

Draft: Toxic Contaminants in the Chesapeake Bay and its Watershed: Extent and Potential

Biological Effects

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**Draft: Toxic Contaminants in the Chesapeake Bay and its Watershed: Extent and Potential
Biological Effects**

Executive Summary

Executive Summary

Need for and Purpose of the Report

Toxic contaminants have adverse effects on fish and wildlife in portions of the Chesapeake Bay and its watershed. The Chesapeake Bay Program (CBP), a federal-jurisdictional partnership, recognized the issue and developed the Toxics 2000 Strategy. Since 2000, new concerns, such as intersex conditions in fish, have arisen. In 2010, the President's Chesapeake Bay Executive Order (EO 13508) Strategy directed Federal agencies to prepare a report summarizing information on the extent and severity of toxic contamination in the Bay and its watershed. The report relied on available information from State integrated water-quality assessment reports (which listed impairments to aquatic life due to toxic contaminants), reports of Federal and State-supported studies, and results of investigations in scientific journals to assess the state of the knowledge about toxic contaminants. Findings from this report will be used by the CBP partnership (during 2013) to consider new goals for reducing toxic contaminants and to develop strategies (by 2015) to carry out the goals. This report also identifies future research and monitoring activities needed to improve the understanding of the occurrence and effects of toxic contaminants in the Chesapeake Bay and its watershed.

Effects of Toxic contaminants on Fish and Wildlife

The effects of toxic contaminants on living resources are a concern in most of the Chesapeake Bay:

- In 2010, the CBP reported that 72 percent of the Bay and its tidal river segments are fully or partially impaired as a result of the presence of toxic contaminants.
- There are advisories on the amount of fish that people can eat on the basis of high levels of certain toxic contaminants in fish in both in the Bay and its watershed.

Other key findings about the effect of toxic contaminants on fish (chapter 3) are based on biological indicators of a degraded ecosystem within the Chesapeake Bay watershed. These indicators show (1) increased incidence of infectious disease and parasite infestations contributing to increased mortality, (2) feminization (male fish with eggs and elevated levels of vitellogenin) of largemouth and smallmouth bass and other signs of endocrine disruption, (3) reduced reproductive success and recruitment of yellow perch in certain highly urbanized tributaries, and (4) tumors in brown bullhead and mummichogs. The weight of the evidence points to an association between indicators of biological effects and exposure to toxic chemicals.

Wildlife in the Chesapeake Bay and its watershed has also been affected by pesticides, polychlorinated biphenyls (PCBs), and flame retardants, but information on the effects of household products, personal care products, and pharmaceuticals is limited (chapter 4).

Concentrations of organochlorine pesticides and their metabolites in tissue have declined and widespread adverse reproductive effects on Chesapeake Bay waterbirds have subsided. However, organochlorine pesticide concentrations remain elevated in a few areas. Unlike concentrations of pesticides, concentrations of PCBs in tissues of many species of Chesapeake Bay wildlife have not declined since the final U.S. Environmental Protection Agency rule restricting the manufacture, processing, and distribution of these compounds became effective in 1979. In

some urbanized regions, exposure to PCBs appears to be substantial and molecular effects are apparent; these compounds may even contribute to localized reproductive problems. Despite nationwide interest and concern about potential effects of household products, personal care products, and pharmaceuticals released from wastewater-treatment plants, septic systems, combined sewer outflows, and landfills, no studies have examined the potential effects of exposure to these chemicals on Chesapeake Bay wildlife.

Major Conclusions about the Extent and Severity of Classes of Compounds

Decision rules that were developed to characterize the extent and severity of classes of compounds are described in chapter 1. The decision rules identified the classes of compounds that have a widespread occurrence and whose concentrations have exceeded ecological thresholds as having “bay-wide” extent and severity. Contaminants that occur only in individual jurisdictions and with noted severity are classified as localized. A summary of the occurrence and severity of major classes of organic compounds, metals, and metalloids is shown in table 1 (see chapter 2 for more discussion). Associated research and monitoring needs are summarized in chapter 5. Key overall conclusions with respect to different classes of compounds are--

- **Widespread extent and severity:** For some contaminants such as PCBs, some herbicides (atrazine, simazine, metolachor, and their degradates), and mercury, available data indicate extensive environmental distribution at concentrations that are known or suspected to compromise the health and quality of the watershed’s living resources. In some cases these contaminants, particularly PCBs and mercury, create a risk to human health through consumption of contaminated fish.

- Localized extent and severity:** For an additional group of contaminants including dioxins/furans, polycyclic aromatic hydrocarbons, petroleum, some chlorinated insecticides (aldrin, chlordane, dieldrin, DDT/DDE, heptachlor epoxide, mirex), and some metals (aluminum, chromium, iron, lead, manganese, zinc), the report identifies localized areas of contamination and severity.
- Need for additional research and monitoring:** For other classes of contaminants such as certain pesticides, pharmaceuticals, household and personal care products, flame retardants, and biogenic hormones, additional monitoring data and effects research are needed to assess the occurrence of the compounds and the associated risk to the watershed's living resources. Moreover, additional research is needed to determine the sublethal effects of the classes of compounds for which widespread or local extent and severity was identified.

Table 1. Summary of extent and severity of major classes of compounds.

Data Availability	Research and Monitoring Gaps?*	Localized Extent and Severity Identified?	Baywide Extent and Severity Identified?
Polychlorinated Biphenyls			
Data available throughout the Chesapeake Bay watershed	No	No	Yes Numerous datasets indicate widespread extent. Concentrations exceed State and Federal benchmarks, and multiple water bodies in most jurisdictions are subject to fish consumption advisories. In some locations, wildlife exposure to PCBs may be substantial and may contribute to adverse reproductive

			effects.
Dioxins and Furans			
Limited data for the Chesapeake Bay watershed	No	Yes Local impairments and two water bodies with fish consumption advisories.	No
Polycyclic Aromatic Hydrocarbons			
Data available throughout the Chesapeake Bay watershed	No	Yes High concentrations in sediment and evidence of adverse effects (such as liver tumors in fish) in several locations. Impairments limited to two sites.	No
Petroleum Hydrocarbons			
Limited data for the Chesapeake Bay watershed	No	Yes Local impairments (oil and grease). Spills result in adverse effects on fish and wildlife.	No
Pesticides			
Data available throughout the Chesapeake Bay watershed	Yes Because of the large number of compounds in this group, data availability and understanding of toxicity effects remain limited.	Yes Localized impairments with respect to organochlorine pesticides and degradates (aldrin, chlordane, dieldrin, DDE/DDT, heptachlor epoxide, mirex).	Yes Extent of triazine herbicides (atrazine, simazine) and acetanilide (metolachlor) and degradates is widespread, with potential adverse effects.
Pharmaceuticals			
Limited data for the Chesapeake Bay watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects are uncertain, but some compounds are known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
Household and Personal Care Products			
Limited data for the Chesapeake Bay watershed	Yes Literature and limited monitoring indicate	No	No

	potential for widespread extent. Effects are uncertain, but some compounds are known to cause adverse ecological effects. Additional research and monitoring needed.		
Polybrominated Diphenyl Ether and other Flame Retardants			
Limited data for the Chesapeake Bay watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects are uncertain, but some compounds are known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
Metals and Metalloids			
Data available throughout the Chesapeake Bay watershed	No	Yes Freshwater impairments in several jurisdictions and some exceedances of State standards (aluminum, chromium, iron, lead, manganese, zinc).	Yes Widespread extent in the Chesapeake Bay watershed and severity noted primarily in freshwater fish tissue (mercury).
Biogenic Hormones			
Limited data for the Chesapeake Bay watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects are uncertain, but some compounds are known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
*A “no” for research and monitoring gaps means that available information is sufficient to define extent and severity but additional research may be needed to address sublethal effects on aquatic life.			

Considerations for Developing Reduction Strategies

The findings in this report will be used during 2013 by the CBP partnership to consider new goals for reducing concentrations of toxic contaminants and to develop strategies by 2015 to carry out the goals. Preliminary considerations for development of goals and reduction strategies (chapter 5) could address:

- **Sources**—Developing a basic understanding of the relative magnitude of sources as well as the nature of their environmental pathways for individual and groups of contaminants is critical in determining the extent to which reductions can be achieved.
- **Regulatory and voluntary controls**—For each contaminant source and environmental pathway, consideration of the current regulatory and/or voluntary controls that can be applied will allow for informed decisions regarding the strengths and limitations of specific reduction actions.
- **Technology limitations and opportunities**—In many cases, technology limitations, including green chemistry, sustainable agricultural and other sustainable practices, wastewater and drinking-water treatment, and best management practices will constrain the extent to which reductions can be expected. Therefore, opportunities for developing and applying new technologies should be considered and promoted through the goals and strategies that are developed.
- **Resource limitations and opportunities**--Both State and Federal entities charged with identifying the contaminants responsible for impairments and pursuing policies and programs to address the effects of those contaminants face substantial financial resource limitations. For this reason the CBP, with its high level of both Federal and State leadership and authorities, represents the best opportunity for efficient resource allocation

that will allow progress to be made in reducing inputs of the contaminants identified in this report.

- **Competing priorities**—In the Chesapeake Bay and its watershed, large-scale efforts to address the occurrence of other high-priority contaminants (e.g., nutrients and sediment) that affect the ecological success of the ecosystem are ongoing. The findings in this report indicate, however, that it is appropriate for the CBP to enhance its investigation of a subset of the toxic contaminants that are compromising the system, particularly those whose presence is widespread and that occur at concentrations that likely are causing adverse ecological effects.

Additional Concerns

In chapter 5, future issues that may affect the severity of toxic contaminants in the Bay and its watershed are discussed. Several trends in land use, environmental condition, and other high-priority restoration activities have the potential to exacerbate the threat from toxic contaminants on the environmental quality of the watershed. The key issues are--

- *Energy-related activities such as the extraction of unconventional sources of fossil fuels by using the technique known as hydraulic fracturing.* Whereas most of the states in the Bay watershed are moving to implement controls to recycle, treat, and otherwise minimize the release of flow-back fluids and produced waters to the environment, this process remains a poorly understood source of potential toxic contaminants and brines to the environment;
- *The environmental outcomes that are projected to occur as a result of changes in climate.* Rising sea level, increases in environmental water temperature, and acidification of environmental waters all have the potential to change the concentrations of,

bioavailability of, and adverse ecological effects that result from toxic contaminants in the environment;

- *Best Management Practices (BMPs) that are designed to achieve the Chesapeake Bay Total Maximum Daily Load for nitrogen, phosphorus, and sediment.* Resource managers need to assess whether some prescribed BMPs lead to increased use of chemicals (e.g., cover crops that require the use of herbicides). Selecting alternative BMP scenarios that achieve the needed nitrogen, phosphorus, and sediment reductions while also minimizing or controlling the use and release of toxic contaminants will provide the maximum benefit to Chesapeake Bay restoration.
- *Technological changes related to genetically modified crops that likely will result in changes in pesticides in the environment.* Similarly, changes in pesticide adjuvant formulations are poorly understood. These factors will require attention with respect to pesticides as environmental contaminants. Like those of pesticides, changes in the development, use, and disposal of all the contaminant classes in this report are likely to occur. These changes could alter the conclusions about the extent and severity of toxic contaminants made in this report. Consequently, additional monitoring is required if toxic environmental contaminants are to be prioritized and their environmental effects minimized in the future.

Research and Monitoring

Additional information is needed about several classes of compounds and also about future issues. The suggestions for future research and monitoring (chapter 5) include--

- Toxicological studies to better identify chemicals that are adversely affecting fish and wildlife.

- Source-to-receptor research to (1) identify the sources of where the chemical are originating, (2) understand their environmental pathways, and (3) determine the most likely exposure effects on fish and wildlife.
- Studies of the effects of contaminants on the health of fish and wildlife, and the extent to which exposure makes them more vulnerable to other environmental stressors such as pathogens.
- Enhanced biological monitoring of the effects of contaminants on the health of fish and wildlife and monitoring of more recent contaminants for which information on occurrence in the Bay and its watershed is lacking.
- Studies of the interaction among and effect on aquatic resources from multiple stressors, including those resulting from landscape changes such as increases in impervious surface.

1.0 Introduction and Background

Toxic contaminants have adverse effects on fish and wildlife in the Chesapeake Bay and its watershed. Some effects are well documented and have been addressed through various approaches, including some direct reduction actions, to minimize the occurrence of targeted contaminants. Other contaminants are poorly understood and are the subject of active research.

The presence of toxic contaminants in the Chesapeake Bay has led to:

- the Chesapeake Bay Program (CBP) adopting the Toxics 2000 strategy,
- impairment of the quality of living-resource conditions to the extent that 72 percent of the Bay and its tidal river segments are fully or partially impaired as a result of toxic contaminants (figure 1), (CBP, 2010),

- advisories on the amount of fish that people can eat as a result of high levels of certain toxic contaminants in both the Bay and its watershed,
- research indicating that conventional toxicological benchmarking approaches may not adequately represent the potential for contaminants to do ecological harm, and
- the realization that contaminants in the environment occur in mixtures that reflect complex combinations of land uses and contaminant sources.
- the President's Chesapeake Executive Order strategy calling for new reduction goals and strategies for toxic contaminants.

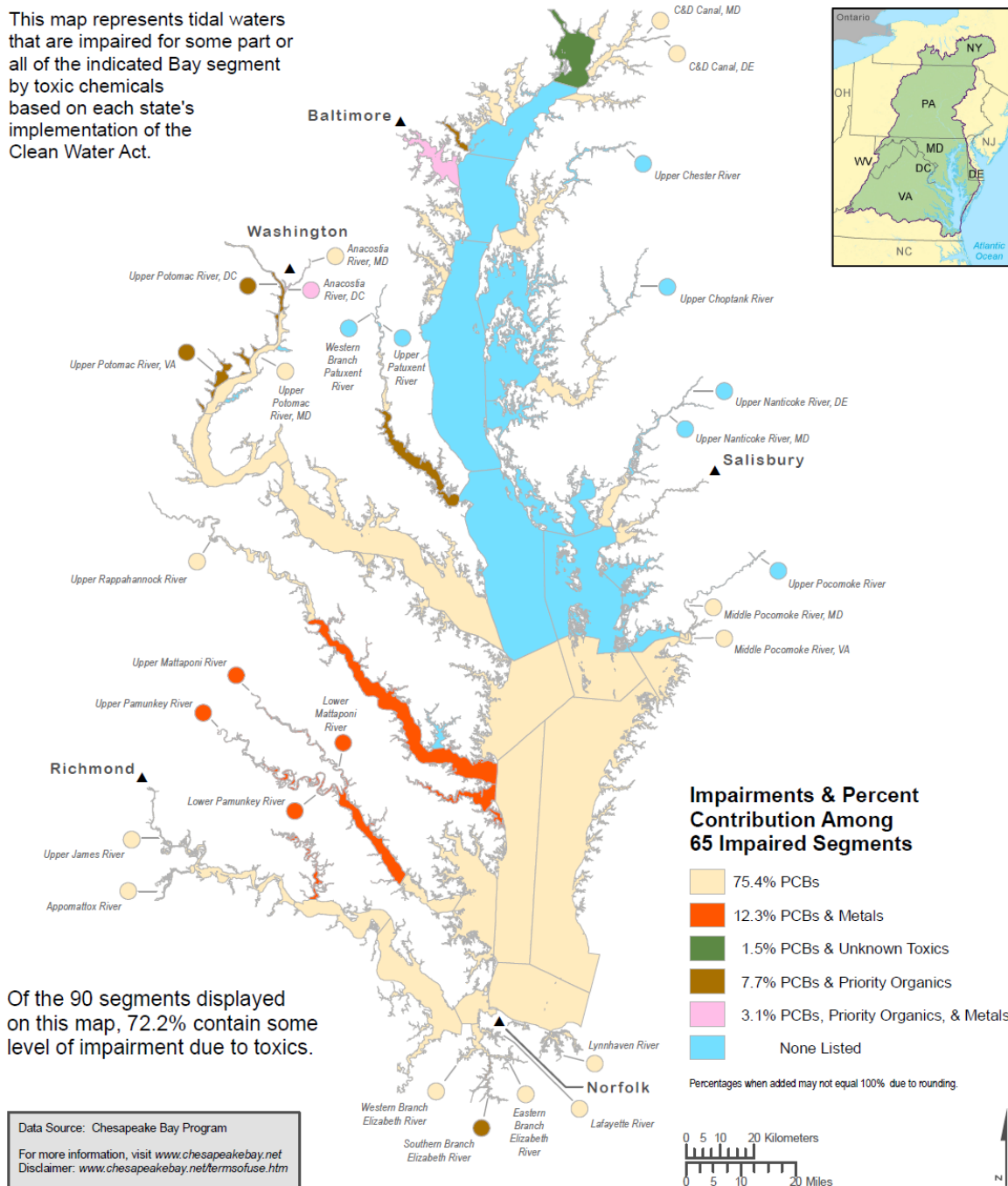
Figure 1 – Tidal Segments With Full or Partial Impairments Due to Toxic Contaminants (next page)

Chemical Contaminants (2010)

Impairments Illustrated Using the
Chesapeake Bay Segmentation Scheme



This map represents tidal waters that are impaired for some part or all of the indicated Bay segment by toxic chemicals based on each state's implementation of the Clean Water Act.



The President's Chesapeake Bay Executive Order (EO 13508, May 12, 2009) Strategy directed Federal agencies to prepare a report summarizing information on the extent and severity of toxic contaminants in the Bay and its watershed. The findings in the report will be used by the U.S. Environmental Protection Agency (EPA) and the jurisdictions in the watershed to consider new goals in 2013 for reducing the input of toxic contaminants and to develop strategies by 2015 to carry out the goals.

Progress on Previous Agreements (*Toxics 2000*)

During December 2000, the CBP Executive Council adopted "Toxics 2000 Strategy: A *Chesapeake Bay Watershed Strategy for Chemical Contaminant Reduction, Prevention, and Assessment*". The agreement made substantial commitments to:

- prevent and reduce chemical contaminant inputs and eliminate toxic impacts on living resources that inhabit the Bay and rivers
- eliminate all chemical contaminant-related fish consumption bans and advisories
- clean up contaminants in the sediment in the three *Regions of Concern* (*Baltimore Harbor, Anacostia River, Elizabeth River*)
- sustain progress in the face of increasing population and expanded development within the watershed.

Since 2000, competing priorities, mostly related to the reduction of nutrient and sediment inputs, have been the main emphasis of CBP activities. This is not to say, however, that progress has not been made by federal and state agencies as well as non-government organizations (NGOs) that are completing ongoing work. Federal agencies such as EPA have continued with numerous contaminated site cleanups that have improved conditions in the Bay and in the watershed. The jurisdictions have continued to enforce permit conditions including industrial

wastewater permits. The jurisdictions have also continued to monitor fish tissue and other environmental media to fulfill their data needs for determining fish consumption advisories and impairment listings. Federal and jurisdiction agencies charged with implementing and enforcing the hazardous material and waste statutes that control the release of toxic contaminants have continued to fulfill their obligations. Federal agencies with science based missions such as USGS, NOAA and USFWS have monitored the presence of chemical contaminants and have assessed possible ecological effects. Many of the outputs of federal monitoring efforts are referred to in this report.

Progress has been made in at least two of the three previously designated Regions of Concern – the Elizabeth River and Anacostia River due in part to the leadership provided by NGOs such as the Elizabeth River Project and Anacostia Watershed Restoration Partnership. For example in the Elizabeth River watershed, contaminated soil at a former naval shipyard was removed and the site was replanted to create a wetland. Multiple industrial sites are being cleaned up in the Elizabeth River to reduce bottom sediment contaminated with PAHs and other pollutants. In the Anacostia, stormwater retrofit projects have been completed to allow for improved treatment of stormwater originating from hundreds of acres in the river's watershed. The Anacostia is benefiting from a TMDL that targets trash, which will reduce inputs of contaminants associated with household products and other industrial sources of waste. An Anacostia watershed restoration plan, developed in 2010, is being implemented through multijurisdictional cooperation and projects that will reduce inputs of toxic contaminants to the river are being completed. During 2012, the EPA Chesapeake Bay Program Office focused one million dollars of grant funds toward the Anacostia. Both the Anacostia and Baltimore Harbor

were chosen for EPA's Urban Waters Initiative, which is working to align federal programs and investments and build local capacity for improving ecological conditions in these watersheds.

In 2006, the CBP completed an analysis of information that led to prioritization of organic pollutants for use in developing management strategies for reducing pollutant inputs. Although several of the compound classes that were identified as high priority in 2006 are also identified in this report, the 2006 prioritization was not substantially referred to in this report because the project team believed more current information was available. Strategies for reduction of those high priority pollutants were in development when the organizational decision was made in the CBP to focus primarily on the nutrient and sediment TMDL.

In 2007, the former CBP Toxics Subcommittee was disbanded to allow for greater focus on the nutrient and sediment Total Maximum Daily Load (TMDL). Prior to 2007, the efforts of the Toxics Subcommittee focused on further characterizing the condition of the Bay with regard to ecological impacts from toxic contaminants. The characterization data generated during that time is referred to in this report.

It is beyond the scope of this report to make quantitative estimates on the progress made on the original commitments in Toxics 2000. According to the environmental indicator maintained by the CBP (see figure 1), which measures the number of tidal segments with a partial or full jurisdiction-listed impairment due to toxic contaminants, a stable or slightly increasing extent of impairment exists in the Bay as compared to the previous version, which was based on 2008 jurisdiction impairment listings. Since the strategy was written, the conditions that existed remain; research has augmented our understanding of sublethal effects of contaminant mixtures; and new issues, such as intersex characteristics in fish in the Bay watershed, have arisen. The focus of this report, therefore, is current conditions of extent and severity of impacts from toxic

contaminants to assist the CBP in revising goals and strategies to reduce risk to the Bay's biological resources.

Report Purpose and Scope

This report summarizes information about the extent and severity of the effects of toxic contaminants in the Bay and its watershed. This report also provides considerations for developing reduction goals and identifies research and monitoring that needs to be conducted to better define extent and severity of classes of compounds.

The scope of the report focuses on using available information to summarize the extent and severity of toxic contaminants and their effects on fish and wildlife in the Bay and its watershed. The report does not address potential effects on human health except in recognizing the status of fish consumption advisories established by the jurisdictions in the watershed.

The extent of toxic contamination is defined for major classes of compounds, such as polychlorinated biphenyls (PCBs) and pesticides, which are known to occur in the Bay and its watershed. Information from the jurisdictions' integrated water-quality assessment reports is a key resource in helping to define the extent and severity of toxic contaminants. Additional information from previously published Federal and academic studies was examined. For some classes of compounds, such as PCBs, polynuclear aromatic hydrocarbons (PAHs), and some pesticides and metals, available information was sufficient to characterize the contaminant as widespread, limited, or not detected. For other classes of compounds, including pharmaceuticals, personal care products, flame retardants, and hormones, data were limited; therefore, conclusions about extent of occurrence are constrained and less certain.

The severity of the impact of toxic contaminants on aquatic communities was assessed, in part, by using results from jurisdiction integrated assessment reports with the recognition that conventional approaches are limited. These reports identified streams and tidal waters that were impaired on the basis of a comparison between environmental concentrations and existing environmental effects benchmarks. The authors also used findings in the national and international literature regarding compounds that have been shown to produce adverse effects (both lethal and sublethal) at environmentally relevant concentrations.

The findings will be used by the CBP to consider new or updated goals for reduction of toxic contaminants. The primary audience is the decision makers in the CBP who are working to manage fisheries, habitat, water quality, and healthy watersheds. Several CBP goal implementation teams (GITs) are concerned with the potential effects of toxic contaminants. The Fisheries GIT needs the findings to better understand the health of fisheries in the Bay and its watershed. The Habitat GIT wants to understand effects on wildlife (especially waterfowl) that use coastal wetlands and submerged aquatic vegetation. Because the Water-Quality GIT is working to make waters both fishable and swimmable, the information developed in this report will help support nutrient and sediment reduction efforts. The Healthy Watersheds GIT is working to reduce impacts of toxic contaminants on healthy watersheds. The Water Quality GIT will coordinate with the other GITs and will use the information to work with CBP leadership groups such as the Management Board and Principal's Staff Committee to consider new goals to reduce toxic contaminants (during 2013) and to develop more detailed strategies to carry out the goals (by 2015).

Decision rules to define extent and severity of toxic contaminants

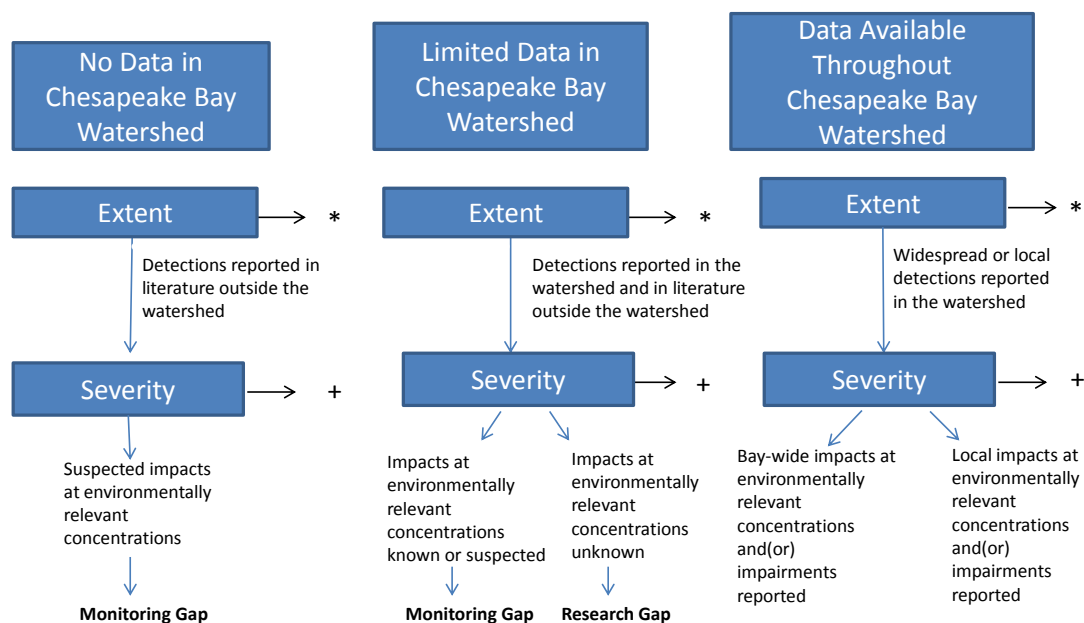
Decision rules were developed to characterize the extent and severity of classes of compounds (see figure 2). The decision rules identified the classes of compounds that have a widespread occurrence and whose concentrations have exceeded ecological thresholds as having “bay-wide” extent and severity. Contaminants that occur in individual jurisdictions are classified as “localized” with noted severity.

The rules identify three possible scenarios that are guided largely by the extent to which monitoring data and toxicity benchmarks are available related to the extent and severity of the distribution of a contaminant class in the Chesapeake Bay watershed:

- **Data Available** - For compound classes for which data for the Chesapeake Bay watershed are readily available, the rules determine whether detections are widespread, limited, or absent (right column on figure 2). If detections are widespread and at concentrations that exceed benchmarks for ecological toxicity, the class of compounds were considered to have “baywide” extent and severity. If contamination is present only in geographically limited areas at concentrations of concern, the classes of compounds were considered to have “local” extent and severity. If available data indicate no detections, the class of compounds are not considered to have extent and severity of environmental concern.
- **Limited Data** - For compound classes for which limited data are available for the Chesapeake Bay watershed, the rules determine whether the data include detections

(middle column on figure 2). If detections are present, the environmental concentrations are compared to available toxicity benchmarks. If there is reasonable cause for concern, the recommendation is for additional monitoring. Detections without applicable benchmarks available result in a recommendation for research to better understand possible toxicity to the ecosystem. If no detections are present in the limited data, and the compound class does not appear to be detected in similar watersheds, the decision rules results in no further consideration in this report.

- **No Data** - For compound classes for which no monitoring data are available for the Chesapeake Bay watershed, the rules ask whether contaminant extent data are available for other, reasonably similar watersheds (left column on figure 2). If so, and if the data from the other watershed(s) indicate substantial presence of the compound class, the rules then apply best judgment on severity of risk. If the distribution is extensive and at concentrations of concern in other watersheds, the recommendation is for increased monitoring in the Chesapeake Bay watershed. If no data are available from comparable watersheds, the classes of compounds have no further summary in this report.



* - Contaminants not analyzed in environmental samples and(or) no detections based on current laboratory capabilities
+ - Unknown and(or) no quantifiable impacts based on current health benchmarks.

Figure 2. Decision rules used to summarize information for each contaminant group.

Assessment typically involved a comparison of contaminant concentrations with State water-quality standards. No standards have been developed for sediment. Guidelines for evaluating the severity of sediment contamination in estuarine and marine sediment are provided by values known as the Effects Range Low (ERL) and the Effects Range Median (ERM). The ERM is the concentration above which toxic effects are predicted to be seen in the field, with acutely toxic impacts occurring 50 percent of the time or more. The ERL is a lower threshold concentration, above which toxic impacts may be seen in the field (Long et al. 1995). For freshwater, consensus-based guidance values were derived based on evaluation of are the Threshold Effects Concentration (TEC) and the Probable Effects Concentration (PEC) (MacDonald et al. 2000a). TECs are intended to identify contaminant concentrations below which harmful effects on

sediment dwelling organisms were not expected. PECs are contaminant concentrations above which harmful effects on sediment-dwelling organisms were expected to occur frequently. All of these guidance values are empirically based. Other more theoretically based guidance values include the equilibrium partitioning approach and evaluation of the relationship between simultaneously extracted metal concentrations and acid volatile sulfide concentrations. For this report, we relied on comparisons with ERL, ERM, TEC, and PEC values provided by the authors of the studies.

2.0 Extent and Severity of Contaminants

2.1 PCBs

Abstract

PCBs are a group of synthetic organochlorine chemicals widely used as dielectric and coolant fluids in transformers and capacitors. In 1977, the United States banned the production of PCBs out of concern for the class's persistence in the environment and evidence indicating that it was bioaccumulative and had the potential to cause toxic impacts. Though the production of PCBs has ceased, there are continued authorized uses of PCB-containing materials which pose the potential for environmental release. The inadvertent production of PCBs in certain manufacturing processes represents an additional contemporary source. The extent of PCB contamination within the Chesapeake Bay watershed is widespread. Concentrations of PCBs in many areas of the watershed exceed state and/or federal benchmarks leading to impairment of Bay resources.

Background

PCBs are a group of synthetic organic chemicals with high thermal stability, making them important in applications such as dielectric fluids in transformers and capacitors, heat transfer fluids, and lubricants. In addition, PCBs were used in plasticizers (e.g., carbonless paper), inks, adhesives, sealants and caulk. There are no natural sources of PCBs to the environment. PCBs typically exist as mixtures of chlorinated biphenyl compounds with varying degrees of chlorination. A total of 209 possible compounds, known as congeners, result from the variation of chlorination (1 – 10 chlorines) around the biphenyl rings (Agency for Toxic Substances and Disease Registry (ATSDR 2000)).

PCBs are relatively insoluble in water with solubility decreasing with increasing chlorination. These hydrophobic compounds dissolve readily in nonpolar organic solvents and in biological lipids. Due to different degrees of chlorination, the physical and chemical properties vary among the congeners (ATSDR 2000). PCBs have been identified as a probable human carcinogen (Integrated Risk Information System (IRIS 2012)).

PCBs have not been produced in the United States since August of 1977 due to evidence that this group of compounds was persistent and bioaccumulative in the environment and had the potential to cause toxic impacts. Aside from the historical contributions of PCBs to the environment, PCBs can continue to be released to the environment through leaks or fires in PCB containing equipment, accidental spills, illegal or improper disposal, burning of PCB containing oils in incinerators, and leaks from hazardous waste sites (Total Maximum Daily Load (TMDL)

reports: MDE 2009a, 2009b, 2009c, 2011a, 2011b, U.S. Environmental Protection Agency (US EPA) 2001, Haywood and Buchanan 2007). Point source discharges should be controlled; however, discharges of PCBs may continue as a result of historical contamination or inadvertent production (Oregon Department of Environmental Quality (ODEQ) 2012, Du 2008, Hu 2010). Specific processes implicated in inadvertent production have been identified as those that involve chlorinated solvents, paints, printing inks, agricultural chemicals, plastics and detergent bars (ODEQ 2012). In addition, there are continued authorized uses of PCBs including transformers and some heat transfer system (ODEQ 2012). ODEQ (2012) provides further information on potential sources in waste materials and recycling operations.

