

Framework for Understanding Contaminants of Emerging Concern in Marine Waters

**Recommendations of the Outfall Monitoring Science Advisory Panel
to the U. S. Environmental Protection Agency (Region 1)
and Massachusetts Department of Environmental Protection**



July 7, 2022

Final Report of the Outfall Monitoring Science Advisory Panel

Greetings:

The three attached documents are based on recommendations of attendees at a November 13, 2018 workshop that reviewed the Massachusetts Water Resources Authority's (MWRA) 25-year monitoring program and raised concerns about emerging contaminants that were not being monitored in wastewater treatment plants. With the MWRA Ambient Monitoring Plan goals as guidance, the Outfall Monitoring Science Advisory Panel (OMSAP) was motivated to examine selected classes of contaminants of emerging concern (CECs) that may be present in wastewater and harmful to humans, and aquatic and marine biota. Three white papers examined the sources, transport, fate and effects of per- and polyfluoroalkyl substances (PFAS), pharmaceutical and personal care products (PPCPs), and microplastics (MPs). These documents and the executive summary have been sent to the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (MADEP). Highlighted recommendations to the agencies summarized the issues in the white papers and include:

1. Identifying priority compounds within the classes of the CECs that may be or are in Massachusetts and Cape Cod Bay;
2. Literature and database searches to identify impacts to marine organisms and humans;
3. Acceptance of agency-approved methodologies;
4. Support of special studies for unknown issues related to monitoring prior to implementation (*i.e.*, monitor with specific goals based on sound science);
5. Sampling of CECs in biota (to be identified).

On behalf of OMSAP, we thank members of the Public Interest Advisory Committee, the Interagency Advisory Committee, and all who participated in the discussions for your continued interest and support as this effort moved forward. We value your input. We also appreciate the timely and helpful cooperation of Betsy Reilley and the MWRA staff, Cathy Coniaris (MADEP), and Matt Liebman (EPA, retired). Photo: J. Pederson

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Executive Summary: A Framework for Understanding Contaminants of Emerging Concern in Marine Waters

Recommendations of the Outfall Monitoring Science Advisory Panel to the U. S. Environmental Protection Agency (Region 1) and Massachusetts Department of Environmental Protection

July 7, 2022

PREFACE

The attached documents are a set of reviews or white papers about three general types of contaminants of emerging concern (CECs) in domestic wastewater effluent, specifically as it applies to the Massachusetts Water Resources Authority's (MWRA) outfall discharge into Massachusetts Bay. These reviews evolved from the discussions during a November 13, 2018 public workshop, *2300 Days at Sea: Monitoring the Impacts of the Outfall on Massachusetts Bay*, hosted by MIT Sea Grant, Save the Harbor/Save the Bay, and the Outfall Monitoring Science Advisory Panel (OMSAP).

As part of its National Pollutant Discharge Elimination System (NPDES) permit, MWRA has developed and implemented a monitoring plan to evaluate whether its discharge adversely impacts Massachusetts Bay. At the November 2018 workshop, participants were asked to review the 25 plus years of MWRA monitoring results, to evaluate whether the current monitoring questions are still relevant, and to determine whether other emerging questions or threats related to the outfall discharge should be addressed by the monitoring program. Attendees concluded that three categories of CECs—persistent or long-lived chemicals, pseudopersistent (short-lived but released frequently) compounds, and microplastics were potential risks for Massachusetts Bay. To better understand the issues associated with the three categories of CECs, OMSAP, a scientific panel that reports to Massachusetts Department of Environmental Protection (MADEP) and the U.S. Environmental Protection Agency (EPA), focused on developing white papers that included per- and polyfluoroalkyl substances (PFAS), a persistent organic chemical group of thousands of compounds; pharmaceuticals and personal care products (PPCPs), a diverse group of relatively short-lived, but consistently released chemicals; and microplastics (MPs), small plastic particles that persist for a few to 100s of years that were either manufactured or broken down from larger pieces and contain over 4,000 additives.

These reviews focus on the potential discharge of CECs from the MWRA outfall; their chemistry, sources, transport, fate and effect in the ecosystem; and their impacts to marine life and human health. EPA and MADEP have recently started adding monitoring requirements for six PFAS compounds to NPDES permits for wastewater treatment plant (WWTP) discharges

with new recommendations that 40 PFAS parameters are to be monitored in drinking water and receiving waters, however, currently there are no monitoring requirements for PPCPs, or MPs.

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To complete these reviews, OMSAP consulted with regional experts who provided overviews of the issues associated with selected CECs and their impacts. We especially appreciate the scientific contributions of Todd Callaghan, Massachusetts Coastal Zone Management Office; Mark Cantwell, EPA; Michaela Cashman, EPA; and Anna Robuck, University of Rhode Island (currently at Icahn School of Medicine at Mount Sinai, as well as contributions from others at EPA and MADEP. Additional reviews by OMSAP members, Kay Ho from EPA, Ken Keay (retired), and Catherine Tobin from the University of Massachusetts at Boston were also appreciated. Bruce Berman and Save the Harbor/Save the Bay generously provided financial and logistic support for the November 2018 workshop that initiated the discussions on contaminants of emerging concern.

Genesis and Rationale for Evaluating Contaminants of Emerging Concerns

In response to EPA and MADEP requests, an Ambient Monitoring Plan (AMP) for the proposed MWRA outfall discharge in Massachusetts Bay was adopted in 1991 to address public concerns:

- Is it safe to eat fish and shellfish?
- Are natural/living resources protected?
- Is it safe to swim?
- Are aesthetics being maintained?

In 2018, OMSAP co-sponsored a public workshop with its Public Interest Advisory Committee (PIAC) to discuss the extent to which monitoring questions were answered, whether the goals of the monitoring program were met, and whether the original questions were still valid thirty years later. After reviewing MWRA's AMP data on key issues, the attendees concluded that "*After 25 plus years of monitoring, the data show that the MWRA outfall has not adversely affected Massachusetts Bay.*" Regarding contaminants in Massachusetts Bay specifically, the workshop summary noted that concentrations of legacy metal contaminants and persistent chemicals such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), and chlordane in sediments impacted by the outfall discharge have either decreased or remained constant since the baseline period. However, the monitoring program has not evaluated other potential issues that are related to WWTP outfalls. CECs are not included in the current monitoring program yet many are potential threats to human health and the ecosystem. At the workshop, the public, coastal managers, researchers, and representatives of environmental groups expressed interest in adapting the monitoring framework to investigate the new concerns and address relevant questions in the AMP.

To better advise EPA, MADEP, and MWRA, in 2019 and 2020 the OMSAP convened *ad hoc* focus groups of academic and government scientists, and members of the PIAC to review the scientific literature for impacts to humans and marine biota from CECs associated with wastewater discharges. Based on these discussions, reviews of three categories of CECs were initiated to highlight the role of WWTPs, specifically the MWRA outfall, in their release to the Massachusetts Bay. These categories include **persistent contaminants** (per- and polyfluoroalkyl substances or PFAS), **pseudopersistent** or short-lived chemicals (pharmaceutical and personal care products or PPCPs), and particles of **plastic** (microplastics or MPs composed of additives) with lifespans of 4–100s of years. These three categories of CECs, *i.e.*, PFAS, PPCPs, and MPS, reflect the concerns that were the focus of the November 2018 workshop, and are, or will be under consideration on a list of priority compounds generated by the MADEP for potential additional regulation or additional review of risks to public health and the environment.

Many CECs and other chemicals identified during the 2018 workshop emerged from the development of new technologies that provide people with therapeutic benefits or improve some aspect of their everyday lives. However, proliferation of these persistent and often toxic chemicals, their disposal in landfills, and their release to fresh and marine waters, may have serious implications for organisms and the environment. Many of these chemicals have been manufactured since the 1940s or earlier, and were known to cause health problems for workers. Research on environmental impacts has not kept pace with releases of these chemicals and has

not addressed their accumulation in humans, wildlife, and ecosystems. The CECs that are the focus of the white papers represent general categories, but specific additional chemicals or compounds may be most relevant to Massachusetts—*e.g.*, tire particles, new generations of fire retardants (*e.g.*, dibromophenyl ethers or DBPE), phthalates (additives to PPCPs and MPs), and nonylphenols (used in over the counter and household products) among others, and would require further review. The goal of the three white papers is to review what is known about three representative categories of CECs that might pose a risk to marine biota and human health, their influent and effluent rates from MWRA and from other WWTP discharges, and how best to reduce or eliminate these contaminants.

Approach to evaluate contaminants of environmental concern in Massachusetts coastal waters

This Executive Summary synthesizes information about the CECs (PFAS, PPCPs, and MPs) reviewed in the attached white papers. Each paper addresses the same issues, to identify: (1) types of chemicals, sources and their likely releases in WWTP effluent; (2) availability of, and transport in marine receiving waters; (3) effects of the contaminants on humans, marine organisms, and ecosystems; and (4) strategies for identifying and prioritizing chemicals for possible mitigation. Where known, current and emerging regulations were identified and recommendations for addressing these issues are proposed.

CECs eventually reach the ocean by vectors that include transport by air, runoff, riverine flow, and outfall discharges. In addition to MWRA, other WWTPs and industrial outfalls discharge to marine waters (see side bar for WWTP contributions to Massachusetts Bay). The dynamic nature of marine habitats makes it challenging to demonstrate cause and effect in natural ecosystems. Consequently, much of the information on biological effects of CECs comes from laboratory experiments that are conducted under controlled conditions but may not accurately predict *in situ* impacts. Fortunately, new technologies and well-designed field studies along with laboratory experiments are providing information on potential effects of CECs to aquatic life and ecosystems in an expanding body of peer-reviewed literature.

The white papers focus on MWRA's commitment to the goals in its AMP; namely its discharge should ensure safe swimming standards, protect the safety of seafood for human consumption, maintain aesthetics, and do no harm to the ecosystem. The three CEC classes identified are known to cause human health and ecosystem impacts. There are many gaps in our knowledge of the relationship between PFAS, PPCPs, and MPs and the contribution from WWTP discharges relative to other sources.

Major WWTP Discharges into Massachusetts Bay

MWRA is the largest, but not the only discharger to Massachusetts Bay. There are nine other WWTPs discharging an average total of 67.2 MGD (0.44-25.8 MGD). Based on the average of 299 MGD by MWRA, it contributes ~82% of WWTP discharge into Massachusetts Bay. Most of the discharges into Cape Cod Bay are from septic-system groundwater with only 6 MGD discharged from a WWTP. The findings from these white papers would also apply to other WWTPs discharging into Buzzards Bay and portions of Mount Hope Bay. MWRA is currently the only discharger with a NPDES permit that requires significant ambient monitoring (data from MADEP, 2022).

Contaminants of Emerging Concern in the marine environment

CECs are generally found in low concentrations in the water column. Some (e.g., PFAS, estrogen-related chemicals found in PPCPs, MPs, and other CECs) are bioaccumulated in marine organisms and both PFAS and MPs are found in sediments, with the highest concentrations observed near sources. Sediment resuspension and ocean currents are known to transport PFAS and MPs to remote areas as far as the Arctic. An overview of the sources, characteristics, transport, fate, and effects of PFAS, PPCPs, and MPs highlight what is known about impacts to humans and marine biota.

Per- and Polyfluoroalkyl Substances (PFAS)

PFAS found in everyday products including food packaging, raingear, stain-resistant furniture and fabrics, nonstick cookware, and firefighting foams. There are an estimated 9000 chemicals characterized as PFAS that are not readily degraded and may form more toxic compounds in the environment. Recent monitoring detected PFAS in MWRA's biosolids and effluent. Most long-chain PFAS are removed during treatment in biosolids, but small-chain compounds may be oxidized and form more toxic compounds during treatment and in the receiving waters. Little is known about the ongoing evolution from legacy PFAS to newer species currently in use, such as high-performance fluorinated polymers (also known as Gen X) and perfluoroalkyl acids. The EPA has a PFAS Strategic Roadmap that is making recommendations for PFAS in drinking water and receiving waters and for inclusion in National Pollutant Discharge Elimination System permits.

Several PFAS are correlated with health effects in humans, marine mammals, and other marine biota. Studies have related PFAS concentrations to effects on metabolism, hematological parameters, body condition, reproduction and growth, and immunotoxicity in marine mammals (polar bears, seals, dolphins, whales) and seabirds, as well as humans (including cancer in firefighters). One pathway for human exposure to PFAS is consumption of seafood. Two states (Michigan and New Jersey) have developed fish-consumption screening values for humans, and Canada has developed advisories for wildlife consumption. Both bioaccumulation and trophic transfer occur in marine biota. In plankton and invertebrates, PFAS have negatively impacted growth of a phytoplankton species, and have caused genotoxicity in bivalves; both may potentially have long-term impacts to the ecosystem. A NOAA study found PFAS in mussels near Deer Island and at three other locations in Massachusetts. In coastal areas of the northwestern Atlantic, some seals have PFAS concentrations above immunotoxicity levels, and concentrations of PFAS along the northeastern coast of the U.S. are higher than in other regions of the North Atlantic.

At the state level, actions taken by MADEP to regulate drinking water highlighted PFAS-contaminated drinking water supplies, many of which are in coastal Massachusetts. Recently EPA and MADEP NPDES permits for WWTPs have included influent, effluent, and biosolids monitoring for 6 PFAS compounds, and effluent PFAS monitoring is also required for industrial dischargers. Additionally, EPA has adopted a program for development of strategic approaches to review hundreds of PFAS and other compounds for potential impact and a timeline for action

if required. A Massachusetts PFAS Interagency Task Force recommends testing of drinking water and ground water, reducing PFAS discharges, and funding for remediation, but it did not address marine ecosystems.

Pharmaceuticals and Personal Care Products (PPCPs)

PPCPs include common household products such as medicines, hormones, stimulants, cosmetics, antimicrobial compounds, sunscreens, and insect repellants. While the detailed transport and fate of PPCPs, including their health and environmental effects, persistence, and derivative compounds are not well understood, it is known that many reach the marine environment via human wastewater, either through WWTPs or onsite septic systems. In a review of the literature, no PPCPs demonstrated toxicity to marine organisms at ambient levels. In Massachusetts marine waters, pharmaceuticals were found in concentrations lower than therapeutic levels for humans and showed temporal and spatial variability. Most pharmaceuticals exhibit short lifespans after discharge into the environment; however, even those that are not considered persistent are likely released continuously via domestic wastewater and therefore organisms within the receiving waters may experience long-term exposure to low-level concentrations.

While many PPCPs do not bioaccumulate, oysters have been shown to not completely depurate or metabolize initial doses of a suite of PPCPs, a recent NOAA study (Mussel Watch) found one or more of 16 PPCPs in mussels at 17 locations in Massachusetts waters, pyrethroid insect repellants have been shown to pass from mother to baby dolphins, and synthetic musks have been found to accumulate in several marine fauna groups. The effect of synthetic hormones is an area of PPCP research that may deserve more investigation given that one study found chronic exposure of fathead minnows to low concentrations of synthetic estrogen resulted in near collapse of the population due to feminization of male fish. Given the breadth of chemicals defined as PPCPs, a strategic approach to identifying chemicals of highest concern in Massachusetts—those that are persistent, bioaccumulative, and toxic—is needed.

Microplastics (MPs)

MPs are small particles of plastic that are physically or chemically degraded or may be manufactured (e.g., microbeads and powders). When plastic degrades into smaller particles they are defined as microplastics at sizes between 1 μm and 5 mm and as nanoplastics when they are $<1 \mu\text{m}$. Plastics are integral to our everyday life as low-cost products such as water bottles, food containers, rugs, clothes, electrical and electronic equipment, and much more. Plastic is produced primarily from petroleum and to a lesser extent from natural products. Over 4,000 additives, many of which are toxic (Bisphenol A or BPA, PFAS, Triclosan, phosgene, and others) provide flexibility, hardness, or other characteristics necessary for the multiple uses of plastic products. As plastics break down they can release additives that are detrimental to humans and marine biota.

In the ocean MPs serve as a substrate for contaminants such as PFAS, Bisphenol A, PCBs, and other persistent chemicals that adsorb to their surfaces, and have deleterious biological effects on marine biota that consume them. Microplastic particles are found in gyres of major ocean systems, in the Arctic and its sediments, at depths of 2000 meters, and in deep ocean sediments.

In landfills, some MPs are biodegraded, *i.e.*, they are biochemically broken down, but little is known about the extent of biodegradation in the ocean.

Secondary and tertiary WWTPs can remove 80 to 99% of microplastics, although microfibers and smaller particles may be released. Recent articles document that plastic particles smaller than 50 nm (*i.e.*, nanoplastics) can enter cells and are found in organs and tissues of fish and other vertebrates, including humans. Microplastics ingested by zooplankton may have negative effects on feeding, reproduction, and life span, impacting important primary consumers at the base of the food web, such as the copepod *Calanus finmarchicus* in Massachusetts Bay.

General Issues: Sources, Screening, Methodologies, and Regulations

Over the past 28 years of monitoring, new contaminants that are potential threats to humans, marine biota, and marine ecosystems are present in Massachusetts Bay but are not included in the current AMP. There are many sources of these contaminants to Massachusetts coastal waters, including wastewater and industrial discharges. OMSAP understands that MWRA is not responsible for all CECs released to Massachusetts Bay, but the AMP and permit require monitoring of major pollutants that pose threats to humans and the ecosystem. Preliminary data suggest that concentrations of all three CECs are low in the water column, but these persistent chemicals and MPs can be found in sediments and reintroduced to the water column.

CECs are generally identified and regulated by state and federal agencies. However, with some notable exceptions, regulatory agencies have generally been slow to respond to contaminants causing harm to humans and the ecosystem. This failure to act has limited society's ability to understand what is being released into receiving waters and their impacts. Unknown issues include basic information such as relative contributions from different sources; treatment and removal from influent by WWTPs; concentrations in effluent; and transport, fate and effects in the ocean. Another important limitation is a lack of consistent approved analytical methodologies. This, however, appears to be changing at both the state and federal level.

In 2020, MADEP adopted a standard of 20 ng/L or parts per trillion for six compounds of PFAS for drinking water. Regulatory limits for PPCPs, or MPs in marine receiving waters have not been developed, but new NPDES permits in Massachusetts require monitoring of these same six PFAS species and More recently, EPA is recommending that 40 PFAS parameters be monitored in drinking water and receiving waters.. In April 2021, an EPA Council on PFAS was established that has resulted a PFAS Strategic Roadmap to address impacts to humans and wildlife, toxicity testing, toxicity assessment, standardized methodologies, and gathering data on 1000 compounds. EPA has drafted and is seeking public input on standard methods and other recently released reports. Similarly, a standardization of identification, measurements, approaches, and processes for evaluating impacts to marine biota and ecosystems are needed for MPs and PPCPs.

Even without regulatory standards or approaches, it is essential to evaluate the role of MWRA, other WWTPs, other dischargers, and groundwater discharges as sources of CECs to receiving waters. The current AMP monitors selected chemicals (but not PFAS, PPCPs, and MPs) in three marine species, winter flounder *Pseudopleuronectes americanus*, lobster *Homarus americanus*,

and the edible blue mussel, *Mytilus edulis*. Currently, MWRA is not conducting biological monitoring of CECs such as PFAS, PPCPs, or MPs.

The OMSAP recommendations in the three white papers and summarized below recognize that there are multiple limitations that need to be faced: the lack of agency identification of chemicals of highest priority; lack of regulations for receiving waters; and limited field and research studies relating concentrations to impacts on wildlife and marine biota. There are, however, intermediate approaches that MWRA, other WWTPs, and other major dischargers can address. These include identification of chemicals and MPs present in discharges, analysis of chemicals and MPs in selected biota, efforts to reduce CEC discharge, and support of special studies.

Recommendations to State and Federal Agencies and MWRA

For the purpose of this document, there are three questions relative to state or federal regulations for the MWRA's Ambient Monitoring Plan:

- (1) To what extent does the MWRA outfall and by extension other industrial and WWTP discharges contribute CECs to Massachusetts Bay?
- (2) To what extent are seafood and other marine biota accumulating CECs?
- (3) To what extent are CECs impacting the Massachusetts Bay ecosystem?

Although there are several ongoing surveys of CECs in the effluent and receiving waters in and around the MWRA outfall, these data are not currently available.

The role of OMSAP has consistently focused on the relevant scientific issues associated with the MWRA discharge. Traditionally, OMSAP serves as the link between ongoing academic and other research with state and federal agencies and convenes *ad hoc* meetings with specialists in relevant scientific areas. The proposed recommendations are consistent with MWRA's responsibility through its Ambient Monitoring Plan goals and permit requirements to address areas where additional scientific information is needed. OMSAP recognizes that increasing knowledge on these groups of CECs is time-critical, and recommends that MWRA should begin developing a forward-looking strategic monitoring plan for CECs that are shown to have negative impacts on humans, biota, and/or the ecosystem. The purpose of the plan would be to identify the extent to which CECs are being released through MWRA to Massachusetts Bay. Initial CEC monitoring should characterize concentrations and distributions in the influent and in-plant effluent. Requirements for ambient monitoring—in the near-field or far-field water column, sediments, or biota—would need to be justified on a case-by-case basis for each CEC as the science matures.

