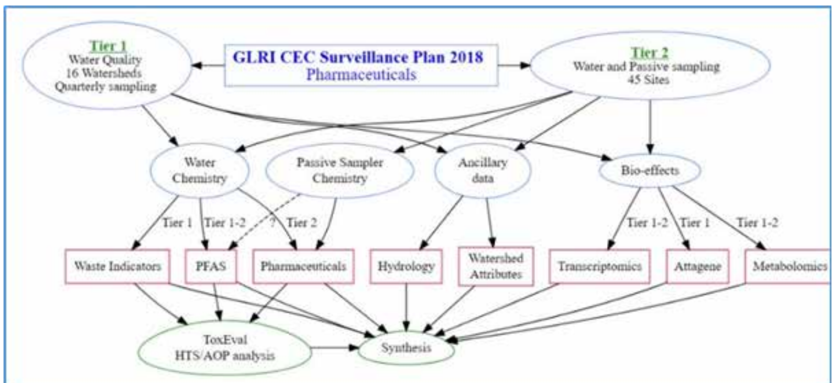
Figure 2. Great Lakes Mussel Watch dreissenid mussel sampling sites across the lower Great Lakes where mussel health indicators have been measured. Sites include river mouths, lake nearshore, lake offshore, and connecting channels (e.g. Detroit River and Niagara River). Site locations of the 2016 Maumee River Integrated Assessment Case Study are shown in the right side map, where red points indicate Asian clam sites; sites marked with red and yellow points are co-located clam and dreissenid mussels.

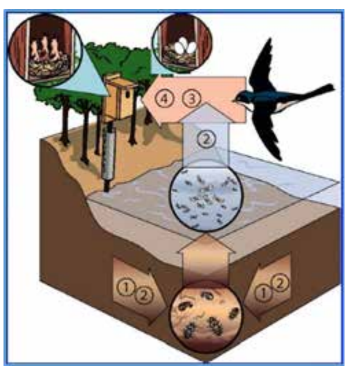
The GLMW assisted with two parts of the strategic plan, Surveillance and Integrated Assessment Case Studies (IACS), and received approximately 2 million dollars in GLRI funding over the period 2016-2019. 125 site visits (Figure 2) generated 562 samples for chemical contaminant analysis in bivalve tissue and passive water samples (video link) plus three bivalve health indicators (metabolomics, DNA damage, and cellular biomarkers).

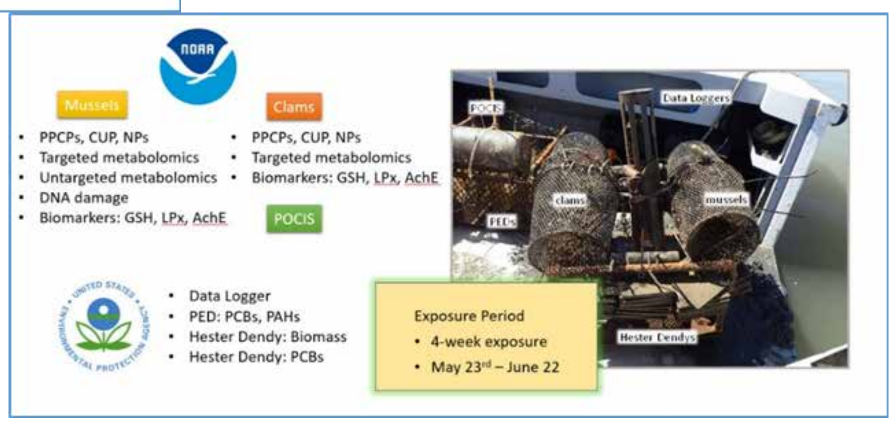
In addition, the CEC Team chose two locations to conduct IACS; the Maumee River (Lake Erie) for its predominantly agricultural land use, and the Milwaukee Estuary (Lake Michigan) for its mixed land use and its three rivers that converge in the urban/industrial harbor-center in downtown Milwaukee, WI. The Maumee River IACS was executed in 2016 and the Milwaukee IACS in 2017/2018.

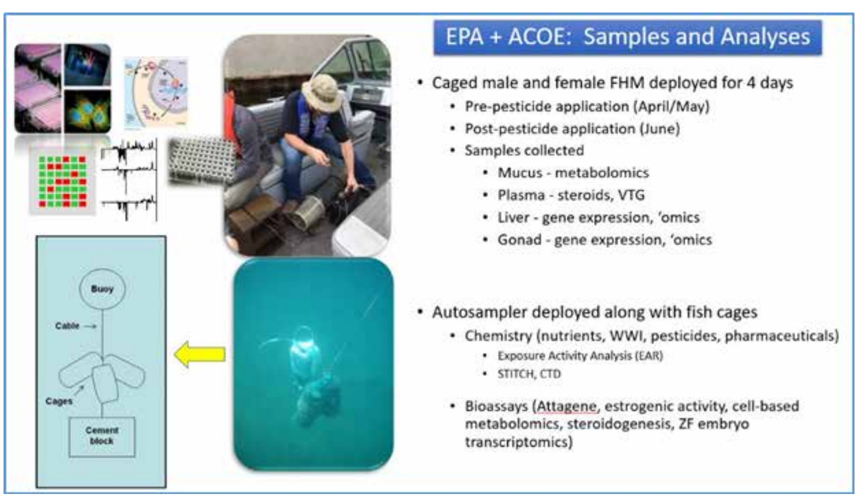
The Maumee River and Milwaukee Estuary are Areas of Concern (AOCs). In 1987 the U.S.-Canada Great Lakes Water Quality Agreement established Areas of Concern, as recommended by the International Joint Commission Great Lakes Water Quality Board. There are 43 AOCs (mostly industrial river-harbors), 25 in the U.S. and 5 more shared by the U.S. and Canada. GLMW visited all U.S. AOCs included the 5 shared with Canada. Since the GLRI began, GLMW has visited all U.S. AOCs including the 5 shared with Canada, and made over 200 unique site visits of rivers (AOC and non-AOC), nearshore lake and offshore lake collections of dreissenid mussels.

The CEC Team collaboration, made possible by the GLRI, is a model example of how federal agencies can work together to leverage resources, data, information, and knowledge (video link). The CEC Team is working on synthesis products facilitated by recently combined Team data into a single database. The first synthesis publication will compare and contrast CECs found in various matrices (tissue, water, sediment) and recommend a short-list of priority CECs for monitoring and assessment based upon risk factors and frequency of detection. The second synthesis publication will focus on the Maumee IACS study of 2016 bringing all the health metrics together to inform on the potential adverse effects to biota including molecular and cellular data that elucidate potential adverse outcome pathways. Clearly the team synthesis efforts are expected to inform and advance our knowledge and understanding beyond what any individual agency might accomplish alone. Some of the contributions of each partner are summarized in Figure 3.









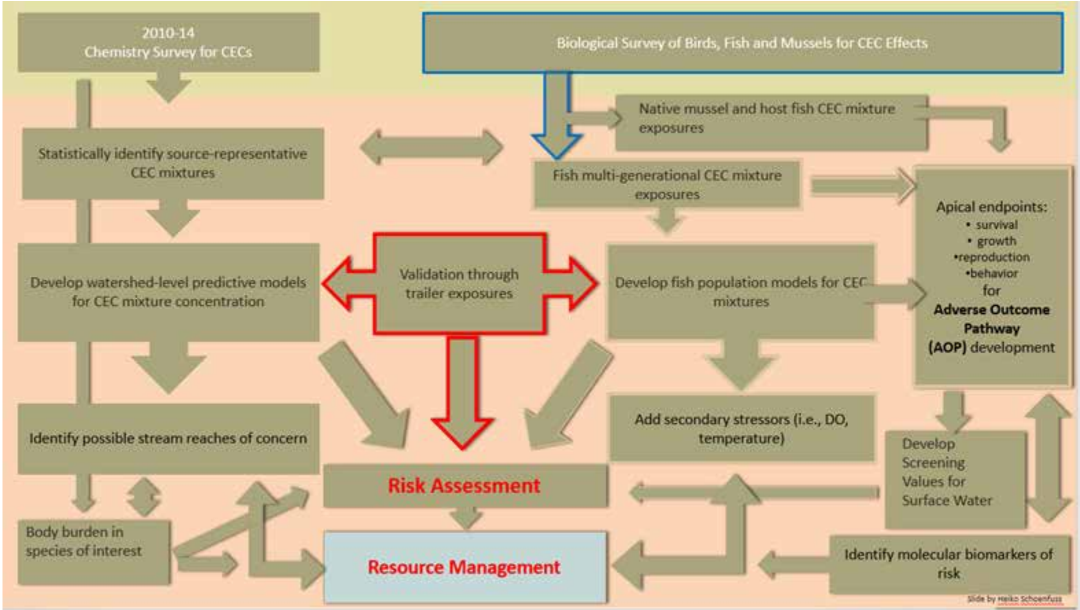


Figure 3. Contributions of each of the federal partners of the CEC Team: a) USGS-Middleton: water and passive water samples for contaminant characterization and Bio-effects assays; b) EPA-Athens: human cell lines exposed to surface water; c) NOAA & EPA: shared moorings – multi indicators – mussels, clams, POCIS, PEDs, Hester Dendy; d) USGS-Lacrosse: tree swallows; e) EPA-Duluth: caged fish; f) FWS: Fish, mussels, water.

Partner	Indicator	matrix
USGS	tissue contaminant body burden	tree swallows
USGS	targeted metabolomics	tree swallows
USGS	transcriptomics	tree swallows
USGS	Contaminants, microplastics, micro-organisms	Water, sediment
FWS	contaminants	Fish, mussels
EPA	metabolomics	Fish mucus
EPA	Steroids, vtg	Fish plasma
EPA	Gene expression, ‘omics	Fish liver, gonad, intestine
EPA	Attagene bioassay	human liver cancer cells (HepG2)
USACE	Transcriptomics (gene expression)	Fish liver, zebrafish embryo, human liver cells (HepG2), human brain cells (LN229)
FWS	Skin tumors	fish
FWS	Blood glucose	fish
FWS	Controlled exposures (Mobile Exposure Lab Trailer)	fish, mussels

The synthesis effort will include for example, metabolomics data across multiple species (mussels, tree swallow, fish). NOAA's mussel and clam samples and USGS tree swallow samples utilized the same laboratory and methodology for targeted metaboloimcis and these data are presently being combined for analysis together.

Preliminary results for NOAA supported efforts focus on river-harbor studies and primarily the 2016 Maumee River IACS effort. This agricultural watershed is the largest in the Great Lakes basin and is well characterized for nonpoint source pollution and discharge of nutrients and pesticides to the western basin of Lake Erie (Dill, 1952; Richards et al. 1996, Baker et al. 2019, Baker 2019). The Maumee River IACS was unique for GLMW because two bivalve organisms were used, dreissenid mussels and Asian clams (Corbicula). The study area is shown in figure 2 along with each clam and mussel sampling location. Each sampling site included passive water samplers (polar organic integrative sampler, POCIS), and water quality data loggers to monitoring dissolved oxygen and water temperature.

Lastly, but of important significance, a temporal study was conducted in 2018 in Lake Michigan. The purpose of this study was to measure indicators (table x) repeatedly over the year at the same mussel site. The location chosen was Lake Michigan at the mouth of the Muskegon River where NOAA maintains a permanent field station with scientists and laboratories, and headquarters of it research vessels operations. GLMW partnered with Ashely Elgin, PhD, a NOAA scientists whose expertise is in benthic ecology and dreissenid mussel biology. The premise for the study was to observe how mussel physiology changes relative to environmental characteristics of the site as the water begins to warm in the spring (after ice out) and the mussels "wake up," grow, reproduce, and store energy for the winter season. This study will help us to better understand the influence of biological and environmental factors on mussel health, which will improve the ability to detect, identify and interpret change related to biology, environment, and/or contaminant exposure. Samples were collected at nine time points 2MAY and ending 27NOV, 2018, before lake ice reforms. An NCCOS supported project will utilize archived samples from this study to conduct transcripomics pilot study.

Targeted and Untargeted Metabolomics

Metabolomics is the systematic study of concentration profiles of endogenous metabolites in biofluids and tissues of a given biological system, and has found applications in many fields including medicine, pharmacology, and more recently in environmental toxicology. Within the field of metabolomics, environmental metabolomics focuses on detecting system-wide biochemical changes in organisms in response to environmental exposure. Mass Spectrometry-metabolite profiling has been used to identify biology function in invertebrates including mussels (Goulitquer, Potin, and Tonon 2012). For example, the effect of a pharmaceutical product has been studied in the Mediterranean mussel M. galloprovincialis by liquid chromatography-high resolution mass spectrometry (Bonnefille et al. 2018) and the effect of an endocrine disruptor compound has been investigated in the unionid mussel Lampsilis fasciola by GC and LC-MS (Leonard et al. 2014). Moreover, untargeted NMR-based metabolomics has been used to investigate the impact of a petrochemical area on caged mussel M. galloprovincialis (Fasulo et al. 2012; Cappello et al. 2017, 2013) and the effect of heavy metals on in situ M. edulis (Kwon et al. 2012). In addition, a comparison study between a field sampling and laboratory exposure demonstrated a lower metabolic variability from the field in M. galloprovincialis confirming the potential of environmental metabolomics for biomonitoring studies (Hines et al. 2007).

Metabolomics is used to investigate metabolic changes within an organism in response to toxicant exposure in laboratory conditions as well as in natural habitats. However, metabolomics data with respect to dreissenid mussels was lacking. Under Action Plan I of the GLRI (2010-2014), GLMW conducted a feasibility study to determine whether mussel metabolomics could augment standard practices for evaluating ecosystem impairment (Watanabe et al., 2015).

GLMW collaborated with its sister bureau, the National Institute of Standards and Technology (NIST), to study the application of NMR-based untargeted metabolomics to the analysis of the whole-body metabolome of dreissenid mussels collected from the three inner harbor sites of Milwaukee Estuary Area of Concern, and a reference site in Lake Michigan in 2012. One of the objectives of this pilot study was to examine whether there were differences in metabolite profiles between impacted sites and the reference site. A total of 26 altered metabolites with significant differences were successfully identified in a comparison of dreissenid mussels from an inner harbor site and the reference site (Figure xx; Watanabe et al., 2015). This study has demonstrated the feasibility of NMR-based metabolomics approach to assess whole-body metabolomics of dreissenid mussels and are being explored further in Phase 2 activities.

GLMW returned to Milwaukee in 2017/2018 as part of the CEC Team IACS and results from that effort including mussel body burden, targeted and untargeted metabolomics, DNA damage and cellular biomarkers are pending. Manuscripts from GLMW's participation in the 2016 Maumee IACS are in preparation.

For the Maumee IACS, preliminary analysis of clam and mussel targeted MS-based metabolomics measurement, using principle component analysis (PCA) and k-means clustering, illustrates an undiscernible distinction among sites, which is associated with variability in metabolite concentration measurements among analytical batches. The linear mixed effects (LME) model was used to enable metabolite concentration comparisons among sites, with correction of the batch effects. PCA of LME metabolite concentration estimates show (Figure x) that technical variability is reduced to visualize site variability more clearly (Davenport et al. submitted Metabolomics 2020).