In the aqueous environment, the higher molecular weight PCBs (i.e., more chlorinated) are typically sorbed to suspended solids and sediment while the lower molecular weight PCBs tend to volatilize to the atmosphere. Once in the environment, PCBs cycle among environmental media (air, water, soil/sediment). Volatilized PCBs are redeposited to land and water through precipitation events (ATSDR 2000). In a draft report studying PCB sources in the Back River in 2011, the Maryland Department of the Environment (MDE 2011a) adapted a conceptual model from Larry Walker and Associates (LWA 2005) to characterize PCB sources. Though this model was intended specifically for the Back River, the conceptual model can be applied to many tributaries to the Chesapeake Bay.

PCBs in the water column can be removed through volatilization at the air-water interface, through sorption to sediments and suspended solids, and by uptake in aquatic organisms (ATSDR 2000). Uptake in aquatic organisms can occur through bioconcentration and/or

bioaccumulation. In bioconcentration, uptake occurs directly from the water column whereas bioaccumulation occurs through the combined uptake of food, water and sediment.

Concentrations of PCBs increase through the higher trophic levels. Due to the lipophilicity of these compounds, they tend to accumulate within the tissues of the organisms (ATSDR 2000).

The U.S. EPA and the International Agency for Research on Cancer (IARC) list PCBs as probable human carcinogens (reviewed by ATSDR 2000). Studies with workers reported that PCBs were associated with cancer of the liver and biliary tract. ATSDR (2000) summarized studies that reported that women who consumed high amounts of PCB-contaminated fish gave birth to babies with lower birth weights. ATSDR noted that infants of these women had abnormal responses to behavior tests and that the infants' problems with motor skills and short-term memory persisted. Thus, there is concern for prenatal exposure and for exposure of children in breast milk. Fish consumption advisories for PCBs are therefore more restrictive for children and women of child-bearing age.

The data for this chapter were captured primarily from the state integrated assessment reports which documents water body compliance with state water quality standards. Water bodies that fail to meet the water quality standards applicable for the state's designated use are categorized as "impaired". These numerical thresholds may differ from state to state. For the purposes of this chapter, comparisons between the state standards will not be made; however, impairment identifications are noted.

Though the integrated assessment reports do not provide quantitative data on PCB concentrations, such data was available from the TMDL reports prepared for several impaired waterways in the Chesapeake Bay watershed. Under the Clean Water Act, states must develop TMDL reports for each impaired water body, identifying the probable sources of impairment and the required load reductions from each source category necessary to comply with the standard. Several TMDL reports in the Chesapeake Bay watershed have been completed for fish tissue impairments and provide a source for quantitative data. NOAA provided an additional source of quantitative data in its sediment survey of the Chesapeake Bay conducted from 1998 – 2001 characterizing PCB concentrations across a wide area of the watershed (Hartwell and Hameedi 2007).

Analytical challenges exist with capturing low-level PCB data. Though not yet promulgated in the Federal Register for Clean Water Act programs, US EPA Method 1668, a low-level PCB method, is being used to support many TMDL studies. Though there is on-going debate and concern about the method's reliability at levels near its reported detection limit and its sensitivity to false positives, EPA indicates that its use in state TMDL programs has been successful (US EPA 2012a).

Water

There are two categories of water quality standards applicable to PCBs: standards developed for the protection of aquatic life and standards developed for the protection of human health.

Documented water column exceedances of the state water quality standards are uncommon. This

could be, in part, attributable to the limitations of the analytical methods most commonly used for the routine state assessment. Routine methods typically quantify a small subset of the total 209 PCB congeners and have analytical detection limits several orders of magnitude above the state standards (US EPA 2012a). Though high resolution data in the water column may not be commonly available, water column data may be estimated through the calculation of bioaccumulation factors (BAFs) (Hartwell 2007).

The Commonwealth of Virginia documents water column impairments in the Potomac and Shenandoah river basins. Approximately 9 river miles are impaired and 1 square mile of estuary is impaired (Virginia Department of Environmental Quality (VA DEQ) 2010).

The multi-jurisdictional Potomac/Anacostia Rivers TMDL identified a range of water column values from below detection – 340 ng/L (congener specific detection limits 2 – 8 pg/L) (Haywood 2007). Completed Maryland TMDL studies reported water column values ranging from 0.09 – 30.71 ng/L (MDE 2011a, MDE 2009a, MDE 2009b, MDE 2009c, MDE 2009d). Virginia and West Virginia collaborated for the Shenandoah River TMDL and measured water column values ranging from 0.0077 – 0.0791 ng/L (USEPA 2001). Pennsylvania's Susquehanna River TMDL reported a water column value of 27.6 ng/L (PA DEP 1999).

Sediment

Maryland documents impairments based on exceedances of screening values in sediment (Bear Creek, Curtis Bay and Baltimore Harbor - MDE 2010). In Virginia, 208 stations were monitored

for PCBs in sediment in conjunction with the Commonwealth's freshwater probabilistic monitoring program. PCBs were detectable in all samples but were below the Probable Effect Concentration screening value of 676 ppb (VA DEQ 2010). The other states in the Chesapeake Bay watershed did not document impairments for PCBs. Historical data from the Nanticoke River in Delaware indicates that PCB concentrations "were not detected at levels expected to pose a significant risk to aquatic life or human health" (DDNREC 1997). More recent sediment core data was collected to support a maintenance dredging project in the Nanticoke (2006).

The National Oceanic and Atmospheric Administration (NOAA) completed a survey of toxic contaminants in sediments bay-wide from 1998 – 2001, including PCB analysis for a list of approximately 22 congeners. Sediment concentrations from samples in the Bay tributaries tended to be higher than those collected from the embayments and mainstem (Hartwell and Hameedie 2007).

In 1994, NOAA released a report documenting sediment contamination in the Chesapeake and Delaware Bays. At that time, sediment concentrations around Fort McHenry (Baltimore, MD) ranked among the highest PCB sediment concentrations in the country (90th percentile). The measured concentration at this site was 679 ppb, above the ERM of 180 ppb. The more recent NOAA report (Hartwell and Hameedi 2007) did not include data from the Fort McHenry area.

None of the sediment concentrations in the NOAA study exceed the ERM level of 180 ppb, however, several sites did document levels above the ERL of 22.7 ppb (Susquehanna Flats, Bay Bridge, and the Elizabeth River). The sediment values for the Chesapeake Bay embayments

were all below the ERL. The study reports sediment concentrations ranging from below detection to 122 ppb (Hartwell and Hameedi 2007).

The Potomac/Anacostia Rivers TMDL identified a range of sediment values from below detection – 1550 ng/g dry weight (congener specific detection limits less than 10 pg/L) (Haywood 2007). Completed Maryland TMDL studies reported sediment values ranging from 1.4 – 59.14 ng/g dry weight (MDE 2011a, MDE 2009a, MDE 2009b, MDE 2009c, MDE 2009d). Virginia and West Virginia collaborated for the Shenandoah River TMDL and measured sediment values ranging from 0.31 – 100 ng/L (USEPA 2001).

PCBs in sediments at concentrations above certain thresholds pose risks to aquatic life through several pathways. First, sediment-bound PCBs serve as a source for bioaccumulation that ultimately results in fish contamination. This topic is covered extensively by Haywood and Buchanan (2007) in the total maximum daily load (TMDL) document for the tidal Potomac River. They calculated bioaccumulation factor (BAF)-based target sediment concentrations of 2.8 to 12.0 ppb. These would translate to fish tissue concentrations at or below the impairment thresholds of the District of Columbia, Maryland, and Virginia. Clearly, a high percentage of the sediments monitored in the tidal Potomac have total PCB concentrations above these targets, hence the TMDL's calculation of the need for a 96% reduction in PCB loading.

Eggs, larvae, and juveniles of Bay fish species are exposed to PCB-contaminated sediments and it is likely that these life stages are more sensitive than adults (Eisler and Belisle 1996). In addition, maternal transfer of PCBs occurs during oogenesis (Fisk and Johnston 1998).

Calculations of sediment thresholds for toxic effects in fish have been conducted for juvenile salmonids by Meador et al. (2002) who evaluated 15 studies that reported total PCB tissue concentrations and toxic effects. Using literature-based biota sediment accumulation factors (BSAFs) and lipid calculations, they suggested a sediment effect threshold concentration ranging from 0.075 to 0.600 ppm dry weight. The range depended on the BSAF and percent total organic carbon in the sediments. Note that these sediment thresholds for the protection of salmonids are higher than the TMDL targets of Haywood and Buchanan (2007).

Fish

Human health concerns

The state water quality standards regulating fish tissue concentrations are designed to protect human health by minimizing dietary exposure to PCBs through fish consumption. These concentrations can be elevated to unacceptable levels as a result of interactions with sediment, the water column and through trophic transfer. Though high resolution data may not be available for sediment and water in waterways that have fish impairments, it is likely in many cases that the sediment and/or water column may have PCB concentrations in excess of state standards.

With the exception of New York, all of the Bay jurisdictions have multiple water bodies listed with fish consumption advisories due to PCB fish tissue concentrations in excess of a state standard or health department threshold. Most limit exposure in terms of meals per week or month and there is variation in the formulas used to calculate the restrictions.

The District of Columbia issued fishing advisories for all its waters out of concern for elevated levels of PCBs and other chemicals in fish tissue (District Department of the Environment (DDOE) 2010). In Virginia, all five Bay tributaries have PCB fish tissue impairments with a total of 456 river miles and 2011 square estuarine miles impacted. The James River has the highest number of impaired river miles (245 miles) while the mainstem Chesapeake Bay and its small coastal basins account for 79% of the impaired estuary footprint (VA DEQ 2010). PCB TMDLs for the Potomac and Shenandoah Rivers have been completed. In the Potomac River TMDL, fish tissue values ranged from non-detect to > 400 ppb.

West Virginia has identified 7 subwatersheds of the Chesapeake Bay as impaired for the state standard: Southern Branch of the Potomac, Northern Branch of the Potomac, the Potomac Drains, Cacapon, Shenandoah Jefferson, and Shenandoah Hardy (West Virginia Department of Environmental Protection (WV DEP) 2010). As indicated in the above discussion, the TMDL for the Shenandoah has been completed in collaboration with the Commonwealth of Virginia. More recently, West Virginia collected data in the Shenandoah which indicates that PCB levels may be declining. The average fish tissue concentration (skin-off) was 0.25 ppm with a range from non-detect – 2.1 ppm (detection limit = 0.01 ppm). All of the fish collected for skin-on analyses were below the WVDHHR screening value of 0.05 ppm (WVDHHR 2012a). The most recent Shenandoah data collected by the Commonwealth of Virginia (2005), however, indicates a continued need for fish consumption advisories (VA DEQ 2012).

The State of Maryland lists more than 30 segments in the Bay watershed for fish tissue impairment. In the Severn River mesohaline segment, the integrated report indicates that fish

tissue concentrations may be low enough to meet the standard; however, additional data are needed for confirmation (MDE 2010). Completed Maryland TMDLs document a range of fish tissue values of 22.1 – 608.9 ng/g (MDE 2009a-d, MDE 2011a).

Within the Chesapeake Bay watershed of Pennsylvania, the Susquehanna River is identified as impaired for fish tissue consumption based on exceedances of the PCB standard (Pennsylvania Department of Environmental Protection (PA DEP) 2010, 2012a, 2012b). This basin accounts for approximately 275 miles of impaired rivers and streams. A TMDL for a portion of the Susquehanna River basin has been completed and identifies a fish tissue value of 0.860 ppm (PA DEP 1999).

Within the entire Bay watershed, the Anacostia and Potomac Rivers in Washington, DC are the areas of greatest concern for PCB fish tissue contamination. The District Department of the Environment (<http://ddoe.dc.gov/service/fishing-district>) currently advises the public not to consume any catfish, carp, or eels from waters of the District of Columbia due to PCBs and other chemicals. The most recent sampling was conducted in 2007 in the Potomac and Anacostia Rivers within the District's waters (Pinkney, 2009). Pinkney (2009) found that the highest total PCB concentrations were in American eel (*Anguilla rostrata*), where the median concentration was 2.18 ppm wet weight, over 100 times the U.S. EPA (2000) screening value of 0.020 ppm. One eel sample contained 4.00 ppm. Median concentrations in carp (*Cyprinus carpio*), channel catfish (*Ictalurus punctatus*), and blue catfish (*I. furcatus*) were all close to 0.80 ppm.

Pinkney (2009) compared PCB fish tissue concentrations in 2007 with those measured in 2000 (Pinkney et al. 2001), using similar methods and fish with similar lengths. Median concentrations of PCBs in American eel, carp, and largemouth bass increased in both the Potomac and Anacostia rivers whereas median PCB concentrations in channel catfish decreased in both rivers. Median PCB concentrations in sunfish decreased slightly. PCB concentrations were generally higher in the Anacostia vs. Potomac fish, but fish from both rivers were well above thresholds.

Ecological concerns

Wenning et al. (2011) and Monosson (1999) reviewed literature on toxicological effects of PCBs on fish. Reported effects include mortality, impaired growth and reproduction, disruption of the endocrine and immune systems, biochemical changes, behavioral alteration, and mutagenicity. Iwanowicz et al. (2009a) documented adverse effects on the brown bullhead immune response, disease resistance and endocrine physiology following intraperitoneal exposure to 5 and 0.5 mg/kg of the PCB mixture Aroclor 1248. Similarly, a significant negative correlation has been documented between PCB body burden and the immune response and endocrine physiology in wild-caught brown bullheads and largemouth bass (Iwanowicz et al. 2012). Barron et al. (2000) attributed an increased prevalence of hepatic tumors and preneoplastic liver lesions in walleye from the PCB-contaminated Green Bay area of Lake Michigan relative to a reference area. They stated that while these results did not show causation, they are consistent with studies that indicate that PCBs are liver tumor promoters in fish (Weisburger and Williams 1991).

Wenning et al. (2011) concluded that data were inadequate to establish no observable effect concentrations (NOECs) based on PCB tissue residues. Meador et al. (2002) in their review of

salmonid toxicity data suggested a tissue residue threshold of 2.4 mg PCBs/kg (=ppm) lipid, which corresponds to 0.14 mg PCBs/kg (=ppm) wet weight tissue (D. MacDonald, MacDonald Environmental Services Ltd, personal communication). TAMS Consultants Inc. and Menzie-Cura Associates Inc. (2000) addressed the toxicological effects associated with PCB residues as part of the Hudson River Ecological Risk Assessment. Based on their literature review, they recommended a no observable adverse effects level (NOAEL) of 1.9 mg PCBs/kg (=ppm) whole body weight and a lowest observable adverse effect level of 9.3 mg/kg (=ppm) body weight. These NOAELs and LOAELs were applied to species that are resident to the Hudson River, most of which are also Chesapeake Bay species. Using a whole body to fillet ratio of 1.7 from Amrhein et al. (1999), these are converted to 1.1 ppm fillet (NOAEL) and 5.5 ppm fillet (LOAEL). Others have reported whole body: fillet ratios ranging from 1.7 to 3.1 (D. MacDonald, MacDonald Environmental Services Ltd, personal communication), which would lower the estimated fillet concentration thresholds.

Based on TAMS Consultants Inc. and Menzie-Cura Associates Inc. (2000) and Meador et al. (2002), it is reasonable to suggest that total PCB fillet concentrations above about 1.0 ppm may be associated with adverse biological effects in Bay watershed species. Such concentrations have been reported in bottom-dwelling fish in urban areas such as the District of Columbia (Pinkney 2009; Velinsky et al. 2011) and near U.S. EPA National Priority List sites where PCBs are a contaminant of concern (such as the Marine Corps Base Quantico, Pinkney and McGowan 2006).

Wildlife

Human health concerns

In 1994, a total of 23 snapping turtles (*Chelydra serpentina*) were collected in the upper Chesapeake (U.S. Army Environmental Hygiene Agency (USAEHA) 1994). Aroclor 1260 was detected in skeletal muscle of only 3 of the turtles collected in Canal and Watson Creeks, with concentrations ranging from 0.20 to 0.709 ppm wet weight. The cancer and non-cancer risk to humans consuming turtle meat from these two creeks was within an acceptable range.

Ecological concerns

Studies on Chesapeake Bay bald eagles (*Haliaeetus leucocephalus*) from the late 1960's to 1990 revealed that total PCB concentrations in addled eggs averaged about 25 ppm wet weight (ranged from 8.9 to 218 ppm) (Wiemeyer et al. 1984, 1993). In the past 20 years, total PCBs concentrations have only been reported for a few bald eagle eggs. A single addled egg collected at Aberdeen Proving Ground in Harford County, Maryland in 2008 contained 33.69 ppm wet weight (Mojica and Watts 2008), and two addled eggs collected from the Naval Support Facility Indian Head in Charles County Maryland in 2008 and 2009 contained 18.4 and 18.3 ppm (Mojica and Watts 2011). Concentrations of total PCBs from blood samples of 58 nestling eagles from these same sites ranged from 7 to 106 ppb wet weight (Mojica and Watts, 2008, 2011), and are below the toxicity threshold for impaired reproduction of 189 ppb (Elliott and Harris 2002; Henny and Elliott 2007).

Between the 1960's and 1990, total PCBs in osprey eggs ranged up to 18 ppm (Wiemeyer et al. 1988, Audet et al. 1992). In a large-scale osprey study conducted in 2000 and 2001, total PCB concentrations in eggs collected from Baltimore Harbor and the Patapsco River, and the

Anacostia and middle Potomac Rivers averaged 7.25 and 9.28 ppm wet weight, respectively (Rattner et al. 2004). The upper extreme value was 19.3 ppm from an egg collected near the Naval Research Laboratory on the middle Potomac, and was actually similar to the greatest historical values reported in Osprey eggs from the Chesapeake (Wiemeyer et al. 1988). Osprey eggs from the Elizabeth River, the location of the largest military naval port in the world, contained the lowest total PCB value, averaging 3.60 ppm. Surprisingly, total PCB concentrations in eggs from the South, West and Rhode Rivers reference area averaged 4.60 ppm, and ranged up to 12.4 ppm. Compared to total PCB values reported in collections in the 1970's and 1980's by Wiemeyer and coworkers (1988), it would appear that total PCB concentrations in osprey eggs have not declined; this trend has also been noted for ospreys eggs for much of the Atlantic coast (Rattner et al. 2005). Levels of 15 arylhydrocarbon (*Ah*) receptor-active PCB congeners (but not dioxins or dibenzofurans) were also quantified in these eggs. Concentrations of the toxicologically most potent coplanar and semi-coplanar congeners (i.e., congeners 77, 81, 105, 126 and 169) did not differ much between study sites. Dioxin toxic equivalents of 15 *Ah* receptor-active congeners did not differ among sites in this Chesapeake Bay study, with average site values ranging from 54.5 to 218 parts per trillion (ppt) wet weight, and on a national scale, values were greater than those observed in the Pacific Northwest (Elliott et al. 2000; Henny et al. 2003), but not unlike toxic equivalents observed in Delaware Bay (Toschik et al. 2005) and the Great Lakes (Martin et al. 2003).

In the past 20 years, three studies have examined total PCB concentrations in nonviable peregrine falcon (*Falco peregrinus*) eggs collected from nests in the Chesapeake. In 1992, 10 eggs nonviable eggs were collected from 7 nests in the Chesapeake Bay region (Morse 1994).

Aroclor 1254 ranged from 2.0 to 5.7 ppm wet weight and Aroclor 1260 ranged from 4.1 to 10.9 ppm. By summing these two Aroclors in the 10 individual eggs, it would appear that total PCBs ranged from 7.1 to 12.9 ppm. Between 1993 and 1999, nine peregrine falcon eggs that failed to hatch from the middle Bay region contained total 4.71 to 6.73 ppm wet weight, while two eggs from the Upper Chesapeake contained 2.85 and 4.65 ppm (Clark *et al.* 2009). Wet weight concentration of *Ah* receptor-active PCB congeners were measured in this study but not reported. However, their concentrations in combination with dioxins and furans were used to estimate dioxin toxic equivalents (results described in subsequent section). Total PCBs were also quantified in 22 addled peregrine falcon eggs collected between 1993 and 2002 from yet other locations in the Chesapeake, and ranged from 3.46 to 12.5 ppm (Potter *et al.* 2009).

A study of black-crowned night-heron (*Nycticorax nycticorax*) pipping embryos collected from Baltimore Harbor, Maryland and Rock Creek Park, Washington, D.C. in 1991 documented that total PCB concentrations were about an order of magnitude greater (range: 0.70 to 18.8 ppm wet weight) when compared to concurrent samples collected from Chincoteague Bay, Virginia (range: not detected to 1.21 ppm) (Rattner *et al.* 1997). Arylhydrocarbon-active PCB congeners and toxic equivalents were up to 37-fold greater in Baltimore Harbor and Rock Creek Park compared to levels in embryos from Chincoteague Bay, Virginia (Rattner *et al.* 1997). Hepatic microsomal activities of benzyloxysorufin-O-dealkylase and ethoxyresorufin-O-dealkylase of embryos from the two most PCB polluted sites were six- to nine-fold greater than those found in embryos from Chincoteague Bay. Total PCB concentrations in 10 day old nestling herons from Baltimore Harbor averaged 1.29 ppm, which was eight times greater than values from the Chincoteague Bay reference site (0.15 ppm). Findings of high concentrations of PCB congeners

and toxic equivalents, as well as cytochrome P450 induction in Baltimore Harbor herons, was the impetus for testing the hypothesis that PCBs might be leading to the declining size of the Baltimore Harbor heron colony (Rattner et al. 2001). Although total PCBs, 12 *Ah* receptor-active PCB congeners and dioxin toxic equivalents were up to 35 times greater in sample eggs from Baltimore Harbor compared to those from the reference area in the southern Chesapeake (Holland Island), overall nest success (0.74) and productivity (2.05 young/hen) were adequate to maintain a stable population. Furthermore, no significant relation was found between hatching, fledging and overall reproductive success and concentrations of PCBs and toxic equivalents. It was concluded that contaminants were not having a dramatic effect on reproduction in the Baltimore Harbor heronry.

In a preliminary study examining potential endocrine disruptive effects of PCBs, common tern eggs collected in 1994 from South Sand Point, off of Barren Island, contained relatively low concentrations of Aroclor 1260 concentrations ranging from 0.44-1.50 ppm wet weight (J.B. French, unpublished data). In testing this hypothesis, eggs were subsequently collected from Bodkin Island, which served as a comparative reference site for the more contaminated samples from Ram Island in Buzzards Bay, Massachusetts. Total PCBs concentrations (<10 ppm lipid weight) were much lower at Bodkin Island compared to Ram Island, but no evidence was obtained to suggest that PCBs were evoking toxic effects in embryos (French et al. 2001). In 2010, common tern eggs were collected from Poplar Island for flame retardant toxicity study, and six that were chemically analyzed were found to have very low total PCB concentrations (range: 0.31 to 0.44 ppm wet weight) (Rattner et al. 2011).

Tree swallow (*Tachycineta bicolor*) eggs and nestlings from the Patuxent Wildlife Research Center in the Chesapeake Bay region generally contained considerably lower concentrations of total PCBs than samples collected from PCB-polluted sites in Indiana, New York and Pennsylvania (eggs: 0.69 ppm wet weight versus 0.94 to 4.6 ppm; nestling body burdens: 0.294 ppm versus 0.169 to 18.46 ppm) (Yorks 1999).

Concentrations of total PCBs and several congener groups (e.g. congeners 118, 138/158, 153/132 and 187; accounted for 66% of the total PCBs in present in liver) were quantified in tissues of juvenile loggerhead (*Caretta caretta*) and Kemp's ridleys (*Lepidochelys kempi*) sea turtles stranded on beaches in the Chesapeake Bay in 1991 (Rybitski et al. 1995). Values in liver ranged from 8.26 to 608 ppb wet weight and levels in subcutaneous fat ranged from 55.4 to 1730 ppb. Concentrations of PCBs and various congeners in muscle and kidney were quite low, and often below the limit of detection. The significance of these concentrations could not be addressed as toxicological thresholds are not adequately established for reptiles.

Concentration of total PCBs in mesentery of dead adult ospreys from Tabbs Creek in York County, Virginia, ranged from 11.3 to 45.3 ppm dry weight (Hale et al. 1996), which appears to be slightly lower than the range of normalized values reported for adult osprey carcasses and brains collected from 1964-1982 (Wiemeyer et al. 1980, 1987). In necropsy reports of the New York State Department of Environmental Conservation on adult birds that apparently succumbed to organochlorine pesticide intoxication from the Chesapeake Bay region, Aroclors 1254 and 1260 were below the limit of detection (New York Department of Environmental Conservation Necropsy Cases 89-07-34, 89-62-29, and 90-22-26).

In general, birds are more tolerant to acute exposure to PCBs compounds than mammals, but a range of effects (e.g., enzyme induction, altered growth and reproduction, chick edema disease, immune dysfunction and endocrine disruption) have been linked to exposure (Rice et al. 2003). In portions of the Chesapeake, including US EPA-designated regions of concern, there is clearly evidence that total PCBs and *Ah*-receptor active PCB congeners induce cytochrome P450-associated monooxygenases, and may evoke adverse effects on some sensitive species of birds. In a few circumstances, PCBs concentrations in eggs are great enough to contribute to the failure of eggs to hatch. Unlike most organochlorine pesticides, concentrations of PCBs in avian eggs have been slow to decline since their use was restricted in the 1970s.

Threshold effects for reduced productivity have been estimated to be about 20 µg total PCB/g wet weight of egg (=ppm) (Elliott and Harris 2002, Henny and Elliott 2007). Thus, it was suggested that the concentration of PCBs, in combination with *p,p'*-DDE, were great enough to contribute to the failure of eagle eggs to hatch (Mojica and Watts 2008).

In a 1995 biomonitoring study conducted at Aberdeen Proving Grounds in Maryland, carcasses of 34 white-footed mice (*Peromyscus leucopus*) from various location were found to contain low levels of total PCBs (Aroclor 1260), with detectable quantities present in only 4 individuals (range: 0.05 to 0.13 ppm wet weight) (Whaley 1996).

Conclusions

Existing data documenting the concentrations of PCBs in fish tissue in the Chesapeake Bay watershed are readily available. Due to the widespread presence of fish consumption advisories within the Chesapeake Bay watershed, it is clear that PCB contamination is negatively impacting watershed resources. The environmental persistence of PCBs is an impediment to quick remediation of the impairments as legacy deposits remain a primary source of PCBs. However, continued authorized uses and the inadvertent production of PCBs remains a potential source of environmental exposure. Though sources of PCBs can be localized, atmospheric transport and deposition of PCBs can have regional impacts.

2.2 Dioxin and Furans

Abstract

Dioxins and Furans is the abbreviated name for a family of toxic substances that all share a similar chemical structure, containing one to eight chlorine atoms attached to the carbon atoms of the parent chemical (dibenzodioxin and dibenzofuran). Dioxins and Furans have no known technical use and are not intentionally produced. They are primarily released to the environment during combustion of fossil fuels (coal, oil, and natural gas) and wood, and during incineration processes (municipal and medical solid waste and hazardous waste incineration). Though data on dioxin contamination in the watershed is limited, what is available indicates that the extent of dioxin contamination within the Chesapeake Bay watershed is localized. Concentrations of dioxins in select areas of the watershed exceed state and/or federal benchmarks leading to impairment of Bay resources.

Background

Dioxins and furans is the abbreviated or short name for a family of toxic substances that all share a similar chemical structure. These chemicals contain one to eight chlorine atoms attached to the carbon atoms of the parent chemical (dibenzodioxin and dibenzofuran). The chlorinated dibenzo-p-dioxins (CDDs) include 75 individual compounds and the chlorinated dibenzofurans (CDFs) include 135 compounds. These individual compounds are referred to as congeners. The most widely studied of these compounds, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), is one of the most toxic to mammals and has received the most attention. Often referred to as “dioxin”, 2,3,7,8-TCDD serves as a reference compound for this class of compounds. The chemicals with properties similar to 2,3,7,8-TCDD are called “dioxin-like” compounds. Only 7 of the 75 congeners of CDD and 10 of the 135 congeners of CDFs are thought to exhibit “dioxin-like” toxicity (USEPA 2012 – *dioxin furan fact sheet website accessed in 2012*, ATSDR 1998).

Dioxins and Furans have no known technical use and are not intentionally produced. Dioxins arise through inadvertent production in processes involving uncontrolled reactions involving chlorine (ATSDR 1998). Air emissions of dioxins and furans result from the combustion and incineration of fossil fuels, municipal and medical solid waste, and hazardous waste (ATSDR 1998). Additional sources include the burning of many materials that may contain chlorine, such as plastics, wood treated with pentachlorophenol (PCP), pesticide-treated wastes and PCB-containing materials. They are also created in the pulp and paper industry from a process that bleaches the wood pulp (ATSDR 1998, USEPA 2012).

Dioxins and furans are persistent and bioaccumulative compounds with very low water solubility. Because of this general lack of solubility in water and overall low volatility, they are likely to be found in soil or condensed on particulate matter. They bind strongly to soil and are more likely to move from soil to water by soil erosion and flooding. Highly persistent, these compounds tend to stick to suspended particles and settled particles in lakes and rivers can remain at the bottom for several years (USEPA 2012).

Atmospheric deposition provides the primary route of exposure to the ecological food chain. Dioxin exposure in waterways can be widespread, resulting from the dispersion of soil particles in erosion and run-off, volatilization from land and water, and resuspension of sediment particles. There is some uncertainty as to whether the atmospheric deposition represents contemporary inputs of dioxins or whether this deposition component is resulting from transfers among the environmental media (USEPA 2001).

Dioxins and Furans are found in the environment together with other structurally related chlorinated chemicals. Therefore, to facilitate risk assessment of exposure to these chemicals, the Toxicity Equivalent Factor (TEF) methodology was developed for assisting in estimating the risk from exposure to these mixtures. Since for many of these chemicals very limited data on toxicity exist, TEFs were developed and validated in studies in animals. TEFs are the result of expert scientific judgment using all of the available data and taking into account uncertainties in the available data. The TEF approach compares the relative toxicity of individual congeners to that of 2,3,7,8-TCDD, which is the most extensively studied. 2,3,7,8-TCDD was assigned a TEF of 1.0 and the TEF for the other congeners range from 1.0 to 0.00001. The toxic potency of a

mixture of congeners (i.e., the Toxicity Equivalent Quantity, or TEQ) is the sum of the products of the TEFs for each congener and its concentration in the mixture.

Dioxins and furans can cause a number of health effects. EPA has said that the most well known 2,3,7,8 TCDD it is likely to be a cancer causing substance to humans. In addition, people exposed to dioxins and furans have experienced changes in hormone levels and high doses of dioxin have caused a skin disease called chloracne. Animal studies show that animals exposed to dioxins and furans experienced changes in their hormone systems, changes in the development of the fetus, decreased ability to reproduce, and suppression of the immune system.

Water and Sediment

No water column data were found in the sources of information reviewed. This is not unusual since dioxins/furans are hydrophobic and tend to attach to soil and settle in sediments.

Three areas were found where with reported or potential dioxin/furan sediment contamination.

The first one is in the Southern Branch of the Elizabeth River in Portsmouth, VA. Dioxin contamination there likely resulted from the Atlantic Wood Industries (AWI) Superfund site.

The site is approximately 12 miles from the Chesapeake Bay. Pentachlorophenol (PCP) was widely used at the AWI facility as a wood preservative, and PCP has been reported to contain dioxin and furan impurities. Sediment sampling conducted as part of the Superfund investigation showed that the dioxin in samples included predominantly 1,2,3,4,6,7,8,9-octachloro dibenzo-p-dioxin (OCDD) with minor amounts of 1,2,3,4,6,7,8,9-heptachloro dibenzo-p-dioxin (HpCDD). Sampling conducted in shallow sediment in the vicinity of the AIW site showed a TEQ (US EPA

1989) of 2674 pg/g (parts per trillion) (maximum concentration). Sediment sampling also showed detections of dibenzofurans, but at lower levels.

The second area with reported dioxin contamination is in the North Branch of the Potomac River. In the late 1980s and early 1990s dioxin contamination in the North Branch of the Potomac River resulted from the discharge from the Westvaco paper mill in Luke, Maryland. Fish consumption advisories were issued at that time by both Maryland and West Virginia for a portion of the Potomac between Luke and Paw Paw, West Virginia. Westvaco implemented control measures to reduce dioxin levels in the discharge and according to Maryland Department of Environment (MDE) personnel, no dioxin levels are detected any longer in the Westvaco discharge. Fish advisories were lifted in the early 90s, but it is not clear the levels of contamination in sediment that could still remain as a result of this past discharge.