1. Identify priority compounds within chemical classes (i.e., PPCPs, PFAS, and MPs) through literature and database searches that indicate chemicals that are or may be occurring in Massachusetts and Cape Cod Bays.
 - For PPCPs, two websites (SCCWRP and HSPH) provide information on likely candidates and estimated risk and the NOAA report identified 31 of 121 PPCP contaminants in the Gulf of Maine of which 16 were present in Massachusetts mussels.

- For PFAS, the recently issued NPDES permits identify six PFAS compounds that of concern for which data on toxicity exists. Over the next three years, EPA is examining several groups of PFAS to identify priority chemicals or groups of chemicals. The first draft report from EPA has identified PFOS and PFOA as priorities compounds (see EPA, April 2022; EPA 842-D-22-005). In April 2022 the Final PFAS Agency Task Force report was released with recommendations for MADEP to identify and remediate PFAS in drinking water, develop standards for groundwater, along with numerous other recommendations on eliminating PFAS from consumer products, ensuring environmental justice, and appropriating funds for the recommendations (PFAS in the Commonwealth of Massachusetts, April 2022).
 - For MPs, data on concentrations of MPs in MWRA's influent and effluent is unknown but impacts are documented in Massachusetts marine organisms as well as human organs and tissues. Recent studies document that PFAS, phthalates, Triclosan are among the over 4,000 additives in high percentages in plastics. As plastics break down, additives that are likely released and consumed, and increased surface areas develop biofilms and adsorb other contaminants.
2. Conduct literature and database searches for health effects of CECs on marine organisms and humans.
- For PPCPs, data on effects of PPCPs on marine organisms are limited for the New England region but the NOAA report identified 1 or more PPCPs at all 17 stations in Massachusetts including Deer Island. Risk assessments by HSPH and SCCWRP identify some PPCPs of concern, but many are unidentified and few are tested at ambient conditions or for prolonged exposure periods.
 - For PFAS, data on marine biota along the Northwest Atlantic coast as well as throughout the North Atlantic primarily are based on bioaccumulation, including mussels near Deer Island and Neponset River. Fewer studies have correlated field-level concentrations with effects in marine biota including seals at levels that may cause immunotoxicity and other marine mammals. Data show higher concentrations of PFAS along the Northwest Atlantic than the Northeast Atlantic
 - For microplastics, impacts to Massachusetts biota indicate impacts on growth of corals but other studies indicate broader impacts, including on the small planktonic crustaceans that are important in the marine food web.
3. Methodologies for monitoring vary and some require approval by state agencies. A review of documented methods for sampling and analysis, detection limits, accuracy and precision of results, and required quality control is necessary to ensure data are useful for regulatory actions. The review of acceptable methodologies can be used to assess the quality of literature and databases for identifying compounds and their effects (i.e., # 1 and 2). EPA is conducting multi-laboratory tests to develop a standardized PFAS methodology.

4. Special studies have provided a successful approach to addressing unknown issues before committing to large-scale monitoring. OMSAP recommends that MWRA should seek opportunities for focused studies that exist through internal funding opportunities and through collaborations with other agencies, e.g., EPA and NOAA, and with other programs such as Sea Grant, other institutions, and not-for profit organizations.
5. OMSAP recommends that sampling for CECs should include sampling of biota, although the target organisms still need additional consideration.
6. OMSAP urges MWRA to continue their commitment of working with community leaders and environmental organizations to keep the public informed of ongoing studies and outcomes.

Although it is not a recommendation for the monitoring plan, the success of reducing legacy contaminants to Massachusetts Bay relied on reduction of discharges from all sources. OMSAP concurs with the Interagency Task Force that reduction of PFAS from all sources should be a high priority.

The focus of these recommendations is to identify CECs of concern to humans, marine biota, and marine ecosystems, to assess the relative input of CECs to marine receiving waters from MWRA, and to assess concentrations in the water, sediments, and biota. We support adoption of short-term special studies, often in collaboration with others, to address unknown issues that include integration of current research with monitoring activities. We recognize that some of the recommendations are beyond expectations of the MWRA's current monitoring plan. In that context we urge MWRA to collaborate, as they have in the past, with local non-government organizations such as PIAC and the Massachusetts Bays National Estuary Partnership in developing outreach materials to reduce use and release of CECs. Although the focus of the white papers has been MWRA's potential role in discharging CECs to Massachusetts and Cape Cod Bay, it is not the sole responsibility of MWRA to respond to these concerns. We urge the Commonwealth of Massachusetts and EPA to develop a state-wide monitoring program that addresses the issues raised by all WWTP discharges for all Massachusetts marine waters, including north coastal Massachusetts, Cape Cod, Buzzards and Mount Hope bays and develop a cooperatively funded program that pursue special studies and research in support of sustaining healthy ecosystems.

Per- and Polyfluoroalkyl Substances: Their Sources, Fate, and Effects in Marine Ecosystems

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are persistent organic pollutants that have been found globally and enter the ecosystem from air, soil and water. Over 9,000 PFAS have been identified and are used in industrial processes, household products, food packages, and firefighting products. Several PFAS are shown to cause immunotoxicity, interfere with reproduction and development, impact organs such as liver and kidneys, and may increase risk of certain cancers. Wastewater treatment plant effluent along with groundwater, rivers, nonpoint flows, and air are conduits for PFAS to both freshwater and marine ecosystems. This document examines what is known about the sources of PFAS, their transport, fate and effects on human and ecosystem health. It is worth noting that during the writing of this document, both the Commonwealth of Massachusetts and the U.S. Environmental Protection Agency began requiring PFAS monitoring in discharge permits to surface waters. Thus, it is timely to explore the PFAS contribution of wastewater outfalls to coastal ecosystems and to identify what is known about potential PFAS impacts to marine biota and human health.

Introduction

This document is part of a series of reviews about contaminants of emerging concern (CECs) in domestic wastewater effluents, specifically as it applies to the Massachusetts Water Resources Authority's (MWRA) outfall into Massachusetts Bay. In response to state and federal requirements, an Ambient Monitoring Plan (AMP) for the outfall was adopted to address concerns as to whether it is safe to swim, eat seafood, maintain aesthetics, and sustain a healthy ecosystem. After 28 years of monitoring, in 2018 the Outfall Monitoring Science Advisory Panel (OMSAP) organized a workshop to review the monitoring results and the relevancy of the monitoring plan. This workshop concluded that based on what is required to be monitored by the National Pollutant Discharge Elimination System (NPDES) permit and Ambient Monitoring Plan, "After 25+ years of monitoring, the data show that the MWRA outfall has not adversely affected Massachusetts Bay" (OMSAP 2018). The workshop summary also noted that some areas have improved or remained the same (e.g., concentrations of legacy metal contaminants have decreased in sediments), but some classes of CECs, specifically per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), and microplastics, have not been addressed (OMSAP 2018).

This section reviews what is known about PFAS and their sources, transport and fate, and effects examined in the context of wastewater treatment plant outfalls and impacts to the ecosystem and human health. The literature review summarizes information related to two questions identified in the AMP; namely, is it safe to eat seafood and are natural and living resources protected?

Although previous publications identify 4,700 PFAS, a recent listing in the EPA Computational Toxicology Database (CompTox) identifies 9,000¹ chemicals. PFAS enter the environment by air, soil, and water that eventually reach the ocean (OECD 2018). Some legacy persistent organic pollutants with originally unclear impacts, such as polychlorinated biphenyls (PCBs); chlordane; and dichloro-diphenyl-trichloroethane and its derivatives went through regulatory reviews resulting in cessation of their production and appropriate ways of disposing of the chemicals. PFAS have only recently been identified as persistent organic pollutants in need of regulation in Massachusetts (ATSDR 2020). The Massachusetts Department of Environmental Protection (MADEP) has developed PFAS standards for contaminated sites and drinking water; is in the process of developing standards for residuals (including biosolids); and will develop standards for wastewater and receiving waters (MADEP 2020). The U.S. Environmental Protection Agency (EPA) has issued a health advisory for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate acid (PFOS) in drinking water. The status regulations and advisories are discussed in a section at the end of the report. To date, two other groups of CECs, pharmaceuticals and personal care products (PPCPs) and microplastics, have not been specifically addressed in either state or federal regulations; however, the Massachusetts State Water Quality Standards at 314 CMR 4.05(5)(e) states that “*All surface waters shall be free from pollutants in concentrations or combinations that are toxic to humans, aquatic life or wildlife*”.

In order to gain insights into the role of PFAS in the environment, the Outfall Monitoring Science Advisory Panel (OMSAP) invited an *ad hoc* focus group of experts to review and present information related to PFAS and adopted the following goals for review: (1) the types of chemicals that are classified as PFAS, (2) sources and transport of PFAS to the environment, (3) exposure pathways for humans and marine wildlife, (4) the potential for effects from PFAS on organisms and humans, and (5) strategies identifying and prioritizing chemicals of interest from an extensive candidate list, including the status of monitoring for PFAS in Boston Harbor and Massachusetts Bay. The focus remains on the extent to which effluent from MWRA, and by extension other coastal wastewater treatment plants, may be discharging PFAS into marine receiving waters with potentially detrimental impacts on human health and ecosystems.

The OMSAP will make recommendations to MADEP and EPA on what future actions regarding PFAS should be addressed by MWRA; it is anticipated that some of these recommendations would apply to other coastal wastewater treatment facilities. Presentations on PFAS were made at meetings on 24 April 2019, 10 September 2019, 3 October 2019, and 16 December 2019.

Throughout this document, PFAS concentrations are expressed either by wet weight (ww), dry weight (dw), whole body (WB) or specific to tissues and organs. To provide the reader with a consistent frame of reference, the values have been converted to parts per billion (ppb) or ng/L or parts per trillion (PPT) to distinguish it from the familiar parts per thousand (ppt) used in oceanography.

What are per- and polyfluoroalkyl substances?

Per- and polyfluoroalkyl substances are a group of human-created chemicals that have been manufactured since the late 1940s (OECD 2018). Compounds and subgroups are considered PFAS if they include at

¹ https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster

least one perfluoroalkyl moiety (C_nF_{2n+1}) associated with a minimum of three carbon-fluorine bonds (Buck *et al.* 2011). To assist with referencing PFAS compounds, the major subclasses, and individual compounds mentioned in this paper, a list of abbreviations are provided at the end of the document. In addition, a family tree of PFAS subclasses, their chain length, precursors, and those restricted by global regulations or voluntary frameworks is available in a supplemental document (Supplemental Document 1). Many PFAS are often separated into two broad categories; “legacy” chemicals that have been produced and in use for decades (*e.g.*, PFOS, PFOA) and novel or replacement compounds such as GenX (hexafluoropropylene oxide dimer and its ammonium salt (HFPO-DA)), and ADONA (dodecafluoro-3H-4,8-diozamonannoate).

Non-polymer PFAS are further categorized as perfluoroalkyl substances or polyfluoroalkyl substances based on the degree of fluorination present within the molecule (Figure 1). Polyfluoroalkyl acids (PFAAs) include both perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs). For example, PFOS is a specific long-chain PFSA. The polyfluoroalkyl substances include fluorotelomer-type substances, perfluoroalkane sulfonamido substances, among others. The “precursor” compounds that readily transform into PFCAs, PFSAs, or other stable PFAS under environmental conditions as well as per- and polyfluoroalkyl ether acids (PFEAs) may fall under either the perfluoroalkyl substance or polyfluoroalkyl substance designation (Buck *et al.* 2011). PFEAs include the perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs). A relatively new replacement compound referred to as Gen X, or HFPO-DA is one specific PFECA. Each of these sub-groups and individual molecules vary based on molecular structure and functional groups (Buck *et al.* 2011).

The wide range of PFAS also possess similarities in physicochemical behavior and environmental fate (Buck *et al.* 2011; OECD 2018; Kwiatkowski *et al.* 2020). Generally, PFAS particularly PFAAs, are often referred to by chain length, *i.e.* by the number of carbons that make up the backbone of the molecule. Legacy PFCAs are considered long-chain with seven or more alkyl carbons, while legacy PFSAs are considered long-chain with six or more alkyl carbons (Buck *et al.* 2011).

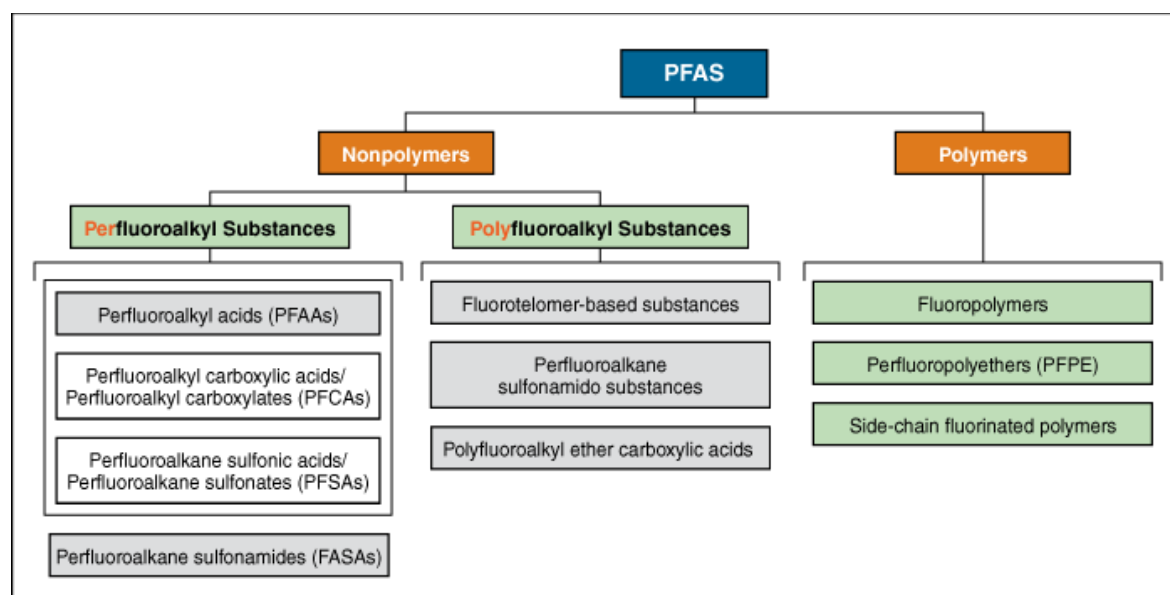


Figure 1. A schematic presenting some of the main groups of PFAS (ITRC, section 2.2., 2020a). Further details about PFAS nomenclature and groups can be found in Buck *et al.* (2011).

The carbon-fluorine (C-F) bond is one of the most stable single bonds identified in organic chemistry and defines PFAS behavior while also making them remarkably persistent in the environment and not readily degraded (Kissa 2001; Yamashita *et al.* 2008). Some PFAS are capable of degrading to some extent via *in situ* or *in vivo* oxidation, but because of the stability of the C-F bond, they often degrade into other, more stable PFAS structures (Ellis *et al.* 2004; Martin *et al.* 2010). For example, a sub-group of PFAS called fluorotelomer alcohols (FTOHs) transform in the environment into the more persistent and toxic PFCA sub-group (Ellis *et al.* 2004; Wallington *et al.* 2006).

As amphiphilic compounds, PFAS associate with both water and oil (Kissa 2001), even as they are used as water and oil repellents (Figure 2). This property means PFAS readily migrate within and beyond the hydrologic cycle (Hu *et al.* 2016; Yeung *et al.* 2017) while also accumulating in living organisms (Guillette *et al.* 2020).

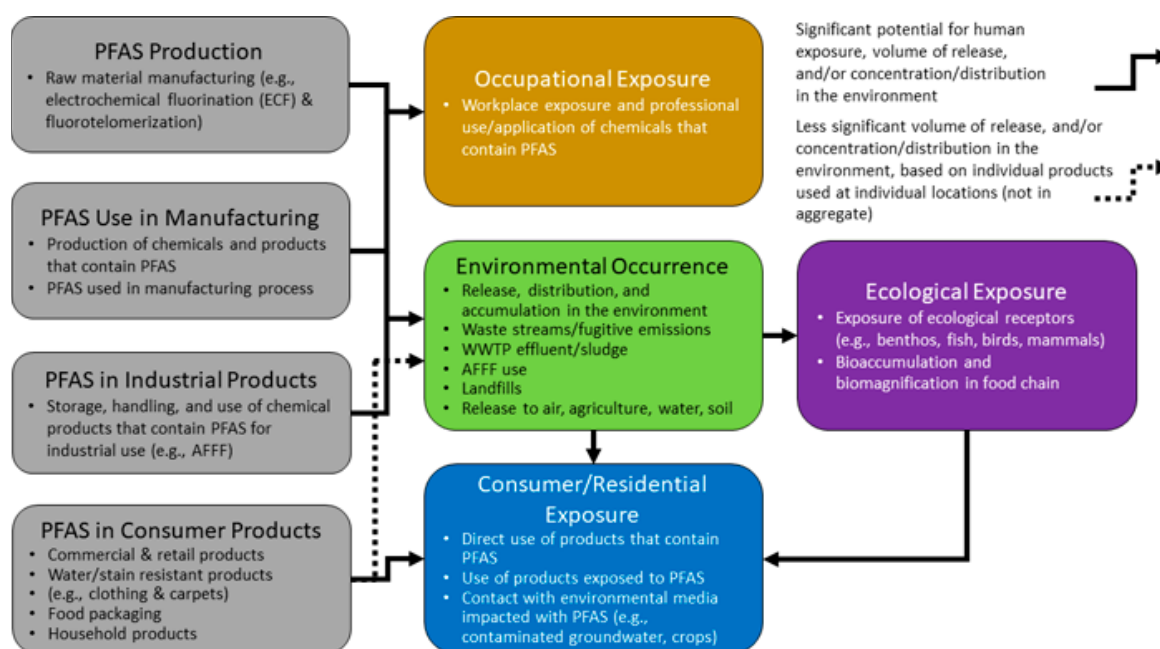


Figure 2. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle (ITRC 2020a). (See Table 1 for additional estimates of exposure for human health).

What are the sources and environmental fates of PFAS?

Initial commercial production of PFAS, primarily PFOS and PFOA started at 3MTM, and subsequently DuPontTM and subsidiaries manufactured PFOA. PFOA was used as a polymerization aid in polymer production such as Teflon[®] and PFOS was the key ingredient in fabric protectors and in older aqueous film forming foams (AFFF) used for firefighting at airports, military bases, and gas operations (Hu *et al.* 2016; ITRC 2020c). Production and use of PFOA and PFOS were primary contributors to the environment (Buck *et al.* 2011; Hu *et al.* 2016; Barzen-Hanson *et al.* 2017; Wang *et al.* 2017; Glüge *et al.* 2020). Subsequent to the phase-out in the United States of PFOS, PFNA, and PFOA by 3MTM and other major manufacturers, some legacy PFAS, e.g., PFOS, continued to be produced until around 2013 (ITRC 2020c). In addition, many PFAS subclasses were manufactured, replacing legacy compounds and released

from their sources via wastewater treatment facilities, runoff, groundwater, rivers, landfill leachate and atmospheric release (Masoner *et al.* 2020; Wang *et al.* 2017).

Systems where PFAS play a central role as current sources to the environment include industrial and workplace processes such as electroplating, electronics manufacture, production of medical equipment, oil recovery, textile manufacture, plastics manufacture, specialty chemical production, fuel cell production, and membrane manufacture (Glüge *et al.* 2020). Due to their unique and desirable chemical qualities, PFAS are found in innumerable household or consumer goods including non-stick pans (Teflon®), food packaging, take-out food containers, paper goods, cleaning products, cosmetics, fire-fighting foams, carpets and furniture (Scotchgard™), ski wax, textiles, waterproof clothing (GORE-TEX®), coatings, paints, and many more consumer products (Schaidler *et al.* 2018; Glüge *et al.* 2020). Recently several PFAS compounds at levels above those considered safe for drinking water were found in a pesticide used by Massachusetts mosquito control (Boston Globe, December 2, 2020). Some polyfluoropolymers breakdown into plastics and releasing additives, such as PFAS, BPA, phthalates and others that are frequently added to plastics (Lohmann *et al.*, 2020).

As with many chemicals, PFAS do not remain confined to products or sites where they are used or discharged. Their environmental persistence coupled with their high aqueous solubility allows them to leach into the environment readily, where they can be subsequently transported via air, water, or solid materials (Armitage *et al.* 2009a,b). They are ubiquitous and are found in polar regions where they are transported by long-range atmospheric and water-borne pathways (Ellis *et al.* 2004; Wallington *et al.* 2006; Pickard *et al.* 2008) and in the deep ocean (Yamashita *et al.* 2008; Yeung *et al.* 2017).

Household and commercial wastewater, industrial discharges, or otherwise PFAS contaminated influents enter domestic wastewater treatment systems (Schultz *et al.* 2006; Guo *et al.* 2010; Arvaniti and Stasinakis 2015; Gago-Ferrero *et al.* 2017; Masoner *et al.* 2020). Figure 3 illustrates a generalized flow of PFAS to and from municipal wastewater treatment plants (Hamid and Li 2016). Although other sources, *e.g.*, direct discharges from industrial sources, landfill run-off, groundwater leachate, overland and storm water flows, and long-range atmospheric transport also contribute to receiving waters and the relative contribution of each of these fluxes is not currently quantified. Recently, there have been discussions of incinerators as a potential significant source of PFAS in the air (Stoiber *et al.* 2020).