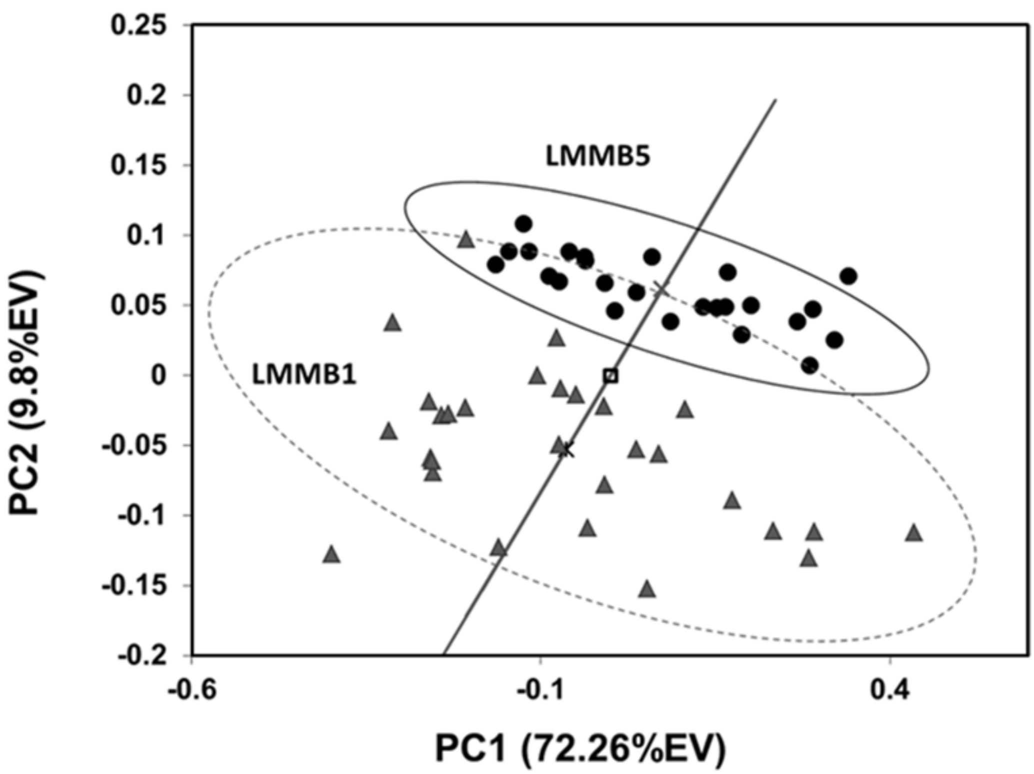
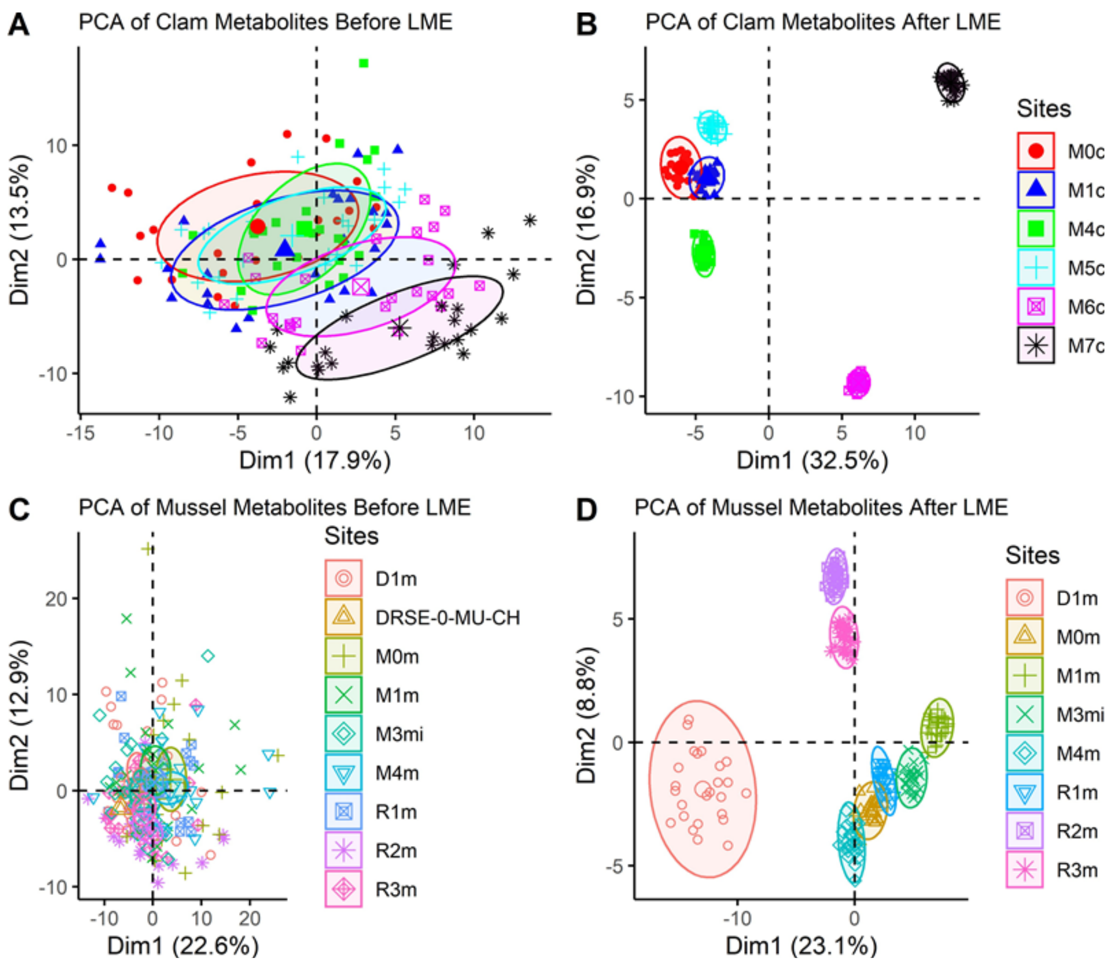


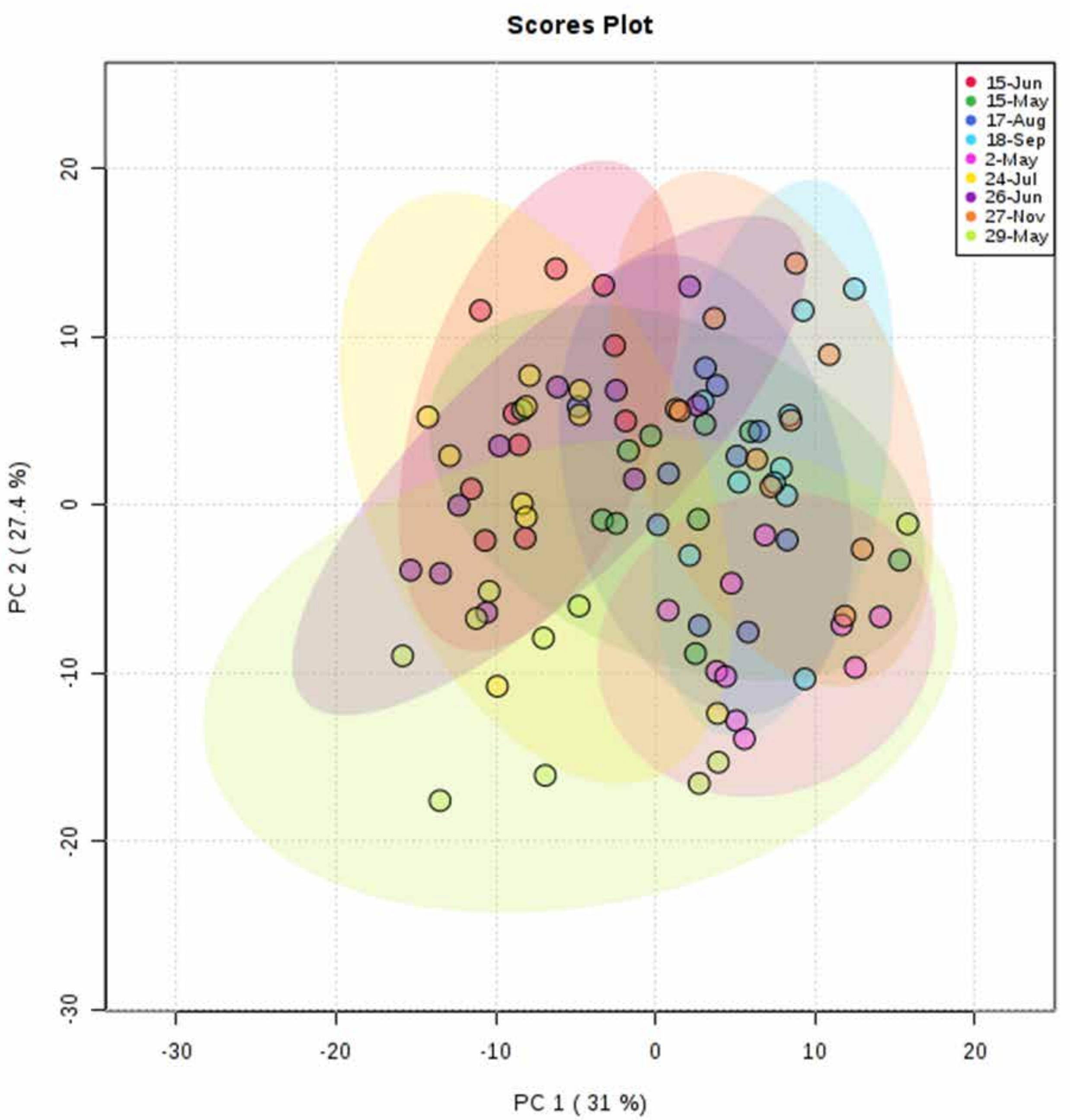
Figure 4: From Figure B.12 of Watanabe et al. 2015. PCA scores plot of the processed 1H NMR spectra data obtained dreissenid mussels from impacted site LMMB1 (▲), and the reference site LMMB5 (●). The ovals indicate the 95% Hoteling's confidence interval. The solid line represents the projection of the scores onto the hybrid scores axis connecting the centers of each group. A Student's t-test for these projected points shows a significant difference between the groups (p= 5.65x10-6).

Figure 5. Principle component analysis before and after the linear mixed effects model was used to control the batch effects.



Results from the Muskegon Temporal Study are pending, but preliminary results will help in the interpretation of the IACS and Surveillance data collected. In addition, metabolomics data collected from this and other sites across the Great Lakes basin will inform basic mussel biology. For example, Figure x shows similarity in metabolomes of a mussel bed sampled during the Muskegon temporal study. The preliminary results may suggest that the mussels in this bed show a more-or-less consistent metabolic pattern with subtle changes throughout a season. Metabolomics data therefore may become a tool for assessment of basic mussel biology across lakes and habitat types (river, nearshore, offshore).

Figure 6. PCA plot of preliminary untargeted metabolomics NMR results (Schock et al. 2020) for dreissenid mussels collected at nine time points throughout 2018 from the Muskegon River mouth, Muskegon, MI (Lake Michigan).



Cellular Biomarkers

Cellular biomarkers represent the most sensitive indicators of sublethal toxicity. Eventually these cellular stress effects would be reflected in more general physiological effects such as decreased growth and reproduction, and ultimately cause significant effects on the sustainability of bivalve populations. A variety of well-established biomarkers have been used worldwide as valuable diagnostic indicators of organismal health (De Lafontaine et al., 2000; Galloway et al., 2004; Tsangaris et al., 2011; Edge et al., 2012; Farrington et al., 2016). These include biomarkers of cellular damage (DNA damage, lysosomal destabilization, lipid peroxidation levels, and acetylcholinesterase levels) and antioxidant status (glutathione, and antioxidant enzymes such as catalase, glutathione peroxidase. A common mode of toxicity of many pollutants is oxidative stress and cellular damage related to oxyradicals, but bivalves and other organisms respond to xenobiotic exposures by inducing antioxidant defense mechanisms to detoxify excess reactive oxygen species, attempting to mitigate significant damage. However this is a delicate balance, and if the damage exceeds the compensatory capacity, more widespread effects on organismal health will occur. It is also recognized that species, life history stages, or populations with reduced antioxidant capacities will be even more susceptible to pollutant impacts. Therefore, cellular damage and antioxidant responses in bivalves and other organisms are valuable biomarkers of stress and organismal health for environmental monitoring.

This integrated program provides a unique opportunity to gather extensive biomarker data on Dressinid mussels and to promote their development as potentially valuable bioindicator organisms. While many of these biomarkers have been used extensively with marine bivalves, less is known about the responses of fresh water bivalves. The biomarker and bivalve health studies conducted throughout the Great Lakes provide important baseline data that will provide a better understanding of normal vs perturbed responses. Furthermore, linking bivalve health indices to tissue contaminant and land use data will facilitate robust ecosystem assessments.

DNA Damage

DNA damage caused by oxygen-derived species including free radicals is the most frequent type encountered by aerobic cells. Free radicals are generated in aerobic organisms from oxygen or nitrogen by endogenous cellular metabolism, or by exogenous sources such as ionizing radiation, ultraviolet radiation, carcinogenic compounds, redox cycling drugs, and environmental pollutants, to name a few. Endogenous and exogenous sources cause free radical-induced DNA damage in living organisms by a variety of mechanisms. The highly reactive hydroxyl radical (●OH) reacts with the heterocyclic DNA bases and the sugar moiety near or at diffusion-controlled rates. Hydrated electron e-aq and H• atom also add to the heterocyclic bases. When this type of damage occurs to DNA it is called oxidative DNA damage and it can produce a variety of modifications in DNA including base and sugar lesions, 8,5′-cyclo-2′-eoxynucleosides, strand breaks, DNA-protein cross-links, and base-free sites. This type of damage can be repaired in living cells by a numerous repair mechanisms. Oxidatively induced DNA modifications that escape repair before replication lead to mutagenesis, which is well known to be a fundamental part of the molecular basis of all cancers. Mutations occur throughout the genome, including in genes that maintain genetic stability (e.g., RB1, TP53), leading to genetic instability, which is a hallmark of cancer. 8,5′-cyclo-2′-eoxynucleosides presence in DNA is generating similar mutagenicity and could lead to cells death by triggering DNA helix distortion, which blocks DNA polymerases what is equal to halt of cells proliferation. Accurate measurement of these modifications is essential for understanding of mechanisms of oxidatively induced damage to DNA and its biological effects. Various analytical techniques exist for the measurement of oxidative damage to DNA. Techniques that employ gas chromatography (GC) or liquid chromatography (LC) with tandem mass spectrometry (MS/MS) simultaneously measure several products and provide their positive identification and accurate quantification. The measurement of multiple products avoids misleading conclusions that might be drawn from the measurement of a single product, because product levels vary depending on reaction conditions and the redox status of cells. GC-MS/MS measurements of oxidatively induced DNA base damage described in this chapter were conducted with use of NIST certified Oxidative DNA Damage Mass Spectrometry Standards, Standard Reference Material® 2396, which includes eight oxidatively-modified, stable isotope-labeled DNA bases. Use of such standards in mass spectrometry assures positive identification of analytes, as well as their precise quantitation.

