NATIONAL STATUS AND TRENDS, MUSSEL WATCH PROGRAM

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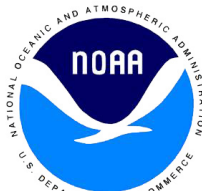
NOAA Technical Memorandum NOS NCCOS 240

An oyster bed in Charleston Harbor, SC.

A Message from the Mussel Watch Program

NOAA's National Status and Trends' (NS&T) Mussel Watch Program has been in operation since 1986, when it was designed to monitor the status and trends of a broad suite of chemical contaminants at sites that represent large coastal areas in order to construct a nationwide assessment. Of the Program's analyte list, there are some legacy compounds that have been banned and whose concetrations have declined over time, while others persist. At the same time, there are new chemicals entering the environment every year and there is often a lack of comprehensive information describing the sources, distribution, persistence, and potential effects of these contaminants of emerging concern (CECs). Previous efforts by NS&T in assessing CECs have been limited to localized studies and only a few classes of emerging contaminants. In 2006, NS&T collaborated with local scientists and stakeholders to conduct a survey of the occurrence of human use pharmaceuticals in the Chesapeake Bay, Biscayne Bay, and the Gulf of Farallones (Pait et al. 2006). Other CEC focused efforts to date include a nationwide Mussel Watch Program assessment of polybrominated diphyenyl ethers in 2009, and a regional CEC characterization led by the Southern California Coastal Water Research Project in 2011.

Mussel Watch is now conducting additional pilot work in other regions of the United States, in order to assess CEC classes for potential inclusion into the national monitoring program. These pilot studies are regional in nature, balancing short-term flexibility in study design against the cost of broad CEC surveys. We tested multiple bivalve species and sediment samples for accumulation of flame retardants, stain resistant compounds, pharmaceutical and personal care products, endocrine-disrupting chemicals, and multi-residue pesticides and industrial chemicals. Our 2014-15 effort was a retrospective analysis of dreissenid (zebra/quagga) mussels collected from other NCCOS studies in our ongoing work under the Great Lakes Restoration Initiative (Kimbrough et al. 2018). In 2015, we had two case studies; a survey of natural oyster beds in a range of land use types around Charleston, SC and a Chesapeake Bay survey which utilized a combination of traditional Mussel Watch sites and caged oyster deployments to target land use and wastewater outfalls.

We conducted a regional assessment of blue mussels in the Gulf of Maine in 2016, combining traditional Mussel Watch sites with those of the GulfWatch Program. Combined with the previous work in California, these pilot studies represent the range of bivalve species and land use types surveyed in the national Mussel Watch Program.

ABSTRACT:

NOAA's National Status and Trends (NS&T) Mussel Watch Program conducted regional pilot studies to assess the magnitude and distribution of contaminants of emerging concern (CEC) in shellfish and sediment from different coastal zones. In 2015, oyster and surficial sediment samples from study areas in the Chesapeake Bay, Maryland, and Charleston Harbor, South Carolina were assessed for CECs, such as pharmaceutical and personal care products (PPCPs), current use pesticides, flame retardants, new industrial chemicals, stain resistant compounds, and endocrine-disrupting chemicals. Results indicated that CECs are being accumulated at various degrees in coastal resources and the environment. Classes of CECs most frequently detected in oyster tissues and sediments from both study areas were the perfluorinated compounds (PFCs), the flame retardants (polybrominated diphenyl ethers; PBDEs), and current use pesticides. In the Chesapeake Bay, at least one PFC and PBDE flame retardant was detected in all sediment samples. In Chesapeake Bay sediment samples, PFCs 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 PFCs 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 (PFCs) 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). Overall occurrence and 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.

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ABOUT THIS DOCUMENT

The goal of this document is to provide a summary of findings from two NCCOS Mussel Watch pilot studies which assessed contaminants of emerging concern (CECs) in 2015 in Chesapeake Bay, Maryland and the Charleston Harbor estuary, South Carolina. The document is organized into five chapters that introduce and explain the rationale, procedures, design, and findings of the studies. Chapter 1 presents introductory materials that provide background information on NCCOS' National Status and Trends' Mussel Watch Program, the study areas, as well as some general information about the environmental fate and transport of CECs measured. Chapter 2 offers a summary of all the results from both Maryland (MD) and South Carolina (SC) studies in order to provide a study-wide perspective of what CECs were found and how often they were detected. Chapter 3 provides information on standard methodologies used by the NCCOS Mussel Watch Program for sample collection as well as the analytical procedures for measured CECs. Chapters 4 and 5 present detailed information and results specific to the MD and SC pilot studies, respectively. These include specific descriptions of the study areas, detailed study design, and concentrations for those CECs that were detected.

Although this report is a summary of the two CEC pilot studies, the results from each study are intended to stand alone. Therefore, some segments of the text have been intentionally repeated in different chapters throughout the document as a way to assist readers and resource managers in preserving the specifics of each study.

Residential development along estuarine shoreline. Photo Credit: NOAA

CHAPTER 1: INTRODUCTION

Since 1986, the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program (MWP) has monitored the nation's coastal waters for chemical contaminants and biological indicators of water quality. With the goal to support ecosystem management nationwide, the MWP and its sister program the National Bioeffects Program, conduct environmental monitoring, assessment, and research to describe the status and trends in the environmental quality of the nation's estuarine and coastal waters. The MWP utilizes a sentinel-based approach to monitoring, by collecting and analyzing sediment and bivalves (oysters and mussels) as surrogates for water pollution and bioaccumulation. The scope of the MWP is nationwide, with monitoring in coastal zones around the US, including the Great Lakes, and in territories such as Puerto Rico. Contaminants monitored by the program include legacy organic chemicals, such as organochlorine pesticides (e.g. DDT), industrial contaminants (e.g. polychlorinated biphenyls), fossil fuel combustion byproducts (e.g. polycyclic aromatic hydrocarbons), and metals (e.g. mercury). However, in response to recent public concerns (Daughton 2004, Sauve and Desrosiers 2014) about the widespread distribution and potential impacts of contaminants of emerging concerns (CECs), NCCOS and the MWP have invested resources directed at the assessment of a suite of CEC compounds for long term monitoring consideration.

The US EPA has loosely defined CECs as pollutants that are not currently regulated nor monitored as part of routine monitoring programs (Ankley et al. 2008). Based on EPA recommendations described by Ankley et al. (2008), classes of CECs to consider for monitoring should include: 1) Persistent organic pollutants (POPs) such as flame retardants, multi-residue pesticides and industrial by-products, 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, 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. Traditionally the list of chemical contaminants to consider for long-term monitoring would be based on factors such as bioaccumulation potential, environmental half-life, biodegration, ecotoxicity and human health information. Many of these factors are poorly understood when it comes to CECs. Other challenges faced by monitoring programs when considering whether or not to include CECs involve the large number of new compounds that are continuously entering the environment from diverse sources, the lack of knowledge about their environmental fate, and most importantly, the lack of adequate analytical methods to measure them in environmental media. NCCOS and MWP are assessing a list of CECs that include classes of chemicals for which some information about health effects is known and analytical methods are available. This list includes compounds that serve as flame retardants, stain resistant compounds, pharmaceutical and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and multi-residue pesticides and industrial by-products (MRES).

The interest of NCCOS in assessing contaminants of emerging concerns (CECs) in the US coastal zone dates back to 2005 when public concerns about the distribution, magnitude and potential effects of these new contaminants were identified. In 2006, NCCOS scientists from the National Status and Trends (NS&T) program worked with local and regional scientists and stakeholders to conduct a survey detailing the occurrence of human use pharmaceuticals in the Chesapeake Bay, Biscayne Bay, and the Gulf of Farallones. That study addressed both local and NS&T needs and showed evidence of a downstream gradient of some pharmaceuticals in the estuarine environments of the study areas (Pait et al. 2006). Additionally, NCCOS scientists conducted a national assessment of the magnitude and distribution of polybrominated diphenyl ethers (PBDEs), a class of potentially toxic flame retardant chemicals, in 2009. Using archived MWP sediment and bivalve samples, the study found PBDE flame retardants to be ubiquitous in the coastal and estuarine environment and that their distribution could be linked to human population centers (Kimbrough 2009). Prompted by stakeholder interest, the MWP collaborated in a multiagency pilot project with the Southern California Coastal Water Research Project (SCCWRP) to conduct a CEC assessment along the California coast in 2011. Multiple classes of CEC compounds were evaluated in a variety of matrices (sediment, water, fish and bivalve tissues) from the Southern California Bight. During that project, a broad scan of diverse classes of CECs (PPCPs, MRES contaminants,

phenolic and flame retardant compounds) were evaluated. These pioneering collaborative studies provided insight about the distribution and concentrations of CECs in different environmental media (Dodder et al. 2014, Maruya et al. 2016). Although many of the surveyed CECs were infrequently detected, perhaps as a result of their individual chemical properties, the concentrations of those that were detected increased with urbanization and proximity to storm water discharge outfalls (Maruya et al. 2016). The outcome of these NCCOS CEC studies along with recommendations from Bricker et al. (2014) and Maruya et al. (2016) helped inform future MWP CEC efforts. These recommendations included development of a list of matrix-specific CEC compounds for consideration in coastal monitoring programs based on their occurrence, availability of contaminant data, and robust analytical methods (Anderson et al. 2012, Bricker et al. 2014, Dodder et al. 2014). Scientists advocated for more research assessing CEC fate and transport, bioeffects and bioanalytical screening tool in order to fill data gaps and gain a better understanding of the distribution and risk associated with CECs in the environment (Anderson et al. 2012).

The current aim of the national MWP is to provide actionable information to stakeholders and the scientific community while improving its monitoring approach by incorporating knowledge gained and lessons learned from these previous studies. 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. Beginning in 2013, NCCOS undertook the task of re-designing the MWP to focus on a rotating regional model. Because the geography of the coastal zone around the US presents specific challenges and the resident bivalve species (oyster and mussel) used by the MWP as sentinel organisms differ by region, the MWP initiated pilot studies in different coastal areas in order to build a capacity focused on a more robust regional monitoring effort. Recommendations from the California Bight Pilot Project served as guidance for the MWP in initiating a series of regional assessments using a variety of bivalve species to gain regional insight into the prevalence and magnitude of contaminants. The first of these studies was the assessment of CECs in the Great Lakes. The Great Lakes CEC study, initiated in 2014 as part of an ongoing Great Lakes basin-wide ecosystem health characterization, focused on the potential accumulation of CECs in zebra mussels (*Dreissena polymorpha*). The Great Lakes study included a broad scan of CECs in addition to a toxicity biomarkers assessment in caged and wild zebra mussels (Kimbrough et al. 2018).

This Study

Using the MWP's regional design paradigm initiated with the MWP effort in the Great Lakes, the current studies in Chesapeake Bay, MD and Charleston Harbor, SC in 2015 focused on the oyster, *Crassostrea virginica*. Based on lessons learned from the Great Lakes study, the MWP was able to develop a study design using both caged and wild (in Maryland) and wild only (in South Carolina) oysters as well as sediments in order to describe possible land use influence on the occurrence and distribution of CECs.

The Chesapeake Bay and Charleston Harbor estuaries were selected as the study areas for this CEC study because they represent estuarine environments with different land use types, both for sites within this study and compared to the study areas in the Great Lakes, and also because the study design offered opportunities to leverage resources and build stronger collaborations within NCCOS, as well as state and local resource managers in Maryland and South Carolina. 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. The common objectives of both studies were to: 1) assess the distribution of flame retardants, chemicals that enhance stain-resistance, multi-residue (MRES) 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.

In order to address the goals listed above, build upon the Great Lakes study and expand our understanding of the fate and transport of CECs in different coastal regions, this report discusses the prevalence, frequency of detection in both sediment and tissue, as well as occurrence relatively to land-use categories.

Layout of the Results

The results in this document are presented in three sections. Chapter 2 presents the combined dataset in order to evaluate the overall occurrence of the CECs measured in both the Chesapeake Bay and South Carolina studies. It is important for the reader to remember that the MD study was focused on deployed, caged oysters, while the SC study was able to collect natural populations of oysters at each site. The data are presented by class and matrix as distribution maps of presence (BLUE) and absence (GREY) of the compounds measured at a given site. The frequency of detection (or occurrence) is then presented in tabular format for each CEC class and matrix, with the sites organized by study (Maryland and South Carolina).

Chapters 4 and 5 then describe each regional study design in detail, noting the occurrence and concentrations of CECs measured in both sediment and oyster tissues by general land use classifications. The assignment of land use classifications to sampling areas was based on dominant land use characteristics in the surrounding watersheds, but is only a general classification. Concentrations are reported for sediments in nanogram per gram (ng/g) dry mass (parts per billion; ppb) and for oyster as picogram per gram (pg/g) wet mass (parts per trillion; ppt). Historically, chemical concentrations in bivalve tissue have been reported by the MWP as dry weight fractions (nanograms of chemical per gram of dry tissue) (Lauenstein and Cantillo 1993). However, in this document we chose to report concentrations of contaminants in tissue based on wet weight fractions (picograms of chemical per gram of wet tissue). This allows an easier comparison of findings from this report and a concurrent sampling effort by NOAA in the Great Lakes. Appendix B provides information on how wet weight values could be converted into dry weight values.

It is important for the reader to understand that the notations of presence or absence (Chapter 2) or reported concentrations (Chapters 4 and 5) do not represent a measure of hazard or risk. The number of studies reporting data for CECs is limited (although becoming more common) and there are currently no US regulatory or environmental criteria or guidelines that offer thresholds of risk.

View of marinas lining the Severn River, Chesapeake Bay.

Photo Credit: NOAA

CHAPTER 2: STUDY-WIDE SUMMARY

This chapter provides a study-wide summary of findings for both the Maryland and South Carolina CEC studies. Maps of the study areas (Figures 2.1a and 2.1b) identify the sampling locations (Table 2.1) followed by a brief description of the chemical classes, and CEC results in sediment and oyster tissue. The results in this chapter include illustrations identifying where each analyte was detected among the survey sites in MD and SC, as well as the overall frequency of detection based on the combined total sites from both study areas. Details about the two pilot studies in Chesapeake Bay, MD and Charleston Harbor, SC, including study design, concentration and distribution of detected compounds relative to land use, are summarized in Chapters 4 and 5.

Table 2.1. 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
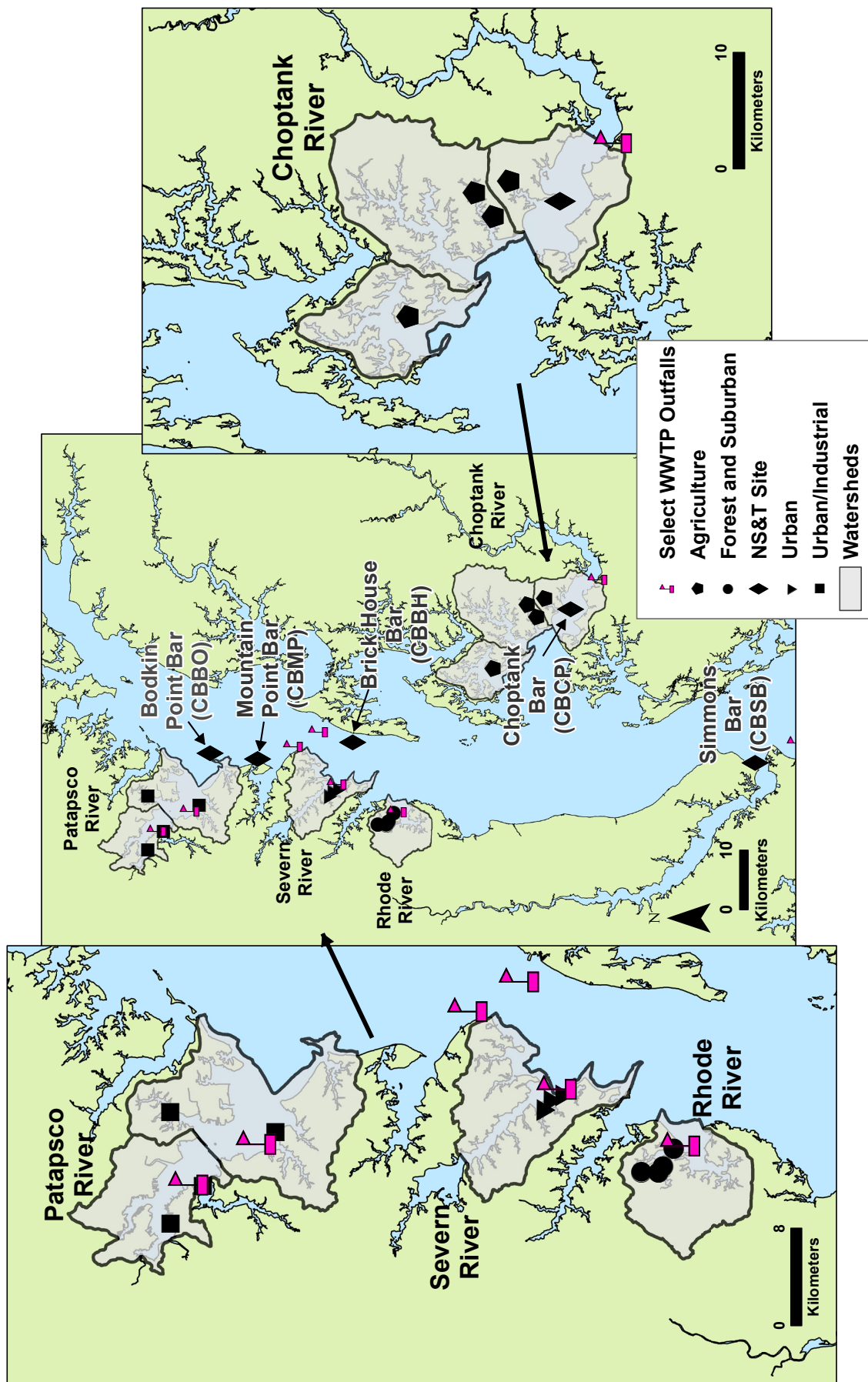
Figure 2.1a General locations for the assessment of contaminants of emerging concern in Chesapeake Bay, Maryland. The central panel shows the entire sampling extent, with side panels showing the tributaries at a smaller scale. All black station markers, except for the diamonds, show the locations of 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 flags.

Figure 2.1b 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 flags.

Contaminants of Emerging Concern (CECs) Classes and Results Summary

Perfluorinated Compounds (PFCs)

Background

Perfluorinated chemicals (PFC) are a group of fluorine-containing compounds used in industrial processes related to surface protection/coatings, fire fighting foam, insecticides and commercial polymer manufacturing. Typically, PFCs enter the aquatic environment through aqueous industrial effluent or residential wastewater. This class of chemicals appears to accumulate in the environment, and because of their widespread use, they are becoming ubiquitous in sediment and tissue samples from coastal habitats (Chen et al. 2012, CDC 2018). When they are taken up by organisms, PFC are suspected to be endocrine disruptors and can cause developmental problems in animals (Grun and Blumberg 2009). Thus, this class of CECs has garnered increasing environmental research interest in the past 10-15 years and was included in the two studies presented here.

PFC contaminants in sediment from MD and SC

Figure 2.2. Distribution map showing presence (■) and absence (■) of PFC compounds measured in sediment. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.3.

Table 2.2. Perfluorinated compounds frequency of detection in sediment from the MD and SC study areas (overall n = 20). Compound abbreviations are defined in Table 3.3.

Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
PFBS	0	0	0
PFDA	30	40	26
PFDODA	35	100	13
PFDS	0	0	0
PFHPA	0	0	0
PFHXA	0	0	0
PFHXS	0	0	0
PFNA	55	100	40
PFOA	30	40	27
PFOS	55	100	40
PFOSA	10	20	7
PFUNDA	55	80	46

Summary of PFCs in sediment from MD and SC

- Of the 12 PFC compounds measured, seven were detected in sediment (Figure 2.2).

- PFCs were detected in 16 out of 20 sediment samples.

- The most common PFCs detected were PFOS, PFNA and PFUNDA (Table 2.2); all of which were detected in slightly over half of the sediment samples (55% detection frequency).

- The frequency of detections was greater for Maryland samples than for South Carolina sediment samples.

- PFBS, PFHXS, PFDS, PFHXA, and PFHPA were not detected in any sediment samples (Table 2.2).

PFC contaminants in oyster tissue from MD and SC
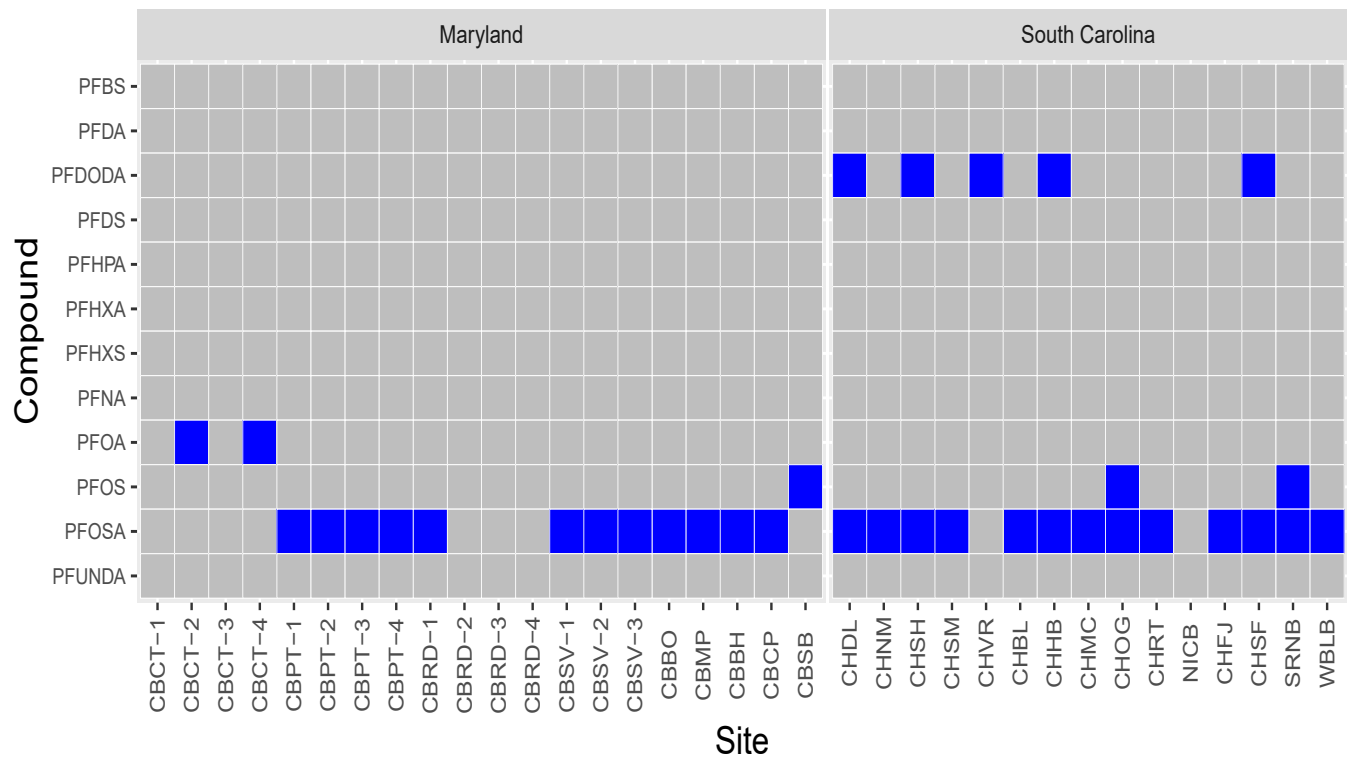
Figure 2.3. Distribution map showing presence (■) and absence (■) of PFC compounds measured in oyster tissue from the MD and SC study areas. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.3.

Table 2.3. Perfluorinated compounds frequency of detection in oyster tissue from the MD and SC study areas (overall n = 35). Compound abbreviations are defined in Table 3.3.

Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
PFBS	0	0	0
PFDA	0	0	0
PFDODA	14	0	33
PFDS	0	0	0
PFHPA	0	0	0
PFHXA	0	0	0
PFHXS	0	0	0
PFNA	0	0	0
PFOA	6	10	0
PFOS	9	5	13
PFOSA	71	60	87
PFUNDA	0	0	0

Summary of PFCs in oyster tissue from MD and SC

• PFCs were detected in 29 of the 35 oyster tissue samples (Figure 2.3).

• Four PFCs were detected in oyster tissues, although no site had greater than two PFCs detected.

• The most common PFC detected was PFOSA which was detected in over half of the tissue samples (71% detection frequency) (Table 2.3).

• PFBS, PFDA, PFDS, PFHSA, PFHXA, PFHXS, and PFNA were not detected in any MD or SC oyster tissue.

Pharmaceutical and Personal Care Products (PPCPs)

Background

Environmental PPCPs include a wide spectrum of therapeutic and consumer-use compounds, such as prescription and over-the-counter medications, hormones, synthetic fragrances, detergents, disinfectants, insect repellants, and antimicrobial agents. In 2009, an estimated 3.9 billion prescriptions were written for the top 300 pharmaceuticals in the US (Lundy 2010). Pharmaceutical companies produce over 50 million pounds of antibiotics annually in the United States, with approximately 60% for human use and 40% for animal agriculture (Levy 1998). PPCPs enter the environment via many pathways, although the primary routes include wastewater discharge after excretion or improper disposal of unused drugs (Daughton and Ternes 1999). Because pharmaceuticals are designed with the intention of having a biological effect, the major concerns of PPCPs in the environment are their potential ecotoxicity and unintentional human health impacts. Potential impacts of PPCPs in the environment include abnormal physiological effects, impaired reproduction, and increased cancer rates (Boyd and Furlong 2002). According to the US EPA, many CECs including PPCPs are suspected to be endocrine disruptors, which alter the normal functions of hormones resulting in a variety of health effects (Ankley et al. 2008). Seventy-three of the 85 PPCP analytes were analyzed in sediments, and 84 PPCPs in tissues. Similar PPCP analyte data quality and reporting issues have been noted in at least one previous CEC study (Klosterhaus et al. 2013).

PPCP contaminants in sediment from MD and SC

Figure 2.4a. Distribution map showing presence (■) and absence (■) of PPCP compounds measured in sediment. Site acronyms (x axis) are defined in Table 2.1.

Figure 2.4b. Distribution map showing presence (█) and absence (█) of PPCP compounds measured in sediment. Site acronyms (x axis) are defined in Table 2.1.

Table 2.4. Pharmaceutical and Personal Care Products frequency of detection in sediment from the MD and SC study areas (overall n = 20).

Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)	Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
Acetaminophen	0	0	0	Metformin	10	20	7
Albuterol	5	0	7	Methylprednisolone	0	0	0
Alprazolam	0	0	0	Naproxen	0	0	0
Amitriptyline	0	0	0	N-Desmethyldiltiazem	0	0	0
Amlodipine	0	0	0	Norfluoxetine	10	0	13
Amphetamine	0	0	0	Norverapamil	5	0	7
Atenolol	5	0	7	Ormetoprim	0	0	0
Atorvastatin	0	0	0	Oxacillin	0	0	0
Benzoylecgonine	0	0	0	Oxolinic Acid	0	0	0
Benztropine	5	0	7	Oxycodone	0	0	0
Bisphenol-A	0	0	0	Paroxetine	0	0	0
Caffeine	0	0	0	Penicillin G	0	0	0
Carbamazepine	0	0	0	Penicillin V	0	0	0
Cimetidine	0	0	0	Prednisolone	0	0	0
Clarithromycin	0	0	0	Prednisone	0	0	0
Clonidine	0	0	0	Promethazine	0	0	0
Cloxacillin	0	0	0	Propoxyphene	5	0	7
Cocaine	0	0	0	Propranolol	0	0	0
Codeine	0	0	0	Ranitidine	0	0	0
Cotinine	0	0	0	Roxithromycin	0	0	0
Dehydronifedipine	0	0	0	Sertraline	0	0	0
Diazepam	10	20	7	Sulfachloropyridazine	5	0	7
Digoxigenin	0	0	0	Sulfadiazine	5	0	7
Digoxin	0	0	0	Sulfadimethoxine	0	0	0
Enalapril	0	0	0	Sulfamerazine	0	0	0
Flumequine	0	0	0	Sulfamethazine	0	0	0
Fluocinonide	0	0	0	Sulfamethizole	0	0	0
Fluoxetine	0	0	0	Sulfamethoxazole	0	0	0
Fluticasone propionate	0	0	0	Sulfanilamide	0	0	0
Furosemide	0	0	0	Sulfathiazole	0	0	0
Gemfibrozil	0	0	0	Thiabendazole	0	0	0
Glipizide	0	0	0	Triamterene	0	0	0
Glyburide	0	0	0	Trimethoprim	0	0	0
Hydrocodone	0	0	0	Tylosin	0	0	0
Hydrocortisone	0	0	0	Verapamil	5	0	7
Ibuprofen	0	0	0	Warfarin	0	0	0
Meprobamate	0	0	0				

Summary of PPCPs in sediment from MD and SC

- Of the 73 individual PPCPs measured, only 11 were detected in sediment samples (Figures 2.4a-b).