The fate of PFAS in wastewater processes depends on their specific structure. Long-chain compounds may preferentially partition to particles and become associated with biosolids, while shorter chain soluble PFAS remain in the aqueous phase. Some precursors may oxidize to other, more stable PFAS (*e.g.*, PFOA), and stable terminal products may remain intact in the aqueous phase and re-enter the water cycle following effluent discharge to receiving waters (Schultz *et al.* 2006; Guo *et al.* 2010). Municipal wastewater treatment processes do not substantially remove PFAS from effluent and those associated with residuals or biosolids (sludge) are often used as fertilizer and soil amendments that may pose environmental risk (Schultz *et al.* 2006; Gómez-Canela *et al.* 2012). In the MWRA service area the magnitude of contributions from households (see Glüge *et al.* 2020 for potential household sources), manufacturers using PFAS compounds, and other specific sources of PFAS to the wastewater infrastructure are largely unknown.

The oceans are the ultimate sink for PFAS, as volatile atmospherically transported PFAS (*e.g.*, FTOHs) may be oxidized (Ellis *et al.* 2004) and washed out of the gas phase into the water cycle (Joeris *et al.* 2020), while water-borne PFAS in rain, rivers, and streams flow to the ocean (Paul *et al.* 2009). The ubiquitous environmental distribution of PFAS in the biosphere is reflected in their presence in freshwater and marine invertebrates and vertebrates. They are present in plants where soils are either contaminated or intentionally amended with biosolids with uptake by plants (Ghisi *et al.* 2019; Wang *et al.* 2020),

domestic animals, agricultural food products (Kowalczyk *et al.* 2013; Scher *et al.* 2018; Munoz *et al.* 2017) and humans (Sunderland *et al.* 2019). In marine biota, PFAS are found across food webs in invertebrates (*e.g.*, crustaceans (Langberg *et al.* 2019), holothurians (Martin *et al.* 2019), and shellfish (Munsch *et al.* 2019) to name a few); fish (Langberg *et al.* 2019; White *et al.* 2019); seabirds (Gebbinck *et al.* 2011); and marine mammals (Dassuncao *et al.* 2017).

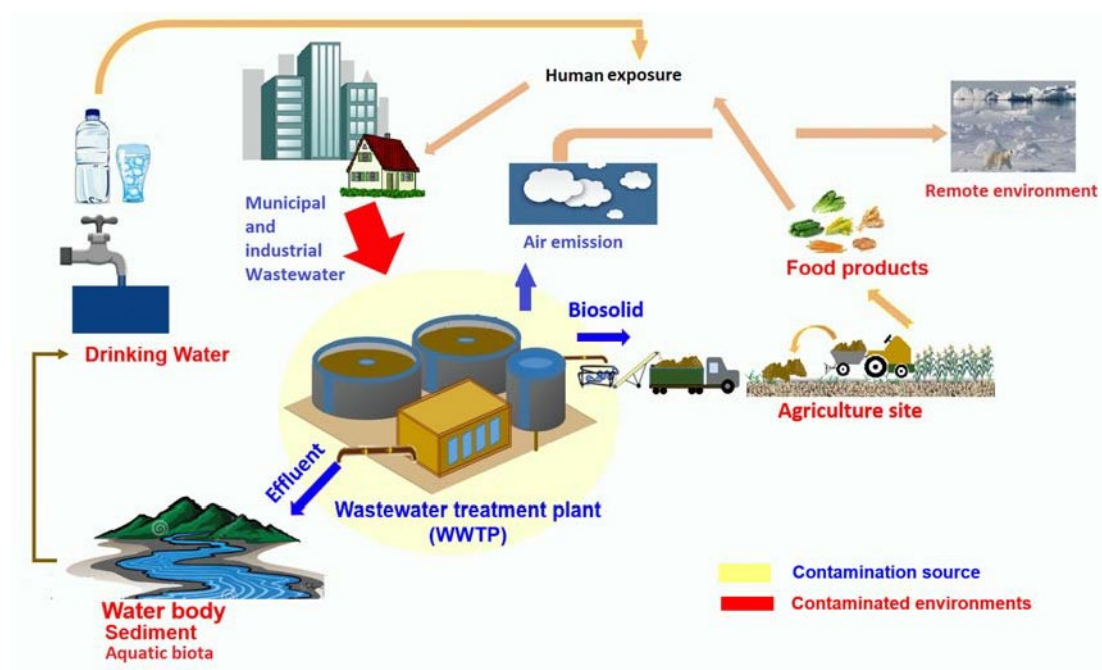


Figure 3. Environmental pathways of per- and polyfluoroalkyl compounds (PFASs) from a wastewater treatment plant (WWTP); Hamid and Li (2016).

How are humans and marine biota exposed to PFAS?

Human Exposure to PFAS

Humans are primarily exposed to PFAS via food, drinking water, and air-borne particles such as dust; whereas dermal and inhalation exposure are relatively minor contributors to adults (Sunderland *et al.* 2019; Table 1, Figure 2). However, for individuals working in an industry that produces or uses PFAS, or those who work with AFFF, inhalation likely represents a significant exposure risk (Sunderland *et al.* 2019). It is generally accepted that seafood is a significant route of exposure of PFAS in humans, particularly in communities where fishing and whaling are primary dietary sources (Dassuncao *et al.* 2018; Hu *et al.* 2018; Sunderland *et al.* 2019). Less well-documented are contributions of PFAS contamination that come from products in direct contact with food, such as: PFAS-treated food wrappers around desserts, burgers and other foods; drinking containers; and other products (Schneider *et al.* 2018). The U.S. Food and Drug Administration (U.S. FDA) has announced a voluntary phase-out by three manufacturers (AR Chroma, AGC Chemicals Americas, Inc., and Daikin America, Inc.) of 6:2 fluorotelomer alcohol (6:2 FTOH) products that often are in contact with food items (U.S. FDA 2020).

Plants grown in areas with PFAS-contaminated soils may also be a source for humans, domestic livestock, and wildlife (Hu *et al.* 2016; Ghisi *et al.* 2019; Wang *et al.* 2020). Drinking water contaminated with PFAS is a major concern (see section on regulations below). The highest levels of contamination in drinking water and groundwater have been associated with proximity to industrial sources, landfills, manufacturing plants, AFFF impacted sites, airports, wastewater treatment plants, and incinerators (Masoner *et al.* 2020; Hu *et al.* 2016; Zhang *et al.* 2016; Stoiber *et al.* 2020). Children may be more exposed via maternal transfer of PFAS *in utero* or through breast milk, as well as via dermal and inhalation exposure through increased proximity to and contact with PFAS-containing textiles used in flame retardant sleepwear and carpets (Sunderland *et al.* 2019).

Table 1. Literature estimates of source contributions (%) to adult PFAS exposures, (modified from Table 1, Sunderland *et al.* 2019). Numbers represent an average percent based on the reported percentages; numbers in parentheses are ranges of reported percentages; n.d. is no data given and were not included in the average; N= number of reported percent from the paper cited. References from Sunderland (2019) are: (1) Trudel *et al.* 2008; (2) Vestergren and Cousins 2009; (3) Haug *et al.* 2011; (4) Lorber and Egeghy 2011; (5) Tian *et al.* 2016; (6) Shan *et al.* 2016; (7) Gebbink *et al.* 2015; (8) Egeghy and Lorber 2011.

PFAS Category	Diet	Dust	Tap Water	Food pkg.	Inhalation	Dermal	Other	References
PFOA	66 (16-99) N=6	8.5 (6-11) N=4	12 (1-37) N=5	29.5 (3-56) ^b N=2	6.3 (1-14) N=3	<1 N=1	9 (2-22) ^{a,c,d} N=3	1,2,3,4,5,6
PFOS	85 (66-100) N=6	8 (1-15) N=4	10 (1-22) N=3	n.d.	2.3 (1-5) N=3	<1 N=1	3.5 (3-4) N=2	1,3,5,7,8
PFBA	n.d.	4 N=1	96 N=1	n.d.	n.d.	n.d.	n.d.	7
PFHxA	38 N=1	4 N=1	18 N=1	n.d.	8 N=1	n.d.	12 ^d N=1	7
PFOA	47 N=1	8 N=1	12 N=1	n.d.	6 N=1	n.d.	22 ^d N=1	7
PFDA	51 N=1	2 N=1	4 N=1	n.d.	15 N=1	n.d.	28 ^d N=1	7
PFDoDA	86 N=1	2 N=1	2 N=1	n.d.	4 N=1	n.d.	5 ^d N=1	7

^a Carpet, ^b Consumer goods, ^c Precursors, ^d Indirect

Marine Biota Exposure to PFAS

Marine biota are exposed to PFAS in the coastal and oceanic environments via water, sediments, and diet, with species showing the greatest concentrations in closest proximity to sources (Munoz *et al.* 2017). The legacy PFAS compounds are the most studied to date with emerging information on replacement compounds, as they are identified and become more measurable. The following studies relate PFAS sources in coastal and open oceans to uptake, bioaccumulation, although species within taxonomic groups may exhibit different metabolic responses. Many of these compounds preferentially partition to proteinaceous or aqueous matrices; this results in different accumulation patterns in food webs compared to hydrophobic legacy compounds. In general, long-chain PFAS compounds tend to bioaccumulate whereas short chain and other chemical forms (telomers, precursors,) may be degraded to terminal compounds *e.g.*, PFOA. Concentrations are expressed as ng/g (parts per billion or ppb) either as wet weight (ww) or dry weight (dw) and may include what has been measured, *i.e.*, soft tissue, whole body (WB), or specific organs or tissues (liver, hepatopancreas, fillet, serum). The following studies focus on PFAS in invertebrates (molluscs and crustaceans), fish, and marine mammals. These are species of interest in the current MWRA AMP, and studies of PFAS in organisms and biomagnification in Massachusetts Bay and the North Atlantic. This section focuses on bioaccumulation, whereas the next section focuses on impacts.

The evidence for bioaccumulation is most compelling for C8 – C11 PFCAs and PFOS, while the biological behavior of novel PFAS and shorter-chain PFAAs is still under investigation or has been

shown to vary between exposure scenarios (Conder *et al.* 2009, ITRC 2020b). Bioaccumulation of PFCAs, PFSAAs, and some novel PFAS have been demonstrated in field settings, although the magnitude of bioaccumulation for different PFAAs has been shown to vary within different food webs or locations. This is largely due to differences in exposure scenario, methods used to calculate bioaccumulation, trophic strategies, or toxicokinetic variables like excretion and metabolism (Conder *et al.* 2009; Galatius *et al.* 2013; Franklin 2015; Reiner and Place 2015). Substantial variability in methods, species, tissues sampled, locations, adequate sample size, and PFAS analyzed (*e.g.*, PFOA, PFOS, precursors and fluorotelomers) call for refined approaches to better understand the impacts and risks to human health, species, and ecosystems.

PFAS bioaccumulation in organisms indicates their availability to biota and potential for impacts. In the Gulf of Maine, PFAS in the blue (edible) mussel, *Mytilus edulis* found PFAS at levels of ng/g or parts per billion at four locations in Boston Harbor, including a site near Deer Island (Apeti *et al.*, 2021). Other locations included a site near the mouth of the Merrimack River, in Buzzards Bay near the Cape Cod Canal and Nauset Harbor on the outer Cape. Several European studies have reported PFAS in invertebrate species such as green shore crab (*Carcinus maenas*), mussels (*Mytilus edulis* and *Mytilus galloprovincialis*), and oysters (*Crassostrea gigas*), along with numerous other invertebrate taxa that serve as food for fish, birds and mammals (Munoz *et al.* 2017; Langberg *et al.* 2019; Munschy *et al.* 2019). PFAS have been reported in teleost fish such as the Atlantic cod (*Gadus morhua*), flatfish such as the European plaice (*Pleuronectes platessa*) and Lemon sole (*Microstomus kitt*) (Langberg *et al.* 2019), several fish species along the in South Carolina coast, (Fair *et al.* 2019) and in forage-fish species in Massachusetts Bay (Robuck 2020).

While research continues to explore specific exposure scenarios, bioaccumulation dynamics, and the environmental, and biological distribution of novel and understudied PFAS beyond what is highlighted above, existing research indicates that long-chain PFCAs and PFOS are bioaccumulating in both invertebrates and vertebrates (Houde *et al.* 2011; Ahrens and Bundschuh 2014) and biomagnification is occurring in marine ecosystems (Kelly 2009; Munoz *et al.* 2019).

What are the impacts of PFAS in humans and biota?

Human Health Impacts of PFAS

Potential human health impacts from PFAS were first identified by internal industry studies in the 1960s, but it took almost four decades before that information was released to the public and action was taken to voluntarily phase out PFOS after the industry developed substitutes (U.S. EPA, accessed 2020; ITRC 2020c). Current understanding of human health effects relies on epidemiological studies conducted with occupationally exposed workers, residents living near facilities producing or using PFAS, and the general population. Using serum levels as a biomarker of individual exposure, these studies pair health assessments with measurements of select PFAS that bind to albumin in the blood (Grandjean and Budtz-Jørgensen 2013; Dassuncao *et al.* 2018). To date, most identified human health impacts fall into four general categories: developmental effects, hormonal (endocrine) and immune disruption, potential carcinogenicity, and changes in blood lipid levels (ATSDR Tox Profile 2018; Sunderland *et al.* 2019).

Many of the health effects are associated with environmentally relevant levels of exposure, while some, like increased risk for some cancers, are associated only with high levels of PFAS exposure (ATSDR 2018; Sunderland *et al.* 2019). Although legacy PFOS and PFOA were phased-out in the U.S, numerous other fluorinated compounds, some of which are highly toxic, are still in commercial production and

widespread use. While some legacy PFAS serum levels decreased, mixtures of PFAS continue to be present in human serum (Grandjean and Budtz-Jørgensen 2013; Dassuncao *et al.* 2018; NHANES 2019).

Table 2. Fish consumption screening values (FSCV) for PFOS (MDHHS 2016).

Michigan Fish Consumption Screening Values			New Jersey Fish Consumption Screening Values		
Meal Category Meals per month	PFOS μg/g (ppm)	Equivalent in ppb (ng/g)	PFOA ng/g (ppb)	PFNA ng/g (ppb)	PFOS ng/g (ppb)
Unlimited meals			0.62	0.23	0.56
16	≤0.009	≤9			
12	>0.009 to 0.013	>9-13			
8	>0.013 to 0.19	>13-19			
4	>0.019 to 0.038	>19-38	4.3	1.6	3.9
2	>0.038 to 0.075	>38-75			
1	>0.075 to 0.15	>75-150	18.6	6.9	17
6 meals per year	>0.15 to 0.3	>150-300			
4 meals per year			57*	21*	51*
1 Meal per year			226*	84*	204*
Limited	NA	NA			
Do No Eat	>0.3	>300	>226*	>84*	>204*

*concentrations not recommended for high risk population

Research detailing the effects of PFAS mixtures on human health is rapidly expanding, yet uncertainties remain regarding how mixtures of PFAS or replacement PFAS like Gen X and other PFEAs may impact human health (Fenton *et al.* 2020). Existing studies suggest that newer PFAS compounds may impart similar impacts to the long-chain PFAAs they seek to replace (Blake *et al.* 2020; Gomis *et al.* 2018). Actions by state and federal agencies are discussed in a later section.

Fair *et al.* (2019) applied fish consumption screening values (FSCV) developed by the Michigan Department of Health and Human Services (MDHHS 2016) to PFOS concentrations in South Carolina southern flounder (*Paralichthys lethostigma*) and spotted seatrout (*Cynoscion nebulosus*) (Table 2) and determined that humans should not eat more than 4 meals/month.

Marine Biota Impacts from PFAS

Very few studies examine PFAS exposure and impacts in marine organisms. Laboratory studies using rodents, birds (chickens), fish and invertebrates indicate that PFAS are associated with adverse impacts on growth, development, reproduction, and metabolism (ATSDR 2018; ITRC Ecological Effects, 2020b). These data serve as the basis for presumed impacts on marine mammals and birds. Most wildlife research to date has focused on the occurrence of PFOA (a PFCA) and PFOS (a PFSA), with investigation of fluorotelomer-based substances, long-chain PFCAs or replacement PFAS (Reiner and Place 2015). Even though legacy PFAS (PFOA, PFOS) and perfluorononanoic acid (PFNA) were generally phased out (ITRC 2020c), PFOS remains one of the major PFAS in wildlife (Reiner and Place 2015). Canada has adopted PFOS Federal Environmental Quality Guidelines (FEQC) for water, fish tissue, diet, and bird egg (Table 3; ECCC 2018). The FEQC guidelines were based on data from freshwater invertebrates, amphibians, birds, and terrestrial mammals and long-term impacts on amphibians, plants, birds, and terrestrial mammals, as well as toxicity studies using rats and monkeys (Seacat *et al.* 2002; 2003).

Regional application of the Canadian FEQC to wild-caught fish from South Carolina found that 83% of the fish had PFAS levels that pose risk to marine mammals (Table 3; Fair *et al.* 2019; see also ITTC 2020b). The concentrations (whole fish ranges from 12.7-33.0 ng/g (ppb) ww and fillets ranges 6.2-12.7 ng/g (ppb) ww) varied with fish species (Fair *et al.* 2019). Preliminary analysis of forage fish from Stellwagen Bank (sand lance, *Ammodytes americanus* and mackerel, *Scomber scombrus*) indicates PFOS (range: 3–10 ppb, whole fish) above thresholds established elsewhere as safe for wildlife diet (>4.6 or >8.2 ppb in mammalian and avian diet, respectively) and above thresholds suggested by the state of New Jersey as safe for human consumption (0.56 ppb and 3.9 ppb, for daily and weekly consumption, respectively (Robuck 2020; see Tables 2 and 3).

Table 3. Canadian Federal Environmental Quality Guidelines for perfluorooctane sulfonate (PFOS) for surface water, fish tissue, wildlife diet for mammalian and avian, and bird egg (adapted from ECCC 2018).

Water (µg/L) (ppb)	Fish Tissue (mg/kg ww)* (ppm or 9,400 ppb)	Wildlife Diet (µg/ww food)** (ppb)		Bird Egg (ng/g ww) (ppb)
6.8	9.4	4.6	8.2	1.9

*ww = wet weight

**The wildlife diet guidelines are intended to protect either mammalian or avian species that consume aquatic biota. The guidelines are the concentration of PFOS in the aquatic biota food item, expressed on whole body, wet weight basis that could be eaten by terrestrial or semi-aquatic mammalian or avian wildlife.

While the occurrence of PFAS may be well-described for many locations and species of wildlife, significant data gaps remain in our knowledge of impacts of PFAS on marine species and food webs. These gaps represent a significant impediment to defining proper management practices as bioaccumulation is not an indicator of effects. Studies that document impacts in wildlife find potential for sub-lethal effects at low concentrations. One laboratory study shows adverse impacts on the phytoplankton (*Chlorella* sp.) growth when exposed to persistent and bioaccumulative chemicals that replace phased-out PFAS at concentrations far below acute toxicity levels (Niu *et al.* 2019). Plankton are at the base of the food web and have the potential to impact higher trophic levels. The green mussel (*Perna viridis*) demonstrated genotoxic responses to perfluorinated chemicals that was related to time and exposure (Liu *et al.* 2014) even though bivalves have low concentrations of PFAS (Munoz *et al.* 2017).

Marine mammal PFAS concentrations from liver, brain and blood plasma were correlated with health effects (Fair and Houde 2018; Table 4). While many of the studies focus on Arctic and Pacific species, a few examined marine mammals from the northwestern Atlantic. Potential effects associated with PFAS vary with species, for example, California sea otters (*Enhydra lutris nereis*) succumb to infectious diseases (Kannan *et al.* 2006). Bottle nose dolphins (*Tursiops truncatus*) have hematopoietic, immune, kidney and liver function effects (Fair *et al.* 2013). The Baikal seal (*Pusa siberica*) had high concentrations in kidneys associated with enzyme changes (Ishibashi *et al.* 2008), and polar bears (*Ursa maritimus*) showed reproductive and hormonal responses (Sonne *et al.* 2009; Pedersen *et al.* 2015, 2016; Bourgeon *et al.* 2017). In the northwestern Atlantic, marine mammals have higher levels of PFAS than other regions of the north Atlantic with some concentrations above levels associated with immunotoxicity (Spaan *et al.* 2020). Seals from Massachusetts were found to contain PFAS above immunotoxicity thresholds established in marine mammals (Shaw *et al.* 2009; Spaan *et al.* 2020).

Although not a marine mammal, several Great Shearwaters in Massachusetts Bay exhibited decreased liver phospholipid content with increasing levels of PFOS (Robuck *et al.* 2020), as well as decreased total body fat, reduced organ weights, and altered wing length in association with a range of C9 – C14 PFCAs,

PFOS, FOSA, and two precursor compounds (Robuck 2020). Some seabirds from Massachusetts Bay have been found to contain PFOS at levels above female-specific toxicity reference values established using controlled studies in chickens (>140 ppb in liver) (Robuck *et al.* 2020).