The third area where dioxin contamination has been reported is in the North Branch Potomac River in Cumberland, Maryland. Sediment sampling was conducted in 2009 as part of a Cumberland Dam Phase I Feasibility Study. Sediment samples collected from within the dam and upstream detected dioxin-like compounds. The 2,3,7,8-TCDD concentration in each sample ranged from 0.57 to 0.93 parts per trillion. The sum of dioxin-like compounds detected in sediment samples ranged from 99.5 to 296.6 parts per trillion. Collection of additional information was recommended in the Feasibility Report. There was no information regarding the source of contamination, however, the report notes that the Westvaco paper mill was investigated for dioxin contamination in the late 1980s. The dam is approximately 28 miles downstream from the Westvaco paper mill.

In regards to contamination that resulted from the Westvaco paper mill, there is the potential that dioxin contamination still remains in the sediments since dioxins attach to solid particles and settle in sediments. However, no information was available on any sediment sampling conducted close to this discharge.

The Feasibility Study conducted as part of the plans to remove a dam in Cumberland County, MD, showed contamination within the dam and upstream from the dam in the Potomac River. The range of the levels detected were from 0.57 to 0.93 parts per trillion, and the report noted that EPA Region III Biological Technical Assistance Group- Freshwater Sediment Screening benchmark for ecological risk assessment for 2,3,7,8-TCDD is 0.85 parts per trillion. The report recommended collection of additional information; however, no further studies have been conducted since that study was completed.

Tissue

Human health concerns

The states use fish advisories as basis for listing streams as impaired by dioxin in their integrated reports. The fish advisories are coordinated with the respective states' Health Departments. Only two states, Virginia and Delaware, listed streams in the Chesapeake Bay watershed, as impaired by dioxins. The listings are reported as “*Dioxin*”, or “*Dioxin, including 2,3,7,8-TCDD*”. Specifically, Delaware listed the Chesapeake and Delaware Canal (C & D Canal), from the Maryland Line to Delaware River (15 miles). The listing was based on an advisory for no

consumption of all finfish due to dioxin, among other pollutants. No source for the dioxin is specified for this segment. Virginia listed the Elizabeth River Southern Branch and its tidal tributaries (23 miles) based on a fish advisory issued for no consumption of blue crab hepatopancreas, but not edible tissue. As stated above, dioxin contamination was reported in the Southern Branch of the Elizabeth River as a result of contamination from the AIW Superfund Site. As part of the Superfund investigation shellfish sampling was conducted as follows (results in parenthesis are maximum detections): crab meat and whole crab (crab meat and hepatopancreas) collected adjacent to the AWI site (Total Dioxin TEQ (1989) 0.00000026 ppm and 0.000012 ppm, respectively); Oyster meat from Oysters collected adjacent to the AIW site (0.0000014 ppm); crab meat and whole crab (crab meat and hepatopancreas) from near Scuffletown Creek (Total Dioxin TEQ (1989) 0.000000023 ppm and 0.0000042 ppm, respectively).

As indicated above, two streams in the Bay were listed as impaired by dioxins, one in the Southern Branch of the Elizabeth River and one in the C&D Canal based on fish advisories. The fish advisories were issued due to the exceedance of each of the states' benchmarks whose purpose is to be protective of human health based on assumptions regarding fish consumption. However, for the C&D Canal currently there is no fish advisory for dioxin. The states' schedule to issue Total Maximum Daily Loads (TMDL) plans for these impairments is from 5 to 10 years. Therefore, addressing contamination in these streams will not occur in the near future. A remedy has been selected for the AIW Superfund in the Southern Branch of the Elizabeth River, which includes dredging of the dioxin-contaminated sediments. This project is still in the design phase.

Wildlife

Apparently, only one study has examined the concentrations of dioxins and dibenzofurans in the Chesapeake Bay wildlife. Addled and post-term peregrine falcon eggs were found to contain dioxin (not detected to 97 parts per trillion wet weight, not adjusted for moisture loss) and dibenzofurans (not detected to 128 parts per trillion, not adjusted for moisture loss) (U.S. Fish and Wildlife Service et al. 2004). These data, in combination with coplanar PCB congener levels, were subsequently concentration corrected for moisture loss to estimate their fresh weight values (Clark et al. 2009). These concentration values were used to estimate dioxin toxic equivalents. Geometric means of the both peregrine egg samples from middle Chesapeake Bay (n=9) and upper Chesapeake Bay (n=2) were at or below the no-observed-adverse-effect-level of 0.23 ppb wet weight derived in the American kestrel (*Falco sparverius*) (US EPA 2003).

Conclusions

Existing data documenting the environmental occurrence of dioxins and furans in the Chesapeake Bay watershed are limited though sediment and fish tissue contamination near areas associated with historical contamination. Dioxin (as measured by 2,3,7,8 TCDD) has been found to be elevated in fish tissue resulting in impairment listing in the Elizabeth River and the C&D Canal. The sediment in the Elizabeth River and portions of the North Branch of the Potomac River are also identified as areas with quantifiable dioxin contamination. Identified exceedances of state and/or federal benchmarks indicate impairment of Bay resources.

2.3 Polynuclear Aromatic Hydrocarbons (PAHs)

Abstract

Polynuclear aromatic hydrocarbons (PAHs) are a class of hundreds of chemicals composed solely of hydrogen and carbon in structures containing two or more benzene rings. They are either petrogenic (derived from petroleum and coal) or pyrogenic (derived from the consumption of fossil fuels or wood products). PAHs are detected more often in sediments than in other media. Whereas PAHs bioaccumulate in invertebrate tissues, they are rapidly metabolized in fish and, therefore, are less frequently measured in fish-tissue monitoring programs than PCBs and metals. PAH detections in fish tissue did result in a listed impairment for 7 river miles in one jurisdiction (Virginia). Several impairments are determined by the jurisdictions on the basis of detections in water. Although the jurisdictions report detectable quantities of PAHs in most sediment samples, there were no identified impairments because concentrations did not exceed the States' benchmarks. In Baywide sediment monitoring, concentrations of PAHs in the tributaries were five times higher in the tributaries than in the mainstem and embayments. Other investigators report some of the highest known PAH concentrations in the Nation in the Anacostia River, Baltimore Harbor, and the Elizabeth River. In contaminated segments of the Elizabeth River, impairments are listed for the benthic community but not for individual compounds or classes; there, sediment remediation projects, with the aim of reducing contaminant concentrations (including PAHs) and associated biological effects, have been completed and are in progress. Modes of ecotoxicity to fish embryos, bottom-dwelling fish, and benthic organisms are well documented. Liver tumors in bottom-

dwelling fish from the Anacostia and Elizabeth Rivers have been statistically associated with exposure to PAH-contaminated sediments. PAH exposure is widespread through the Bay watershed, with localized areas having documented adverse biological effects, and large areas having little evidence of adverse effects. Research and monitoring should focus both on these “hot spots” and on areas that are at the threshold of having toxic effects.

Background

Polynuclear aromatic hydrocarbons (PAHs) are a class of hundreds of chemicals, composed solely of hydrogen and carbon in structures containing two or more benzene rings.

PAHs are hydrophobic and lipophilic, and, like other chemicals with the same properties, are commonly found associated with solid particles. PAHs in water will readily adsorb to sediments (U.S. Environmental Protection Agency (US EPA) 2008b, Van Metre et al. 2006). They may persist in the environment, and some have a half-life of up to 5 years (Greenfield et al. 2004, Oros et al. 2007). There are two types of PAHs: petrogenic PAHs are found naturally in petroleum and coal, whereas pyrogenic PAHs are formed during the burning of gasoline, coal tar, aluminum, fuel oil, and other fossil or modern biomasses. Petrogenic PAHs tend to have lower molecular weights (typically less than (<) 4 carbon rings), whereas pyrogenic PAHs tend to have higher molecular weights (greater than or equal to (\geq) 4 carbon rings). PAHs with higher molecular weights tend to have lower solubility (ATSDR 1995, NIH 2005). With their decreased solubility, the higher molecular weight compounds tend to be found in sediment, whereas the lighter compounds may be found dissolved in water. Studies indicate that the load of PAHs in

Bay tributaries may have a larger proportion of pyrogenic (e.g., combustion byproducts) compounds than the load in the mainstem (Hartwell and Hameedi 2007).

Human health effects of PAHs were summarized in the Agency for Toxic Substances and Disease Registry (ATSDR 1995) toxicological profile. Many PAHs are classified as probable human carcinogens by the US EPA and the International Agency for Research on Cancer (IARC).

Water

In Maryland, two segments of the Patuxent River are listed as impaired by PAHs resulting from an oil spill in 2000.¹ PAH contamination as a result of oil spills resulted in impairment of 0.33 estuarine acres.

In the District of Columbia, there are impairment listings for PAHs in more than 12 stream segments as part of the District's Organics Total Maximum Daily Load (TMDL) (District Department of the Environment (DDOE) 2010). A study titled "Sediment contamination studies of the Potomac and Anacostia Rivers around the District of Columbia" was completed by the Interstate Commission on the Potomac River Basin in 1992. The study included the tidal basin. Results of this study showed higher levels of PAHs at sampled outfalls and storm sewers to the tidal basin than in basin sediments. Results did not indicate a specific outfall as the source. The

¹ The April 7th, 2000, oil spill resulted from a break in a Pepco pipeline; two segments, Craney Creek and Buena Vista, have yet to meet the Phase I or Phase II cleanup status.

study indicated that the primary source of these hydrocarbons likely was much more diffused and probably related to vehicular traffic.

There are no reported impairments resulting from PAH contamination in the other states within the Bay watershed (spell out (DNREC) 2010, (West Virginia Department of Environmental Protection (WV DEP) 2010, Pennsylvania Department of Environmental Protection (PA DEP) 2010, New York State Department of Environmental Conservation (NYSDEC) 2010). In a U.S. Geological Survey (USGS) study of organic wastewater compounds in Pennsylvania streamwater samples in 2007-09, PAHs were occasionally detected in concentrations ranging from 4 to 42 parts per billion (ppb) (Reif et al. 2012).

Sediment

The Chesapeake Bay Program (CBP) funded two sediment triad studies, Pinkney et al. (2005) and Fulton et al. (2007), to focus on Bay tributaries identified by US EPA (1999) as having insufficient data to characterize the extent and magnitude of sediment contamination. Sediment triad studies use synoptically collected samples for sediment chemistry, benthic macroinvertebrate taxonomy, and sediment toxicity tests to evaluate habitat quality. Only the sediment PAH data from those studies are reported here.

Pinkney et al. (2005) collected samples from tidal sections of the Bohemia, Elk, Northeast, and Severn Rivers in Maryland. Total PAH concentrations ranged from 0.717 to 16.9 parts per million (ppm), substantially less than the Effects Range Median (ERM) of 44.792 ppm.

Fulton et al. (2007) collected samples from a total of 60 stations in five areas of the Bay for which data previously had been insufficient: the Chester River, Nanticoke River, Pocomoke River, Lower Mobjack Bay (Poquosin and Back Rivers), and South and Rhode Rivers. In general, total PAH concentrations were highest at stations in the upper section of the South River. The average total PAH concentration in the South River ranged from 2.723 ppm in the lower section to 4.704 ppm (just above the Effects Range Low (ERL) of 4.022 ppm) in the upper section. Total PAH levels were also high at some stations in the upper sections of the Nanticoke and Pocomoke Rivers. Average total PAH concentrations were Chester River, 784 ppb; Nanticoke River, 1,036 ppm; Pocomoke River, 890 ppb; and Rhode River, 777 ppb. The average total PAH concentrations in Lower Mobjack Bay ranged from 167 ppb in the Back River to 309 ppb in the Poquosin River.

Hartwell and Hameedi (2007) reported the results of the National Oceanic and Atmospheric Administration (NOAA) sediment triad study of the Chesapeake Bay conducted at 210 sites in 1998, 1999, and 2001. They found that total PAH concentrations varied from just over 4 ppb to more than 22 ppm. They stated that concentrations at only one mainstem and six tributary stations exceeded the ERL of 4.022 ppm, and no concentrations exceeded the ERM of 44.792 ppm. They stated that the highest tributary concentrations were in Baltimore Harbor, the James and Elizabeth Rivers, and the mouth of the Patuxent River.

The objective of the Hartwell and Hameedi (2007) study was to conduct a broad-scale survey of the Bay; therefore, it did not focus on highly impacted areas. Only two samples were collected

from Baltimore Harbor, none was collected from the Anacostia River, and nine were collected from the Elizabeth River. Sediment PAH data are discussed below.

Velinsky and Ashley (2001) analyzed surface sediment collected at 114 locations in the Anacostia River, including the Washington Channel, for contaminants in 2000. Total PAH concentrations averaged 22.6 ppm, just below the 22.8-ppm freshwater probable effect concentration (PEC) (MacDonald et al. 2000a). The maximum concentration was 90.4 milligrams per kilogram (mg/kg). Samples from 52 of the 114 locations had concentrations above the PEC. Therefore, based on a comparison of concentrations of total PAHs with the PEC, concentrations of total PAHs appear to be frequently detected at concentrations associated with adverse effects on the benthic community. However, in a sediment triad study of 20 locations with total PAHs ranging from 1.005 to 57.907 mg/kg, McGee et al. (2009) reported only sublethal toxicity at the station with the highest total PAH concentration and no evidence of sediment toxicity at the other 19 stations.

The most extensive survey of Baltimore Harbor sediment chemistry and toxicity was conducted in 1996 (Ashley and Baker 1999). Total PAH concentrations ranging from 90 to 46.2 ppm (which exceeds the ERM of 44.8 ppm) were reported for 80 sampling sites. Some of the highest concentrations were found in the Bear Creek area near the Sparrows Point industrial facility. More recently (2009), EA Engineering, Science and Technology, Inc. (2009, 2011) collected sediment, water, and tissue PAH concentration data in the Coke Point Offshore Area near Sparrows Point. Total sediment PAH concentrations in the 18 samples collected in the Coke Point Offshore Area ranged from 5.97 to 7,354 ppm, which greatly exceeds the Baltimore

Harbor average concentration of 3.27 ppm (EA Engineering, Science and Technology, Inc. 2009). EA Engineering, Science and Technology, Inc. (2011) concluded that ecological risks to aquatic organisms from exposure to PAHs existed and that concentrations exceeded those at the nearby Patapsco River Background Area.

Hartwell and Hameedi (2007) reported total PAH concentrations ranging from 1.678 to 24.617 ppm at the nine sites in the Elizabeth River sampled in 2001. The Elizabeth River Project (2008; a grass-roots citizens' organization dedicated to the cleanup of the Elizabeth River) reported that concentrations of PAHs in some areas of the Elizabeth River were as much as 1,000 times the average concentration in the Chesapeake Bay. Concentrations of individual and total PAHs at 16 locations in the Elizabeth River sampled in 2007 ranged from 0.736 to 383.2 ppm (Vogelbein et al. 2008). The highest concentration was found at a Superfund site. This site, operated from 1926 to 1992 as a wood-treating facility, released creosote, pentachlorophenol, metals, and dioxins into the Elizabeth River (<http://www.epa.gov/reg3hscd/npl/VAD990710410.htm#status>).

Tissue

Human health concerns

In Virginia, fish tissue impairments are listed for Pohick Creek (1 square estuary mile due to benzo[k]fluoranthene), 74 acres of lakes, and 7 river miles (Gold Mine Creek in the James River due to benzo(a)pyrene, benzo[b]fluoranthene, and/or benzo[k]fluoranthene) (Virginia Department of Environmental Quality (VA DEQ) and Virginia Department *of what?* (VA DCR) 2010). VA DEQ lists PAH tissue data for fish and invertebrates within the Chesapeake Bay

watershed for 2000, 2001, 2003, 2005, and 2008 on its Web site

(<http://www.deq.state.va.us/Programs/Water/WaterQualityInformationTMDLs/WaterQualityMonitoring/FishTissueMonitoring/FishTissueResults.aspx>). Virginia DEQ uses a screening value of 15 ppb (PEC) for PAHs based on the following seven carcinogenic compounds: benzo(a)pyrene (potency = 1.0), benzo(a)anthracene (0.145), benzo(b)fluoranthene (0.167), benzo(k)fluoranthene (0.020), chrysene (0.0044), dibenzo(a,h)anthracene (1.11), and indeno(1,2,3-c,d)pyrene (0.055). In all the sampling years, no concentration exceeded the PEC. The highest concentration in fish sampled in these years was measured in a composite sample of mummichogs collected from St. Julian Creek in the Elizabeth River watershed.

Fish tissue were analyzed for PAH concentrations as part of monitoring conducted to update fish tissue advisories (Pinkney et al. 2001, Pinkney 2009). In 2007, samples of the following species were collected from the Potomac and Anacostia Rivers: sunfish, largemouth bass, carp, blue catfish, channel catfish, and American eel (Pinkney 2009). PAH concentrations were compared with the US EPA (2000) screening value of 0.00547 ppm wet weight, which is based on the cancer slope factor for benzo(a)pyrene, the most potent PAH carcinogen. Concentrations were also evaluated with respect to Toxic Equivalent Factors (TEFs) by using the values of Nisbet and LaGoy (1992), which relate the toxicities of various PAHs to that of benzo(a)pyrene. For the TEF approach, the screening values developed by the Delaware Department of Natural Resources and Environmental Control (DNREC) and the Delaware Department of Health and Social Services (DHSS) were used (DNREC-DHSS 2005).

In general, the two- and three-ring PAHs such as naphthalene and anthracene were detected at

higher concentrations than the five- and six-ring compounds such as benzo(a)pyrene (Pinkney 2009). Concentrations of PAHs in all samples except one sunfish sample exceeded the screening value of 0.00547 ppm (table 1). The highest total PAH concentrations by far were detected in carp and ranged from 0.0706 ppm in the lower Potomac River sample to 0.384 ppm in the upper Potomac River sample. The median concentration (0.184 ppm) was about 34 times the screening level. Median total PAH concentrations in the other species ranged from 0.0079 ppm in the single smallmouth bass sample (from the lower Potomac River) to 0.0814 ppm in American eel. By using the TEF approach, however, no concentrations in any of the samples for any species exceeded the DNREC-DHSS (2005) screening value of 7 ppb. Median TEF concentrations ranged from 0.002 ppb in smallmouth bass to 0.129 ppb in carp. The highest TEF, 0.217 ppb, was measured in a carp sample from the upper Potomac River.

The District of Columbia's (D.C.) advisory is not linked to a specific chemical but states that the advisory is due to presence of "PCBs and other chemicals" (<http://green.dc.gov/service/fishing-district>). In view of the uncertainty regarding the risk from PAHs in fish tissue, it is reasonable to attribute most of the risk from fish consumption in D.C. waters to PCBs and chlorinated pesticides rather than to PAHs (on the basis of data in Pinkney (2009)).

Ecological concerns

Logan (2007) reviewed the ecotoxicology of PAHs on fish. Although PAHs can be detected in fish muscle tissue, these compounds tend to be metabolized by vertebrates and eliminated through the liver. Elimination results in detoxification but also the generation of genotoxic metabolites (French et al. 1996). Therefore the most common biomarkers used to monitor PAH

exposure in fish are bile PAH-like metabolites (Leadly et al. 1999) and DNA adducts (Reichert et al. 1998).

Chronic exposure of fish embryos to PAHs may result in death, deformities, or decreased growth. Narcosis is believed to be an important mechanism of toxicity and is attributable to low molecular weight volatile PAHs (French-McCay 2002). In addition, there is concern about sediment toxicity to bottom-dwelling organisms, which can be associated with phototoxicity (Barron 2007). A diminished benthic biomass could affect the survival, growth, and reproduction of their fish predators. Third, there are documented cases of liver tumors in bottom-dwelling fish that have been causally linked with exposure to PAH-contaminated sediments (Myers et al. 2003; Baumann and Harshbarger 1998). In the Chesapeake Bay watershed, the clearest linkages between liver tumors in fish and PAH exposure are in the Anacostia (Pinkney et al. 2009) and Elizabeth Rivers (Vogelbein and Unger 2006). Fourth, there are genetic changes associated with long-term exposure to PAHs. In a laboratory study with Elizabeth River sediments, Ownby et al. (2002) documented an increased tolerance to the acute toxic effects of creosote. The authors found that tolerance was heritable, indicating that it resulted from natural selection.

Pinkney et al. (2001b, 2004) used biomarkers of exposure and response, tumor data, and sediment data to evaluate the association between PAHs and liver tumors in brown bullheads. In both studies, the concentrations of biliary PAH-like metabolites were examined as an indicator of PAH exposure. Pinkney et al. (2004) also measured concentrations of polynuclear aromatic compound (PAC)-DNA adducts, which are bulky molecules attached to the DNA that serve as an indicator of response to PAHs. A specific pattern (diagonal radioactive zone (DRZ)) in the radiographic determination of these adducts is indicative of PAC adducts. Using logistic

regression, the authors reported a statistical association between liver tumors and biliary PAH-like metabolites. They also reported equally high concentrations of PAC-DNA adducts in 1- to 2-year-old fish, which already had a 10 to 17% liver tumor prevalence, as in the 3-year-old and older fish, which had a 50 to 68% tumor prevalence. Therefore, the younger age classes are likely to have a high prevalence as they reach age 3 or greater. The finding of high concentrations of PAC-DNA adducts with a strong DRZ signal, elevated bile PAH-like metabolites, and elevated sediment PAHs (15–31 ppm total PAHs within 1 kilometer of the fish collection sites) provide strong evidence linking the liver tumors with exposure to PAH-contaminated sediments.

Monitoring efforts have been conducted over the past 25 years to monitor the status of sediment contamination in the Elizabeth River by using mummichog liver pathology. Vogelbein et al. (1990) reported total PAH concentrations as high as 2,200 ppm in sediments from a creosote-contaminated site. They reported that 35.0% of mummichogs collected near this site exhibited hepatocellular neoplasms and 73.3% of them had foci of cellular alteration, which are hypothesized to be pre-neoplastic lesions. They also noted a variety of other pathologies, including elevated prevalences of exocrine pancreatic (Vogelbein and Fournie 1994; Fournie and Vogelbein 1994) and vascular neoplasms (oral commun., 2012). In contrast, mummichogs from two relatively uncontaminated study sites exhibited no proliferative liver lesions or other pathologies.

Vogelbein et al. (1990) demonstrated a strong positive association between sediment PAH concentrations derived from creosote spills and development of proliferative liver lesions. On the

basis of the study results, the Virginia DEQ and the Elizabeth River Project adopted the mummichog as a sentinel of chemical contamination. Since the late 1990s, this fish has been used in a long-term field monitoring program in the Elizabeth River (Elizabeth River Project 2008). Results of these studies indicate that liver histopathology in mummichogs is an effective bioindicator of sediment chemical contamination in the Elizabeth River (Vogelbein et al. 1997, 1999, 2008; Vogelbein and Zwerner 1999; Vogelbein and Unger 2003). Mummichog liver lesion prevalence tracked closely with a sediment PAH gradient. The greatest liver disease prevalence was found in fish from the most heavily contaminated sites and the lowest disease prevalence occurred in fish from the least contaminated sites. When coupled with sediment chemical analyses, use of mummichog liver pathology is an effective way to characterize environmental quality within the Elizabeth River. This approach was possible because mummichogs are abundant throughout the system and are found in large, self-sustaining populations in habitats ranging from relatively uncontaminated to heavily contaminated. Because mummichogs are largely nonmigratory, in the Elizabeth River they constitute stable, semi-isolated subpopulations that intermix minimally and are resident year-round.

Currently, mummichog liver histopathology and sediment PAH measurements are being used in association with ongoing sediment remediation efforts in the Elizabeth River. During 2009, a sediment remediation effort within the southern branch of the Elizabeth River at Money Point was begun. This site was the location of the Eppinger and Russell wood treatment facility that, for many years, used creosote to pressure-treat timbers such as railroad ties and telephone poles. Portions of the adjacent riverine and shoreline habitats have remained severely contaminated with PAHs of creosote origin. Remediation efforts included nearshore sediment dredging and

sand capping, and construction of a new onshore salt marsh. Concurrent with sediment remediation, a mummichog liver pathology and sediment PAH monitoring study was initiated at the site with the goal of applying these measurements to quantify environmental recovery and remediation success. Results of these studies indicated that the constructed inshore salt marsh has created a refuge for aquatic life from the sediment chemical contaminants found just offshore. Results also indicate that remediation efforts at the Money Point site reduced the bioavailability of sediment PAHs, which has already caused a decrease in liver lesion prevalence at the site (Vogelbein and Unger 2011).

Wildlife

Human health concerns

From 1986 to 1988, 35 muskrats (*Ondatra zibethicus*) were trapped on the Elizabeth and Nanesmond Rivers in Virginia. Twenty-two of 35 carcasses had detectable concentrations of PAHs (naphthalene, phenanthrene, anthracene, fluorine, pyrene, chrysene), and the muskrat with the greatest concentration (phenanthrene) contained 0.15 micrograms per gram ($\mu\text{g/g}$) dry weight (Halbrook et al. 1993). To the best of the authors' knowledge, PAH concentrations have not been reported in other wildlife species in the Chesapeake Bay.

2.4 Petroleum Hydrocarbons

Abstract

Petroleum hydrocarbons are a mixture of several hundred chemicals originating from crude oil. The chemical components of this group of compounds vary considerably in

chemical properties (i.e., some are characterized by relatively high vapor pressures, whereas others have low vapor pressures). The compounds vary with regard to solubility in water, with the lower molecular weight aromatic hydrocarbons exhibiting a relatively high degree of solubility (benzene, toluene, ethylbenzene, xylene (BTEX)). For petroleum compounds, states typically evaluate compliance with a narrative standard (i.e., no visible sheen) or with a numeric standard, such as that for oil and grease compounds (which include petroleum and non-petroleum-based oils). Data on reported spills and/or observable sheens are readily available, though concentration-based data are limited. Available data indicate that petroleum contamination within the Chesapeake Bay watershed is predominantly localized to areas with heavy boating or shipping activity. In selected areas of the watershed, the concentrations of oil and grease exceed State and/or Federal benchmarks, leading to impairment of Bay resources. Local reduction strategies are recommended for petroleum.

Background

Petroleum hydrocarbons are a mixture of several hundred chemicals originating from crude oil. The chemical components of this group of compounds vary considerably in chemical properties (i.e., some are characterized by relatively high vapor pressures, whereas others exhibit low vapor pressures). Compounds with high vapor pressures, such as those commonly found in gasoline, volatilize readily, whereas those with low vapor pressures tend to remain in liquid form. The individual compounds vary with regard to solubility in water, with the lower molecular weight aromatic hydrocarbons exhibiting a relatively high degree of

solubility (benzene, toluene, ethylbenzene, xylene (BTEX)). The individual petroleum compounds have widely ranging organic carbon-water partition coefficients, indicating that some compounds partition preferably to solids and sediment that may be present in the water column, whereas others remain in water. Those compounds remaining in the aqueous fraction are highly mobile and can be transported considerable distances from the point of entry into the environment. Of the BTEX compounds, benzene is classified as a mobile compound whereas toluene, ethylbenzene, and xylene are classified as intermediately mobile. Upon exposure of these compounds to the environment, microbial populations capable of utilizing petroleum hydrocarbons as a carbon source begin to biodegrade them, provided that nutrients are also readily available. Horel et al. (2012) determined that addition of inorganic nutrients to the sandy beaches in the northern Gulf of Mexico both stimulated and enhanced the biodegradation of these compounds following the Deepwater Horizon accident in 2010.

Petroleum hydrocarbon contamination can arise from a number of sources, given the common use of petroleum-derived products (e.g., gasoline, kerosene, asphalt). Combustion and accidental releases of these products into the environment are common and are associated with the use of any tool, vehicle, or equipment that requires their use (*spell out agency name* (DDOE) 2003). The most commonly used methods to assess risk to aquatic life and human health involve the measurement of surrogates such as the BTEX compounds or oil and grease.

Chesapeake Bay jurisdictions assessing their waters for aquatic life protection commonly refer to either a narrative standard (“no visible sheen”) or a numeric standard for oil and

grease promulgated by the U.S. Environmental Protection Agency (US EPA) in 1986. A water standard for total petroleum hydrocarbons has not been developed; however, this measurement of oil and grease includes plant-based oils as well as those derived from petroleum products. The measurement of oil and grease, like that of total petroleum hydrocarbons, captures a wide array of organic compounds, each with distinct physical, chemical, and toxicological properties (US EPA 1986).

The data for this chapter were derived primarily from the State integrated assessment reports, which document water-body compliance with State water-quality standards. Water bodies that fail to meet the water-quality standards applicable for the State's designated use are categorized as "impaired." Additionally, quantitative data were extracted from any completed Total Maximum Daily Load (TMDL) reports available for the Chesapeake Bay watershed.

Water

Only two jurisdictions cite oil and grease impairments within the Chesapeake Bay watershed: the District of Columbia (DC) and Pennsylvania (DDOE 2010, Pennsylvania Department of Environmental Protection (PA DEP 2010)). DC identifies approximately 1.7 miles as impaired; all but 0.6 miles have a completed TMDL. In Pennsylvania, approximately 5 river miles in the watershed are identified as impaired for this contaminant, with slightly more than half in the Conococheague River.

Water-column data generated during the preparation of the Anacostia/Hickey Run TMDL ranged from less than detection (less than 5 milligrams per liter (mg/L)) to 116 mg/L. Of the 37 samples collected during this effort, concentrations in 5 were at or above the water-quality standard of 10 mg/L. However, although the most recently approved integrated assessment report from the DC Department of Environmental Quality indicated the presence of a visible sheen in Hickey Run, it noted that the suspected sources are currently being addressed (DDOE 2003).

Petroleum is released to the environment through spills both small and large, including chronic releases from crankcase oil from vehicles and discharges from boat engines. The National Response Center (NRC) staffed by U.S. Coast Guard personnel is to be contacted upon discharge of a “harmful quantity” of oil, defined as “any quantity that violates state water quality standards, causes a film or sheen on the water’s surface, or leaves sludge or emulsion beneath the surface” (Oil Discharge Reporting Requirements, US EPA, Office of Emergency Management, EPA-550-F-06-006, December 2006, http://www.epa.gov/osweroe1/content/spcc/factsheet_spill_reporting_dec06.htm). Minor spills occur frequently within the Bay watershed and are reported to the NRC. For the 5-year period from 2007 to 2011, U.S. Fish and Wildlife Service personnel received 2,734 spill-response notifications from the NRC for the Chesapeake Bay region. Fortunately, most spills were very small and none involved wildlife. Though the majority of these spills could not be attributed to a known source, many were associated with boating or shipping activity. Virginia had the most reports. Within the State of Virginia, the largest number of oil and

hazardous chemical spill incidents are reported in the Elizabeth River area (S. Lingenfelser, U.S. Fish and Wildlife Service, oral communication).

Because of the wide variety of compounds present in the general category of “petroleums,” completing a risk assessment for the group as a whole is challenging. In 1976, US EPA promulgated a water-quality criterion for oil and grease to protect aquatic life from the harmful effects of petroleum and nonpetroleum oils. The potential effects identified were sublethal effects on cellular activity as well as physiological processes affecting feeding and reproduction. These sublethal effects resulting from chronic exposure could occur when general petroleum concentrations are as low as 10 ppb. In many cases, the most toxic and long-lived components of petroleum in the water column are PAHs. The toxicology of PAHs is complex and is discussed in more detail in another section of this report.

Both petroleum and non-petroleum oils can cause deleterious physical effects on aquatic organisms by coating gill surfaces; by increasing biochemical oxygen demand in the water body, potentially leading to fish kills; and by combining with surface debris to form tarballs that settle out of the water column and become lethal to benthic organisms. Though the physical effects of non-petroleum-based oils are the same as those of petroleum-based compounds, vegetable-based oils are non-toxic (US EPA 1976).

Sediment and Tissue

Sediment and tissue residue data for petroleums were not available. See the section of this report on PAHs for more information.

Wildlife

Since the early 1990's, two moderate-sized oil spills have resulted in wildlife kills in the Chesapeake Bay. On March 28, 1993, a 36-inch high-pressure pipeline running from the Gulf of Mexico to Maine ruptured and released more than 400,000 gallons of heating oil into Sugarland Run Creek and the Potomac River, affecting a 9-mile stretch. Twenty-three oiled birds, including wood ducks (*Aix sponsa*), Canada geese (*Branta canadensis*), mallards (*Anas platyrhynchos*), and a kingfisher (*Megasceryle alcyon*), were observed, 18 of which succumbed despite rehabilitation efforts (Research Planning, Inc. 1993). Undoubtedly, more birds were affected by this spill. Another oil spill on April 7, 2000, involved a pipeline rupture that released 126,000 gallons of fuel oil at the Potomac Electric Power Company Chalk Point Facility near Aquasco, Maryland. The spill spread to Swanson Creek, a tributary of the Patuxent River; 55 dead birds (principally waterfowl, but also osprey, herons, gulls, and terns) were found, and 109 birds were collected for rehabilitation (12 of these died) (Cardona et al. 2001). This spill occurred near osprey nests and, although 10 adult ospreys were observed to be oiled, there was no evidence of effects on reproductive success (Michel et al. 2001). In addition, some visible evidence of oiling from this spill was found on 10 snapping turtles (*Chelydra serpentina*), 7 diamondback terrapins (*Malaclemys terrapin*), 1 Eastern box turtle (*Terrapene carolina*), 18 common mud turtles (*Kinosternon subrubrum*), 2 Eastern painted turtles (*Chrysemys picta picta*), 1 garter snake (*Thamnophis sirtalis*), and 8 Northern water snakes (*Nerodia sipedon*) (Tri-state Bird Rescue and Research 2000). The National Oceanic and Atmospheric Association (2009) summarized the injury to the aquatic

receptors (separate from wildlife) as follows: the oiling of 76 acres of wetlands and 10 acres of beaches; the deaths of 122 diamondback terrapins and an estimated 10% loss in hatchlings for the year 2000; and the biomass loss of 2,464 kilograms (kg) of fish and shellfish and 2,256 kg in benthic communities.