Numerous DNA lesions have been identified in cells and tissues at steady-state levels and upon exposure to free radical generating systems, including environmental pollutants and their metabolites. Tissues of bivalves exposed to xenobiotic substances are threatened by the production of elevated levels of reactive oxygen and nitrogen species as a result of the metabolism or direct reactions of pollutants. Overproduction of free radicals can cause damage to biomolecules including DNA. Biomarkers of oxidatively induced damage, i.e., modified DNA bases and nucleosides in DNA of dreissenid mussels can be used as bioindicators for environmental genotoxicity.

MWP in collaboration with National Institute of Standards and Technology (NIST) conducted a pilot project to study the applicability of quantitative mass spectrometric assessment of oxidatively induced DNA base damage in dreissenid mussels in 2014. The aim of this pilot was to see whether oxidatively induced DNA lesions could serve as early warning biomarkers for pollution and specifically, to determine whether samples from polluted sites can be differentiated from those collected from reference sites based on DNA damage. Mussel samples from 2 sites in the outer Ashtabula harbor, a historically polluted harbor and a reference site in Lake Erie, approximately 6.5 km east of the Ashtabula River mouth were analyzed for DNA damage.

Scuba divers removed dreissenid mussels from rock substrate using stainless steel scrapers, placed them in a nylon mesh bag, and upon surfacing transferred them to coolers containing site water. Within one hour of collection, the mussels were rinsed free of debris with site water, placed in 5 Ziploc bags in composites of approximately 20 to 30 mussels each. The bagged mussels were then placed in a cooler of dry ice and shipped blind coded to the NIST laboratory, where they were transferred to a freezer at -80 0C. For DNA damage analyses, mussels were thawed on ice, then washed with ice-cold deionized water. To minimize the influence of body mass and age of studied animals on the results of measurements of markers of oxidatively induced DNA damage, similar size (≈2 cm) mussels have been selected for each group. Mussel tissues (≈100 mg) separated from shells with a scalpel were processed according to the product manual of E.Z.N.A. Mollusc DNA Kit, Omega Bio-tek (Norcross, Georgia) with modification involving homogenization with Bullet Blender Storm 24 high-throughput bead-mill homogenizer (Next Advance, Averill Park, New York). Tissues were placed in the 1.5 mL Rhino Screw cap tubes (Next Advance) kept on ice, containing 350 mL of ML1 Buffer from the kit and three 2 mm zirconium oxide beads. Tubes were transferred into the Bullet Blender kept in the refrigerator at 4 0C and processed 2 x 30 s at speed 12 with 30 s break between runs. Subsequently 25 mL of Proteinase K from the kit was added and samples were incubated for 2 h at 60 0C. Then, subsequent steps of the Mollusc DNA Kit protocol were applied. For the final DNA elution, two portions of 100 mL of sterile high-performance liquid chromatography grade water (Sigma- Aldrich, St. Louis, Missouri) warmed to 70 0C were used. The UV absorbance spectrum of each DNA sample was recorded by absorption spectrophotometry between the wavelengths of 200 nm and 350 nm to ascertain the quality of DNA and to measure the DNA concentration at 260 nm (absorbance of 1 = 50 mg of DNA per mL).

Aliquots (50 mg) of DNA samples were dried in 1.5 mL deoxyribonuclease-free Eppendorf tubes in a SpeedVac under vacuum and then kept at –80 0C for further analysis. Gas chromatography-tandem mass spectrometry with isotope-dilution was used to identify and quantify modified DNA bases and 8,5' -cyclopurine-2'-deoxynucleosides. Six modified DNA bases (5 hydroxy-5-methylhydantoin (5-OH-5-MeHyd), thymine glycol (ThyGly), 5,6-dihydroyuracil (5,6-diOH-Ura), 4,6-diamino-5-formamidopyrimidine (FapyAde), 2,6-diamino-4-hydroxy-5-formamidopyrimidine (FapyGua) and 8-hydroxyguanine (8-OH-Gua)) and three 8,5′-cyclopurine-2′-deoxynucleosides ((5'S)-8,5′-cyclo-2′-deoxyadenosine (S-cdA), (5'R)-8,5′cyclo-2′-deoxyguanosine (R-cdG) and (5'S)-cyclo-2′-deoxyguanosine (S-cdG)) were identified and quantified in the mussels’ tissue samples.

Results show that the mussels from one site in the outer harbor had significantly greater levels of oxidatively induced DNA bases, except for 5,6-diOH-Ura (p=0.7873), and 8,5'-cyclopurine-2'-deoxynucleosides than those from the reference site (Table xx; Jaruga et al., 2017). Further evaluation of this monitoring tool was conducted with mussels collected from other Great Lakes

Table 3: From table B.1 of Jaruga et al. 2017. The mean and SE of DNA bases and nucleosides measured in mussels from the harbor site (LEAR-1). All but one were significantly different from those measured at the reference site (LEAB).

	LEAB	LEAR1			
DNA base	mean	SE	mean	SE	significant
FapyAde	3.26	0.41	7.15	0.49	*
FapyGua	7.49	1.05	15.7	0.78	*
8-OH-Gua	1.35	0.06	2.14	0.08	*
ThyGly	5.86	0.89	9.94	0.57	*
5-OH-5-MeHyd	6.65	0.33	8.38	0.42	*
5,6-diOH-Ura	8.21	0.37	8.41	0.57	
S-cdA	0.039	0.003	0.216	0.033	*
R-cdG	0.954	0.173	2.19	0.105	*
S-cdG	2.32	0.40	5.89	0.29	*

harbors in agricultural, and industrial watersheds, for comparison with reference sites as part of a larger strategic plan to identify and assess adverse impacts of CECs in Great Lakes tributaries; results from this effort is forthcoming.

Oxidatively induced damage of Dreissenid mussels' DNA was detected in samples collected from 9 sites located at Maumee River, along Detroit River and from 3 sites, caged mussels, Rogue River. Significantly higher concentrations of four modified bases (5-OH-5-MeHyd, FapyGua, FapyAde and 8-OH-Gua and two cyclodeoxypurines (S-cdAdo and R-cdGuo) were found in the in-situ mussels collected at Hennepin Point/Trenton Channel, Detroit River, MI. Considered possible factors triggering elevated levels of oxidatively induced damage of mussels' DNA include transition metals (Fe, Cu, Ni, Cr) possibly present in the sediments (Hennepin Point is the former BASF salt mining and tailings disposal place) and a wide spectrum of pesticides, herbicides and drugs and their metabolites present in mussels' tissues (channel blockers, antidepressants, etc.), reacting with nitrites abundant in discharge and overflows from water treatment facility (upstream, opposite to samples collection site) and forming this way DNA-damaging N-nitroso compounds. Simply, metabolism of numerous pesticides and drugs in mussels' tissues involve reactions when ●OH radical damaging their DNA is generated. Considering entire variety of possible compounds' reactions and their metabolic interactions leading to generation of reactive species, e.g., ●OH, and ●NO is quite impossible to name an individual source of oxidatively induced DNA damage.

Significantly elevated concentrations of two modified bases (5-OH-5-MeHyd and 5-OH-Ura) and four nucleosides R-cdAdo, S-cdAdo, R-cdGuo and S-cdGuo) were found in DNA of in situ mussels collected between May and October 2018 from Muskegon Lake, MI. Observed maximums of measured concentrations of oxidatively induced mussels DNA damage correspond to the maximum concentrations (ng/g wet tissue) of analyzed pharmaceuticals and pesticides.

- Such biomarkers can be used to determine whether xenobiotics have impacted the health of aquatic species at a contaminated site vs. reference organisms,
- Biomarkers of this type of DNA damage may provide accurate data reflecting specific genotoxicity of certain groups of contaminants

present in the monitored environment and serve as sensitive indicators of the effectiveness of remedial actions.

- More data search/analysis (e.g., in vitro exposure to specific pollutants/compounds or their selected mixtures) is required to correlate oxidatively induced DNA damage with a specific contaminant(s) or their reactions/metabolism products.

Lipid Peroxidation (LPx) and Glutathione (GSH)

Lipid peroxidation reflects oxidative damage to lipid-rich components such as cell membranes that occurs as a result of increased OH• radicals. Moreover, the free radical induced damage propagates additional cytotoxic products that can damage DNA and enzymes (Kehrer, 1993; Yu, 1994; Halliwell and Gutteridge, 2007). Increased lipid peroxidation has been demonstrated in response to contaminant exposures (metals and organics such as PAHs, PCBs, pesticides, etc) in fish and bivalves (Di Giulio et al. 1989; Viarengo et al., 1990; Ringwood et al., 1998; Livingstone, 2001; McCarthy et al., 2013). Damaged lipids, especially in membranes will impair fundamental functions (loss of fluidity, falls in membrane potential, impairment of transporters, etc. Antioxidants can help defend against oxidative stress by preventing radical formation, intercepting radicals when formed, repairing oxidative damage caused by radicals, and increasing the elimination of damaged molecules. However when oxidative damage exceeds antioxidant responses, the damage can be irreversible.

Glutathione (GSH) is the most abundant cellular antioxidant, and maintenance of baseline levels is essential for cellular homeostasis and resisting toxicity from oxidative and contaminant stress. This abundant tripeptide is regarded as one of the most important "first-line" defense mechanisms of cells to metals and oxyradicals, and numerous GSH-related enzymes are important components of detoxification pathways for organic pollutants. Animals can respond to contaminants by increasing GSH levels as well as other amelioration or detoxification mechanisms (metallothioneins, multidrug transporters, heat shock proteins, etc.) in an effort to reduce adverse effects. An increase in GSH levels suggest that cells are responding to a stressor and can be compensatory. However, if the detoxification mechanisms are overwhelmed, GSH production can be impaired, leading to decreased or depleted GSH levels. Glutathione depletion can occur as a result of oxidation by metals or radicals, and reflects an imbalance in antioxidants and oxyradicals that will ultimately lead to oxidative stress. Glutathione depletion has been observed in mammalian systems as well as marine organisms, and it is recognized that GSH depletion is both a signal of stress and a predisposing factor for increased adverse effects (Meister and Anderson, 1983; Viarengo et al., 1990; Regoli and Principato, 1995, Conners and Ringwood, 2000).

MWP ran a pilot project from 2010-2014 to examine the feasibility of using two cellular biomarkers- total glutathione (GSH) and lipid peroxidation (LPx) in wild populations of dreissenid mussels collected from around the Great Lakes to help identify highly impacted sites. The methods for analysis of these biomarkers in dreissenid mussels were optimized and tested for both whole body samples and hepatopancreas tissue. Our results indicate that the GSH and LPx biomarker responses were inversely correlated (ANCOVA, $r2 = 0.40$; Figure X) and the pattern of response was identical for whole body samples and hepatopancreas tissue samples suggesting that laborious work of isolating organ tissues can be avoided. Based on known biochemical mechanisms, high LPx and low GSH in animals are typically indicative of stress and in this study, we were able to rank the sites as 'normal', 'intermediate stressed' and 'highly stressed'. Additional results of analyses linking biomarker data and mussel tissue burden data will be summarized in Ringwood et al. (Manuscript in Preparation).

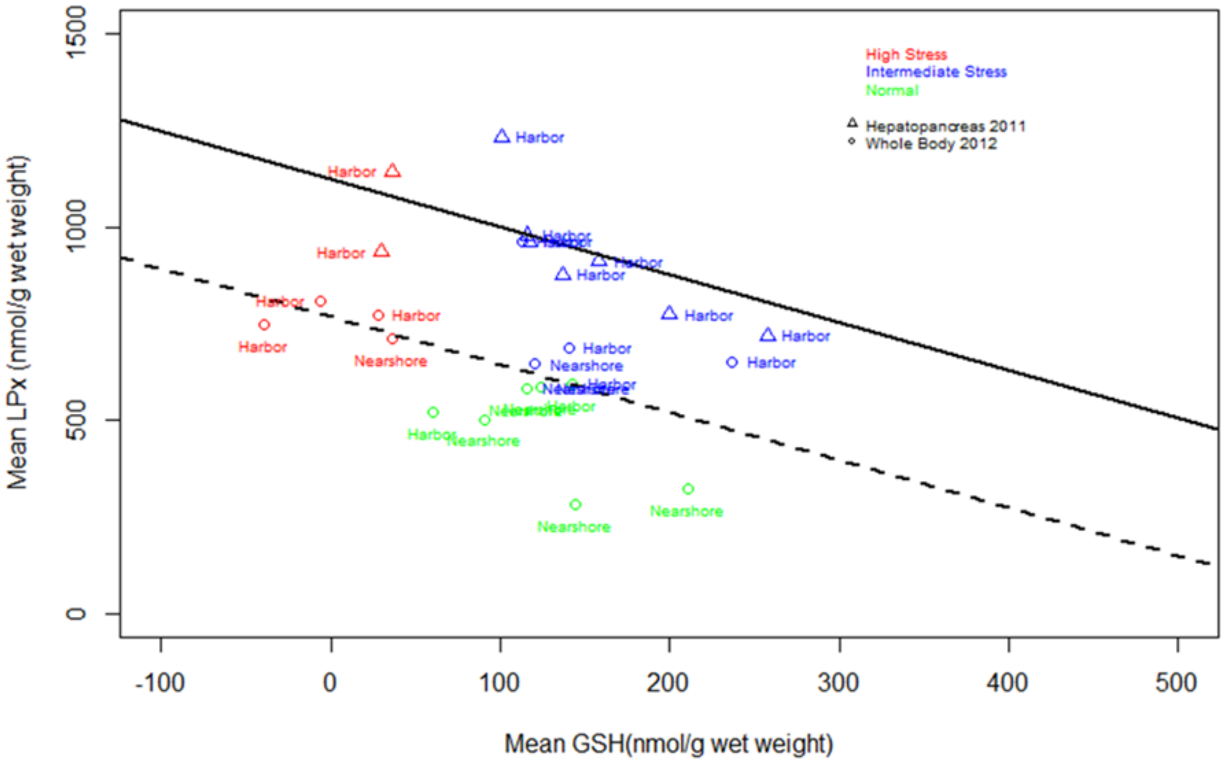


Figure 7: From Ringwood et al., manuscript in preparation. Inverse correlation (ANCOVA, r2 = 0.40) of glutathione (GSH) and lipid peroxidation (LPx) in mussel samples (hepatopancreas and whole body) collected from several locations around the Great Lakes.

Acetylcholinesterase (AChE)

Cellular biomarker responses of organismal health were conducted with caged bivalves (dreissenid mussels) in the Maumee River system during 2015 and 2016. This system is dominated by agricultural input, and high levels of pesticides in mussel tissues have been found. Therefore in addition to the LPx and GSH biomarkers, the acetylcholinesterase (AChE) biomarker was included for these studies. Acetylcholinesterase is the primary cholinesterase in living organism located in the neurotransmitter synapses that hydrolyzes acetylcholine into choline and acetic acid, a process that is required for cholinergic neurons to return to a resting state after activation and for normal central and peripheral nervous system functions (Colovic et al. 2013; Lionetto et al. 2013). While changes in cellular damage and antioxidants can be related to a variety of contaminants, AChE is tightly linked to pesticide toxicity, so this biomarker can provide important insights regarding causation. The enzyme activity has been used as a valuable biomarker for pesticide exposure and effects in many animals, including bivalves (Doran et al. 2001; Binelli et al. 2005; Cooper et al. 2006; Beltran et al. 2010). Moreover, The expected levels of AChE for dressenid mussels can be estimated mathematically based on water temperature (Binelli et al., 2005).