- PPCPs were detected in 45% of all sediment samples.

- The PPCPs detected in sediments from either MD or SC (Table 2.4) included albuterol, atenolol, benztropine, diazepam, metformin, norfluoxetine, norverapamil, propoxyphene, sulfachloropyridazine, sulfadiazine, and verapamil.

- Individual PPCP compounds were detected at frequencies ranging from 5% to 10% in sediment.

- With only 13% of PPCPs detected and a maximum of 10% detection frequency, the results indicated that PPCPs are not prevalent in sediment from the study areas.

PPCP Contaminants in oyster tissue from MD and SC

Figure 2.5a. Distribution map showing presence (■) and absence (■) of PPCP compounds measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1.

Figure 2.5b. Distribution map showing presence (■) and absence (■) of PPCP compounds measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1.

Table 2.5. Pharmaceutical and Personal Care Products frequency of detection in oyster tissue from the MD and SC study areas (overall n = 35).

Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)	Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
10-hydroxy-amitriptyline	0	0	0	Lomefloxacin	0	0	0
Acetaminophen	29	30	27	Meprobamate	3	5	0
Albuterol	0	0	0	Metformin	0	0	0
Alprazolam	3	5	0	Methylprednisolone	0	0	0
Amitriptyline	0	0	0	Metoprolol	0	0	0
Amlodipine	6	10	0	Naproxen	0	0	0
Amphetamine	0	0	0	N-Desmethyldiltiazem	0	0	0
Atenolol	0	0	0	Norfloxacin	0	0	0
Azithromycin	0	0	0	Norfluoxetine	3	5	0
Benzoylecgonine	3	5	0	Norverapamil	6	5	7
Benztropine	3	5	0	Ofloxacin	0	0	0
Bisphenol-A	0	0	0	Ormetoprim	0	0	0
Caffeine	14	20	7	Oxacillin	3	5	0
Carbamazepine	0	0	0	Oxolinic Acid	0	0	0
Cimetidine	0	0	0	Oxycodone	0	0	0
Clarithromycin	0	0	0	Paroxetine	6	10	0
Clinafloxacin	0	0	0	Penicillin G	3	0	7
Clonidine	0	0	0	Penicillin V	3	5	0
Cloxacillin	6	10	0	Prednisolone	3	5	0
Cocaine	0	0	0	Prednisone	3	5	0
Codeine	0	0	0	Promethazine	0	0	0
Cotinine	0	0	0	Propoxyphene	0	0	0
Dehydronifedipine	0	0	0	Propranolol	3	5	0
Diazepam	0	0	0	Ranitidine	0	0	0
Digoxigenin	0	0	0	Roxithromycin	0	0	0
Digoxin	6	5	7	Sarafloxacin	3	5	0
Diltiazem	3	0	7	Sertraline	3	5	0
Diphenhydramine	3	5	0	Sulfachloropyridazine	0	0	0
Enalapril	0	0	0	Sulfadiazine	17	10	27
Enrofloxacin	0	0	0	Sulfadimethoxine	3	5	0
Erythromycin	0	0	0	Sulfamerazine	0	0	0
Flumequine	9	5	13	Sulfamethazine	6	5	7
Fluocinonide	3	5	0	Sulfamethizole	0	0	0
Fluoxetine	0	0	0	Sulfamethoxazole	0	0	0
Fluticasone propionate	3	5	0	Sulfanilamide	3	5	0
Furosemide	0	0	0	Sulfathiazole	0	0	0
Gemfibrozil	3	5	0	Thiabendazole	0	0	0
Glipizide	0	0	0	Triamterene	0	0	0
Glyburide	3	5	0	Trimethoprim	0	0	0
Hydrocodone	0	0	0	Tylosin	0	0	0
Hydrocortisone	3	5	0	Verapamil	0	0	0
Ibuprofen	0	0	0	Warfarin	0	0	0

Summary of PPCPs in Oyster Tissues from MD and SC

- A total of 32 individual PPCPs of the 84 measured were detected in oyster tissues from either MD or SC (Figures 2.5a and 2.5b).

- PPCPs were present in 60% of oyster tissue samples.

- Detection frequency of PPCP compounds that were detected varied from 2% to 29%. As illustrated in Figure 2.5, the detected PPCPs were mostly at a single site (CBPT-1). However, PPCPs such as acetaminophen, sulfadiazine, caffeine, and flumequine were detected at multiple sites.

- Overall, PPCPs appeared to be more prevalent in oyster tissue compared to sediment (Table 2.5).

Alkyl Phenol Compounds (APs)

Background

Alkylphenols (APs) are a class of chemicals used as detergents and surfactants in industrial processes (EPA 2014a). Some household detergents (i.e. laundy soaps) also include APs. The most common sources of APs to aquatic systems are wastewater and septic system discharges (Ying et al. 2002). These compounds tend to be persistent in the environment, have a strong affinity for suspended particles, and are well preserved in bottom sediments (Ying et al. 2002). In the environment, alkylphenol ethoxylate surfactants biodegrade into more environmentally stable metabolites, such as the alkylphenol n-ethoxylates, alkylphenoxy acetic and alkylphnoxypolyethoxy acetic acids, and alkylphenols (EPA 2014a). This study focused on four AP metabolites in both sediment and oyster tissues. Two of the compounds, 4-nonylphenol (4-NP) and 4 -n-octylphenol (4-n-OP), are degradation products of 4-nonylphenol mono-ethoxylate (NP1E0) and 4 nonylphenol di-ethoxylate (NP2E0), which are byproducts of the parent alkylphenol polyethoxylate. These degradation products are more stable and more toxic than the parent compounds and are hormone mimics (Ying et al. 2002).

AP Contaminants in Sediment from MD and SC
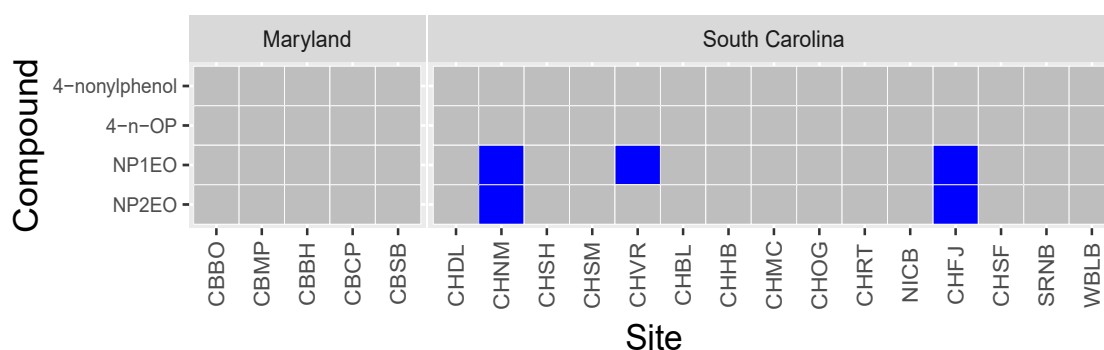
Figure 2.6. Distribution map showing presence (■) and absence (■) of AP compounds measured in sediment from the MD and SC study areas. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.5.

Table 2.6. Alkyl Phenols frequency of detection in sediment from the MD and SC study areas. Compound abbreviations are defined in Table 3.5.

Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
4-nonylphenol	0	0	0
4-n-OP	0	0	0
NP1EO	15	0	20
NP2EO	10	0	13

Summary of APs in sediment from MD and SC

- Of the four phenolic compounds measured, two were detected in sediment (Figure 2.6).

- The phenolic compounds detected included nonylphenol monoethoxylate (NP1EO), and nonylphenol diethoxylate (NP2EO).

- These phenolic compounds were only detected in sediment from SC at 20% and 13% frequency, respectively (Table 2.6).

AP Contaminants in oyster tissue from MD and SC

Figure 2.7. Distribution map showing presence (■) and absence (■) of AP compounds measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.5.

Table 2.7. Alkyl Phenols frequency of detection in oyster tissue from the MD and SC study areas. Compound abbreviations (y axis) are defined in Table 3.5.

Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
4-nonylphenol	0	0	0
4-n-OP	0	0	0
NP1EO	6	10	0
NP2EO	0	0	0

Summary of APs in Oyster Tissue

- Of the four phenolic compounds measured, only one, nonylphenol monoethoxylate (NP1EO), was detected in oyster tissue (Figure 2.7).

- The detected phenolic compound was found in oyster tissue samples from MD only (Table 2.7).

- The NP1EO compound was detected in only 6% of the overall oyster samples.

Polybrominated Diphenyl Ethers (PBDEs) Flame Retardants

Background

Polybominated diphenyl ethers (PBDEs) are a group of chemicals that are used as flame-retardants in consumer and household products. Commercially, three types of PBDE industrial mixtures were available, the pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE) and the decabromodiphenyl ether (deca-BDE) mixtures (EPA 2014b). As these products age and degrade, PBDEs can enter the environment. PBDEs are structurally similar to PCBs with 209 possible unique structures or congeners. PBDEs have been measured in household dust, human breast milk, sediment and wildlife (ATSDR, 2015). The toxicology of PBDEs is not well understood, but PBDEs have been associated with tumors, neurodevelopmental toxicity and thyroid hormone imbalance. Due to ubiquitous distribution, potential persistance and toxicity, the manufacture of the 'penta' and 'octa' PBDEs mixtures have been phased out starting in 2004, and for the deca mixture in 2013 (EPA 2014b, Schreder and La Guardia 2014). However, as persistent organic pollutants (POPs), PBDEs will be present in every compartment of the environment for years. Less brominated PBDEs, like tetra-, penta- and hexa-BDE, demonstrate high affinity for lipids and tend to bioaccumulate in animals and humans, while highly brominated PBDEs like deca-BDE tend to absorb more onto sediment and soil.

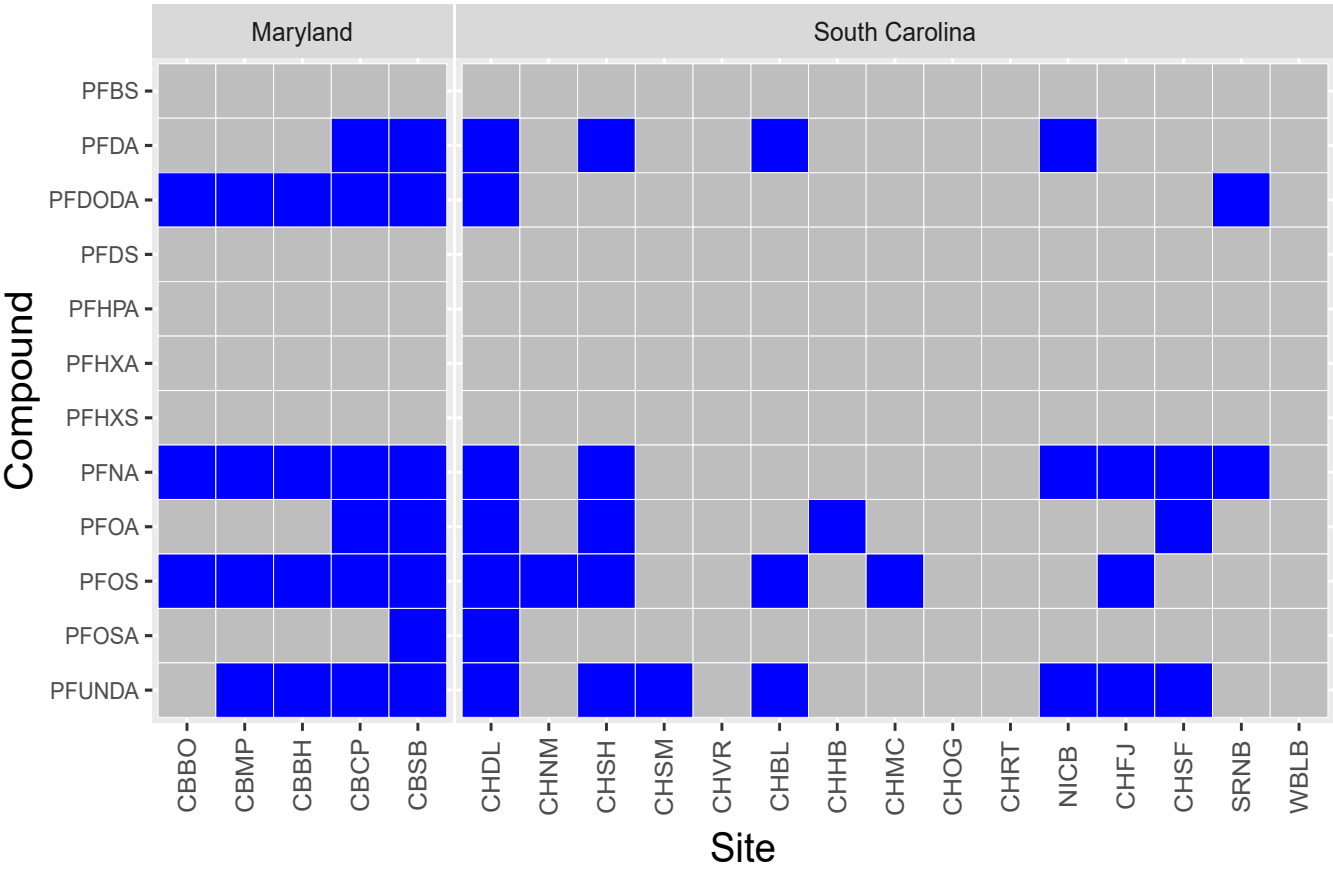*PBDE contaminants in sediment from MD and SC*
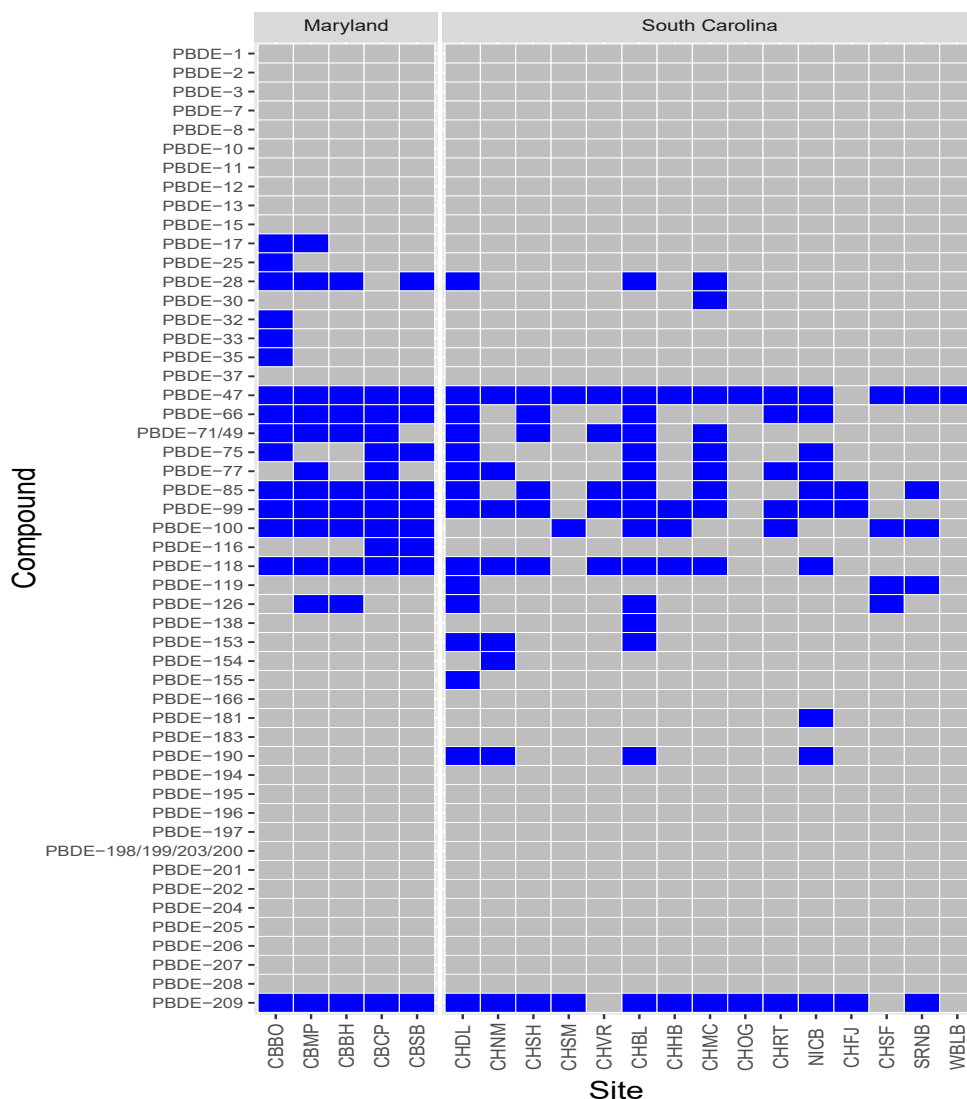
Figure 2.8. Distribution map showing presence (■) and absence (■) of PBDE congeners measured in sediment. Site acronyms (x axis) are defined in Table 2.1; congener abbreviations (y axis) are defined in Table 3.6.

Table 2.8. Polybrominated Diphenyl Ethers frequency of detection in sediment from the MD and SC study areas. Congener abbreviations are defined in Table 3.6.

Congener	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)	Congener	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
PBDE-1	0	0	0	PBDE-116	10	40	0
PBDE-2	0	0	0	PBDE-118	65	100	53
PBDE-3	0	0	0	PBDE-119	15	0	20
PBDE-7	0	0	0	PBDE-126	25	40	20
PBDE-8	0	0	0	PBDE-138	5	0	7
PBDE-10	0	0	0	PBDE-153	15	0	20
PBDE-11	0	0	0	PBDE-154	5	0	7
PBDE-12	0	0	0	PBDE-155	5	0	7
PBDE-13	0	0	0	PBDE-166	0	0	0
PBDE-15	0	0	0	PBDE-181	5	0	7
PBDE-17	10	40	0	PBDE-183	0	0	0
PBDE-25	5	20	0	PBDE-190	20	0	27
PBDE-28	35	80	20	PBDE-194	0	0	0
PBDE-30	5	0	7	PBDE-195	0	0	0
PBDE-32	5	20	0	PBDE-196	0	0	0
PBDE-33	5	20	0	PBDE-197	0	0	0
PBDE-35	5	20	0	PBDE-198/199/203/200	0	0	0
PBDE-37	0	0	0	PBDE-201	0	0	0
PBDE-47	95	100	93	PBDE-202	0	0	0
PBDE-66	50	100	33	PBDE-204	0	0	0
PBDE-71/49	45	80	33	PBDE-205	0	0	0
PBDE-75	35	60	27	PBDE-206	0	0	0
PBDE-77	40	40	40	PBDE-207	0	0	0
PBDE-85	65	100	53	PBDE-208	0	0	0
PBDE-99	75	100	67	PBDE-209	85	100	80
PBDE-100	55	100	40				

"/" denotes co-eluting congeners

Summary of PBDEs in Sediment from MD and SC

- From a total of 55 individual PBDE congeners (51 analytically identifiable groups) measured, 26 groups were detected in sediments from MD and SC (Figure 2.8).

- PBDEs were detected in 100% of the sediment samples.

- The overall frequency of detected PBDE congeners ranged from 5 to 100% (Table 2.8).

- The most frequently detected PBDEs were PBDE-47, PBDE-209, PBDE-99, PBDE-85, PBDE-118, PBDE-100, and PBDE-66, which were detected in more than 50% of the sediment samples.

PBDE Contaminants in oyster tissue from MD and SC
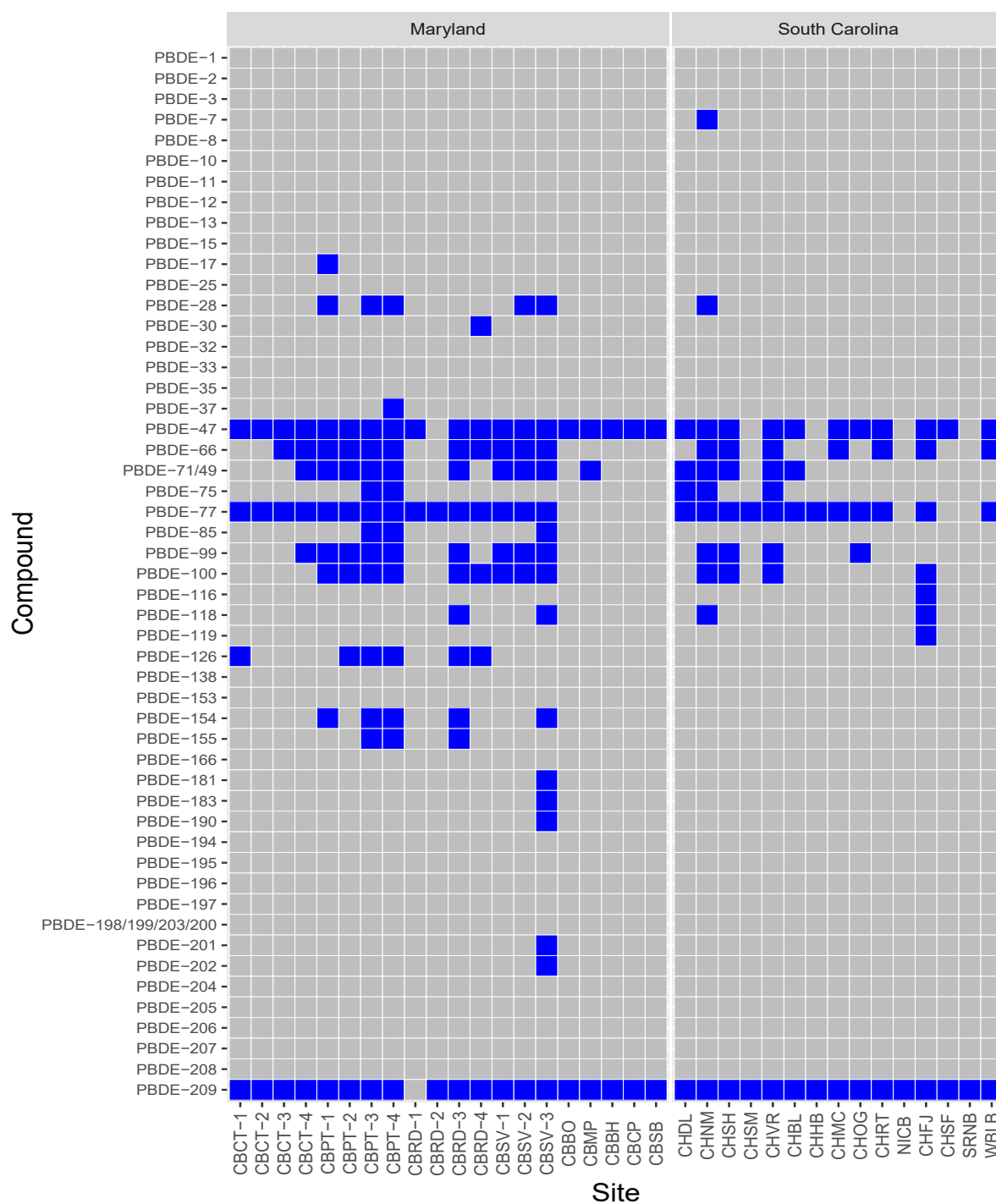
Figure 2.9. Distribution map showing presence (■) and absence (■) of PBDE congeners measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.6.

Table 2.9. Polybrominated Diphenyl Ether frequency of detection in oyster tissue from the MD and SC study areas. Congeners abbreviations are defined in Table 3.6.

Congener	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)	Congener	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
PBDE-1	0	0	0	PBDE-116	3	0	7
PBDE-2	0	0	0	PBDE-118	11	10	13
PBDE-3	0	0	0	PBDE-119	3	0	7
PBDE-7	3	0	7	PBDE-126	17	35	0
PBDE-8	0	0	0	PBDE-138	0	0	0
PBDE-10	0	0	0	PBDE-153	0	0	0
PBDE-11	0	0	0	PBDE-154	14	25	0
PBDE-12	0	0	0	PBDE-155	9	15	0
PBDE-13	0	0	0	PBDE-166	0	0	0
PBDE-15	0	0	0	PBDE-181	3	5	0
PBDE-17	3	5	0	PBDE-183	3	5	0
PBDE-25	0	0	0	PBDE-190	3	5	0
PBDE-28	17	40	7	PBDE-194	0	0	0
PBDE-30	3	5	0	PBDE-195	0	0	0
PBDE-32	0	0	0	PBDE-196	0	0	0
PBDE-33	0	0	0	PBDE-197	0	0	0
PBDE-35	0	0	0	PBDE-198/199/203/200	0	0	0
PBDE-37	3	5	0	PBDE-201	3	5	0
PBDE-47	86	95	73	PBDE-202	3	5	0
PBDE-66	51	55	47	PBDE-204	0	0	0
PBDE-71/49	43	50	33	PBDE-205	0	0	0
PBDE-75	14	10	20	PBDE-206	0	0	0
PBDE-77	77	75	80	PBDE-207	0	0	0
PBDE-85	9	15	0	PBDE-208	0	0	0
PBDE-99	37	45	27	PBDE-209	97	95	100
PBDE-100	37	45	27	Total PBDEs	100	100	100

"/" denotes co-eluting congeners

Summary of PBDEs in oyster tissue from MD and SC

- From a total of 55 individual PBDE congeners (51 analytically identifiable groups) measured, 25 groups were detected in oyster tissue from both MD and SC (Figure 2.9).

- The PBDEs were detected in 100% of the oyster samples. At least one PBDE group was detected in oyster tissue from both study areas.

- The overall frequency of detected PBDE congeners ranged from 3% to 100% (Table 2.9).

- The most frequently detected PBDEs in oyster were PBDE-209, PBDE-47, PBDE-77, PBDE-66, PBDE-71/49, PBDE-99, and PBDE-100, which were detected in more than 50% of the oyster samples.

Alternative Flame Retardants (AFRs)

Background

Alternative flame retardants (AFRs) are added to a wide variety of industrial and consumer products, such as textiles, rugs, furniture and plastics (de Wit 2002). For this study, several groups of chemicals were combined under the title of alternative flame retardants, including chlorinated organophosphate (CPP) and the polybrominated biphenyls (PBBs). PBBs are primarily used in firefighting materials but they differ from PBDEs by their chemical structure (the absence of an ether group within the biphenyl core structure). Due to potential toxicity, the application of PBBs is now controlled as a hazardous substance (Safe 1984). The brominated flame retardants (BFRs), such as hexabromo-cyclododecane (HBCDs), are primarily used in household consumer products, such as upholsteries and textiles. The chlorinated or-ganophosphate flame retardants, such as tris(1,3-dichloroisopropyl)phosphate (TDCPP), are mainly used as additives in textiles, and tend to leach over time into water and air. In the environment, TDCPP can accumulate in animal fat tissues (Andresen et al. 2004). AFRs are ubiquitous in the environment, but their ecotoxicity is not well understood.