Conclusions

Existing data on the occurrence of petroleum spills or observable sheens is readily available through the National Response Center (NRC). However, concentration-based data is much more limited and typically present in the form of the surrogate parameter “oil and grease”. Review of the NRC data indicates that the extent of petroleum contamination within the Chesapeake Bay watershed is predominantly localized to areas with heavy boating or shipping activity. In select areas of the watershed, the concentrations of oil and grease exceed state and/or federal benchmarks leading to impairment of Bay resources.

2.5 Pesticides

Abstract

Unlike most of the other toxic contaminant groups (other than polynuclear aromatic hydrocarbons) discussed in this report, pesticides are intentionally applied to land and water surfaces throughout the Chesapeake Bay watershed. In addition, pesticides are specifically designed to kill or otherwise harm targeted organisms. Recently, a consortium of stakeholders from government, academia, and industry published a study (Maryland Pesticide Network, 2009) recommending that reduction of current levels of

pesticides be a priority for agencies working to protect the Bay. Occurrence data on pesticides as a group, in the Bay watershed and elsewhere, are available and therefore do not limit general interpretations about their extent. Because pesticides represent such a diverse group of herbicides, insecticides, and fungicides (among other compounds), however, relevant environmental and toxicological data for any one pesticide or group of pesticides are variable. In addition, recent laboratory and field research indicates that pesticides and related mixtures can cause adverse sublethal effects on receptor organisms, including microbes, insects, plants, and animals, at environmentally relevant concentrations. The severity of pesticide occurrence in terms of conventional benchmarking approaches has been documented in individual integrated state assessment reports by the number of river miles that are considered to be impaired; however, the emerging literature regarding concerns about the limitations of conventional benchmarking approaches in assessing the sublethal and other effects of pesticides, their degradates, and their mixtures indicates that additional research is needed to accurately assess the severity of pesticide occurrence in the Chesapeake Bay watershed.

Background

Generally chemical or biological agents, pesticides are used for a range of governmental, residential, industrial, and agricultural applications. This report summarizes chemical pesticides only. The U.S. Environmental Protection Agency (US EPA) defines the term “pesticide” to include many kinds of ingredients in products, such as insect repellants, weed killers, disinfectants, and swimming pool chemicals, which are designed to prevent, destroy, repel, or

reduce pests (<http://www.epa.gov/opp00001/factsheets/registration.htm>). Some pesticides target only one or a few species, whereas others are broad-spectrum pesticides and target all similar species. Pesticides can be classified or grouped by (1) similarities in the target organism(s) (e.g., herbicide, insecticide, fungicide, etc.); (2) similarities in the molecular structure (e.g., organophosphates, organochlorines, carbamates, etc.); or (3) the mode of action (e.g., acetylcholinesterase inhibition, inhibition of sterol biosynthesis, growth regulation, etc.). Application rates and procedures vary greatly depending on the targeted organism(s), mode of action, chemistry, and other factors. For example, some pesticides are applied before plants emerge, whereas others are applied after they emerge. Some are applied directly to plant or animal tissue, whereas others are applied to the soil or other physical components of habitat (e.g., open-water surfaces). The mode of delivery includes through irrigation waters, aerial spraying, and tractor applied. The application rates and procedures and the associated environmental pathways dictate to a large extent how and where the active ingredients will be mobilized, deposited, and/or transformed. These pathways then determine the extent to which receptors (included target and nontarget organisms) are exposed. In order to facilitate application and uptake, various adjuvants are commonly used in pesticide mixtures. Consideration of pesticide adjuvants, although they are potentially important toxic chemicals, is beyond the scope of this chapter, which focuses on active pesticide ingredients and their degradation products.

Pesticides are used on approximately 900,000 farms and in 70 million households in the United States (citation needed – ncsu factsheet). Agricultural uses account for about 75% of all pesticides, but at least one pesticide is stored in 85% of U.S. households, and one to five pesticides are stored in 63% (citation ncsu factsheet).

<http://ipm.ncsu.edu/safety/factsheets/pestuse.pdf>.) Therefore, virtually all land uses in the Chesapeake Bay watershed are potential sources of pesticides, and many provide direct pathways to the environment. Keily et al. (2004) estimate a per capita home, garden, and personal-care pesticide loading of 0.42 pounds per year in the Chesapeake Bay watershed, which results in a loading to the watershed of about 6.5 million pounds annually, not including agricultural uses. Hively et al. (2011) showed that the fate of herbicides (atrazine and metolachlor) is related to landscape features and characteristics in 15 subwatersheds in the Choptank River system. Although agricultural and residential uses account for much of the pesticide use in the watershed, other land activities associated with golf courses, control of invasive or non-native species, and weed control on rights-of-way are also potential sources of these contaminants.

In 2009, a study of pesticides in the Chesapeake Bay watershed was published with input from a range of stakeholders and technical experts, including representatives of Federal and State agencies, academia, and industry (MPN 2009). The report noted that, although more data are needed, pesticides have been shown to have potential adverse effects on the watershed. Basing their recommendations on previously published work, the authors of the report concluded that “reducing current levels of chemical pesticides flowing into the Bay should be a priority for agencies working to protect the Bay.”

Many previous studies have prioritized pesticides on the basis of combinations of occurrence (extent) and toxicity (severity) as potential environmental contaminants. For example, the Chesapeake Bay Program Toxics Subcommittee (2006) recently assessed more than 1,000 chemicals, including a range of pesticides previously documented to occur in the Bay, to occur in

its tidal tributaries, or to have been used in the watershed with potential to reach the Bay. The report further prioritized 35 contaminants, including 10 organochlorine and 2 organophosphate pesticides, for additional study on the basis of the following criteria: (1) the chemical appeared on lists of priority chemicals submitted by the Chesapeake Bay Program Toxics Subcommittee, (2) loading estimates for the chemical were available in the 1999 Chesapeake Bay Toxics Loading and Release Inventory, and (3) detections of the chemical were reported in the 1999 Toxics Characterization Report. These 12 compounds represent the results of only one attempt to prioritize pesticides in the watershed, with the acknowledgment that other prioritization schemes may yield different results. This report does not rely on the prioritization study in its recommendations; however, the prioritization is another indication that multiple pesticides warrant attention as potential environmental contaminants in Chesapeake Bay watershed.

There are many point and nonpoint sources of the pesticides that enter the Chesapeake Bay watershed every day. As previously mentioned, these chemicals are deliberately applied to the land and water surfaces. In addition to intentional applications, spills and other sources and indirect pathways to the environment, such as wastewater effluents (solid and/or liquid), landfill leachates, spray drift, runoff to surface water, and leaching to groundwater, must be considered. These sources are all closely related to the usage and use patterns of pesticides. A multitude of pesticides, each with its own “footprint” in terms of geographic extent and location, is used in the Chesapeake Bay watershed. Pesticide usage changes over time as new products are registered, old ones are phased out, and pest-control needs and strategies evolve. There are many reasons for phasing out or modifying older pesticides in favor of new ones: loss of effectiveness due to increased resistance in target organisms; technological advances that enable the same level of

effectiveness to be achieved with smaller quantities of pesticides (e.g., increases in potency of active ingredients); and changes associated with re-registration processes. For example, Hartwell (2011) notes that the total mass of pesticides being applied to the Chesapeake Bay watershed declined during the period 1985 to 2004; however, because the potency of these chemicals increased during the same period, the “toxic units” (a measure of the toxicity of the active ingredients to a range of animal and plant species) remained approximately static or increased depending on the bioassay test organism(s) used. In addition, recent agricultural uses of pesticides have begun to shift toward the use of transgenic crops. Two of the most common examples include those that are resistant to targeted pesticides (e.g., “roundup-ready corn”) and/or are capable of creating pesticides through otherwise normal metabolic activities (e.g., “Bt corn”). In 2009, more than 85% of U.S. corn crops were genetically modified to repel pests and/or resist herbicide exposure, with Bt corn accounting for about 63% (<http://www.sciencedaily.com/releases/2010/09/100927155324.htm>). As a result of transgenic crops, pesticide usage and geographic patterns change. For example, glyphosate herbicide usage increases where roundup-ready corn is grown, whereas usage of other herbicides (e.g., atrazine) decreases. Toxins produced in situ by transgenic crops such as Bt corn are released to the environment in unquantified amounts, but recent studies have documented their occurrence (<http://www.pnas.org/content/early/2010/09/22/1006925107.abstract>).

The fate and transport properties of pesticide formulations in the environment vary with active ingredient, adjuvant characteristics and purposes, application procedures, seasonality, and other factors. Generally, pesticides are biologically active agents capable of persisting long enough to

be effective in environmental applications. Therefore, the half-life of all currently registered active pesticide ingredients ranges from hours to days to weeks to months depending on the nature of the molecule. Some pesticides are water soluble and can be expected to be mobile in aquatic environments, whereas others are hydrophobic and are likely to sorb to solids. Foster et al. (2000) documented that measured concentrations of organophosphorus pesticides in tributaries to the Chesapeake Bay varied mainly in response to the timing of their application, whereas the particle-reactive organochlorine insecticides were more directly correlated with stream discharge. Finally, although not a focus of the summaries in this report, atmospheric transport of pesticides has been shown by a number of studies across the globe to be an important ecological pathway for exposure (Majewski and Capel, 1996). Kuang et al. (2003) detected metolachlor, atrazine, simazine, endosulfan, and chlorpyrifos in air and rain, with maximum concentrations during the time when crops were planted; they suggested that an atmospheric source from outside the watershed was likely contributing to some of the high values. Summarizing the environmental behavior of all pesticides is beyond the scope of this report; however, information on half-life/persistence and the potential for the active ingredient to enter and move in aquatic environments are part of the registration process considerations required by US EPA (citation). Many documented cases show long-term persistence of pesticides and/or their degradates (e.g., DDT/DDE; citation needed) as well as mobility in the environment (e.g., atrazine; citation needed). In addition, the environmental behaviors exhibited by the environmental transformation products of pesticides can be very different from those of the parent active ingredient.

Pesticide occurrence in ambient water resources, as residues on produce and other food products, and in our drinking waters has been documented by a number of nationally relevant studies. The USGS National Water-Quality Assessment (NAWQA) program has monitored and assessed the extent of pesticide occurrence in the Nation's water resources since the early 1990's. These assessments have targeted a range of insecticides, herbicides, and some fungicides, and have shown close relations between pesticide applications and occurrence in nearby water resources throughout a range of hydrogeologic environments (Gilliom et al. 2007). Other factors such as the physiochemical characteristics of the pesticide molecules, the nature and properties of associated soils, and other hydrogeologic controls have been shown to be related to pesticide occurrence in water resources. Gilliom et al. (2007) note that the major findings of the NAWQA program with respect to pesticides include (1) pesticides are frequently present in streams and groundwater; (2) pesticides are seldom present at concentrations that exceed human-health benchmarks; however, current benchmarks have been, and will be continuously, updated and revised as understandings of pesticide modes of actions in nontarget organisms, mixture effects, and other nonconventional toxicological effects are advanced; and (3) pesticides occur in many streams at concentrations that may have effects on aquatic life or fish-eating wildlife. The U.S. Department of Agriculture (USDA) publishes annual summaries of the Pesticide Data Program that include occurrence data for pesticide residues on a range of food commodities and drinking-water sources in several states across the Nation, including some samples collected in Maryland, New York, Pennsylvania, and Virginia (citation needed: USDA, 2011. Pesticide Data Program – Annual Summary Calendar Year 2009). Although individual State data were not summarized for this report, nationally representative findings include (1) 17% of food samples analyzed contained residue of only one pesticide; (2) 40% of food samples analyzed contained more than

one pesticide; (3) 29 different pesticide residues (including metabolites) representing 19 parent compound pesticides were detected in the 278 groundwater samples collected from farm wells, schools, and domestic wells; (4) 53 different pesticide residues (including metabolites) representing 42 pesticides were detected in the 306 finished municipal drinking-water samples analyzed; and (5) 49 different pesticide residues (including metabolites) representing 38 pesticides were detected in 306 samples of untreated (at intake locations) municipal drinking water.

As mentioned above, pesticides are a unique group of toxic contaminants because they are applied directly to land surfaces in a variety of land-use settings across the U.S. and because they are designed to kill or harm living organisms at prescribed application rates and procedures. As a result of advances in modern detection technologies such as mass spectroscopy and gas or liquid chromatography and the range in their hydrophilic and lipophilic properties, pesticide residues (including parent and degradate compounds) are likely to be found in detectable concentrations in various environmental matrices including water, sediment, air, and fish tissue. Because the US EPA pesticide registration process requires testing and data, many sources of information about individual pesticide toxicities and potential behavior in the environment are available (cite EPA), particularly for the high levels likely to be found as a result of pesticide applications in the field. This and other information sources (e.g., the Safe Drinking Water Act) have produced benchmarks to interpret environmental pesticide data. For example, the US EPA Office of Pesticides Program Aquatic Life benchmark for atrazine is 65 micrograms per liter ($\mu\text{g/L}$); however, Tillett et al. (2010) showed that chronic exposures to concentrations as low as $0.5 \mu\text{g/L}$ will cause fathead minnows to spawn less frequently and to produce fewer eggs than controls.

Recently, the usefulness of conventional “benchmarks,” which have been, and continue to be, developed on a contaminant-by-contaminant basis for a limited range of toxicological endpoints, has been questioned (Feingold et al. 2010).

Water

Many sources of data and information on pesticide extent in waters of the United States at local, regional, and national levels are available. Among the federally funded national programs that address pesticide occurrence in the environment, two examples, the U.S. Geological Survey’s NAWQA Program and the USDA’s Pesticide Data Program, are summarized here. Examples from local and regional studies, including the state integrated assessments as well as those from other governmental agencies and academia, are also included. Other examples of important data on pesticides in water, such as the complete list of individual academic studies and municipal drinking-water compliance monitoring, were not assembled for this report.

Water samples collected in Chesapeake Bay tidal waters during spring 2000 and late summer 2004 were analyzed for a range of pesticides (McConnell et al. 2007). Of all pesticide groups analyzed for, agricultural herbicides were detected most frequently. Among the herbicides analyzed for, the parent compounds atrazine, simazine, and metolachlor were detected at maximum concentrations of 1.29, 0.49, and 0.61 $\mu\text{g/L}$, respectively. Degradates of these parent compounds were also frequently detected, with the metolachlor degradation product, metolachlor ethane sulfonic acid (MESA), found in greater concentrations (2.9 $\mu\text{g/L}$) than the parent compound in almost all of the tidal regions assessed. Atrazine was detected in 100% of the

samples collected in 2004. McConnell et al. (2007) noted that herbicides and associated products are present within both agricultural and nonagricultural tidal areas of the Chesapeake Bay throughout the year, even though they are used primarily in the spring. Hall et al. (1999) sampled the major mainstem tributaries to the Chesapeake Bay, smaller tributaries, and representative small agricultural streams, and found much higher concentrations of atrazine (maximum 98 µg/L) and metolachlor (maximum 68 µg/L). Citing the observation that the concentration of atrazine exceeded the No Observed Effects Concentration (NOEC) of 20 µg/L during only one event, the authors concluded that the ecological risk from both atrazine and metolachlor was low.

Recognizing the need to develop estuarine criteria for low levels of pesticides in the Chesapeake Bay, Hall et al. (1997) studied the chronic toxicity of atrazine to Sago pondweed (*Potamogeton pectinatus*) under varying conditions of salinity. This study showed that toxicity as well as bioavailability was influenced by salinity and highlights the typically subtle and complicating factors involved in determining conventional “benchmarks.” Since then, many other studies have concluded that conventional benchmarking approaches to decision making are inadequate for a variety of reasons. For example, Fatima et al. (2007) exposed goldfish to environmentally relevant mixtures of herbicides (atrazine, simazine, diuron, and isoproturon) and observed biomarkers indicative of immune suppression. They concluded that these common environmental exposures cause immune suppression in goldfish, thereby representing an endpoint and exposure scenario that are not quantified in conventional benchmarking studies.

Hall et al. (2009) studied the potential effects of irgarol (an algicide used as an anti-fouling agent in paints for boat hulls) and its major metabolite on phytoplankton in the Port Annapolis marina and Severn River system, Maryland. These sites were chosen to represent a range in use of irgarol including a high-use area (marina) and a background site (Severn River near its confluence with the Chesapeake Bay). In the study, a probabilistic approach was used to determine ecological risk by comparing exposure data with toxicity endpoints (NOEC). Field data could not confirm the microcosm NOEC in the high-exposure area (marina).

Whitall et al. (2010) analyzed water samples collected from seven sites in the Choptank River estuary, *state*, during base flow and documented the seasonal signal in herbicide (atrazine, simazine, and metolachlor) concentrations known to dominate pesticide occurrence in streams throughout the Nation. Observed concentrations of individual herbicides did not approach established levels of concern (10--20 µg/L) for aquatic organisms (US EPA 2006b) and were below the US EPA drinking-water standard for atrazine (3 µg/L). Total triazine concentrations (atrazine, simazine, CIAT, and CEAT), however, exceeded 3 µg/L in eight samples, highlighting the importance of assessing the effects of mixtures. Additionally, the degradation products (CIAT, CEAT, MESA, and MOA) were associated with groundwater pathways and were frequently found in higher concentrations than the parent compounds (Whitall et al. 2010). Hladik et al. (2006) also documented that degradates of triazine herbicides were found in higher concentrations than parent products in the upper Chesapeake Bay, and noted the importance of assessing degradate compounds in ecological studies.

As noted above, there are many local environmental studies that assessed pesticide occurrence in the Chesapeake Bay watershed. Ferrari et al. (1997) analyzed 463 surface-water samples from sites in the Mid-Atlantic area collected as part of the USGS NAWQA program and showed that most of the pesticides analyzed for were detected at least once (reporting levels were generally below 1 µg/L). Analytical procedures at that time did not focus on degradate compounds; therefore, the pesticide occurrence data in Ferrari et al. (1997) reflect a combination of the analytical capabilities at that time, the pesticides that were used before and during the study period, and the hydrogeologic and other factors controlling pesticide fate and transport at that time. Since the publication of Ferrari et al. (1997), passive-sampler technologies have been used to detect a broader range of pesticides in the Potomac River Basin (Alvarez et al. 2009). In general, pesticide occurrence data from several more recent studies including Ator and Denver (2006), Chambers and Leiker (2006), McConnell et al. (2007), Battaglin et al. (200x), Loper et al. (2009), and Hively et al. (2011) reflect changes in pesticide trends (e.g., increases in glyphosate use) as well as changes in sampling and analytical methods to include a wider range of degradate compounds.

Kingsbury et al. (2008) collected raw and treated drinking water from nine community water systems ranging in size from a system serving about 3,000 people to one that serves about 2 million people. The study included one site on the Potomac River where simazine, atrazine, DEA, and metolachlor were consistently detected throughout the year (i.e., 100% detection frequency). Other pesticides frequently detected include 2,4-D (58%), 2-hydroxyatrazine (92%), acetochlor (17%), benomyl (8%), carbaryl (33%), diazinon (33%), deisopropylatrazine

(8%), 3,4-dichloroaniline (17%), diuron (25%), fipronil (17%), prometon (92%), MCPA (33%), and tryclopypyr (17%).

In Virginia, along the Potomac and Shenandoah Rivers, 7 river miles are impaired as a result of the insecticides heptachlor epoxide (five impaired segments) and chlordane in the James River Basin, impairments are listed from chlordane (3 impaired miles) and from other insecticides (aldrin and DDE/DDT), totaling 9 impaired river miles; mirex, also an insecticide, impairs 5 river miles in the James River and 49 miles in the Rappahannock River (VA DEQ and DCR, 2010). Two river segments in Maryland, the Back River and the Baltimore Harbor, and one impoundment, Lake Roland, are listed as impaired waters for chlordane. One location in the northwest portion of the Anacostia River in Maryland is listed as impaired by heptachlor epoxide contamination (MDE and MD DNR, 2010). In the District of Columbia in many branches of the Potomac and Anacostia Rivers chlordane, DDE, DDD, DDT, dieldrin, and heptachlor epoxide all contribute to impairments (DDOE, 2010). Pesticides are also responsible for the impairment of 17 river miles in the Susquehanna River Basin of Pennsylvania (PA DEP, 2010). New York and West Virginia do not report any pesticide contamination entering the Chesapeake Bay from their portions of the watershed (New York State Department of Environmental Conservation (NYSDEC) 2010, West Virginia Department of Environmental Protection (WV DEP) 2010). (Note that the impairments cited in this paragraph are related to legacy pesticides that are no longer in use.)

Sediment

The National Oceanic and Atmospheric Association (NOAA) Contaminated Sediment report identifies organophosphate-type pesticides as having the highest yield of all organic materials present in tidal sediment, with the largest concentration spikes reported for the Choptank and Nanticoke River watersheds in Maryland during spring runoff. Elevated levels of insecticides including chlordanes, heptachlors, nonachlors, aldrin, dieldrin, endrin, and endosulfan were found in sediments in the Elizabeth River in Virginia, and trace amounts of insecticides were found throughout the other tidal portions of the Bay. Hexachlorocyclohexane (HCH) concentrations were elevated in the Patuxent, Potomac, and Eastern Shore tributaries of Maryland. DDT was found throughout the Bay but was concentrated mainly in the upper Bay, and exceeded the ERM only in the Elizabeth River. Other pesticides detected were mirex, chlorpyrifos, butyltins, tributyltin (TBT), and chlorinated benzenes (Hartwell and Hameedi 2007).

Fish

Human health concerns

Although human-health perspectives and research on pesticides are focused on occupational, and household, exposures due to application and handling activities, additional perspective is being addressed by the Centers for Disease Control (CDC) as part of its biomonitoring program. The CDC has documented the presence of a range of pesticides and pesticide metabolites in human blood and urine (cite CDC). In addition, the detections of some pesticides cited above in sources

of drinking water indicate the likelihood of at least one other potential exposure route that is unrelated to the workplace or application of pesticides. The presence of these contaminants in human tissue and drinking water does not necessarily indicate adverse health effects; however, in referring to low-level environmental exposures of pesticide residues from food sources (another exposure pathway for humans and animals), the National Institutes of Health notes that “scientists do not yet have a clear understanding of the health effects of these pesticide residues” (<http://www.niehs.nih.gov/health/topics/agents/pesticides/index.cfm>).

Ecological concerns

Surveys in DC have shown elevated levels of chlordane in the tissue of certain fish species across many portions of the Anacostia and Potomac Rivers. Chlordane is included with other pesticides in the DC area mentioned previously (DDOE 2010). Blazer et al. (2010) analyzed organ-specific fish tissue from fish in the Potomac River watershed; the following pesticides were measured in at least one tissue analyzed: chlorpyrifos, the phenyl pyrazole pesticides (fipronil, fenprothion, and desulfenylfipronil), hexachlorobenzene, pentachloronitrobenzene, pentachloroanisole, oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, dieldrin, and DDX (DDE, DDD, DDT). One or more organochlorine pesticides were found in all tissues of both sexes. In addition, the ovary from a female smallmouth bass collected in the South Branch Potomac River contained 30.5 micrograms per kilogram ($\mu\text{g/kg}$) total organochlorine pesticides, with 13.6 $\mu\text{g/kg}$ DDX; skin from the same individual contained 6.4 $\mu\text{g/kg}$ total organochlorine, with 2.6 $\mu\text{g/kg}$ from DDX. Pesticide compounds detected in individual organ tissue varied in presence and magnitude; muscle tissue generally contained the lowest concentrations.

Wildlife

Rohr et al. (2008) exposed tadpoles to environmentally relevant concentrations of four individual pesticides (atrazine, glyphosate, carbaryl, and malathion) and concluded that these exposures will elevate nematode infections in these amphibians. They also concluded that adequate assessments of lethal as well as sublethal effects on parasite as well as host organisms are critical to understanding parasite transmission and virulence and the associated potential effects on environmental health. An increasing number of additional studies have shown sublethal and other effects on receptor organisms exposed to low levels of pesticides. For example, Hayes et al. (2003) showed that atrazine can induce hermaphroditism in leopard frogs (*Rana pipiens*), and Blakely et al. (1999) showed immunotoxicological effects of pesticides to a variety of organisms. In more recent work within the Chesapeake Bay watershed, Kolpin et al. (oral commun., 2012) have shown statistically significant correlations between atrazine concentrations in the water column of streams in the Potomac River Basin and intersex in smallmouth bass.

Conclusions

Because of the diverse uses, modes of action, and chemical characteristics of pesticides, the available data on environmental occurrence and related toxicology range from minimal to extensive. In addition, some pesticides are included in current monitoring programs, whereas many others are not. On the basis of data collected within the Chesapeake Bay watershed, herbicides as a group are known or are suspected to be widely extensive. The likelihood that

current and future land uses will include regular and widespread applications of herbicides largely in agricultural areas, but also in association with any land use where lawns and other plantings are maintained, also increases their potential to be widely extensive in the environment. Specifically, atrazine and its degradates are widely distributed throughout the agricultural parts of the watershed, and recent studies have shown the potential for atrazine to cause adverse ecological effects at environmentally relevant concentrations. Insecticides and fungicides, though potentially important environmental contaminants as a result of their potential effects on nontargeted insects, fungi, and other organisms (e.g., broad-spectrum insecticides, systemic fungicides), have not been monitored as broadly or as consistently as herbicides; however, some of the more recent studies indicate the potential for a range of effects related to insecticides and fungicides at environmentally relevant concentrations. Therefore the occurrence of herbicides, and specifically atrazine, simazine, metolachlor, and their degradates, is identified as extensive and severe Bay-wide. Insecticides such as aldrin, chlordane, dieldren, DDE/DDT, heptachlor epoxide, mirex, and their degradates occur in localized areas at levels severe enough to indicate that adverse effects are likely. Additional targeted monitoring is recommended for pesticides generally, including some current-use and some legacy pesticides. Finally, additional research on the potential sublethal effects of low concentrations of pesticides (and degradates) and their mixtures (including adjuvants, etc.) in the environment is needed for poorly understood pesticides.

2.6 Pharmaceuticals

Abstract

Pharmaceuticals are chemicals used in the diagnosis, mitigation, treatment, cure, and prevention of disease in humans and other animals. Occurrence and toxicological data for pharmaceuticals are limited in the Chesapeake Bay watershed are limited; however, there is substantial evidence of the widespread occurrence of some pharmaceutical compounds in the environment due to the abundant human (e.g., municipal wastewater-treatment plant discharges) and animal waste (e.g., livestock feeding and related activities) sources in the watershed. The few occurrence studies in the watershed as well as many studies elsewhere in the United States and across the globe have documented pharmaceuticals as environmental contaminants. In addition, although effects on receptor organisms are still poorly understood, several studies have shown biological uptake in a wide variety of exposed aquatic and other species, as well as a range of sublethal effects at environmentally relevant concentrations. Although data are insufficient to warrant specific reduction action recommendations (other than those already in place, such as drug buy-back programs, etc.), there is evidence that these compounds are of concern as toxic contaminants in the Bay watershed. Targeted monitoring and support for effects research are need for pharmaceuticals and their mixtures.

Background

Pharmaceutical compounds have been considered to be potential environmental contaminants since the 1960's (Richardson and Bowron, 1985) and their occurrence in rivers of the United States has been documented for many years (Kolpin et al., 2002). Although broader definitions of pharmaceuticals include herbal preparations, nutraceuticals, cosmeceuticals, and other remedies, this section focuses on the conventional prescription and nonprescription pharmaceuticals as noted in the Food, Drug and Cosmetic Act (FD&C Act, sec. 201(g)(1)).

Excipients, which are additives in pharmaceuticals that give a drug its form, control its release into the bloodstream, facilitate its transport to targeted sites in the body, preserve its shelf life, and enhance its taste, are beyond the scope of this report but could be important compounds for future research on environmental contaminants generally. This report focuses only on the active pharmaceutical ingredients. In addition, biological drugs or so-called "biopharmaceuticals" such as vaccines that are typically administered by injection in the doctor's office are not considered here. The chemically derived prescription and nonprescription drugs covered in this report range from popular over-the-counter analgesics to rigorously controlled chemotherapy or other drugs. The World Health Organization supports a chemical classification system for pharmaceuticals based on the organ or system on which they act. This classification system includes alimentary/digestive tract and metabolism, blood and blood-forming organs, cardiovascular system, dermatologicals, genitourinary system/sex hormones, systemic hormonal preparations, antiinfectives, antineoplastic and immunomodulating agents, musculoskeletal, nervous system, antiparasitic, respiratory, sensory organs, and various others. The Centers for Disease Control (CDC) showed that human use of pharmaceuticals has increased since 2000.

Prescription pharmaceuticals are also commonly used to treat domestic pets as well as livestock. Livestock usages include growth promotion, estrus modulation, and various purposes that are not common goals of human pharmaceutical usage. Many human-use pharmaceuticals are also used as veterinary pharmaceuticals, though many veterinary pharmaceuticals are restricted to animal use only. In addition, many over-the-counter pharmaceuticals are used for domestic pets and livestock. Veterinary drugs are administered for a variety of reasons, including nervous system (anesthetic), digestive tract and metabolism (antacid), antiparasitic (anthelmintic, antibacterial, antimicrobial, antiseptic, astringent, anti-infective), respiratory (antihistamine), steroidal and nonsteroidal anti-inflammatory, respiratory (bronchodilator), genitourinary (diuretic, emetic), estrus synchronization (sex hormones), nervous system (sedative, tranquilizer), other (growth promotant) purposes.

According to 1995 Toxics Release Inventory (TRI) data, facilities released (discharged to the air, water, or land without treatment) and transferred (shipped off-site) a total of 177 million pounds of contaminants, made up of 104 different chemicals (EPA/310-R-97-005). This amount represents about 3 percent of the 5.7 billion pounds of TRI chemicals released and transferred by all manufacturers in that year. In comparison, the chemical industry as a whole produced 1.7 billion pounds that year, accounting for about 30 percent of all releases and transfers. Of the pharmaceutical industry's TRI releases, 57% go to the atmosphere, 25% go to underground injection, 17% go to surface waters, and 1% go to the land. The reported chemical releases from pharmaceutical manufacturing facilities are not commonly active pharmaceutical ingredients (APIs), but rather volatile organic compounds (VOCs) (e.g., solvents) and other chemicals used in the manufacturing process itself. It is not possible at this time to summarize the API releases.

US EPA defines high-production-volume chemicals as those produced or imported at quantities exceeding 1 million pounds per year; therefore, some pharmaceuticals and classes of pharmaceuticals are considered high-production-volume chemicals whereas many are not. For this reason, production volume may not be a good indicator of the potential for a pharmaceutical to do ecological harm because some of them (e.g., synthetic hormones) may be potent at very low levels in the environment.

Currently (2012), several hundred pharmaceuticals are available as prescriptions or over the counter, with about 500 new compounds registered since 1996 (FDA 2010). Approximately half of the U.S. population takes at least one prescription drug during any given month, with several drugs being common in the older populations (CDC). Therefore, as more than 17 million people live in the Chesapeake Bay watershed, about 8.5 million prescription drugs are consumed in any given month, or about 102 million per year. Nonprescription drug use is more difficult to track, but for many types of drugs (e.g., analgesics, antihistamines, etc.), can far exceed prescription usage. Typical therapeutic maintenance dosages for most pharmaceuticals are less than 1 gram per adult (<http://drugs.com>). (Because dosage depends on type of drug, type of therapy, and many other factors, there is no “representative” dose for all pharmaceuticals. A conservative estimate of 100 milligrams (mg) is used here for estimation purposes.) With a conservative estimate of 100 mg per pharmaceutical dose, the total mass consumed by humans in the Chesapeake Bay watershed in a year is approximately 225,000 pounds. The actual mass that is released to the environment would have to be adjusted for metabolic losses and processes, losses due to wastewater, and other treatment processes, and environmental factors such as dilution and transformation. It is beyond the scope of this report to assess and summarize the

mass of pharmaceuticals manufactured and released in the Chesapeake Bay watershed; however, it is clear that they are manufactured in large quantities throughout the United States, are consumed within the Bay watershed by the majority of the population, and therefore are being released to the environment in human and animal wastes and through waste-management activities.