Table 4. Health-related impacts on marine mammals associated with PFAS modified from Fair and Houde (2018) with additions relevant to marine mammals and birds in the northwestern Atlantic, including Massachusetts Bay. PFAS abbreviations are in Appendix A.

Organism	Region	Years	Tissue	Concentration as ng/g (ppb) unless noted	Effects	Study*
Sea otter, <i>Enhydra lutris nereis</i>	California, U.S.	1992-2002	Liver:	PFOS: healthy: 31; emaciated 39; diseased: 95 PFOA: healthy: 49; emaciated: 62; diseased: 89	Emaciated and diseased livers were significantly associated with higher concentrations	1
Bottlenose dolphin <i>Tursiops truncatus</i>	Charleston, South Carolina, U.S.	2003-2005	Blood plasma	ΣPFAS 1970	Multiple immunological and hematological parameters	2
Baikal Seal <i>Pusa siberica</i>	Lake Baikal	1992	Liver; In vitro	PFDA <0.56-35; PFNA, PFDA, PFUnA with LOEC at 62.5-125 μM	Hematological parameters; hepatic CYP4A correlated with PFNA and PFNA	3
Polar bear <i>Ursa maritimus</i>	East Greenland	1990-2006	Liver	PFOS: 3108	Risk Quotient >1 for reproduction	4
Polar bear <i>Ursa maritimus</i>	East Greenland, Scoresby Sound	2011-2012	Brain	ΣPFSA (91% PFOS): 25; ΣPFCA (79% PFUnA, PFDoA, PFTTrDA): 88	MAO brain activity; negative correlation to dopamine	5
Polar bear <i>Ursa maritimus</i>	East Greenland, Scoresby Sound	2011-2012	Brain	ΣPFSA (91% PFOS): 25; ΣPFCA (79% PFUnA, PFDoA, PFTTrDA):88	Positive interaction between 2 hormones, testosterone and 17α-hydroprogesterone	6
Polar bear <i>Ursa maritimus</i>	Barents Sea, Svalbard, Norway	2012-2013	Brain Plasma	ΣPFAS: 353 ΣPFSA: 264 ΣPFCA: 88	Alterations of thyroid homeostasis	7
Pilot whale <i>Globicephala melas</i>	U. S. North Atlantic	1994-2002; (2006-2013)	Juvenile, muscle	ΣFOSA: 20(10); ΣPFOS: 2.7 (4.6); ΣPFOA: 0.1(0.1); ΣPFSA: 0.2 (0.16); ΣPFCA: 2.1 (7.1)	Exposure: 1999-2002 (2006-2013)	8
Harbor porpoise <i>Phocoena phocoena</i>	U.S. Atlantic Coast	2006-2012	Liver	ΣPFCA: 26.6; ΣPFSA: 69.5; ΣPFAS: 288.1; TF: 1560.3	Total exposure is underestimated	9
Grey seal <i>Halichoerus grypus</i>	U.S. Atlantic Coast	2000-2004	Liver	ΣPFCA: 65.9; ΣPFSA: 178.6; ΣPFAS: 285.2 TF: 1433.7	Above immunotoxicity levels; total level underestimated	9
Harbor seal <i>Phoca vitulina</i>	U.S. Atlantic Coast	2000-2008	Liver	ΣPFCA: 27.7; ΣPFSA: 52; ΣPFAS: 233.6; TF: 1138.8	Above immunotoxicity levels; total level is underestimated	9
Pygmy sperm whale <i>Kogia breviceps</i>	U.S. Atlantic Coast	2007	Liver	ΣPFCA: 70; ΣPFSA: 7.1; ΣPFAS:106.2; TF 559.7	Total exposure is underestimated	9
Great shearwater <i>Ardenna gravis</i>	Massachusetts Bay	2020	Liver	PFAS 11-280; (58% of all PFAS)	Decreased liver phospholipid content with PFOS	10

*1 = Kannan *et al.* 2006; 2 = Fair *et al.* 2013; 3 = Ishibashi *et al.* 2008; 4 = Sonne *et al.* 2009; 5 = Pedersen *et al.* 2015; 6 = Pedersen *et al.* 2016; 7 = Bourgeon *et al.* 2017; 8 =Dassuncao *et al.* 2017; 9=Spaan *et al.* 2020; 10 = Robuck *et al.* 2020.

Current Studies

The MWRA shares information with the Massachusetts Office of Technical Assistance (OTA) to inform them of industrial users so that OTA can offer them free technical assistance to reduce PFAS in their

industrial discharges to MWRA's sewer system. MWRA collaborates with researchers from state and federal agencies, non-government agencies, and academia. MWRA is participating in two Water Research Foundation (WRF) research projects: 5031—Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants; and 5042—Assessing Poly- and Perfluoroalkyl Substance Release from Finished Biosolids. These projects seek to evaluate PFAS occurrence in U.S. wastewater treatment plants and conduct a mass-balance approach calculation to determine the fate of PFAS compounds during wastewater treatment processes. As part of its programmatic research on contaminants of emerging concern the USEPA-ORD laboratory in Narragansett is conducting research on PFAS and PCPPs in Massachusetts Bay. The purpose of this study is to evaluate the presence, dilution, and attenuation of these compounds, as well as estimate exposure to aquatic life in Massachusetts Bay. The status of this project was last reported to OMSAP at the October 3, 2019 meeting. The USEPA-ORD laboratory has sampled Massachusetts Bay twice but analysis of samples from this project has been delayed by laboratory shutdowns associated with the COVID-19 pandemic.

Regulation of PFAS

The manufacture and use of specific PFAS are internationally restricted by the Stockholm Convention², including PFOS and PFOA and related compounds. Currently, PFAS are not regulated at the federal level in the U.S., however the EPA disseminating Health Advisory Guidelines of 70 PPT for PFOA and PFOS individually or in combination, and under the Toxics Substance Control Act³. Short-chain chemicals or structurally diverse analogs incorporating ethers, chlorine, polyfluorination, or other functionalities have supplanted the phased-out legacy PFAS, some of which are precursors and may form PFOS or PFOA (Wang *et al.* 2017; Liu *et al.* 2019). Additional information on the Toxic Use Reduction Program can be found in the 2018 annual report (OTA, TURI and MADEP 2018). In fiscal year 2020, EPA added 172 PFAS compounds to the Toxic Release Inventory (TRI)⁴. Industries covered under TRI must report the use of these chemicals. Massachusetts's released revisions to its Toxic Use Reduction Act (TURA) regulations incorporated these additions at the end of calendar year 2020⁵. Health advisories provide information on contaminants that can cause human health effects and are known or anticipated to occur in drinking water. EPA has issued a health advisory on PFAS to provide technical information to state agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination. The EPA recommended the health advisory level of 70 parts per trillion (PPT) for individual or combined concentrations of PFOA and PFOS offers a margin of protection for all receptors from adverse health effects resulting from exposure to PFOA and PFOS in drinking water.

Currently, many New England states are working on setting standards for PFAS in drinking water. During the preparation of this paper, Massachusetts adopted a maximum contaminant level, or MCL, of 20 ng/L or PPT for the sum of six specific PFAS compounds, perfluorohexanesulfonic acid (PFHxS),

² Although the U.S. has not accepted ratification or entry into force, in 2001 it was a signatory of the Stockholm Convention on Persistent Organic Pollutants which *"is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment"* (Stockholm Convention, 2020).

³ <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas>

⁴ https://www.epa.gov/sites/production/files/2021-01/documents/tri_non-cbi_pfas_list_1_8_2021_final.pdf

⁵ <https://www.mass.gov/tura-regulations-and-amendments>

perfluoroheptanoic acid (PFHpA), PFNA, PFOS, PFOA, and perfluorodecanoic acid (PFDA)⁶. All drinking water suppliers will be required to test for PFAS in drinking water. The six PFAS compounds have been identified in public water supplies in Massachusetts at levels exceeding the state MCL of 20 ng/L (PPT)⁷. The American Water Works Association has compiled a list of state policies for drinking water and drinking water sources as of November 1, 2020⁸. See also Boxer et al. (2016) for an interactive, up-to-date map of areas with high PFAS in drinking water.

Testing for PFAS in drinking water has begun in Massachusetts for municipal and individual wells and sources of drinking water. The state has funds to support testing and remediation (C. Coniaris, pers. comm., 2021).

Other actions include a Massachusetts interagency task force focused investigating “PFAS detection in multiple environmental media, known and potential exposure pathways, associated health and environmental impacts, possible sources of contamination, state and federal action, costs and challenges, and potential solutions on PFAS” (PFAS Interagency Task Force 2022). Although the task force did not address marine outfalls or impacts, their recommendations include reducing and eliminating PFAS discharges, minimizing use, and assigning accountability.

In April 2021, an EPA Council on PFAS was established that has resulted in several strategic actions to address impacts to humans and wildlife, toxicity testing, toxicity assessment, standardized methodologies, and gathering data on groups of PFAS. In April 2022 EPA’s PFAS Strategic Road Map has begun to evaluate draft aquatic (freshwater) life criteria PFOA and PFOS were recommended, reduction of PFAS through NPDES permits guidance is being developed, and a new method for detecting fluoride in the water is being tested among other actions (EPA 2022).

There are limited regulations or remediation guidelines offered for wastewater effluent at the state or federal level, making it difficult to implement PFAS monitoring or remediation for wastewater effluent. Several states are exploring guidelines or regulation of biosolids and some have or are in the process of developing standards. Recently, MADEP and EPA in draft and final National Pollutant Discharge Elimination System (NPDES) permits are including the same six PFAS chemicals for monitoring in wastewater treatment facilities (WWTP) that are used for monitoring drinking water. A study is currently underway for individuals living near Pease Airport in Portsmouth, New Hampshire, and surrounding areas, where residents were exposed to contaminated drinking water from 2004 to 2014⁹. The study has been delayed due to COVID-19.

Related to the lack of discharge or cleanup guidelines, there are no federal standards for PFAS in marine or freshwater surface waters although that may be changing (see EPA 2022). Few states have developed or are working to develop guidelines for PFAS in surface waters supporting human or aquatic life use. The state of New Hampshire is developing surface water standards protective of human use, fish and shellfish consumption, and aquatic life use; surface water guidelines of varying regulatory significance designed to protect human or non-human uses are also in place in Oregon, Florida, Minnesota, and Michigan. Australia and the European Union offer surface-water guidelines for PFOS specifically protective of marine wildlife at 0.4 and 0.13 PPT, respectively. Fish consumption advisory guidelines for PFAS only exist in a handful of states, including New Jersey, Michigan, and Minnesota. A lack of fish

⁶<https://www.mass.gov/doc/per-and-polyfluoroalkyl-substances-pfas-drinking-water-regulations-quick-reference-guide/download>

⁷ <https://www.mass.gov/info-details/per-and-polyfluoroalkyl-substances-pfas#pfas-detected-in-drinking-water-supplies-in-massachusetts->

⁸ https://www.awwa.org/LinkClick.aspx?fileticket=Ve9Ygub_2ZM%3d&portalid=0

⁹ <https://www.atsdr.cdc.gov/pfas/activities/pease/community-fact-sheet.html>

consumption guidelines explicitly protective of wildlife health in the US is in contrast to Canada which appears to be the only government entity that has offered diet guidelines for the protection of mammals and birds that eat fish in their Chemicals Management Plan¹⁰.

Relevance to OMSAP and MWRA Operations

The primary concern of this white paper is the extent to which PFAS may occur in MWRA effluent, its contribution to Massachusetts Bay, and its impact on seafood and the protection of natural and living resources. Currently MWRA meets the EPA and Massachusetts requirements for sludge treatment for use as fertilizer; for example the MADEP “has begun developing screening levels for residuals and approving laboratories for analysis, and is continuing to require entities that sell, distribute, and apply biosolid products to test for PFAS” (C. Vakalopoulos, MADEP).

Preliminary data from research underway indicate that PFAS are present in MWRA effluent and ambient Massachusetts Bay waters (A. Robuck, URI-GSO currently at Mount Sinai Medical School and M. Cantwell, US EPA, pers. comm. 2020) and is consistent with findings of PFAS in municipal wastewater effluent globally (Coggan *et al.* 2019). The occurrence of PFAS in ambient waters is expected, given the proximity of Massachusetts Bay to human populations and multiple effluent inputs from MWRA and other wastewater facilities (Hu *et al.* 2016) and other sources. The dilution provided by the MWRA diffuser’s design and location likely contributes to the low levels observed or hypothesized to occur in Massachusetts Bay.

Summary Recommendations and Uncertainties

Recommendations for consideration submitted by the Outfall Monitoring Science Advisory Panel to the Massachusetts Department of Environmental Protection, the U.S. Environmental Protection Agency, and the Massachusetts Water Resources Authority

- PFAS are present in MWRA’s outfall and necessitates characterization of which PFAS are present in the influent, effluent, their concentration levels, and availability in the ecosystem. Depending on the results of ongoing studies, there may be other issues that emerge that require short-term special studies.
- At a regional and national level, long-term studies of these persistent organic pollutants should address issues such as bioaccumulation and biomagnification in the ecosystem and their effects on humans and marine biota. While the occurrence of PFAS may be well-described for many locations and species, data gaps remain in our knowledge of impacts of PFAS on marine species, food webs, and ecosystems. These gaps represent an impediment to defining proper management practices and to developing risk assessments for humans and the ecosystem that should be pursued by national funding agencies such as the National Science Foundation, the National Institute of Environmental Health Sciences, and National Institute of Health, as well as foundations dedicated to healthy ecosystems.

¹⁰ <https://www.canada.ca/en/health-canada/services/chemical-substances/chemicals-management-plan.html>

- The body of literature indicates a significant potential for impacts of legacy and novel PFAS on humans, yet they remain a sustained presence in our everyday lives from food packages, wrappers, cell phones, rain gear, stain resistant fabrics and rugs, and nearly all plastic products found in households, plus industrial processes and manufacturing. Unfortunately, most of the population is unaware of the risk associated with PFAS that may affect children disproportionately. A concerted public outreach effort is needed to inform the public of the risks and how to mitigate them.
- During preparation of this document, EPA has initiated a PFAS Strategic Roadmap with a goal of protecting human health and the environment and hold polluters responsible (EPA 2022). They have issued advisories for PFOS and PFOA, examined toxicity of GenX compounds, and are examining other PFAS groups. In Massachusetts, newly issued NPDES permits will require monitoring for six PFAS compounds of interest (*i.e.*, PFHxS, PFHpA, PFNA, PFOS, PFOA, and PFDA) that may eventually include other PAFS at the ng/L PPT level. EPA is conducting multi-laboratory tests to develop a standardized PFAS methodology.

The primary points of uncertainty and relevance to inform future monitoring and decision-making related to outfall operation in Massachusetts Bay are:

1. ***What are the concentrations of PFAS and specifically compounds of interest to MADEP/EPA within MWRA effluent and Massachusetts Bay, and what compounds could potentially impact biota and ecosystems?***

Initially there should be a screening of PFAS to identify compounds in the effluent of interest to MADEP and EPA. Current studies are underway examining PFAS in MWRA's effluent and their presence and dilution in Massachusetts Bay. As noted above, monitoring requirements for six PFAS compounds of interest are being added to newly issued NPDES permits (*i.e.*, PFHxS, PFHpA, PFNA, PFOS, PFOA, and PFDA) at the ng/L PPT level. EPA is currently reviewing groups of PFAS to protect humans and the environment and has issued aquatic life criteria for PFOS and PFOA.

2. ***Are there major sources or many sources of PFAS from small manufacturers and users of PFAS compounds?***

Massachusetts through its Toxic Use Reduction Act (TURA) program (OTA, Toxic Use Reduction Institute (TURI), MADEP 2018) should continue to develop a list of manufacturers of PFAS precursors or other PFAS, and those using PFAS compounds or precursors in production of household goods, industrial processes and other activities that may result in discharge to the MWRA and other coastal WWTPs. Developing such a list may be a collaboration between state and federal agencies and MWRA, and may be included in current regulations for pretreatment prior to discharge, similar to the success of MWRA's Toxics Reduction and Control (TRAC) Department that focused on reducing legacy pollutants.

3. ***Are concentrations of PFAS increasing or decreasing in effluent?***

In order to evaluate what is present, selected PFAS monitoring should include biota and sediments in the adjacent outfall environment, as well as the effluent. To properly design and implement a monitoring program, a preliminary study is required that can define the variability of the PFAS species being monitored temporally and spatially. This may include short-term special

studies that examine PFAS concentrations in the biota and sediments in close proximity of the diffusers where effects are likely to be impacted.

4. *Are there indications in the adjacent environment of the diffusers of bioaccumulation in marine biota of currently studied species and/or relevant species?*

The scope of PFAS in marine biota evaluation in Massachusetts Bay should reflect species where PFAS may be a concern. OMSAP recommends screening for bioaccumulation of PFAS compounds in organisms, with choice of organisms dictated by feasibility and best science. Ongoing discussions about appropriate organisms or other approaches (e.g. passive samplers) continue during the ongoing review of the AMP.

5. *What is an appropriate way to address the complexity of PFAS in effluent?*

The EPA PFAS Strategic Roadmap has begun to evaluate PFAS chemicals and methodologies for analyzing PFAS. The state and federal agencies will adopt a wastewater/surface water method for PFAS analyses in wastewater permits. OMSAP recommends collaborative special studies to investigate PFAS issues that are relevant to the AMP.

Summary

As with many persistent organic pollutants, PFAS are a complicated and challenging suite of chemicals with approximately 9,000 compounds that are ubiquitous in their distribution.

For the purpose of this document, there are two questions relative to the Ambient Monitoring Plan: (1) to what extent does the MWRA outfall contribute PFAS to Massachusetts Bay and (2) what are the impacts on seafood and other marine organisms, including marine mammals.

1. Early unpublished data and the presence of PFAS in biosolids indicates they are present in MWRA's effluent and discharged to Massachusetts Bay.
2. There is a need to evaluate the contribution from MWRA's outfall to Massachusetts Bay that requires identifying other sources and their contributions.
3. New regulations for drinking water were promulgated in 2020. The Massachusetts MCL for drinking water is 20 ng/L (PPT) for six PFAS compounds. An EPA draft PFAS method for eight different environmental media, including wastewater, surface water, groundwater, and soils has recently been validated. Consensus on identification, evaluation and ranking of effects associated with PFAS compounds is an ongoing discussion.
4. Concentrations of PFAS in sport and commercially harvested seafood from Massachusetts Bay are unknown, but based on the scientific literature it is hypothesized that they are present and, in some species, may exceed recommended safe consumption levels for humans and wildlife. Scientific literature on uptake, bioaccumulation, and biomagnification in marine plankton and invertebrates is expanding. Data exist that correlate concentrations of PFAS in marine mammals (seals, porpoises, dolphins and whales) and sea birds from the northwestern Atlantic and Massachusetts Bay with health outcomes such as immunotoxicity and liver malfunction.
5. There are many gaps in our knowledge of the relationship between PFAS and their impacts that will require research beyond the scope of recommendations for MWRA.