AFR Contaminants in sediment from MD and SC
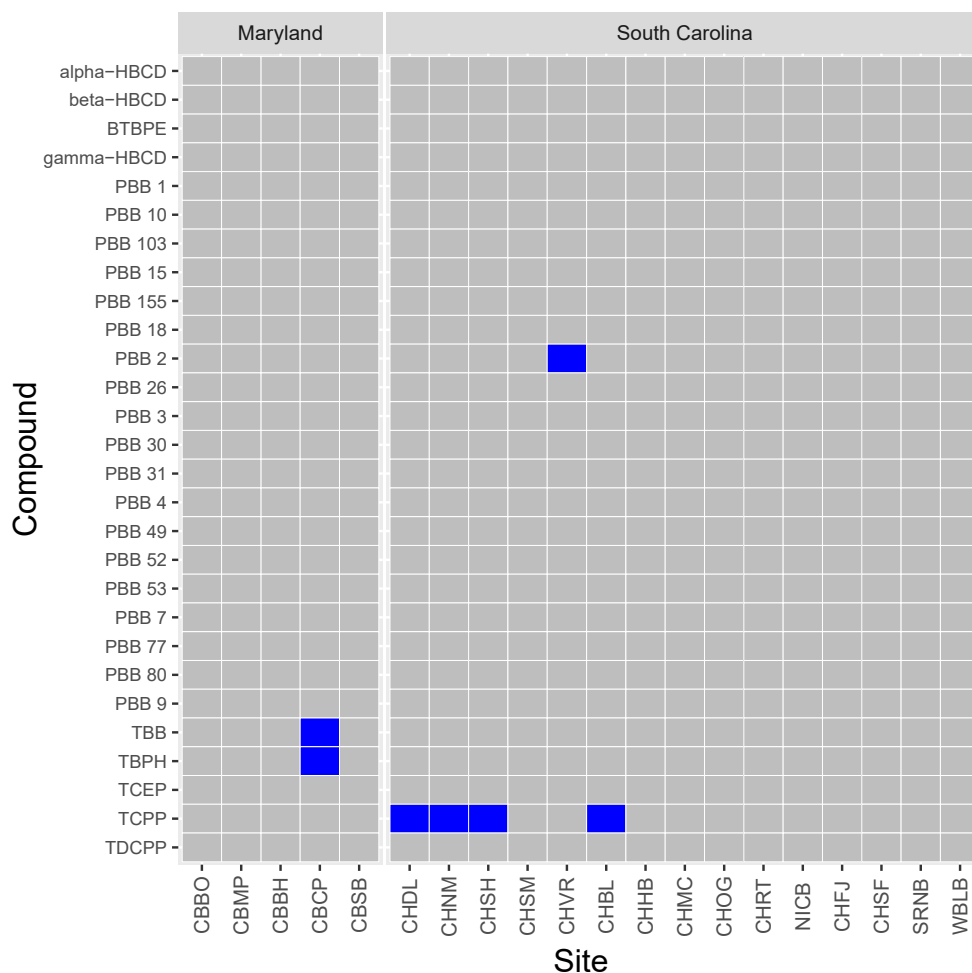
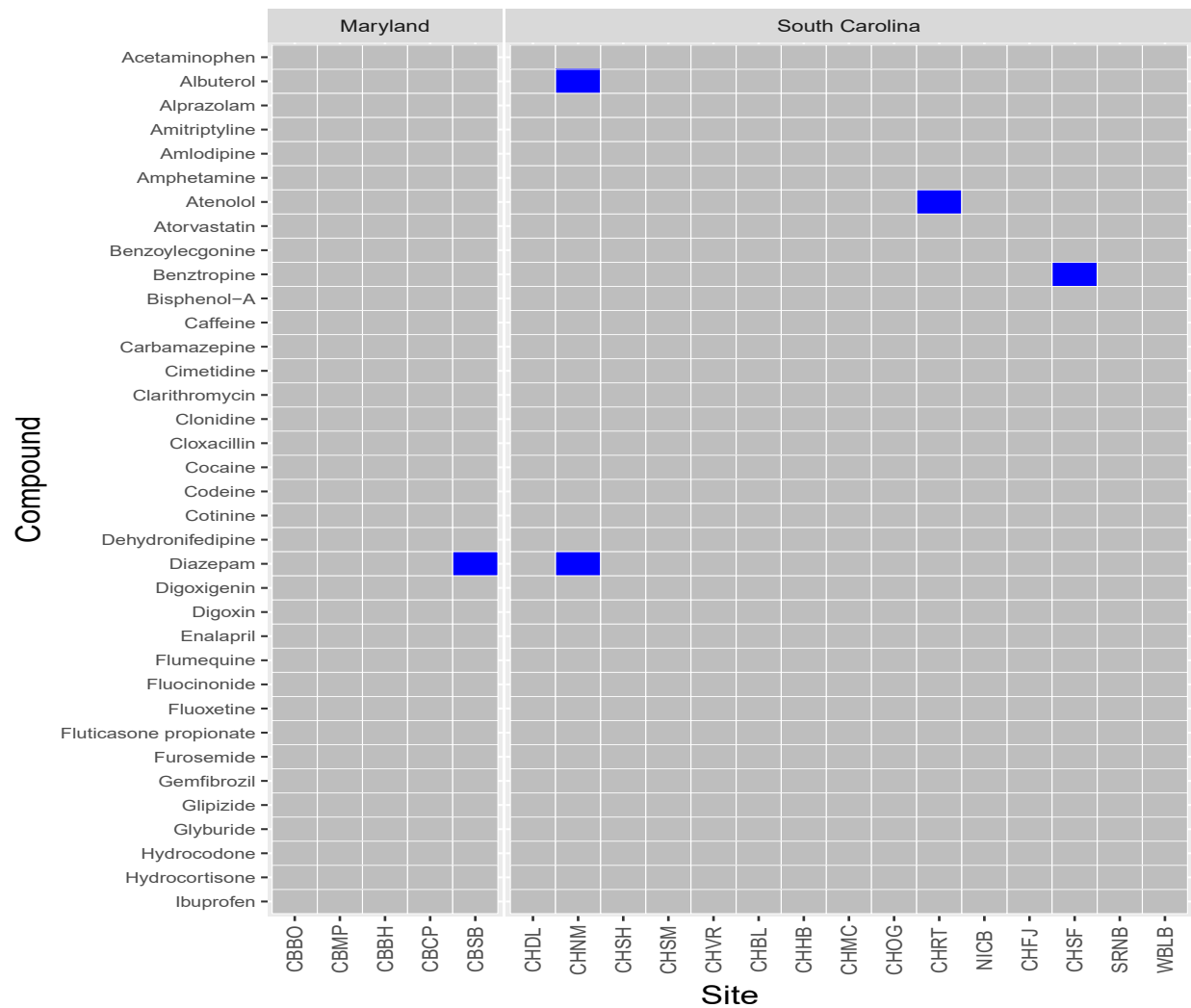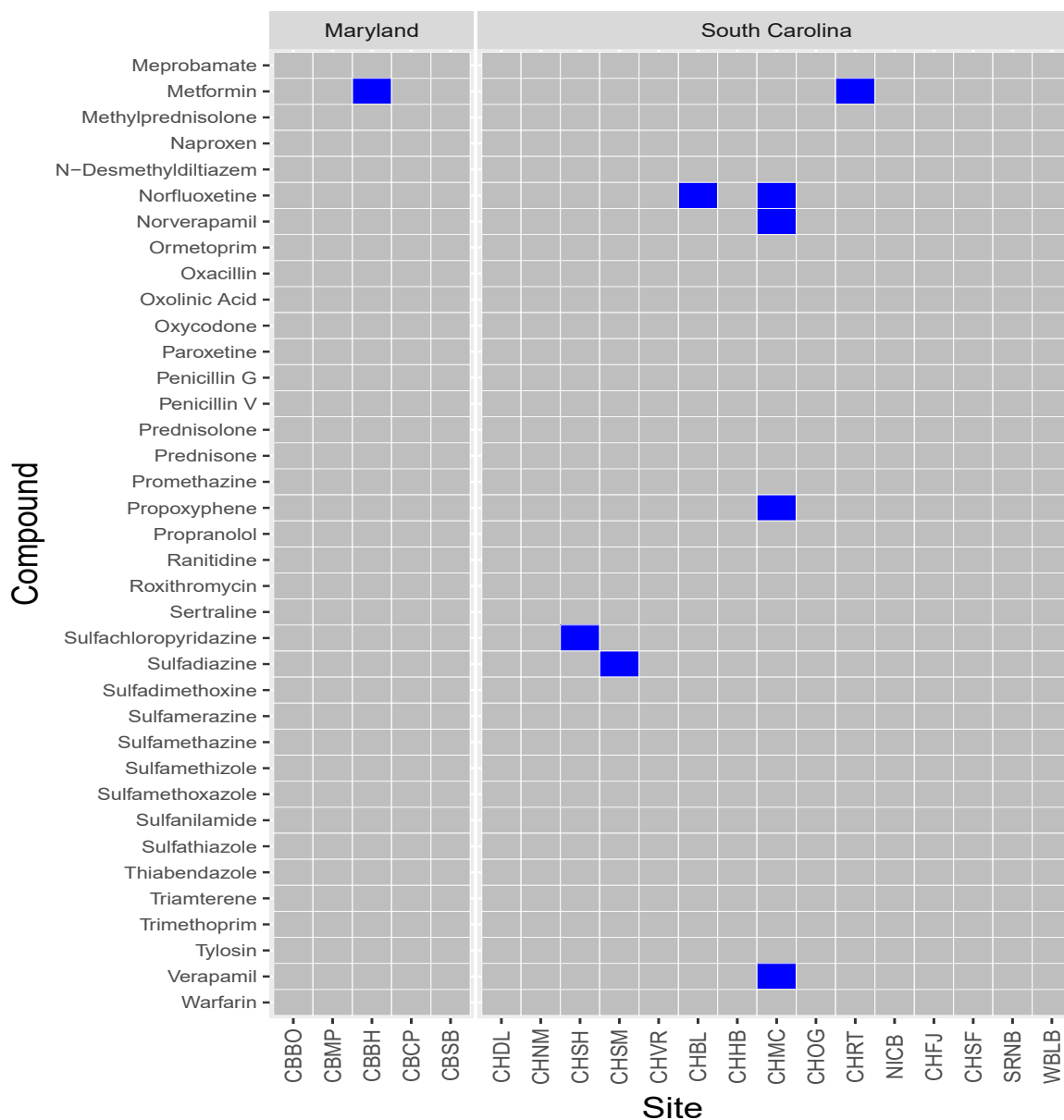**Figure 2.10.** Distribution map showing presence (■) and absence (■) of AFR compounds measured in sediment. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.7.

Table 2.10. Alternative Flame Retardants frequency of detection in sediment from the MD and SC study areas (overall n = 20). Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.7.

Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
BTBPE	0	0	0
PBB 1	0	0	0
PBB 10	0	0	0
PBB 103	0	0	0
PBB 15	0	0	0
PBB 155	0	0	0
PBB 18	0	0	0
PBB 2	5	0	7
PBB 26	0	0	0
PBB 3	0	0	0
PBB 30	0	0	0
PBB 31	0	0	0
PBB 4	0	0	0
PBB 49	0	0	0
PBB 52	0	0	0
PBB 53	0	0	0
PBB 7	0	0	0
PBB 77	0	0	0
PBB 80	0	0	0
PBB 9	0	0	0
TBB	5	20	0
TBPH	5	20	0
TCEP	0	0	0
TCPP	20	0	27
TDCPP	0	0	0
alpha-HBCD	0	0	0
beta-HBCD	0	0	0
gamma-HBCD	0	0	0

Summary of AFRs in sediment from MD and SC

- Of the 28 individual compounds defined as alternate flame retardants in these studies, only four were detected in sediments (Figure 2.10).

- The polybrominated biphenyl congener TBB and the brominated compound TBPH were only detected in MD, while PBB-2 and the chlorinated organophosphate TCPP was found only in sediment from SC.

- The frequency of detection for individual AFRs ranged from 0% to 27% of the sampling sites (Table 2.10).

- The most commonly detected AFR was TCPP, detected at 20% of all sample sites.

- The polybrominated biphenyl congener PBB-2 and the brominated compounds TBB and TBPH were found in 5% of the sediments.

AFR Contaminants in oyster tissue from MD and SC
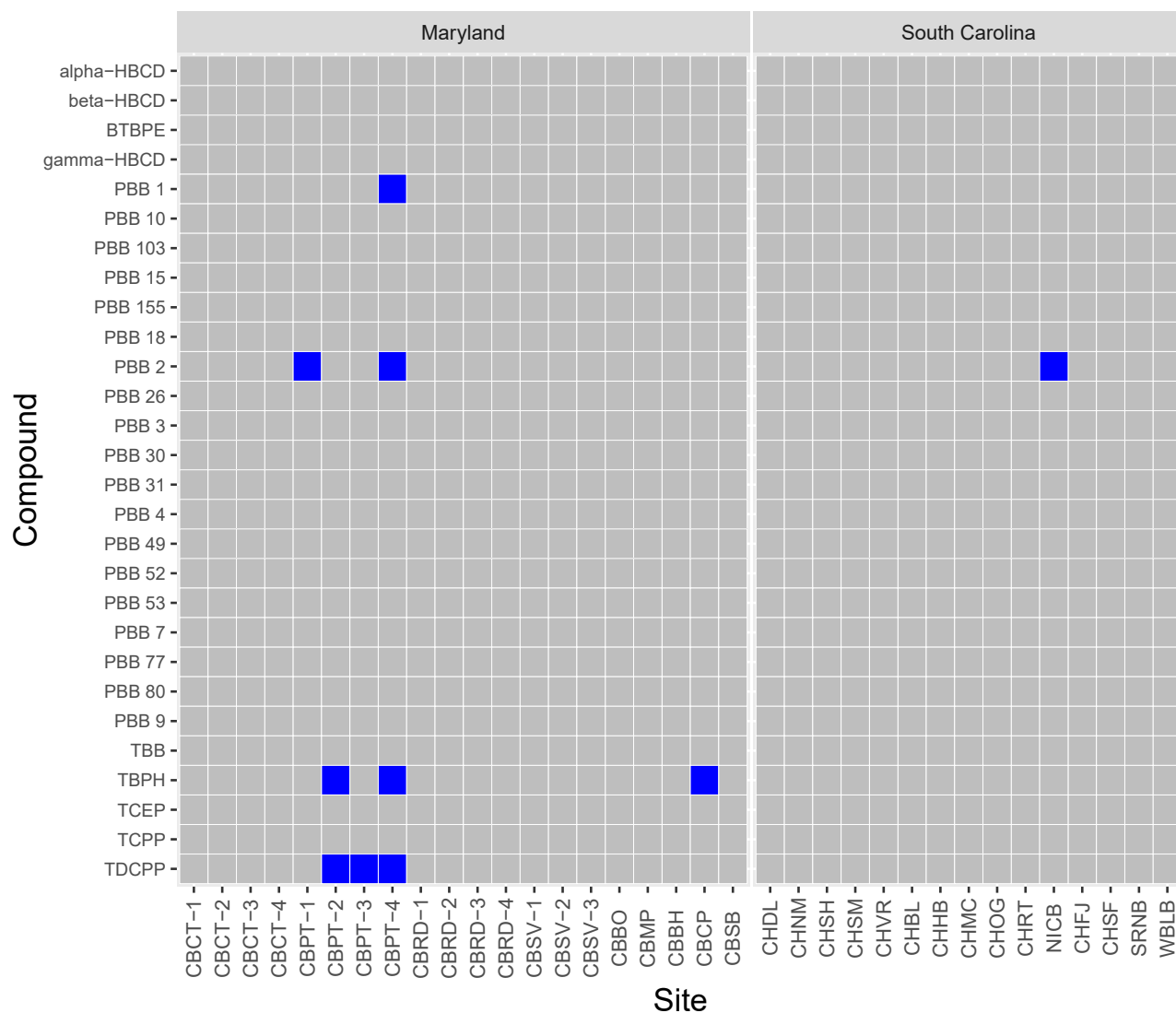
Figure 2.11. Distribution map showing presence (■) and absence (■) of AFR compounds measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1; compound abbreviations (y axis) are defined in Table 3.7.

Table 2.11. Alternate Flame Retardants frequency of detection in oyster tissue from the MD and SC study areas (overall n = 35). Compound abbreviations are defined in Table 3.7.

Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
BTBPE	0	0	0
PBB 1	3	5	0
PBB 10	0	0	0
PBB 103	0	0	0
PBB 15	0	0	0
PBB 155	0	0	0
PBB 18	0	0	0
PBB 2	9	10	7
PBB 26	0	0	0
PBB 3	0	0	0
PBB 30	0	0	0
PBB 31	0	0	0
PBB 4	0	0	0
PBB 49	0	0	0
PBB 52	0	0	0
PBB 53	0	0	0
PBB 7	0	0	0
PBB 77	0	0	0
PBB 80	0	0	0
PBB 9	0	0	0
TBB	0	0	0
TBPH	9	15	0
TCEP	0	0	0
TCPP	0	0	0
TDCPP	9	15	0
alpha-HBCD	0	0	0
beta-HBCD	0	0	0
gamma-HBCD	0	0	0

Summary of AFRs in oyster tissue from MD and SC

- From a total of 28 individual AFR compounds measured, four were detected in oyster tissues from either MD or SC (Figure2.11).

- Two polybrominated biphenyls (PBB 1, and PBB 2) were detected in 3% and 9% of the samples, respectively (Table 2.11).

- The brominated flame retardant compounds (TBPH) and the chlorinated organophosphate chemicals (TDCPP) were also detected in 9% of the oysters (Table 2.11).

- Overall, frequency of detection of the AFR compounds was low.

Multi-Residue (MRES) Contemporary Contaminants

Background

In this study, multi-residue (MRES) contemporary contaminants include the class of current use pesticides and contemporary industrial by-product chemicals, such as octachlorostyrene. MRES contaminants are generally a group of semi-volatile chemicals that span multiple chemical classes and are measured using the same analytical method. In this report, MRES includes current use pesticides, degradation products and the industrial by-product octachlorostyrene. Current use pesticides include a number of chemicals that serve as insecticides, herbicides and fungicides. These chemicals are typically more water soluble than the legacy organochlorine pesticides and tend not to bioaccumulate in organisms. It has been estimated that in 2007, over 565 million kg of current use pesticides were used in the US (EPA 2011). While agricultural application accounts for over 60% of pesticides used, urban usage is also increasing in the US (EPA 2011). Pesticides enter the environment seasonally through surface run-off, direct discharge and through atmospheric long-range transport (EPA 2011). Octachlorostyrene is a by-product of industrial processes involving aluminium refining and combustion of chlorinated compounds. Listed in the EPA priority list of most bioaccumulative compounds, octachlorstyrene is highly toxic and extremely persistent when released to the environment (Chu et al. 2003). Octachlorostyrene is included in this study as it has been found in the environment at increasing concentrations, particularly in industrial areas (Chu et al. 2003).

MRES Contaminants in sediment from MD and SC
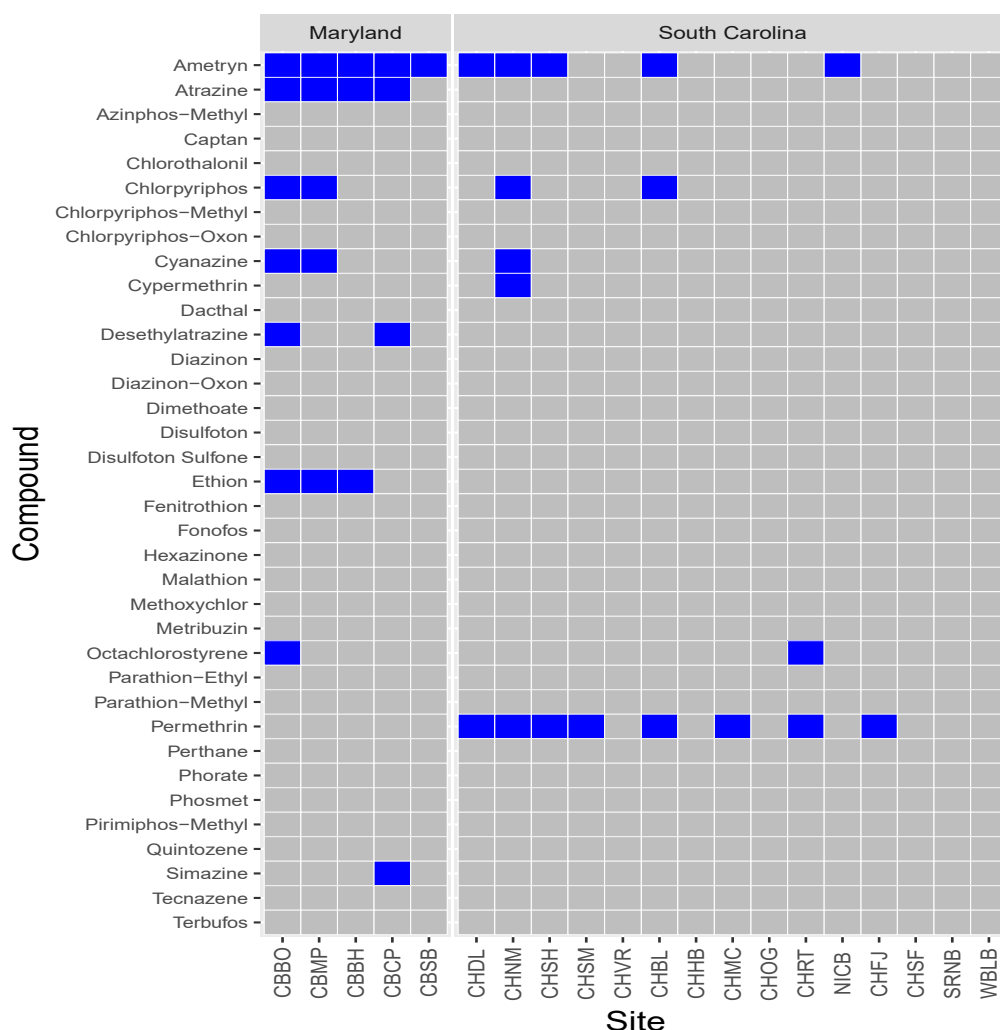
Figure 2.12. Distribution map showing presence (■) and absence (■) of MRES compounds measured in sediment. Site acronyms (x axis) are defined in Table 2.1.

Table 2.12. Multi-Residue Contemporary Contaminants frequency of detection in sediment from the MD and SC study areas.

Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)	Compound	Overall % (n=20)	Maryland % (n=5)	South Carolina % (n=15)
Ametryn	50	100	33	Fenitrothion	0	0	0
Atrazine	20	80	0	Fonofos	0	0	0
Azinphos-Methyl	0	0	0	Hexazinone	0	0	0
Captan	0	0	0	Malathion	0	0	0
Chlorothalonil	0	0	0	Methoxychlor	0	0	0
Chlorpyrifos	20	40	13	Metribuzin	0	0	0
Chlorpyriphos-Methyl	0	0	0	Octachlorostyrene	10	20	7
Chlorpyriphos-Oxon	0	0	0	Parathion-Ethyl	0	0	0
Cyanazine	15	40	7	Parathion-Methyl	0	0	0
Cypermethrin	5	0	7	Permethrin	40	0	53
Dacthal	0	0	0	Perthane	0	0	0
Desethylatrazine	10	40	0	Phorate	0	0	0
Diazinon	0	0	0	Phosmet	0	0	0
Diazinon-Oxon	0	0	0	Pirimiphos-Methyl	0	0	0
Dimethoate	0	0	0	Quintozene	0	0	0
Disulfoton	0	0	0	Simazine	5	20	0
Disulfoton-Sulfone	0	0	0	Tecnazene	0	0	0
Ethion	15	60	0	Terbufos	0	0	0

Summary of MRES in sediment from MD and SC

- A total of 36 individual MRES compounds were measured; of those, 10 were detected in sediment samples from both MD and SC (Figure 2.12).

- Most detected MRES were observed in sediment from both MD and SC. However, the herbicides atrazine, aes-ethylatrazine, and simazine were only found in MD sediment, while the insecticides permethrin and cypermethrin were detected in SC sediments.

- The overall frequency of detection ranged from 0% to 50% (Table 2.12).

- The insecticides ametryn (in 50% of the samples) and permethrin (in 40% of the samples) were the most prevalent MRES in sediment. The herbicide atrazine and insecticides chlorpyrifos, cyanazine, and ethion were also detected in 15% of the sediments (Table 2.12).

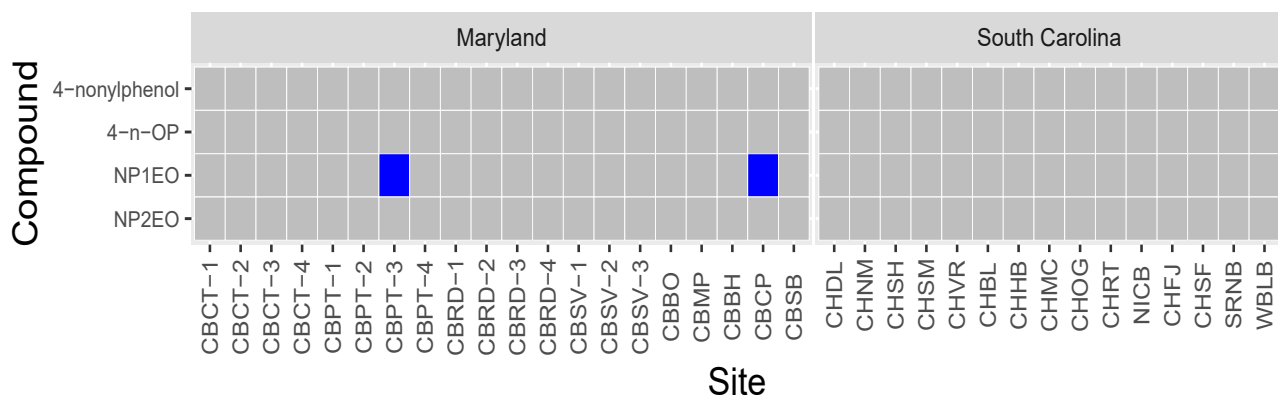*MRES Contaminants in oyster tissue from MD and SC*
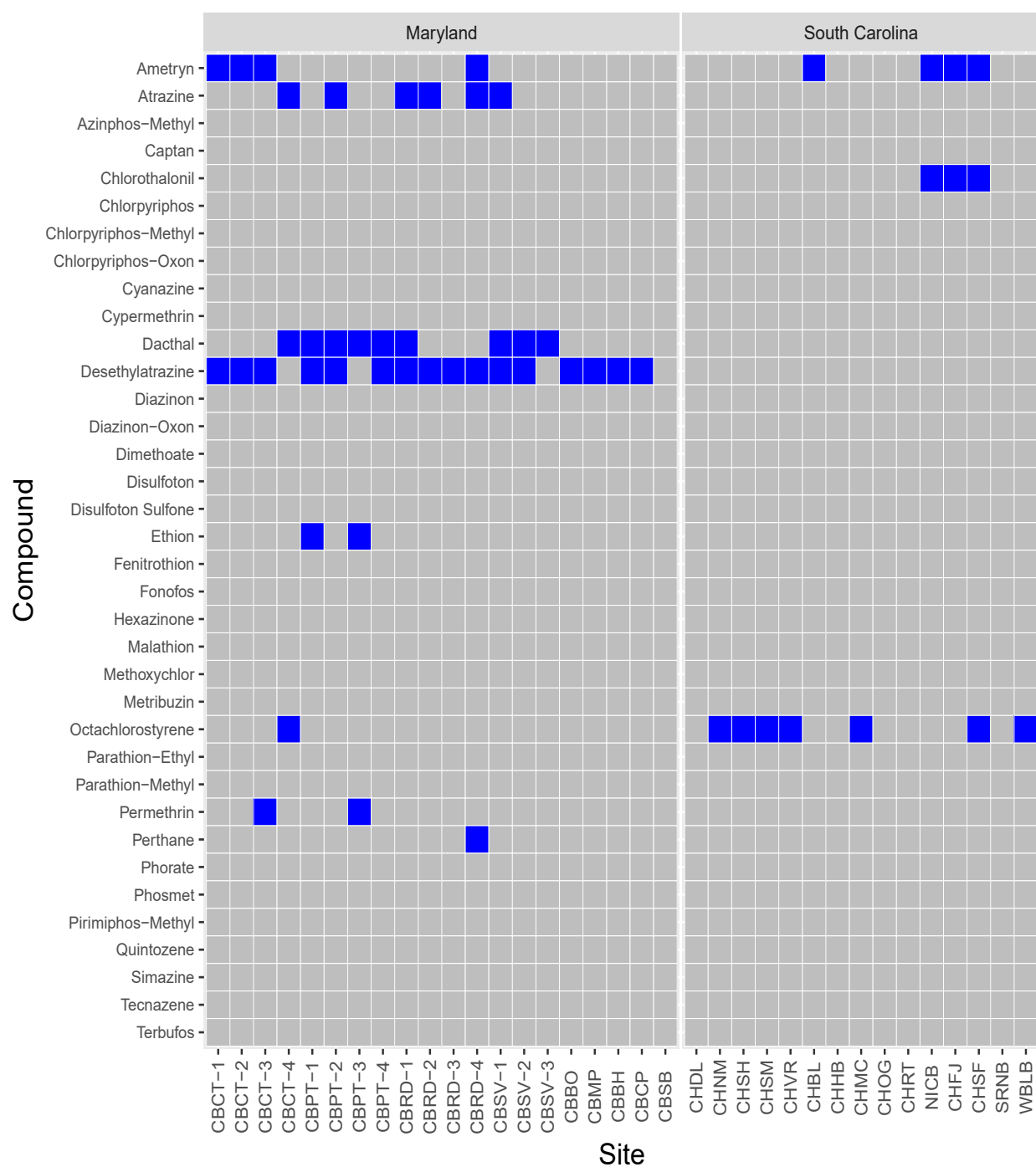
Figure 2.13. Distribution map showing presence (■) and absence (■) of MRES contaminants measured in oyster tissue. Site acronyms (x axis) are defined in Table 2.1.