As a group, pharmaceuticals are complex molecules with various acidic and basic functionalities; they exhibit a range of neutral, cationic, anionic, or zwitterionic behaviors in the environment, are of high molecular weight (commonly ranging from 300 to 1,000), and are biotransformed in the body, commonly resulting in changes in their physical and chemical properties upon excretion (Kummerer 2004). For example, Sarmah et al. (2006) listed selected antibiotics and showed the range of physical and chemical properties that exists for this one group of pharmaceuticals. Once in the environment, APIs can further undergo a range of potential transformations including photolysis, bacterially mediated degradation, hydrolysis, and dilution. Generally, APIs are biologically active and are mobile because they have high water solubilities in relation to molecular weight (Kummerer 2004). Therefore, although some generalizations can be made regarding the expected environmental persistence of some individual or classes of pharmaceuticals, accurate understanding of the ultimate fate of these compounds requires site-specific assessments.

Pharmaceuticals are associated with point as well as nonpoint sources and pathways to the environment. In sewerred areas, pharmaceuticals are transported from human excretion or disposal in residential settings to municipal wastewater-treatment plants (WWTPs). In this way,

WWTPs represent centralized locations where various residential, hospital, manufacturing, and other potential pharmaceutical wastes are accumulated before being discharged as a point source of mixtures of APIs and their metabolites to receiving water bodies. Approximately 75% of households in the U.S. are connected to municipal sewers (US EPA), which often include hospitals as well as pharmaceutical manufacturing facilities within the same sewersheds as well. Therefore, point sources of wastewater effluent are the primary source pathways of human-use pharmaceuticals to the environment in the Chesapeake Bay watershed, as they are elsewhere in the United States. Although WWTPs are not designed to remove APIs or their metabolites, studies have shown that existing treatment processes can decrease the concentrations of some parent compounds, in some cases to below detection (Phillips et al. 2011, Drewes et al. 2009) before being discharged to receiving water bodies. Other APIs, however, are discharged relatively unchanged because of their ability to resist the type of treatment typically found in municipal WWTPs. Other studies (Benotti et al. 2007, Stackelberg et al. 2007) have shown that drinking-water treatment is effective in decreasing concentrations of parent pharmaceutical compounds in many cases; in some limited cases, however, the pharmaceutical compounds are recalcitrant. In addition, the prevalence and magnitude of individual and mixtures of APIs can vary widely depending on sources in the sewershed (citation). Other sources of human-waste-related APIs include leachate from onsite sewage disposal such as septic tanks (citation).

Pharmaceuticals are also associated with nonpoint sources and pathways to the environment where agricultural land uses, particularly animal feeding operations, are present (Sarmah et al. 2006). Sources of APIs include feed or drinking-water additives, direct injections, implants, drenches, and pastes. The use and length of treatment and whether the drug is delivered to an

individual animal or to a herd or flock determine, in part, how a specific drug is delivered and ultimately determines the potential pathways to the environment (Sarmah et al. 2006). Potential pathways to the environment reflect overall manure management practices and include composting and/or application of biosolids/manures on crop or other lands, deposition by animals in liquid or solid wastes excreted directly into surface-water bodies, releases of liquid animal wastes from lagoons or other holding tanks, etc., as well as the local hydrologic condition. Therefore, the potential agricultural sources and the pathways depend, in large part, on how animals and their wastes are managed. In a recent summary of the literature on animal manures, the US EPA showed that the amount of manure per area of farmland in states within the Chesapeake Bay watershed is among the highest in the Nation. Phillips et al. (2011), in an analysis of effluent from WWTPs in New York State (outside the Chesapeake Bay watershed) with a focus on sewersheds that contain pharmaceutical manufacturing facilities, conclude that manufacturing practices can result in pharmaceuticals concentrations from 10 to 1,000 times higher than those typically found in WWTP effluents.

As a group, pharmaceuticals represent a wide array of potentially biologically active compounds with a variety of potential mechanisms of action. Additionally, although these compounds are designed for specific pharmacological purposes, they also can exhibit a range of unintended effects on target as well as nontarget species at therapeutic doses. The toxicity of therapeutic doses of pharmaceuticals is well understood because these chemicals are intentionally ingested and because the FDA registration process requires it (FDA). The effects of pharmaceuticals on aquatic or terrestrial organisms at environmentally relevant concentrations are less well understood. Recent research is focused on the potential effects on organisms that are exposed to

low concentrations of pharmaceuticals in the environment. Currently (2012), no aquatic-life or related water-quality or sediment-related benchmarks exist for pharmaceuticals; however, several studies have documented a range of lethal as well as sublethal effects on receptor organisms in laboratory, mesocosm, and field settings. One of the first studies to link environmental exposures of a pharmaceutical to an adverse ecological effect was Swan et al. (2006). Vultures (*Gyps* spp) in South Asia feeding on cattle carcasses with high levels of diclofenac (a veterinary pharmaceutical) died of renal failure in numbers that threatened their extinction. Since then an increasing number of studies, many focused on aquatic organisms, have been undertaken. In addition, there continue to be more efforts to demonstrate and quantify biological uptake of environmental pharmaceuticals in various species and environmental source pathways. For example, Kinney et al. (2012) documented bioaccumulation of wastewater indicator compounds (commonly indicative of sources of environmental pharmaceuticals) in earthworms exposed to biosolids. Other studies, such as Ramirez et al. (2009), Bringolf et al. (2010), and Schultz et al. (2011), are providing baseline data and information on biological uptake of targeted pharmaceuticals by various species living in municipal wastewater-affected streams. In related work, Li et al. (2012) documented a range of antibiotics including quinolones, macrolides, and sulfonamides in mollusks collected from the Bohai Sea of China.

This chapter summarizes the extent and severity of pharmaceutical occurrence in the Chesapeake Bay watershed. Although representative studies conducted in the watershed are highlighted, several studies conducted outside the watershed are included for illustrative purposes. A short list of representative laboratory, mesocosm, and field studies that have linked various categories of environmental exposures to three major classes of pharmaceuticals (hormones,

antidepressants, and antibiotics) to a range of adverse effects on biological receptors is included. This list is meant for illustrative purposes only and does not represent a complete literature review.

Water

Human-health or ecologically based water-quality standards are not common for environmental pharmaceuticals and they are not regulated water-quality constituents, consequently, they are not commonly monitored in the environment. However, a few research-based datasets for the Chesapeake Bay watershed and a few for the Nation as a whole are available. State integrated assessments did not include pharmaceuticals, but the few studies that assessed pharmaceuticals as environmental contaminants in the Bay watershed are summarized below. Several studies that provide a national perspective are summarized as well.

Kolpin et al. (2002) was the first to document the widespread occurrence of pharmaceuticals in streams of the United States. Glassmeyer et al. (2008) reviewed and summarized the available literature on the occurrence of pharmaceuticals and personal-care products in the environment worldwide and showed that most of the current papers originated in the United States. Although the individual studies summarized in the report included a variety of compounds with different analytical methods, detection limits, and research objectives, it is clear that some groups of pharmaceuticals tend to be detected more frequently than others in the aquatic environments sampled (including groundwaters, surface waters, WWTP influents, and WWTP effluents, as well as biosolids and streambed sediments). Sixty-seven compounds were found in wastewater

influent, 105 were detected in wastewater effluents, and 22 were present in biosolids. One-hundred twenty-four compounds were detected in surface waters, 35 were detected in groundwaters, and 4 were found in bed sediments. Of the 126 compounds measured in at least one matrix, 18, including analgesics, antibiotics, antihyperlipidemics, an antiepileptic, and other compounds such as galaxolide and tonalide, which are used as fragrances in personal-care products, were detected in more than 10 different studies. In another national study by the U.S. Geological Survey (USGS) (Focazio et al. 2008), 25 groundwater and 49 surface-water sites that are sources of drinking water were sampled for the occurrence of 100 targeted chemicals including pharmaceuticals, personal-care products, and other organic wastewater compounds. Forty percent of the 36 pharmaceuticals analyzed for were detected at least once, and carbamazepine was the most commonly detected pharmaceutical in both surface water and groundwater. In these and other, similar studies that monitored for a range of organic compounds, pesticides, fragrances and flavors, sterols, nonprescription pharmaceuticals, plasticizers, flame retardants, and detergent metabolites tended to be detected more frequently than prescription pharmaceutical compounds.

Phelan and Miller (2010) reported results of a collaborative effort between the USGS and the National Park Service Police Aviation Group. In this study, a high-resolution, low-altitude aerial thermal infrared survey of the Washington, D.C., section of Rock Creek Basin within the Rock Creek National Park boundaries was conducted to identify specific locations where warm water was discharging from seeps or pipes to the creek. Samples collected from 23 stream sites in the park that were selected on the basis of the thermal infrared images were analyzed for a suite of nine human-use pharmaceuticals. Butalbital and oxycodone were detected but concentrations

could not be quantified as a result of analytical uncertainties. Although the sources of the warm water were not specifically linked to pharmaceutical detections, they nevertheless indicate the presence of leaking municipal wastewater pipes or other anthropogenic influences on the water.

Loper et al. (2007) present environmental and quality-control data from analyses of water samples from 11 streams and 6 wells in south-central Pennsylvania for 46 pharmaceuticals (31 of which were human and veterinary antibiotics). The objective of this project was to conduct a reconnaissance of selected emerging contaminants in streams and well water in nine counties in Pennsylvania. Five of the streams received municipal wastewater and six received runoff from agricultural areas dominated by animal-feeding operations. For all 11 streams, samples were collected at locations upstream and downstream from the municipal effluents or animal-feeding operations. All six wells were in agricultural settings. For the stream samples, 24 pharmaceuticals (the authors of this report included caffeine and its metabolite as pharmaceutical compounds) were detected at least once. Of the pharmaceuticals detected, 11 were antibiotics. Seventy-eight percent of all detections were in samples collected downstream from municipal-wastewater effluents. The maximum concentrations of compounds other than caffeine include azithromycin (1.65 parts per billion (ppb); antibiotic), sulfamethoxazole (1.34 ppb; antibiotic), carbamazepine (0.516 ppb; antiepileptic), ofloxacin (0.329 ppb; antibiotic), ibuprofen (0.277 ppb; nonsteroidal anti-inflammatory), and trimethoprim (0.256 ppb; antibiotic). Concentrations and detections were much lower in streams receiving runoff from animal-feeding operations than in those receiving municipal-wastewater effluents. The pharmaceuticals detected were acetaminophen, carbamazepine, diphenhydramine, oxytetracycline, sulfadimethoxine, sulfamethoxazole, and tylosin. The maximum concentration for all pharmaceuticals was 0.157

ppb. In samples from wells used to supply livestock, 3 of the 24 pharmaceutical compounds were detected—diphenhydramine, tylosin, and sulfamethoxazole. There were five detections in all the well samples. The maximum concentration detected in well water was 0.024 ppb (estimated), for cotinine.

Alvarez et al. (2008) used passive samplers to assess the occurrence of a limited number of pharmaceuticals and other wastewater indicator compounds at nine locations in the Shenandoah River Basin and two in the James River Basin, Virginia. The objective of this study was to test the general hypothesis that declining fish health is linked to stream chemistry, but not to examine possible sources or source pathways. Detections included codeine (a narcotic analgesic) and carbamazepine (an anticonvulsant drug), each of which was detected at several sites.

Trimethoprim, an antibiotic commonly prescribed in tandem with sulfamethoxazole, was detected at 8 of 10 sites; however, sulfamethoxazole was detected only at 1 of these sites. The antidepressant venlafaxine, currently the 13th most prescribed drug in the United States was detected at several sites.

Arikan et al. (2006) collected water samples from 22 stream sites in the Choptank River, state, including 7 sites on the mainstem and 15 on tributaries. Samples were collected in all four seasons (April, June, September, and December) in a reconnaissance effort to assess the occurrence of key tetracycline and sulfur classes of antibiotic compounds. Of the sulfur class of antibiotics, sulfamethoxazole (19% detection) and sulfadimethoxine (12% detection) were detected at the mainstem stations at maximum concentrations of 0.002 and 0.003 ppb, respectively. The most frequently detected compounds at the tributary stations were

sulfamethoxazole (5% detection) and sulfadimethoxine (14% detection), with maximum concentrations of 0.007 and 0.009 ppb, respectively. Of the tetracycline class of antibiotics, chlortetracycline (19% detection) and oxytetracycline (15% detection) were the most frequently detected of the tetracycline group of antibiotics at the mainstem stations, with maximum concentrations of 0.034 and 0.047 ppb, respectively. Tetracycline and doxycycline were detected only once (4% detection) at the mainstem stations, at concentrations of 0.005 and 0.020 ppb, respectively. Chlortetracycline (21% detection) and oxytetracycline (18% detection) were the most frequently detected tetracycline antibiotics at the tributary stations, with maximum concentrations of 0.180 and 0.084 ppb, respectively. Tetracycline and doxycycline were detected at 5% of the tributary stations, with maximum concentrations of 0.003 and 0.146 ppb, respectively. In this limited dataset, seasonal trends were not clear; however, the authors report more samples with detections for antibiotics in December (chlortetracycline was detected in 14 of 19 samples collected in December) than in the other seasons. The highest concentration for all sulfur antibiotics was 0.694 ppb for sulfamerazine in a sample collected in April.

Barnes et al. (2006) reported datasets used in a national reconnaissance of pharmaceuticals and other organic wastewater compounds in untreated sources of drinking water in 25 states throughout the United States, including three states in the Chesapeake Bay watershed (six wells in Pennsylvania, three wells in West Virginia, and four surface-water intakes in Virginia). Results indicated that sulfamethoxazole (antibiotic) was detected in a Pennsylvania well and none of the compounds analyzed for were detected in the West Virginia wells. Sarafloxacin (antibiotic) and carbamazepine (antiepileptic) were each detected once in samples from Virginia surface-water sites.

The USGS is conducting ongoing research throughout the Chesapeake Bay watershed to determine whether fish health is related to chemical exposure. Initial research included the sampling of water and bed sediment at seven active smallmouth bass nesting sites during spawning (Kolpin et al. 2012, oral commun.). During this study, 14 prescription and nonprescription pharmaceuticals (including caffeine and its metabolite as well as cotinine, a metabolite of nicotine) were detected in the water samples collected. The two most frequently detected compounds were caffeine (86%, stimulant) and iso-chlorotetracycline (71%, antibiotic degradate). Other pharmaceuticals detected include acetaminophen (29%, analgesic), azithromycin (14%, antibiotic), carbamazepine (29%, antiepileptic), diphenhydramine (14%, antihistamine), epi-iso-chlorotetracycline (15%, antibiotic degradate), epi-tetracycline (29%, antibiotic degradate), oxytetracycline (43%, antibiotic degradate), sulfamethazine (29%, antibiotic), sulfamethoxazole (29%, antibiotic), sulfathiazole (14%, antibiotic), tetracycline (57%, antibiotic), and tylosin (14%, antibiotic).

Sediment

Very few analyses of sediment and no tissue analyses have been published for samples collected in the Chesapeake Bay watershed; however, Glassmeyer et al. (200~~x~~), in a national summary of pharmaceutical and other organic wastewater data, note that whereas the concentrations of pharmaceuticals in liquid effluents typically are in the range of low parts per billion to high parts per trillion (low micrograms per liter ($\mu\text{g/L}$) to high nanograms per liter (ng/L)), they are found in biosolids at parts per million (milligrams per kilogram (mg/kg)) concentrations. These values

reflect, in part, the affinity of many of these compounds to attach to solid particles and the manner in which solid wastes from municipal wastewater-treatment plants and other sources are managed. Additionally, several studies conducted outside the watershed have shown that pharmaceuticals such as antidepressants can be detected in the brain tissue of fish (Schultz et al. 2010) where the fish have been exposed to wastewater effluents in aquatic environments.

Arikan et al. (2006) analyzed bed sediment from four sites on the Choptank River.

Chlortetracycline (100% detection) and sulfamethoxazole (75% detection) were the most frequently detected of the antibiotics. The maximum concentrations were 10.0 and 0.15 ppb dry weight, respectively. Sulfamethazine was detected at one site at a concentration of 0.82 ppb dry weight. Chlortetracycline and sulfamethoxazole were also the most frequently detected antibiotics in water samples at these sites. Oxytetracycline, the second most frequently detected compound in water samples from these sites, was not detected in bed-sediment samples. Kolpin et al. (2012, oral commun.) also analyzed bed sediment for a limited number of compounds.

Fish and Wildlife

Pharmaceutical hormones:

In this report, “pharmaceutical” (or synthetic) hormones are considered separately from naturally occurring (or biogenic) hormones (see the “Biogenic Hormones” section of this report).

Although their modes of action are similar, their potencies, sources, and other factors are different. For simplicity, therefore, these two major groups of hormones have been separated. A third group with similar hormone-related modes of action includes other chemicals that have

been shown to interfere with normal endocrine functioning through antagonistic or synergistic effects on hormone receptors. These other known, or suspected, “endocrine-disrupting” chemicals, which include some pesticides, surfactants (e.g., alkylphenol ethoxylates), ingredients in plastics (e.g., bisphenol A), and flame-retardant mixtures (e.g., polybrominated diphenyl ethers), are discussed in other sections of this report.

Much of the environmental research regarding pharmaceutical hormones has focused on the synthetic sex hormones such as ethinyl estradiol, the active ingredient in human birth control pills. Leet et al. (2011) summarized the state of the science on the role of exposure to estrogens and androgens in sexual differentiation during early life stages of fish. Other hormonally active pharmaceuticals such as those used for thyroid-related therapies, corticoid-related therapies, and others are beginning to receive more attention as potential environmental contaminants; however environmentally relevant studies of these other pharmaceutical hormone groups are not common (Kugathas and Sumpter 2011).

Some of the earliest work linking reproductive endocrine disruption effects and potential environmental exposures to pharmaceuticals (ethinyl estradiol and diethylstilbestrol) was demonstrated in Japanese quail by Halldin et al. (1999). The study showed embryonic exposure to these synthetic estrogens can affect sexual differentiation and cause reproductive impairment. More recently, Kidd et al. (2007) dosed a Canadian lake with environmentally relevant concentrations of synthetic estrogen (17 α -ethinyl estradiol) (i.e., concentrations detected by other studies in environmental waters) over a 3-year period. Population-level effects including intersex and severe reproductive failure were observed in fathead minnows (*Pimephales*

promelas) from the dosed lake but not in those from two control lakes. Populations returned to normal when the contaminant dosing was discontinued.

Other research has shown that in some cases exposure to estrogens at environmentally relevant concentrations can result in immunosuppressive effects (Milla et al. 2011). For example, Roberston et al. (2010) have shown that expression of a protein critical to immune suppression (hepcidin) can be disrupted in fish exposed to exogenous estrogens at environmentally relevant concentrations (also see the “Biogenic Hormones” section of this report). Cubero-Leon et al. (2010) have documented that natural (estradiol) as well as synthetic (ethinyl estradiol) estrogen can disrupt serotonin receptor functioning as well as mRNA expression levels of cyclooxygenase (an enzyme critical to production of prostaglandins) in the marine bivalve *Mytilus edulus*. Other studies have shown that total estrogenicity of common mixtures of contaminants (composed of natural, pharmaceutical, and other hormonally active compounds) such as those commonly found in municipal wastewater effluents can cause intersex in exposed fish (Vajda et al. 2011). Critically, once the wastewater-treatment plant was updated with treatment technologies capable of removing these estrogenic compounds, the intersex conditions in fish were no longer evident (Alan Vajda, University of Colorado, oral comm. 2012). Yonkos et al. (2010) exposed fathead minnows (*P. promelas*), sheepshead minnows (*Fundulus heteroclitus*), and mummichogs (*Cyprinodon variegatus*) to solutions leached from poultry litter. The minnows exhibited intersex conditions, whereas the mummichogs were unresponsive in all trials. The potential mixture of hormonally active chemicals in the litter likely includes biogenic hormones as well as other endocrine disruptors; however, this study did not test for individual chemicals. A positive

controlled exposure experiment with 17 β -estradiol (biogenic estrogen) had no effect on the mummichogs but did have effects on the minnows.

Pharmaceutical antidepressants:

Schultz et al. (2011) exposed fathead minnows (*P. promelas*) to environmentally relevant concentrations of antidepressants (bupropion, fluoxetine, sertraline, and venlafaxine) and observed anatomical and physiological effects, including the presence of intersex biomarkers such as elevated plasma vitellogenin in male fish as well as severe effects on male secondary sexual characteristics. Some exposures to venlafaxine (305 ng/L) and sertraline (5.2 ng/L) resulted in mortality. Painter et al. (2009) showed that predator avoidance behaviors were adversely affected in larval fathead minnows (*P. promelas*) exposed to these antidepressants at environmentally relevant concentrations. Avoidance success decreased significantly in individuals exposed to these pharmaceuticals, thus potentially compromising survival and reproductive fitness.

Pharmaceutical antibiotics:

It is well known that antibiotic therapies can create antibiotic resistance in clinical settings as a result of repeated exposures of bacteria to individual antibiotics. The potential for antibiotics that have been released to the environment to enhance resistance patterns in receptor microbial communities is not well understood; however, recent research has focused attention on this topic. For example, D'Costa et al. (2011) discuss potential effects on resistance patterns of indigenous soil microbial communities exposed to antibiotics, and Duriez and Topp (2007) explore various manure management techniques at swine farms and their influence on antibiotic

resistance patterns in the manure. Haack et al. (2012) showed that microbial community composition and structure can be affected by environmentally relevant exposures to an antibiotic (sulfamethoxazole). These investigators also noted that ecological function could be affected at concentrations two to three orders of magnitude smaller than those used in clinical applications and could promote antibiotic resistance through the selection of naturally resistant bacteria. In a related experiment, Underwood et al. (2011) showed that sulfamethoxazole exposures at environmentally relevant concentrations can affect the denitrifying activity of indigenous soil microbial populations in an aquifer that previously received wastewater effluents. LaPara et al. (2011) have identified tertiary treated municipal wastewater effluents to be significant point sources of antibiotic resistance genes to receiving surface waters in Minnesota. In another example of pharmaceutical antibiotic effects in the environment, Ebert et al. (2011) researched potential risks to photoautotrophic aquatic organisms (an alga, a cyanobacterium, and two macrophytes) resulting from exposure of fluoroquinolone antibiotics (ciprofloxacin, enrofloxacin). The study identified risks (growth inhibition effects) to two of the test species at environmentally relevant concentrations of ciprofloxacin (risks were not identified at these concentrations for enrofloxacin).

Conclusions

Existing data documenting the environmental occurrence of pharmaceuticals in the Chesapeake Bay watershed are limited. However the limited data indicate a potentially wide extent of some pharmaceuticals for several reasons; 1) the sources of pharmaceuticals, which include human and animal waste management operations such as municipal wastewater treatment effluents and animal agriculture, are widely distributed throughout the watershed; 2) the few studies that have

been completed in the watershed have detected some pharmaceutical and related indicator chemicals in some streams, groundwater, and streambed-sediment; and 3) other studies conducted across the United States and elsewhere consistently point to a wide extent of pharmaceuticals wherever source pathways to aquatic environments exist. The severity of pharmaceuticals as environmental contaminants is the subject of active research. However several studies in the United States and elsewhere have linked some of these chemicals to adverse sublethal effects in a range of exposed organisms at environmentally relevant concentrations. Therefore pharmaceuticals are likely to occur extensively in the watershed at concentrations that may cause adverse impacts but additional monitoring and research is required before conclusions can be made regarding the severity of these compounds.

2.7 Household and Personal Care Products

Abstract

Household and personal-care products (PCPs) represent a wide range of potential organic chemicals that we use in our daily lives in residences, workplaces, and other locations. Used for a variety of reasons such as cosmetics, detergents, soaps, pest control, and food additives these products are often formulated as a mixture of ingredients. These contaminants can enter the environment a number of ways but the predominant pathways are all related to management and disposal of residential and human wastes such as landfills, on-site septic, and municipal wastewater treatment plants. Findings of the few local and regional occurrence datasets in Chesapeake Bay Watershed tend to mirror national and other studies of these compounds as potential environmental contaminants.

For example the compounds often detected in the environment include N,N, diethyltoluamide (insect repellent known as DEET), surfactants (i.e. alkyl phenols), triclosan (an antimicrobial), and musks (tonalide, galaxolide). The environmental-health implications of the presence of these contaminants in the environment are poorly understood however it is clear that: 1) these compounds often occur in complex mixtures; 2) the concentrations detected in environmental settings tend to be low as compared to the few existing health-based benchmarks; 3) some studies are showing that targeted compounds in low level environmental exposures; and 4) the low-level sublethal effects are where more research is required before a complete understanding of the “severity” of these contaminants can be realized

Background

Household and personal-care products (PCPs) include a wide range of inorganic as well as organic chemicals that we use in our daily lives in residences, workplaces, gyms, and other locations. These products, such as cosmetics, detergents, soaps, and food additives, are typically formulated as a mixture of ingredients. For example, some soaps and toothpastes include antimicrobial compounds in their formulation (e.g., triclosan and triclocarban); some cosmetics include compounds that provide fragrance (galaxolide and tonalide); detergents and cleaning products consist of several ingredients, including surfactants (nonylphenol ethoxylates, alkylphenol ethoxylates, and octylphenol ethoxylates); and other organic compounds (e.g., menthol) are used to enhance flavors in a range of products.

Chemical constituents in household products and PCPs can enter the environment through a variety of pathways. Solid forms of these products are commonly placed in trash receptacles destined for landfills, whereas liquid forms are flushed in toilets or poured into sink drains. Therefore, most source pathways to the environment are associated directly or indirectly with human-waste management activities such as municipal wastewater-treatment facility effluent discharges, septic tanks, and landfill leachates. Chemical constituents associated with household products and PCPs can have a variety of sources and therefore are not always associated with household wastes.

Water and Sediment

These chemical constituents associated with PCPs could derive from a variety of waste sources. Therefore, the analytes listed in this section are referred to as “indicators” of household products and PCPs when detected in the environment. Water-quality standards generally do not exist for all chemicals that are indicators of household products and PCPs; therefore, these analytes are not commonly monitored in the Chesapeake Bay watershed. Several studies conducted throughout the United States and elsewhere, however, have provided monitoring data and perspective on the few local data that are available. Most of the environmental data for these chemicals are for concentrations in water and some sediment samples. Tissue analyses are not available.

Kolpin et al. (2002) were among the first to document the widespread occurrence of chemical indicators of household products and PCPs in streams in the United States. Glassmeyer et al.

(2008) reviewed and summarized the available literature on the occurrence of pharmaceuticals and chemical indicators of household products and PCPs in the environment worldwide and showed that 124 different compounds were detected in surface waters, 35 were detected in groundwaters, and 4 were detected in bed sediments. Of the 126 compounds measured in at least one matrix, 18, including galaxolide and tonalide (which are used as fragrances in PCPs), were detected in more than 10 different studies.

Phelan and Miller (2010) reported results from base-flow, stormwater, and bed-sediment synoptic sampling of 23 sites in Rock Creek Park, D.C. Of the indicators of household products and PCPs analyzed for, N,N-diethyltoluamide (insect repellent), organophosphate, flame retardants, and galaxolide (musk) were detected at more than half the sites. Other indicators of household products and PCPs detected in water samples included alkyl phenol surfactants, triclosan (antimicrobial additive in soaps), and tonalide (musk). Compounds detected in bed-sediment samples include N,N-diethyltoluamide, galaxolide, and surfactants.

Alvarez et al. (2008) used passive samplers to assess the occurrence of a limited number of pharmaceuticals and other wastewater indicator compounds at nine locations in the Shenandoah River Basin and two in the James River Basin, Virginia. The objective of this study was to test the general hypothesis that declining fish health is linked to stream chemistry, but not to determine possible sources or source pathways. Detections of indicators of household products and PCPs included celestolide, galaxolide, phantolide, tonalide, and traseolide (musks used in a variety of cosmetics and other PCPs), N,N diethyltoluamide (insect repellent applied topically to

clothing and skin), as well as several phosphate-based flame retardants used in a variety of consumer products such as clothes and furniture.

Barnes et al. (2006) reported datasets used in a national reconnaissance of pharmaceuticals and other organic wastewater compounds in untreated sources of drinking water in 25 states throughout the United States. Sites in the Chesapeake Bay watershed were located in Virginia, Maryland, and Pennsylvania. Synthetic surfactants that are common in several types of detergents and cleaning products were detected at several sites. Other indicators of PCPs detected included triclosan, menthol, and N,N, diethyltoluamide.

Reif et al. (2012) conducted reconnaissance sampling from 2006 to 2009 to identify contaminants of emerging concern in (1) groundwater from wells used to supply livestock, (2) streamwater upstream and downstream from animal feeding operations, (3) streamwater upstream from and streamwater and streambed sediment downstream from municipal wastewater effluent discharges, (4) streamwater from sites within 5 miles of drinking-water intakes, and (5) streamwater and streambed sediment where fish health assessments were conducted. Analytes included a range of indicators of household products and PCPs.

Kolpin et al. (oral commun., 2012) analyzed discrete (grab samples) and integrated (passive samplers) water samples as well as bed sediment from smallmouth bass nesting sites in the Potomac River Basin in State. Chemical indicators of household products and PCPs detected in water samples include a range of surfactants, camphor, galaxolide, N,N, diethyltoluamide, tonalide, and triclosan.

Fish and Wildlife

Residues of household products and PCPs have yet to be reported in tissues of wildlife (amphibians, reptiles, birds, and mammals) in Chesapeake Bay. Ramirez et al. conducted a survey of five wastewater-effluent-dominated streams across the United States and analyzed fish tissue for a range of pharmaceuticals and PCPs. Galaxolide and tonalide (musks) and triclosan were among the compounds detected.

Perfluorinated compounds are surface protectors and surfactants that are distributed worldwide. Perfluorooctanoic acid, an active ingredient of Scotch Guard®, was voluntarily removed from the marketplace in 2000 because it was increasingly being detected in the environment, wildlife, and people. Several perfluorinated compounds were detected in osprey eggs collected in the Chesapeake Bay watershed in 2000 and 2001, with upper extreme concentrations of 428 ppb wet weight for perfluorooctanesulfonate, 671 ppb for perfluorodecanesulfonate, 13.7 ppb for perfluorodecanoic acid, and 27.1 ppb for perfluoroundecanoic acid (Rattner et al. 2004). Recent controlled exposure studies and risk assessments in Northern bobwhite (*Colinus virginianus*) and mallards concluded that environmental exposure does not pose a significant risk to avian populations (Newsted et al. 2005).

A series of alkylphenol and ethoxylate surfactants were also analyzed in 15 osprey eggs collected from the Chesapeake Bay watershed in 2000 and 2001. Nonylphenol was detected in all egg samples, with the extreme concentration being 16.7 ppb wet weight. Nonylphenol ethoxylates,

octylphenol, and octylphenol ethoxylates were generally not detected, with the exception of octylphenol ethoxylate in 1 of 15 eggs at a concentration of 14.6 ppb.

Lozano et al. (2012) documented seasonal variations in concentrations of alkylphenol and alkylphenol ethoxylate surfactants in tissue samples collected from largemouth bass living downstream from municipal wastewater-treatment plants in Chicago, Illinois. In comparison the tissue concentrations of other persistent organic compounds such as PCBs, poly brominated diphenyl ethers (PBDEs), and some legacy pesticides such as DDT did not vary over time. Although these analyses were not done in the Chesapeake Bay watershed, the contaminants associated with wastewater (e.g., surfactants) are similar.

The toxicological effects of PCPs in the environment are an area of active research. Some compounds, such as the antimicrobials triclosan and triclocarban, have been shown to have various sublethal effects at environmentally relevant concentrations ranging from stimulation of embryo production in freshwater snails (*Potamopyrgus antipodaru*) (Guidice and Young 2009) to disruption of thyroid homeostasis (Dann and Hotela 2010). Dann and Hotela (2010) also point out that mammalian toxicity studies of triclosan have shown that it is not acutely toxic, carcinogenic, mutagenic, or a developmental toxicant; however, they also note that some aquatic species such as algae, invertebrates, and some fish are sensitive to triclosan. Bedoux et al. (2012) reviewed the literature on triclosan toxicity and environmental occurrence and showed that benchmarks such as EC50 generally were much lower ($\mu\text{g/L}$ or lower) in plants than in animals, with toxicities to animals well above most environmentally relevant concentrations. On the other hand, some indigenous soil bacteria and aquatic algal species did exhibit sublethal and

other effects (e.g., inhibition of soil microbial respiration) at environmentally relevant concentrations. Evidence of the biological effects of PCPs in the environment can be found for other contaminants as well. For example, APE surfactants can elevate plasma vitellogenin in male largemouth bass living in streams receiving wastewater effluents (Lozano et al. 2012).