During 2015, caging studies with dressenid mussels were conducted in the Maumee River. The results indicated severe inhibition of AChE at all sites, indicating significant neurotoxicity associated with pesticide exposures. Based on Binelli’s equation, the AChE levels were more than 50% lower than predicted at almost all sites. Moreover, using the same techniques with mussels deployed in the Niagara River in 2014, the AChE levels in mussels from many of the sites were much higher than those from the Maumee, and were at predicted levels. Perturbation of the biomarker responses related to oxidative stress (glutathione and lipid peroxidation) was also observed at some sites. Therefore the biomarker studies, especially the significant AChE inhibition, suggest wide-spread cellular and physiological impacts throughout the Maumee watershed that are related to pesticide exposures.

During 2016, caging studies were conducted in the Maumee River with Asian clams (Corbicula fluminea) as well as dreissenid mussels to compare the relative sensitivity and feasibility of using either or both as an indicator species. In general, clams had higher AChE levels and less oxidative stress (higher glutathione and lower lipid peroxidation). The database of clams is too limited at this time to make final conclusions, but the preliminary results suggest that Asian clams may not be as sensitive as dreissenid mussels.

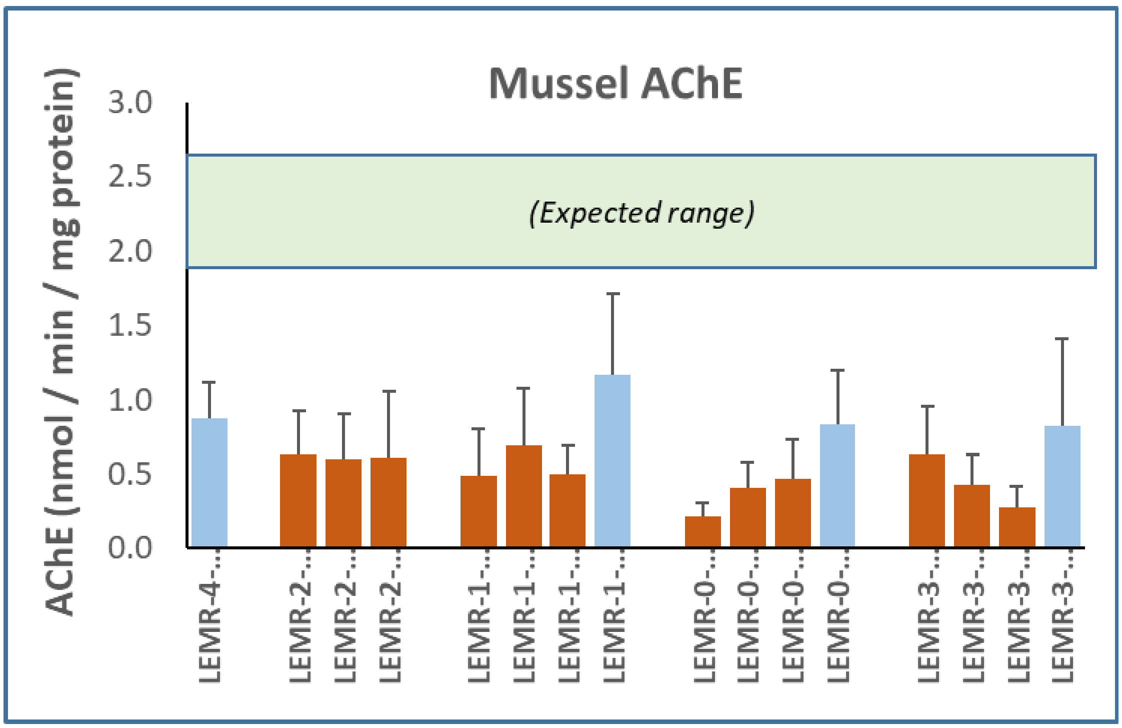


Figure X. The AChE activity of caged dreissenid mussels (whole tissues) deployed in the Maumee River during 2015 and 2016. Dreissenid mussels were collected in the month of May, June, and July in 2015 and June in 2016. Shaded box indicates expected AChE activities of dreissenid mussels at ambient temperatures of 19-25ºC based on the Binelli et al (2005) equation (manuscript in preparation).

Conclusions

A variety of bivalve health indicators were evaluated throughout the Great Lakes and preliminary results were presented for the Maumee River IACS and Muskegon (Lake Michigan) temporal study. Results are forth coming for the Milwaukee 2017/2018 IACS and a summary of Great Lakes surveillance monitoring of the lower lakes (Lake Michigan, Huron, Erie, and Ontario), which includes 15 river mouths, 8 nearshore sites, 13 offshore lake sites, and 4 sites in connecting channels (Detroit River and Niagara River).

In general, the bivalve health biomarkers provided relevant information that was consistent with the environmental conditions (contaminants) where they were exposed, and indicated when bivalve health was impacted. The cellular damage and antioxidant biomarkers measure targeted endpoints. Metabolomic profiles indicate potential perturbation to specific metabolic pathways and physiological conditions that could affect their susceptibility to contaminant stress. Significant progress has been made toward developing the library of metabolic profiles and their associated contaminant profiles in rivers, lake nearshore, and offshore lake areas across the basin. NOAA is working collaboratively with dreissenid mussel ecologist, Ashely Elgin (NOAA/GLERL) to potentially utilize this growing library of site-metabolomes in the assessment of mussel populations across the basin.

The integration of cellular and molecular biomarkers of organismal health with tissue and environmental contaminant monitoring will facilitate identification of impacts as well as contaminant levels. The biomolecular basis and outcome pathways for these health indicators are well understood, and their successful use in marine bivalves (including the application of integrated health indices using suites of biomarkers) provide important interpretative frameworks for using freshwater bivalves as valuable bioindicator organisms. NOAA is confident that as these approaches are refined and eventually applied routinely in other regions of the country, they will become essential diagnostic tools for the National Status and Trends Program. Characterizing organismal health will be essential for assessing and monitoring ecosystem health, especially since contaminated areas can be impacted by pollutant mixtures or emerging contaminants that are difficult to adequately assess using purely physico-chemical measurements. Clearly, environmental monitoring must evolve to include valuable diagnostic monitoring with biomarker tools/techniques that provide managers with early warnings regarding state of health of the resource and that are also sufficiently sensitive to identify improvements related to remediation strategies.

In addition to the NOAA publications cited here in, a number of publications are in various stages of completion:

NOAA led bivalve health products:

- Ringwood et al. Biomarker Responses of Freshwater Mussels and Clams to Pesticide Pollution, (ET&C)
- Davenport et al. Integrated assessment of targeted metabolomics and chemical body burden to link exposure to effects in bivalves, (Metabolomics)
- Legrand et al. Contribution of untargeted metabolomics analysis of dreissenid mussels to biomonitoring effort in the Great Lakes (Metabolomics)
- Davenport et al. Integration of metabolomics results from co-located mussel and tree swallow in in the Maumee River and Milwaukee Estuary watersheds.
- Johnson et al. Temporal changes in mussel health indicators in a Lake Michigan tributary.

CEC Team Synthesis Products:

- Synthesis 1: Contaminants of Emerging Concern identified as priority for monitoring and assessment.
- Synthesis 2: Molecular and cellular responses of biota and evidence supporting adverse outcome pathways.

References

Bai, Xuelian, and Kumud Acharya. 2019. "Uptake of Endocrine-Disrupting Chemicals by Quagga Mussels (Dreissena Bugensis) in an Urban-Impacted Aquatic Ecosystem." Environmental Science and Pollution Research 26 (1): 250–58. https://doi.org/10.1007/s11356-018-3320-4.

Bajt, Oliver, Andreja Ramšak, Vesna Milun, Bruno Andral, Giulia Romanelli, Alfonso Scarpato, Milena Mitrić, et al. 2019. "Assessing Chemical Contamination in the Coastal Waters of the Adriatic Sea Using Active Mussel Biomonitoring with Mytilus Galloprovincialis." Marine Pollution Bulletin 141 (April): 283–98. https://doi.org/10.1016/J.MARPOLBUL.2019.02.007.

Baker, K. 2019. The National Center for Water Quality Research at Heidelberg University 1969-2019. Heidelberg University, Tiffin, OH. 250pp. (link)

Baker, D.B., L.T. Johnson, R.B. Confesor, J.P. Crumrine, T. Guo, N.F. Manning, 2019. Needed: Early-term adjustments for Lake Erie phosphorus target loads to address western basin cyanobacterial blooms. 2019. Journal of Great Lakes Research, doi.org/10.1016/j.jglr.2019.01.011

Beltran, Kimberly S., and Glorina N. Pocsidio. "Acetylcholinesterase activity in Corbicula fluminea Mull., as a biomarker of organophosphate pesticide pollution in Pinacanauan River, Philippines." Environmental monitoring and assessment 165.1-4 (2010): 331-340.

Binelli A., F. Ricciardi, C. Riva, A. Provini. 2005. Screening of POP pollution by AChE and EROD activities in zebra mussels from the Italian Great Lakes. Chemosphere 61: 1074-1082.

Binelli, A., C. Della Torre, S. Magni, and M. Parolini. 2015. "Does Zebra Mussel (Dreissena Polymorpha) Represent the Freshwater Counterpart of Mytilus in Ecotoxicological Studies? A Critical Review." Environmental Pollution 196 (January): 386–403. https://doi.org/10.1016/J.ENVPOL.2014.10.023.

Bonnefille, Bénilde, Elena Gomez, Mellis Alali, David Rosain, Hélène Fenet, and Frédérique Courant. 2018. "Metabolomics Assessment of the Effects of Diclofenac Exposure on Mytilus Galloprovincialis: Potential Effects on Osmoregulation and Reproduction." Science of The Total Environment 613–614 (February): 611–18. https://doi.org/10.1016/J.SCITOTENV.2017.09.146.

Cappello, Tiziana, Maria Maisano, Angela Mauceri, and Salvatore Fasulo. 2017. "1H NMR-Based Metabolomics Investigation on the Effects of Petrochemical Contamination in Posterior Adductor Muscles of Caged Mussel Mytilus Galloprovincialis." Ecotoxicology and Environmental Safety 142 (August): 417–22. https://doi.org/10.1016/J.ECOENV.2017.04.040.

Cappello, Tiziana, Angela Mauceri, Carmelo Corsaro, Maria Maisano, Vincenzo Parrino, Giuseppe Lo Paro, Giuseppe Messina, and Salvatore Fasulo. 2013. "Impact of Environmental Pollution on Caged Mussels Mytilus Galloprovincialis Using NMR-Based Metabolomics." Marine Pollution Bulletin 77 (1–2): 132–39. https://doi.org/10.1016/J.MARPOLBUL.2013.10.019.

Colovic, M., Krstic, D., Lazarevic-Pasti, T., Bondzic, A. and Vasic, V. 2013. Acetylcholinesterase Inhibitors: Pharmacology and Toxicology. Current Neuropharmacology, 11(3), 315-335.

Conners, D. E. and Ringwood, A. H. 2000.   Effects of glutathione depletion on copper cytotoxicity in oysters (Crassostrea virginica). Aquatic Toxicology. 50: 341-349.

Cooper, Naomi L., and Joseph R. Bidwell. "Cholinesterase inhibition and impacts on behavior of the Asian clam, Corbicula fluminea, after exposure to an organophosphate insecticide." Aquatic Toxicology 76.3 (2006): 258-267.

De Lafontaine, Y, Gagné, F, Blaise, C, Costan, G, Gagnon, P, Chan, HM. 2000. Biomarkers in zebra mussels for the assessment and monitoring of water quality of the St. Lawrence River (Canada). Aquatic Toxicology. 50: 51-71.

Dill, B.M. 1952. Pollution Study of the Maumee River Basin, Sewage and Industrial Wastes Vol. 24, No. 10 (Oct., 1952), pp. 1288-1302 (link)

Doran, W. J., Cope, W. G., Rada, R. G., & Sandheinrich. "Acetylcholinesterase inhibition in the threeridge mussel (Amblema plicata) by chlorpyrifos: implications for biomonitoring." Ecotoxicology and Environmental Safety 49.1 (2001): 91-98.

Edge, Katelyn J., Emma L. Johnston, Anthony C. Roach, Amy H. Ringwood. 2012. Indicators of environmental stress: cellular biomarkers and reproductive responses in the Sydney rock oyster (Saccostrea glomerata). Ecotoxicology 21: 1415-1425

Farrington, J. W., B. W. Tripp, S. Tanabe, A. Subramanian, J. L. Sericano, T. L. Wade, A. H. Knap. 2016. Edward D. Goldberg's proposal of "the Mussel Watch": reflections after 40 years. Mar. Poll. Bull. 110: 501–510

Fasulo, Salvatore, Francesco Iacono, Tiziana Cappello, Carmelo Corsaro, Maria Maisano, Alessia D'Agata, Alessia Giannetto, et al. 2012. "Metabolomic Investigation of Mytilus Galloprovincialis (Lamarck 1819) Caged in Aquatic Environments." Ecotoxicology and Environmental Safety 84 (October): 139–46. https://doi.org/10.1016/J.ECOENV.2012.07.001.

Galloway, T. S., R.J. Brown, M.A. Browne, A. Dissanayake, D. Lowe, M.B. Jones, M.H. Depledge. 2004. A multibiomarker approach to environmental assessment. Environ Sci Technol. 38: 1723-1731

Goulitquer, Sophie, Philippe Potin, and Thierry Tonon. 2012. Mass Spectrometry-Based Metabolomics to Elucidate Functions in Marine Organisms and Ecosystems. Marine Drugs. Vol. 10. https://doi.org/10.3390/md10040849.

Halliwell, Barry, and John M. C. Gutteridge. Free Radicals in Biology and Medicine. Oxford, Oxford University Press, 2007

Hameedi, M. J., W. E. Johnson and K. L. Kimbrough. 2006. Status of Contaminant Levels in Biota and Sediments of the St. Lucie Estuary. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 32. 40 pp. https://repository.library.noaa.gov/view/noaa/17798

Hameedi, M.J. (2005). Environmental indicators as performance measures for improving estuarine environmental quality, pp. 451-465, in: Bortone, S.A.; Estuarine indicators. CRC Marine Science Series. CRC Press: Boca Raton. ISBN 0-8493-2822-5. 531 pp.

Hameedi, M.J. "Toxicological Assessment of Environmental Conditions: The Role of Environmental Indicators. Proceedings of the Third Joint Meeting of the Coastal Environmental Science and Technology Panel of the United States-Japan Cooperative Program in Natural Resources, Yokusuka, Japan: 327-342 (2002)

Hameedi, M.J., A.S. Pait, and R.A. Warner "Environmental Contaminant Monitoring in the Gulf of Maine," a discussion paper presented at the Northeast Coastal Monitoring Summit, Durham, NH (December 2002) (published as part of a meeting proceedings)

Hameedi, M.J., 1997. Chapter 8: Strategy for Monitoring the Environment in the Coastal Zone, in: Coastal Zone Management Imperative for Maritime Developing Nations. Edited by B.U. Haq, Gunnar Kullenberg, Jan H. Stel. Kluwer Academic Publishers (Dordrecht/Boston/London) ISBN 0-7923-4765-X

Hines, Adam, Wai Ho Yeung, John Craft, Margaret Brown, Jill Kennedy, John Bignell, Grant D. Stentiford, and Mark R. Viant. 2007. "Comparison of Histological, Genetic, Metabolomics, and Lipid-Based Methods for Sex Determination in Marine Mussels." Analytical Biochemistry 369 (2): 175–86. https://doi.org/10.1016/j.ab.2007.06.008.