Table 2.13. Multi-Residue Contemporary Contaminants frequency of detection in oyster tissue from the MD and SC study areas (overall n = 35)

Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)	Compound	Overall % (n=35)	Maryland % (n=20)	South Carolina % (n=15)
Ametryn	23	20	27	Fenitrothion	0	0	0
Atrazine	17	30	0	Fonofos	0	0	0
Azinphos-Methyl	0	0	0	Hexazinone	0	0	0
Captan	0	0	0	Malathion	0	0	0
Chlorothalonil	9	0	20	Methoxychlor	0	0	0
Chlorpyrifos	0	0	0	Metribuzin	0	0	0
Chlorpyriphos-Methyl	0	0	0	Octachlorostyrene	23	5	47
Chlorpyriphos-Oxon	0	0	0	Parathion-Ethyl	0	0	0
Cyanazine	0	0	0	Parathion-Methyl	0	0	0
Cypermethrin	0	0	0	Permethrin	6	10	0
Dacthal	26	45	0	Perthane	3	5	0
Desethylatrazine	46	80	0	Phorate	0	0	0
Diazinon	0	0	0	Phosmet	0	0	0
Diazinon-Oxon	0	0	0	Pirimiphos-Methyl	0	0	0
Dimethoate	0	0	0	Quintozene	0	0	0
Disulfoton	0	0	0	Simazine	0	0	0
Disulfoton-Sulfone	0	0	0	Tecnazene	0	0	0
Ethion	6	10	0	Terbufos	0	0	0

Summary of MRES in oyster tissue from MD and SC

- A total of 36 individual MRES contaminants were measured and 9 were detected in oyster samples from MD and SC (Figure 2.13).

- The herbicides atrazine, dacthal, and insecticides ethion, permethrin were only detected in MD, while the fungicide chlorothalonil was detected in oyster tissue from SC.

- The overall frequency of detection ranged from 0% to 46% (Table 2.13).

- The insecticides desethylatrazine (in 46% of the samples), dacthal (in 26% of the samples) and ametryn (in 23% of the samples); and the industrial by-product octachlorostyrene (in 23% of the samples) were the most prevalent MRES in oyster tissue. The herbicide atrazine and the fungicide chlorothalonil were also detected in more than 3 oyster samples (Table 2.13).

Study-Wide General Findings

Evaluating each CEC class shows that overall detection frequencies were generally quite low (<50%; Table 2.14). 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 PFCs. The highest detection frequency found in oysters was 11.5% for PBDEs in MD samples.

Table 2.14. 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	40.0	16.7	6.3	11.1
PPCP	0.5	1.1	2.5	1.3
AP	0.0	8.3	2.5	0
PBDE	21.1	12.0	11.5	8.1
AFR	1.4	1.2	1.6	0.2
MRES	10.0	3.3	5.7	2.6

Detections for most individual CEC compounds were generally low relative to minimum analytical detection levels. The highest frequencies of detection were for particular compounds in the class of PFCs, such as PFOSA in oyster tissues, and the PBDEs. In general, alkyl phenols and alternative flame retardants were not detected in most samples, suggesting that these classes of CECs may not readily accumulate in the environmental media surveyed in this study. A few of the current use pesticides were more commonly detected, although detections of these compounds tended to differ between Maryland and South Carolina. For Maryland, the atrazine degradation product desethylatrazine was found in most oyster tissues, while the herbicides atrazine and ametryn were common in sediment samples. In South Carolina, permethrin and octachlorostyrene were detected in roughly half of the sediment and tissue samples, respectively. Although pharmaceuticals were not commonly found across multiple sites, the presence of a large number of compounds at one site in the Patapsco River, Maryland, highlights the potential importance of point sources for these chemicals in oyster tissues.

CHAPTER 3: METHODS

Study Area

The Maryland study area was located in upper Chesapeake Bay, within the tributaries of the Patapsco, Severn, Rhode and Choptank Rivers, which were selected to represent different land use types (Figure 3.1). A total of 15 targeted survey sites were selected within the tributaries as described in Table 3.1. Because wild oysters were not present in these tributaries, caged oysters, purchased from a local grower were deployed. Additionally, five of the 14 historical MWP monitoring sites in the Chesapeake Bay (Figure 3.1) were included in the study design to contrast the historic, open bay sites against the riverine deployed sites (Table 3.1). More details about the Chesapeake Bay study design are provided in Chapter 4.

The South Carolina study area was generally located within the Charleston Harbor estuary (Figure 3.2). A total of 10 survey sites were selected that represent different land uses within the study area (Table 3.2). One site was selected within NOAA's North Inlet National Estuarine Research Reserve (NERR). In addition, four historical MWP monitoring sites in the area were included. The 11 land use based sites (e.g. non-MWP sites) were selected based on previous work developing the relationship between tidal creek sediment and water quality with changing land use (Sanger et al. 1999a, b). Unlike the caged-oyster approach used in the Chesapeake Bay, the study design for CEC assessment in SC was based on oysters available from natural beds. More details about the South Carolina study design are provided in Chapter 5.
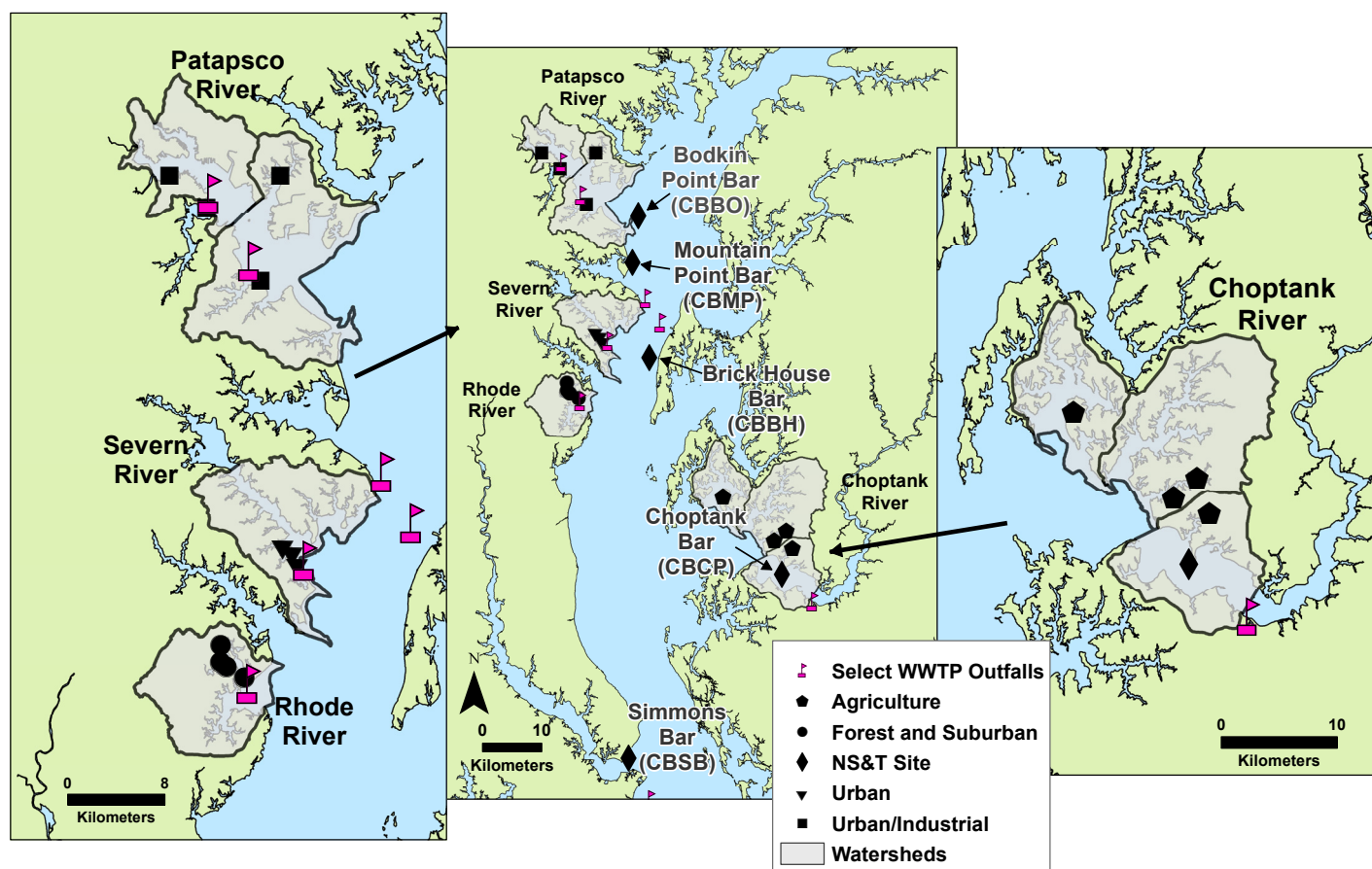
Figure 3.1. General locations for the assessment of contaminants of emerging concern in Chesapeake Bay, Maryland. The central panel shows the entire sampling extent, with side panels showing the tributaries at a smaller scale. All black station markers, except for the diamonds, show the locations of 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 3.2. 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 3.1. Survey site locations and description in the Chesapeake Bay, MD study area

Site	Specific location	Latitude	Longitude	Site type
CBCT-1	Choptank River	38.6502	-76.0967	Agriculture
CBCT-2	Choptank River	38.6620	-76.1324	Agriculture
CBCT-3	Choptank River	38.6767	-76.1092	Agriculture
CBCT-4	Choptank River	38.7272	-76.2326	Agriculture
CBPT-1	Patapsco River	39.1705	-76.5070	Heavy Urban/Industrial
CBPT-2	Patapsco River	39.2489	-76.4899	Heavy Urban/Industrial
CBPT-3	Patapsco River	39.2239	-76.5598	Heavy Urban/Industrial
CBPT-4	Patapsco River	39.2474	-76.5955	Heavy Urban/Industrial
CBRD-1	Rhode River	38.8742	-76.5163	Forested/Suburban
CBRD-2	Rhode River	38.8819	-76.5335	Forested/Suburban
CBRD-3	Rhode River	38.8853	-76.5393	Forested/Suburban
CBRD-4	Rhode River	38.8980	-76.5392	Forested/Suburban
CBSV-1	Severn River	38.9594	-76.4704	Urban
CBSV-2	Severn River	38.9680	-76.4754	Urban
CBSV-3	Severn River	38.9730	-76.4844	Urban
CBBH	Brick House	38.9386	-76.3798	Mussel Watch site
CBBO	Bodkin Point	39.1554	-76.4055	Mussel Watch site
CBCP	Choptank River	38.6098	-76.1163	Mussel Watch site
CBMP	Mountain Point	39.0828	-76.4152	Mussel Watch site
CBSB	Simon Bar	38.3259	-76.4076	Mussel Watch site

Table 3.2. Survey site locations and description in the Charleston Harbor, SC Bay study area

Site	Specific location	General location	Latitude	Longitude	Land Use
CHDL	Charleston Harbor	Diesel Creek	32.8155	-79.9633	Urban
CHNM	Charleston Harbor	New Market Creek	32.8062	-79.9401	Urban
CHSH	Charleston Harbor	Shipyard Creek	32.8392	-79.9452	Urban
CHSM	Charleston Harbor	Shem Creek	32.7933	-79.8803	Urban
CHVR	Charleston Harbor	Vardell Creek	32.8027	-79.9317	Urban
CHBL	Charleston Harbor	Bull Creek	32.8263	-80.0176	Suburban
CHHB	Charleston Harbor	Horlbeck Creek	32.8657	-79.8222	Suburban
CHMC	Charleston Harbor	Metcalf Creek	32.7461	-79.9535	Suburban
CHOG	Charleston Harbor	Orange Grove Creek	32.8055	-79.9775	Suburban
CHRT	Charleston Harbor	Rathall Creek	32.8598	-79.8884	Reference
NICB	North Inlet	Clam Bank	33.334	-79.1932	Reference
CHFJ	Charleston Harbor	Fort Johnson	32.7532	-79.8979	Mussel Watch site
CHSF	Charleston Harbor	Shutes Folly	32.7769	-79.9144	Mussel Watch site
SRNB	Santee River	North Bay	33.1634	-79.2479	Mussel Watch site
WBLB	Winyah Bay	Lower Bay	33.2433	-79.1972	Mussel Watch site

Sampling Method

Oyster and sediment sample collection for both Chesapeake Bay and Charleston Harbor pilot studies occurred during August and September of 2015. Sampling methods followed the NS&T Program's standard field protocols (Apeti et al. 2012). Oyster and sediment samples from the Chesapeake Bay were collected under the scientific collection permit SCP201581AB provided by the Maryland Department of Natural Resources Fisheries Service. South Carolina samples were collected under the SC Department of Natural Resources scientific collection permit #3773. Sampling details specific to each study area are provided in Chapters 4 and 5. The field activities were designed to have negligible impacts on the environment as called for by the NCCOS environmental compliance policy.

In this study, multiple classes of CEC compounds were measured in sediment and tissue samples. Traditionally, the list of contaminants that should be considered for monitoring would be based on potential for accumulation, environmental half-life, biodegration, ecotoxicity and human health information. Since this information does not currently exist or is not fully established, NCCOS and the MWP are assessing a list of CECs for which methods are established and for which literature indicates their potential environmental persistence and ecological and human toxicity. This includes classes of chemicals that serve as flame retardants, stain resistant compounds, pharmaceutical and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and multi-residue contemporary contaminants (MRES). During the Southern California Bight project in 2008, a broad scan of diverse classes of CECs (PPCPs, MRES, and phenolic and flame retardant compounds) were evaluated in a variety of matrices (sediment, water, fish and bivalve tissues). This collaborative study provided insight about the detection and concentrations of CECs in different environmental media (Dodder et al. 2014, Maruya et al. 2016), and served as guidance for defining the contaminant lists in these subsequent pilot studies.

Contaminants Analyzed

Perfluorinated Compounds (PFCs)

There are thousands of PFCs pollutants that are not currently regulated and or routinely monitored in the environment. The MWP program is measuring 14 PFCs (Table 3.3) which are considered toxic and for which methodologies are well developed. In this study, measurement of PFCs in sediment and tissue samples was conducted by AXYS Analytical Services Ltd. The analytical methods are proprietary and confidential. Hence, only the method name (MLA-043 REV.08.06) is mentioned in this document, along with contact information (AXYS Analytical Services Ltd, 2045 Mills Road W., Sidney, BC, Canada, V8L 5X2. Tel. (250) 655-5800, fax (250) 655-5811) for further references.

Table 3.3. Perfluorinated Compounds measured in oyster tissue and sediment

Chemical code	Chemical name	Chemical code	Chemical name
PFBS	Perfluorobutane sulfonate	PFHXS	Perfluorohexane sulfonate
PFDA	Perfluorodecanoic acid	PFNA	Perfluorononanoic acid
PFDODA	Perfluorododecanoic acid	PFOA	Perfluorooctanoate
PFDS	Perfluorohexane sulfonate	PFOS	Perfluorooctane sulfonate
PFHPA	Perfluoroheptanoic acid	PFOSA	Perfluorooctane sulfonamide
PFHXA	Perfluorohexanoic acid	PFUNDA	Perfluoroundecanoic acid

Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceutical and personal care products represent a diverse class of emerging contaminants among which selected compounds are measured by the MWP. The PPCPs analyzed in this study are grouped by analytical methods identified as PPCP-I, PPCP-II, PPCP-IV, and PPCP-V (Table 3.4). 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). Detailed description of the analytical methods are provided in Appendix A.

Table 3.4. Group-1 Pharmaceutical and Personal Care Products (PPCP-I) measured in oyster tissue and sediment by acidic extraction

Chemical group	General use	Chemical name	Chemical group	General use	Chemical name
PPCP-I	Pain Reliever	Acetaminophen[s,t]	PPCP-I	Antiprotozoa	Ormetoprim[t]
PPCP-I	Antibiotic	Azithromycin[t]	PPCP-I	Antibiotic	Oxacillin[s,t]
PPCP-I	Stimulant	Caffeine[s,t]	PPCP-I	Antibiotic	Oxolinic Acid[s,t]
PPCP-I	Muscular	Carbamazepine[s,t]	PPCP-I	Antibiotic	Penicillin G[s,t]
PPCP-I	Antibiotic	Clarithromycin[s,t]	PPCP-I	Antibiotic	Penicillin V[s,t]
PPCP-I	Antibiotic	Clinafloxacin[s,t]	PPCP-I	Antibiotic	Roxithromycin[s,t]
PPCP-I	Antibiotic	Cloxacillin[t]	PPCP-I	Antibiotic	Sarafloxacin[s,t]
PPCP-I	Cardiovascular	Dehydronifedipine[s,t]	PPCP-I	Antibiotic	Sulfachloropyridazine[t]
PPCP-I	Steroid	Digoxigenin[s,t]	PPCP-I	Antibiotic	Sulfadiazine[s,t]
PPCP-I	Cardiovascular	Digoxin[s,t]	PPCP-I	Antibiotic	Sulfadimethoxine[s,t]
PPCP-I	Cardiovascular	Diltiazem[s,t]	PPCP-I	Antibiotic	Sulfamerazine[s,t]
PPCP-I	Antihistamine	Diphenhydramine[t]	PPCP-I	Antibiotic	Sulfamethazine[s,t]
PPCP-I	Antibiotic	Enrofloxacin[t]	PPCP-I	Antibiotic	Sulfamethizole[s,t]
PPCP-I	Antibiotic	Erythromycin[t]	PPCP-I	Antibiotic	Sulfamethoxazole[s,t]
PPCP-I	Antibiotic	Flumequine[t]	PPCP-I	Antibiotic	Sulfanilamide[s,t]
PPCP-I	Psychiatric	Fluoxetine[s,t]	PPCP-I	Antibiotic	Sulfathiazole[s,t]
PPCP-I	Antibiotic	Lomefloxacin[s,t]	PPCP-I	Fungicide	Thiabendazole[s,t]
PPCP-I	Antibiotic	Norfloxacin[t]	PPCP-I	Antibiotic	Trimethoprim[s,t]
PPCP-I	Antibiotic	Ofloxacin[t]	PPCP-I	Antibiotic	Tylosin[s,t]

s = sediment, t = oyster tissue

Table 3.4 (cont'd). Group-3 Pharmaceutical and Personal Care Products (PPCP-III) measured in oyster tissue and sediment by acidic extraction

Chemical group	General use	Chemical name
PPCP-III	Plastic Additive	Bisphenol-A[s,t]
PPCP-III	Fluid Reducer	Furosemide[s,t]
PPCP-III	Cholesterol Reducer	Gemfibrozil[s,t]
PPCP-III	Antidiabetic	Glipizide[s,t]
PPCP-III	Antidiabetic	Glyburide[s,t]
PPCP-III	Pain Reliever	Ibuprofen[s,t]
PPCP-III	Pain Reliever	Naproxen[s,t]
PPCP-III	Cardiovascular	Warfarin[s,t]

s = sediment, t = oyster tissue

Table 3.4 (cont'd). Group-4 Pharmaceutical and Personal Care Products (PPCP-IV) measured in oyster tissue and sediment by basic extraction

Chemical group	General Use	Chemical name
PPCP-IV	Cardiovascular	Albuterol[s,t]
PPCP-IV	Psychiatric	Amphetamine[s,t]
PPCP-IV	Cardiovascular	Atenolol[s,t]
PPCP-IV	Cholesterol Reducer	Atorvastatin[s]
PPCP-IV	Acid Reducer	Cimetidine[s,t]
PPCP-IV	Cardiovascular	Clonidine[s,t]
PPCP-IV	Pain Reliever	Codeine[s,t]
PPCP-IV	Recreational Drug	Cotinine[s,t]
PPCP-IV	Cardiovascular	Enalapril[s,t]
PPCP-IV	Stimulant	Hydrocodone[s,t]
PPCP-IV	Antidiabetic	Metformin[s,t]
PPCP-IV	Pain Reliever	Oxycodone[s,t]
PPCP-IV	Acid Reducer	Ranitidine[s,t]
PPCP-IV	Cardiovascular	Triamterene[s,t]

s = sediment, t = oyster tissue

Table 3.4 (cont'd). Miscellaneous group-5 Pharmaceutical and Personal Care Products (PPCP-V) measured in oyster tissue and sediment by acidic extraction

Chemical group	General use	Chemical name	Chemical group	General use	Chemical name
PPCP-V	Psychiatric	10-hydroxy-amitrip-tyline[t]	PPCP-V	Cardiovascular	Metprololt
PPCP-V	Psychiatric	Alprazolam[s,t]	PPCP-V	Cardiovascular	N-Desmethyldiltiazem[s,t]
PPCP-V	Psychiatric	Amitriptyline[s,t]	PPCP-V	Psychiatric	Norfluoxetine[s,t]
PPCP-V	Cardiovascular	Amlodipine[s,t]	PPCP-V	Cardiovascular	Norverapamil[s,t]
PPCP-V	Recreational Drug	Benzoylecgonine[s,t]	PPCP-V	Psychiatric	Paroxetine[s,t]
PPCP-V	Muscular	Benztropine[s,t]	PPCP-V	Steroid	Prednisolone[s,t]
PPCP-V	Recreational Drug	Cocaine[s,t]	PPCP-V	Steroid	Prednisones,t
PPCP-V	Psychiatric	Diazepam[s,t]	PPCP-V	Depressant	Promethazine[s,t]
PPCP-V	Steroid	Fluocinonide[s,t]	PPCP-V	Pain Reliever	Propoxyphene[s,t]
PPCP-V	Steroid	Fluticasone propionate[s,t]	PPCP-V	Cardiovascular	Propranolol[s,t]
PPCP-V	Steroid	Hydrocortisone[s,t]	PPCP-V	Psychiatric	Sertraline[s,t]
PPCP-V	Psychiatric	Meprobamate[s,t]	PPCP-V	Cardiovascular	Verapamil[s,t]
PPCP-V	Steroid	Methylprednisolone[s,t]			

s = sediment, t = oyster tissue

Alkyl Phenol Compounds (APs)

Among the diverse group of alkylphenols, nonylphenol ethoxylates (NPEOs), metabolites of commercial detergents, and their environmental degradation products nonylphenols (NPs), were included in the EPA New Use Rules list of 15 toxic AP compounds (EPA 2014a). In this study, the MWP measured two NPEO and two NP compounds (Table 3.5.) 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).

Table 3.5. Phenolic compounds measured in oyster tissue and sediment.

Chemical code	Chemical name
4-nonylphenol	4-nonylphenol
4-n-OP	4-n-octylphenol
NP1EO	nonylphenol monoethoxylate
NP2EO	nonylphenol diethoxylate

Polybrominated Diphenyl Ethers (PBDEs) Flame Retardants

The brominated PBDE flame retardants include 209 possible congeners. The list of 51 PBDE congener groups measured by the MWP is presented in Table 3.6. In this study, the analyses were performed by TDI-Brooks International Inc. following procedures used by the NOAA NS&T Program (Kimbrough et al. 2007).

Table 3.6. Polybrominated Diphenyl Ethers measured in oyster tissue and sediment.

Congener	Congener
PBDE-1	PBDE-116
PBDE-2	PBDE-118
PBDE-3	PBDE-119
PBDE-7	PBDE-126
PBDE-8	PBDE-138
PBDE-10	PBDE-153
PBDE-11	PBDE-154
PBDE-12	PBDE-155
PBDE-13	PBDE-166
PBDE-15	PBDE-181
PBDE-17	PBDE-183
PBDE-25	PBDE-190
PBDE-28	PBDE-194
PBDE-30	PBDE-195
PBDE-32	PBDE-196
PBDE-33	PBDE-197
PBDE-35	PBDE-198/199/203/200
PBDE-37	PBDE-201
PBDE-47	PBDE-202
PBDE-66	PBDE-204
PBDE-71/49	PBDE-205
PBDE-75	PBDE-206
PBDE-77	PBDE-207
PBDE-85	PBDE-208
PBDE-99	PBDE-209
PBDE-100	

Alternative Flame Retardants (AFRs)

Like PBDEs, polybrominated biphenyls (PBBs) are brominated flame retardants with a possible 209 unique congeners. PBBs measured in this study are presented in Table 3.7. Chemical analyses were performed following procedures routinely used by the NOAA NS&T Program described in Kimbrough et al. 2007.

Measurements of the other alternate flame retardants compounds, such as the hexabrocyclododecanes (HBCD) and organophosphorous flame retardants (OPFR) listed in Table 3.7, were conducted by AXYS Analytical Services Ltd. The analytical methods are proprietary and confidential. Hence, only method names (MLA-070 REV.02.03 for Hexabromocyclododecane and MLA-101 REV.01.02 for organophosphates) are mentioned in this document, along with contact information (AXYS Analytical Services Ltd, 2045 Mills Road W., Sidney, BC, Canada, V8L 5X2. Tel. (250) 655-5800, fax (250) 655-5811) for further references.

Table 3.7. Alternate Flame Retardants measured in oyster tissue and sediment

Chemical code	Chemical name
alpha-HBCD	α-Hexabromocyclododecane
beta-HBCD	β-Hexabromocyclododecane
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
gamma-HBCD	γ-Hexabromocyclododecane
TBB	4,5,6,7-tetrabromobenzotriazole
TBPH	bis(2-ethylhexyl) tetrabromophthalate
TCEP	Tris(2-chloroethyl) phosphate
TCPP	Tris (chloroisopropyl) phosphate
TDCPP	Tris(1,3-dichloroisopropyl)phosphate
PBB 1	PBB 1 (2-MonoBB)
PBB 10	PBB 10 (2,6-DiBB)
PBB 103	PBB 103 (2,2',4,5',6-PentaBB)
PBB 15	PBB 15 (4,4'-DiBB)
PBB 155	PBB 155 (2,2',4,4',6,6'-HexaBB)
PBB 18	PBB 18 (2,2',5-TriBB)
PBB 2	PBB 2 (3-MonoBB)
PBB 26	PBB 26 (2,3',5-TriBB)
PBB 3	PBB 3 (4-MonoBB)
PBB 30	PBB 30 (2,4,6-TriBB)
PBB 31	PBB 31 (2,4',5-TriBB)
PBB 4	PBB 4 (2,2'-DiBB)
PBB 49	PBB 49 (2,2',4,5'-TetraBB)
PBB 52	PBB 52 (2,2',5,5'-TetraBB)
PBB 53	PBB 53 (2,2',5,6'-TetraBB)
PBB 7	PBB 7 (2,4-DiBB)
PBB 77	PBB 77 (3,3',4,4'-TetraBB)
PBB 80	PBB 80 (3,3',5,5'-TetraBB)
PBB 9	PBB 9 (2,5-DiBB)

Multi-Residue (MRES) Contemporary Contaminants

There are dozens of un-regulated or un-monitored contemporary contaminants, such as current use pesticides (or-ganophosphate, neonicotinoids, pyrethroids, n-methyl carbamates, and insect growth regulator hormones) and in-dustrial by-products such as octachlorostyrene, which can be classified as MRES. However, the list of MRES chemicals measured in this study (Table 3.8) is restricted by available analytical methods. AXYS Analytical Services Ltd. conducted these measurements. The analytical methods are proprietary and confidential but generally detect a group of semi-volatile chemicals that span multiple chemical classes. Hence, only the method name (MLA-035 REV.07.04) is men-tioned in this document, along with contact information (AXYS Analytical Services Ltd, 2045 Mills Road W., Sidney, BC, Canada, V8L 5X2. Tel. (250) 655-5800, fax (250) 655-5811) for further references.

Table 3.8. Multi-Residue (MRES) Contemporary Contaminants measured in oyster tissue and sediment.