Conclusions

Household and personal care products represent another group of contaminants covered in this report with many potential uses and a diverse array of chemicals. Many studies throughout the world have shown these contaminants to be associated with a wide range of wastewater sources such as municipal effluents, on-site septic tanks, and other waste management operations (e.g. landfills). Therefore, although the existing occurrence data are limited in the watershed, the sources such as wastewater effluents are widespread indicating a potential for widespread occurrence of some of the commonly used chemicals within this group. Toxicological understandings at environmentally relevant concentrations currently are limited; however, this is an active area of research. Additional monitoring and research is warranted in order to determine the severity of these compounds in the watershed (fig. 1).

2.8 Polybrominated Diphenyl Ether Flame Retardants

Abstract

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in a range of consumer products since the 1970s. As a contaminant group, PBDEs include more than 200 potential congeners, making this one of the most extensive groups in this report in terms of total number of individual chemicals. Unlike many other contaminants in this report, however, PBDE congeners are highly hydrophobic and therefore are more likely to be found in sediments and tissue than in the water column. In addition, PBDEs are known to bioaccumulate; therefore, environmental monitoring for PBDEs has been focused on animal tissue (e.g., fish, shellfish, and a range of terrestrial animals) in the Chesapeake Bay watershed and around the world, including remote regions of the Arctic. Also known to exist in coastal marine sediments globally, PBDEs are well documented in terms of their extent. On the other hand, the potential toxicological and ecological effects, or “severity” of PBDEs as environmental contaminants are less well understood. Currently there are no fish consumption advisories for PBDEs in the Chesapeake Bay watershed; however, research on sublethal effects of PBDEs on living resources of the Bay watershed at environmentally relevant concentrations is limited. More research on the potential impacts of low level exposures is needed.

Background

Polybrominated diphenyl ether (PBDE) flame retardants have been commonly used as fire retardants in textiles, electronics, polymers, and other materials since the 1970s. Although the deca-BDE mixture has been produced in the greatest volumes, the demand for penta-BDE in North America has exceeded that in other markets by an order of magnitude (Hale et al. 2006). Pathways for PBDEs to enter the environment are poorly understood and quantified. Because PBDEs are chemically incorporated into consumer products, the most likely environmental pathways include air emissions from manufacturing and product usage. Hale et al. (2002) suggest that these compounds enter the environment as polyurethane foams, disintegrate, and release congeners in the resulting fragments.

Because PBDEs are hydrophobic and lipophilic, the majority of environmental occurrence studies for PBDEs are focused on animal tissue and soils or bed sediment. Hale et al. (2002) found elevated concentrations of PBDEs in soils, bed sediment, and bluegill tissues downwind and downstream from a polyurethane foam manufacturing plant in the Roanoke River watershed (outside the Chesapeake Bay watershed).

Water and Sediment

Because PBDEs have low solubility and there are no regulatory standards for PBDEs, no water-column data for these compounds were identified in the literature or found in any of the data searched for this report.

Kimbrough et al. (2009) measured concentrations of PBDEs (mono- through hepta- congeners) in paired sediment and oyster tissues (see below) collected at the National Oceanic and Atmospheric Administration (NOAA) nationwide Mussel Watch stations from 2004 to 2007. None of the Chesapeake Bay stations were listed as having elevated concentrations, and the Chesapeake Bay was placed in the lowest of three clusters (low, medium, and high) for paired sediment and tissue concentration data. Two of these sites were designated as having medium concentrations in sediment (0.1 and 0.3 ppb dry weight), whereas PBDEs were not detected in sediment at the other four sites. Of the seven Virginia sites, three had nondetectable PBDE sediment concentrations, two were not sampled, and two had medium concentrations of 0.1 and 0.4 ppb.

Fish and Shellfish Tissue

Human health concerns

According to the Agency for Toxic Substances and Disease Registry (ATSDR 2004), the main source of human exposure to PBDEs may be through foods with high fat content, such as fatty fish. Some lower brominated PBDEs have been detected in air samples, indicating that people can also be exposed by inhalation. The ATSDR (2004) public health statement provides the following information on PBDE effects:

“Rats and mice that ate food containing moderate amounts of lower brominated PBDEs for short periods of time had mainly thyroid effects. Rats and mice that ate smaller amounts over several weeks or months developed effects in the liver and in the thyroid. It is speculated that many of the thyroid effects of PBDEs are specific to the species of test animals, suggesting that they are less likely to occur in humans. Subtle behavioral changes have been observed in animals exposed to PBDEs as infants. One possible explanation for the behavioral effects might be related to changes in the thyroid, because development of the nervous system is dependent on thyroid hormones. PBDEs have not

caused other kinds of birth defects in animals, but more studies are needed to determine if PBDEs can impair reproduction. Preliminary findings from short-term animal studies suggest that some PBDEs might impair the immune system. Animals exposed to PBDEs by skin contact showed signs of skin irritation only if they had been scratched. We don't know if PBDEs can cause cancer in people, although liver tumors developed in rats and mice that ate extremely large amounts of decaBDE throughout their lifetime. On the basis of evidence for cancer in animals, decaBDE is classified as a possible human carcinogen by EPA. Lower brominated PBDEs have not yet been tested for cancer.”

There are no fish tissue advisories for PBDEs in the Chesapeake Bay watershed. PBDE concentrations were included as part of monitoring conducted to update fish tissue advisories (Pinkney 2009). In 2007, samples of the following species were collected from the Potomac and Anacostia Rivers: sunfish, largemouth bass, carp, blue catfish, channel catfish, and American eel (Pinkney 2009). Total PBDE concentrations were compared with the Virginia Department of Health (VDH) Guidance Value of 5 ppm (R. Tripathi, VDH, personal communication) because no US EPA fish-tissue screening value exists for PBDEs. The maximum concentration was 0.136 ppm in a channel catfish sample. No concentration in any of the other samples exceeded 0.1 ppm.

Ecological concerns

In their review of the literature on the toxicity of PBDEs, Wenning et al. (2011) stated that PBDEs are expected to be toxic to aquatic organism but that dose-response relationships have not been developed.

Recent studies of single PBDE compounds in the laboratory demonstrate a range of sublethal effects. For example, Kuiper et al. (2008) exposed zebrafish (*Danio rerio*) to a purified pentabromodiphenylether (congener BDE-71) in water in a 30-day exposure that focused on egg

production and fertilization. Eggs were hatched and exposure continued until 45 days post-hatch. The authors also measured whole-body BDE-71 concentrations in adults and juveniles. They found that, although larval survival was significantly reduced, the adult tissue concentration associated with the exposure (126 ppm wet weight) was more than 55 times the highest reported environmental concentrations in wild fish (burbot, *Lota lota* in a Norwegian lake at 2.27 ppm wet weight). In contrast, Chou et al. (2010) reported adverse effects on swimming speed and level of activity in juvenile zebrafish (*D. rerio*) exposed to the pentabromodiphenylether BDE-47 from day 21 through day 54 post-hatch. They stated that these effects occurred at concentrations approaching those reported in environmental samples of wild fish.

As stated above, Kimbrough et al. (2009) measured concentrations of PBDEs (mono- through hepta- congeners) in paired sediment and oyster tissues collected at NOAA's nationwide Mussel Watch stations from 2004 to 2007. None of the Chesapeake Bay stations were listed as having elevated concentrations, and the Chesapeake Bay was placed in the lowest of three clusters (low, medium, and high) for paired sediment and tissue concentration data. The six Maryland stations were designated as having medium concentrations in oyster tissue (7.1–24.1 ppb total PBDEs). Two of these sites were designated as having medium sediment concentrations (0.1 and 0.3 ppb dry weight), whereas the other four sites did not have detectable PBDE concentrations. Of the seven Virginia sites, three had nondetectable PBDE sediment concentrations, two were not sampled, and two had medium concentrations (0.1 and 0.4 ppb). Six of the seven sites had medium oyster concentrations of 1.2 to 14.8 ppb and the seventh site had no detectable PBDEs. Kimbrough et al. (2009) concluded that the toxicity and ecosystem effects of PBDEs on marine biota have not been well studied.

Wildlife

In osprey eggs collected in 2000 and 2001, BDE congeners 47, 99, 100, 153, and 154 were detected in all samples from Chesapeake Bay regions of concern and the South, West, and Rhode Rivers reference sites near Annapolis, Maryland (Rattner et al. 2004). Total PBDE concentrations ranged up to 928 ppb wet weight (some of the greatest concentrations reported in bird eggs to date), and approach the lowest-adverse-effects-level of 1,800 ppb eggs for pipping and hatching success derived in American kestrels (McKernan et al. 2009). Tetra- and penta-BDE congeners typically dominate eggs of piscivorous birds. In a collection of addled peregrine falcon eggs from 13 nests in the Chesapeake Bay watershed (Potter et al. 2009), total PBDE concentrations ranged from 32.8 to 354 ppb wet weight. The deca-BDE congener 209 was detected at concentrations ranging up to 48.2 ppb, and levels of this congener were found to be positively correlated with human population density in proximity to the nests (Potter et al. 2009). Polybrominated biphenyl congener 153 was also quantified in many of the peregrine eggs, ranging from 5.88 to 51.8 ppb wet weight, although toxicity thresholds in avian eggs are unknown. In 2010, six common tern eggs collected from Poplar Island were analyzed for PBDEs. These eggs contained low levels of BDE congeners (total PBDE ranged from 10.2 to 51.0 ppb wet weight), making them ideal for their intended use in a controlled exposure penta-BDE egg injection (Rattner et al. 2011).

Congeners of PBDEs detected in penta- and octa-BDE formulations bioaccumulate and biomagnify in food chains (de Wit 2002), and detailed investigations in captive and free-ranging

birds have documented developmental, endocrine, immunologic, and reproductive effects at environmentally relevant concentrations (Chen and Hale 2010).

Conclusions

It is clear that PBDEs can be found in the tissue of a range of aquatic and terrestrial organisms throughout the watershed. It is notable that recent research on the adverse effects of PBDEs is focusing on specific congeners. Additional research on sublethal effects is required before conclusions can be drawn as to their severity.

2.9 Biogenic Hormones

Abstract

By definition, biogenic hormones are created, biologically processed, and excreted by humans and other organisms. Therefore, their extent in the environment is widespread. Recent monitoring studies have focused on natural and synthetic estrogens as well as several other chemicals that are known or suspected to interfere with normal estrogen receptor functioning in a range of organisms. Monitoring results have shown that municipal wastewater effluents as well as animal agricultural activities can be major pathways for biogenic hormones to reach the environment. Other studies have shown that exposures to these environmental hormones cause intersex and other abnormalities such as immune suppression in fish and other species. Many of these compounds, although they may be significant contaminants in the environment, do not have immediate lethal effects; however, they may have more subtle effects on developmental and maturational processes and may diminish individual fitness and reproductive life span.

These key sublethal effects are typically difficult to detect in wild populations and present an insidious challenge to the health of fish and wildlife. Currently (2012), the weight of evidence indicates that environmental exposures to these sources of biogenic hormones cause adverse effects to some receptor organisms. Reductions in animal and human wastes entering the environment will decrease these effects on living resources (Barber et al. 2012). Targeted monitoring and research is required in order to determine their severity in the Chesapeake Bay watershed.

Background

The presence of natural hormones in the environment, a result of animal and plant waste excretion and other natural biological processes, can be anthropogenically enhanced by various waste-management practices. As a compound group, natural hormones are not commonly monitored by regulatory agencies as contaminants.; however, the combination of potentially large quantities of these compounds reaching the environment as a result of waste-management activities and the fact that they are biologically active at low concentrations has increased research attention on these compounds as potential environmental contaminants.

All multicellular organisms including plants and animals produce hormones. Hormones are required for a variety of biological functions and include, for example, estrogen and androgen, which are critical for normal sexual reproduction in vertebrate animals. Other examples of animal hormones include tyrosine-based hormones associated with thyroid functioning and

corticosteroids produced in the adrenal cortex and associated with a range of stress and immune responses as well as a range of metabolic processes. Phytoestrogens are produced by plants and, although they are weakly estrogenic compared to animal estrogens, they are produced in abundance, and their environmental pathways also are affected by waste-management activities. This section of the report focuses on naturally produced hormones because of current related research on fish health and intersex in the Chesapeake Bay watershed (Vajda et al. 2011; Ciparis et al. 2011) and elsewhere in the world. Current research is focused on the naturally occurring steroidal hormones as well as other environmental contaminants that bind to or otherwise affect estrogen and androgen receptors; however, there is a growing list of other chemical compounds that are known or suspected to interact with hormone receptor signaling pathways. These other compounds are not considered in this section of the report, but some of them are discussed can be found elsewhere in this report.

Because these compounds are key components of all animal and plant life their environmental sources are ubiquitous. Some management activities associated with human, animal, and plant wastes and associated biological material can be key point and(or) nonpoint source pathways for hormones in the environment. Municipal wastewater treatment plants are centralized locations where human wastes (and associated hormones) are treated before being discharged to the environment. These treatment systems are not specifically designed to remove hormones and consequently some municipal wastewater effluents are potential point sources of natural hormones to the environment. Consequently successful removal (or biochemical transformation) of parent hormone compounds as they pass through existing wastewater treatment plants can be highly variable (Chimchirian et al. 2007). Khanal et al. (2006) showed that estradiol

concentrations in effluents can be lowered when compared to influent concentrations at wastewater treatment plants using existing treatment technologies whereas estrone concentrations may not be reduced. Effluent from WWTPs can be a significant source of natural estrogens from human excretion to surface waters (Lagana et al. 2004; Muller et al. 2008; Petrovic et al. 2002; Ying et al. 2008). Finally, because sewersheds can encompass large land areas and various sources the treatment plants can become central locations where hormone-laden wastes accumulate and potentially become concentrated before release to the environment. Other sources include land uses and related operations where animal manure is created and accumulated (e.g. lagoons at livestock feeding operations) and inadvertently (or intentionally) released to the environment as point sources. Rangeland or pasture grazing of livestock can be another source of hormones to the environment especially where livestock have direct access to streams or other water bodies (Kolodziej and Sedlak 2007). Other agricultural activities such as where animal manures are spread on cropland as a source of soil fertility, biosolid uses, and compost operations accumulate animal and plant wastes and eventually release them to the environment in various forms and conditions of decomposition. The latter are important nonpoint sources of hormones to surface and groundwater during runoff and leaching events (Finlay-Moore et al. 2000; Kjaer et al. 2007; Matthiessen et al. 2006; Shore et al. 1995).

Metabolic processes associated with plants and animals produce a range of parent and conjugated forms of hormones. Therefore, hormones excreted from animals can be in the original parent form as well as a range of conjugated forms such as glucuronides and sulfur compounds, which in turn are subject to further transformation processes. Where environmental conditions are amenable, the conjugated forms can be cleaved to the parent compound and other

processes can produce the conjugated forms again

(<http://www.ncbi.nlm.nih.gov/pubmed/22327963>). Several studies have documented concentrations of parent steroids as well as their glucuronide and sulfate conjugated metabolites in livestock manures and municipal biosolids destined for land applications (Hanselman et al. 2003; Andaluri et al. 2012). The glucuronide metabolites have been shown to deconjugate back to the parent steroid in the environment (Ternes et al. 1999; Panter et al. 1999). In contrast, current evidence on sulfate conjugates indicates they are much more resistant to transformation (Johnson and Williams 2004; D'Ascenzo et al. 2003). Hutchins et al. (200x) analyzed samples from several different lagoons at confined animal-feeding operations and concluded that estrogen conjugates contribute to the overall estrogen load. Therefore, fate and transport studies of natural plant and animal hormones must account for the parent as well as the conjugated forms, especially when their role as hormonally active environmental contaminants is being investigated.

Hanselman et al. (2003) completed a literature review to assess the current state of science regarding estrogen physicochemical properties, livestock excretion, and the fate of manure-borne estrogens in the environment. Unconjugated steroidal estrogens have low solubility in water (0.8-13.3 milligrams per liter (mg/L) and are moderately hydrophobic (log K_{ow} 2.6-4.0). Cattle excrete mostly 17 α -estradiol, 17 β -estradiol, estrone, and respective sulfated and glucuronidated counterparts, whereas swine and poultry excrete mostly 17 β -estradiol, estrone, estriol, and respective sulfated and glucuronidated counterparts.

Kanal et al. (2006) reviewed the literature and summarized on the fate, transport, and biodegradation of natural estrogens in the environment. Although the environmental fate of estrogens is not clearly known, Hanselman et al. (2003) summarized the results of laboratory-based studies that found the biological activity of these compounds is greatly reduced or eliminated within several hours to days as a result of degradation and sorption. Bradley et al. (2010) studied the biodegradation of 17 β -estradiol, estrone, and testosterone in three streams in the United States that receive wastewater-effluent effluents. The results showed that biodegradation of these hormones in conjunction with sorption to bed sediments can be mechanisms for the attenuation of hormonal endocrine disruptors in effluent-affected streams. Gray and Sedlak (2005) showed that constructed wetlands function to remove or transform estrogenic contaminants. Approximately 36% of the 17 β -estradiol was attenuated, with the most likely cause being sorption to hydrophobic surfaces in the wetland coupled with biotransformation. However, the attenuation processes in these studies were still not sufficient to completely mineralize or sequester these compounds. Other studies (Kanal et al. 2006) have demonstrated that estrogens are sufficiently mobile and persistent to affect surface-water and groundwater quality and, therefore, aquatic organisms can be exposed to these hormones even in locations that are removed from their sources or pathways to the environment.

Khanal et al. (2006) summarized recent literature and found that conventional wastewater treatment is efficient in the removal of 17 β -estradiol, but estrone removal is relatively poor. The removal occurs mainly through sorption by sludge and subsequent biodegradation. Barber et al. (2012) showed that estrogenic compounds were removed from treated wastewater by upgrading a wastewater-treatment plant from a trickling-filter/solids-contact process to an activated-sludge

process, as a result, in large part, to the increase in hydraulic retention time and the solids retention time. Before the upgrade, 17 β -estradiol was partially removed by the trickling filter, whereas estrone concentrations actually increased in the effluent, likely as a result of biologically mediated oxidation of 17 β -estradiol. Concentrations of estriol, 17 β -estradiol, and estrone in treated effluent decreased to below detection levels after the upgrade.

Previous research on synthetic and other exogenous hormones has improved understanding of the effects of hormones in the environment regardless of whether the hormones are derived from natural sources, synthetic hormones, or other chemicals that are known to interfere with normal hormone-receptor functioning in vertebrates. For example, the effect of embryonic diethylstilbesterol (DES, a synthetic estrogen) exposure demonstrated that estrogenic chemicals affect the differentiation of estrogen target organs (Colborn et al. 1993). Data on androgen- and thyroid-active compounds reveal similar deleterious potential for long-term effects from these compounds through different mechanisms of action (Custer et al. 1999; Chen et al. 2008; Zoeller 2008).

Studies and monitoring data on steroidal hormones in the Chesapeake Bay watershed are limited. A few example studies conducted by Federal agencies and academia are cited below; however, available information is insufficient to warrant separate sections on water, sediment, and tissue at this time.

Water and Sediment

Many studies have documented the presence of steroidal hormones in aquatic environments (Kolpin et al. 2002). Most of these studies have focused on dissolved constituents in the water column, with fewer studies of those in bed sediment. Kinney et al. (2006) analyzed biosolids produced from wastewater-treatment-plant sources and detected several steroidal hormones including 3- β -coprostanol, cholesterol, β -sitosterol, and stigmastanol at high concentrations relative to the concentrations of other organic compounds detected. These commercially available biosolids are commonly applied to land surfaces as soil amendments and are therefore potential source pathways for steroidal hormones to the environment. Data on phytoestrogen occurrence in aquatic environments is much more limited; however, Kolpin et al. (2010) analyzed water from 15 streams draining agricultural land in Iowa for a range of phytoestrogens. Target compounds that were frequently detected include formononetin (80%), equol (45%), daidzein (32%), biochanin A (23%), and genistein (11%).

Reif et al. (2012) analyzed 270 streamwater samples collected near drinking-water intakes in Pennsylvania for a range of biogenic hormones. Six of the 17 hormones and 2 of the animal sterol compounds were detected at least once. The most frequently detected hormones were estrone (18% of samples; maximum concentration 3.1 ng/L), cis-androsterone (5% of samples; maximum concentration 6.2 ng/L), and 4-androstene-3,17-dione (3% of samples; maximum concentration 1.8 ng/L). All other hormones were detected in fewer than 1 percent of samples. Only 1.5% of all 5,130 analyses resulted in hormone detections.

Dorabawila and Gupta (2005) documented the presence of estradiol (17 β -estradiol) in water samples from the Wicomico, Manokin, and Pocomoke Rivers, with moderate levels of estradiol

in surface water from coastal bays. Concentrations of estradiol were highest downstream from sewage-treatment plants.

Ciparis et al. (2012) sampled tributaries in the Shenandoah River watershed during three different seasons and analyzed the water by using an estrogen assay. The bioluminescent yeast estrogen screen (BLYES) indicates the presence of compounds that can bind to the estrogen receptor. In this way, BLYES is an indicator of “total estrogenicity” of the water and includes activities associated with all natural and synthetic estrogens or other chemicals that are estrogen agonists or antagonists. The total concentration of estrogenic compounds in the water samples relative to 17 β -estradiol (E2) is reported by this assay as E2 equivalents (E2Eq). Concentrations in 18 samples from 10 sites were >1 ng/L E2Eq, and animal feeding operation (AFO) densities in the watersheds of most of these sites were >1 per 1,000 acres. An E2Eq > 1 ng/L was the predicted no-effect concentration of total estrogens on fish reproduction. This study documented statistically significant ($R^2=0.39-0.75$) relations between watershed densities of AFOs and in-stream concentrations of E2Eq. The range in estrogenic activity observed during this study was similar to estrogen concentrations and total activity measured in other studies across the United States, including (1) streams with concentrated sources, such as streams draining fields that receive wastes from poultry AFOs; (2) streams adjacent to pastures receiving waste from dairy and beef AFOs; and (3) rangeland streams directly accessed by grazing cattle. A similar range in estrogenic activity has been measured in treated WWTP effluent (Salste et al. 2007) and in rivers receiving effluent from WWTPs (Vermeirssen et al. 2005).

Arikan et al. (2006) analyzed 26 water samples from seven river stations and 56 water samples from 15 subwatershed stations in the Choptank River Basin for several biogenic hormones. Estriol (12 ng/L) and estrone (13 ng/L) were each detected once in subwatersheds, and progesterone was detected in three different subwatersheds (12, 12, and 14 ng/L). The synthetic estrogen 17 α -ethinylestradiol was also detected in one subwatershed water sample. Testosterone (16 ng/L) was detected once at a river station. One other hormone (17 β -estradiol) was analyzed for but not detected in any water sample.

As part of a national AFO study, the USGS has monitored runoff from streams and ditches draining a pastured cattle operation in the Rappahannock River Basin. Samples were collected during a range of high and low flows by using both grab samples and passive samplers. Preliminary results indicate detections of steroidal hormones in water and bed sediment, including cholesterol, cis-androsterone, coprostanol, estrone, epitestosterone, testosterone, 4-androstene-3, 17-dione, 17 α -estradiol, and 17 β -estradiol (Kolpin, D.W., USGS, oral comm., 2012).

In a continuing investigation regarding the potential connections between contaminants and fish health and intersex in the Chesapeake Bay watershed, the USGS collected samples of water and bed sediment at six active smallmouth bass nesting stream sites and one control site during spawning (Kolpin, D.W., USGS, oral commun., 2012). Although hormone analyses in this study have been limited, the steroidal hormones detected in water and sediments include 17 α -estradiol, 17 β -estradiol, cholesterol, estrone, sitosterol, and stigmasterol.

Fish

Although natural endogenous steroidal hormones are present in all animals, hormone concentrations in tissue such as blood plasma are potentially useful indicators or markers of exposures to environmental or exogenous sources of hormones. Iwanowicz et al. (2009b) analyzed blood plasma of smallmouth bass collected from two tributaries in the Chesapeake Bay watershed for an estrogen (17- β estradiol) and an androgen (testosterone). Fish upstream and downstream from municipal wastewater effluents were compared. The general increase in blood plasma hormone concentrations in fish downstream from wastewater sources indicates likely exposures to these or other hormonally active compounds in the wastewater effluents.

Citing weight of evidence for endocrine disruption in fish, the Environment Agency of England and Wales recently focused on risk-management strategies for natural (and all other) estrogenically active effluents that discharge to the aquatic environment (Gross-Sorokin et al. 2006). To date (2012), most studies of environmental hormones have focused on estrogenicity and related effects. Khanal et al. (2006) cited estrogenicity monitoring studies in more than 30 countries and concluded that natural steroidal estrogens such as estrone, 17 β -estradiol, estriol, and 17 α -estradiol are potent endocrine disrupters found in the environment. Phytoestrogens are structurally similar to 17 β -estradiol (estrogen in vertebrate animals) and their interaction with vertebrate estrogen receptors is a topic of active research in human and ecological health sciences. Currently (2012), research on other natural hormones as potential environmental contaminants is limited.

Recent research has linked environmental exposures of estrogenic compounds to fish intersex in Boulder Creek, Colorado, and the Potomac River Basin, Virginia (Vajda et al. 2008; Blazer et al. 2011). Because the sources of biogenic hormones in human and animal wastes are consistently associated with other estrogenic chemicals, these intersex studies have not linked specific effects to individual naturally occurring animal or plant hormones. For example, among the targeted chemicals analyzed by Vajda et al. (2008) that are known or suspected endocrine disruptors, 17 β -estradiol, estrone, estriol, and 17 α -ethynylestradiol as well as estrogenic alkylphenols and bisphenol A were identified and their mixtures were linked to intersex conditions in fish. However, VanDenBelt et al. (2004) compared the estrogenic potencies of 17 β -estradiol, estrone, 17 α ethinyl estradiol, and nonylphenol (surfactant) and showed that 17 α ethinyl estradiol can be as estrogenic as, or many times more estrogenic than 17 β -estradiol (estrogenic potencies are commonly reported relative to 17 β -estradiol), but nonylphenol is likely orders of magnitude less potent. Therefore, the naturally occurring estrogens are likely critical components of total estrogenicity in terms of potency and therefore must be considered key environmental contaminants.

Wildlife

A primary mode of exposure to exogenous steroids or environmental chemicals in birds is through maternal deposition (Adkins-Regan et al. 1995; Ottinger et al. 2005), which is significant across a range of endocrine disruptors and contaminants, with the distribution of the toxicant in the egg dependent on the chemical characteristics of that compound (Lin et al. 2004; Ottinger et al. 2005). This potential route of exposure is supported by a study in which Japanese

quail hens were given estradiol implants (Adkins-Regan et al. 1995). Assay of plasma samples showed increased circulating estradiol levels, with either daily estradiol injections or with a silastic implant containing crystalline estradiol. Eggs produced by treated females contained significantly greater estradiol concentrations in the yolks than those produced by control females; therefore, these data provide evidence for maternal transfer of steroid hormones to the offspring through the yolk (Adkins-Regan et al. 1995). Similarly, other lipophilic compounds, including the soy phytoestrogens, also transfer from the hen into the egg and, more specifically, the yolk (Lin et al. 2004).

Embryonic exposure to exogenous steroid hormones alters sexual differentiation in birds and results in reproductive impairment in adults (Adkins-Regan et al. 1990, 1995; Halldin et al. 1999; Ottinger and vom Saal 2002; Ottinger et al. 2005). Embryonic exposure to estradiol or androgen greatly affects sexual differentiation, whereas adult exposure is ineffective (Adkins-Regan et al. 1990; Ottinger and Abdelnabi 1997). Similar results have been observed in bobwhite quail and also in mammals, indicating that this effect may be common across species and even phyla (Lien et al. 1987).

Yonkos et al. (2010) exposed fathead minnows (*Pimephales promelas*), sheepshead minnows (*Cyprinodon variegatus*), and mummichogs (*Fundulus heteroclitus*) to solutions leached from poultry litter. The minnows exhibited intersex conditions whereas the mummichogs were unresponsive in all trials. Again, the potential mixture of hormonally active chemicals in the litter likely includes biogenic hormones as well as other endocrine disruptors; however, this study did not test for individual chemicals. In contrast, in a positive controlled exposure

experiment, 17 β -estradiol (biogenic estrogen) had no effect on the mummichogs but did have effects on the minnows (Yonkos et al, 2010).

Conclusions

Although only few studies have been conducted on the occurrence of biogenic hormones in the watershed, it is clear that these naturally occurring compounds are widespread. Previous studies have shown that wastewater management operations such as municipal sewer systems can result in point sources of biogenic hormones that are reflective of the combined inputs within the sewershed. Animal agricultural practices, particularly those associated with manure management and others where livestock have direct access to streams are also known sources of these contaminants. In addition, although these contaminants are naturally occurring they are likely to be elevated in concentrations above background downstream from these pathways to the environment. Hormones are known to be physiologically active at very low levels and previous and current research are addressing the need to further understand how these contaminants may be impacting aquatic environments. Because of the potential widespread extent of these contaminants and their potential to interfere with normal physiological functions of a variety of vertebrate, and other, species at low, environmentally relevant, concentrations additional monitoring and research is warranted.

2.10 Metals and Metalloids

Abstract

Parsing the effects of metals in the environment is a complex process as a result of the presence of naturally occurring metals and of the variability in biological availability of the metals under differing environmental conditions. Although the concentrations of trace metals have declined slowly since the 1980s, elevated concentrations remain in some regions of the Bay. The most prevalent cause of impairment is the presence of mercury in fish tissue at concentrations in excess of State guidelines, affecting more than 600 river miles and approximately 20,000 impoundment acres in the Chesapeake Bay watershed. In the water column, other metals are present at concentrations in excess of State standards for the protection of aquatic life. Both Maryland and West Virginia have identified impairments for aluminum and iron. Maryland listed additional impairments for chromium, lead, and zinc in sediment. In addition, a NOAA report documented sediment concentrations in excess of the ERM for nickel. Based on the spatial extent of the listed impairments and the additional data collected by NOAA, the extent of mercury contamination within the Bay watershed is considered to be widespread, whereas contamination with other metals is more localized. Exceedances of State standards and ERMs are indicators that some metals concentrations are adversely affecting Bay resources. Baywide and local reduction strategies are recommended for mercury. Additional metals impairments may be remediated through application of local reduction strategies.

Background

Metals are ubiquitous in the environment as constituents of both rock and sediment, and concentrations vary across geographic regions. They may be delivered to aquatic environments through natural erosion and weathering but also from anthropogenic sources. When concentrations in aquatic environments exceed natural background levels as a result of human activities, metals are considered contaminants. The term “metals” as used in this report refers to true metals, metalloids and, organometals.

Risk from metal contamination in aquatic environments is complex because of the unique nature and behavior of elements. For example, because metals occur naturally in all environmental media, they typically are present in the environment in mixtures. Some metals are nutrients that are essential for life and maintaining the health of humans, animals, plants, and microorganisms. Unlike organic contaminants, metals are not degraded or destroyed by chemical or biological processes, but instead those processes can transform metals from one species to another (valence states) and can convert them between organic and inorganic forms. These factors, along with differing characteristics for each metal, create highly variable biological and ecological effects in the environment, making ecological risk assessment uniquely challenging. Extended exploration of these topics is beyond the scope of this report. Moreover, this chapter is not intended to be an exhaustive review of all metal contaminants; its focus is on those metals that have been found within the Chesapeake Bay watershed.

According to Kimbrough et al. (2008), fossil fuel and waste burning, mining and ore processing, chemical production, and agriculture are the sources largely responsible for the elevated environmental metal concentrations observed in coastal waters. Metals are transported to coastal waters primarily through runoff and atmospheric deposition. The relative contribution from each source varies by metal, proximity to sources, and chemical phase (dissolved or particulate-bound).

Mercury, one of the most prevalent of the metals contaminants, is delivered to most aquatic ecosystems by deposition from the atmosphere, primarily through precipitation (USGS 1995). Anthropogenic sources of mercury contamination in the atmosphere include coal combustion, chlorine alkali processing, waste incineration, and metal processing (USGS 1995). Once deposited in aquatic ecosystems, mercury may be transformed to methylmercury; an organic form of mercury that is the most toxic and that readily bioaccumulates and is biomagnified (USGS 2000). Methylation occurs in sediments of freshwaters, estuaries, and coastal zones; however the rate of net methylmercury creation from different sediment types is highly variable, with higher methylation rates occurring in the organically rich, anoxic sediments common in wetland areas (Luoma and Rainbow 2008). According to the U.S. EPA's Region 5 Superfund Division, mercury is highly toxic and is a known mutagen, teratogen, and carcinogen (U.S. EPA, 2011). Factors such as chemical form; dose; route of ingestion; and the species, sex, age, and overall health of the exposed organism play a role in determining the level of toxicity and the environmental effects. Acute exposure to mercury most commonly affects the central nervous system and kidneys in fish, birds, and mammals (U.S. EPA 2011).