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Disclaimer

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

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Abbreviations and Short Descriptions

ADONA	Dodecafluoro-3H-4,8-dioxanonanoate
AFFF	Aqueous film forming foam (e.g., used at airports and military bases among others)
AMP	MWRA's Ambient Monitoring Plan
ATSDR	Agency for Toxic Substances and Disease Registry

CEC	Contaminants of environmental concern
EPA	U.S. Environmental Protection Agency
EOF	Extractable organofluoride
FCSV	Fish consumption screening values based on Michigan Department of Health and Human Services
FTOH	Fluorotelomer alcohols
6:2 FTOH	6:2 fluorotelomer alcohol
Gen-X	High performance fluorinated polymers composed primarily of hexafluoropropylene oxide (HFPO-DA) dimer and its ammonium salt
HBCD	Hexabromocyclododecanes (added to flame retardants)
HFPO-DA	Hexafluoropropylene (with ammonium salt is called Gen-X)
Nafion™	(Sulfonated tetrafluoroethylene)
MADEP	Massachusetts Department Environmental Protection
MCL	Maximum contaminant level
MWRA –	Massachusetts Water Resources Authority
NPDES	National Pollutant Discharge Elimination System
OMSAP	Outfall Monitoring Science Advisory Panel
PCB	Polychlorinated biphenyl
PFAAs	Perfluoroalkyl acids include PFCAs and PFSA
PFAS	Per and polyfluoroalkyl substances of which 9000 are estimated to have been manufactured.
PFBA	Perfluorobutanesulfonic acid
PFOA	Perfluoroalkyl carboxylic acid between C4-C16 carbons
PFDA	Perfluorodecanoic acid*
PFDODA or PFDaA	Perfluorododecanoic acid
PFEA	Perfluoroalkyl ether acid
PFECA	Perfluoroalkyl ether carboxylic acid
PFESA	Perfluoroalkyl ether sulfonic acid
PFHpA	Perfluoroheptanoic acid*
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid*
PFNA	Perfluorononanoic acid*
PFOA	Perfluorooctanoic acid, also known as C8*
PFOS	Perfluorooctanesulfonate acid (bioaccumulates)*
PFSA	Perfluoroalkyl sulfonic acids between C4-C16 carbons
PFTTrDA	Perfluoroheptanoic acid
PFUnA	Perfluoroundecanoic acid
PIGE	Particle-induced gamma ray emission (PIGE) used to measure PFAS where typical methods for PFAS measure only 16% of the fluorine in the body.
PPCPs	Pharmaceuticals and personal care products
STEEP	U.S.EPA-ORD laboratory and University of Rhode Island Sources, Transport, Exposure and Effects of PFASs
TF	Total fluoride
TOF	Total organofluoride
TRAC	Toxics Reduction and Control is a program designed to reduce contaminants entering wastewater treatment plants.
TURA	Toxic Use Reduction Act
TURI	Toxic Use Reduction Institute
WWTP	Wastewater Treatment Plant
*PFAS compounds with monitoring requirement in draft and final NPDES permits	

Appendix A. Members of Panel and Committee

Outfall Monitoring Science Advisory Panel (OMSAP)

Judith Pederson, Massachusetts Institute of Technology Sea Grant
Bob Beardsley, Woods Hole Oceanographic Institution
Peter Burn, Suffolk University
Ginny Edgcomb, WHOI
Loretta Fernandez, Northeastern University
Mark Patterson, Northeastern University
Jeff Rosen, Corona Environmental Consulting
Julie Simpson, Massachusetts Institute of Technology Sea Grant
Juanita Urban-Rich, University of Massachusetts Boston

Public Interest Advisory Committee

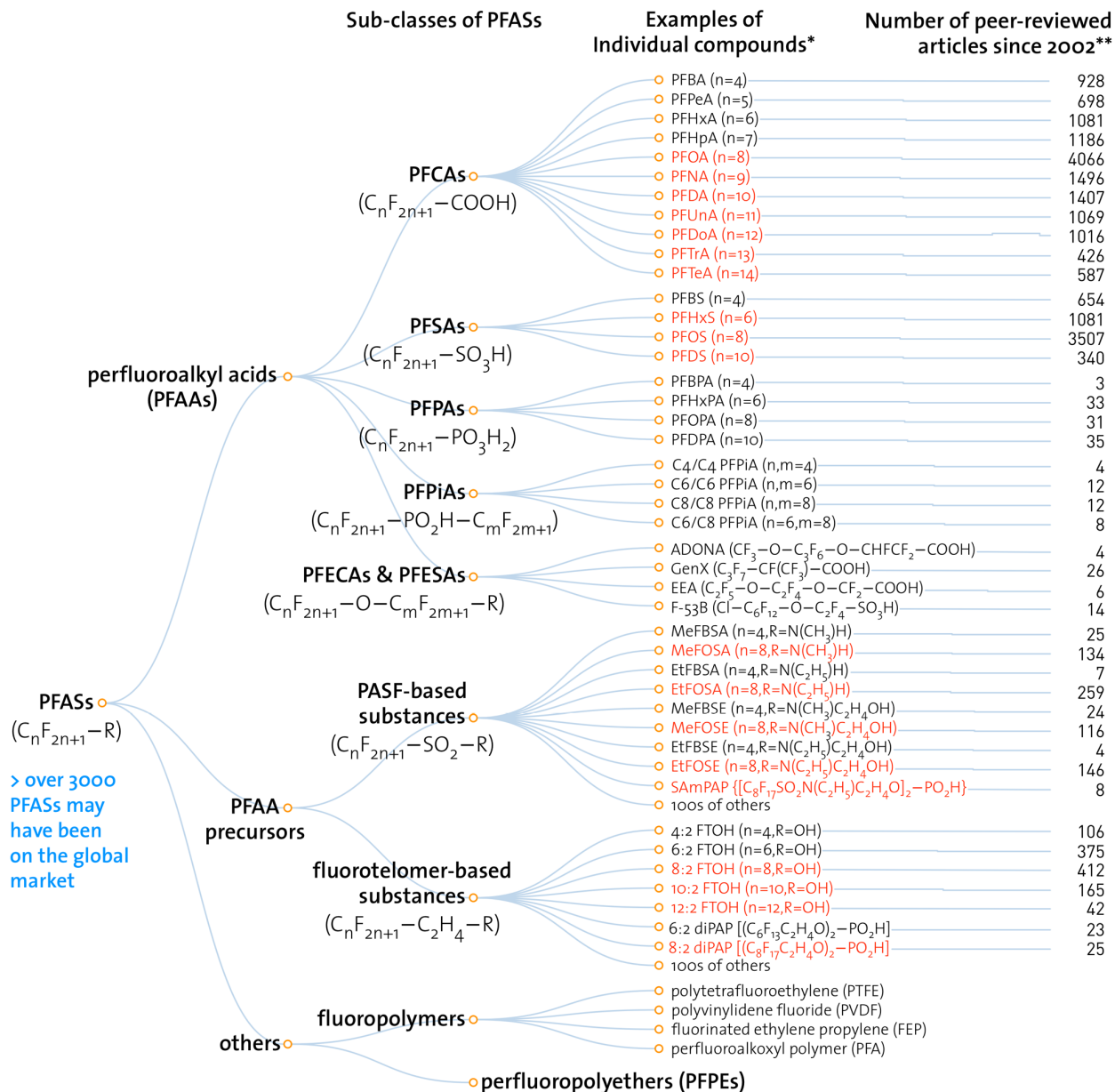
Bruce Berman, Save the Harbor/Save the Bay
Priscilla Brooks, Conservation Law Foundation
Robert Buchsbaum, Mass Audubon (retired)
Rich Delaney, Provincetown Center for Coastal Studies (retired)
Pam DiBona, Massachusetts Bays National Estuary Partnership
Andreae Downs, MWRA Wastewater Advisory Committee
Joe Favaloro, MWRA Advisory Board
Heather McElroy, Cape Cod Commission
Jo Ann Muramoto, Association to Preserve Cape Cod
Jack Murray, Boston Harbor Now
Vi Patek, Safer Waters in Massachusetts

Interagency Advisory Committee

Todd Callaghan, Massachusetts Coastal Zone Management
Ben Haskell, Stellwagen Bank National Marine Sanctuary
Matthew Liebman, United States Environmental Protection Agency (retired)
Jeff Kennedy, Massachusetts Division of Marine Fisheries
Pam DiBona, Massachusetts Bays National Estuary Partnership
Cathy Vakalopoulos, Massachusetts Department of Environmental Protection
Steve Wolf, U. S. Army Corps of Engineers, currently at U.S. Environmental Protection Agency

Appendix B: Supplemental Document 1. Family Tree of PFAS

“Family tree” of PFASs, including examples of individual PFASs and the number of peer-reviewed articles on them since 2002 (most of the studies focused on long-chain PFCAs, PFSAAs and their major precursors) (Wang 2017).



* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. <http://oe.cd/1AN>).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Pharmaceuticals and Personal Care Products: Their Sources, Fate, and Effects in Marine Ecosystems

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Abstract

An ad hoc focus group of scientists, government agencies, and members of the public interested in the Massachusetts Water Resources Authority (MWRA) sewage discharge to Massachusetts Bay convened in 2019 and 2020 to review the scientific literature on impacts to marine organisms from contaminants of emerging concern (CECs) associated with wastewater discharges. A subset of the ad hoc group focused specifically on pharmaceuticals and personal care products (PPCPs). Here we summarize what the ad hoc focus group learned about: 1) the types of chemicals that are classified as PPCPs and their origins; 2) where PPCPs are found in the aquatic environment; 3) the effects of PPCPs on marine organisms; and 4) strategies for identifying and prioritizing chemicals of interest from an extensive candidate list. In recent years, advances in instrumentation have allowed for the detection of PPCPs in water, sediment, and biota, typically at concentrations on the order of parts per billion or trillion. At such low levels, PPCPs have not been shown to have acute effects, although there is evidence that at ambient concentrations several classes of PPCPs can induce chronic effects in marine taxa including: oxidative stress, neurotoxicity, inhibited development, metabolic changes, and reduced mobility. In addition, several studies document the bioaccumulation of PPCPs under ambient aquatic conditions. Recommendations are offered to address the issue of PPCPs entering Massachusetts Bay from the MWRA outfall.

Introduction

The Massachusetts Water Resources Authority (MWRA) manages the drinking water and wastewater treatment for over three million people across 60 communities in the greater Boston region. The MWRA operates a secondary treatment wastewater facility on Deer Island, Boston that discharges approximately 330 million gallons per day of effluent out of a nine-and-a-half-mile long outfall pipe to a series of diffuser heads in 80-100 feet of water in Massachusetts Bay (Werme et al. 2019). In 1998, an Outfall Monitoring Science Advisory Panel (OMSAP) was convened to advise the Massachusetts Department of Environmental Protection (MassDEP) and the U.S. Environmental Protection Agency (USEPA)¹¹ on technical and scientific matters related to the MWRA outfall in Massachusetts Bay and any potential impacts of the effluent on

¹¹ EPA and MassDEP jointly issue the National Pollutant Discharge Elimination System (NPDES) permit regulating pollutants discharged from the MWRA outfall.

receiving waters.¹² Recent meetings of the OMSAP¹³ supported the conclusions of previous evaluations of monitoring results and identified that the Deer Island Treatment Plant (DITP) had largely been working as planned and that impacts to marine biota and human health associated with the conventional pollutants (bacteria, solids, nutrients) and legacy contaminants (metals, pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs)) in the discharge of treated effluent were minimal (October 3, 2019 OMSAP meeting notes; Werme et al. 2019).

In November 2018, the OMSAP co-sponsored a public workshop with MWRA, USEPA, and MassDEP to discuss the results of over 25 years of monitoring the MWRA outfall's effects. At the workshop the public, coastal managers, and environmental groups expressed interest in adapting the monitoring framework to investigate new concerns.¹⁴ With this in mind, in 2019 the OMSAP turned its attention to other classes of chemicals, contaminants of emerging concern (CECs), many of which can be present in wastewater and may have deleterious effects on humans, aquatic life, and the ecosystem. Advances in analytical instrumentation (Arpin-Pont et al. 2016, Yang et al. 2017) have allowed for the identification and study of CECs that are present at very low concentrations, parts per billion (ppb) or parts per trillion (ppt). In addition, the information on their potential effects to aquatic life and ecosystems in the peer-reviewed literature is expanding (Klosterhaus 2010, Arnold et al. 2013, Liu and Wong 2013, Andradi-Brown 2015, Muir et al. 2017).

With the objective of learning more about potential CECs in the MWRA effluent discharge to Massachusetts Bay, an ad hoc focus group¹⁵ of scientists and government agency representatives, as well as the OMSAP Public Interest Advisory Committee, convened in 2019 and 2020 to review the scientific literature on impacts to marine organisms and ecosystem effects from CECs. The goal was to determine if there was a suite of compounds that should be monitored in the MWRA effluent and the marine environment and if so, to make recommendations to the OMSAP on a course of action. After an initial meeting with presentations and discussions about several classes of CECs, the ad hoc group decided to focus specifically on three groups of CECs: pharmaceuticals and personal care products (PPCPs), poly- and perfluoroalkyl substances (PFAS), and microplastics.

This document summarizes what the ad hoc focus group learned about: 1) the types of chemicals that are classified as PPCPs and their origins; 2) where PPCPs are found in the aquatic environment, including the results of monitoring for PPCPs in Boston Harbor and Massachusetts Bay; 3) the potential for effects from PPCPs released in wastewater effluent on marine organisms and humans; and 4) strategies for identifying and prioritizing chemicals of interest from an extensive candidate list. Lastly, this document provides recommendations to the OMSAP for how MWRA might address this broad class of chemical compounds.

¹² <https://www.epa.gov/npdes-permits/outfall-monitoring-science-advisory-panel>

¹³ http://www.mwra.com/harbor/html/omsap_briefing.htm

¹⁴ [https://seagrant.mit.edu/wp-](https://seagrant.mit.edu/wp-content/uploads/2019/05/Transcript_OutfallMonitoringSciAdvPanelWorkshop_11_13_2018.pdf)

[content/uploads/2019/05/Transcript_OutfallMonitoringSciAdvPanelWorkshop_11_13_2018.pdf](https://seagrant.mit.edu/wp-content/uploads/2019/05/Transcript_OutfallMonitoringSciAdvPanelWorkshop_11_13_2018.pdf)

¹⁵ <https://www.epa.gov/npdes-permits/outfall-monitoring-science-advisory-panel#charter>

What chemicals are classified as PPCPs and what are their sources?

PPCPs include a wide variety of over-the-counter and prescription drugs as well as cosmetics (Juliano and Magrini 2017) and other “personal care products.” Table 1 lists the major classes of PPCPs and some of the common examples that have been found in wastewater or in the environment.¹⁶

Table 1. Common names of chemicals from across various PPCP classes referenced in this document.

PPCP Class	Examples from Studies Cited in This Document
Analgesic	acetaminophen
Antacid	ranitidine
Antianxiety/antiseizure	diazepam, oxazepam
Anticonvulsant	carbamazepine
Antidepressant	citalopram, fluoxetine, sertraline
Antihypertensive	atenolol, diltiazem, gemfibrozil, hydrochlorothiazide, losartan, metoprolol, valsartan, verapamil
Antimicrobial	erythromycin, sulfamethoxazole, triclocarban, triclosan, ¹⁷ trimethoprim
Blood sugar regulation	metformin
Cosmetic	magnesium laureth sulfate
Diuretic	furosemide, triamterene
Fragrance (musk)	galaxolide
Hormone	estrone, 17-beta estradiol
Insect repellant	DEET, permethrin
Non-steroidal anti-inflammatories	diclofenac, ibuprofen
Stimulant	amphetamine, caffeine
Sunscreen	benzophenone, oxybenzone

What are the pathways for PPCPs to enter coastal waters?

One major source of pharmaceuticals to the environment is domestic wastewater, from both centralized wastewater treatment outfalls (Ort et al. 2010) and decentralized septic systems (Schaidt et al. 2014, 2016). Another source may be wastewater from the pharmaceutical manufacturing industry, which in the metro-Boston area would also be treated at the DITP and transported through the MWRA outfall. In agricultural areas, pharmaceuticals may also enter the environment from Confined Animal Feeding Operations (CAFOs) (Bernot et al. 2013); however, there are no CAFOs located within coastal Massachusetts. Pharmaceuticals also enter the

¹⁶ In this document, “environment” refers broadly to freshwater and marine waters, sediments beneath these waters, and various aquatic organisms and life stages.

¹⁷ Triclosan was banned by the U.S. Food and Drug Administration in 2016 but continues to be found in the environment.

environment after therapeutic use by humans or after being administered to agricultural animals that then excrete a residual fraction of the initial dose. Some pharmaceuticals may also enter sewage treatment facilities directly when unused portions are disposed of down bathroom drains. Thus, pharmaceuticals may be delivered to the marine environment via treated wastewater, combined sewer overflows (CSOs), residential treatment system leachate, or stormwater runoff (Anderson et al. 2012). Topically applied personal care products (e.g., antimicrobial agents, fragrances, sunscreens, and insect repellants) can wash off of human skin and hair in domestic settings and similarly enter sewage treatment systems or can be rinsed off of humans while they are swimming or recreating on the water (Langford and Thomas 2008).

Where have PPCPs been found in ocean and coastal environments?

PPCPs are ubiquitous in freshwater environments (Richmond et al. 2017) and their prevalence in coastal and marine waters is becoming more well-documented (e.g., Anderson et al. 2012). PPCPs have been found in marine bivalves (Li et al. 2020), crustaceans (Nakata et al. 2007), fish (Barreto et al. 2018), birds (Nakata et al. 2007), and mammals (Alonso et al. 2015). On May 19, 2020, the ad hoc focus group received an overview presentation on PPCPs from three of its members: Dr. Peter Burn from Suffolk University (an OMSAP member), Dr. Todd Callaghan from the Massachusetts Office of Coastal Zone Management, and Dr. Mark Cantwell from the USEPA's Office of Research and Development (USEPA-ORD) laboratory in Narragansett, Rhode Island.¹⁸ The presentation covered the breadth of aquatic environments and organisms where PPCPs have been found; discussed the Southern California Coastal Water Research Project (SCCWRP), its framework for identifying chemicals of monitoring interest, and its extensive PPCP studies in freshwater, estuaries, and marine environments; and presented the results of several PPCP studies in the northeast. Below is a summary of the extensive work done by SCCWRP in California as well as several PPCP studies done by USEPA-ORD and others in the northeast.

California

In California, SCCWRP identified 82 CECs in the aquatic environment. Of these, 62 were PPCPs found in treated municipal sewage, as well as in the sediment, water, and biota adjacent to regional municipal wastewater discharges. SCCWRP also found PPCPs in surface waters and stormwater downstream of agricultural areas (Anderson et al. 2012). Six of the PPCPs (diclofenac, 17-beta estradiol, estrone, galaxolide, ibuprofen, and permethrin) were given greater focus because they had a monitoring trigger quotient above 1 (i.e., their concentration in the environment was greater than the concentration known to have effects on biota).

Ocean sediments in southern California were found to contain three PPCPs in the ppb range: carbamazepine, diazepam, and triclosan (Maruya et al. 2011), while several PPCPs were found in estuarine sediments in the ppb range including: DEET, erythromycin, sulfamethoxazole, triamterene, triclocarban, triclosan, trimethoprim (Klosterhaus 2010), and permethrin (Lao et al. 2010).

¹⁸ Now called the Atlantic Coastal Environmental Sciences Division.

The SCCWRP researchers found multiple PPCPs in mussels including: atenolol (0.3 ppb), amphetamine (4 ppb), carbamazepine (5 ppb), erythromycin (0.1 ppb), sertraline (1 ppb), triamterene (0.6 ppb), and triclocarban (0.2 ppb) (Ramirez et al. 2009, Klosterhaus 2010, Maruya et al. 2011). Lastly, SCCWRP found diazepam (110 ppb) in a marine flatfish's liver (Maruya et al. 2011).

New York/Connecticut

In a USEPA-ORD study of the Hudson River, 70 stations from Albany to New York Harbor were sampled for 24 PPCPs (Cantwell et al. 2018). The study identified several antihypertensives (atenolol, gemfibrozil, losartan, metoprolol, and valsartan), two antimicrobials (sulfamethoxazole and trimethoprim), the anticonvulsant carbamazepine, and the analgesic acetaminophen in the ppt range, with spikes in the low ppb range at the locations of major sewage treatment outfalls. These locations, in close proximity to outfalls, were identified as sites of “pseudopersistence” for many PPCPs because even though the chemicals degrade or are diluted to much lower levels relatively rapidly, their supply is continually replenished by the wastewater outfalls.

Additional research and monitoring in Long Island Sound (Cantwell et al. 2019) found several of the same pharmaceutical compounds present in the ppt range, as well as sucralose¹⁹ and caffeine, and identified a dilution trend across the sound from west to east, consistent with an increase in salinity and flushing from the Atlantic Ocean. This study also identified that the chemical sweetener sucralose is a useful tracer to monitor PPCP dispersal.

Rhode Island

In Narragansett Bay, the USEPA-ORD investigated the influence of several large wastewater facilities at the northern end of the bay on PPCPs across the Bay (Cantwell et al. 2016b). Again, a strong gradient in PPCP concentration was found, in this case from north to south, with concentrations in the low to mid ppt range. In this study, samples were taken monthly from May 2014 to April 2015. This work demonstrated the seasonal and temporal influence on PPCP concentrations. For example, the highest concentrations of the antihypertensive gemfibrozil were found in March and April, while the highest concentrations of the antimicrobial sulfamethoxazole were found between June and August. These data point to the temporal and spatial variation in PPCP concentrations in the aquatic environment.

Massachusetts

Research by the Silent Spring Institute (Schneider et al. 2014, 2016) and the Center for Coastal Studies²⁰ identified PPCPs in groundwater, drinking water, marshes, embayments, and oysters on Cape Cod and concluded that the primary sources were residential onsite treatment systems.

¹⁹ Sucralose is an artificial sweetener that is used extensively in processed food products and beverages and is the main ingredient of Splenda.

²⁰ <https://coastalstudies.org/cape-cod-bay-monitoring-program/monitoring-projects/contaminants-of-emerging-concern/pharmaceuticals-in-the-waters-of-cape-cod-bay-and-nantucket-sound/>

In the Boston Harbor watershed, the USEPA-ORD conducted a study in 2015 that documented that caffeine had declined significantly since the 1990s, when the MWRA outfall and CSOs discharged directly into the Harbor (Cantwell et al. 2016a). In the same study, USEPA-ORD sampled for numerous pharmaceuticals and found the antihypertensives diltiazem and verapamil in all waters tested (Charles, Neponset, and Mystic Rivers as well as Boston, Dorchester, and Quincy Harbors).²¹ The antihypertensives gemfibrozil and hydrochlorothiazide were also found routinely. Finally, the antacid ranitidine was found only in the Mystic and Charles Rivers. Concentrations of these PPCPs were relatively low, which was attributed to source reduction due to the termination of DITP discharges to Boston Harbor in 2000 and declines in the number and volume of untreated sewage discharges via CSOs.