Compound	Application	Compound	Application
Ametryn	unrestricted or General Use Pesti-cide (GUP)	Fenitrothion	phosphorothioate (organophosphate) insecticide
Atrazine	herbicide, used to prevent pre- and postemergence broadleaf weeds in crops	Fonofos	organothiophosphate insecticide primarily used on corn
Azinphos-Methyl	a broad spectrum organophos-phate acetylcholinesterase inhibitor insecticide	Hexazinone	organic compound that is used as a broad spectrum herbicide
Captan	fungicide, gup	Malathion	pesticide that is widely used in agriculture, residen-tial landscaping
Chlorothalonil	a broad spectrum, nonsystemic fungicide,	Methoxychlor	insecticide to protect crops, ornamentals, livestock, and pets
Chlorpyriphos	an organophosphate pesticide used to kill a number of pests including insects and worms	Metribuzin	herbicide used both pre- and post-emergence in crops including soy bean, potatoes, tomatoes and sugar cane. It acts by inhibiting photosynthesis
Chlorpyriphos-Methyl	an organophosphate pesticide used to kill a number of pests including insects and worms	Parathion-Ethyl	known as "Folidol", is an organothiophosphate insecticide
Chlorpyriphos-Oxon	an organophosphate pesticide used to kill a number of pests including insects and worms	Parathion-Methyl	Parathion methyl is used as an insecticide on crops (cotton)
Cyanazine	herbicide	Permethrin	is a medication and insecticide. As a medication it is used to treat scabies and lice. As an insecticide it can be sprayed on clothing or mosquito nets
Cypermethrin	an insecticide in large-scale com-mercial agricultural applications	Perthane	insecticide
Dacthal	a preemergent herbicide. It kills grass and many common weeds ...	Phorate	an organophosphate used as an insecticide and acaricide
Desethylatrazine	Herbicide, a breakdown product of atrazine	Phosmet	non-systemic, organophosphate insecticide used on plants and animals

Table 3.8. (cont'd.) Multi-Residue (MRES) Contemporary Contaminants measured in oyster tissue and sediment.

Compound	Application	Compound	Application
Diazinon	a nonsystemic organophosphate insecticide formerly used to control cockroaches, silverfish, ants, and fleas in residential	Pirimiphos-Methyl	a phosphorothioate used as an insecticide
Diazinon-Oxon	a nonsystemic organophosphate insecticide formerly used to control cockroaches, silverfish, ants, and fleas in residential	Quintozene	used as a fungicide
Dimethoate	organophosphate insecticide and acaricide. an acetylcholinesterase inhibitor	Simazine	an herbicide of the triazine class. The compound is used to control broad-leaved weeds and annual grasses
Disulfoton	organophosphate acetylcholinesterase inhibitor used as an insecticide	Tecnazene	fungicide
Disulfoton Sulfone	organophosphate acetylcholinesterase inhibitor used as an insecticide.	Terbufos	insecticides and nematicides
Ethion	organophosphate insecticide	Octachlorostyrenes	industrial by-products

Data Analysis

Data management and analysis were conducted using a combination of R, Excel and JMP-SAS software.

Differences in total chemical group concentrations for sites associated with different land uses (e.g. Urban/Industrial, Suburban/Low Developed, Reference and Open Water Mussel Watch sites) were analyzed using a Wilcoxon nonparametric test on ranks. When chemical concentrations from different land use classifications were identified as statistically different, the means were compared using a Wilcoxon each pair test (JMP version 12). For the South Carolina study, chemical concentrations noted at Mussel Watch sites were described separately from other sites since the four SC MWP sites do not classify to a specific land use according to Sanger et al. (1999a, 1999b).

CHAPTER 4: CHESAPEAKE BAY

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 a two month 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 4.1).
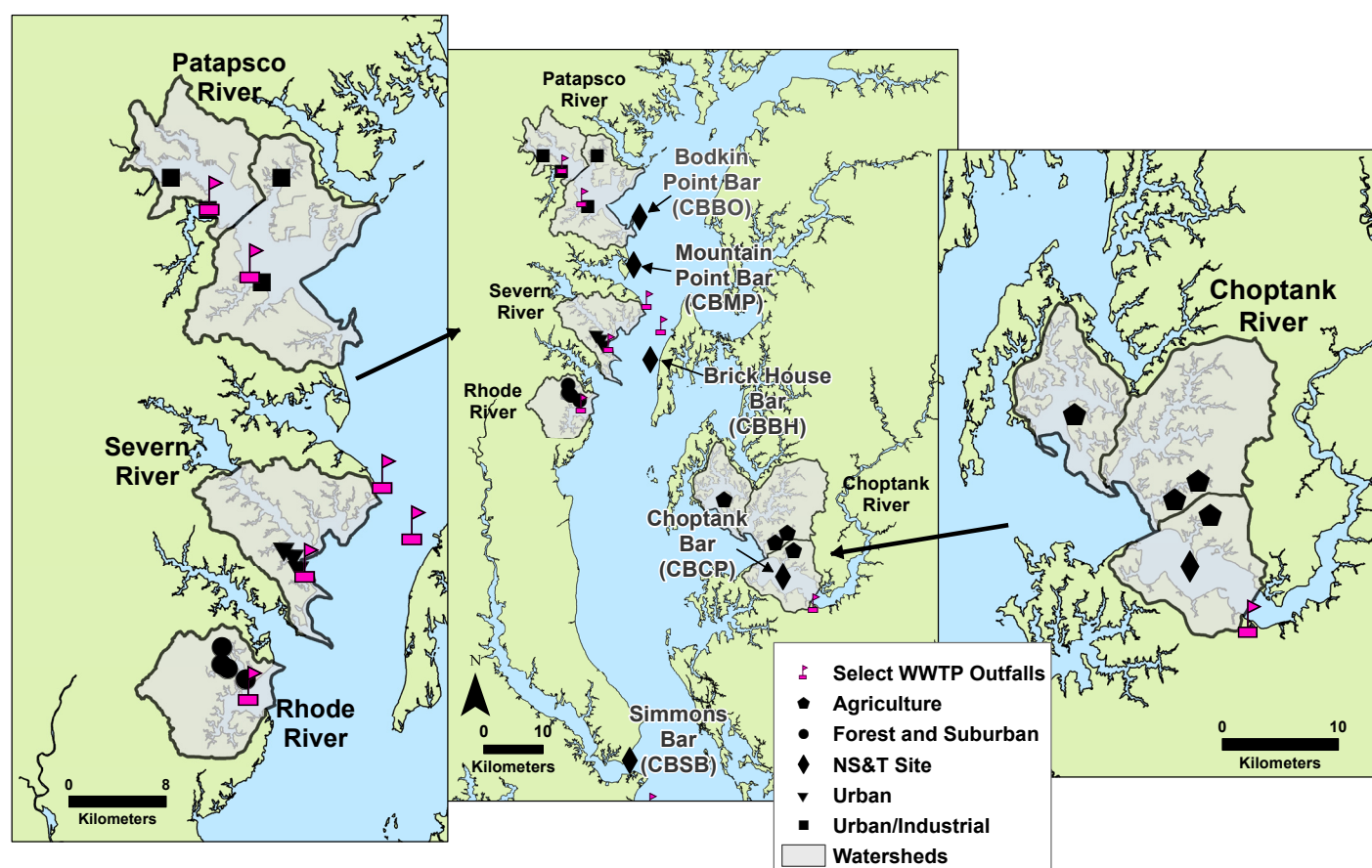
Figure 4.1. General locations for the assessment of contaminants of emerging concern in Chesapeake Bay, Maryland. The central panel shows the entire sampling extent, with side panels showing the tributaries at a smaller scale. All black station markers, except for the diamonds, show the locations of 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.

Chesapeake Bay Facts

- The Chesapeake Bay is the largest estuary in the contiguous United States.

- The Bay's watershed covers over 64,000 square miles, and includes parts of six states.

- The human population in the Chesapeake Bay watershed, currently estimated at 18.1 million people, has risen by over 110% since 1950 and is projected to exceed 21 million people by the year 2040 (EPA 2017).

Study Design

Deployed Oysters

Oysters were purchased from an aquaculture facility on the Chesapeake Bay and stored at the Cooperative Oxford Laboratory (COL) in Oxford, Maryland for less than one week. The oysters were then deployed to the sampling locations in cages, which were suspended from piers, at mid-water column depth (Figure 4.2), from June to August of 2015. Approximately 40-50 oysters were placed in each cage, and two cages were deployed at each site. Cages for deployment were borrowed from the Maryland Department of Natural Resources (MDDNR) - Marylanders Grow Oysters Program (MDDNR 2016). Approximately every 2-3 weeks the cages and oysters were cleaned with brushes to dislodge biofouling organisms, and to check for any oyster mortality.

Figure 4.2. Deployment of caged oysters at a survey site. Photo credit: NOAA.

Oyster Deployment Tributaries

Patapsco River

- The Patapsco was selected due to heavy urbanization, including the City of Baltimore, and industrial complexes in the watershed.

- Four locations in the Patapsco were identified where salinity was sufficient for oyster survival and growth.

- The Patapsco has been recognized by the Chesapeake Bay Program as one of only three 'Regions of Concern', meaning that chemical contaminants have been found at concentrations above thresholds associated with adverse effects, and that these chemicals appear to be causing toxic effects on living resources (EPA 1999).

- Two wastewater treatment facilities are located on the Patapsco River, with a combined average discharge of about 66 million gallons per day (mgd) (MDE 2017). A large number of septic systems are also concentrated on the southern shore of the Patapsco River.

- An earlier NOAA study of select human-use pharmaceuticals in Chesapeake Bay waters detected 11 of 24 compounds analyzed from five sites in Patapsco River (Pait et al. 2006).

Severn River

- The lower Severn River was selected as an urbanized watershed, with hardened shorelines and extensive marinas.

- The Severn River drains large sections of the city of Annapolis and the Naval Academy grounds.

- Oysters were deployed in cages at three locations in the Severn River, one in Spa Creek, one in Back Creek, and one further downstream along the southern shore of the Severn.

- Benthic sediments in the area have been shown to contain metals, PAHs, and legacy pesticides, leading to its classification as an 'Area of Emphasis' by the Chesapeake Bay Program, where chemical contaminant data are elevated above thresholds associated with adverse effects, but where there is limited or no evidence of actual effects (EPA 1999).

- The Annapolis Water Reclamation Facility (AWRF), a WWTP located near the mouth of the Severn, discharges roughly 9.6 mgd on average (MDE 2017).

- An earlier NOAA study of pharmaceuticals in Chesapeake Bay waters included samples from a site at the AWRF outfall and found two compounds (carbamazepine and cotinine) at detectable levels (Pait et al. 2006).

Rhode River

- The Rhode River was selected to represent low development land use.

- The Rhode River is located south of the Severn along the western shore of the Bay.

- The watershed primarily contains forested and light-residential and suburban areas.

- Deployed oysters were placed at four locations spread throughout the river, with one location in Sellman Creek and three sites along the mainstem of the river.

- Two studies of benthic condition in the Rhode River have noted variable chemical contaminant levels, with some mainstem sites containing chemical contaminants at elevated levels, particularly for metals and a few PAHs, while other sites had very low levels of chemical contaminants (Fulton et al. 2007, Leight et al. 2011).

- A relatively small wastewater treatment facility discharges an average of 0.5 mgd into the mouth of the river at the furthest point of land toward the Bay (MDE 2017).

Choptank River

- The Choptank River was selected due to extensive agricultural land use in the watershed.

- It is located across the Bay from the other three rivers on the Eastern Shore of Chesapeake Bay.

- Sample locations from this river, similar to those for the Severn, were distributed between several smaller tributaries that feed into the lower Choptank, including LaTrappe Creek, Island Creek, and Broad Creek.

- Oysters were deployed in three tributaries of the Choptank at four locations, one in LaTrappe Creek, two in Island Creek, and one in Broad Creek.

- A moderately sized wastewater treatment facility is located in the town of Cambridge and discharges an average of 2.7 mgd into the lower Choptank River (MDE 2017). Effluent from this plant may impact the long-term Mussel Watch site in the lower Choptank (CBCP), but is not likely to have a large influence on the deployed oyster sites, which were located in tributaries of the Choptank.

Sediments and Wild Oysters from Mussel Watch Sites

- The MWP has 14 long-term monitoring sites located in the Chesapeake Bay (Maryland and Virginia).

- Five of these sites were selected for this study based on their proximity to the rivers where caged oysters were deployed. These Mussel Watch sites were primarily in the mainstem of the Bay or close to the mouth of the tributaries selected for this study.

- For this study, wild oysters and sediment were collected from each of the five selected MWP sites.

Sample Collection and Analysis

Sample collection followed MWP standard procedures as briefly described in Chapter 3 and described further in Apeti et al. (2012). In MD, caged oysters were deployed and collected by hand from a small boat. Cages were deployed June 22-29, and collected between August 27-31. Oysters and sediments from the Mussel Watch locations were collected using the NOAA research vessel Chesapeake. The samples from the Mussel Watch sites were collected using a benthic grab sampler (sediments) and a small dredge (oysters) in August 2015 (Figure 4.3). Sediment samples were collected using a modified Van-Veen sampler and preserved on ice or in refrigerators until shipped to the laboratory. Additionally, at least 60 oysters (3-5 inch) were collected for chemical contaminant analyses.
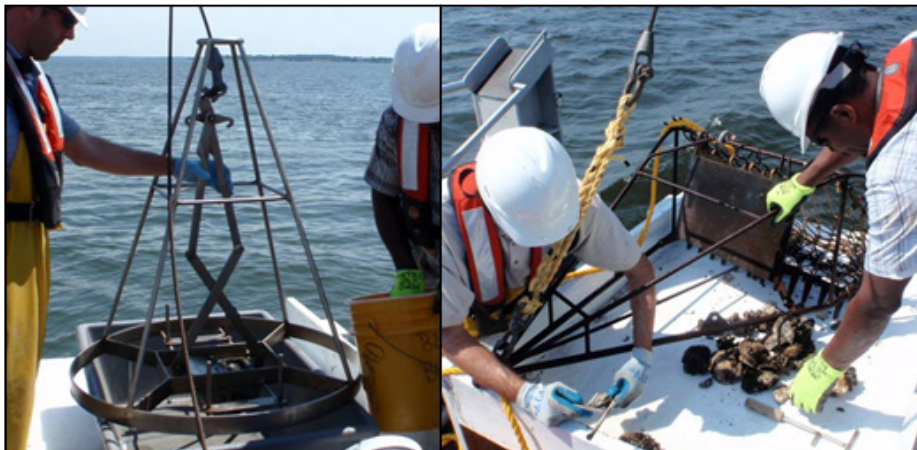
Figure 4.3. Bottom grab sampler (left) used to collect sediments, and oyster dredge (right) used to collect wild oysters from natural bars. Photo Credit: NOAA

Data Analysis

Differences in total chemical group concentrations for sites associated with different land uses were analyzed using a Wilcoxon nonparametric test on ranks. When chemical concentrations from different land use classifications were identified as statistically different, the means were compared using a Wilcoxon each pair test (JMP version 12). Chemical concentrations noted at Mussel Watch sites were described separately since the five Chesapeake Bay MWP sites are largely open water sites and do not classify to a specific land use.

Distribution and Magnitude of CECs in the Chesapeake Bay Study Area

Perfluorinated Compounds (PFCs) in Chesapeake Bay

Background

Perfluorinated chemicals (PFC) are a group of fluorine-containing compounds that are used in industrial processes related to surface protection/coatings, fire fighting foam, insecticides and commercial polymer manufacturing. Typically, PFCs enter the aquatic environment through aqueous industrial effluent or residential wastewater. This class of chemicals appears to accumulate in the environment, and because of their widespread use, are becoming ubiquitous in sediment and tissue samples from coastal habitats (Chen et al. 2012, CDC 2018). When they are taken up by organisms, PFCs are suspected to be endocrine disruptors and can cause developmental problems in animals (Grun and Blumberg 2009). Thus, this class of CECs has garnered increasing environmental research interest in the past 10-15 years.

PFCs in Chesapeake Bay Sediment

Table 4.1. Magnitude of PFC compounds found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	PFOSA	PFOS	PFOA	PFNA	PFDA	PFUNDA	PFDODA
Mussel Watch	Open Water	CBBO	0	0.319	0	0.329	0	0	0.196
		CBMP	0	0.729	0	0.362	0	0.323	0.244
		CBBH	0	0.372	0	0.308	0	0.366	0.283
		CBCP	0	0.917	0.411	0.708	0.188	0.509	0.313
		CBSB	0.236	1.08	0.274	0.529	0.314	0.489	0.601
Sample Detect Frequency (%)			20	100	40	100	40	80	100

Summary of PFCs in Chesapeake Bay Sediment

Mussel Watch Highlights

- 12 Perfluorinated compounds (PFCs) were surveyed in sediment samples.

- Seven different PFCs were detected in sediment samples collected from the historic Mussel Watch sites.

- PFCs were found in all sediment samples, with concentrations ranging from 0.20 to 1.08 ng/g (Table 4.1).

- PFOS, PFNA, and PFDODA were detected in all five sediment samples.

PFCs in Chesapeake Bay Oyster Tissues

Table 4.2. Magnitude of PFCs compounds found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	PFOA	PFOS	PFOSA
Choptank	Agriculture	CBCT-1	0	0	0
		CBCT-2	454	0	0
		CBCT-3	0	0	0
		CBCT-4	591	0	0
Patapsco	Urban/ Industrial	CBPT-1	0	0	4310
		CBPT-2	0	0	3290
		CBPT-3	0	0	2910
		CBPT-4	0	0	3320
Rhode	Forest/ Light Development	CBRD-1	0	0	1100
		CBRD-2	0	0	0
		CBRD-3	0	0	0
		CBRD-4	0	0	0
Severn	Urban	CBSV-1	0	0	891
		CBSV-2	0	0	1670
		CBSV-3	0	0	1920
Mussel Watch	Open Water	CBBO	0	0	3360
		CBMP	0	0	1900
		CBBH	0	0	1400
		CBCP	0	0	837
		CBSB	0	1050	0
Sample Detect Frequency (%)			10	5	60

Summary of PFCs in Chesapeake Bay Oyster Tissue

Chemical Highlights

- Only three of the 12 PFCs surveyed were detected in oyster samples (Table 4.2).

- Fifteen of the 20 tissue samples contained a PFC.

- PFOSA (perfluorooctanesulfonamide) was detected most frequently (12 samples).

- Concentrations of PFCs were generally higher in tissues than in sediments (1000 picograms equals one nanogram).

Land Use Highlights

- PFCs were detected at all sites in the urbanized Patapsco and Severn Rivers and at significantly higher concentrations (p value > 0.05) in the urban/industrial Patapsco than the agricultural Choptank or forested Rhode Rivers.

- The highest concentration of PFCs (4310 pg/g) was found in oyster tissues at the deployed oyster site in Patapsco River CBPT-1.

Mussel Watch Highlights

- Oyster tissues from at each of the five Mussel Watch sites contained a PFC.

Pharmaceuticals and Personal Care Products (PPCPs) in Chesapeake Bay

Environmental PPCPs include a wide spectrum of therapeutic and consumer-use compounds. These are residues of prescription and over-the-counter medications, hormones, synthetic fragrances, detergents, disinfectants, insect repellants, and antimicrobial agents. In 2009, an estimated 3.9 billion prescriptions were written for the top 300 pharmaceuticals in the US (Lundy 2010). Pharmaceutical companies produce over 50 million pounds of antibiotics annually in the United States, with approximately 60% for human use and 40% for animal agriculture (Levy 1998). There are numerous pathways by which PPCPs are introduced into the environment, although the main ones are release through excretion and the improper disposal of unused drugs (Daughton and Ternes 1999). Because pharmaceuticals are designed with the intention of having a biological effect, the major concerns of PPCPs in the environment are their potential ecotoxicity and unintentional human health impacts. Potential impacts of PPCPs in the environment include abnormal physiological effects, impaired reproduction, and increased cancer rates (Boyd and Furlong 2002). According to the US EPA, many CECs, including PPCPs, are suspected to be endocrine disruptors, which alter or interfere with the normal functions of hormones resulting in a variety of health effects (Ankley et al. 2008). Seventy-three of the possible 85 PPCP analytes were analyzed in sediments and 84 PPCPs in tissues. Similar PPCP analyte data quality and reporting issues have been noted in at least one previous CEC study (Klosterhaus et al. 2013).

PPCPs in Chesapeake Bay Sediment

Table 4.3. Magnitude of PPCP compounds found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	Antidiabetic	Psychiatric
			Metformin	Diazepam
Mussel Watch	Open Water	CBBO	0	0
		CBMP	0	0
		CBBH	21.2	0
		CBCP	0	0
		CBSB	0	9.38
Sample Detect Frequency (%)			**20**	**20**

Summary of PPCPs in Chesapeake Bay Sediment

Mussel Watch Highlights

- Only two PPCPs were detected in Chesapeake Bay sediment samples (Table 4.3).
- The antidiabetic drug Metformin was detected in sediments from the Brickhouse Bar (CBBH).
- The anti-anxiety drug Diazepam was detected in sediments from the Simmons Bar (CBSB).

Summary of PPCPs in Chesapeake Bay Oyster Tissues

Table 4.4. Magnitude of PPCP compounds found in MD oyster samples (pg/g wet mass)

Location	Land Use	Site	Antibiotic									Antidiabetic	Antihistamine	Cardiovascular			
			Cloxacillin	Flumequine	Oxacillin	Penicillin V	Sarafloxacin	Sulfadiazine	Sulfadimethoxine	Sulfamethazine	Sulfanilamide	Glyburide	Diphenhydramine	Amlodipine	Digoxin	Norverapamil	Propranolol
Choptank	Agriculture	CBCT-1	0	345	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBCT-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBCT-3	0	0	0	676	0	0	0	0	17700	0	0	0	0	0	0
		CBCT-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Patapsco	Urban/ Industrial	CBPT-1	1120	0	736	0	2400	1550	0	196	0	0	0	1410	856	163	685
		CBPT-2	1770	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBPT-3	0	0	0	0	0	0	0	0	0	0	1720	0	0	0	0
		CBPT-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rhode	Forested/ Light Development	CBRD-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBRD-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBRD-3	0	0	0	0	0	3090	0	0	0	0	0	0	0	0	0
		CBRD-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Severn	Urban	CBSV-1	0	0	0	0	0	0	404	0	0	0	0	0	0	0	0
		CBSV-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBSV-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mussel Watch	Open Water	CBBO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBMP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBBH	0	0	0	0	0	0	0	0	0	1840	0	1770	0	0	0
		CBCP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBSB	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sample Detect Frequency (%)			10	5	5	5	5	10	5	5	5	5	5	10	5	5	5

Table 4.4 (cont'd). Magnitude of PPCP compounds found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	Cholesterol Reducer	Muscular	Pain Reliever	Psychiatric					Recreational Drug	Steroid					Stimulant
			Gemfibrozil	Benztropine	Acetaminophen	Alprazolam	Meprobamate	Norfluoxetine	Paroxetine	Sertraline	Benzoylecgonine	Fluocinonide	Fluticasone propionate	Hydrocortisone	Prednisolone	Prednisone	Caffeine
Choptank	Agriculture	CBCT-1	0	0	5680	0	0	0	0	0	0	0	0	0	0	0	4650
		CBCT-2	0	0	13900	0	0	0	0	0	0	0	0	0	0	0	0
		CBCT-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBCT-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Patapsco	Urban/Industrial	CBPT-1	0	0	41400	225	3520	1030	4930	0	736	9360	8850	47400	5620	144000	26600
		CBPT-2	0	0	0	0	0	0	1480	0	0	0	0	0	0	0	0
		CBPT-3	0	0	23300	0	0	0	0	1440	0	0	0	0	0	0	0
		CBPT-4	0	0	17100	0	0	0	0	0	0	0	0	0	0	0	0
Rhode	Forested/Light Development	CBRD-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBRD-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBRD-3	0	0	4130	0	0	0	0	0	0	0	0	0	0	0	9690
		CBRD-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Severn	Urban	CBSV-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBSV-2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBSV-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3030
Mussel Watch	Open Water	CBBO	0	512	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBMP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBBH	900	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBCP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		CBSB	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sample Detect Frequency (%)			5	5	30	5	5	5	10	5	5	5	5	5	5	5	20

Chemical Highlights

- 30 different PPCP compounds were detected in oyster tissues, including antibiotics, pain relievers, antidepressants, and caffeine (Table 4.4).

- Acetaminophen was the most common PPCP detected, found in oyster tissues at 6 sites.

Land Use Highlights

- PPCPs were detected at 10 of the 15 deployed oyster sites.

- At least one PPCP chemical was detected in tissues of deployed oysters from each river.

- Most PPCP chemicals detected were in oyster tissues at one site in the Patapsco River (CBPT-1).

- However, there were no statistical differences in total PPCP concentrations between the four rivers ($p > 0.05$).

- The high numbers of PPCP chemicals and concentrations at CBPT-1 site may be due to the downstream proximity of the sample site to two large wastewater treatment plants.

Mussel Watch Highlights

- Four PPCPs were detected in Mussel Watch oyster samples, three compounds at CBBH and one at CBBO.

- Three of the four compounds detected in Mussel Watch oysters were found only in oysters.

Alkyl Phenols (APs) in Chesapeake Bay

Alkylphenols are a class of chemicals used as detergents and surfactants in industrial processes. Some household detergents (i.e. laundy soaps) also include APs. The most common sources of APs to aquatic systems are wastewater and septic system discharges (Ying et al. 2002). These compounds tend to be persistent in the environment, have a strong affinity for suspended particles, and are well preserved in bottom sediments (Ying et al. 2002). In the environment, alkylphenol ethoxylate surfactants biodegrade into more environmentally stable metabolites, such as the alkylphenol n-ethoxylates, alkylphenoxy acetic and alkylphnoxypolyethoxy acetic acids, and alkylphenols (EPA 2014a). This study focused on four AP metabolites in both sediment and oyster tissues. Two of the compounds 4-nonylphenol (4-NP) and 4 -n-octylphenol (4-n-OP) are degradation products of 4-nonylphenol mono-ethoxylate (NP1E0) and 4 nonylphenol di-ethoxylate (NP2E0), which are byproducts of the parent alkylphenol polyethoxylate. These degradation products are more stable and more toxic than the parent compounds and are hormone mimics (Ying et al. 2002).

APs in Chesapeake Bay Sediment

- No alkyl phenols were found at detectable level in any of the Maryland sediment samples.

APs in Chesapeake Bay Oyster Tissues

Table 4.5. Magnitude of AP compounds found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	4-nonylphenol	4-n-OP	NP1EO	NP2EO
Choptank	Agriculture	CBCT-1	0	0	0	0
		CBCT-2	0	0	0	0
		CBCT-3	0	0	0	0
		CBCT-4	0	0	0	0
Patapsco	Urban/ Industrial	CBPT-1	0	0	0	0
		CBPT-2	0	0	0	0
		CBPT-3	0	0	29100	0
		CBPT-4	0	0	0	0
Rhode	Forested/ Light Development	CBRD-1	0	0	0	0
		CBRD-2	0	0	0	0
		CBRD-3	0	0	0	0
		CBRD-4	0	0	0	0
Severn	Urban	CBSV-1	0	0	0	0
		CBSV-2	0	0	0	0
		CBSV-3	0	0	0	0
Mussel Watch	Open Water	CBBO	0	0	0	0
		CBMP	0	0	0	0
		CBBH	0	0	0	0
		CBCP	0	0	13100	0
		CBSB	0	0	0	0
Sample Detect Frequency (%)			**0**	**0**	**10**	**0**

Summary of APs for Chesapeake Bay Oyster Tissue

Chemical Highlights

- Nonylphenol monoethoxylate (NP1EO) was the only one of the four APs tested that was detected (Table 4.5).

Land Use Highlights

- The only AP detected in deployed oysters was found at the site CBPT-3 in Patapsco River (Fig. 4.1).

Mussel Watch Highlights

- The only AP detected in oysters from Mussel Watch sites was found at the Choptank River site (CBCP).