The presence of ecological and biological effects resulting from metal contamination have been evident since the height of the Industrial Revolution; a substantial amount of literature related to metals in the environment dates as far back as the mid 1800s (Kapustka et al. 2004). Trace metal concentrations in the Chesapeake Bay peaked in the 1970s and have slowly declined since the 1980s; despite this downward trend, however, concentrations remain elevated in some regions of the Bay (Hartwell and Hameedi 2007).

Occurrence information for this chapter was gathered primarily from the 2010 integrated assessments. This chapter identifies impairments and occurrences and does not attempt to compare loadings among jurisdictions. In addition to the Integrated Reports, information was captured from State fish consumption advisories, fish tissue monitoring program data from Maryland and Virginia, various reports from NOAA and other Federal agencies, and several studies related to metal contamination throughout the Chesapeake Bay region.

Because in-depth review of the biological and ecological effects is beyond the scope of this report, a focus has been placed on selected metal contaminants that have occurred within the Chesapeake Bay watershed. The exclusion of a particular metal in this discussion of severity does not imply insignificance. Although the science surrounding metals and their biological and ecological effects continues to be studied intensively and is evolving rapidly, information in some areas is insufficient to support a quantitative assessment (US EPA 2007).

Water Column

Mercury

Available data from Mason et al. (1999) indicate that overall mercury concentrations in the Chesapeake Bay were <15 mg/L except at sites in highly urbanized areas such as the Baltimore Harbor and the confluence of the Anacostia and Potomac Rivers in State. Total mercury concentrations in the upper Bay and in the subestuaries decreased down-estuary, coinciding with decreases in suspended particulate matter. Increased concentrations of mercury, especially methylmercury, were observed during seasonal bottom water anoxic conditions at the Baltimore Harbor. None of the Chesapeake Bay jurisdictions reported impairments for mercury in the water column.

Other Metals

Maryland, Pennsylvania, and West Virginia each identified impairments for metals other than mercury. Both Maryland and West Virginia listed water impairments for aluminum, iron, and manganese, with iron causing more than 300 miles of impairments. Copper and selenium were identified in excess concentrations. Pennsylvania's impairment of 203 river miles was attributed to "other metals" (metals other than mercury).

Sediment

Mercury

Concentrations of mercury in sediment in the Baltimore Harbor region have been found at levels below impairment benchmarks (Mason 1999). None of the Bay jurisdictions documented sediment impairments for mercury.

Other metals

Maryland was the only state to identify any sediment impairments specifically attributable to metals concentrations. Zinc was the most widespread of the metals contaminants, affecting an area smaller than 10 square estuarine miles. Sediment concentrations in excess of the State standards for the identified metal compounds have the potential adversely affect aquatic life.

In order to characterize the extent and magnitude of contaminated sediments in the Chesapeake Bay, Hartwell and Hameedi (2007) analyzed sediment samples for a suite of metals and metaloids: Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, and Zn. The report documented metals enrichment in nearly all locations. The authors noted declining concentration trends with some site-specific exceptions, such as the Patuxent River and several southeastern tributaries, that demonstrate high levels of cadmium. According to the report, Baltimore Harbor is one of the most contaminated sites in the Bay and metal concentrations in sediment near Ft. McHenry, the Patapsco River, and the Potomac River are elevated. The Elizabeth River is also heavily contaminated; concentrations of most constituents are in the 75th percentile. In the northern part of the Bay, metals enrichment rates are higher than in the middle and southern parts of the Bay, specifically for concentrations of manganese, nickel, chromium, and lead, which are elevated by factors of 1.5 to 2.0. Throughout the Bay, concentrations of copper and zinc are elevated by factors of 1.5 to 3.0. Sites near heavily developed areas, such as the Magothy River in Maryland and Broad Bay in Virginia Beach, also exhibited elevated levels of metal enrichment. Large western tributaries of the Bay demonstrated slightly higher concentrations than the lower

mainstem. The authors attribute the high degree of variability in metals concentrations from site to site to interactions involving sediment grain size, proximity to sources, and the inherent particle reactivity of the elements.

Fulton et al. (2007) inventoried toxic contaminants in five selected areas of the Bay for which data previously had been insufficient: the Chester River, Nanticoke River, Pocomoke River, Lower Mobjack Bay (Poquosin and Back Rivers), and the South and Rhode Rivers. In the study, sediment, water-column and benthic analyses were examined to characterize the bio-effects of the contaminants. Total metal concentrations were found to be highest in the lower South River and the middle Chester River. Of the 60 stations, only 2 had contaminant concentrations that exceeded the ERM for any analyte; in the upper South River, concentrations at 2 stations exceeded the ERM (51.6 ppm) for nickel. The most common metal ERL exceedances, by river system, were arsenic, nickel, and zinc in the Chester River, arsenic and nickel in the Nanticoke River, and arsenic in the Pocomoke River.

Based on guidance, in the instance of the documented exceedance of the ERM for nickel acutely toxic impacts can be expected at least 50% of the time (Fulton et al., 2007). Individually, the other metals were not present in high enough concentrations to affect aquatic life.

Fish

Mercury

The primary method of human exposure to mercury is through ingestion of contaminated seafood (USGS 2000). States monitor levels in fin fish tissue and issue fish consumption advisories for the species found to have elevated levels in specific areas in order to protect human health. An advisory recommends a particular number and size of meals safely consumed by the general public, pregnant women, and children; avoidance recommendations advise that no meals should be eaten regardless of meal size or population demographics.

Maryland currently has fish consumption advisories due to mercury for 10 species of fish in rivers, lakes, and reservoirs within the Chesapeake Bay watershed. The number of recommended meals per month for the general population ranges from one to eight. The State of Maryland reported impairments for approximately 12,500 acres of impoundments. A TMDL report has been completed for nearly 8,200 of those acres.

The State of Virginia currently has fish consumption advisories for mercury for nine species in the Chesapeake Bay and small coastal basin, James River, Rappahannock River, and York River Basins. The number of recommended meals for the general population is no more than two per month for all species. Virginia does not have any avoidance recommendations due to mercury in fish tissue at this time. Virginia reported a total of approximately 5,980 acres in impoundments, approximately 300 miles in rivers and streams, and approximately 23 square miles in estuaries as impaired by mercury in fish tissue.

The District of Columbia advises the general population avoid carp, eel, and catfish from the Potomac and Anacostia Rivers; however, the cause of advisory is not specified. No

impairments specifically attributable to mercury in fish tissue have been reported in Washington, D.C.

The State of New York notes impairment in the lower Susquehanna River. The State advises that up to one meal of walleye longer than 22 inches from the Susquehanna River may be consumed by the general population as a result of mercury contamination.

The State of West Virginia has issued statewide advisories of one to two meals per month for more than 10 species within waters flowing to the Chesapeake Bay as a result of mercury contamination. There is an avoidance recommendation for carp in the Shenandoah River, and a limit of one meal per month for smallmouth bass longer than 12 inches as a result of mercury contamination. West Virginia did not list any of the free-flowing streams to the Chesapeake Bay as impaired with respect to mercury in the 2010 Integrated Report.

The State of Pennsylvania has issued advisories for 37 water bodies within the Susquehanna River Basin as a result of mercury contamination; consumption recommendations are for one to two meals per month. One lake within the Potomac River Basin has an advisory of two meals of walleye per month as a result of mercury contamination. In the 2010 Integrated Report, Pennsylvania reported that approximately 290 miles of rivers and streams within the Chesapeake Bay watershed are considered impaired as a result of mercury in fish tissue. Approximately 2,052 acres of impoundments are considered impaired as a result of mercury in fish tissue.

The State of Delaware does not have any fish consumption advisories as a result of mercury in fish tissue within waters flowing into the Chesapeake Bay watershed.

The toxicity of mercury in fish tissue is associated with methylmercury, a highly toxic compound that crosses biological membranes, accumulates in the exposed species, and can be biomagnified up the food chain (Sandheinrich and Wiener 2011). State monitoring programs commonly measure only total mercury, and criteria (such as U.S. EPA 2001) are typically stated as criteria for methylmercury. Because there is little difference in the fish-tissue concentrations when both compounds are measured, conversion from total mercury to methylmercury requires a decrease of 10% at most.

The U.S. EPA (2001) issued a water-quality criterion for methylmercury of 0.3 ppm wet weight fish tissue for the protection of human health. This criterion was developed on the basis of a review of high-dose exposures (i.e., Minimata Bay, Japan) that have resulted in neurotoxic effects, including mental retardation, cerebral palsy, deafness, blindness in utero, and sensory and motor impairment in adults. Studies of chronic low-level mercury exposure have shown developmental effects in children, including abnormalities in memory, attention, and language. Other studies have reported cardiovascular and immunological effects.

Within the Bay watershed, Virginia's South River is the area of greatest concern with respect to mercury contamination. Except for stocked trout, which spend little time in the river, no fish consumption is recommended. From 1929 to 1950, mercury was used as a catalyst in fiber production at the DuPont plant in Waynesboro, Virginia. During that time, strict

storage and disposal regulations did not exist, and mercury was released into the South River. A serious contamination problem was discovered in the 1970s (South River Science Team 2009); the Virginia Department of Health subsequently issued advisories for fish consumption along the South River and on the South Fork Shenandoah River. As part of a settlement agreement, DuPont paid a penalty and established a State-administered (by VA DEQ) trust fund to support a 100-year mercury-monitoring program for fish, water, and river sediment. The most recent fish-sampling data listed on the VA DEQ (2012) Web site are from 2007. At several sampling locations downstream from the plant, mercury concentrations frequently exceeded 1.5 ppm (five times the U.S. EPA (2001) criterion) in smallmouth bass (*Micropterus dolomieu*), redbreast sunfish (*Lepomis auritus*), and white sucker (*Catostomus commersoni*).

Sandheinrich and Wiener (2011) reviewed the toxic effects of methylmercury by evaluating the relation between tissue concentrations and toxic effects. Mercury exposure can adversely affect the survival, growth, and reproduction of fish. Wiener and Spry (1996) reported that mortality due to mercury poisoning is observed only at extremely high tissue concentrations (6--20 ppm wet weight in muscle). Behavioral effects include hyperactivity and altered shoaling activity (Webber and Haines 2003), which occurred in a laboratory study with golden shiners (*Notemigonus crysoleucas*). The fish were fed a diet containing 0.96 ppm methylmercury and had whole-body concentrations of 0.52 ppm wet weight. Reduced spawning success occurred in fathead minnows (*Pimephales promelas*) at whole-body minus gonad concentrations of 0.71 to 0.92 ppm wet weight (Drevnick and Sandheinrich 2003). Methylmercury causes oxidative stress in fish tissues through the formation of radical oxygen

species and lipid peroxidation. Organs affected include the brain and liver (summarized in Sandheinrich and Wiener 2011).

On the basis of their literature review, Sandheinrich and Wiener (2011) concluded that effects on fish biochemical processes, damage to cells and tissues, and reduced reproduction have been demonstrated at methylmercury concentrations of about 0.3 to 0.7 ppm in the whole body or 0.5 to 1.2 ppm in muscle tissue. Given the high concentrations present in fish in Virginia's South River, there is a great likelihood that fish in this water body are being adversely affected by methylmercury exposure.

Other Metals and Metalloids

No impairments were reported by any states for metals other than mercury in fish tissue in waters flowing to the Chesapeake Bay. According to the Maryland Department of the Environment's (MDE) human-health screening study of finfish tissue collected from 1985 to 1997, tissue concentrations in finfish from the Maryland portion of the Chesapeake Bay did not exceed the established conservative human-health risk-based screening values for arsenic, silver, cadmium, chromium, copper, mercury, nickel, or zinc (MDE, nd). Although concentrations of inorganic arsenic in a few individual bluefish, striped bass, and white perch exceeded the screening values, the MDE noted that those species exhibit migratory behavior and therefore are not considered a target species in the Core Monitoring Program (MDE, nd). It should be noted that this report is 15 years old; some screening values may be different now (2012). Additionally, this report focuses on human-health criteria only; aquatic-life criteria are not examined.

Virginia conducted a statewide fish-tissue monitoring survey most recently in 2008. A review of the data for waters within the Chesapeake Bay watershed indicates that concentrations of arsenic in 83 of 477 samples from the Bay watershed exceeded the Virginia Department of Environmental Quality's screening value for arsenic (VA DEQ 2008). Although arsenic is detected at concentrations in excess of the screening value, VA DEQ has not identified these water bodies as impaired. This is in acknowledgement of the fact that the fish-tissue data are based on the concentration of total arsenic, whereas toxicity is associated only with inorganic arsenic. Inorganic arsenic may be a very small portion of the total arsenic value. VA DEQ uses this information to identify areas where additional study is needed and has indicated that a method for analyzing inorganic arsenic may be utilized for these efforts (VA DEQ 2010). Concentrations in several samples exceeded the detection limits of <0.1 ppm wet weight for lead and <0.5 ppm wet weight for selenium (VDEQ 2008). Because available data were insufficient to identify a threshold associated with a risk of human toxicity, these waters were not identified as impaired.

Wildlife

Mercury

Mercury concentrations in blood have been measured in several species of birds in the Chesapeake Bay watershed. Levels in osprey nestlings from regions of concern and reference sites ranged from 0.105 to 0.470 (Rattner et al 2008); adult tree swallow samples collected at a contaminated site in the South River (tributary of the Shenandoah River, which flows into the Potomac River) had mean concentrations of <3.56 ppm wet weight (Brasso

and Cristol 2008, Hawley et al. 2009), and values were <0.5 ppm wet weight in Nelson's sparrow (*Ammodramus nelsoni*) and the saltmarsh sparrow (*A. caudacutus*) from several Bay locations. With the exception of tree swallow samples from the South River, mercury concentrations observed in these species generally were less than the 0.400-ppm wet weight that has been associated with adverse sublethal effects in birds (Scheuhammer et al. 2007), although recent studies suggest that such concentrations could evoke endocrine disruptive effects in nestlings (Wada et al. 2009).

Mercury is readily incorporated into feathers in growing birds and adults following molt. Mercury levels in feathers of 14- to 16-day-old nestling black-crowned night herons from Baltimore Harbor and Holland Island did not differ, and ranged only from 0.04 to 0.23 ppm dry weight (Golden et al. 2003b). Mercury concentrations in feathers of 40- to 45-day-old osprey nestlings were greater in the Elizabeth River (0.26-2.40 ppm dry weight) than in Baltimore Harbor and the Patapsco River, Anacostia River, the middle Potomac River, and the South, West, and Rhode Rivers (values ranged from 0.01-1.53 ppm) (Rattner et al. 2008). Molted feather samples collected from 83 occupied bald eagle nests in the Chesapeake Bay watershed averaged 3.82 ppm dry weight (Cristol et al. 2010). Feathers from adult tree swallows in the vicinity of the South River in Virginia had averaged mercury concentrations of 13.55 ppm dry weight (Brasso and Cristol 2008). With the exception of samples collected in the mercury-contaminated South River location in Virginia, values were generally well below the concentration commonly associated with adverse effects (7.5 ppm dry weight) (Eisler 1987).

Mercury was detected in muscle tissue from 4 of 21 snapping turtles collected from Canal Creek in the upper Chesapeake Bay watershed in 1994, with values ranging from 0.10 to 0.20 ppm, which are less than the Food and Drug Administration (FDA) action level of 1 ppm (U.S. Army Hygiene Agency 1994).

Since 1988, several studies in which eggs from ospreys (Rattner et al. 2004), peregrine falcons (Morse 1994, U.S. Fish and Wildlife Service et al. 2004, Clark et al. 2009), common terns (French et al. 2001), and bald eagles (Mojica and Watts 2008, 2011) indicated that mercury concentrations averaged well below 0.5 to 1.5 ppm wet weight, the generally accepted toxicity threshold for reproductive effects in bird eggs (Wiener et al. 2003).

In an unpublished study of dabbling and diving ducks collected in Baltimore Harbor and the Rhode River from 1987 to 1989 (M.W. Tome, USGS, unpublished data), mercury concentrations in 174 liver samples from mallards, black ducks, canvasbacks, ruddy ducks (*Oxyura jamaicensis*), and scaup ranged from 0.03 to 1.6 ppm dry weight. In long-tailed ducks collected in 1994, mercury concentrations in liver samples ranged from 0.11 to 1.2 ppm dry weight (Mashima et al. 1998). Mercury concentration in the kidney of a bald eagle found dead along the James River in 2001 was determined to be 8.80 ppm wet weight (Southeastern Cooperative Wildlife Disease Study Case Number CC63-02). These values in adult birds are well below the 20-ppm level in liver or kidney tissue that is associated with toxicity (Wiener et al. 2003).

Other Metals and Metalloids

Considerable historic data exist for the concentrations of metals in tissue of wildlife in the Chesapeake Bay region. Heinz and Wiemeyer (1991) pointed out that metals did not seem to be involved in the decline of bald eagle and osprey populations in the Chesapeake Bay watershed and, with the exception of lead exposure from spent shot, concentrations of several other metals were less than the adverse effect threshold for several species of waterbirds. Mercury and selenium have been measured in eggs, liver, and kidney, whereas other metals (e.g., lead, cadmium, nickel) generally have been quantified in liver and kidney because they are poorly transferred into eggs.

The Contaminants Exposure and Effects–Terrestrial Vertebrates (CEE-TV) database contains more than 50 records for Chesapeake Bay waterbirds from 1988 to the present (2012) that describe lead concentrations in liver tissue (Rattner and McGowan 2007, Rattner, unpublished data). For 26 of these records (representing 84 individuals including waterfowl, geese, and bald eagles), lead concentration in liver tissue exceeded 2 ppm wet weight, a value associated with subclinical poisoning in waterfowl (Franson and Pain 2011), and ranged up to 183 ppm dry weight in one of the bald eagles (> 10 ppm wet weight is compatible with death; Franson and Pain 2011). Many of these necropsy reports were related to the ingestion of spent lead shot that historically was used for hunting waterfowl but was phased out of use by 1991. Lead can be incorporated into feathers of growing birds (Golden et al. 2003a), and has been proposed as a sensitive minimally invasive indicator of exposure. Concentrations in feathers of black-crowned night-heron nestlings from Chincoteague Bay and Holland Island were lower (≤ 0.13 ppm dry weight) than those in feathers of 14- to 16-day-old nestlings from

Baltimore Harbor (0.32 ppm) (Golden et al. 2003b). A similar tendency was noted in concentrations in feathers of 40- to 45-day-old osprey nestlings collected from Baltimore Harbor in 2000 (geometric mean: 1.25 ppm dry weight) compared to those in feathers of nestlings from the South River reference area near Annapolis (0.66 ppm), whereas those in samples from the middle Potomac River watershed were intermediate (0.96 ppm) (Rattner et al. 2008). Concentrations in osprey nestling feather samples collected from the Elizabeth River in 2001 (1.47 ppm dry weight) were significantly greater than in those from the South, West, and Rhode Rivers reference site (0.54 ppm) (Rattner et al. 2008). Although lead concentrations of concern in feathers of waterbirds in Chesapeake Bay are elevated compared to those in bird feathers from reference sites, it is not possible to relate the concentrations to toxicity thresholds or assess the risk of lead in feathers to overall waterbird health.

Reports of lead in liver tissue of wild mammals in the Chesapeake Bay region are far more limited, and are focused on military sites with known or suspected contamination. Lead was not detected in liver or kidney tissue of woodchucks (*Marmota monax*) collected in the vicinity of small arms and skeet ranges at Aberdeen Proving Grounds in Maryland, although low levels were detected in blood (mean values ≤ 0.92 nanograms per milliliter (ng/mL) wet weight) and bone (mean values ≤ 13 ppm dry weight), indicating its bioavailability (Johnson et al. 2004). In 1993, tissues were collected from 150 white-tailed deer (*Odocoileus virginianus*) in the vicinity of Aberdeen Proving Grounds in the upper Chesapeake Bay watershed and analyzed for metals (U.S. Army Center for Health Promotion and Preventative Medicine 1995a). Lead concentrations at six study sites ranged from 0.035 to 4.59 ppm in muscle tissue and from 0.012 to 1.75 ppm in liver tissue. A human-health risk assessment

indicated a likely elevated risk to humans consuming these tissues, but lead was not a principal toxicological driver in this analysis. In a 1995 biomonitoring study conducted at Aberdeen Proving Grounds in Maryland, only 1 of 34 carcasses of white-footed mice (*Peromyscus leucopus*) collected from various locations was found to contain lead, but the concentration (3.28 ppm wet weight) and was considered to represent background concentrations (Whaley 1996).

Lead was detected in each of six snapping turtles (*Chelydra serpentina*) collected from Watson Creek in the upper Chesapeake Bay from Canal Creek in 1994, ranging from 0.39 to 2.29 ppm (U.S. Army Hygiene Agency 1994). The toxicological risk of these concentrations to the turtles and to humans consuming turtles was not addressed in this study. In a biomonitoring study at Aberdeen Proving Grounds, 22 anuran samples (Southern leopard frog (*Rana utricularia*) and green frog (*R. clamitans*)) were collected and analyzed for metals (U.S. Army Center for Health Promotion and Preventative Medicine 1995b). Whole-body burdens of lead were detectable in 5 of the 22 samples (2.10-86.4 ppm), and it was suggested that reproductive performance could possibly be affected by these concentrations.

Cadmium concentrations in livers of dabbling and diving ducks from Baltimore Harbor and the Rhode River averaged <2 ppm dry weight (M.W. Tome, USGS, unpublished data). The mean concentration in livers of long-tailed ducks collected during the Chesapeake Bay avian cholera outbreak in 1994 was 2.65 ppm dry weight, but was much greater in kidney tissue, averaging 22.7 ppm and ranging up to 81 ppm (Mashima et al. 1998). The mean cadmium concentration in livers of mute swans collected at Blackwater and Eastern Neck National

Wildlife Refuges was 16 ppm dry weight, and ranged up to 94 ppm (Beyer et al. 1998). The toxicity threshold for cadmium in liver and kidney has not been adequately established for birds (perhaps >100 ppm wet weight; Beyer 2000), and seemingly elevated concentrations in individuals may merely reflect that cadmium values increase with age. Cadmium is rarely detected in eggs, and is poorly transferred into feathers of nestlings. Cadmium was not detected in blood of osprey nestlings collected in regions of concern, and concentrations in feathers were <0.28 ppm dry weight (Rattner et al. 2008).

Cadmium concentrations in 150 white-tailed deer (*O. virginianus*) collected in the vicinity of Aberdeen Proving Grounds ranged from 0.012 to 0.37 ppm in muscle and 0.012 to 0.74 ppm in liver (U.S. Army Center for Health Promotion and Preventative Medicine 1995a). A human-health risk assessment indicated the likelihood of an elevated risk to humans consuming these tissues, but cadmium was not a principal toxicological driver in this analysis.

Selenium concentrations in common tern and peregrine falcon eggs averaged <2.6 micrograms per gram ($\mu\text{g/g}$) dry weight (Morse 1994; French et al. 2001; U.S. Fish and Wildlife Service et al. 2004; Clark et al. 2009; J.B. French, USGS-Patuxent Wildlife Research Center, unpublished data), and were clearly less than levels that cause embryotoxicity, although this threshold is contentious (Ohlendorf 2003). Concentrations of selenium in the liver of waterfowl (M.W. Tome, USGS, unpublished data) and mute swans (Beyer 1998) averaged < 20 ppm dry weight and, when converted to wet weight, were less than sublethal adverse effects in young and adults (Heinz 1996). Notably, livers of male

ruddy ducks collected on the Rhode River in 1987-89 appeared to be higher, averaging 29.8 ppm dry weight with a maximum value of 140 ppm (M.W. Tome, USGS, unpublished data). Selenium was present in blood of nestling ospreys at concentrations ranging from 2.34 to 18.2 ppm dry weight, and in feathers at concentrations ranging from 0.71 to 9.73 ppm, and did not approach levels associated with toxicity (Rattner et al. 2008).

Concentrations of aluminum, boron, chromium, copper, iron, manganese, strontium, and zinc were frequently detected in tissues and eggs of Chesapeake Bay waterbirds collected since 1988, and were generally in the range of values for healthy captive birds. Arsenic, barium, beryllium, molybdenum, nickel, and vanadium were commonly analyzed for but rarely detected in tissues and eggs. Arsenic concentrations in 150 white-tailed deer (*O. virginianus*) collected in the vicinity of Aberdeen Proving Grounds ranged from 0.07 to 0.91 ppm in muscle and 0.06 to 1.14 ppm in liver (U.S. Army Center for Health Promotion and Preventative Medicine 1995a). A human-health risk assessment for arsenic suggested the possibility of an elevated risk to humans consuming these tissues from deer collected at some of the study sites.

Conclusions

Plentiful data exists on concentrations of metals and metalloids in the various media as a result of both federal and routine jurisdiction monitoring. Mercury impairments dominate the 303(d) listings identified for metals with more than 600 river miles and 20000 acres of impoundments listed for fish tissue impairments. Though impairments in the water column are not as common, both Maryland and West Virginia have identified impairments for aluminum and iron. In addition, Maryland has identified sediment impairments for chromium, lead and zinc. The impact of mercury contamination on fish tissue is widespread and baywide based on documented fish consumption advisories. However, contamination from other metals is more localized as

evidenced by the cited impairments. When considering severity, exceedances of state standards and ERMs are indicators that some metals concentrations are adversely impacting Bay resources.

3.0 Integrative Responses of Fish to Contaminants

In addition to cataloging the extent and severity of toxic effects in the Bay by contaminant class, there is a need to describe studies that indicate the adverse effects of fish exposure to complex mixtures of both legacy contaminants and contaminants of emerging concern (CEC). These complex mixtures can have additive (Silva et al. 2002; Brian et al. 2005; Correia et al. 2007) as well as synergistic or antagonistic effects (Micael et al. 2007; Santos et al. 2006; Sárria et al. 2011). In addition, it is increasingly recognized that many chemicals, particularly those that affect the endocrine and immune systems, may not elicit the typical dose-response curves. Significant effects may be observed at very low levels, and nonmonotonic (nonlinear) dose responses are increasingly demonstrated (Welshons et al. 2003; Vandenberg et al. 2012). Additionally, most monitoring of chemical concentrations is a snapshot in time, and the results depend on sampling time and numerous environmental factors such as climatic conditions and flow. For instance, atrazine concentrations measured in the Monocacy River, State, in the spring were 100 times those measured in the fall (Alvarez et al. 2009), yet short-term exposures, particularly in early life stages, can have long-lasting effects on both the endocrine and immune systems (Leet et al. 2011; Milston et al. 2003; Mcallister and Kime 2003; Liney et al. 2005).

For these reasons, biological effects monitoring is increasingly recognized as an important factor in assessing the effects of toxic chemicals on ecosystem health (Dubé et al. 2006; Ankley et al. 2010). The following biological indicators of a degraded ecosystem have been observed within the Chesapeake Bay watershed: increased incidence of infectious disease and parasite infestations contributing to increased mortality; feminization (intersex, plasma vitellogenin) of largemouth and smallmouth bass and other signs of endocrine disruption; reduced reproductive success and recruitment of yellow perch in certain highly urbanized tributaries; and liver and skin tumors of brown bullhead. It is important to describe these effects and the weight-of-evidence approach that indicates possible associations with exposure to toxic chemicals. Furthermore, many of these measurements of biological exposure and response can be used as environmental indicators to evaluate status and trends on varying spatial scales.

Infectious Diseases, Parasites, Immune Responses, and Fish Kills

Substantial increases in disease reports for fishes, amphibians, and crayfish have been reported from 1970 to 2009 (Johnson and Paull 2010), and anthropogenic drivers, including toxic chemicals, may play direct and indirect roles in these increases. Recent studies indicate that increased disease incidence can be related to human-induced land-use changes (Patz et al. 2004), increased nutrient concentrations (McKenzie and Townsend 2007), climate change (Karvonen et al. 2010), and toxicants (Feingold et al. 2010). Exposure to a range of chemicals has been shown to cause immune-system effects that can increase susceptibility to disease, increase the persistence and hence shedding of infectious organisms, and alter the severity of disease. Hence,

understanding disease epizootics in wild populations is complex and requires a multidisciplinary approach.

A number of epizootic diseases have been documented in the Chesapeake Bay in recent decades. Ulcerative skin lesions of menhaden (*Brevoortia tyrannus*) were determined to be caused by the oomycete *Aphanomyces invadans* (Blazer et al. 1999, 2002; Kiryu et al. 2002), a pathogen responsible for major mortalities in freshwater and estuarine fishes worldwide (Baldock et al. 2005). Skin and internal lesions have also been observed in a high percentage (> 50%) of striped bass (*Morone saxatilis*) from the Bay and its tributaries. Disease in striped bass has been attributed to a variety of *Mycobacteria* spp. (Ottinger and Jacobs 2006; Gauthier and Rhodes 2009). Mycobacteriosis is a chronic disease; however, negative population-level effects have been demonstrated, indicating the importance of disease in management and stock assessment (Gauthier et al. 2008). The role of toxic chemicals in susceptibility to these infectious diseases is currently unknown.

In 2002, major mortality of smallmouth bass (*Micropterus dolomieu*) and other freshwater fishes was observed in the South Branch Potomac River, State(s). Similar fish kills occurred in the North Fork of the Shenandoah River in 2004, the South Fork Shenandoah River in 2005, and the Monocacy River in 2009. Adult fishes during the spring are affected, and most dead and dying fish exhibit a variety of external skin lesions. A number of potential pathogens, including the bacteria *Aeromonas salmonicida*, *Flavobacterium columnare*, *Aeromonas hydrophila*, and other motile Aeromonads, and internal trematode and myxozoan parasites, as well as external parasites including trematodes and leeches, have all been identified or cultured; however, no consistent

pathogen or parasite was identified as a single cause of the mortalities at all sites (Blazer et al. 2010). These findings indicate that certain sensitive (immunocompromised) species are affected by a variety of opportunistic pathogens, eventually leading to lesions and(or) death.

Raised skin lesions, which range from hyperplasia (proliferation of normal epidermal cells) to papillomas (benign neoplasia), are observed in adult bass from the Potomac (Blazer et al. 2010) and Susquehanna Rivers. The cause of these lesions is currently unknown; however, similar lesions have been described in a variety of fish species. In some instances viral particles have been observed in similar lesions by using electron microscopy (Anders and Möller, 1985; Lee and Whitfield 1992; Quackenbush et al. 2001); in other cases, investigators have attempted to culture and(or) visualize viruses by using electron microscopy and have not found any indication of a viral etiology. There are a number of reports of increased prevalence of these types of papillomas at site impacted by industrial and(or) sewage effluent (Korkea-aho et al. 2006, 2008), increased by exposure to androgens (Kortnet et al. 2003) and they, together with numerous other indicators, are used by the International Council for the Exploration of the Sea (ICES) as an indicator of environmental condition (need refBucke et al. 1996).

All of the affected watersheds are also areas in which a high prevalence and severity of intersex or testicular oocytes have been documented (see below; Blazer et al. 2007a, 2011). The co-occurrence of skin lesions/mortalities and signs of endocrine disruption further indicate that exposure to chemical contaminants and other stressors may contribute to the reduced health of these populations. For instance, whereas exposure to estrogenic compounds is considered a primary cause of feminization (testicular oocytes and plasma vitellogenin) of male fishes,

estrogens have also been shown to modulate disease resistance (Iwanowicz and Ottinger, 2009; Robertson et al. 2009). Exposure to atrazine, a commonly detected herbicide in the Chesapeake Bay watershed, including sites where fish kills have occurred (Alvarez et al. 2008, 2009), has been shown to increase susceptibility of silver catfish to *A. hydrophila* at sublethal concentrations (Kreutz et al. 2010), and is also associated with increased trematode infections in some amphibians (Rohr et al. 2008). Arsenic, used in pesticides, used as an additive in poultry feed, and found naturally, has been reported to modulate the immune response of fishes (Hermann and Kim, 2005; Lage et al. 2006) and is also associated with skin lesions in humans (Kazi et al. 2009). Exposure to arsenic was shown to enhance the ability of *A. hydrophila* to colonize and disseminate within exposed catfish (Datta et al. 2009) and to inhibit the ability of zebra danio to clear viral or bacterial infections (Nayak et al. 2007). A substantial increase in arsenic concentrations in the skin and anterior kidney (major immune organ of fish) from March to May (leading up to the fish kills) was demonstrated in smallmouth bass from the Shenandoah River (Blazer et al. 2010).