IOOS. Linking Elements of the Integrated Ocean Observing System (IOOS) With the Planned National Water Quality Monitoring Network Proceedings from the NOAA-Supported Workshop 19-21 September, 2005. Edited by: Peter M. Rowe; M. Jawed Hameedi, and Michael P. Weinstein. NOAA Technical Memorandum NOS NCCOS 48 https://repository.library.noaa.gov/view/noaa/2426

Jaruga P, Coskun E, Kimbrough K, Jacob A, Johnson WE, Dizdaroglu M: "Biomarkers of oxidatively induced DNA damage in dreissenid mussels: A genotoxicity assessment tool for the Laurentian Great Lakes". Environmental Toxicology, June 1, 2017;32:2144–2153. doi: 10.1002/tox.22427. (link)

Kwon, Yong-Kook, Young-Sang Jung, Jong-Chul Park, Jungju Seo, Man-Sik Choi, and Geum-Sook Hwang. 2012. “Characterizing the Effect of Heavy Metal Contamination on Marine Mussels Using Metabolomics.” Marine Pollution Bulletin 64 (9): 1874–79. https://doi.org/10.1016/J.MARPOLBUL.2012.06.012.

Lafontaine, Yves de, François Gagné, Christian Blaise, Georges Costan, Pierre Gagnon, and H.M. Chan. 2000. “Biomarkers in Zebra Mussels (Dreissena Polymorpha) for the Assessment and Monitoring of Water Quality of the St Lawrence River (Canada).” Aquatic Toxicology 50 (1–2): 51–71. https://doi.org/10.1016/S0166-445X(99)00094-6.

Leonard, Jeremy A., W. Gregory Cope, M. Christopher Barnhart, and Robert B. Bringolf. 2014. “Metabolomic, Behavioral, and Reproductive Effects of the Synthetic Estrogen 17 α-Ethinylestradiol on the Unionid Mussel Lampsilis Fasciola.” Aquatic Toxicology 150 (May): 103–16. https://doi.org/10.1016/J.AQUATOX.2014.03.004.

Lionetto, M. G., Caricato, R., Calisi, A., Giordano, M. E., & Schettino, T. 2013. Acetylcholinesterase as a biomarker in environmental and occupational medicine: new insights and future perspectives. BioMed research international, 2013: 8 pages

Markich, Scott J., and Ross A. Jeffree. 2019. “The Euryhaline Pygmy Mussel, Xenostrobus Securis, Is a Useful Biomonitor of Key Metal Contamination in the Highly Urbanised Sydney Estuary, Australia.” Environmental Pollution 252 (September): 813–24. https://doi.org/10.1016/J.ENVPOL.2019.05.131.

McCarthy, M.P., D. L. Carroll, A. H. Ringwood. 2013. Tissue specific responses of oysters, Crassostrea virginica, to silver nanoparticles. Aquat. Toxicol. 138–139: 123–128

NOAA Unmanned Systems. February 2020a.

https://nrc.noaa.gov/NOAA-Science-Technology-Focus-Areas.

NOAA Artificial Intelligence Strategy. February 2020b.

https://nrc.noaa.gov/NOAA-Science-Technology-Focus-Areas.

NOAA ‘Omics Strategy Strategic Application of Transformational Tools. February 2020c. https://nrc.noaa.gov/NOAA-Science-Technology-Focus-Areas.

Richards, R. Peter., David B. Baker, Jack W. Kramer, D. Ellen Ewing, 1996. Annual Loads of Herbicides in Lake Erie Tributaries of Michigan and Ohio, Journal of Great Lakes Research, Volume 22, Issue 2, Pages 414-428, ISSN 0380-1330, https://doi.org/10.1016/S0380-1330(96)70966-8. (http://www.sciencedirect.com/science/article/pii/S0380133096709668)

Ringwood, A. H. , M. J. Hameedi, R. F. Lee, M. Brouwer, E. C. Peters, G. I. Scott, S. N. Luoma, and R. T. DiGiulio. 1999. Bivalve biomarker workshop: overview and discussion group summaries. Biomarkers 4: 391-399.

Tsangaris, C., K. Kormas, E. Strogyloudi, I. Hatzianestis, C. Neofitou, B. Andral, and F. Galgani. 2010. “Multiple Biomarkers of Pollution Effects in Caged Mussels on the Greek Coastline.” Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology 151 (3): 369–78. https://doi.org/10.1016/J.CBPC.2009.12.009.

Tsangaris, C., I. Hatzianestis, V. A. Catsiki, K. K. Kormas, E. Strogyloudi, C. Neofitou, B. Andral, F. Galgani. 2011. Active biomonitoring in Greek coastal waters: Application of the integrated biomarker response index in relation to contaminant levels in caged mussels. Sci. Total Environ. 412–413: 359-365.

Watanabe, Miki, Kathryn A. Meyer, Tyler M. Jackson, Tracey B. Schock, W. Edward Johnson, and Daniel W. Bearden. 2015. “Application of NMR-Based Metabolomics for Environmental Assessment in the Great Lakes Using Zebra Mussel (Dreissena Polymorpha).” Metabolomics. http://dx.doi.org/10.1007/s11306-015-0789-4. https://repository.

library.noaa.gov/view/noaa/13686

VIII. Presentations

2020. Jaruga, P., Kimbrough, K., Jacob, A., Johnson, W.E. ”Contaminants Contributing to Oxidatively Induced DNA Damage of Exposed Dreissenid Mussels in the Detroit River”, SETAC SciCon, SETAC EUROPE 30th Annual Meeting, May 3-7, 2020.

2019 Legrand E., Bearden D.W., Casu, F., Hagiwara, K.A., Jacobs, A., Johnson, W.E., Schock, T.B. Biomonitoring in the Great Lakes by untargeted metabolomics of dreissenid mussels. 28th Annual Carolina SETAC Meeting, Mar. 13-15, Charleston, SC.

2019 Legrand E., Bearden D.W., Casu, F., Hagiwara, K.A., Edwards, M., Jacobs, A., Johnson, W.E., Schock, T.B. Biomonitoring in the Great Lakes by targeted and untargeted metabolomics of zebra mussels. 20th International Symposium on Pollutant Responses In Marine Organisms (PRIMO), May 19-22, Charleston, SC.

2018 Schock, T.B., Legrand, E., Casu, F., Watanabe, M., Hagiwara, K., Bearden, D.W. Davenport, E., Kimbrough, K., Jacob, A., Johnson, W.E. Considerations for Metabolomic Evaluation of Dreissenid Mussels as an Indicator of Aquatic Environments in the Great Lakes. 40th Annual SETAC North America Meeting, Nov 4-8, Sacremento, CA,.

2018. Jaruga, P., Coskun, E., Kimbrough, K., Jacob, A., Johnson, W.E., Dizdaroglu, M. “OXIDATIVELY-INDUCED DNA DAMAGE AS BIOINDICATOR FOR ENVIRONMENTAL GENOTOXICITY”, 4th International Congress on Occupational & Environmental Toxicology (ICOETox2108), 24 - 26 October 2018 in Matosinhos – Porto, Portugal, invited talk.

2018. Jaruga, P., Coskun, E., Kimbrough, K., Jacob, A., Johnson, W.E., Dizdaroglu, M., “The impact of environmental contaminants on aquatic life; measurement of biomarkers of oxidatively induced DNA damage in dreissenid mussels by GC-MS/MS”, Society of Environmental Toxicology and Chemistry North America 39th Annual Meeting, 4–8 November 2018, Sacramento, California, invited talk.

2018. T. Phan, T. Thomason, E. Johnson, A. Jacob, K. Kimbrough, A.H. Ringwood. Cellular Biomarker Responses of Freshwater Bivalves to Chlorpyrifos (SETAC, Sacramento, CA, November 2018).

2017. Jaruga, P., Coskun, E., Jacob, A., Kimbrough, K., Johnson, W.E., Dizdaroglu, M. “Oxidatively induced DNA damage in aquatic animals as a biomarker to evaluate the impact of environmental genotoxins”, 6th EU-US Conference on Repair of endogenous DNA damage, University of Udine, Italy, Sep 24th-28th 2017.

2016. Jaruga, P., Coskun, E., Jacob, A., Kimbrough, K., Johnson, W.E., Dizdaroglu, M. “Measurement of biomarkers of oxidative DNA damage in zebra mussels by GCMS/MS to evaluate the impact of environmental contaminants on aquatic life”, 21st INTERNATIONAL MASS SPECTROMETRY CONFERENCE, Toronto, Ontario, Canada, Aug 20–26, 2016.

2016. A.H. Ringwood, E. Johnson, A. Jacob, K. Kimbrough, M. Lowder, B. Khan, T. Gaspar, Dane Thomason, Tuan Phan.. Zebra Mussels as Bioindicators of Habitat Quality of the Great Lakes USA (SETAC, Orlando, FL, November 2016).

2015. M. Lowder, B. Khan, A. Jacob, K. Kimbrough, E. Johnson, A.H. Ringwood. Zebra Mussels (Dreissena polymorpha) as Bioindicators of Habitat Quality in the Great Lakes, USA (PRIMO18, Trondheim, Norway, May 2015).

Data Management Evolution

Kimani Kimbrough

Introduction

The Monitoring and Assessment Branch (MAB) data evolution goal is to mine data from all MAB studies and find patterns to gain chemical contaminant information not attainable at the site or programmatic level. As with all previous MAB monitoring and assessment initiatives, data management drives the effort along with concomitant data analysis techniques.

MAB data management changed from managing data by program to managing data by type (chemistry, organism health, ancillary measurements) irrespective of program, study, or collection date. This evolution results in the generation of larger data sets, as like measurements from all MAB programs, projects and studies are combined.

Enhancing MAB data management necessitated the use of new machine learning (ML) techniques. We highlight this relationship between data management and data analysis throughout the document and seek to convey the message that implementation of new analytical techniques that allow scientists to get more out of MAB data, are not possible without significant data management resources.

The MAB data evolution has been continuous throughout the history of the program, here we detail how the current initiative builds on past data management and analysis enhancements. For example,the MAB Mussel Watch Program (MWP) monitored the status and trends of contaminant for decades. From the beginning all MWP data was managed by data type, not by project or year. This was needed because the associated MWP analyses assessed trends in contamination. The MAB data management evolution can be thought of as an expansion of MWP data management techniques to the all MAB data. Cluster analysis and machine learning were used to find patterns in MWP data and Identify groups by concentration (low, medium, high). The MWP Great Lakes Restoration Initiative, built on MWP to include chemicals of emerging concern (CECs), and bivalve health (metabolomics, DNA damage). The evolving sampling design and analyses necessitated enhanced data management and enhanced analyses. As a result MWP began using ML for analysis to find patterns in the data in addition to statistics to test the data. In essence, a shift towards descriptive stats was made for the largest datasets.

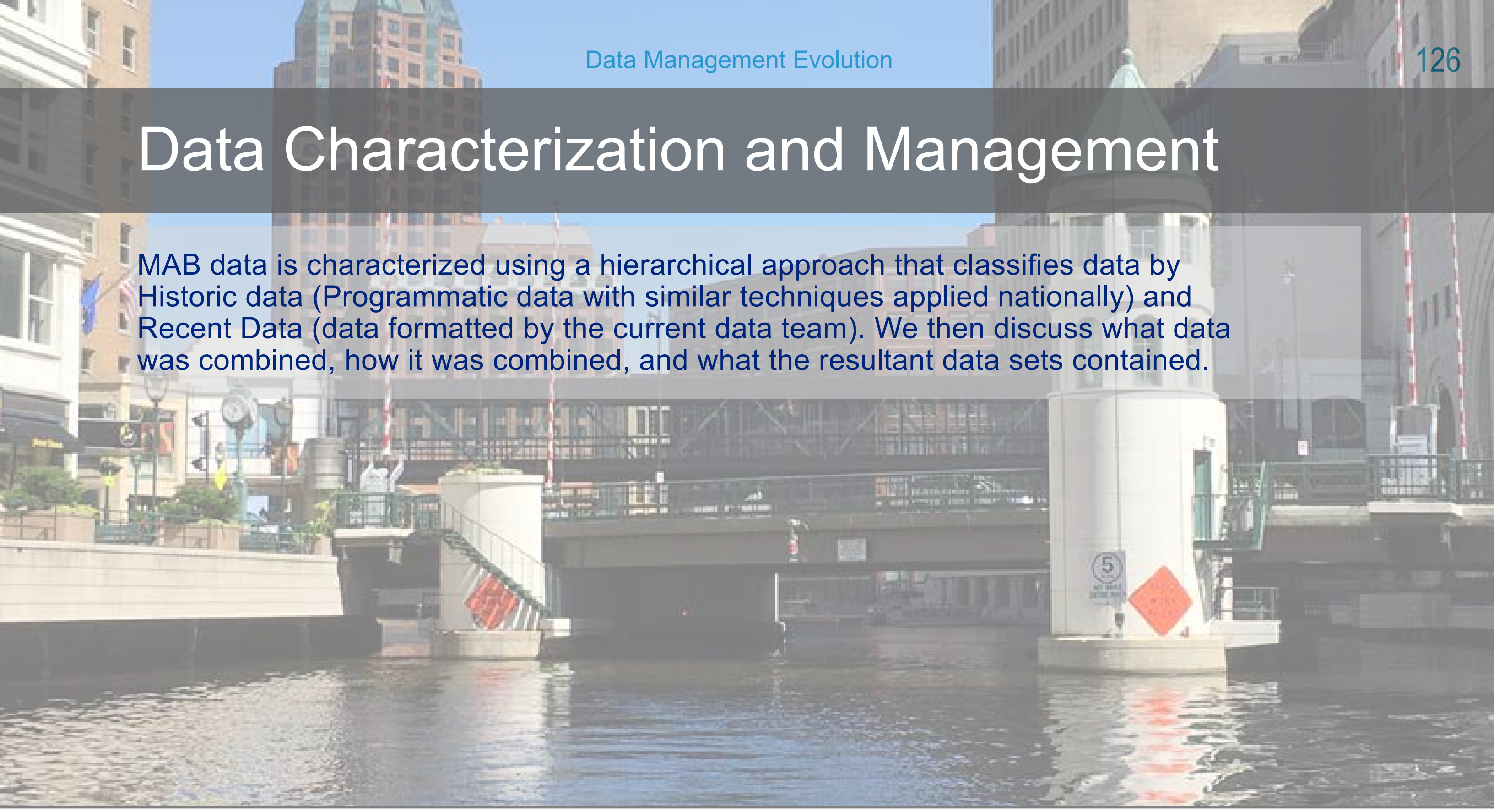
The current phase is combining national data for sediment from all programs in addition to smaller projects, building on earlier data and combining it with more recent data. These large data sets include data from large and small studies from around the Nation, derived from different programs, with different sampling methods. This data represents a gold mine of data with respect to spatial extent, but because they were not originally collected to be analyzed together, descriptive analysis techniques were need.