Polybrominated Diphenyl Ethers (PBDEs) in Chesapeake Bay

Polybominated diphenyl ethers (PBDEs) are a group of chemicals that are used as flame-retardants in consumer and household products. Commercially, three types of PBDE industrial mixtures were available, the pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE) and the decabromodiphenyl ether (deca-BDE) mixtures (EPA 2014b). As these products age and degrade, PBDEs can enter the environment. PBDEs are structurally similar to poly-chlorinated biphenyls (PCBs) with 209 possible unique structures or congeners. PBDEs have been measured in house-hold dust, human breast milk, sediment and wildlife (ATSDR, 2015). The toxicology of PBDEs is not well understood, but PBDEs have been associated with tumors, neurodevelopmental toxicity and thyroid hormone imbalance. Due to ubiquitous distribution, potential persistance and toxicity, the manufacture of the 'penta' and 'octa' PBDEs mixtures have been phased out starting in 2004, and for the deca mixture in 2013 (EPA 2014b, Schreder and La Guardia 2014). However, as persistent organic pollutants (POPs), PBDEs will be present in every compartment of the environment for years. Less brominated PBDEs, like tetra-, penta- and hexa-BDE, demonstrate high affinity for lipids and tend to bioac-cumulate in animals and humans, while highly brominated PBDEs like deca-BDE tend to absorb more onto sediment and soil.

PBDEs in Chesapeake Bay Sediments

Table 4.6. Magnitude of PBDE congeners found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	PBDE Congener									
			17	25	28	32	33	35	47	66	71/49	75
Mussel Watch	Open Water	CBBO	0.14	0.107	0.053	0.126	0.019	0.037	0.307	0.088	0.226	0.062
		CBMP	0.167	0	0.075	0	0	0	0.414	0.14	0.324	0
		CBBH	0	0	0.026	0	0	0	0.131	0.019	0.048	0
		CBCP	0	0	0	0	0	0	0.107	0.017	0.037	0.041
		CBSB	0	0	0.03	0	0	0	0.204	0.066	0	0.066
Sample Detect Frequency (%)			40	20	80	20	20	20	100	100	80	60

"/" denotes co-eluting congeners

Table 4.6. (cont'd) Magnitude of PBDE congeners found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	PBDE Congener								Total PBDEs	Ratio of PBDE209/ all PBDEs
			77	85	99	100	116	118	126	209		
Mussel Watch	OPEN WATER	CBBO	0	0.237	0.195	0.031	0	0.103	0	59.983	61.7	0.972
		CBMP	0.028	0.374	0.268	0.032	0	0.17	0.035	55.761	57.8	0.965
		CBBH	0	0.134	0.099	0.058	0	0.046	0.016	9.707	10.3	0.942
		CBCP	0.019	0.204	0.114	0.043	0.038	0.022	0	2.963	3.61	0.821
		CBSB	0	0.208	0.153	0.062	0.114	0.035	0	7.038	7.98	0.882
Sample Detect Frequency (%)			40	100	100	100	40	100	40	100		

"/" denotes co-eluting congeners

Summary of PBDEs in Chesapeake Bay Sediment

Mussel Watch Highlights

- Fifty-five PBDE congeners were surveyed in Chesapeake Bay sediments.

- PBDEs were pervasive in sediment samples collected from the Mussel Watch sites, with 18 different congeners detected in at least one sample and seven congeners detected in all samples (Table 4.6).

- Total PBDE concentrations ranged from 3.61 ng/g at the Choptank site (CBCP) to 61.7 ng/g at the Bodkins Point Bar site (CBBO) (Figure 4.1, Table 4.6).

PBDEs in Chesapeake Bay Oyster Tissue

Table 4.7. Magnitude of PBDE congeners found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	PBDE Congener											
			17	28	30	37	47	66	71/49	75	77	85	99	100
Choptank	Agriculture	CBCT-1	0	0	0	0	73.7	0	0	0	99.2	0	0	0
		CBCT-2	0	0	0	0	58.8	0	0	0	211	0	0	0
		CBCT-3	0	0	0	0	69.2	29.2	0	0	172	0	0	0
		CBCT-4	0	0	0	0	117	19	88.1	0	728	0	50.2	0
Patapsco	Urban/ Industrial	CBPT-1	150	51.1	0	0	993	121	414	0	235	0	120	182
		CBPT-2	0	0	0	0	444	80.7	213	0	88.7	0	58.1	124
		CBPT-3	0	139	0	0	5130	152	536	90.9	63.6	59.1	964	939
		CBPT-4	0	179	0	19.4	4660	208	1040	146	78.9	78.9	1060	1120
Rhode	Forested/ Light Development	CBRD-1	0	0	0	0	160	0	0	0	96.1	0	0	0
		CBRD-2	0	0	0	0	0	0	0	0	52.2	0	0	0
		CBRD-3	0	0	0	0	131	25.4	149	0	75	0	17.4	40.2
		CBRD-4	0	0	208	0	61.4	61.4	0	0	372	0	0	75.6
Severn	Urban	CBSV-1	0	0	0	0	375	52.9	97.8	0	114	0	83.4	97.8
		CBSV-2	0	28.8	0	0	631	44	194	0	106	0	114	133
		CBSV-3	0	36	0	0	1120	44.6	333	0	86.4	21.6	307	249
Mussel Watch	Open Water	CBBO	0	0	0	0	88.5	0	0	0	0	0	0	0
		CBMP	0	0	0	0	80.9	0	43.1	0	0	0	0	0
		CBBH	0	0	0	0	46.5	0	0	0	0	0	0	0
		CBCP	0	0	0	0	30	0	0	0	0	0	0	0
		CBSB	0	0	0	0	39.1	0	0	0	0	0	0	0
Sample Detect Frequency (%)			5	25	5	5	95	55	50	10	75	15	45	45

"/" denotes co-eluting congeners

Table 4.7. (cont'd) Magnitude of PBDE congeners found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	PBDE Congener										Total PBDEs	Ratio of PBDE209/ all PBDEs
			118	126	154	155	181	183	190	201	202	209		
Choptank	Agriculture	CBCT-1	0	12.8	0	0	0	0	0	0	0	154	339.7	0.456
		CBCT-2	0	0	0	0	0	0	0	0	0	131	400.8	0.327
		CBCT-3	0	0	0	0	0	0	0	0	0	120	390.4	0.308
		CBCT-4	0	0	0	0	0	0	0	0	0	99	1100	0.090
Patapsco	Urban/ Industrial	CBPT-1	0	0	76.7	0	0	0	0	0	0	366	2710	0.135
		CBPT-2	0	67.7	0	0	0	0	0	0	0	203	1280	0.159
		CBPT-3	0	63.6	179	28.8	0	0	0	0	0	209	8550	0.024
		CBPT-4	0	83.4	195	25.3	0	0	0	0	0	200	9090	0.022
Rhode	Forested/ Light Devel- opment	CBRD-1	0	0	0	0	0	0	0	0	0	0	256.1	0.000
		CBRD-2	0	0	0	0	0	0	0	0	0	142	194.2	0.735
		CBRD-3	12.1	8.03	9.37	9.37	0	0	0	0	0	177	654	0.270
		CBRD-4	0	56.7	0	0	0	0	0	0	0	370	1210	0.307
Severn	Urban	CBSV-1	0	0	0	0	0	0	0	0	0	83.4	904.3	0.092
		CBSV-2	0	0	0	0	0	0	0	0	0	155	1410	0.110
		CBSV-3	8.64	0	44.6	0	3.31	7.2	9.5	0.576	0.432	138	2410	0.057
Mussel Watch	Open Water	CBBO	0	0	0	0	0	0	0	0	0	283	372	0.762
		CBMP	0	0	0	0	0	0	0	0	0	203	327	0.621
		CBBH	0	0	0	0	0	0	0	0	0	239	285.5	0.835
		CBCP	0	0	0	0	0	0	0	0	0	27.6	57.6	0.477
		CBSB	0	0	0	0	0	0	0	0	0	151	190.1	0.794
Sample Detect Frequency (%)			10	30	25	15	5	5	5	5	5	95		

"/" denotes co-eluting congeners

Summary of PBDEs in Chesapeake Bay Oyster Tissue

Chemical Highlights

- Fifty-five PBDE congeners were surveyed in oyster samples.

- Twenty-two of the fifty-five PBDE congeners were detected in the oyster tissues (Table 4.7).

- Total PBDE concentration by site ranged from <1 pg/g of oyster tissue to 5130 pg/g wet tissue mass.

Land Use Highlights

- PBDE congeners were detected in all deployed oyster samples.

- The three highest concentrations of total PBDEs were found in the urban Patapsco River sites.

- Oysters from the Severn River sites (suburban areas) contained much lower concentrations of PBDEs than oysters from the Patapsco.

- Total PBDE concentrations in the Patapsco were significantly higher (p value = 0.03) than concentrations found in the Rhode River sites.

- Total PBDE concentrations in the Patapsco River were elevated but not significantly compared to concentrations in the Choptank or Severn Rivers.

Mussel Watch Highlights

- Total PBDE concentrations in wild oyster from the Mussel Watch sites ranged from 372 pg/g at the furthest up-Bay site (CBBO) to 57.6 pg/g at the oyster bar inside the Choptank River (CBCP).

Alternative Flame Retardants (AFRs) in Chesapeake Bay

Alternative flame retardants are chemicals that are added to a wide variety of industrial and consumer products, such as textiles, rugs, furniture and plastics to reduce their flammability (de Wit 2002). For this study, several groups of chemicals were combined under the title of alternative flame retardant, including the brominated flame retardants (BFRs), chlorinated organophosphate (CPP) chemicals and the polybrominated biphenyls (PBBs). PBBs are manufactured chemicals primarily used in firefighting materials; their application is now controlled as a hazardous substance (Safe 1984). The BFRs such as hexabromo-cyclododecane (HBCDs) are primarily use in household consumer products such as upholstery and textiles. HBCDs are ubiqutous in the environment, but their ecotoxicity is not well understood. The chlorinated organophosphate flame retardants such as tris(1,3-dichloroisopropyl)phosphate (TDCPP) are mainly used as additives in textiles. As additives, chlorinated organophosphate flame retardants tend to leach out over time into water and air. In the environment, TDCPP can accumulate in animal fat tissues (Andresen et al. 2004).

AFRs in Chesapeake Bay Sediment

Table 4.8. Magnitude of AFR compounds found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	TBB	TBPH
Mussel Watch	Open Water	CBBO	0	0
		CBMP	0	0
		CBBH	0	0
		CBCP	1.73	1.00
		CBSB	0	0
Sample Detect Frequency (%)			20	20

Summary of AFRs in Chesapeake Bay Sediments

Mussel Watch Highlights

- 28 AFRs were surveyed in sediment samples.

- Only two AFRs were detected in Chesapeake Bay sediment samples collected from the historic Mussel Watch sites (Table 4.8).

- Both detections were of brominated flame retardants (BFRs) at the Choptank River site.

AFRs in Chesapeake Bay Oyster Tissues

Table 4.9. Magnitude of AFR compounds found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	PBB 1 (2-MonoBB)	PBB 2 (3-MonoBB)	TBPH	TDCPP
Choptank	Agriculture	CBCT-1	0	0	0	0
		CBCT-2	0	0	0	0
		CBCT-3	0	0	0	0
		CBCT-4	0	0	0	0
Patapsco	Urban/ Industrial	CBPT-1	0	112	0	0
		CBPT-2	0	0	561	16900
		CBPT-3	0	0	0	20800
		CBPT-4	923	89.3	23400	23100
Rhode	Forested/ Light Development	CBRD-1	0	0	0	0
		CBRD-2	0	0	0	0
		CBRD-3	0	0	0	0
		CBRD-4	0	0	0	0
Severn	Urban	CBSV-1	0	0	0	0
		CBSV-2	0	0	0	0
		CBSV-3	0	0	0	0
Mussel Watch	Open Water	CBBO	0	0	0	0
		CBMP	0	0	0	0
		CBBH	0	0	0	0
		CBCP	0	0	262	0
		CBSB	0	0	0	0
Sample Detect Frequency (%)			5	10	15	15

Summary of AFRs in Chesapeake Bay Oyster Tissues

Chemical Highlights

- Four of the 28 AFRs surveyed, two polybrominated biphenyls and two brominated flame retardants, were detected in oyster tissues (Table 4.9).

- Concentrations of the HBCD compounds tended to be higher than those for the PBB compounds.

Land Use Highlights

- For deployed oyster samples, all four AFRs detected were found only in the Patapsco River.

Mussel Watch Highlights

- One BFR, the brominated flame retardant TBPH, was detected in oysters from the Choptank River site at a concentration comparable to one of the upstream Patapsco River sites (CBPT-2), and an order of magnitude lower than the most downstream Patapsco River site (CBPT-4).

Multi-Residue (MRES) Contemporary Contaminants in Chesapeake Bay

Multi-residue contemporary contaminant (MRES) are generally a group of semi-volatile chemicals that span multiple chemical classes and can be analyzed concurrently. In this report, MRES chemicals includes pesticides, degradation products and the industrial by-product octachlorostyrene. These MRES current use pesticides are typically more water soluble than the legacy organochlorine pesticides and often do not bioaccumulate in organisms. It has been estimated that in 2007, over 565 million kg of current-use pesticides were used in the USA (EPA 2011). Among pesticides, herbicides accounted for 40% of total usage, and insecticides 17% (EPA 2011). While agriculture application accounts for over 60% of pesticides used, urban usage is increasing. Pesticides enter the environment seasonally through surface run-off, direct discharge and through atmospheric long-range transport (EPA 2011).

Octachlorostyrene is a by-product of industrial processes involving aluminium refining and combustion of chlorinated compounds. Listed in the EPA priority list of most bioaccumulative compounds, octachlorstyrene is highly toxic and extremely persistent when released to the environment (Chu et al. 2003). Octachlorostyrene is included in this study as it has been found in the environment at increasing concentrations, particularly in industrial areas (Chu et al. 2003).

MRES in Chesapeake Bay Sediment

Table 4.10. Magnitude of MRES contaminant found in MD sediment samples (ng/g dry mass).

Location	Land Use	Site	Ametryn	Atrazine	Cyanazine	Desethylatrazine	Ethion	Octachlorostyrene	Simazine
Mussel Watch	Open Water	CBBO	0.033	0.572	0.785	0.091	0.598	0.003	0
		CBMP	0.072	0.835	0.83	0	0.755	0	0
		CBBH	0.226	0.174	0	0	0.092	0	0
		CBCP	0.105	0.271	0	0.027	0	0	0.081
		CBSB	0.479	0	0	0	0	0	0
Sample Detect Frequency (%)			100	80	40	40	60	20	20

Summary of MRES in Chesapeake Bay Sediment

Mussel Watch Highlights

- Sediments from the Maryland Mussel Watch sites were surveyed for 36 MRES chemicals.

- All sediment samples from the historic Mussel Watch sites were shown to contain measurable values of at least one of MRES contaminants measured (Table 4.10).

- Seven MRES compounds, mostly herbicides, were detected at different concentrations in Chesapeake Bay sediment (Table 4.10).

- Ametryn, an herbicide to control broadleaf weeds and grasses, was found in all samples.

- Ethion, the only insecticide found in sediments, occurred at the three sites furthest up the Bay.

MRES in Chesapeake Bay Oyster Tissues

Table 4.11. Magnitude of MRES compounds found in MD oyster samples (pg/g wet mass).

Location	Land Use	Site	Ametryn	Atrazine	Dacthal	Desethylatrazine	Ethion	Octachlorostyrene	Permethrin	Perthane
Choptank	Agriculture	CBCT-1	116	0	0	31	0	0	0	0
		CBCT-2	66	0	0	32	0	0	0	0
		CBCT-3	204	0	0	34	0	0	4140	0
		CBCT-4	0	606	26	0	0	3	0	0
Patapsco	Urban/Industrial	CBPT-1	0	0	40	37	315	0	0	0
		CBPT-2	0	463	36	43	0	0	0	0
		CBPT-3	0	0	35	0	3310	0	1080	0
		CBPT-4	0	0	23	43	0	0	0	0
Rhode	Forested/Light Development	CBRD-1	0	364	23	33	0	0	0	0
		CBRD-2	0	341	0	32	0	0	0	0
		CBRD-3	0	0	0	31	0	0	0	0
		CBRD-4	48	392	0	38	0	0	0	643
Severn	Urban	CBSV-1	0	259	35	39	0	0	0	0
		CBSV-2	0	0	32	42	0	0	0	0
		CBSV-3	0	0	26	0	0	0	0	0
Mussel Watch	Open Water	CBBO	0	0	0	30	0	0	0	0
		CBMP	0	0	0	30	0	0	0	0
		CBBH	0	0	0	28	0	0	0	0
		CBCP	0	0	0	33	0	0	0	0
		CBSB	0	0	0	0	0	0	0	0
Sample Detect Frequency (%)			**20**	**30**	**45**	**80**	**10**	**5**	**10**	**5**

Summary of MRES in Chesapeake Bay Oyster Tissues

Chemical Highlights

- Oyster tissues were surveyed for 36 MRES chemicals.

- Eight MRES contaminants were detected, with the herbicide Desethylatrazine being detected most often (80% of samples) (Table 4.11).

- Although Desethylatrazine was detected in most samples, the parent compound atrazine was only detected in six samples.

- MRES contaminants were mostly undetected in wild oysters from the open water Mussel Watch sites except the herbicide Desethylatrazine. Except for the Simon Bar site (CBSB) furthest down bay (and Figure 4.1.), Desethylatrazine was found in all the other wild oyster samples from the historic Mussel Watch sites.

Land Use Highlights

- The highest concentration of MRES was the insecticide permethrin, with a concentration of 4140 pg/g found in oyster tissues at a site in the agriculturally-dominated Choptank River (CBCT-3).

- The herbicide ametryn appeared to be more prevalent in oyster tissue from agricultural area, while desethylatrazine, another herbicide, was found all survey areas in caged as well as in wild oysters.

- There were no significant differences (p > 0.05) between the different land use types (rivers) based on Total MRES concentrations.

Mussel Watch Highlights

- Desethylatrazine was the only MRES contaminant detected in oysters from the Mussel Watch sites, ranging from 28 to 33 pg/g. It was detected at all sites except for the CBSB site.

Chesapeake Bay General Findings

Chemical Highlights

Detections for most CEC classes in oyster tissue and sediment samples from Maryland sites were generally low relative to the reporting limits (Table 4.12). The two classes of CECs most frequently encountered were the PFCs in sediment samples (40%) and the PBDEs in sediment samples (21.1%). PBDEs were also the most commonly detected CEC group found in oyster tissues, but only at 11.5% of all potential detections. In contrast, the Alternative Flame Retardants had the lowest frequency of detection. Although the PPCPs were infrequently detected, the three highest concentrations found for all CECs in Maryland tissue samples were for pharmaceuticals (prednisone, hydrocortisone, and acetamino-phen; Table 4.4).

Table 4.12. Summary data for the frequency of reported values from MD sediments and oysters.

CEC Class	# of Analytes		Potential # Detects		Reported # Detects		Detection Frequency (%)	
Class	Sediment	Tissues	Sediment	Tissues	Sediment	Tissues	Sediment	Tissues
PFC	12	12	60	240	24	15	40.0	6.3
PPCP	73	84	365	1680	2	42	0.5	2.5
AP	4	4	20	80	0	2	0.0	2.5
PBDE	55	55	275	1100	58	126	21.1	11.5
AFR	28	28	140	560	2	9	1.4	1.6
MRES	36	36	180	720	18	41	10.0	5.7
Total	**208**	**219**	**1040**	**4380**	**104**	**235**	**10.0**	**5.4**

Land Use Highlights

Land use likely played a role in the detection and/or concentrations of CECs in Maryland oyster tissue samples. For APs and BFRs, the only compounds detected in deployed oysters were found in the heavily urbanized Patapsco River. They were not detected in samples from the less densely urbanized Severn River. Although detections of PFCs were common for all four rivers, concentrations of PFCs were significantly higher in the urbanized rivers (Patapsco and Severn) than in the agricultural river (Choptank). The number of detections of PPCPs was much greater in the Patapsco than the other rivers (Table 4.13), likely due to the downstream location of one site (CBPT-1) to two large wastewater treatment facilities, but the concentrations of PPCPs was not statistically different from other rivers when compared on a river-wide basis. PBDEs showed a trend with land use, with the number of PBDEs detections and total PBDE

concentrations being highest in the heavily urbanized Patapsco, followed by the urban Severn River. The number of detections and total concentrations of current use pesticides did not differ significantly between rivers, despite the Choptank River being agriculturally-dominated. It appears that the combination of very dense development in the Patapsco River along with the large wastewater treatment plants that serve the human population there may have contributed to higher detections and concentrations of particular CECs in oysters deployed to that river.

Table 4.13. Summary of the number of detections by Land Use.

CEC Class	Location	Use	Tissue
PFC	Mussel Watch	Open Water	5
	Choptank	Agriculture	2
	Patapsco	Urban/Industrial	5
	Rhode	Forested/ Light Development	1
	Severn	Urban	3
PPCP	Mussel Watch	Open Water	4
	Choptank	Agriculture	6
	Patapsco	Urban/Industrial	27
	Rhode	Forested/ Light Development	3
	Severn	Urban	2
AP	Mussel Watch	Open Water	1
	Choptank	Agriculture	0
	Patapsco	Urban/Industrial	1
	Rhode	Forested/ Light Development	0
	Severn	Urban	0
PBDE	Mussel Watch	Open Water	11
	Choptank	Agriculture	17
	Patapsco	Urban/Industrial	45
	Rhode	Forested/ Light Development	22
	Severn	Urban	31
AFR	Mussel Watch	Open Water	1
	Choptank	Agriculture	0
	Patapsco	Urban/Industrial	8
	Rhode	Forested/ Light Development	0
	Severn	Urban	0
MRES	Mussel Watch	Open Water	4
	Choptank	Agriculture	10
	Patapsco	Urban/Industrial	11
	Rhode	Forested/ Light Development	10
	Severn	Urban	6
Total	Mussel Watch	Open Water	26
	Choptank	Agriculture	35
	Patapsco	Urban/Industrial	97
	Rhode	Forested/ Light Development	36
	Severn	Urban	42

CHAPTER 5: SOUTH CAROLINA

The coastal waters of Charleston, SC and the adjacent areas (Figure 5.1) have long served as a base for environmental research and contaminant monitoring. The National Status and Trends Mussel Watch Program (MWP) established monitoring sites along the SC coast at its inception in 1986 (Kimbrough et al. 2008), and multiple detailed regional studies have been conducted in this region since the mid-1990s (Long et al. 1998, Sanger et al. 1999b). Legacy contaminants have been the primary focus of these studies and it is common for contamination in the local Charleston area to be similar to the national median or lower than contaminant concentrations measured in other regional studies (Long et al. 1998, Lauenstein et al. 2002, Kimbrough et al. 2008). In the early 1990s, the South Carolina Department of Natural Resources (SC DNR) initiated a tidal creek study that focused on the upstream segments of 28 tidal creeks with assigned land use in order to understand the distribution of contaminants in smaller estuarine creek systems and the relationship between land use and contamination (Sanger et al. 1999a, b). In 1999, the SC DNR next established the South Carolina Estuarine and Coastal Assessment Program (SCECAP) that monitors contaminant concentrations and water quality parameters annually along the SC coast (Van Dolah et al. 2002). This effort has continued through 2018. These previously published studies have almost exclusively focused on legacy contaminants, including

Figure 5.1. 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.

heavy metals, polychlorinated biphenyls (PCBs), organochlorine pesticides, chlordane, and polycyclic aromatic hydro-carbons (PAHs). From these studies, we are able to understand the spatial and temporal trends of these contaminant classes in both sediment and oysters from the Charleston estuarine environment.

Within the past decade, research has attempted to identify the occurrence, distribution and magnitude of CECs in the environment. Kolpin et al. (2002) published some of the first national survey data focusing on 95 CECs, such as hormones, pharmaceuticals, personal care products, pesticides and surfactants in US streams. Of these 95 analytes, none were detected in all 139 stream samples (maximum detection frequency ~86%) and many were not detected in any stream (Kolpin et al. 2002). Limited CEC occurrence such as that reported by Kolpin et al. (2002) is not unique (e.g. Hedgespeth et al. (2012)) and has led to several efforts to prioritize those CECs that should be included (or would be most likely to present risk) in environmental monitoring efforts. The physical and chemical properties of many CECs are not similar to the properties of legacy contaminants (i.e. PCBs) that result in chemicals being persistent and bioac-cumulative in sediments and tissues. Thus, a new strategy for monitoring CECs is required (Scott et al. 2012). Several working groups and panels have examined and discussed monitoring CECs in the environment (Diamond et al. 2011, Keith et al. 2014).

The objective of this regional study was to determine if a point specific, watershed based monitoring design would be an effective model for evaluating the occurrence and magnitude of CECs for a large-scale contaminant program like Mussel Watch. Using a land use based approach, sediment and oysters from previously categorized creeks from

Extensive South Carolina tidal marsh. Photo Credit: NOAA

around the greater Charleston, SC estuaries (Sanger et al. 1999a, b) were analyzed for a suite of historical Mussel Watch Program contaminants as well as an extensive list of CECs. The results of this study will help to understand the benefits and limitations of a field monitoring approach to CEC fate and distribution.

Study Design

South Carolina sampling sites (15 sites; Figure 5.1) were selected based on previously collected information from Sanger et al. (1999a, 1999b) and historical Mussel Watch sites. Of these 15 sites, four (CHFJ, CHSF, SRNB and WBLB) are assigned as Mussel Watch sites. Two of these sites are located in the Charleston Harbor estuary proper (CHFJ and CHSF). One Mussel Watch site is located in the North Bay of the Santee River (SRNB), and the final MWP site is located in the lower bay area of the Winyah Bay (WBLB). Mussel Watch sites were originally selected in order to describe na-tional and regional contaminant distribution and to avoid areas of direct input or "hot spots" of contamination (Lauen-

stein et al. 2002, Farrington et al. 2016). The 11 remaining SC sites included a site (North Inlet / Clambank; NICB) selected from within NOAA's North Inlet National Estuarine Research Reserve (NERR). The remaining ten creeks sampled in this study serve as tributaries within the Charleston Harbor estuary and were selected for study based upon land use classification and contaminant characterization from previous studies (Sanger et al. 1999b). Sanger et al. (1999b) classified 28 Charleston Harbor creeks (including the ten selected in this study) based on predominant watershed land cover and watershed demographic data. For this study, creeks were classified into either "Suburban" or "Urban" categories based on land use characterizations and assignments from Sanger et al. (1999a). Two Charleston Harbor creeks experienced enough development over the past two decades to be re-classified. Shem Creek (CHSM) was reclassified from "Suburban" to "Urban" and Horlbeck Creek (CHHB) was re-classified as a "Suburban" creek rather than an "Upland Reference" creek in Sanger et al. (1999a). NICB served as a "Reference" site. An additional "Reference" creek from within the Charleston Harbor estuary was also included in this study; Rathall Creek (CHRT).

Sample Collection and Analysis

Sample collection followed MWP standard procedures as previously described (Apeti et al. 2012). In SC, sampling was performed from a small boat at or near low tide. Briefly, at each site water quality was measured (temperature, dissolved oxygen and salinity). Sediment samples were collected using a modified Van-Veen sampler and stored on ice or in refrigerators until shipped to the laboratory. Additionally, at least 60 oysters (3-5 inch in length) were collected into three subsets. Samples were kept on ice until frozen in the laboratory.

Oyster collection in a South Carolina tidal marsh. Photo Credit: NOAA

Data Analysis

Sites categorized as urban, suburban or reference within each chemical class were analyzed using a Wilcoxon nonparametric test on ranks. When Land Use classifications were identified as statistically different, the means were compared using a nonparametric Kruskall Wallace test for means (JMP version 12). Chemicals concentrations noted at Mussel Watch sites were described separately since the four of these sites do not classify to a specific land use according to Sanger et al. (1999a, 1999b).

Distribution and Magnitude of CECs in the Charleston Harbor, SC Study Area

Perfluorinated Compounds (PFCs) in South Carolina

Perfluorinated chemicals (PFC) are a group of fluorine-containing compounds that are used in industrial processes related to surface protection/coatings, fire fighting foam, insecticides and commercial polymer manufacturing. Typically, PFCs enter the aquatic environment through aqueous industrial effluent or residential wastewater. This class of chemicals appears to accumulate in the environment, and because of their widespread use, they are becoming ubiquitous in sediment and tissue samples from coastal habitats (Chen et al. 2012, CDC 2018). When they are taken up by organisms, PFC are suspected of being endocrine disruptors and can cause developmental problems in animals (Grun and Blumberg 2009). Thus, this class of CECs has garnered increasing environmental research interest in the past 10-15 years.

PFCs in South Carolina Sediment

Table 5.1. Magnitude of PFC compounds found in SC sediment samples (ng/g dry mass).