What are the effects of PPCPs on marine organisms and humans?

Pharmaceuticals are designed to be biologically active at low doses and target specific metabolic, enzymatic, or cell signaling pathways to elicit their desired therapeutic effects (Franzellitti et al. 2015). The pharmaceuticals found in wastewater effluent or in the marine environment are at concentrations (i.e., ppb or ppt) well below therapeutic levels for humans (Cantwell, pers. comm.). However, the effects of most PPCPs on marine biota at low concentrations are not well understood.

Chemicals can be classified for the potential to have harmful effects using persistence, bioaccumulation, and toxicity (PBT) criteria (USEPA 2012). Many PPCPs are known to have relatively short persistence of months to years in the environment (Monteiro and Boxall 2009) and are likely to degrade (Kreuzig and Höltege 2005), while others exhibit long term persistence in environmental compartments (e.g., water, soil, air) or degrade to long-lived metabolites (Liu and Wong 2013). PPCPs that enter the environment via wastewater outfalls may exhibit pseudopersistence because they are continually added to the environment, presenting sustained localized exposure to aquatic life (Daughton and Ternes 1999). Many pharmaceuticals, a class of PPCPs, are easily metabolized and are assumed to be less bioaccumulative than pesticides or industrial pollutants because they are more water soluble (Daughton and Brooks 2010). Though the published literature on bioaccumulation in aquatic organisms is relatively sparse for many PPCPs, there is evidence that specific PPCPs do bioaccumulate (Nakata 2005, Nakata et al. 2007, Daughton and Brooks 2010, Muir et al. 2017, Horricks et al. 2019, Elizalde-Velázquez and Gómez-Aliván 2020, Li et al. 2020). Also, while some organisms may be able to recover following an initial dose or exposure to a mixture of PPCPs, the recovery might not be complete. For example, a laboratory study looking at metabolic changes in oysters subjected to a suite of PPCPs found changes in metabolism associated with both PPCPs alone and in a mixture. After a period of depuration, the extent of metabolic change was decreased, but none of the treatments returned to control values, suggesting that oysters were only able to partially recover from PPCP exposure and accumulation after a depuration period (Brew et al. 2020). Several studies have identified the toxic effects of specific PPCPs to marine organisms (Breitholtz and Wollenberger 2003, Breitholtz et al. 2003, DeLorenzo et al. 2008, Kusk et al. 2011, Chariton et al. 2014, Li et al. 2020), but all were laboratory studies where concentrations were several orders of magnitude

²¹ These data are unpublished but were presented to the OMSAP ad hoc focus group.

higher than what has been recorded in the marine environment. While we acknowledge that we have not fully explored the PPCP literature, the studies we reviewed did not identify toxic effects of PPCPs at concentrations found in the environment.

The PBT classification system is generally a useful screening tool for prioritizing efforts to remediate pollution; however, chronic effects of PPCPs on aquatic organisms may be overlooked, especially in cases where PPCP concentrations are too low to detect persistence or toxicity. For example, a whole-lake experiment in Canada conducted over five years identified that chronic exposure of fathead minnows (*Pimephales promelas*) to low concentrations of synthetic estrogen (17 α -ethynylestradiol) resulted in near collapse of the minnow population due to feminization of male fish (Kidd et al. 2007). Richmond et al. (2017) reviewed several freshwater studies documenting sublethal but significant ecological effects of several pharmaceuticals (e.g., citalopram, diclofenac, fluoxetine, oxazepam) at low concentrations (ppt) that include changes in feeding activity, changes in biomass, suppression of primary productivity, and changes in the timing of metamorphosis. While the two studies above were both conducted in freshwater, they underscore that a chemical need not have all or any of the PBT characteristics in order to have significant detrimental effects on biota. Indeed, studies have shown behavioral effects (Barreto et al. 2018) as well as metabolic, reproductive, and developmental effects (Li et al. 2020) in marine organisms exposed to PPCPs at environmental concentrations.

Overall, PPCPs comprise a broad range of chemicals with individual classes spanning a wide range of persistence, bioaccumulative capacity, toxicity, and sublethal effects in the marine environment. Appendix C (Table 2) contains a list of results from a limited selection of studies identifying lethal and sublethal effects on marine organisms across several PPCP classes. Literature C contains the complete list of studies reviewed by the authors.

Strategies for identifying PPCPs that should be monitored

SCCWRP, using the broad expertise of many scientists, evaluated the risk associated with various CECs to develop an adaptive and phased monitoring approach and research program (Anderson et al. 2012). As part of its efforts, SCCWRP developed monitoring trigger levels (MTLs) for CECs that pose the greatest potential risk to aquatic systems based upon published effects concentrations. SCCWRP calculated the monitoring trigger quotient (MTQ) as the ratio of the environmental concentration of a contaminant (either measured directly or estimated by a model) divided by the monitoring trigger level. MTQs greater than 1 indicate that a potential for risk exists and therefore, according to SCCWRP scientists, the chemical should be included in a monitoring program. Of note is that none of the PPCPs for which data were available had an MTQ greater than 1 in the marine environment (Anderson et al. 2012, p. 40). No PPCPs were recommended to be part of the SCCWRP marine monitoring program; however, several were recommended to be included in its freshwater and/or estuarine monitoring program including: the hormones estrone and 17-beta estradiol, the non-steroidal anti-inflammatories ibuprofen and diclofenac, the fragrance galaxolide, and the antimicrobial triclosan.

The Harvard School of Public Health (HSPH) has a webpage describing a program to prioritize PPCPs based upon a PPCP's "relative toxic load" (Harvard School of Public Health 2020; Dong et al. 2013). According to HSPH, a PPCP's toxic load is defined as its mass loading divided by its toxic dose.²² The goal of this program is to iteratively develop a list of PPCPs that may be of human or ecological significance. It is not clear at this time if the HSPH has advanced this program.

At the November 2018 OMSAP workshop, MassDEP presented a list of CECs that are priorities for action. Several PPCPs are on MassDEP's action list, but no recommendations have been made to prioritize or screen which compounds would pose the greatest risk to humans or aquatic life. Since there is no regulatory standard for these chemicals, occurrence monitoring helps to assess concentrations, exposures, trends, and possible risks. MassDEP has an internal Emerging Contaminant Workgroup charged with identifying and assessing public health and environmental problems associated with currently unregulated or under-regulated contaminants and recommending agency strategies for addressing them (Cathy Vakalopoulos, pers. comm.).²³

Recommendations to the OMSAP, MassDEP, and USEPA regarding MWRA

PCPPs have been detected in treated wastewater (e.g., Ort et al. 2010), downstream from wastewater treatment plants in estuaries across the northeast (Cantwell et al. 2016a, 2016b, 2018, 2019), and in various marine environments, often in concentrations in the ppt range (Anderson et al. 2012, Richmond et al. 2017). PPCPs in some estuaries were documented to be at low concentrations (i.e., ppt) due to dilution from seawater and other factors (Cantwell et al. 2019). Thus, it may be that the roughly 100:1 dilution²⁴ provided by the MWRA diffuser's design and location will also result in very low levels of PPCPs in Massachusetts Bay. Preliminary results from a pilot study suggest that MWRA effluent contains several PPCPs and that PPCPs are detectable at low levels surrounding the MWRA outfall in Massachusetts Bay (Anna Robuck, Mark Cantwell pers. comm).

While studies to date suggest that the design of the MWRA DITP and diffuser appear to be adequate to protect human health and the marine ecosystem from the deleterious effects of conventional pollutants (Werme et al. 2019), there was hesitation among the ad hoc focus group to conclude that OMSAP should ignore the PPCP class of chemicals or that it could be stated with certainty that there are no expected effects to marine biota—that not knowing is not the same as no harm. For example, the studies by USEPA-ORD in several estuaries discussed above did not include hormones, a class of pharmaceuticals of concern to the public. Indeed, Kidd et al. (2004) found significant population-level effects of synthetic estrogen on freshwater fish. Further, the effects of pharmaceuticals once in the environment are largely unknown and "there is concern that some PPCPs may disrupt key processes in sensitive non-target organisms, including certain human populations" (Harvard School of Public Health 2020). Thus, the consensus of the ad hoc focus group was that it would be prudent for the MWRA to conduct

²² <https://www.hsph.harvard.edu/water/research/ppcp/>

²³ <https://www.mass.gov/info-details/emerging-contaminants>

²⁴ <http://www.mwra.com/harbor/enquad/pdf/2002-07.pdf>

special studies, within its existing marine monitoring program and in collaboration with local researchers, to better understand MWRA's contribution of PPCPs to Massachusetts Bay and whether there are significant risks to public health and the marine ecosystem. We are aware that the MWRA is already conducting collaborative studies on PPCPs. MWRA is a participant in two Water Research Foundation (WRF) research projects: *Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants* (RFP 5031) and *Assessing Poly- and Perfluoroalkyl Substance Release from Finished Biosolids* (RFP 5042).²⁵

As part of its programmatic research on contaminants of emerging concern, the USEPA-ORD laboratory in Narragansett, Rhode Island is conducting research on PFAS and PPCPs in Massachusetts Bay. The purpose of the study is to evaluate the presence, dilution, and attenuation of these compounds, as well as estimate exposure to aquatic life in Massachusetts Bay. The status of this project was last reported to OMSAP at the October 3, 2019 meeting. The USEPA-ORD laboratory has sampled Massachusetts Bay twice but analysis of samples from this project has been delayed by laboratory shutdowns associated with the COVID-19 pandemic. Moving forward, MWRA should be encouraged to continue to collaborate on CEC research in Massachusetts Bay and to keep its staff and the OMSAP informed of the results of future studies.

Below are recommendations from the ad hoc focus group on PPCPs for the OMSAP to consider:

- Conduct a literature search and risk assessment to identify PPCPs that demonstrate persistent, bioaccumulative, and toxic properties. Attention should be given to identifying chemicals for monitoring that have the greatest potential for imparting adverse biological effects. This white paper reviewed two approaches for identifying a short list of chemicals from a list of thousands, but other approaches are available.²⁶
- Conduct a literature review on influent and effluent removal rates for all major classes of PPCPs. The WRF project 5031 should provide important information toward addressing this issue. Couple the literature review with an investigation of emerging technologies and strategies to reduce PPCPs through wastewater treatment. Several studies summarized in Anderson et al. (2012, p. 18) determined that tertiary treatment is largely ineffective at removing PPCPs; however, several studies demonstrated that certain PPCPs react with chlorine in treated wastewater and can be reduced to below detection levels.
- Monitor influent and effluent levels of selected PPCPs at the MWRA DITP to determine treatment removal efficacy.
- Enact source reduction through industrial discharger education and management. The reduction of PPCPs at their industrial sources might reduce quantities reaching the ocean via the MWRA outfall. A first step would be to identify the existing, large dischargers of PPCPs (e.g., industries, schools, hospitals) within the MWRA system and to make note of any new PPCP dischargers entering the MWRA collection system for targeted education.

²⁵ Project 5031 is in its start-up phase; MWRA has provided facility process information to the project team from CDM Smith. The description from the Request for Proposal is at:

https://www.waterrf.org/sites/default/files/file/2019-09/RFP_5031.pdf. The project page for 5042 is at <https://www.waterrf.org/research/projects/assessing-poly-and-perfluoroalkyl-substance-release-finished-biosolids>

²⁶ <https://www.waterrf.org/resource/decision-making-framework-prioritization-research-constituents-concern>

- Continue monitoring for PPCPs in the marine environment. We recommend that OMSAP evaluate the feasibility of a pilot study to employ passive samplers and mussels in the field and in wastewater to estimate long-term mean concentrations. Such a study might focus on indicators (e.g., tracer compounds) to establish spatial/temporal distribution and to monitor if any future engineering or operational solutions reduce concentrations.
- Conduct modeling to better understand the fate of discharged PPCPs. There are some PPCPs whose levels are correlated with the concentration of relatively easy to monitor compounds such as sucralose. Therefore, modeling the distribution and concentration of sucralose or another suitable tracer would give an indication of the extent of some PPCPs. The MWRA Massachusetts Bay model could be utilized to better understand the fate and transport of PPCPs.
- Enact source reduction public education. Expand outreach and continue to encourage the public to not flush old or unused drugs down toilet or sink drains, but rather to use pharmaceutical deposit boxes at police stations.²⁷
- Form an advisory group to keep interested parties apprised of the current literature, any actions by governments or non-government organizations, and periodically summarize the latest laboratory and field work, with a focus on monitoring studies and programs from organizations such as SCCWRP and the San Francisco Estuary Institute (<https://www.sfei.org/>).

Looking more broadly at wastewater discharges besides the MWRA outfall, the ad hoc focus group recommends that MassDEP and USEPA encourage all wastewater operators to participate in an education plan to encourage their various domestic and industrial contributors to keep PPCPs, especially pharmaceuticals, from reaching surface and ground waters in Massachusetts.

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Disclaimer

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²⁷ <https://www.mass.gov/service-details/find-a-waste-medication-kiosk>

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Annotated bibliography of references reviewed for this paper (Excel spreadsheet) is available upon request.

List of acronyms used in this paper

CAFOs: Confined Animal Feeding Operations
CECs: contaminants of emerging concern
CSOs: combined sewer overflows
DEET: N,N-diethyl-meta-toluamide
DITP: Deer Island Treatment Plant
HSPH: Harvard School of Public Health
MassDEP: Massachusetts Department of Environmental Protection
MTL: monitoring trigger level
MTQ: monitoring trigger quotient
MWRA: Massachusetts Water Resources Authority
OMSAP: Outfall Monitoring Science Advisory Panel
PAHs: polycyclic aromatic hydrocarbons
PBT: persistence, bioaccumulation, and toxicity
PCBs: polychlorinated biphenyls
PFAS: poly- and perfluoroalkyl substances
Ppb: parts per billion
PPCPs: pharmaceuticals and personal care products
Ppt: parts per trillion
RFP: request for proposals
SCCWRP: Southern California Coastal Water Research Project
USEPA: U.S. Environmental Protection Agency
USEPA-ORD: U.S. Environmental Protection Agency Office of Research and Development
WRF: Water Research Foundation

Appendix A. Presentations to the OMSAP and the Ad Hoc Group on CECs:

April 24, 2019

- Contaminants of Emerging Concern in Massachusetts Bay: Preliminary Discussion. Anna Robuck and Mark Cantwell, University of Rhode Island Graduate School of Oceanography and USEPA Atlantic Ecology Division.

September 10, 2019

- Existing CEC Monitoring Efforts: SCCWRP, Center for Coastal Studies, Silent Spring Institute, and NOAA. Todd Callaghan, Massachusetts Office of Coastal Zone Management.

October 3, 2019

- Summary of WWTP monitoring of CECs. Todd Callaghan, Massachusetts Office of Coastal Zone Management.
- Massachusetts Focus on CECs. Cathy Vakalopoulos, Massachusetts Department of Environmental Protection.
- Contaminants of Emerging Concern in Massachusetts Bay: Preliminary Study Update. Anna Ruth Robuck, Mark G. Cantwell, Pete DeCola, David R. Katz, Christine L. Gardiner, Michael A. Thompson, David N. Wiley, and Rainer Lohmann. University of Rhode Island Graduate School

of Oceanography, US EPA Atlantic Ecology Division, and NOAA Stellwagen Bank National Marine Sanctuary, respectively.

May 19, 2020

- Contaminants of Emerging Concern: Pharmaceuticals and Personal Care Products (PPCPs) by Todd Callaghan, Peter Burn, and Mark Cantwell. Massachusetts Office of Coastal Zone Management, Suffolk University, and USEPA Atlantic Ecology Division, respectively.

Appendix B.

***Members of the ad hoc focus group to study PPCPs**

Outfall Monitoring Science Advisory Panel (OMSAP)

Judith Pederson, Massachusetts Institute of Technology Sea Grant*

Bob Beardsley, Woods Hole Oceanographic Institution*

Peter Burn, Suffolk University*

Ginny Edgcomb, WHOI*

Loretta Fernandez, Northeastern University*

Mark Patterson, Northeastern University*

Jeff Rosen, Corona Environmental Consulting*

Julie Simpson, Massachusetts Institute of Technology Sea Grant*

Juanita Urban-Rich, University of Massachusetts Boston*

Public Interest Advisory Committee

Bruce Berman, Save the Harbor/Save the Bay*

Priscilla Brooks, Conservation Law Foundation

Robert Buchsbaum, Mass Audubon (retired)

Rich Delaney, Provincetown Center for Coastal Studies

Pam DiBona, Massachusetts Bays National Estuary Partnership

Andreae Downs, Massachusetts Water Resources Authority (MWRA) Wastewater Advisory Committee

Joe Favalaro, MWRA Advisory Board

Heather McElroy, Cape Cod Commission*

Jo Ann Muramoto, Association to Preserve Cape Cod*

Jack Murray, Boston Harbor Now

Vi Patek, Safer Waters in Massachusetts

Interagency Advisory Committee

Todd Callaghan, Massachusetts Coastal Zone Management*

Ben Haskell, Stellwagen Bank National Marine Sanctuary*

Matthew Liebman, United States Environmental Protection Agency (retired)*

Jeff Kennedy, Massachusetts Division of Marine Fisheries*

Prassede Vella, Massachusetts Bays National Estuary Partnership

Cathy Vakalopoulos, Massachusetts Department of Environmental Protection*

Steve Wolf, United States Army Corps of Engineers, currently at U.S. Environmental Protection Agency

Appendix C.

Table 2. Documented lethal (acute) and sublethal (chronic) effects of various classes of PPCPs on marine organisms.

PPCP Class	Chemical Reference	Effect
Antimicrobial ppt ¹	Triclosan Delorenzo et al. 2008	Increased mortality in grass shrimp (<i>Palaemonetes pugio</i>) at 150-650
		Toxicity to green alga (<i>Dunaliella tertiolecta</i>) at 4 ppt ¹
		Reduced benthic diversity at 180 mg/kg
Cosmetic	Chariton et al. 2014 Magnesium laureth sulfate Amouroux et al. 1999	Inhibited urchin egg development at 30 ug/ml
Hormone <i>beryllina</i>)	17-beta estradiol and estrone Mehinto et al. 2018	Impaired gonadal development in the inland silverside (<i>Menidia</i>
Insect Repellent <i>guianensis</i>) to fetuses	Pyrethroids Alonso et al. 2015	Transferred from mother dolphins (<i>Franciscana spp.</i> and <i>Sotalia</i>
Pharmaceutical 1.5 ug/l	Gemfibrozil Barreto et al. 2018	Reduced seabream (<i>Sparus aurata</i>) ability to swim against current at
ug/l		Induced oxidative stress in seabream (<i>Sparus aurata</i>) at 15-15,000
Stimulant	Caffeine ² Li et al. 2020	Bioaccumulated in green mussels (<i>Perna viridis</i>)
		Induced oxidative stress in polychaetes (<i>Diopatra neapolitana</i> and
<i>Arenicola marina</i>) at 0.5-18 ug/l		
		Induced neurotoxicity and metabolic effects in clams (<i>Ruditapes</i>
<i>philippinarum</i>) at 0.5-50 ug/l		
0.01-15 ug/l		Decreased sea urchin (<i>Paracentrotus lividus</i>) egg development at
		Decreased metabolic activity in amphipods (<i>Ampelisca brevicornis</i>) at
0.15-1500 ng/g		
<i>(Palaemonetes pugio)</i> at 20 mg/l		Increased time to hatching and decreased embryo size in shrimp
		Affected enzyme activity in green crab (<i>Carcinus maenas</i>) at 50 ug/l
Sunscreen	2,4-dihydroxybenzophenone (BP1) Kusk et al. 2011	Induced toxicity to copepods (<i>Acartia tonsa</i>) at 2.6 mg/l ³
		Inhibited development of copepods (<i>Acartia tonsa</i>) at 0.49 mg/l ³
Synthetic Musk	Celestolide Breitholtz et al. 2003	Increased mortality of copepods (<i>Nitocra spinipes</i>) at 0.3 ppm ⁴
	Galaxolide	Affected larval development of copepods (<i>Nitocra spinipes</i>) at 0.02
ppm ⁴		
	Musk ketone	Reduced population growth of copepods (<i>Nitocra spinipes</i>) at 0.1
ppm ⁴		
		Bioaccumulation of synthetic musks in marine clams, crabs, fish,
	birds	Nakata et al. 2007
		Bioaccumulation of synthetic musks in sharks and marine mammals
		Nakata 2005

1. Triclosan has been banned in the U.S. since 2016 but persists in the environment. Experimental concentrations of triclosan were greater than the ambient concentration, which was 0.001 ppt.
2. Experimental concentrations of caffeine used were likely several orders of magnitude above ambient as Li et al. (2020) reported that globally 50% of reported sea water caffeine concentrations were > 18 ng/l with 99% < 1091 ng/l.
3. Experimental concentrations were several orders of magnitude above a mean concentration of 0.123 ug/l oxybenzone (a similar class of sunscreens) that Horricks et al. (2019) found in nearshore seawater in Grenada.
4. Authors acknowledge that experimental concentrations were above ambient.