Feminization of Male Bass

Two indicators of feminization of male fishes that have been used worldwide are testicular oocytes (intersex) and vitellogenin. Experimental exposures of various fish species to natural and synthetic estrogens have shown that the most sensitive stage for induction of oocytes within the testes is during sexual differentiation, within 2 to 3 weeks after hatching. It has also been shown that exposures at these early life stages can lead to a greater sensitivity to estrogenic exposures later in life (Liney et al. 2005). Plasma and liver vitellogenin mRNA may be indicative of more

recent exposure. Estrogens induce vitellogenin production by the liver. Normally this process occurs only in egg-producing females; however, exposure to abnormal concentrations of estrogens can induce immature or male fishes to produce vitellogenin.

Studies in the Chesapeake Bay watershed have concentrated on smallmouth and largemouth (*M. salmoides*) black bass species, although species comparisons have been conducted in some areas. Results of the U.S. Geological Survey Biomonitoring of Environmental Status and Trends program showed black bass species to be sensitive species for reproductive endocrine disruption studies. In surveys conducted from 1995 to 2004 in nine river basins (Mississippi, Columbia, Rio Grande, Colorado, Yukon, Pee Dee, Apalachicola, Savannah, and Mobile), intersex was most prevalent in smallmouth and largemouth bass. Largemouth bass were collected at 52 of the 111 sites sampled and at least one male with testicular oocytes was collected at 23 (44%) of these sites, with an overall prevalence of 18%. Smallmouth bass were collected at 16 sites and at 7 (44%,) at least one male with testicular oocytes was observed, with an overall prevalence for smallmouth bass of 33% (Hinck et al. 2009). Similarly, largemouth bass within the Potomac River drainage also show signs of feminization, but may be less sensitive than smallmouth bass (Blazer et al. 2007a; Iwanowicz et al. 2009). The prevalence of intersex in smallmouth bass in the Potomac River is considerably higher than that observed in the national survey, ranging from 50 to 100% (Blazer et al. 2007a, 2012).

With respect to reproductive endocrine disruption, most studies to date have focused on the prevalence and severity of, and factors that contribute to, feminization (intersex and vitellogenin in male fishes). Because aquatic organisms may be exposed to complex mixtures of chemicals

that can have additive, synergistic, or antagonistic effects, it is difficult to identify one chemical or one source of the estrogenic compounds. Hence, biological effects, as well as chemical monitoring, were used to determine the extent of reproductive endocrine disruption throughout the Potomac River and nearby drainages, to identify potential causes, sources, and associated land-use practices and to document effects. Initial biological effects monitoring indicated that the prevalence of testicular oocytes varied from 100% at some sites in the Shenandoah River to low or background levels (10-14%) at selected out-of-basin sites such as the Gauley, Tygart, and Cheat Rivers. Prevalence in the South Branch of the Potomac River in West Virginia was intermediate, with 50 to 75% of the male bass affected. These early surveys indicated a probable gradient of intersex in West Virginia and Virginia associated with human population and agricultural land use in the counties containing the sites. Although sample sizes of male smallmouth bass were small at some sites, there was an indication that, even within out-of-basin rivers such as the Greenbrier River, prevalence of intersex at downstream sites increased with human population and agricultural land use (Blazer et al. 2007a). Further studies within the Bay watershed are in progress.

Feminization of male fishes has most commonly been associated with exposure to human wastewater-treatment plant (WWTP) effluents or other point sources. Hence, an early study in the Potomac River watershed to identify chemical compounds and associated point sources focused on sites upstream and downstream from WWTPs on the Monocacy River and Conococheague Creek, Maryland (Alvarez et al. 2009; Iwanowicz et al. 2009). Although some biomarkers such as gonadosomatic index and female plasma vitellogenin concentrations were adversely affected downstream from these WWTPs, the prevalence of males with testicular

oocytes or plasma vitellogenin was not consistently higher downstream. A similar lack of increased prevalence of intersex downstream from WWTPs was found in the Susquehanna River drainage. Whereas prevalence was not significantly different, severity increased downstream, indicating that other sources may be inducing intersex early in development but that WWTP effluent may contribute to increased severity. The Pennsylvania project also demonstrated that white sucker collected at the same sites as small mouth bass had no signs of testicular oocytes, but male suckers did show vitellogenin (Blazer et al. USGS, oral communication, 2012).

These findings led to investigation of other sources such as agriculture. A spring spawning study was conducted in which fish were collected just prior to spawning for a suite of reproductive endpoints. Sediment samples were collected from the smallmouth bass nests, integrative samplers were placed near nesting areas to bracket spawning, and discrete water samples were collected at the time of fish sampling. Because many of the chemicals currently of concern have biological effects at very low levels—commonly close to or below analytical capabilities—two approaches were used to assess water samples in conjunction with the biological effects in the fish. First, integrative passive samplers were deployed for approximately 30 days at the various sites, allowing the capture not only of cumulative base flow but also runoff events that may occur during the same time period. Second, extracts of discrete water samples as well as the integrated samples were tested for total estrogenicity. Results of the biological effects monitoring over two spring spawning seasons demonstrated a reduction in sperm and in the motility of the sperm in bass from the Potomac River with respect to those at the reference site in the Gauley River, and an inverse relation between testicular oocyte severity and sperm motility. Second, a seasonal difference in intersex and vitellogenin in male bass was found. Third, for the various

land-use characteristics (human population density, number of WWTPs, WWTP flow, and various agricultural attributes), intersex prevalence was associated only with percent agriculture and animal density in the catchment above the site. Intersex severity was associated with these two variables, as well as total animal feeding operations (AFOs), number of poultry houses, and WWTP flow (Blazer et al. 2011), also indicating that factors associated with agricultural runoff may be responsible for induction of intersex in these areas, whereas multiple sources increase intersex severity over the life of the fish.

Chemical analysis results obtained during the spawning study indicated that 39 of 201 target chemicals were detected in at least one discrete water sample. Atrazine and its degradate, simazine (both herbicides), iso-chlorotetracycline (antibiotic), and caffeine (stimulant) were the most frequently detected. In contrast, 100 compounds, including four biogenic hormones, were detected in extracts from the integrated samplers. Concentrations of atrazine in the discrete water samples and of total hormones and sterols in the sediment were significantly related to the prevalence and severity of testicular oocytes (Kolpin et al. USGS, oral communication, 2012).

A landscape-scale study, conducted by researchers from Virginia Polytechnic Institute and State University (Blacksburg, Virginia) in smaller watersheds of the Shenandoah River Basin, assessed the effects of WWTPs and AFOs on nutrients and estrogenic activity by using the bioluminescent yeast estrogen screen. _____ at 18 sites representing a gradient of AFO influence combined with the presence/absence of WWTP discharge was sampled during both low- and high-flow periods. Strong relations ($R^2 = 0.39\text{--}0.75$) were found between watershed densities of

AFOs and estrogen equivalents at all sampling times. There was no consistent relation between estrogenicity and WWTP discharges (Ciparis et al. 2012).

Reproductive Impairment of Yellow Perch

Several Chesapeake Bay tributaries, including the Severn and South Rivers, were closed to yellow perch fishing for nearly 20 years. Despite both recreational and commercial fishing regulations, a continued lack of recruitment has occurred. Hence, the streams were reopened for recreational fishing in 2009. The rationale (for the Severn, South, and West Rivers) was that these watersheds are extremely degraded habitat, reproductive output is low, and, therefore, recreational harvest would not affect the total reproductive capacity (Maryland Fisheries Service 2012).

Larval presence, L_p , is defined as the proportion of 0.5-meter plankton tows with larvae during the peak weeks from late March through early May, and is used as an indicator of year class strength. The L_p index integrates egg production, egg hatching success, and survival of first-feeding larvae. Brackish systems with small watersheds and high levels of development (South, Severn, and Magothy Rivers) have exhibited a persistent depression in L_p to below a reference minimum since 2002. Regression analyses indicated that development (percent impervious surface in the watershed--i.e., pavement, rooftops, and compacted soils) was negatively related to L_p . Other systems may exhibit wide variation in larval presence, but low levels similar to those seen in these urbanized subestuaries are not common; however, since 2008 spawning site loss for

anadromous fishes is evident in the developing Mattawoman Creek watershed (Uphoff et al. 2011a,b).

Despite numerous studies, the contributing factors to the lack of reproductive success have not been identified. Neither excessive adult mortality nor reduced growth has been observed in Severn River (YP). Severn River broodstock induced to spawn in the hatchery produced visually abnormal egg chains and too few viable eggs to support hatchery production. Hence, the depressed egg and larval survival are hypothesized to be critical factors suppressing resident YP populations in western shore subestuaries whose watersheds are subject to high levels of development (Uphoff et al. 2005). In recent surveys that assessed a suite of bioindicators, a number of biological effects were found in yellow perch from the Severn and South Rivers and, to a lesser degree, Mattawoman Creek. An apparent lack of final maturation, abnormal yolk, and zona pellucida (egg shell) were noted in ovaries collected during the spawning run. In the males, abnormal proliferation of Leydig cells was noted (Blazer et al. USGS, oral communication, 2012).

Skin and Liver Tumors in Bottom-Dwelling Fish

Although liver tumors have been clearly associated with sediment exposure to polycyclic aromatic hydrocarbons (PAHs) in bottom-dwelling fish (see Section 3), it is likely that exposure to other chemicals contributes either as an initiator or a promoter. Evidence that polychlorinated biphenyls (PCBs) and estrogen are believed to promote liver tumors is summarized in Section 3.

In contrast, the causes of skin tumors in brown bullheads are more uncertain and are the subject of intense investigation. These tumors are commonly grotesque in appearance and alarming to the public. From 1992 to 2008, the U.S. Fish and Wildlife Service conducted surveys in the following streams: Potomac River (Quantico Embayment), Anacostia River, Rhode River, South River, Severn River, Back River, Furnace Creek, Farm Creek, Marumsco Creek, Neabsco Creek, Choptank River, Little Blackwater River, and Tuckahoe River (Pinkney et al. 2009, 2011). An early goal of the tumor surveys was to systematically evaluate tumor prevalence in bullheads from the Anacostia River in Washington, D.C., where there was anecdotal evidence of fish with visible mouth lesions. The linkage between liver tumors and PAHs in this river is described in Section 3. (Studies relating liver tumors and PAH exposure in mummichogs in the Elizabeth River and its use in monitoring cleanups are also described in Section 3)

A second goal of the bullhead surveys has been to understand the relation between skin tumors and exposure to environmental contaminants. High prevalence of skin tumors has been observed in the Anacostia, South, Severn, Little Blackwater, and Neabsco Rivers (Pinkney et al. 2009, 2011). The skin-tumor prevalence in the South River, in particular, attracted widespread attention as a result of the grotesque appearance of several individuals. Results of the first survey in 2005 revealed a 53% prevalence of skin tumors, (Pinkney and Harshbarger 2005), a prevalence as high as any reported in North America. A follow-up study was conducted with an archived sample from 2004 and multiple samples from 2007 and 2008, as well as samples collected from the nearby Rhode and Severn Rivers (Pinkney et al. 2011). Skin tumor prevalence in the South River bullheads ranged from 19 to 58%. Prevalence of liver tumors was low in most collections, ranging from 0 to 6% in all collections but one, in which prevalence was 20%. As

part of the study, biliary PAH-like metabolites as well as PAC-DNA adducts in skin and liver tissues were measured. The authors also investigated the concentrations of alkyl-DNA adducts, which arise from interactions of alkylating agents such as nitrosamines with DNA. South River sediment total PAH concentrations averaged 3.6 milligrams per kilogram (mg/kg) within 2 kilometers of the collection site; concentrations from the other rivers were smaller. Neither the sediment PAH concentrations, the PAH-like metabolite data, nor the PAC-DNA adduct data show a linkage between exposure to PAHs and liver or skin tumors in these rivers. The alkyl-DNA adduct data also were not consistent with liver- or skin-tumor prevalence (Pinkney et al. 2011). Therefore, no chemical class has been associated with the high skin-tumor prevalence in the South River. On a broader scale, Pinkney et al. (2009) produced scatterplots of skin-tumor percentages in relation to sediment total PAH concentrations near the Chesapeake Bay bullhead collection sites, but no pattern in the relation between for skin tumors and PAH concentrations was observed.

A third goal was to use logistic regression to statistically analyze the Chesapeake Bay bullhead tumor database to determine which covariates must be considered when comparing tumor prevalence among collections and locations. This analysis was used to compare bullhead tumor prevalence to U.S. Environmental Protection Agency criteria for environmental indicators (U.S. EPA 2006). On the basis of the 1992-2008 database, Pinkney et al. (2009) reported that length and sex (with females having a higher ratio) were significant covariates for liver tumors, and length was a significant covariate for skin tumors.

An environmental indicator was defined by U.S. EPA (2006) as “a numerical value derived from actual measurements of a pressure, ambient condition, exposure or human health or ecological condition over a specified geographic domain, whose trends over time represent or draw attention to underlying trends in the condition of the environment.” Six criteria were used by U.S. EPA to select indicators for a National Report on the Environment: (1) importance: it makes an important contribution towards answering a question; (2) objective: it is developed and presented in an unbiased manner; (3) sound collection and quality assurance of data; (4) trends: data are available to describe changes or trends and the latest data are timely; (5) comparable across time and space and representative of the target population; and (6) transparent and reproducible: the data, assumptions, and statistical procedures are clearly stated.

Pinkney et al. (2009) used the six criteria to evaluate the Chesapeake Bay bullhead tumor data as an environmental indicator. They stated that criteria 1, 2, 3, 5, and 6 were fully met in the rationale for conducting tumor surveys: the random sampling; consistent laboratory and diagnostic methods (Blazer et al. 2006, 2007b); and the sound statistical approach. The limited home range (Sakaris et al. 2005) and abundance at salinities up to about 8 parts per thousand (ppt) makes this species ideal for monitoring many Bay tributaries. Criterion 4, however, was only partially met. Although recent (2005 and 2006) data are included in the database, few locations (only the Anacostia, Tuckahoe, and Neabsco Rivers) were sampled in different years, making it difficult to analyze trends. Recently (20xx), Pinkney (unpublished data) obtained new collections of bullheads from the Anacostia River in 2009, 2010, and 2011 to allow a further analysis of temporal trends. Therefore, it appears that the bullhead liver tumors would be a useful environmental indicator in lower-saline waters of the Bay watershed. The use of

mummichog liver histopathology as an environmental indicator, especially in the Elizabeth River Program monitoring studies (Chapter 3, e.g., Vogelbein and Unger 2011), make it a useful complement to the bullhead in higher salinity waters of the Chesapeake Bay watershed.

4.0 Integrative Responses of Wildlife to Contaminants

On the basis of earlier reviews (Ohlendorf and Fleming 1988; Heinz and Wiemeyer 1991; Rattner and McGowan 2007) and the present analysis, tissue concentrations of organochlorine pesticides and their metabolites have declined and widespread adverse reproductive effects on Chesapeake Bay waterbirds have subsided. Nevertheless, in a few locations concentrations of organochlorine pesticides remain elevated, eggshell thinning associated with *p,p'*-DDE is apparent, reproduction may be impaired, and organochlorine pesticide-linked lethality has even been observed in high-trophic-level predatory birds. In numerous instances, organophosphorus and carbamate pesticides have been linked to avian die-off events in agricultural regions of the Chesapeake Bay watershed, although use of the most hazardous anticholinesterases (e.g., granular formulations of carbofuran and diazinon, parathion) has been curtailed. Residue data in wildlife are not available for many categories of pesticides (e.g., herbicides, fungicides, rodenticides), likely because most have very low potential to bioaccumulate and have short environmental half-lives. The toxicological effects of chronic low-level exposure to newer pesticides and mixtures are unknown.

Unlike concentrations of pesticides, concentrations of PCBs in tissues of many species of Chesapeake Bay wildlife have not declined since the final U.S. EPA rule restricting the

manufacture, processing, and distribution became effective in 1979 (Rice et al. 2003). In some locations (e.g., Chesapeake Bay regions of concern), exposure to PCBs appears to be substantial, molecular effects are apparent (arylhydrocarbon-receptor active PCBs induce cytochrome P450-associated monooxygenases), and these compounds may even contribute to localized reproductive problems. Concentrations of dioxins and dibenzofurans, which evoke toxicity by a similar mechanism to coplanar PCB congeners, are low in peregrine falcon eggs, but limited sampling-location data and the absence of exposure information in other species do not permit Bay-wide conclusions. A human fish-consumption advisory, related in part due to dioxin, is in effect in the southern branch of the Elizabeth River (Virginia Department of Environmental Quality (DEQ) 2012).

Moderate to high concentrations of polybrominated diphenyl ether flame retardants (PBDEs) have been detected in eggs from predatory birds in the Chesapeake Bay watershed, and approach the lowest-observed-adverse-effect level for pipping and hatching success. Use of the penta-, octa-, and deca-BDE formulations is being phased out, however, and residues in tissues of wildlife are likely decline. Exposure and effects data for other groups of new flame retardants (e.g., hexabromocyclododecane and organophosphate flame retardants including tris(3,5-dimethylphenyl)phosphate and tris(1,3-dichloro-2-propyl)phosphate) are lacking for Chesapeake Bay wildlife, although some exposure monitoring has been undertaken with surfactants, such as alkylphenols and ethoxylates, and concentrations of perfluorinated compounds were found to be low, and seemingly well below effect thresholds in wildlife.

On average there are about 500 reportable oil spill events in the Chesapeake Bay annually, but no major spill events have resulted in large-scale wildlife die-offs. Small spills and seepage of

oil from marine vessels, and possibly pump facilities and industrial sites, are thought to be pervasive. The effects of chronic exposure to aliphatic and aromatic hydrocarbons in Chesapeake Bay wildlife have not been monitored, and are unknown.

Despite nationwide interest and concern about potential effects of household products, personal care products, and pharmaceuticals released from wastewater-treatment plants, septic systems, combined sewer outflows, and landfills, there have been no studies examining exposure and potential effects of these chemicals on Chesapeake Bay wildlife. Efforts are currently underway that are examining a suite of compounds (analgesics, antibiotics, anti-inflammatories, antihypertensives, antihistamines, antilipemics, antiseizures, anticoagulants, stimulants, psychostimulants, parasiticides, antidepressants, and antiseptics) in blood of osprey nestlings. The extent of exposure and potential effects of these compounds on wild birds is as yet unknown.

Although use of lead shot for hunting waterfowl was phased out by 1991, lead exposure and its resulting adverse effects are not uncommon in the Chesapeake Bay watershed, particularly in industrialized regions. However, the threat of other metals, including cadmium, mercury, and arsenic, do not seem to be a significant stressor to wildlife in most of the Chesapeake Bay and its tributaries.

Interest in the effects of biotoxins, particularly those associated with harmful algal blooms (HABs), on wildlife has increased. Since 2001, a protracted series of heron die-offs that may be linked to microcystins, a potent hepatotoxin from cyanobacteria found in harmful algal blooms, has occurred. Global climate change could cause an increase in HABs in the Chesapeake Bay

watershed, and adverse effects on waterbird health may be a prominent issue in the foreseeable future.

In comparison to contemporary wildlife data on contaminant exposure in other estuaries in the United States (Rattner et al. 2005), environmental contaminant exposure of Chesapeake Bay wildlife appears to have been moderate, occasionally harming individuals, but not evoking widespread adverse effects at the population level (Rattner and McGowan 2007). From an ecotoxicological perspective, some parts of the Chesapeake Bay watershed, such as Baltimore Harbor and the Anacostia and Elizabeth Rivers, have been studied intensively in the past 20 years, whereas other regions have not. At least two tributaries may merit attention with respect to research and monitoring in the near future--the Susquehanna River, the largest freshwater inflow to the Chesapeake Bay, which provides a large component of the total nutrient contamination entering the Bay, and the Rappahannock River, a region for which wildlife contaminant data are limited. An ongoing monitoring program examining contaminant exposure and potential effects in wildlife is needed. Such an effort should include thorough necropsies and toxicological analyses of individuals found dead, and a rigorously designed collection and analysis scheme for waterfowl (perhaps collected from recreational hunters), osprey eggs, and blood samples in order to document spatial and temporal trends.

5.0 Summary and Conclusions

Summary of extent and severity of contaminants.

Based on the information in Chapter 2, the key overall conclusions with respect to different classes of compounds are--

- **Widespread extent and severity:** For some contaminants such as PCBs, some herbicides (atrazine, simazine, metolachor, and their degradates), and mercury, available data indicate extensive environmental distribution at concentrations that are known or suspected to compromise the health and quality of the watershed's living resources. In some cases these contaminants, particularly PCBs and mercury, create a risk to human health through consumption of contaminated fish.
- **Localized extent and severity:** For an additional group of contaminants including dioxins/furans, polycyclic aromatic hydrocarbons, petroleum, some chlorinated insecticides (aldrin, chlordane, dieldrin, DDT/DDE, heptachlor epoxide, mirex), and some metals (aluminum, chromium, iron, lead, manganese, zinc), the report identifies localized areas of contamination and severity.
- **Need for additional research and monitoring:** For other classes of contaminants such as certain pesticides, pharmaceuticals, household and personal care products, flame retardants, and biogenic hormones, additional monitoring data and effects research are needed to assess the occurrence of the compounds and the associated risk to the watershed's living resources. Moreover, additional research is needed to determine the

sublethal effects of the classes of compounds for which widespread or local extent and severity was identified.

The availability of Chesapeake watershed monitoring data and established toxicity benchmarks is variable for the toxic contaminant classes assessed in this report. For some pollutants such as PCBs, PAHs, herbicides, and mercury, the data indicate extensive environmental distribution at concentrations that are known or suspected to compromise the health and quality of the watershed's living resources. For an additional group of pollutants - dioxin, petroleum, chlorinated insecticides and some metals - the report identifies localized areas of contamination that should continue to be monitored and addressed through existing federal and state authorities and programs. For other classes such as certain pharmaceuticals, household products, personal care products, flame retardants and biogenic hormones, there are some data available that suggest the contaminants are in the Bay system; however, more monitoring data and effects research are needed to assess the actual risk to the watershed's living resources. Finally, there are classes of toxic contaminants such as certain pesticides and pharmaceuticals for which monitoring data are needed to determine whether they are present in the watershed system, preceding any decisions on risk reduction actions. The summary table (table 5.1) provides more detailed information.

The assessment made through this report has noteworthy limitations. It relies on available data from state and federal environmental monitoring, most of which is short term in nature and does not allow for longitudinal assessment of trends. In addition, peer-reviewed literature that included data from outside the Chesapeake Bay watershed was used to provide additional perspective on potential extent and severity for contaminants that were either not monitored in

the Chesapeake Bay watershed or where monitoring data were spatially insufficient. The cost of analytical tests for detection, quantification, and biological effects of toxic contaminants is significant and therefore the spatial coverage of the data is limited even where monitoring programs exist. The method that underlies the report's conclusions is single-stressor oriented (or groups of chemically similar stressors such as congeners of PCBs) and does not consider the full risk presented by additive or synergistic effects of multiple chemical, biological, or physical stressors. The latter is a major limitation to present paradigms in adequately addressing the severity of toxic contaminants in the environment and is a rapidly evolving research topic in environmental chemistry and toxicology. Where appropriate, however, references to this limitation have been discussed and relevant published research has been cited.

The conclusions of the report, therefore, appropriately suggest that for a limited number of toxic contaminant classes, sufficient data to characterize as they have “baywide” or “local” extent and severity and the CBP partnership consider reduction goals and reduction strategies in the future. For other contaminants, recommendations for support of further monitoring and research would be a valid action to better understand to extent and severity of their potential effect on aquatic health.

Table 5.1: Summary of extent and severity of classes of compounds			
Data Availability	Research and Monitoring Gaps?*	Localized Extent and Severity Identified	Baywide Extent and Severity Identified
PCBs			
Data available throughout the Chesapeake watershed	No	No	Yes Numerous datasets indicate widespread extent. Concentrations exceed state and federal benchmarks, and multiple water bodies in most

			jurisdictions are subject to fish consumption advisories. In some locations wildlife exposure to PCBs may contribute to reproductive effects.
Dioxins and Furans			
Limited data in Chesapeake watershed	No	Yes Local impairments and two water bodies with fish consumption advisories.	No
Polycyclic Aromatic Hydrocarbons (PAHs)			
Data available throughout the Chesapeake watershed	No	Yes High concentrations in sediment and evidence of adverse effects (such as liver tumors in fish) in several locations. Impairments limited to two sites.	No
Petroleum Hydrocarbons			
Limited data in Chesapeake watershed	No	Yes Local impairments (oil and grease). Spills result in adverse effects on fish and wildlife impacts.	No
Pesticides			
Data available throughout the Chesapeake watershed	Yes Because of the large number of compounds in this group, data availability and understanding of toxicity effects remain limited.	Yes Localized impairments with respect to organochlorine pesticides and degradates (aldrin, chlordane, dieldrin, DDE/DDT, heptachlor epoxide, mirex).	Yes Extent of triazine herbicides (atrazine, simazine) and acetanilide (metolachlor) and degradates is widespread, with potential adverse impacts.
Pharmaceuticals			
Limited data in Chesapeake watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects are uncertain, but some compounds known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
Household and Personal Care Products			

Limited data in Chesapeake watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects are uncertain, but some compounds known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
Polybrominated Diphenyl Ether Flame Retardants			
Limited data in Chesapeake watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects uncertain, but some compounds known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
Metals and Metalloids			
Data available throughout the Chesapeake watershed	No	Yes Freshwater impairments in several jurisdictions and some exceedances of State standards (aluminum, chromium, iron, lead, manganese, zinc)	Yes Widespread extent in Bay watershed and severity noted primarily in freshwater fish tissue (mercury).
Biogenic Hormones			
Limited data in Chesapeake watershed	Yes Literature and limited monitoring indicate potential for widespread extent. Effects uncertain, but some compounds known to cause adverse ecological effects. Additional research and monitoring needed.	No	No
* “No” indicates sufficient data is available to draw conclusions on extent and severity for the needs of this report. Any future management actions will benefit from additional monitoring.			

The key findings about the effect of toxic contaminants on fish show (1) increased incidence of infectious disease and parasite infestations contributing to increased mortality, (2) feminization (male fish with eggs and elevated levels of vitellogenin) of largemouth and smallmouth bass and other signs of endocrine disruption, (3) reduced reproductive success and recruitment of yellow perch in certain highly urbanized tributaries, and (4) tumors in brown bullhead and mummichogs. The weight of the evidence points to an association between indicators of biological effects and exposure to toxic chemicals.

Wildlife in the Chesapeake Bay and its watershed has also been affected by pesticides, polychlorinated biphenyls (PCBs), and flame retardants, but information on the effects of household products, personal care products, and pharmaceuticals is limited. Concentrations of organochlorine pesticides and their metabolites in tissue have declined and widespread adverse reproductive effects on Chesapeake Bay waterbirds have subsided. However, organochlorine pesticide concentrations remain elevated in a few areas. Unlike concentrations of pesticides, concentrations of PCBs in tissues of many species of Chesapeake Bay wildlife have not declined since the final U.S. Environmental Protection Agency rule restricting the manufacture, processing, and distribution of these compounds became effective in 1979. In some urbanized regions, exposure to PCBs appears to be substantial and molecular effects are apparent; these compounds may even contribute to localized reproductive problems. Despite nationwide interest and concern about potential effects of household products, personal care products, and pharmaceuticals released from wastewater-treatment plants, septic systems, combined sewer outflows, and landfills, no studies have examined the potential effects of exposure to these chemicals on Chesapeake Bay wildlife.

Considerations for the Development of Federal-State Toxic Reduction Goals and Strategies

The findings in this report will be used during 2013 by the CBP partnership to consider new goals for reducing concentrations of toxic contaminants and to develop strategies by 2015 to carry out the goals. Preliminary considerations for development of goals and reduction strategies could address:

Sources – Some individual contaminants have unique profiles with regard to the origin of the ongoing inputs in the watershed. However other contaminants and groups of contaminants such as pesticides have overlapping and varied sources and source pathways to the environment. Developing a basic understanding of the relative magnitude of sources as well as the nature of their environmental pathways for individual and groups of contaminants is critical in determining the extent to which reductions can be achieved. Without this first step most reduction actions are limited to addressing the symptoms of the problem rather than the cause.

Regulatory and Voluntary Controls – For each contaminant source and environmental pathway, consideration of the current regulatory and/or voluntary controls that can be applied will allow for informed decisions regarding the strengths and limitations of specific reduction actions. It is expected that an element of the strategies for reduction would involve development of new regulatory controls and/or new voluntary programs as well as support for additional monitoring and research.

Technology Limitations and Opportunities – In many cases, technology limitations, including green chemistry, sustainable agricultural and other sustainable practices, wastewater and drinking water treatment, and best management practices will limit the extent to which reductions can be expected. Therefore, opportunities for developing and applying new technologies should be considered and promoted through the goals and strategies that are developed. However, technological advances alone are not likely to completely reduce the risk of toxic contaminants and therefore adequate attention to socioeconomic and cultural aspects related to increases in existing and new sources of these toxic contaminants should be acknowledged and addressed.

Resource Limitations and Opportunities - Both state and federal entities charged with identifying pollutants responsible for impairments and pursuing policies and programs to address those pollutants face significant resource limitations. This is precisely why the CBP, with its high level of both federal and state leadership and authorities, represents the best opportunity for resource allocation that would allow progress to be made in reducing inputs of the pollutants identified in this report. Any goals and strategies should be considerate of resource limitations but also not underestimate the opportunities that exist for creative solutions that may result in the application of new resources.

Competing Priorities – In the Chesapeake Bay and its watershed, there are ongoing efforts of a historically large scale that are addressing other high priority pollutants (e.g., nutrients and sediments) that impact the ecological success of the system. Goals and strategies should be attenuated by this fact; however, this report suggests it is appropriate to reaffirm the need for the

CBP to apply itself to a subset of the toxic contaminants that are compromising the system, particularly those that are widespread and occurring at concentrations that are likely to be having adverse ecological effects. High level policy decisions will be needed on priorities. There would be a need for support of all phases of goal setting and implementation across jurisdictional boundaries.

Progress Assessment and Environmental Response Monitoring

Management of established goals and strategies requires measurement of implementation progress and monitoring of resulting changes in environmental condition. Because the analyses needed for contaminant monitoring can be relatively expensive, the breadth of established goals should consider the ability to adaptively manage the goal strategy including the monitoring and measurements that are needed to guide strategic actions. Consideration of how to use existing state and federal monitoring programs, self-reported data sets, and new monitoring systems may help in keeping this factor from limiting the scope of reduction goals and strategies.

Recommendations for Further Research and Monitoring

Current paradigms used to set reduction goals continue to rely on conventional toxicological benchmarks based on single contaminant exposures. These approaches, although moderately useful tools to target reductions caused by single contaminants and, to a lesser extent, congener groups, are disconnected from goals needed to address the potential biological effects caused by mixtures.

This report, therefore, suggests the following categories of research and monitoring:

- Toxicological studies to better define which chemicals are impacting fish and wildlife
- Source-to-receptor research to improve understanding of where the chemical inputs are originating, their pathways to the environment, and the most likely exposure scenarios
- Studies on the effects of contaminants on the health of fish and wildlife and whether exposure makes them more vulnerable to other environmental stressors such as pathogens
- Enhanced monitoring to include biological monitoring of the impacts of contaminants on the health of fish and wildlife and monitoring of the newer contaminants where there is a lack of information on their occurrence in the Bay and its watershed
- Studies on the interaction and impact on aquatic resources from multiple stressors, including those resulting from landscape changes such as increases in impervious surface, on aquatic resources

Potential future issues impacting extent and severity of contaminants in Chesapeake Bay watershed

There are several trends in land use, environmental condition, and other high priority restoration activities that have the potential to exacerbate the threat from toxic contaminants to the

watershed's environmental quality. These trends and activities should be considered in the strategies that are developed to achieve contaminant reductions. Examples of rapidly emerging activities and issues likely to exacerbate effects of contaminants in the environment now and in the near future include: 1) *energy-related activities such as the extraction of unconventional sources of fossil fuels using the technique known as hydraulic fracturing*. While most of the Bay watershed states where this activity is undertaken are moving to implement controls to recycle, treat, and otherwise minimize the release of flow-back fluids and produced waters to the environment, this remains a poorly understood source of potential toxic contaminants and brines to the environment; 2) *the environmental outcomes projected to occur due to changes in climate*. Rising sea level, increases in environmental water temperature, and acidification of environmental waters all have the potential to change the concentrations, bioavailability, and adverse ecological effects that result from toxic contaminants in the environment; and 3) *Best Management Practices that are designed to achieve the Chesapeake Bay Total Maximum Daily Load for nitrogen, phosphorus, and sediment*. Resource managers should assess whether some prescribed BMPs lead to greater use of chemicals (e.g., cover crops that require the use of herbicides). Alternative BMP scenarios are needed that achieve the needed nitrogen, phosphorus, and sediment reductions but also minimize or control the use and release of toxic contaminants should be selected.

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