Land Use	Site	PFOSA	PFOS	PFOA	PFNA	PFDA	PFUNDA	PFDODA
Urban	CHDL	0.124	5.21	0.653	0.76	1.16	0.556	0.403
	CHNM	0	0.633	0	0	0	0	0
	CHSH	0	2.04	0.329	0.621	1.5	0.742	0
	CHSM	0	0	0	0	0	0.141	0
	CHVR	0	0	0	0	0	0	0
Suburban	CHBL	0	1.79	0	0	0.276	0.28	0
	CHHB	0	0	0.297	0	0	0	0
	CHMC	0	0.387	0	0	0	0	0
	CHOG	0	0	0	0	0	0	0
Reference	CHRT	0	0	0	0	0	0	0
	NICB	0	0	0	0.36	0.191	0.336	0
Mussel Watch	CHFJ	0	0.533	0	0.28	0	0.144	0
	CHSF	0	0	0.234	0.262	0	0.132	0
	SRNB	0	0	0	0.245	0	0	0.184
	WBLB	0	0	0	0	0	0	0
Sample Detect Frequency (%)		7	40	27	40	20	47	13

Summary of PFCs in South Carolina Sediment

Chemical Highlights

- Sediments were surveyed for 12 PFCs.

- Seven different PFCs were detected in SC sediments (Table 5.1).

- PFOS and associated PFCs were detected a total of 30 times (out of a total of 180 possible detections, overall SC detection frequency of 16.7%).

Land Use Highlights

- There were no difference among the different Land Use classifications (Chi^2=0.22).

- The average concentration of PFCs detected trended downward from Urban>Suburban>Reference.

- The highest PFC concentrations detected in this study generally occurred at Urban sites, and were highest in sediments at CHDL.

Mussel Watch Highlights

- PFCs were detected at three of the four MWP sites (CHFJ, CHSF, and SRNB).

- Five of the 12 PFCs were detected at MWP sites.

PFCs in South Carolina Oyster Tissues

Table 5.2. Magnitude of PFC compounds found in SC oyster tissue samples (pg/g wet mass).

Land Use	Site	PFDODA	PFOS	PFOSA
Urban	CHDL	400	0	1480
	CHNM	0	0	1450
	CHSH	391	0	1740
	CHSM	0	0	1180
	CHVR	463	0	0
Suburban	CHBL	0	0	4150
	CHHB	330	0	797
	CHMC	0	0	1740
	CHOG	0	406	1160
Reference	CHRT	0	0	673
	NICB	0	0	0
Mussel Watch	CHFJ	0	0	139
	CHSF	656	0	656
	SRNB	0	1310	846
	WBLB	0	0	624
Sample Detect Frequency (%)		33	13	87

Summary of PFCs in South Carolina Oyster Tissues

Chemical highlights

- Only three of the 12 PFCs were detected in SC oyster samples (Table 5.2).

- PFOSA was the analyte most often detected, and was measured in 13 of the 15 oyster samples.

- The overall PFC detection frequency in SC oysters was 11.1%; 20 detections out of the 180 possible.

- No SC site had more than two PFCs detected, and NICB (Reference) was the only site where there were no reported PFCs in oysters.

Land Use Highlights

- There were no significant differences among Land Use classifications (Chi^2=0.52).

- The highest reported PFC concentration was found at the Suburban site (CHBL; PFOSA at 4150 pg/g wet mass).

Mussel Watch Highlights

- All four MWP sites in SC have reportable PFC concentrations.

- The highest SC oyster concentration in this study was reported at SRNB (PFOS at 1310 pg/g wet).

Pharmaceutical and Personal Care Products (PPCPs) in South Carolina

Environmental PPCPs include a wide spectrum of therapeutic and consumer-use compounds. These are residues of prescription and over-the-counter medications, hormones, synthetic fragrances, detergents, disinfectants, insect repellants, and antimicrobial agents. In 2009, an estimated 3.9 billion prescriptions were written for the top 300 pharmaceuticals in the US (Lundy 2010). Pharmaceutical companies produce over 50 million pounds of antibiotics annually in the United States, with approximately 60% for human use and 40% for animal agriculture (Levy 1998). Also, it has been estimated that there are about 70,000 human-produced compounds used daily in the US (Nilsen et al. 2007). There are numerous pathways by which PPCPs are introduced into the environment, although the main ones are release through both excretion and the improper disposal of unused drugs (Daughton and Ternes 1999). Because pharmaceuticals are designed with the intention of having a biological effect, the major concern of PPCPs in the environment are their potential ecotoxicity and unintentional human health impacts. Potential impacts of PPCPs in the environment include abnormal physiological effects, impaired reproduction, and increased cancer rates (Boyd and Furlong 2002). According to the US EPA, many CECs including PPCPs are suspected to be endocrine disruptors, which alter the normal functions of hormones resulting in a variety of health effects (Ankley et al. 2008). In this study, Seventy-three of the 85 PPCP analytes were analyzed for sediments and 84 PPCPs in tissues.

PPCPs in South Carolina Sediments

Table 5.3. Magnitude of PPCP compounds found in SC sediment samples (ng/g dry mass).

Land Use	Site	Antibiotic Sulfachloropyridazine	Antibiotic Sulfadiazine	Antidiabetic Metformin	Cardiovascular Albuterol	Cardiovascular Atenolol	Cardiovascular Norverapamil	Cardiovascular Verapamil	Muscular Benztropine	Pain Reliever Propoxyphene	Psychiatric Diazepam	Psychiatric Norfluoxetine
Urban	CHDL	0	0	0	0	0	0	0	0	0	0	0
Urban	CHNM	0	0	0	10.8	0	0	0	0	0	8.19	0
Urban	CHSH	17.3	0	0	0	0	0	0	0	0	0	0
Urban	CHSM	0	3.41	0	0	0	0	0	0	0	0	0
Urban	CHVR	0	0	0	0	0	0	0	0	0	0	0
Suburban	CHBL	0	0	0	0	0	0	0	0	0	0	44.7
Suburban	CHHB	0	0	0	0	0	0	0	0	0	0	0
Suburban	CHMC	0	0	0	0	0	24.6	26.7	0	24.4	0	61
Suburban	CHOG	0	0	0	0	0	0	0	0	0	0	0
Reference	CHRT	0	0	8.65	0	1.95	0	0	0	0	0	0
Reference	NICB	0	0	0	0	0	0	0	0	0	0	0
Mussel Watch	CHFJ	0	0	0	0	0	0	0	0	0	0	0
Mussel Watch	CHSF	0	0	0	0	0	0	0	27.5	0	0	0
Mussel Watch	SRNB	0	0	0	0	0	0	0	0	0	0	0
Mussel Watch	WBLB	0	0	0	0	0	0	0	0	0	0	0
Sample Detect Frequency (%)		7	7	7	7	7	7	7	7	7	7	13

Summary of PPCPs in South Carolina Sediment

Chemical highlights

- There were a total of 12 detections for all SC sediments from the 73 PPCP chemicals (Table 5.3).

- The detection frequency for PPCPs in SC sediments was 1.11%.

- Eleven PPCPs were detected in SC sediment samples representing six general drug use categories (Antibiotic, Antidiabetic, Cardiovascular, Muscular, Pain Reliever and Psychiatric).

- Cardiovascular and Psychiatric drugs were the most detected in SC sediments.

Land Use Highlights

- There were no significant differences among Land Use categories (Chi^2=0.79).

- Eight sites did not have reported PPCP concentrations, suggesting a patchy distribution in SC estuaries.

- Suburban sites generally had the highest concentrations of reported PPCPs.

Mussel Watch Highlights

- CHSF was the only MWP site where PPCPs were reported in sediment and it was only one compound (Benztropine).

PPCPs in South Carolina Oyster Tissues

Table 5.4. Magnitude of PPCP compounds found in SC oyster samples (pg/g wet mass).

Land Use	Site	Antibiotic				Cardiovascular			Pain Reliever	Stimulant
		Flumequine	Penicillin G	Sulfadiazine	Sulfamethazine	Digoxin	Diltiazem	Norverapamil	Acetaminophen	Caffeine
Urban	CHDL	0	0	0	0	0	0	0	0	0
	CHNM	0	0	722	0	0	407	0	0	0
	CHSH	0	1950	6430	0	22200	0	0	0	0
	CHSM	0	0	0	404	0	0	0	0	0
	CHVR	561	0	0	0	0	0	0	37200	0
Suburban	CHBL	0	0	0	0	0	0	0	0	0
	CHHB	0	0	280	0	0	0	0	0	1960
	CHMC	0	0	0	0	0	0	600	28900	0
	CHOG	0	0	0	0	0	0	0	33900	0
Reference	CHRT	0	0	0	0	0	0	0	0	0
	NICB	0	0	0	0	0	0	0	0	0
Mussel Watch	CHFJ	0	0	0	0	0	0	0	0	0
	CHSF	0	0	0	0	0	0	0	0	0
	SRNB	756	0	0	0	0	0	0	0	0
	WBLB	0	0	778	0	0	0	0	8280	0
Sample Detect Frequency (%)		13	7	27	7	7	7	7	27	7

Summary of PPCPs in South Carolina Oyster Tissues

Chemical Highlights

- There were a total of 16 detections for all SC oysters for the 84 PPCP chemicals (Table 5.4).

- The detection frequency for PPCPs in SC sediments was 1.46%.

- Nine PPCPs were detected in SC oyster samples representing four general drug use categories (Antibiotic, Cardiovascular, Pain Reliever and Stimulant).

- Cardiovascular and antibiotic drugs were frequently detected in SC oysters.

- Acetaminophen and sulfadiazine were the most commonly detected PPCPs in SC oysters, and each was reported in 27% of all sites.

- The highest reported PPCP concentration in SC oysters was recorded for acetaminophen and digoxin.

Land Use Highlights

- There were no significant differences among Land Use categories (Chi^2=0.21).

- Six sites did not have reported PPCP concentrations suggesting a patchy distribution in SC estuaries.

- The number of detections followed the Urban>Suburban>Reference trend.

Mussel Watch Highlights

- SRNB (Flumequine) and WBLB (Sulfadiazine and Acetaminophen) were the only two SC MWP sites with reported PPCP concentrations.

Alkyl Phenols (APs) in South Carolina

Alkylphenols are a class of chemicals used as detergents and surfactants in industrial processes. Some household detergents (i.e. laundy soaps) also include APs. The most common sources of APs to aquatic systems are wastewater and septic system discharges(Ying et al. 2002). These compounds tend to be persistent in the environment, have a strong affinity for suspended particles, and are well preserved in bottom sediments (Ying et al. 2002). In the environment, alkylphenol ethoxylate surfactants biodegrade into more environmentally sable metabolites such as the alkylphenol n-ethoxylates, alkylphenoxy acetic and alkylphnoxypolyethoxy acetic acids, and alkylphenols (EPA 2014a). This study focused on four AP metabolites in both sediment and oyster tissues. Two of the compounds 4-nonylphenol (4-NP) and 4 -n-octylphenol (4-n-OP) are degradation products of 4-nonylphenol mono-ethoxylate (NP1E0) and 4 nonylphenol di-ethoxylate (NP2E0), which are byproducts of the parent alkylphenol polyethoxylate. These degradation products are more stable and more toxic than the parent compounds and are hormone mimics (Ying et al. 2002).

APs in South Carolina Sediments

Table 5.5. Magnitude of AP compounds found in SC sediment samples (ng/g dry mass).

Land Use	Site	NP1EO	NP2EO
Urban	CHDL	0	0
	CHNM	43	24.3
	CHSH	0	0
	CHSM	0	0
	CHVR	17	0
Suburban	CHBL	0	0
	CHHB	0	0
	CHMC	0	0
	CHOG	0	0
Reference	CHRT	0	0
	NICB	0	0
Mussel Watch	CHFJ	51.5	94.4
	CHSF	0	0
	SRNB	0	0
	WBLB	0	0
Sample Detect Frequency (%)		20	13

Summary of APs in South Carolina Sediments

Chemical highlights

- Only two APs, nonylphenol mono-ethoxylate (NP1EO) and nonylphenol di-ethoxylate (NP2EO), were detected in SC sediments and both are degradation products of nonylphenol n-ethoxylate (Table 5.5).

- NP2EO, with a concentration of 94.4 ng/g found in sediment from the Fort Johnson site in Charleston Harbor, was the highest AP concentration reported in this study.

Land Use Highlights

- There were no differences in AP sediment concentrations measured among Land Use categories (Chi^2=0.15).

Mussel Watch Highlights

- CHFJ is the only SC Mussel Watch site where APs were reported.

- The concentrations reported at CHFJ were the highest for NP1EO and NP2EO.

APs in South Carolina Oyster Tissues

Table 5.6. Magnitude of AP compounds found in SC oyster samples (pg/g wet mass).

Land Use		Site	4-nonylphenol	4-n-OP	NP1EO	NP2EO
Urban		CHDL	0	0	0	0
		CHNM	0	0	0	0
		CHSH	0	0	0	0
		CHSM	0	0	0	0
		CHVR	0	0	0	0
Suburban		CHBL	0	0	0	0
		CHHB	0	0	0	0
		CHMC	0	0	0	0
		CHOG	0	0	0	0
Reference		CHRT	0	0	0	0
		NICB	0	0	0	0
Mussel Watch		CHFJ	0	0	0	0
		CHSF	0	0	0	0
		SRNB	0	0	0	0
		WBLB	0	0	0	0
SC Detection Frequency (%)			**0**	**0**	**0**	**0**

Summary of APs in South Carolina Oyster tissues

- There were no Alkyl Phenol compounds detected in SC oysters.

Polybrominated Diphenyl Ethers (PBDEs) in South Carolina

Polybominated diphenyl ethers (PBDEs) are a group of chemicals that are used as flame-retardants in consumer and household products. Commercially, three types of PBDE industrial mixtures were available, the pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE) and the decabromodiphenyl ether (deca-BDE) mixtures (EPA 2014b). As these products age and degrade, PBDEs can enter the environment. PBDEs are structurally similar to PCBs with 209 possible unique structures or congeners. PBDEs have been measured in household dust, human breast milk, sediment and wildlife (ATSDR, 2015). The toxicology of PBDEs is not well understood, but PBDEs have been associated with tumors, neurodevelopmental toxicity and thyroid hormone imbalance. Due to ubiquitous distribution, potential persistance and toxicity, the manufacture of the 'penta' and 'octa' PBDEs mixtures have been phased out starting in 2004, and for the deca mixture in 2013 (EPA 2014b, Schreder and La Guardia 2014). However, as persistent organic pollutants (POPs), PBDEs will be present in every compartment of the environment for years. Less brominated PBDEs, like tetra-, penta- and hexa-BDE, demonstrate high affinity for lipids and tend to bioaccumulate in animals and humans, while highly brominated PBDEs like deca-BDE tend to absorb more onto sediment and soil.

PBDEs in South Carolina Sediment

Table 5.7. Magnitude of PBDE congeners found in SC sediment samples (ng/g dry mass)

Land Use	Site	PBDE Congener										
		28	30	47	66	71/49	75	77	85	99	100	118
Urban	CHDL	0.062	0	0.538	0.11	0.282	0.177	0.197	2.17	0.386	0	0.41
	CHNM	0	0	2.42	0	0	0	0.418	0	1.65	0	0.785
	CHSM	0	0	0.044	0	0	0	0	0	0	0.048	0
	CHSH	0	0	0.654	0.183	0.404	0	0	1.59	0.582	0	0.295
	CHVR	0	0	0.177	0	0.076	0	0	0.206	0.116	0	0.124
Suburban	CHBL	0.049	0	0.392	0.075	0.171	0.138	0.129	1.18	0.236	0.038	0.274
	CHHB	0	0	0.04	0	0	0	0	0	0.042	0.07	0.043
	CHMC	0.021	0.028	0.152	0	0.041	0.097	0.081	0.809	0.109	0	0.116
	CHOG	0	0	0.071	0	0	0	0	0	0	0	0
Reference	CHRT	0	0	0.064	0.027	0	0	0.042	0	0.047	0.052	0
	NICB	0	0	0.164	0.158	0	0.064	0.085	1.29	0.156	0	0.067
Mussel Watch	CHFJ	0	0	0	0	0	0	0	0.106	0.041	0	0
	CHSF	0	0	0.043	0	0	0	0	0	0	0.016	0
	SRNB	0	0	0.026	0	0	0	0	0.027	0	0.046	0
	WBLB	0	0	0.019	0	0	0	0	0	0	0	0
Sample Detect Frequency (%)		20	7	93	33	33	27	40	53	67	40	53

"/" denotes co-eluting congeners

Table 5.7. (cont'd.) Magnitude of PBDE congeners found in SC sediment samples (ng/g dry mass).

Land Use	Site	119	126	138	153	154	155	181	190	209	Total PBDEs	BDE 209 / Total BDE ratio
Urban	CHDL	0.039	0.129	0	0.187	0	0.045	0	0.702	14.9	20.3	0.73
	CHNM	0	0	0	0.398	0.233	0	0	0.754	64.2	70.9	0.91
	CHSM	0	0	0	0	0	0	0	0	0.321	0.413	0.78
	CHSH	0	0	0	0	0	0	0	0	22.7	26.4	0.86
	CHVR	0	0	0	0	0	0	0	0	0	0.699	0
Suburban	CHBL	0	0.064	0.286	0.158	0	0	0	0.444	8.589	12.2	0.7
	CHHB	0	0	0	0	0	0	0	0	0.506	0.701	0.72
	CHMC	0	0	0	0	0	0	0	0	2.83	4.28	0.66
	CHOG	0	0	0	0	0	0	0	0	0.77	0.841	0.92
Reference	CHRT	0	0	0	0	0	0	0	0	1.04	1.27	0.82
	NICB	0	0	0	0	0	0	0.105	0.717	8.31	11.1	0.75
Mussel Watch	CHFJ	0	0	0	0	0	0	0	0	0.875	1.02	0.86
	CHSF	0.017	0.037	0	0	0	0	0	0	0	0.113	0
	SRNB	0.019	0	0	0	0	0	0	0	0.487	0.605	0.8
	WBLB	0	0	0	0	0	0	0	0	0	0.019	0
Sample Detect Frequency (%)		**20**	**20**	**7**	**20**	**7**	**7**	**7**	**27**	**80**	**100**	

Summary of PBDEs in South Carolina Sediment

Chemical highlights

- Twenty PBDE congeners were detected in SC sediments (Table 5.7).

- PBDEs were measured at all SC sites.

- PBDE-47, 99, and 209 were the most commonly detected PBDE congeners; detection frequencies in SC sediments for these three congeners were >60%.

Land Use Highlights

- There were no significant differences among Land Use categories (Chi^2=0.83).

- Average Total PBDE trends indicated followed Urban (23.7 ng/g dry) > Reference (6.19 ng/g dry) > Suburban (4.51 ng/g dry).

- It was observed that the Urban site CHNM contained the highest PBDE concentrations for most PBDE congeners.

Mussel Watch Highlights

- PBDE concentrations at SC Mussel Watch sites was to ≤1 ng/ng dry.

PBDEs in South Carolina Oyster Tissues

Table 5.8. Magnitude of PBDE congeners found in SC oyster samples (pg/g wet mass).

Land Use	Site	7	28	47	66	71/49	75	77	99	100	116	118	119	209	Total PBDEs
Urban	CHDL	0	0	94.6	0	51.9	31.8	292	0	0	0	0	0	44.2	514
Urban	CHNM	52.6	11.2	236	16.2	63.2	42.6	340	103	56.6	0	7.84	0	137	1064
Urban	CHSH	0	0	128	35.6	157	0	1759	46.7	15	0	0	0	14.2	2159
Urban	CHSM	0	0	0	0	0	0	263	0	0	0	0	0	30	293
Urban	CHVR	0	0	164	80.9	95	39.6	325	62	36.3	0	0	0	56.2	859
Suburban	CHBL	0	0	67	0	49.4	0	216	0	0	0	0	0	13.8	347
Suburban	CHHB	0	0	0	0	0	0	322	0	0	0	0	0	41.5	364
Suburban	CHMC	0	0	87.4	28.4	0	0	430	0	0	0	0	0	69.9	617
Suburban	CHOG	0	0	110	0	0	0	290	31.5	0	0	0	0	39.2	470
Reference	CHRT	0	0	62.8	20.8	0	0	375	0	0	0	0	0	59	519
Reference	NICB	0	0	0	0	0	0	0	0	0	0	0	0	37.8	37.4
Mussel Watch	CHFJ	0	0	209	213	0	0	448	0	59.2	2.09	3.48	5.57	68.2	1010
Mussel Watch	CHSF	0	0	165	0	0	0	0	0	0	0	0	0	54.6	221
Mussel Watch	SRNB	0	0	0	0	0	0	0	0	0	0	0	0	19.7	19.4
Mussel Watch	WBLB	0	0	67.6	43.8	0	0	218	0	0	0	0	0	29.5	360
Sample Detect Frequency (%)		7	7	73	47	33	20	80	27	27	7	13	7	100	100

"/" denotes co-eluting congeners

Summary of PBDEs in South Carolina Oyster Tissues

Chemical highlights

- Thirteen of the 55 PBDE congeners were detected in SC oysters (Table 5.8).

- BDE 47 and 209 were the two most detected congeners, with detection frequencies that were greater than 70%.

Land Use Highlights

- There were significant differences identified among the Land Use categories (Chi2=0.02).

- Urban PBDE levels were determined to be significantly different from both Suburban (p-value=0.035) and Reference (p-value=0.027) PBDE levels.

- Average Total PBDE concentrations decreased from Urban (978 pg/g wet) > Suburban (449 pg/g wet) > Reference (278 pg/g wet).

Mussel Watch Highlights

- CHFJ had the second highest Total PBDE level reported in this study (1010 pg/g wet).

Alternative Flame Retardant (AFRs) in South Carolina

Alternative flame retardants are added to a wide variety of industrial and consumer products, such as textiles, rugs, furniture and plastics (de Wit 2002). For this study, several groups of chemicals were combined under the title of alternative flame retardants, including the brominated flame retardants (BFRs), chlorinated organophosphate (CPP) chemicals and the polybrominated biphenyls (PBBs). PBBs are manufactured chemicals primarily used in firefighting materials; their application is now controlled as a hazardous substance (Safe 1984). The BFRs, such as hexabromo-cyclododecane (HBCDs), are primarily use in household consumer products such as upholstery and textiles. HBCDs are ubiqutous in the environment, but their ecotoxicity is not well understood. The chlorinated organophosphate flame retardants, such as tris(1,3-dichloroisopropyl)phosphate (TDCPP), are mainly used as additives in textiles. As additives, chlorinated organophosphate flame retardants tend to leach out over time into water and air. In the environment, TDCPP can accumulate in animal fat tissues (Andresen et al. 2004).

AFRs in South Carolina Sediments

Table 5.9. Magnitude of AFR compounds found in SC sediment samples (ng/g dry mass).

Land Use	Site	PBB 2	TCPP
Urban	CHDL	0	19.2
	CHNM	0	89.1
	CHSH	0	47
	CHSM	0	0
	CHVR	0.1	0
Suburban	CHBL	0	10.3
	CHHB	0	0
	CHMC	0	0
	CHOG	0	0
Reference	CHRT	0	0
	NICB	0	0
Mussel Watch	CHFJ	0	0
	CHSF	0	0
	SRNB	0	0
	WBLB	0	0
Sample Detect Frequency (%)		7	27

Summary of AFRs in South Carolina Sediment

Chemical Highlights

- SC sediments were surveyed for 28 alternative flame retardants and only two compounds were detected; a polybrominated biphenyl (PBB2) and a chlorinated organophosphate [tris(2-chloroethyl) phosphate; TCPP] (Table 5.9).

Land Use Highlights

- There were no significant differences found among Land Use categories (Chi^2=0.27).

- Four of the five AFR detections in SC were observed in sediments from urban sites.

Mussel Watch Highlights

- There were no AFRs detected in sediment from SC Mussel Watch sites.

AFRs in South Carolina Oyster Tissues

Table 5.10. Magnitude of AFR compounds found in SC oyster samples (pg/g wet mass).

Land Use	Site	PBB 2
Urban	CHDL	0
	CHNM	0
	CHSH	0
	CHSM	0
	CHVR	0
Suburban	CHBL	0
	CHHB	0
	CHMC	0
	CHOG	0
Reference	CHRT	0
	NICB	49.5
Mussel Watch	CHFJ	0
	CHSF	0
	SRNB	0
	WBLB	0
Sample Detect Frequency (%)		**7**

Summary of AFRs in South Carolina Oyster Tissues

Chemical Highlights

- SC oysters were surveyed for 28 alternative flame retardants and only one compound was observed in SC oysters; the polybrominated biphenyl (PBB-2) at NICB (Table 5.10).

Land Use Highlights

- There were no significant differences measured among the Land Use categories (Chi^2=0.11).

Mussel Watch Highlights

- The only AFR (PBB) detected in oysters form SC was found at NICB, a reference sites.

Multi-Residue (MRES) Contemporary Contaminants in South Carolina

Multi-residue contemporary contaminants (MRES) are generally a group of semi-volatile chemicals that span multiple chemical classes and can be analyzed concurrently. In this report, MRES chemicals includes pesticides, degradation products and the industrial by-product octachlorostyrene. The MRES current use pesticides are typically more water soluble than the legacy organochlorine pesticides and often do not bioaccumulate in organisms. It has been estimated that in 2007 over 565 million kg of current-use pesticides were used in the USA (EPA 2011). Among pesticides, herbicides accounted for 40% of total usage, and insecticides 17% (EPA 2011). While agriculture application accounts for over 60% of pesticides used, urban usage is increasing. Pesticides enter the environment seasonally through surface run-off, direct discharge and through atmospheric long-range transport (EPA 2011).

Octachlorostyrene is a by-product of industrial processes involving aluminium refining and combustion of chlorinated compounds. Listed in the EPA priority list of most bioaccumulative compounds, octachlorstyrene is highly toxic and extremely persistent when released to the environment (Chu et al. 2003). Octachlorostyrene is included in this study as it has been found in the environment at increasing concentrations, particularly in industrial areas (Chu et al. 2003).

MRES in South Carolina Sediments

Table 5.11. Magnitude of MRES compounds found in SC sediment samples (ng/g dry mass).

Land Use	Site	Ametryn	Chlorpyrifos	Cyanazine	Cypermethrin	Octachlorostyrene	Permethrin
Urban	CHDL	0.27	0	0	0	0	421
	CHNM	0.253	0.495	8.76	1590	0	6890
	CHSH	0.169	0	0	0	0	0.286
	CHSM	0	0	0	0	0	155
	CHVR	0	0	0	0	0	0
Suburban	CHBL	0.649	0.029	0	0	0	207
	CHHB	0	0	0	0	0	0
	CHMC	0	0	0	0	0	129
	CHOG	0	0	0	0	0	0
Reference	CHRT	0	0	0	0	0.002	46.8
	NICB	0.038	0	0	0	0	0
Mussel Watch	CHFJ	0	0	0	0	0	56.7
	CHSF	0	0	0	0	0	0
	SRNB	0	0	0	0	0	0
	WBLB	0	0	0	0	0	0
Sample Detect Frequency (%)		**33**	**13**	**7**	**7**	**7**	**53**

Summary of MRES in South Carolina Sediment

Chemical Highlights

- Six of the 36 MRES were found in SC sediments and included, the pesticides ametryn, chlorpyrifos, cyanazine, cypermethrin, and permethrin, and the industrial by-product octachlorostyrene (Table 5.11).

- Two of the six MRES reported in SC are pyrethroid insecticides (cypermethrin and permethrin).

- The highest CEC concentration measured in SC found in this study was for permethrin (6890 ng/g dry).

Land Use Highlights

- There were no significant differences found among the Land Use categories (Chi^2=0.46).

- The number of detections within each Land Use category was greatest in Urban (10), followed by Suburban (4) and then Reference (3).

Mussel Watch Highlights

- Only one MRES chemical was detected in sediments from MWP sites (56.7 ng/g permethrin found at CHFJ).

MRES in South Carolina Oyster Tissues

Table 5.12. Magnitude of MRES compounds found in SC oyster samples (pg/g wet mass).

Land Use	Site	Ametryn	Chlorothalonil	Octachlorostyrene
Urban	CHDL	0	0	0
	CHNM	0	0	4
	CHSH	0	0	7
	CHSM	0	0	3
	CHVR	0	0	3
Suburban	CHBL	102	0	0
	CHHB	0	0	0
	CHMC	0	0	3
	CHOG	0	0	0
Reference	CHRT	0	0	0
	NICB	301	24	0
Mussel Watch	CHFJ	116	29	0
	CHSF	1180	23	6
	SRNB	0	0	0
	WBLB	0	0	3
SC Frequency of detect (%)		27	20	47

Summary of MRES in South Carolina Oyster Tissues

Chemical Highlights

- SC oysters were surveyed for 36 MRES contaminants, two pesticides (ametryn, chlorothalonil) and the toxic industrial by-product octachlorostyrene.