Microplastics:

Their Sources, Transport, and Fate in the Ocean

Authors: Judith Pederson¹, Robert Kenney², and Virginia Edgcomb³, with contributions from Peter Burn⁴, Todd Callahan⁵, Loretta Fernandez⁶, Kay Ho⁷, Ken Keay⁸, Mark Patterson⁶, Jeffrey Rosen⁹, Catie Tobin¹⁰, Juliet Simpson¹⁰, and Juanita Urban-Rich¹¹.

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Abstract

Iconic photos of plastic trash around the necks of seabirds and seals and the formation of plastic-laden ocean gyres have raised awareness in the public, but that has not reduced our continued use and discard of plastics. Less often seen are microplastics (MPs), small particles (5 mm–1 µm) of plastic broken down or degraded by mechanical, photochemical, oxidative, or biochemical actions. Plastics are transported by air, runoff, riverine input, and outfall discharges and ultimately reach the ocean. It is estimated that 8 million tons of plastic reach the ocean each year and that amount is continuing to increase. The lack of standardized methodologies in identifying MP types in water, sediments, and tissues limits accurate assessments of how much plastic is in the ocean and the ability of researchers to compare MP effects on biota. Current knowledge of MP uptake, concentrations of MPs in organisms, and metabolic and physiological responses are based on field studies, lab experiments, and for marine mammals and some sea birds, assessments of stranded animals. Data show impacts to reproduction, metabolism, and growth in marine biota. Less well understood are impacts of biofilms, associated contaminants, additives, and breakdown products on marine vertebrates, especially marine mammals. Wastewater treatment plants remove of 80–98% of MP particles during treatment; however, this may not include fibers and smaller particles. Guidance and protocols from agencies are needed to identify permissible levels of MPs that protect humans and the ecosystem.

Introduction

This document is one of three reviews addressing contaminants of emerging concern (CECs) in domestic wastewater effluents, specifically as applied to the Massachusetts Water Resources Authority's (MWRA) discharge into Massachusetts Bay. In response to state and federal requirements, an Ambient Monitoring Plan (AMP) for the outfall (MWRA 1991, 1997, 2004, 2010, 2021) was adopted to address four general concerns:

- Is it safe to swim?
- Is it safe to eat seafood?
- Are aesthetics being maintained?
- Are there adverse effects to the ecosystem?

In 2018, after 28 years of monitoring, the Outfall Monitoring Science Advisory Panel (OMSAP) organized a workshop to review the monitoring results and the relevancy of the monitoring plan. This workshop concluded based on monitoring requirements established in MWRA's National Pollutant

Discharge Elimination System (NPDES) permit and AMP, that “*After 25+ years of monitoring, the data show that the MWRA outfall has not adversely affected Massachusetts Bay*” (OMSAP 2018). The workshop summary also noted that some areas have improved or remained the same (*e.g.*, concentrations of legacy metal contaminants have decreased in sediments), but some classes of persistent chemicals and compounds, specifically per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products (PPCPs), and MPs, have not been addressed (OMSAP 2018).

This document reviews what is known about MPs and their sources, transport, fate, and effects in marine ecosystems and the role of wastewater treatment plant (WWTP) outfalls, specifically as they relate to MWRA’s discharges into Massachusetts Bay. The literature review summarizes information related to the questions of seafood safety and adverse environmental effects identified in the MWRA monitoring plan.

As with all classes of CECs, MPs are found in the air, soil, and water and are ubiquitous and persistent. Plastics are generally considered disposable by the public and have increased in production over the past few decades. The concentration of plastics throughout all ecosystems and their persistence, as well as the additives used to make plastics adaptable for a wide variety of uses can cause environmental harm or constitute a human public health risk. Plastics²⁸ and their degraded or fragmented particles are increasing in the environment at unprecedented rates and are not readily biodegraded to basic chemical structures. As such they are considered persistent organic chemicals (Hale *et al.* 2020). This white paper addresses two questions; 1) to what extent are wastewater treatment plant outfalls contributing MPs to coastal waters and 2) what are the documented or potential impacts of MPs to biota, human health and ecosystems?

What are Microplastics?

The first synthetic plastic, Bakelite was invented in 1907 but it was not until after World War II that plastic manufacturing increased and replaced natural materials in nearly all aspects of our lives—household products, construction, clothing and other industry and manufacturing areas except for cement and steel (Geyer *et al.* 2017). It is estimated that around 10 billion tons of plastic have been manufactured since 1950. By 2015 over 350 million tons of plastic are discarded each year of which approximately 8 million tons (*e.g.*, between 4 and 12.7 metric tons in 2010; Jambeck *et al.* 2015) enter the ocean each year and break down into smaller particles forming MPs and nanoplastics that sink and eventually settle in the sediments (Geyer *et al.* 2017; Geyer 2020). In 2017 estimates of recycling, incineration and discard rates for 380 million tons discarded plastics was 18%, 26% and 55%, respectively, although the U.S. only recycles about 9% annually (Geyer 2020). The annual amount of plastics manufactured is estimated to double by 2030 (Hale *et al.* 2020) adding increasing levels of MPs to the ocean ecosystems. These data are based on reports from countries that keep records using estimates of populations living within 50 miles of the coast (Geyer *et al.* 2017, Geyer 2020, Jambeck *et al.* 2015). Lebreton *et al.* (2017) The coastal population data may not include the global estimates of between 1.3 and 2.6 million tons of plastic that enter the ocean from rivers mostly from Asia (67%). The Mississippi River drains ~ 40% of the continental U.S. into the Gulf of Mexico (Cizdziel 2020) but it is not listed as one of the top 20 rivers adding plastic to the ocean²⁹.

Throughout this document the focus is on identifying the questions of how much plastic and MPs are in the ocean, how are MPs identified and measured, and to what extent MPs impact human health and marine ecosystems. The lack of standardized approaches including definitions of MPs, characterizations

²⁸ Plastics may be further designated as macroplastics (2.5 cm–1 m) and mesoplastics (5mm –2.5 cm) but these terms are rarely used in the literature.

²⁹ <https://ourworldindata.org/grapher/plastic-top-20-rivers>

of sizes and types, and scientifically designed experiments (Hartman 2019; Zantis 2021) limit comparison of results.

Microplastics are plastics manufactured from petroleum, sugar cane, or cornstarch and additives that bestow the desired characteristics of a wide variety of types. Microplastics (5 mm to 1 μm) are manufactured for specific purposes (*e.g.*, microbeads) or formed from larger plastics that are broken down by mechanical (abrasion and friction), photochemical, oxidative, and biochemical degradation processes. For this discussion, we use the term **degradation** or **fragmentation** when plastic is broken down to smaller-sized items such as MPs and nanoplastics ($>1\ \mu\text{m}$) whereas **biodegradation** refers to the complete breakdown of plastics to carbon, hydrogen, and oxygen (Amaral-Zettler *et al.* 2020). Plastics that are more readily biodegradable include three hydrolysable polyethylene terephthalates (PETs), polyurethanes (PURs) and possibly polycarbonates (PCAs) but they constitute a small percentage of total plastics manufactured each year (Amaral-Zettler *et al.* 2020; Geyer 2020). Although known enzymes break down PET, biodegradation in the ocean is complicated by suboptimal conditions, limited field studies, and the unknown role of microbial and fungal communities (Amaral-Zettler *et al.* 2020).

Types and Composition of Plastics

This section describes the petroleum and organic-based plastics and some specific additives, particularly those considered toxic. Two common plastics are polyethylene (PE) and polypropylene (PP) both of which are composed of hydrogen and carbon from petroleum byproducts differentiated by the number of carbon-carbon units in each unit of polymer chain (Table 1). Polyethylene chains are formed from monomers where shorter chains generally form more flexible structures and longer chains form harder structures. Polypropylene chains are composed of propene or polypropene monomers and form crystalline and harder structures. Polypropylene is widely used in packaging textiles and other consumer products such as detergents and other liquids as it does not react with dilute acids or bases.

Plastics are categorized as thermoplastics or thermosets (Table 1). Thermoplastics can be heated to a liquid, formed and solidified when cooled and may be reheated and reformed, but they often crack and break and are not generally reused. Thermoset plastics are formed into a hard structure and cannot be reheated into a liquid. They include PURs along with other resins (Geyer 2020). They can be combined with thermoplastics and be used in structures such as boat hulls and blades of wind turbines (Geyer 2020).

In general plastics are not readily biodegradable and those found in the ocean develop biofilms and attract contaminants in the water column. Plastics, whether petroleum-based or organic, are valued for their plasticity, *i.e.*, the ability to be molded or altered, as well as their low density, toughness, low electrical conductivity, and transparency. Many of these characteristics are due to additives that represent between 0.1 and 80% in plastics as a percent of total weight (hereafter by weight) and vary greatly depending on the types of additives (*e.g.*, plasticizers) and types of plastics (Hahladakis *et al.* 2019). While biodegradable plastics require less energy to manufacture and release less CO_2 (carbon dioxide) than petroleum-based plastics, they have higher potential to lead to eutrophication and acidification than petroleum-based plastics (Gironi 2011). In addition, both petroleum and bioplastics have additives that are released to the environment as they degrade or biodegrade (Gironi 2011).

Additives

Additives can be used to create plastics with particular characteristics, *e.g.*, high or low impact resistance, high transmission to light, and ease of forming into shapes. There are four general types of additives:

functional additives (*e.g.*, stabilizers, plasticizers, flame retardants, biocides, etc.), colors (soluble azocolorants, pigments etc.), fillers (various clays and minerals, calcium carbonate, barium sulfate), and high-impact reinforcements (*e.g.*, glass and carbon fibers) (Hahladakis *et al.* 2018). About 80% of plasticizers are phthalates (esters of phthalic acid), which are used for PVCs and about 20% for organic plastics (Hahladakis *et al.* 2018).

Table. 1. General categories of plastics, their chemical bonds, likelihood of photo- or biochemical degradation and uses.

Plastic types (% of total production) ^a	Abbreviations	Elemental formulas ^b	Rate of Photo- or biochemical degradation ²	Life Span (years) ^{d,e}	Uses ³	Comments
Polypropylene (21%)	PP	(C ₂ H ₆) _n	Photo- medium Bio-very low	10-600	Fibers, ropes, carpets	Thermoplastic
Polyethylene (15%) (High density polyethylene)	PE	(C ₂ H ₄) _n	Photo- medium Bio-low	No data (>600)	Packaging, bags, films, detergent, toiletries	Thermoplastic
Low density and linear low density polyethylene (18%)	LDPE, LLDPE	(C ₂ H ₄) _n	Photo-medium Bio-low	10-600	Packaging, bags, films, detergent, toiletries	Thermoplastic
Polyethylene terephthalate (8%)	PET or PETE	(C ₁₀ H ₈ O ₄) _n	Photo-medium Bio- medium	450	Shopping bags, beverage bottles, containers, coatings	Thermoplastic; 30% is biodegradable ^d
Polyvinyl chloride (17%)	PVC	(C ₂ H ₃ Cl) _n	Photo-low Bio-very low	60-150	Plumbing pipes, construction, garden hoses,	Thermoplastic
Polystyrene (9%)	PS	(C ₈ H ₈) _n	Photo-high Bio-low	50-80	Food containers	Thermoplastics
Polyethylene terephthalate (8%)	PET or PETE	(C ₁₀ H ₈ O ₄) _n	Photo-medium Bio- medium	450	Shopping bags, beverage bottles, containers, coatings	Thermoplastic; 30% is biodegradable ^d
Others (12%) incl. acrylate copolymers (<i>e.g.</i> , nylon or polyamide (PA))	PUR, resins, nylon	No Data			Foams, coatings, footwear, insulation	Thermosets
Polycarbonate*	PCA	No Data	Photo- occurs Bio-limited		DVDs	Biodegradable [#]
Polylactic acid*	PLA	No Data	Photo- occurs Bio-limited		Bottles, medical devices	Biodegradable [#]

^aHahladakis *et al.* 2018; ^bStubbins *et al.* 2021; ^cShah *et al.* 2008; ^dGeyer 2020; ^eMohanan *et al.* 2020; *Organic-based plastics, many are semi-synthetic; [#]Polycarbonates and polyactic acids are not readily or fully biodegradable and represent a small total of all plastics.

Many of plastic additives have been correlated with human health impacts Table 2. One of the most common plasticizers, bis (2-ethylexyl) phthalate (DEHP), has been banned from children's plastic toys and is permitted in other uses. For example, DEHP may be 50% by weight in PVC (Babinsky 2006; EPA 2017). Other ortho-phthalates are implicated in effects on brains of children (Ejaredar *et al.* 2015) and metabolic effects in adults (Radke *et al.* 2019). It is estimated that 4.9 million metric tons of phthalates are produced each year (Engel 2021).

Table 2. Categories of chemical additives and percentage by weight (adapted from Hahladakis *et al.*, 2018).

Category or type of additive with examples	% by weight additive/plastic	General purpose and comments
Plasticizers bis (2-ethylexyl) phthalate (DEHP), Bis compounds, phthalates, many others)	10–80	Provide flexibility, durability elasticity. Used in PVC, cling films, and PET and more.
Flame retardants (bromated flame retardants, phosphate esters, and others)	0.7–25	Intended to retard start or growth of fires in clothing, furniture, etc. Amount varies with bromated retardants used
Stabilizers, antioxidants, and UV stabilizers (Bisphenol A (BPA), metals, phosphates, many others)	0.05–3	Stabilize food packaging when exposed to light, temperature, and microwaves. Phosphates are used in higher amounts, phenolics lower amounts
Heat stabilizers (lead, cadmium and phenolic salts)	0.5–3	Prevent degradations when exposed to high temperature; used in PVCs
Slip agents, lubricants, anti-statics (fatty acids)	0.1–3	Reduce surface frictions; amounts vary with chemical and use (less in anti-static, some hydrophilic
Curing and blowing agents (formaldehyde hydrazine, others)	0.1–2	Amounts vary, especially for blowing agents
Biocides (arsenic, organic tin compounds, Triclosan)	0.001–1	Used in foams and soft PVC; Triclosan banned
Colorants (water soluble azocolorants); organic (cobalt based); inorganic pigments (metals and fluorescence substances)	0.25–5; 0.001–2.5; 0.01–10	Provide colors to transparent goods, other plastics and fluorescence. Depending on the use, found in polystyrene, cellulose and other plastics.
Filler (Calcium carbonate, other inorganics, asbestos, glass microspheres and more chemicals, wood, clay, others)	up to 50	Reduces cost of plastics. Adds characteristics to plastic for a variety of purposes.
Glass reinforced plastic or reinforcements (glass fibers in plastic), also called fiber glass	15–30	Reduces amount of plastic, creates strong, flexible materials. Used to create hulls, sheets, toys to bridges.

Although BPA is prohibited in children’s bottles, infant formula containers and sippy cups by the U.S. Food and Drug Administration (FDA), BPA can be found in plastic products such as water bottles, dental sealants, and cash register paper; in liners of cans; and many other products (FDA 2012a). It has been deemed not a major health threat based on data prior to 2012 and continues to persist in the environment (FDA 2014); however Vandenberg *et al.* (2013) examined hundreds of publications and concluded that low-dose BPA is of concern for mammals. Other chemical additives in plastics include oxybenzone, fluoride, parabens, butylated hydroxyanisole (BHA), perchlorate, decabromodiphenyl ether (deca-BDE),

asbestos, and perfluorooctanoic acid, some of which are considered toxic and undergoing review by EPA's Toxics Substance Control Act³⁰.

Some additives are endocrine disruptors and are released when plastics breakdown, but generally are in low concentrations and not considered problematic by EPA and FDA (EPA 2010, 2017; FDA 2012a, b; Hahladakis *et al.* 2018). However, a number of studies find impacts to humans, wildlife, and marine biota (Vandenberg *et al.* 2013; Zantis *et al.* 2021). One study demonstrated negative impacts of low doses of BPA and that the lowest observed adverse effect level (LOAEL) of 50 mg/kg/day should be 1–4 orders of magnitude lower than currently stated (Vandenberg *et al.* 2013). Nonetheless, neither the FDA nor EPA have taken further action about BPA in drinking bottles and plastic films.

Shapes and Composition

Microplastics are also categorized in large part on size as well as shape and types of plastics (Hartmann *et al.* 2019; Figure 1). Microplastic shapes are assigned to four groups: granules pellets and microbeads,

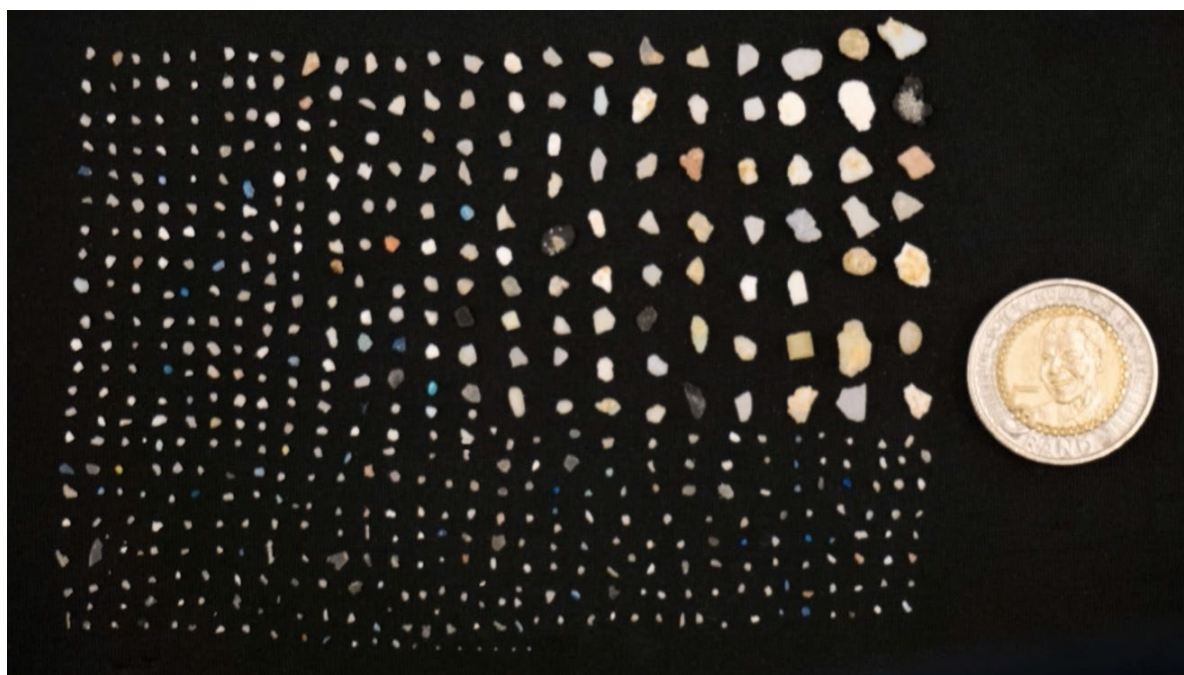


Figure 1. Examples of microplastics color and shape with South African Krugerrand for scale. Sample collected approximately 500 km off the coast of South Africa. Credit: Ethan Edson, Ocean Diagnostics Inc. (Victoria, British Columbia, Canada).

rigid irregular fragments, films, and fibers (including fishing lines and lint) (Hartmann *et al.* 2019). Identifying and measuring MPs either by shape or type, especially when they are combined in a sample is challenging without sophisticated equipment and even with specialized equipment may have false positive and negative results or miss small particles (Table 3). Samples of MPs collected by towing nets in the water often undercount microfibers and small particles (Barrows *et al.* 2018). Grab sampling generally report higher concentrations of microfibers and small MPs (Tobin and Urban Rich, 2022)

³⁰ <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/chemicals-undergoing-risk-evaluation-under-tsca>

Several new approaches are modifying current technologies to improve *in situ* assessments. Automated sampling was used to capture microplastic concentrations across large areas of the ocean surface (Edson and Patterson, 2015). Adaptation of Raman spectroscopy for use in the ocean provided insights into the distribution of microparticle distribution in Monterey Bay, which is a promising option for improved real-time analysis of MPs for Massachusetts Bay and other areas (Araujo *et al.* 2018). In addition to combining two techniques (*e.g.*, visual and Raman) others are modifying equipment to monitor particles at depth. A recently developed technology (in the lab of Anna Michel, Woods Hole Oceanographic Institution) that robustly, accurately, and quickly measures microplastics is currently being developed for environmental use fresh and marine waters³¹.

Table 3. Advantages and limitations of analysis techniques for determining microplastic shape, composition, and number (Smith *et al.* 2019 and cited and modified from Burton 2017, Shim *et al.* 2017, Duis and Coors 20016, and Rocha-Santos and Duarte 2014).