The evolution of MAB data management discussed in this document combines previous data management initiatives, and removes programmatic stovepipes, paving the way for advanced data analysis and automation. To understand data management evolution this document:

- Characterizes data at the programmatic level
- Highlights the relationship between data management and data analysis
- Provides representative case studies that detail analytical techniques.

Data Characterization and Management

MAB data is characterized using a hierarchical approach that classifies data by Historic data (Programmatic data with similar techniques applied nationally) and Recent Data (data formatted by the current data team). We then discuss what data was combined, how it was combined, and what the resultant data sets contained.



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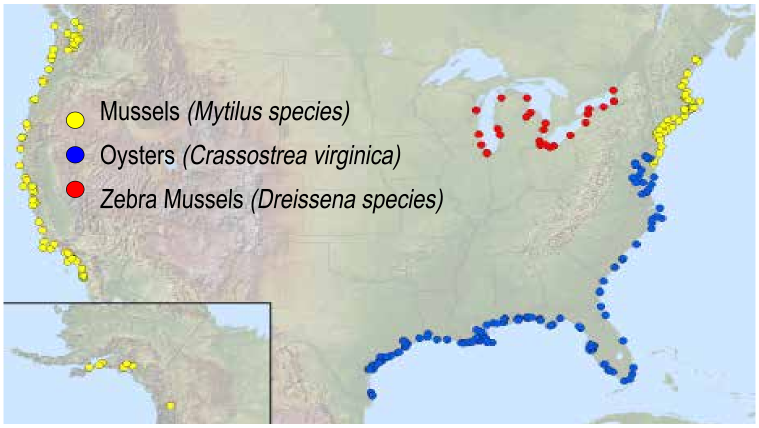

Figure 1. Distribution of oysters (Crassostrea virginica), mussels (Mytilus species), and zebra mussels (Dreissena species) collected and measured as part of the Mussel Watch Program.

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- Highlights the relationship between data management and data analysis, and
- Provides representative case studies that detail analytical techniques.

To make the discussion of MAB data more digestible, we break it up into historic data (data already formatted by previous data managers), recent data (data collected over approximately the past decade) and combined data (derived from historic and recent data). Ancillary, spatial and organism health data in recent years have added hundreds of new columns to each contaminant measurements which necessitates the use of new data management and statistical techniques at the study level and at the combined data level.

Historic data includes the Mussel Watch Program (MWP), the Bioeffects Program (BE), and Special Projects that all characterize the distribution of chemical contaminants in aquatic environments at different spatial scales. Method and results for the other programs, projects and initiatives are detailed elsewhere. Here we examine them from a data perspective including focusing on what data was combined, how was it analyzed and major findings. A few current initiatives are highlighted as examples of how the data has been used.

From a data management evolution perspective, this report is focused on data that can be combined and is derived from common methods (sediment and tissue). Data not common to multiple studies is not discussed.

The importance and relevance of this exercise was to develop spatially robust data sets to answer larger questions that site based studies cannot. By utilizing temporal and spatial data collected throughout the Nation we can better characterize spatial contaminant distribution and use the results to more efficiently model and assess new contaminants. This initiative also supports the NCCOS move to the cloud, and need to make data available to the public.

Historic data

MWP is a monitoring program that uses bivalves and sediment to assess the status and trends of contaminants nationally and regionally.
With respect to data management evolution the primary data used from the historic MWP are sediment and tissue measurements. Other long-term MWP data sets such as gonadal index and histopathology exist, but they are program specific and cannot be combined with other MAB data. MWP sampling design include, temporal and regional sampling, focused on baseline and background measurements. Early in MWP three duplicate samples were taken. Nationally bivalve and sediment samples were collected and analyzed primarily for contaminant assessment (legacy organics, trace elements, and later contaminants of emerging concern).

MWP has always managed data using a format that combined similar types of data, which is reflected in the national/regional reports. In the past, MWP used nominal sites because they continually sampled the same sites year after year. Historic MWP site locations were primarily limited to areas where *in situ* bivales were found. Caged mussels were not a major part of the historic MWP.

As a result of duplicate sampling in the early years, MWP provided data about spatial variability at a site. This is crucial to interpreting newer data where site replication is not performed. Collection of samples from nominal sites year after year allows for the characterization of temporal variability at each site.

With respect to bivalve sampling, three primary bivalve types were collected (Figure 1). This limits the bivalve data analysis to sub-national assessments based on the distribution of similar organisms. Sediment samples from all years and all geographic regions can be combined into one national data set for analysis.

For more than 20 years, Bioeffects (BE) focuses on place-based characterization of contaminants and toxicity using the sediment triad approach (sediment, sediment toxicity, and benthic infauna characterization). BE is national in scope and included studies in remote and highly impacted areas. In contrast to MWP, BE is a site characterization program that uses multiple strata to characterize contamination and impacts at a location. As a result, BE data is useful for assessing within location variability and adds a robust spatial component at each study location because it is not limited by species distribution. BE is a sediment based assessment program that shares a similar list of chemical contaminant analytes with MWP. The benthic infauna characterization and sediment toxicity data were not used as part of this data management evolution effort as they were specific to BE and cannot be combined with other MAB data sets. However, the opportunity exists to combine all of the BE studies and analyze the data together. At this time, the only BE data that is being combined with other MAB data is sediment chemistry data.

A combined vertical file with all BE data was not developed until the early 2000s. For most of its existence BE data was stored in a study based format and the reports reflect this. After being combined no characterization was completed that analyzed all of the BE data together.

Special Projects are those studies that were performed in response to disasters, oil spills and executive initiatives. Special Projects have historically been published as unique assessments and the data management was treated accordingly. In the early 2000s, all studies were combined into one data set. Special studies are included in the historic data section because they were primarily performed using methods derived from the MWP or BE program.

Recent data

Data collected over approximately the last decade is identified as recent, data here for discussion purposes and was created by the new data management team. During this period a higher percentage of data was generated from outside funding relative to base funding. As a result scientists generated data that addressed the needs of the stakeholder building on historic MAB methods and evolving to include new analyses and methods as needed. As with BE, many of the studies funded with outside monies focused on regional or place based assessments. As a result, data management change to accommodate programmatic changes associated with a move from consistent, program based analytical methods, to more dynamic study based methods used to generate the more recent data. It is a change from managing data in a consistent format to data with unique formats. For example, MAB studies began to utilize caged mussels and abiotic matrices as a significant part of sampling. Contaminants of emerging concern that included hundreds of new compounds from several different laboratories were introduced as a regular component of sampling. MWP changed sampling methods to a regional approach that does not solely rely on established sites. In addition to sampling changes more data was generated for each sample in the form of ancillary data.

Descriptive and analytical ancillary data for each sample and measurements adds columns to each site measurements and expands the dimension of our data sets, for some samples adding hundreds of new columns. Currently ancillary data includes environmental, spatial, and health data. Health analyses included metabolomics, bivalve health, cellular biomarkers and transcriptomics. Spatial data was generated that included relevant data such as social data, landcover, and population.

The additional analyses, changes in sampling design and introduction of ancillary data necessitated a change in data management techniques and the use of new analytical techniques at the program, regional, location and site levels. The evolution of sampling designs that generate exponentially more data, and the initiative to utilize combined data sets, increases the substantial resources needed to manage data for scientific analysis and release to the public.

As part of the data management evolution initiative:

- New data handling methods were developed (Azure cloud, Python/R).
- All recent data was formatted using python code to semi automate the procedure, include QA/QC information, and save in similar vertical formats.
- QA protocols were developed that flagged/ removed questionable observations and visualized data.
- Historic and recent data were combined using python to create large data sets for publications.

The new data evolution started approximately three years ago with a new data management team. Recent data is managed by laboratory analytical method, not by program as in the past. This was done for efficiency and to address a backlog of data and the different needs of the various data types (chemistry, bivalve health). To address this need a data handling document was developed (Figure 2). Python code was developed to format raw data into a vertical format that could be easily combined. Jupyter notebooks were used to format the recent data starting with raw excel files so all changes to the original data is documented. The data formatting effort consumed a significant amount of MAB resources. The data formatting update that captured addition QA data was used to accommodate partners who serve our data to the public that require QA data such as blanks and method detection limits that were not included in the historic data management.

Historic and recent data were combined using python to create large data sets for publications with decades of data including MAB MWP, BE, Special Projects and recent data. This was treated like a data mining initiative. The new combined data sets were used to enhance placed based assessments and also created a new branch of study for MAB solely focused on its analysis.

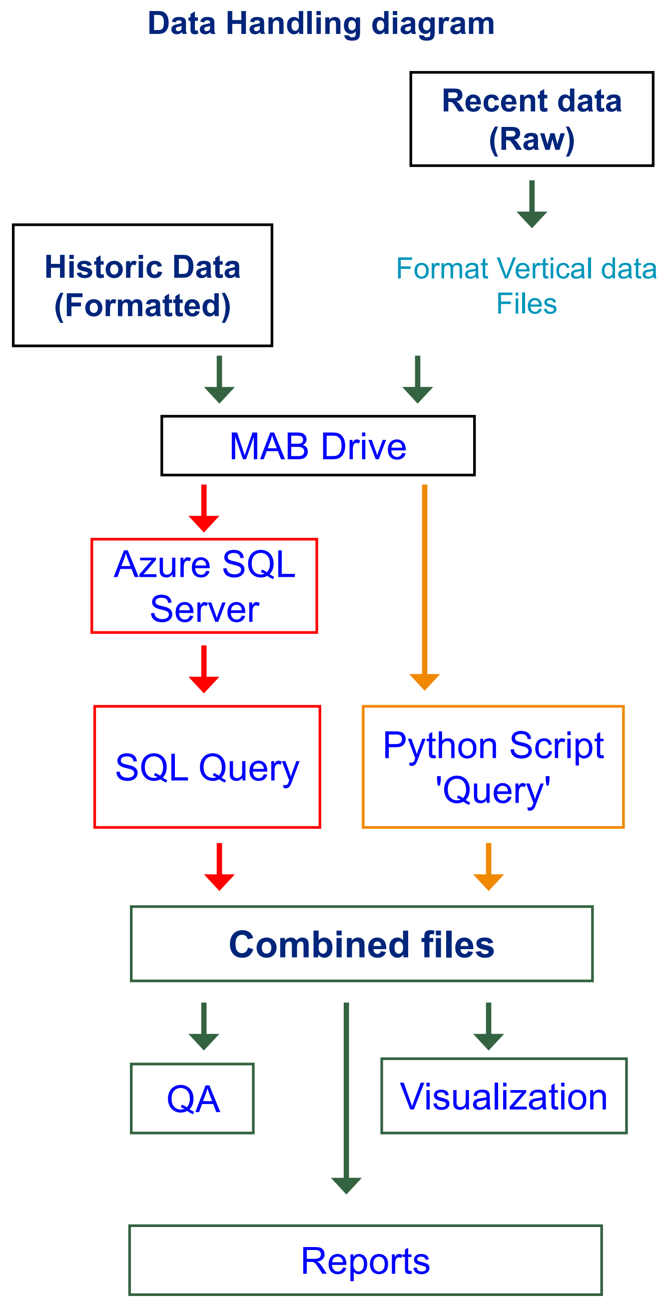

Figure 2. Green arrows represent the data flow now and in the future. Orange represent flow currently and red represents flow in the future. Bold writing represent data files.

Case studies

Case studies are used to highlight how the combined data sets are being used to enhance MAB studies and some of the new analytical techniques needed to produce results. Specifically, we provide case studies examples that include:

- Reference/baseline identification,
- Relative site comparison,
- National and regional contaminant characterization,
- Sample design improvement/prediction.

Case Studies: Data Characterization

Historic Mussel Watch sampled *in situ* bivalves nationally using different species. Due to the distribution and location of bivalves, historic data from MWP is a good measure of baseline and background measurements of contaminants in the U.S. In contrast, BE and Special Projects focused more on impacted areas of the Nation including estuaries, rivers, and responses to disasters. Assessment studies were not limited to those areas where bivalves can survive. The combination of all MAB data includes decades of impacted and baseline sediment measurements.

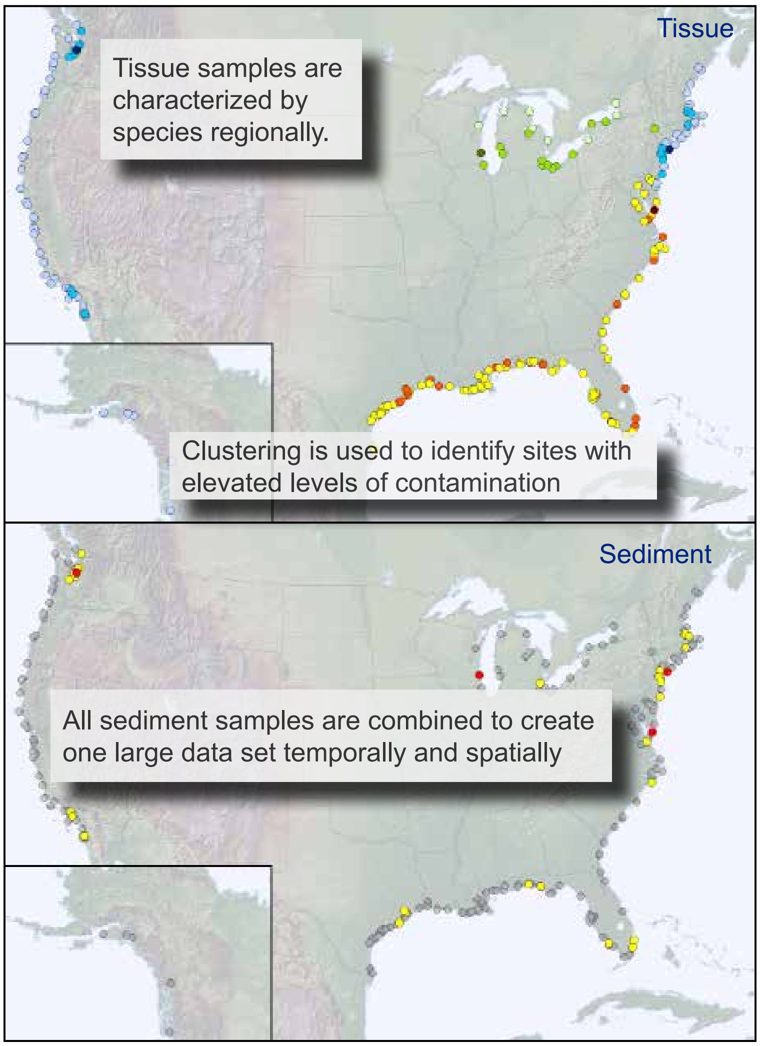

Figure 3 Tissue figure displays distribution of oysters, Crassostrea virginica (red/yellow); mussels, Mytilus species (blues); and zebra/quagga mussels, Dreissena species (greens) collected and measured as part of the Mussel Watch Program. Sediment figure displays high (red) and medium (yellow) clusters.

MWP has used relative concentration to bring perspective to data by employing cluster analysis to group tissue and sediment concentrations. Tissue samples are group by species while all sediment are analyzed together (Figure 3). Sediment contaminants have threshold levels used to identify impacts, but with bivalves the relative concentrations characterizations are more important because reliable threshold levels for do not exist for all contaminants. Clustering techniques were used to identify elevated levels of contamination and, where resources were available, conduct follow up studies to determine the cause or impacts of elevated contaminant concentrations.