Land Use Highlights

- There were no differences observed among Land Use categories (Chi^2=0.76).

Mussel Watch Highlights

- Surprisingly, the number of MRES detected overall in SC oysters was highest at the Mussel Watch sites, which are supposed to be open water locations.

South Carolina General Findings

Chemical Highlights

Detection frequencies for most CEC classes were generally quite low; less than 20% for each of the CEC classes examined in this study. PBDEs are most often detected (based on count) in both SC sediments and oysters, but the frequency of detection in SC sediments and oysters for the perfluorinated compounds is highest, 16.7 and 11.1% respectively (Table 5.13). The highest concentrations reported in SC sediments were MRES associated with the insecticides pyrethroid permethrin (6890 ng/g dry mass at found at CHNM) and cypermethrin (1590 ng/g dry mass at CHNM). These were easily the highest CEC concentrations reported in this report from SC samples.

Table 5.13. Summary data for the frequency of reported values from SC sediments and oysters.

CEC Class	# of Analytes		Potential # Detections		Reported # Detections		Detection Frequency (%)	
	Sediment	Tissues	Sediment	Tissues	Sediment	Tissues	Sediment	Tissues
PFC	12	12	180	180	30	20	16.7	11.1
PPCP	73	84	1095	1260	12	16	1.1	1.3
AP	4	4	60	60	5	0	8.3	0
PBDE	55	55	825	825	99	67	12.0	8.1
AFR	28	28	420	420	5	1	1.2	0.2
MRES	36	36	540	540	18	14	3.3	2.6
Total	**208**	**219**	**3120**	**3285**	**164**	**118**	**5.2**	**3.6**

Land Use Highlights

Land use appears to be associated with the occurrence of CEC analytes, although further study is required to confirm this association. Table 5.14 summarizes the total number of reported concentrations greater than the detection limit for each class by Land Use categorization. The number of reported concentrations at Urban sites is roughly twice the number of detections reported in Suburban samples. The same relative difference was observed between Suburban

and Reference classified sites. The number of detected PBDEs makes up the majority of concentrations reported for both sediments and tissues, likely related to the physical and chemical properties of PBDEs that cause them to be bio-accumulative, thus partitioning into sediments and tissues.

Table 5.14. Summary of the number of CEC detections by Land Use.

CEC Class	Land Use Category	Number of Detections	
		Sediment	Tissue
PFC	Urban	14	7
	Suburban	5	6
	Reference	3	1
	Mussel Watch	8	6
PPCP	Urban	4	8
	Suburban	5	5
	Reference	2	0
	Mussel Watch	1	3
AP	Urban	3	0
	Suburban	0	0
	Reference	0	0
	Mussel Watch	2	0
PBDE	Urban	38	33
	Suburban	32	14
	Reference	16	5
	Mussel Watch	13	15
AFR	Urban	4	0
	Suburban	1	0
	Reference	0	1
	Mussel Watch	0	0
MRES	Urban	10	4
	Suburban	4	2
	Reference	3	2
	Mussel Watch	1	6
Total	Urban	73	52
	Suburban	47	27
	Reference	24	9
	Mussel Watch	25	30

Mussel Watch Highlights

While the four SC MWP sites are not classified by a given land use, the underlying paradigm used by the MWP to select these sites (i.e. away from "hot spots" of contamination) may still be able to offer important insight into the occurrence and distribution of CECs within coastal SC waters. In sediments, the number of total detections for MWP sites (n=4 sites) within each class is very similar to the number of detections found at SC Reference sites (n=2 sites) (Table 5.14). As identified in Land Use Highlights, the two CEC classes with the most detections for MWP sites were for PFCs

and PBDEs. The maximum concentrations of CECs found at MWP sites were generally lower than maximum concentrations observed at SC reference sites (Tables 5.1 (PFCs), 5.3 (PPCPs), 5.5 (APs), 5.7 (PBDEs), and 5.11(MRES)). In tissues from MWP sites, the highest number of detections were observed for PCFs and PBDEs as well, but the number of detections observed at MWP sites were greater than the number of detections observed in Reference sites for PFCs, PPCPs, PBDEs and MRES. The magnitude of these detections were also greater at the MWP sites relative to Reference sites for PFCs (Table 5.2), PPCPs (Table 5.4), PBDEs (Table 5.8) and MRES (Table 5.14). In many cases, the concentrations reported at a MWP site was the maximum reported concentration for that chemical. In each of the following cases, the MWP tissue concentration was the highest reported; PFDODA, PFOS, flumequine, NP1EO, NP2EO, PBDE-66, PBDE-100, PBDE-116, PBDE-119, ametryn and chlorothalonil (Tables 5.2, 5.4, 5.8, 5.10, and 5.12). The same trend is not the case with sediments. The concentration for benztropine was the only analyte where the maximum was observed at a MWP sediment site (Table 5.3).

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APPENDIX A. Detail AP and PPCP analytical protocols used in MWP 2015 sediment and tissue analysis.

Summary of Extraction Methods for PPCPs and APs

Sample extraction, clean-up and quantitation for PPCPs (groups 1, 3, 4 and 5) were based on the methods detailed in EPA 1694 (EPA 2007) and Klosterhaus et al. (2013). Methods for alkyl phenols (APs) were based on Petrovic et al. (2002) and Loyo-Rosales et al. (2003). A brief detail of the methods and the modifications are described below. All samples were stored at -40°C until sample analysis. Sample batch sizes consisted of ten samples plus a blank, reagent spike and two matrix spikes.

Method Summary for PPCP (Groups 1, 3 and 5) Tissue and Sediment Samples

Tissue aliquots (1.80-2.00 g) or sediment aliquots (0.80-1.00 g) were weighed into 50 mL homopolymer polypropylene tubes (Environmental Express, Charleston SC) containing 1 g of 1 mm zirconium oxide beads (Next Advance, Averill Park, NY). Internal standards (Table A.1) were added to all unknown and QC samples. Samples were extracted three times. For tissues, extraction with 20 mL acetonitrile was followed by two extractions with 20 mL acetonitrile and 15 mL pH 2 phosphate buffer. For sediment samples, two extractions were with 15 mL pH 2 phosphate buffer and 20 mL acetonitrile followed by an extraction with 20 mL acetonitrile only. For each extraction, samples were placed in a sonicator bath for 15 minutes, and then centrifuged for 5 minutes at 3000 rpm. After extraction, samples were filtered through GF/F paper. Sediment samples underwent an additional step for sulfur removal using activated copper wool. Copper wool was added to the first solvent extract, and as the second and third solvent extracts were added the copper wool was allowed to react with any additional sulfur present. The copper wool sat in the sample extracts for 45-60 minutes.

Samples were concentrated in a water bath (50°C) under a gentle stream of nitrogen (14 psi) to a volume of ~30mL (TurboVap II, Biotage, Inc.). After concentration, 200 mL of Milli-Q water and 500 mg of $Na_4EDTA \bullet 2H_2O$ were added to each sample prior to clean-up with HLB SPE (Waters, Oasis HLB 20 cc/1g). After clean-up, samples were concentrated to a final volume of 4 mL. For instrumental analysis, 1 mL was removed and spiked with recovery standards. Samples were analyzed using LC-MS/MS in ESI+ and ESI- modes in order to quantitate those compounds listed in Tables A.2, A.3 and A.4; the remaining 3 mL were stored at 4°C.

Method Summary for PPCP (Group 4) Tissue and Sediment Samples

Tissue aliquots of 1.80-2.00 g or sediment aliquots of 0.80-1.00 g were weighed into 50 mL homopolymer polypropylene tubes containing 1 g of 1 mm zirconium oxide beads. Internal standards (Table A.1) were added to all unknown and QC samples. Samples were extracted three times. For tissues, the first extraction was with 20 mL acetonitrile, in the two subsequent extractions, 15 mL of Milli-Q water was added, samples were adjusted to pH 10 with ammonium hydroxide and 20 mL of acetonitrile were added. For sediment samples, in the first two extractions samples were adjusted to pH 10 with ammonium hydroxide and then extracted with 15 mL Milli-Q water and 20 mL acetonitrile, the last extraction was with 20 mL acetonitrile only. For each extraction, samples were placed in a sonicator bath for 15 minutes, and then centrifuged for 5 minutes at 3000 rpm. After extraction, samples were filtered through GF/F paper. Sediment samples underwent an additional step for sulfur removal using activated copper wool.

Samples were concentrated in a water bath (50°C) under a gentle stream of nitrogen (14 psi) to a volume of ~30mL. After concentration, 200 mL of Milli-Q was added to each sample and the pH was adjusted to pH=10 prior to clean-up with HLB SPE (20 cc/1g). After clean-up, samples were concentrated to a final volume of 4 mL. For Group 4 analysis (Table A.5), 1 mL was removed and spiked with recovery standards and run on LC-MS/MS is ESI+ and ESI- modes; the remaining 3 mL were stored at 4°C.

Method Summary for Alklyphenols & Alkylphenol Ethoxylates (AP)

For tissue and sediment samples, roughly 2.00 g of material was weighed into a glass mortar bowl containing 28 g of anhydrous sodium sulfate. Samples were thoroughly ground with a pestle until dry and then placed into an ASE (accel-

erated solvent extraction) cell. Internal standards were added to each unknown and QC sample (Table A.1). Samples were either extracted with 100% dichloromethane (tissues) or 50:50 acetone/hexane (sediments) according to the parameters in Tables A.6 and A.7.   After ASE, sediment samples were treated with activated copper wool for sulfur removal and then filtered through additional anhydrous sodium sulfate to removed residual water from the extraction process. Tissue samples were immediately filtered through anhydrous sodium sulfate post ASE.

After residual water removal, samples were concentrated in a water bath (40°C) under a gentle stream of nitrogen (14 psi). Sediment samples were solvent exchanged to hexane then cleaned-up using NH_2 SPE cartridges (Supelco, 3 mL/0.5 g). Tissue samples were cleaned-up with gel permeation chromatography (GPC, J2-Scientific). A glass column containing 50 g of SX-3 biobeads with a mobile phase of 100% dichloromethane was used to fractionate the samples. After the clean-up step (either NH_2 SPE or GPC), samples were concentrated, solvent exchanged to methanol and spiked with recovery standards prior to LC-MS/MS analysis.

Table A.1. Internal standards used for PPCP groups 1, 3, 4, 5 and APs. Internal standards were purchased from Cambridge Isotopes (Tewksbury, MA), Santa Cruz Biotechnology (Dallas, TX), C/D/N Isotopes (Quebec, CA), and Sigma Aldrich (St. Louis, MO).

Internal Standard	Group	conc (µg/mL)	Parent Ion	Daughter Ion
13C2, 15N-Acetaminophen	1	4	155.2	111
13C3,15N-Ciprofloxacin	1	4	336.1	318
13C3-Caffeine	1	3	198	140
13C3-Trimethoprim	1	1	294	233.1
13C6-Sulfamethoxazole	1	1	260	162
d10-Carbamazepine	1	2	247	204.2
d6-Thiabendazole	1	1	208.1	180.9
d6-Fluoxetine	1	1	315.3	153
13C2-Erythromycin - H2O	1	1	736.4	160
13C6-Sulfamethazine	1	1	285.1	162
d5-Warfarin	3	1	312	160.9
d6-Gemfibrozil	3	1	208.2	163
d6-Bisphenol A	3	1000	232.9	168.9
13C3-Ibuprofen	3	4	455	319
13C-d3-Naproxen	3	3	495	170
d11-Glipizide	3	3	233	214.8
d3-Glyburide	3	3	255	121
d5-propoxyphene	5	4	345.2	58.1
d8-benzoylecgonine	5	4	298.4	171.1
d3-Benztropine	5	4	311.3	167
d3-Cocaine	5	4	307	185.1
d3-Promethazine	5	4	288	198
d4-Hydrocortisone	5	200	367.2	121.1
d5-Alprazolam	5	4	314.2	285.9
d5-Diazepam	5	4	290.1	198
d6-Amitriptyline	5	4	284	233
d7-Metoprolol	5	4	275.1	190.9
d6-norfluoxetine	5	4	302.4	140
d6-paroxetine	5	4	336.3	197.8
d7-Propranolol	5	4	267.2	116
d5-amphetamine	4	4	141.1	93
d6-codeine	4	4	306.1	218
d3-Albuterol	4	4	243.1	151.1
d3-Cimetidine	4	4	256.1	162
d3-cotinine	4	4	180	80
d4-Clonidine	4	4	243	47.9
d5-Enalapril	4	4	382	238.8
d6-Metformin	4	4	136.2	60.1
d7-Atenolol	4	4	274	145.2
d3-hydrocodone	4	4	303.3	198.9
d6-oxycodone	4	4	322.1	262.1
13C6-4-Nonylphenol	APs/APEOs	4	225.2	112.2
13C6-nonylphenol monoethoxylate	APs/APEOs	25	288.3	127.2
d17-4-n-octylphenol	APs/APEOs	25	222.5	108

Table A.2. PPCP (Group 1) analytes; Standards were purchased from Santa Cruz Biotechnology (Dallas, TX), C/D/N Isotopes (Quebec, CA), Sigma Aldrich (St. Louis, MO) and Toronto Research Chemicals (Ontario, CA). [1]Analytes were quantified in tissues only.

Group 1 - Acid Extraction, ESI + LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
Acetaminophen	13C2, 15N-Acetaminophen	151.8	109.9	2.5
Azithromycin[1]	d6-fluoxetine	749.9	591.6	0.0625
Caffeine	13C3-Caffeine	195.1	138.1	0.625
Carbamazepine	d10-Carbamazepine	237.1	194	0.0625
Clarithromycin	13C6-Sulfamethazine	748.8	158.1	0.0625
Clinafloxacin[1]	13C3,15N-Ciprofloxacin	366.1	348.1	0.25
Cloxacillin	d6-fluoxetine	468.1	160.1	0.125
Dehydronifedipine	d6-fluoxetine	345.4	160.1	0.025
Digoxigenin	d6-fluoxetine	391.2	355.2	0.25
Digoxin	d6-fluoxetine	798.5	651.4	0.625
Diltiazem[1]	d6-fluoxetine	415.3	178.1	0.0125
Diphenhydramine[1]	d6-fluoxetine	256.4	167.1	0.025
Enrofloxacin[1]	13C3,15N-Ciprofloxacin	360.2	316.3	0.125
Erythromycin[1]	13C2-Erythromycin - H2O	734.7	158.1	0.0125
Flumequine	d6-fluoxetine	262	174.1	0.0625
Fluoxetine	d6-fluoxetine	310.3	148.1	0.0625
Lomefloxacin[1]	13C3,15N-Ciprofloxacin	352.2	308.1	0.125
Norfloxacin[1]	13C3,15N-Ciprofloxacin	320.2	302.2	0.625
Ofloxacin[1]	13C3,15N-Ciprofloxacin	362.3	318.3	0.0625
Ormetoprim	13C3-Trimethoprim	275.1	259.1	0.025
Oxacillin	d6-fluoxetine	434.3	160	0.125
Oxolinic Acid	d6-fluoxetine	269.1	243.9	0.025
Penicillin G	d6-fluoxetine	367.3	160.1	0.125
Penicillin V	d6-fluoxetine	393.3	160.1	0.125
Roxithromycin	13C6-Sulfamethazine	837.9	679.6	0.0125
Sarafloxacin[1]	13C3,15N-Ciprofloxacin	386	299.1	0.5625
Sulfachloropyridazine	13C6-Sulfamethazine	285.1	156.1	0.0625
Sulfadiazine	13C6-Sulfamethazine	251	156	0.0625
Sulfadimethoxine	13C6-Sulfamethoxazole	311	156	0.0125
Sulfamerazine	13C6-Sulfamethazine	265	156	0.025
sulfamethazine	13C6-Sulfamethazine	279.1	156	0.025
Sulfamethizole	13C6-Sulfamethoxazole	271.1	155.9	0.025
Sulfamethoxazole	13C6-Sulfamethoxazole	254.1	156	0.025
Sulfanilamide	13C6-Sulfamethazine	190.1	155.9	0.625
Sulfathiazole	13C6-Sulfamethoxazole	256.2	156	0.0625
Thiabendazole	d6-Thiabendazole	202.2	175	0.0625
Trimethoprim	13C3-Trimethoprim	291.3	230.3	0.0625
Tylosin	13C6-Sulfamethazine	916.9	772.6	0.25

Table **A.3.** Group 3 analytes; Standards were purchased from Santa Cruz Biotechnology (Dallas, TX), C/D/N Isotopes (Quebec, CA), Sigma Aldrich (St. Louis, MO) and Toronto Research Chemicals (Ontario, CA).

Group 3 - Acid Extraction, ESI - LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
Bisphenol A	d6-Bisphenol A	227	211.9	125
Furosemide	13C-d3-Naproxen	329	204.8	10
Gemfibrozil	d6-Gemfibrozil	249	121	0.375
Glipizide	d11-Glipizide	444	319	1.5
Glyburide	d3-Glyburide	492.2	169.8	0.75
Ibuprofen	13C3-Ibuprofen	205	161	3.75
Naproxen	13C-d3-Naproxen	228.9	168.9	0.75
Warfarin	d5-Warfarin	307.1	160.9	0.375

Table **A.4.** Group 5 analytes; Standards were purchased from Santa Cruz Biotechnology (Dallas, TX), C/D/N Isotopes (Quebec, CA), Sigma Aldrich (St. Louis, MO) and Toronto Research Chemicals (Ontario, CA). [1]Analytes were quantified in tissues only.

Group 5 - Acid Extraction, ESI + LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
10-hydroxy-amitriptyline[1]	d7-Propranolol	294.2	215	0.0375
Alprazolam	d5-Alprazolam	309.1	281.2	0.075
Amitriptyline	d6-Amitriptyline	278.3	233.1	0.075
Amlodipine	d6-norfluoxetine	409.3	237.8	0.375
Benzoylecgonine	d8-benzoylecgonine	290	167.8	0.075
Benztropine	d3-Benztropine	308.2	166.9	0.075
Cocaine	d3-Cocaine	308.2	166.9	0.0375
N-Desmethyldiltiazem	d3-Promethazine	401.2	177.9	0.0375
Diazepam	d5-Diazepam	285	193	0.075
Fluocinonide	d5-Diazepam	495.2	337.1	1.5
Fluticasone propionate	d5-Diazepam	501.1	293	0.5
Hydrocortisone	d5-Diazepam	363.1	120.9	15
Meprobamate	d5-Diazepam	219	161	1
Methylprednisolone	d5-Diazepam	375.2	357	1
Metoprolol[1]	d7-Metoprolol	268.2	190.8	0.375
Norfluoxetine	d6-norfluoxetine	296.1	133.9	0.375
Norverapamil	d6-Amitriptyline	441.5	165	0.0375
Paroxetine	d6-paroxetine	330	192	1
Prednisolone	d5-Diazepam	361.2	343.1	1.5
Prednisone	d5-Diazepam	359.2	340.9	5
Promethazine	d3-Promethazine	285.1	198	0.1
Propoxyphene	d5-propoxyphene	340.2	57.9	0.075
Propranolol	d7-Propranolol	260.1	115.9	0.5
Sertraline	d6-Amitriptyline	306.2	274.9	0.1
Verapamil	d6-Amitriptyline	455.4	165	0.0375

Table A.5. Group 4 analytes; Standards were purchased from Santa Cruz Biotechnology (Dallas, TX), C/D/N Isotopes (Quebec, CA), Sigma Aldrich (St. Louis, MO) and Toronto Research Chemicals (Ontario, CA). *Analytes quantified in sediments only.

Group 4 - Base Extraction, ESI + LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
Albuterol	d3-Albuterol	240.3	148.2	0.075
Atenolol	d7-Atenolol	267.1	145	0.15
Atorvastatin*	d7-Atenolol	559.2	440.1	0.375
Cimetidine	d3-Cimetidine	253	159	0.15
Clonidine	d4-Clonidine	230.1	44.1	0.375
Codeine	d6-codeine	300.3	214.9	0.75
Cotinine	d3-cotinine	177	98	0.375
Enalapril	d5-Enalapril	377.1	233.9	0.075
Hydrocodone	d3-hydrocodone	300.2	198.9	0.375
Metformin	d6-Metformin	130.1	60	0.75
Oxycodone	d6-oxycodone	316.2	241	0.15
Ranitidine	d6-oxycodone	315.2	175.9	0.15
Amphetamine	d5-amphetamine	136.1	90.8	0.375
Triamterene	d6-oxycodone	254	236.9	0.075

Table A.6. Alkylphenol and Alkylphenol exthoxylate analytes. Standards were purchased from Accustandard (New Haven, CT) and Sigma Aldrich (St. Louis, MO).

Alkylphenols - ASE extraction, ESI - LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
4-nonylphenol (4-NP)	13C6-4-Nonylphenol	219	106	1
4-n-octylphenol (4-n-OP)	d17-4-n-octylphenol	205.2	106	1

Alkylphenol Exthoxylates - ASE Extraction, ESI + LC-MS/MS analysis				
Analyte	*IS for Quantitation*	*Parent Ion*	*Daughter Ion*	*Low Cal Pt (ng)*
NP1EO (nonylphenol monoethoxylate)	13C6-nonylphenol monoethoxylate	282.3	127.2	1
NP2EO (nonylphenol diethoxylate)	13C6-nonylphenol monoethoxylate	326.3	183	1

Table A.7. Extraction conditions used for alkylphenols and alklyphenol ethoxylates from sediment and tissue samples. (Dionex ASE 200, Sunnyvale, CA)

ASE operating conditions	
Solvent	100% dichloromethane or 50:50 acetone/hexane
Pre-heat	5 min
Static	5 min
Cycles	2
Purge	60 s
Flush	50
PSI	1500
Temperature	60 °C

Instrumental Acquisition

All sample analyses for APs and PPCPs were run on an Agilent 1100 HPLC/API 4000 MS/MS in MRM (multiple reaction monitoring) mode. Analyst software was used for data quantitation. Analytes and internal standards were quantified by monitoring parent/daughter ion transitions, and their corresponding peak areas. Six separate instrumental runs were required to acquire the data for groups 1, 3, 4, 5 and alkylphenols (APs)/alkylphenol ethoxylates (APEOs). Groups 1, 4, 5 and APEOs were run in ESI+ mode, group 3 and APs were run in ESI- mode. Instrumental parameters for each acquisition method can be found in the following tables. Each batch of samples was run with a calibration curve containing at least seven calibration points. The coefficient of determination (r^2) for all analytes was greater than or equal to 0.99.

Groups 1 and 5					
HPLC Parameters				*MS Parameters*	
Time (min)	*Flow Rate (uL/min)*	*% A*	*% B*	*Mode*	*ESI +*
0	200	90	10	*Collision Gas*	10
5	200	90	10	*Curtain Gas*	20
6	300	90	10	*Nebulizer Gas*	25
24	300	40	60	*Heater Gas*	40
30	300	0	100	*Voltage*	4500
31	200	90	10	*Temperature (°C)*	350
50	200	90	10		
Injection Vol (uL)	2				
Autosampler Tray (°C)	4				
Column Oven (°C)	40				
Solvent A	0.1% formic acid + 0.1 % ammonium formate in water				
Solvent B	1:1 acetonitrile/methanol				
Column	Waters XTerra MS C18 3.5 um 2.1x100 mm				

Group 3					
HPLC Parameters				*MS Parameters*	
Time (min)	*Flow Rate (uL/min)*	*% A*	*% B*	*Mode*	*ESI -*
0	200	90	10	*Collision Gas*	10
0.5	200	90	10	*Curtain Gas*	25
10	200	0	100	*Nebulizer Gas*	25
20	200	0	100	*Heater Gas*	30
20.5	200	90	10	*Voltage*	-4300
30	200	90	10	*Temperature (°C)*	350
Injection Vol (uL)	2				
Autosampler Tray (°C)	4				
Column Oven (°C)	40				
Solvent A	0.1% ammonium acetate + 0.1% acetic acid in water				
Solvent B	1:1 acetonitrile/methanol				
Column	Waters XTerra MS C18 3.5 um 2.1x100 mm				

Group 4					
HPLC Parameters				*MS Parameters*	
Time (min)	*Flow Rate (uL/min)*	*% A*	*% B*	*Mode*	*ESI -*
0	350	5	95	*Collision Gas*	10
5	350	30	70	*Curtain Gas*	30
6	400	30	70	*Nebulizer Gas*	30
12	400	30	70	*Heater Gas*	30
12.5	350	5	95	*Voltage*	4500
20	350	5	95	*Temperature (°C)*	400
Injection Vol (uL)	5				
Autosampler Tray (°C)	4				
Column Oven (°C)	40				
Solvent A	0.1% acetic acid/ammonium acetate in water				
Solvent B	acetonitrile				
Column	Atlantis HILIC 10 cm, 2.1 mm i.d., 3.0 um				

Alkylphenol Ethoxylates (APEOs)					
HPLC Parameters				*MS Parameters*	
Time (min)	*Flow Rate (uL/min)*	*% A*	*% B*	*Mode*	ESI +
0	200	60	40	*Collision Gas*	4
10	200	100	0	*Curtain Gas*	10
18	200	100	0	*Nebulizer Gas*	20
20	200	60	40	*Heater Gas*	35
30	200	60	40	*Voltage*	5000
				Temperature (°C)	300
Injection Vol (uL)	25				
Autosampler Tray (°C)	ambient				
Column Oven (°C)	40				
Solvent A	10 mM ammonium acetate in methanol				
Solvent B	10 mM ammonium acetate in water				
Column	Waters XTerra MS C18 3.5 um 2.1x100 mm				

Alkylphenols (APs)					
HPLC Parameters				*MS Parameters*	
Time (min)	*Flow Rate (uL/min)*	*% A*	*% B*	*Mode*	ESI -
0	200	60	40	*Collision Gas*	10
10	200	100	0	*Curtain Gas*	15
18	200	100	0	*Nebulizer Gas*	35
20	200	60	40	*Heater Gas*	20
30	200	60	40	*Voltage*	-4500
				Temperature (°C)	350
Injection Vol (uL)	25				
Autosampler Tray (°C)	ambient				
Column Oven (°C)	40				
Solvent A	methanol				
Solvent B	water				
Column	Waters XTerra MS C18 3.5 um 2.1x100 mm				

APPENDIX B

Tissue Sample Data Necessary to Convert from Wet Weight to Dry Weight Concentrations

Historically, chemical concentrations in bivalve tissue have been reported by the Mussel Watch Program as dry weight fractions (nanograms of chemical per gram of dry tissue) (Lauenstein and Cantillo 1993). However, in this document we choose to report concentrations of contaminants in tissue based on wet weight fractions (picograms of chemical per gram of wet tissue). This allows an easier comparison of findings from this report and a concurrent sampling effort by NOAA in the Great Lakes. In order to compare the wet weight concentrations presented in this report to the historic Mussel Watch data or any other report that might have concentrations presented in dry weight concentrations, we provide the following equation and the relevant data in this appendix to convert from wet to dry concentrations.

Eq 1. Concentration (pg/g_wet)*(1/(dry_fraction))*(1/1000 ng/pg)= Concentration (ng/g_dry)

Table B.1. Percent of dry fraction for oyster tissue samples from each sampling site.

Chesapeake Bay, MD oyster tissue		Charleston Harbor oyster tissue	
Site	Dry Fraction	Site	Dry Fraction
CBBO	0.076	CHBL	0.042
CBMP	0.076	CHDL	0.078
CBBH	0.069	CHFJ	0.070
CBCP	0.079	CHHB	0.076
CBSB	0.093	CHMC	0.109
CBCT-1	0.142	CHNM	0.056
CBCT-2	0.151	CHOG	0.059
CBCT-3	0.154	CHRT	0.047
CBCT-4	0.136	CHSF	0.119
CBPT-1	0.160	CHSH	0.079
CBPT-2	0.161	CHSM	0.071
CBPT-3	0.152	CHVR	0.083
CBPT-4	0.149	NICB	0.062
CBRD-1	0.148	SRNB	0.082
CBRD-2	0.116	WBLB	0.095
CBRD-3	0.134		
CBRD-4	0.158		
CBSV-1	0.160		
CBSV-2	0.152		
CBSV-3	0.144		

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