In the Great Lakes the approximatly 25 original MWP monitoring sites were primarily located in the nearshore and in a few harbors because all sites used in situ mussels. Most of the original sites were asymptotic background sites with respect to PAH concentrations. As a result of funding from the Great Lakes Restoration Initiative (GLRI) additional *in situ* monitoring sites were added in impacted urban and agricultural watersheds for a total of 54 sites. The additional sites made for a more balanced sample design with respect to land use. In subsequent years GLRI funding allowed for the expanded use of caged mussels and a new focus on site based assessments (Figure 4). In the Great Lakes, study design permanently change from primarily *in situ* sampling to a balanced sample design to support prediction, baseline

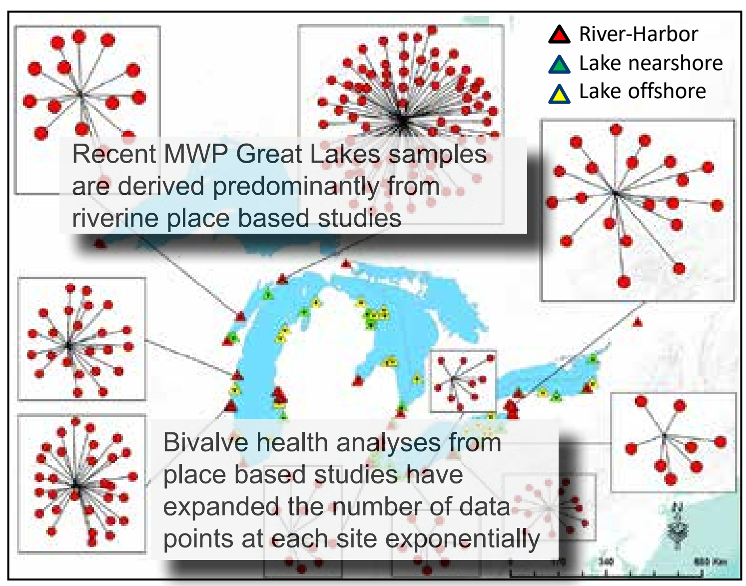

Figure 4. The original and expanded MWP monitoring sites are primarily found in nearshore (green, yellow) and the place based sites are found in the red call out boxes.

characterization, and reference site selection. The aformentioned study design change was used when planning sited based sampling and more importantly from year to year allowing the sample design to have a long-term temporal component. For example, an opportunity to collaborate with EPA was used to obtain offshore samples to identify reference/baseline measurements in deep offshore waters. Year to year planning has been used to fill gaps in our data set. For example, the year after Milwaukee, a highly urbanized location, was sampled, less impacted rivers in eastern Lake Michigan were sampled to bring balance to the Great Lakes data set. The data gap was identified as a result of using random forest to predict PAH concentrations. Specifically, the model predicted concentration at sites from the highest and lowest cluster with better accuracy than sites from the middle two clusters. As a result, we sampled more moderately impacted areas. In addition, the sampling seeks to balance sampling with respect to bivalve health measurements.

Currently, more samples generated from site based assessments than for long-term monitoring in the Great Lakes. In the Great Lakes the historic and recent tissue data was merged into a combined data set. The Great Lakes sediment data was merged into a national sediment PAH data set that will be discussed in another section of his document.

Data characterization

The new combined tissue data set was well balanced and contained samples from monitoring and place based assessments. For MWP and GLRI, density and box plots can be used to identify good reference sites (Figure 5). The first cluster includes nearshore and offshore sites and highlights baseline concentrations.

As more data was collected, more impacted areas were found and we addressed the need for water body specific characterizations (Figure 5). A box plot of all concentration cluster indicates that the highest concentration clusters have the most variability, as a result, sampling was changed to

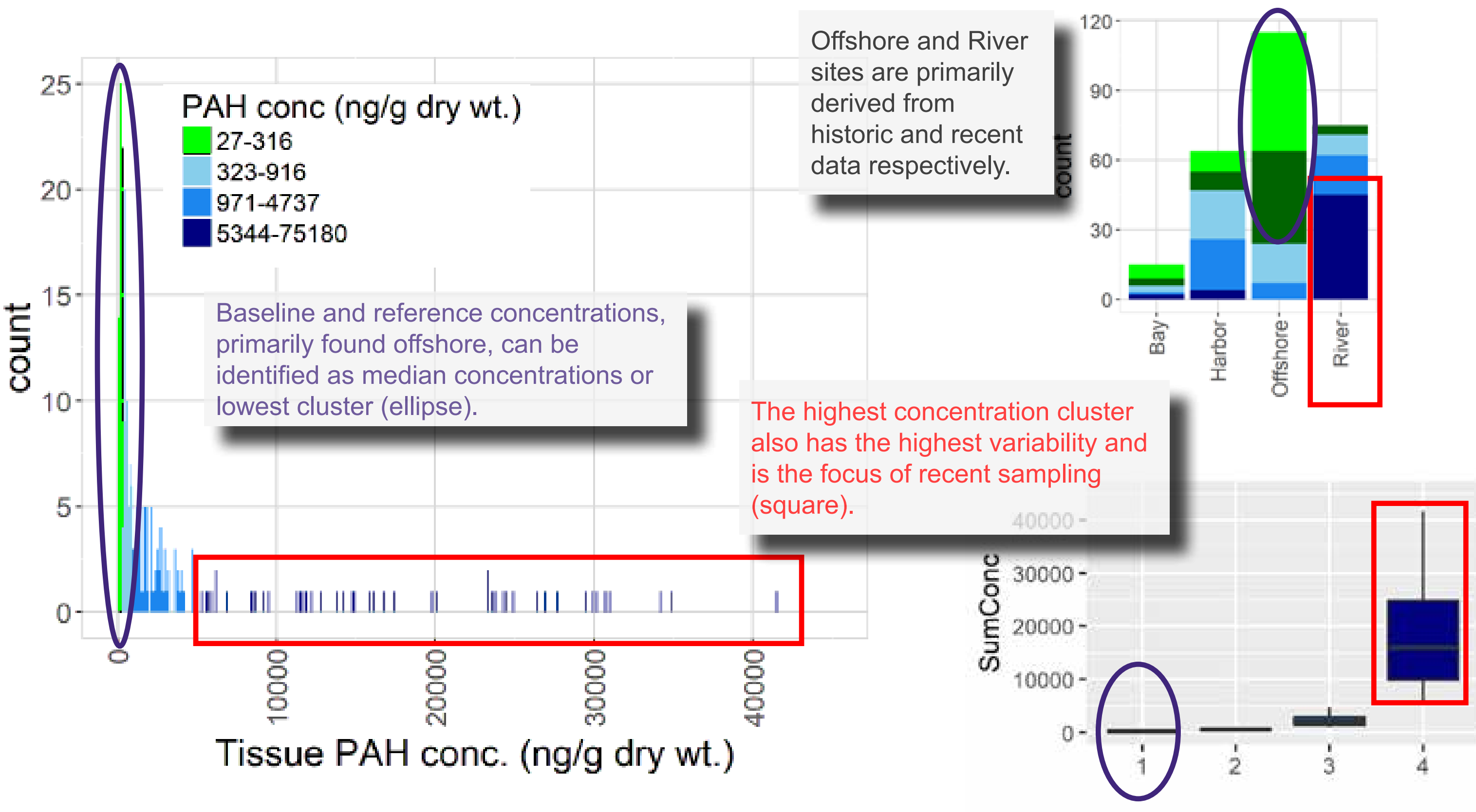

Figure 5. Spatial and graphical depiction of combined tissue PAH data for the Great Lakes basin (monitoring and place based data). Outliers were remove for better visualization. All figures except water body type use the same legend and represent the sum of 16 parent PAHs. The water body figure has an additional green cluster that further divides low concentrations and is presented to show the differences between River and Offshore sites.

focus more on impacted areas (early years of GLRI) that were predominantly found in rivers and harbors (Figure 5). In addition, fewer resources were used to sample offshore sites where the concentration range/variability was the lowest and where decades of monitoring data already existed.

Here we show how simple analyses can be used to characterize a combined data set for the entire Great Lakes basin through:

- Reference/baseline identification,
- Regional contaminant characterization,
- Sample design improvement.

Machine learning techniques were implement for more complex tasks of fingerprinting and prediction using this data. These techniques will be discussed later in this report.

Case Studies: Relative Site Comparisons

As part of the site comparison section we use larger data for comparison to a smaller place based study or regional summary. This type of analysis was first used for MWP. Subsequently, it has been used for placed based assessments to bring perspective. For example, when characterizing a location(region, estuary) significant differences in concentration may be found between sites within a study. Comparisons to the MAB combined data sets bring another dimension to the location based comparison. Studies from Alaska and Milwaukee are use d to highlight the relevance of this technique.

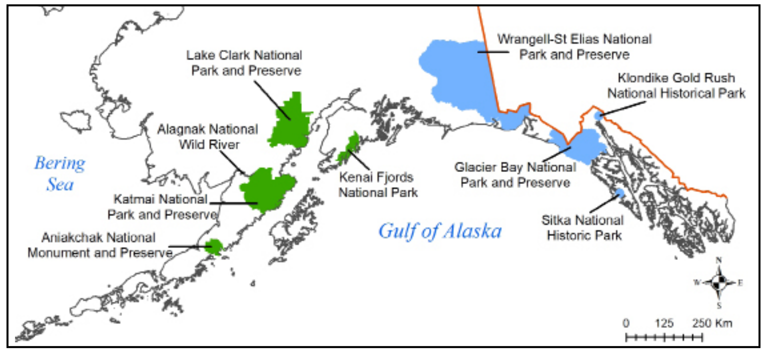

Figure 6. Alaska study site.

As part of a resent Alaska report that summarized mussel concentrations from the Gulf of Alaska (Figure 6), heat maps were used to depict concentrations clusters for study data and compare the data to concentration clusters derived from a larger National Status and trends (NS&T/MAB) data set (Figure 7). Both study and NS&T/MAB depictions of the same data with different clusters are useful and provide different information. For example, the high Mercury measurement from the Alaska summary are low in the national comparison to NS&T/MAB data, while the opposite is true for Cadmium and Copper. The organic compounds Total Butyltins -Total PCBs comparison between the Alaska summary and National comparison provide unique results. For example, many of the organic MWP organic compounds are elevated (high, medium) in the Alaska Summary, however, none are elevated in the national comparison.

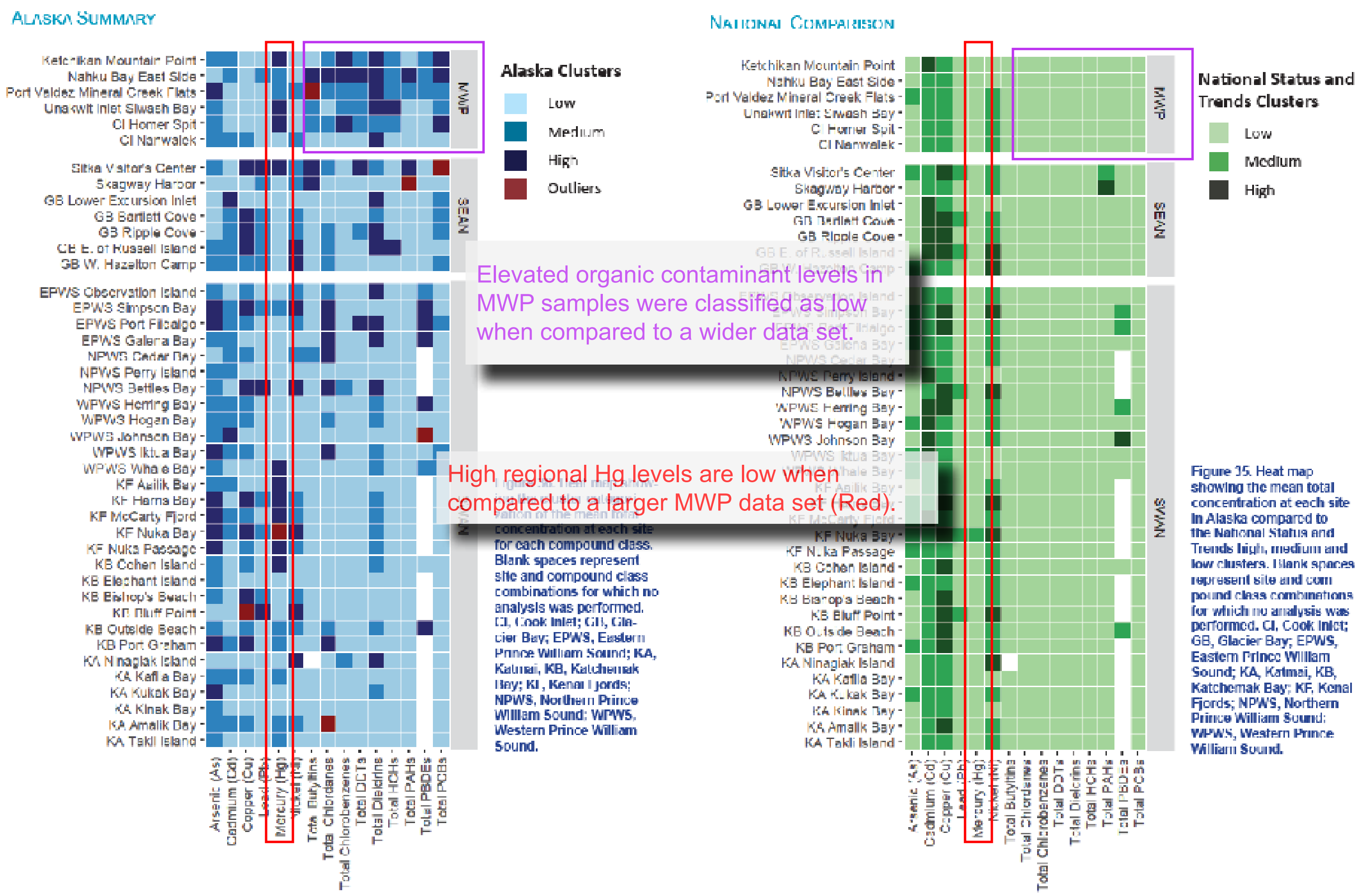

Figure 7. Results from an upcoming MWP Alaska report show the relevance of using historic data from a national data set to compare with study based characterizations. The heat maps are results for mussel body burden clusters.

Case Studies: Machine Learning

Both characterizations are needed to thoroughly characterize the study sites.

The recent data has more variables than historic data resulting in a need to use different analysis techniques. Polycyclic aromatic hydrocarbons are a suite of hundreds of organic compounds that are formed primarily through the incomplete combustion of fossil fuel and in oil and have been measured by all MAB programs and most initiatives. PAHs are one of the most analyzed MAB contaminants. Due to the wealth of MAB data, PAHs were the first analysis machine learning was used to generate new knowledge from our combined data set. Specifically, Random Forest was used to characterize multivariate data sets and for prediction.

The largest data set generated so far is the sediment PAH data set that includes concentration results for more than three decades from MWP, BE, Special Studies, GLRI, and place based studies (Figure 8). As part of a intra-NCCOS MSE-MAB collaboration, researchers were funded to build contaminant prediction model using ML. Ancillary spatial data was generated for all combined data sites and used for predicting where the most elevated concentration levels were found. By combining spatial and contaminant data, dozens of addition columns were added to the combined sediment and Great Lakes tissue data sets.

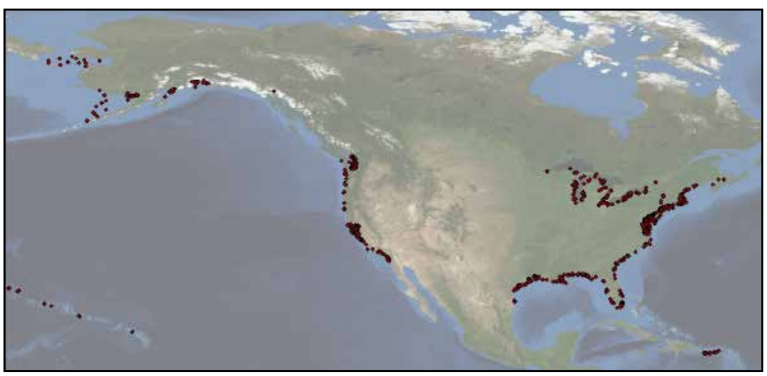

Figure 8. Map of National MAB sediment sites.

The large combined data set was not set up to be tested and there is no sample design. Hence, ML is used to find patterns in the data. Spatial data allows for prediction of contaminant concentrations based on land cover, population and other land based measurements. As discussed earlier, the Random Forest ML model predicted concentrations at sites from the highest and lowest cluster with better accuracy than sites from the middle two clusters.

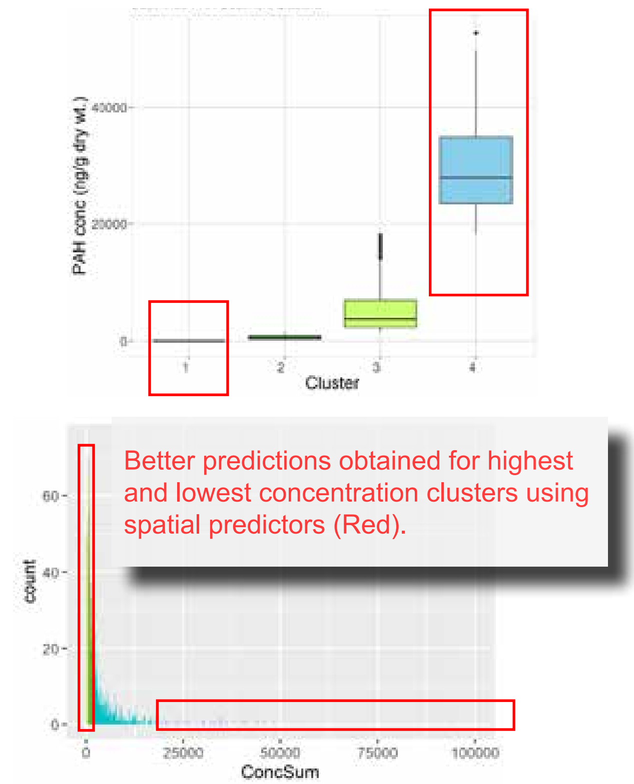

Figure 8. Concentration ranges for sum of 16 parent PAHs range from 0 - 10^6 (ng/g dry weight sediment). Several outliers have been removed for better visualization of the data.

A Quantitative Adverse Outcome Pathways (qAOP) Process and its Role in Monitoring and Assessment of Biological Stress in Compromised Environments

Erik Davenport

Felipe Arzayus

Summary

As the number and complexity of environmental contaminants increase, our ability to monitor and assess their impact via traditional methods becomes less efficient or cost-effective. In addition, the accuracy and precision of an increasingly broad number of chemical analyses confounds their potential use as management tools (timeliness and reproducibility). With the advent of genomic tools that look at the biological stress – and the organismal response resulting from exposure to contaminants, a new contaminant monitoring paradigm is beginning to form – rather than looking at an increasing portfolio of standard contaminants for every tissue, sediment and water sampled to develop contaminant trends, use organismal response (genes and phenotypes) to pinpoint contaminant types and mixtures, and use acuteness of stress as a proxy for contaminant concentration. This is a nascent use of these technologies, and the proposed development of a qAOP, will take us a few steps closer to operationalize this new paradigm by using a collection of metabolomics and transcriptomics data and information from Mussel Watch bivalve organisms. We will use these information for the development of a computational model focused on applied monitoring and assessment of biological stress in compromised environments.

qAOP development Rationale

As the field of 'omics research advances, the potential uses and products resulting from these new tools continuous to grow at unprecedented levels, bringing with it an ever-larger amount of data and information that allow us to go well beyond the traditional LC50 studies and into a more comprehensive 'health' assessment of individual organisms within an ecosystem context.

SDI's Monitoring & Assessment Branch (MAB), through its Federal participation with the Great Lakes Restoration Initiative (GLRI), has utilized the standard National Mussel Watch protocol to assess the concentration of a standard set of contaminants in bivalve mollusks (mussels and oysters) and sediments in the Great Lakes waters to monitor bivalve health and by extension the health of their local and regional environment. In addition to following this protocol, MAB increased the number of survey sites and expanded the chemical analyses performed on bivalve tissues in an effort to identify sites where these organisms show signs of contaminant-derived stress. Some of these added analyses included: DNA damage, GSH, lipid peroxidase, and metabolomics data.

Eco-Metabolomics is the application of metabolomic techniques to ecology to characterize biochemical impacts on organisms resulting from environmental perturbations across different spatial and temporal scales. Metabolomics and chemical body burden data collected by MAB from caged zebra mussels at sites upstream and downstream (fig. 1A) of a wastewater treatment plant in the Maumee river found site associated differences in their metabolomes. A list of metabolites with significantly different concentrations among sites were submitted to the KEGG metabolomics pathway database (https://www.genome.jp/kegg/kegg1.html), which identified multiple biochemical pathways possibly impacted (fig. 1C and 1D) by the Maumee river contaminants.

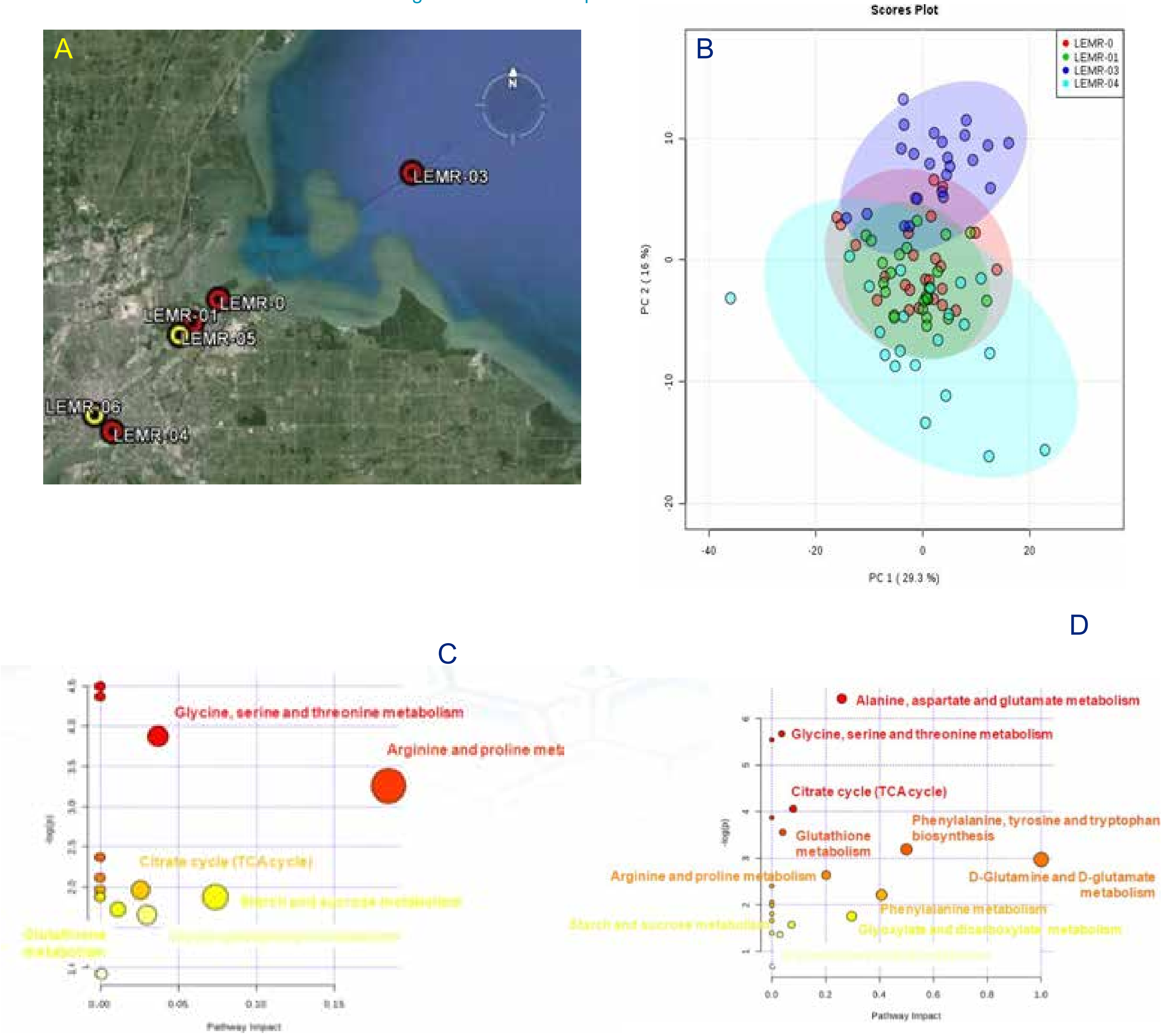

Figure 1. The metabolomes of mussels collected from sites in the Maumee River (A) show their greatest differences at LEMR- 03 and LEMR-04 (B). In addition, significant differences in metabolite concentrations between LEMR-03 vs. LEMR-01 (C) and LEMR-03 vs LEMR-04 (D) were associated with multiple metabolic pathways

While metabolomics identify possible impacted pathways by flagging the up/down regulation of a set of genes, adding transcriptomics – or the ability to determine the different states of a gene, and how many phenotypes are present/absent, enables a higher level of detail by describing key biochemical events that identify a unique pathway. This information can then be used to determine a source of potential adverse health impacts. The incorporation of molecular-level measurements (i.e., metabolomics and transcriptomics) and associated environmental chemical perturbations into an ecological assessment is challenging. The Adverse Outcome Pathway (AOP) is a conceptual framework that enables evaluation of several biologically plausible and empirically supported links between different levels of the biological organization, including molecular and biochemical measurements (Ankley et al., 2010; Villeneuve et al., 2014a). A quantitative adverse outcome pathway (qAOP) enables the linkage between a chemical perturbation within the environment and the biochemical pathways of the organisms.

From the stakeholder perspective, the addition of this toolset to NCCOS and SDI includes new information that would potentially reduce the number of sites, and frequency of sampling as the source of stress – that is, the types and classes of contaminants will be known from the number of gene expressions, and the rate of stress will serve as a proxy for contaminant loads and concentration, for example. The advantages of using a qAOP approach include: 1) a qAOP requires a fundamental need to quantify differences between 'no adverse' and 'adverse' outcomes pathways; and 2) qAOPs integrates exposure models to inform dose-response assessment (fig 2).

We are developing a multi- year effort that leverages resources across SDI toward the development a qAOP that will provide a tool for ecological health assessment (EHA). The purpose for development of the qAOP is the application of a framework that will enhance Mussel Watch monitoring with a tool for assessing health impacts to bivalves. This year's effort is to ensure that transcriptomics and metabolomics patterns are consistent by extracting transcriptomics from samples collected during the GLRI studies in 2016 (Maumee River) and 2018 (Muskegon) and compare it with metabolomics and body burden chemistry currently being analyzed. Preliminary results from the analysis of select number of Contaminants of Emerging Concerns (CEC) with the metabolomes of zebra mussels in the 2016 Maumee River study suggest that the metabolome patterns maybe associated with specific chemical contaminants. If the transcriptome is consistent with the metabolome, it will tell us more specific details about the state of 'health' for the zebra mussel populations in the Maumee River and Muskegon sites.

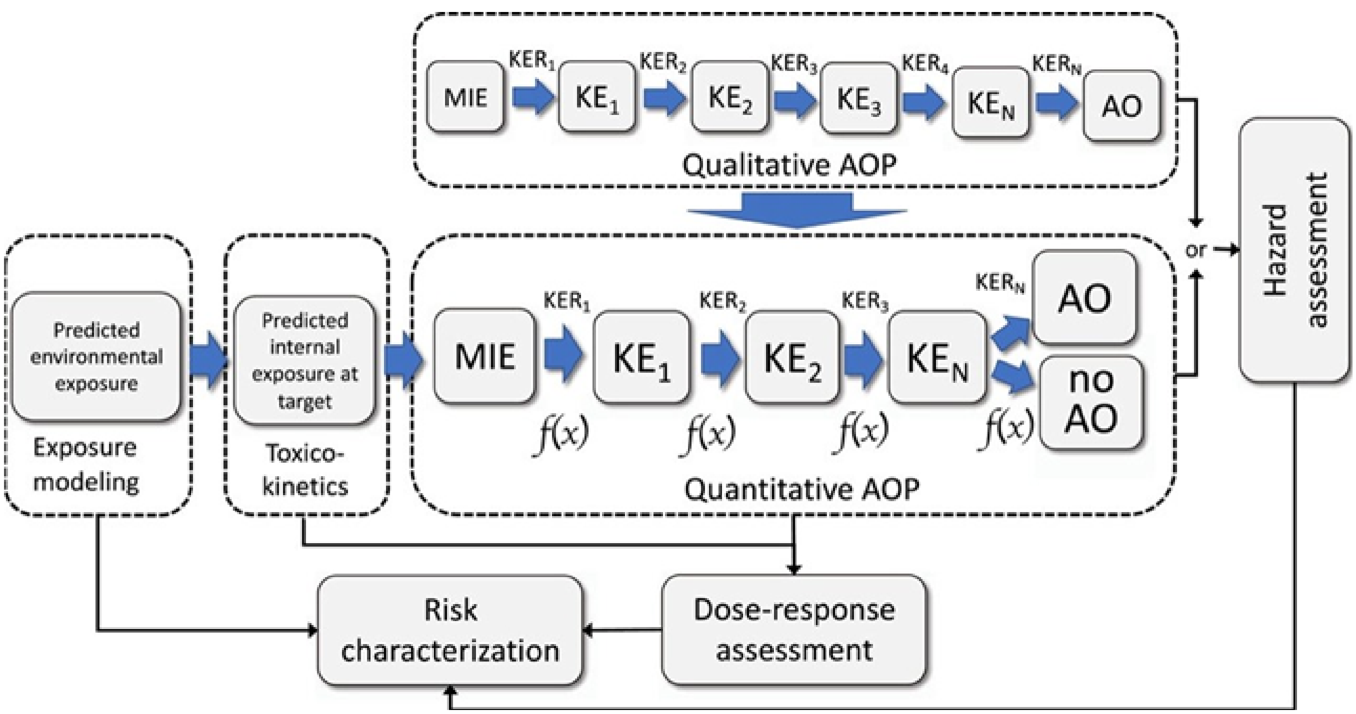

Figure 2. Conceptual diagram of the qualitative AOP vs quantitative qAOP from Perkins et al. 2019

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