Methods	Advantages and Limitations
Microscopy	Simple, visual observations are fast, sample preparation and counting can be slow, inexpensive, high false positive and negative identifications, no chemical composition
ESEM-DDSa	Elemental composition and surface morphology
Microscopy–FTIR/Ramanb	Confirm subset MP and type, filtration required, some false positive and negative, only subset, so may miss types and sizes, color interferes
FTIR spectroscopyc	No false positive, few false negatives, visualization no preparation, expensive, slow, best method for routing analysis*
Raman spectroscopyd	As FTIR + pigment interference
AFM-IRe	No false positives, few false negatives, size to nano-levels, identifies number, size, shape, and chemical content; expensive and slow
Thermal (pyro-GC/MS applied as TGA-GC/MS, TDC-GC/MS, and possibly with FPA-FTIRf	Analyze polymers and additives, applicable to various water matrices, applicable to few polymers, complex, expensive; small particles may be missed and weathered polymers can be problematic

^aESEM-DDS–Environmental scanning electron microscopy–energy dispersive x-ray spectroscopy, ^bMicroscopy–FTIR/Raman; ^cFTIR–Fourier transform infrared spectroscopy, ^dMicroscopy–FTIR/Raman–together identify structural distribution and chemical purity, ^eRaman spectroscopy identifies structural fingerprint of molecules, ^fAFM–IR–atomic force microscopy–infrared spectroscopy ^gThermal– (pyro-GC/MS–pyrolysis-gas chromatography with mass spectrometry, TDS-GC/MS–thermodesorption gas chromatography with mass spectrometric detection, TGA-GC–thermogravimetry gas chromatograph, and FPA-FTIR–focal plane array-Fourier transform infrared spectroscopy), *Shim *et al.* 2017.

Sources and Environmental Fate of Microplastics

Plastics are ubiquitous in our daily lives and are used, discarded and rarely reused. When used for construction products (*e.g.*, water supply and drainage pipes, electrical wires and conduits) they may last a long time; other prolonged uses include everyday household products and items, electronics, computers, and printers. Short-term uses include clothing and cell phones and one-time uses include disposable utensils and tableware, water bottles and plastic bags (Geyer *et al.* 2017). The majority of plastics end up in landfills (about 80%) of which up to 10% may be lost (*e.g.*, winds, loss during loading, runoff, etc.), before reaching the disposal facility (Geyer *et al.* 2017).

³¹ <https://www.tripleringtech.com/news-and-events/jan-11-2022-triple-ring-technologies-and-woods-hole-oceanographic-institution-collaborate-on-microplastic-sensing-in-water-with-epa-grant>

Despite efforts to designate plastics as recyclable, only about 10–15% of plastics are recycled, and usually materials are only done so once. It is estimated that 75% of current recyclable plastics end up in landfills (Geyer 2020). Plastics that are not recycled, incinerated (~12%) or sent to landfills are considered “mismanaged” plastics; meaning they are carried by wind, runoff, or rivers and ultimately reach the ocean and lakes (Jambeck *et al.* 2015). Until recently, the U.S. was exporting “recyclable” plastics to China, India, Malaysia, Turkey, Indonesia, and several other countries (McCormick *et al.* 2020). Currently very little of that plastic is recycled and for countries accepting plastic, it is often incinerated creating hazards for local populations or is mishandled or discarded improperly.

The primary sources of MPs are from manufacturing plants that produce micro-sized plastics (*e.g.*, lentil-sized pellets or “nurdles”), plastic industrial scrubbers used in air blasting (as a replacement for sand), powders used in molding products, and waste particles derived from the manufacture of clothing, textiles, cosmetics, toothpaste, and paints—most of which ends up in WWTPs (Mason *et al.* 2018; Sun *et al.* 2018; Dey *et al.* 2021). Other sources of MPs include fishing gear and plastic particles from car and truck tires that enter by road runoff, rivers, and non-point sources³² (Kole *et al.* 2017). In Europe, plastics from tires represent approximately 110,000 tons/year and is the equivalent of land-fill plastics (OSPAR³³ 2017 see their Figure 1, p. 5). It is estimated that 40% of the MPs reaching the ocean come from road tire wear (0.5 μm –< 10 μm) with the highest concentrations in highly populated areas such the U.S. Northeast, northern Europe and Asia (Evangelidou *et al.* 2020). While microbeads have been banned in “over the counter” cosmetics in numerous countries including the U.S., Canada, Australia, China, India, Italy, and most of the European Union countries as of 2020³⁴, they continue to be used in applications such as air blasting and scrubbing compounds. Microbeads are primarily, PE, PP, PET, polymethyl methacrylate, and nylon (PA). Secondary sources are the degradation or breakdown of large pieces of plastic under different environmental conditions, *e.g.*, mechanical fragmentation, ultraviolet light, sunlight, microorganisms, and water movement (Walsh *et al.* 2021).

As with much of the literature on microplastics, hard data are lacking, research and design of experiments and ask different questions, and approaches may or may not use concentrations comparable to those in the water column or sediments (Burton 2017; Koelmans, *et al.* 2016). Others note that MPs and microfibers are undercounted that underscores the need for standardized approaches for consistency (Conkle, *et al.* 2018).

Transport and fate of microplastics

Mismanaged plastics and MPs are distributed by air, runoff, and streams and rivers, and ultimately find their way to the ocean (Jambeck *et al.* 2015; Schmidt *et al.* 2017). It is estimated that U.S. plastic production increased 26% from 2010 to 2016, and calculations of plastic reaching the ocean may not include current mismanaged plastics (Schmidt *et al.* 2017). Globally the U.S. has the third highest level mismanaged plastic discard (Law *et al.* 2020). Floatable plastics in the oceans are mixed with plants and other floating debris that accumulate in five oceanic gyres found in the North and South Atlantic, North and South Pacific and Indian oceans. The best known and most studied is the northern “Great Pacific Garbage Patch”, which that is twice the size of Texas (Cózar *et al.* 2017, Egger *et al.* 2020; Lebreton *et al.*

³²The runoff from the Zakim Bridge in Boston discharges directly into the Charles River while other parts of the highway discharge directly into Boston Harbor as do several major coastal highways (*e.g.*, I-9).

³³ OSPAR is named for the OSlo and PARis convention. “OSPAR is the mechanism by which 15 Governments & the EU cooperate to protect the marine environment of the North-East Atlantic;” <https://www.ospar.org/about>.

³⁴ Numerous online reports from countries; <https://en.wikipedia.org/wiki/Microbead>.

2017). The North Atlantic garbage patch is several hundred kilometers wide with an estimated concentration of 200,000 pieces of debris per square kilometer (Law *et al.* 2010; Jambeck *et al.* 2015; Wilcox *et al.* 2020).

Ultimately plastics are fragmented by light, waves and other physical actions, biotic consumption and egestion, and microbial activity. These particles begin to gather biofilms and fouling organisms often forming heteroaggregations of particles and plankton. The heteroaggregations are heavier than individual particles, causing them to sink at varying speeds (Egbeocha *et al.* 2018). Settlement of heteroaggregations from the surface removes food for lower trophic level organisms and may interfere with nutrient uptake for organisms ingesting the particles (Egbeocha *et al.* 2018).

Until recently little was known about the fate of the MP particles. Examination of the vertical distribution of plastics in the Great Pacific Garbage Patch from the surface to depths of 2000 m found particles decreased in both size and abundance from the surface to depths (Egger *et al.* 2020; Johnson-Groh 2020). Microplastics at depth represent heavier plastics such as polyesters, PA, and acrylics whereas which PP and PE tend to remain at the surface (Erni-Cassola *et al.* 2019). The finding of MPs at depths underscores the amount of plastics ending up in the ocean (one estimate is >800 billion tons since the 1950s) but it does not estimate the amount of plastics that are in the sediments (Cashman *et al.* 2020). The debris in the oceanic garbage patches are expected to double in weight by 2030 and quadruple by 2060 (Isobe 2019). A common assumption is that floating plastic accounts for only 1% of the plastics in the ocean. The remaining 99% is assumed to be below the surface, in sediments, or biodegraded but that is not well documented (Amaral-Zettler *et al.* 2020).

In addition to the accumulation of plastics in gyres, deeper currents also carry plastics and MPs to locations far from where they enter the ocean. The distribution of plastics in the ocean provide insights into oceanographic dynamics in nearshore, offshore, and deeper waters (Van Sebille *et al.* 2020). While most of the plastics are found near coastal areas with high populations (Stubbins *et al.* 2021), even remote regions like the Arctic have substantial levels (Cózar *et al.* 2014, 2017).

Coastal areas are a primary region for plastic accumulation largely driven by physical factors and proximity to anthropogenic sources with additional accumulation in deeper waters and sediments (Olivelli *et al.* 2020). Coastal areas are habitats for birds, marine mammals and other vertebrates resulting in iconic photos of plastic impaired seabirds, seals, turtles and other wildlife. Although not photographically compelling, other marine organisms (*e.g.*, plankton, amphipods, and polychaetes), also ingest smaller plastic particles and fibers that may negatively affect their nutrition and growth. Generally most of the particles in coastal zones and surface waters are single-use plastics, PE (*e.g.*, packaging and bags) and PP (*e.g.*, fishing lines), but with recent sampling protocols researchers are finding smaller MPs, especially fibers that consist of PE, PA and polyester (Barrows *et al.* 2018; Carr 2017).

Microplastics discharged to WWTPs come from domestic and industrial wastewater and include PPCPs, detergents, washing synthetic clothing, and other sources of plastics (Carr *et al.* 2016; Boucher and Froit 2017). Until June 2017, microplastic beads used in rinseable cosmetics contributed to a significant amount of MPs in receiving waters, but they have been banned both globally and in the U.S. (Benson and Reczek 2020). However, microbeads are also used in air blasting and other cosmetics and continue to be produced and released (Benson and Reczek 2020).

Two primary treatment processes separate plastics at WWTPs. At the MWRA plant most floatable plastics, oils, fats and sticks are removed by gravity and centrifuge thickening processes forming scum that is and subsequently landfilled (Figure 1; MWRA 2021; B. Reilley, pers. comm. 2021).

Studies at other WWTPs demonstrate that 80-99% microplastics are removed during secondary and tertiary treatment, at 0.2% and 14% depending on the process (Carr *et al.* 2016; Sun *et al.* 2019; Dey *et al.* 2020) sequestering them in biosolids (Rolsky *et al.* 2020). Many WWTP operators incinerate biosolids, however MWRA dehydrates and pelletizes its biosolids that are then used in agriculture, landscaping, or reclamation and are available at nurseries (MWRA 2021). As noted earlier, MPs and their additives may be released into the air and as runoff at each stage of the WWTP process including the land-based use of biosolids. The annual estimated amount of MPs in biosolids ranges from 44,000–300,000 and 63,000–400,000 tons for European and U.S. applications respectively annually. These MP estimates in biosolids exceed the estimated total MP in the surface of ocean of 93,000-236,000 tons (Nizzetto *et al.* 2016).

Over 2 million tons of microplastics reach the ocean each year (Tobin and Urban-Rich 2022). Studies of MPs removal from seven major California wastewater treatment facilities found that very few MP fibers of sizes measured as (28 mm-0.3 mm) came through the systems with tertiary treatment (Carr *et al.* 2017).

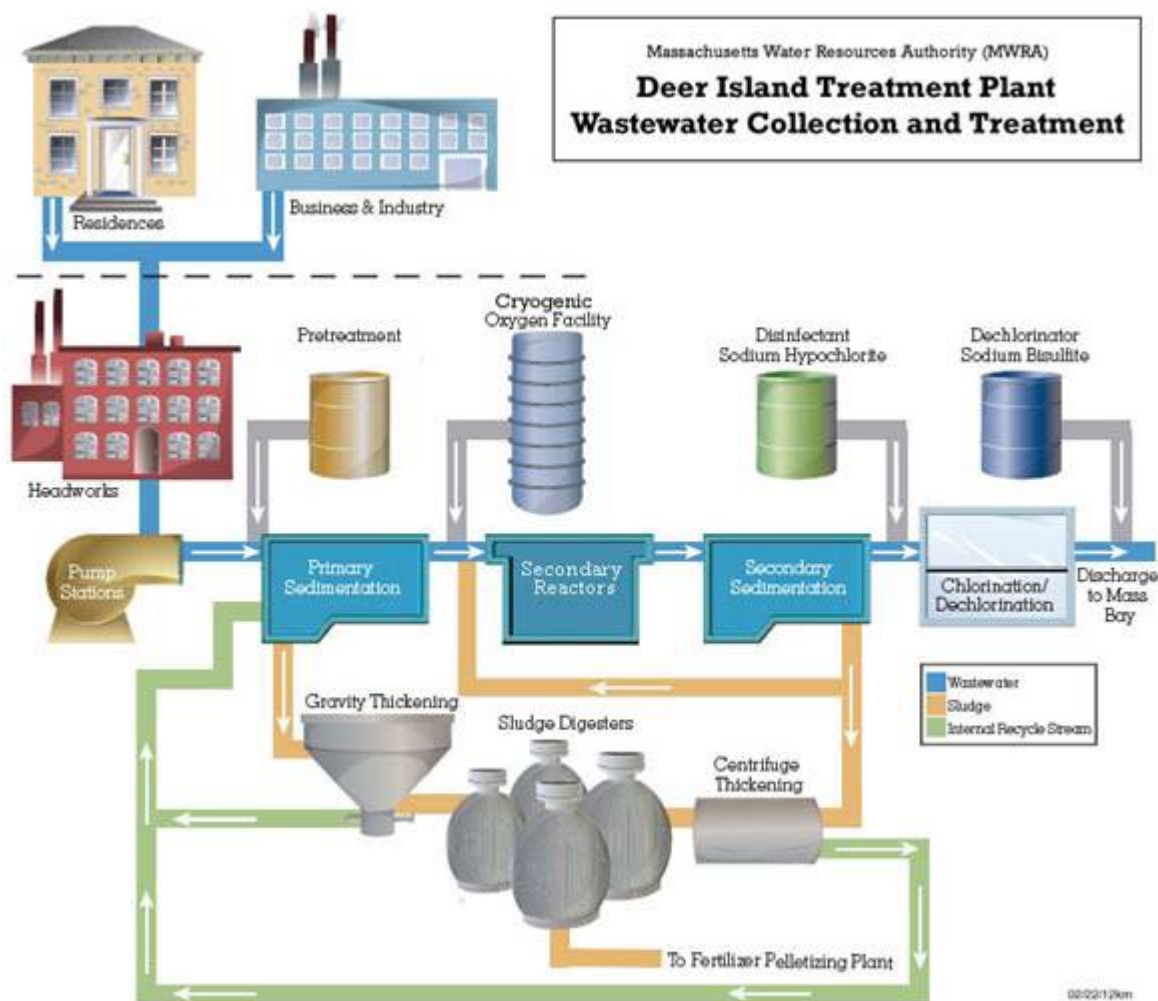


Figure 1. Diagram of the MWRA Deer Island wastewater treatment plant collection and discharge system (courtesy of B. Reilley, 2021, MWRA).

However, other studies claim it is unclear if the estimated removal effectiveness includes MPs smaller than 100 μm or fibers (Talvitie *et al.* 2017) underscoring the need for standardized methods and approaches.

With secondary treatment, it is estimated that WWTPs release over 4–7 million microparticles (including MPs and natural fibers) per facility per day (Mason *et al.* 2016; Carr *et al.* 2017); Carr (2017 estimate that 0.8 microfibers/1L are discharged from WWTPs. If applied to MWRA, an estimated 1.13 billion fibers are released per day (assuming an average flow of 299 million gallons/day based on Massachusetts Department of Environmental Protection (MADEP) NPDES analysis (C Vakalopoulos, MADEP, pers. comm. 2021). Approximately 57% of fibers are synthetic (microplastic fibers), ~12% are semi-synthetic such as rayon and ~31% are natural or non-synthetic such as wool and cotton (Barrows *et al.* 2018). The lack of clarity about microfiber identification adds to the many challenges in assessing the role of or the amount of MPs and fibers in the ocean (Barrows *et al.* 2018; Amaral-Zettler *et al.* 2020). An in-depth discussion of MP fiber analysis identifies sources, issues associated with sampling and analysis of presence and concentrations, data gaps and mitigation strategies (Tobin and Urban-Rich 2022)

Plastics degrade both physically into smaller particles, and by microbial and enzymatic mechanisms. In addition to the type of plastic, the rate of biochemical degradation varies with environmental conditions such as temperature, depth and microbial community. Specifically, biodegradation is more rapid in surface waters than in the deep sea (Amaral-Zettler *et al.* 2020; Dey *et al.* 2021). Efforts to develop bacteria and fungi to biodegrade MPs are being pursued as potential options for reducing microplastics in the environment, but it is unclear if these approaches are feasible for marine waters (Amaral-Zettler *et al.* 2020).

Marine Biota and Human Exposure to Microplastics

Marine Biota

Marine biota are exposed to MPs in all regions of the ocean from nearshore habitats to the deepest areas of the sea floor including the Arctic and Antarctic basins. The lack of standardized methodologies for identifying microplastic types in water and sediments limits accurate assessments of how much plastic is in the ocean as well as the ability to compare impacts on biota. Current knowledge of microplastic uptake, total MPs in organisms, and metabolic and physiological responses is based on field studies, lab experiments, and for marine mammals and some sea birds, assessments of stranded animals (Cole *et al.* 2014; Karlsson *et al.* 2017; Lusher *et al.* 2017; Egbeocha *et al.* 2018). Each approach has benefits and limitations in drawing conclusions about uptake and retention of MPs and their effects. The advantage of the laboratory experiments is the ability to control exposure levels to specific MP types and contaminants of known biological test species. However, it is difficult to design controlled experiments that are meaningful in the absence of clear understanding of the MP concentrations *in situ* (Zhang *et al.* 2020).

Plankton

Microplastics are found in, and clearly impact both photosynthetic plankton (phytoplankton) and heterotrophic plankton (zooplankton). The plankton includes microscopic bacteria, archaea and protists (including microalgae and diatoms), and metazoans (including cnidarians, ctenophores, crustaceans and diverse larvae). Data suggest microplastics can inhibit growth and/or metabolic activities of phytoplankton and zooplankton (Zhang *et al.* 2020; Prinz and Korez 2018). Microplastics are ingested by diverse zooplankton, with individual species ingesting particular shapes and sizes of microplastics that often mimic their natural prey (Botterell *et al.* 2020). Once ingested by zooplankton, these microplastics that enter marine food webs have negative effects on feeding behavior, growth, development, reproduction, and lifespan of many taxa, including some such as the copepod *Calanus*, known to play key roles in marine food webs, and are transferred up trophic levels (Botterell *et al.* 2019; Cole *et al.* 2015). Because zooplankton such as copepods and euphausiids are a primary food source for many commercially

important fish species, microplastic ingestion by zooplankton lead to the transfer of this plastic into trophic levels relevant to the human food supply, where plastic fragments and fibers are detected in fish and bivalves collected for human consumption (Rochman *et al.* 2015; Li *et al.* 2015). Further, consumption of microplastics by zooplankton has the potential to exacerbate ocean deoxygenation by reducing the grazing by zooplankton on phytoplankton, leading to increased carbon export to deeper waters and associated remineralization of that carbon (Kvale *et al.* 2021). Biofouling of microplastics occurs when bacteria and other plankton utilize them as substrates where they form biofilms on the surface. Formation of biofilms causes the microplastics to become less buoyant, and to sink faster, thus shielding them from degradation by ultraviolet light near the ocean surface, and increasing their consumption at depth by predatory organisms (Sudhakar *et al.* 2007). Since microplastics can adsorb and concentrate organic pollutants and heavy metals up to 1 million times over ambient pollutant concentrations, ingestion of small plastic particles is a probably route for biomagnification of toxic chemicals in the marine food web (Egbeocha *et al.* 2018; Carbery *et al.* 2018; Zhang *et al.* 2020). There is still much to learn about the toxic effects of trophic transfer of MPs and their adsorbed contaminants through marine food webs, including into commercially valuable fisheries of tremendous value to humans.

Other Invertebrates

Many bivalves have selective ingestion and reject MPs as pseudofeces without consuming them or may ingest MP without consuming them and eliminate them quickly (Ward *et al.* 2019a, b). Often a small number of MPs (fewer than 10 particles/organism) may be retained (K Ho, EPA, pers. comm., 2020). In the lab microplastic beads, covered with a variety of chemicals and substances, are often used to assess feeding preferences and to monitor uptake in bivalves relating size of the particles, coverings, and rate of ingestion and egestion (Ward *et al.* 2019a, b). Determining factors that affect MP ingestion in the field is complex and more challenging (Cole *et al.* 2014). The North Atlantic coral, *Astrangia poculata* appears to ingest MPs, especially microbeads and microfibers, both in the field (Rhode Island) and lab (Rotjan *et al.* 2019). Field-collected polyps had an average of 112 particles per animals and showed a preference for microbeads over similarly sized zooplankton. When fed microbeads with *Escherichia coli* biofilms *A. poculata* polyps died within a few weeks, but polyps that ingested non-biofilmed microbeads did not show mortality. The preference for microplastics and their retention may inhibit nutritive update and reduce energy availability (Rotjan *et al.* 2019). Oysters, scallops, and mussels have different size preferences and capture and eject particles differently. In general, mussels are highly selective and while some plastics are retained, overall they reject most particles either as pseudofeces or feces and may not be the ideal organisms for assessing plastic contamination in the ocean (Ward *et al.* 2019a, b). In contrast, Zhang *et al.* (2020) have summarized research on a variety of bivalves with data suggesting that microbeads are retained from 4 hours or less to over a month in mussels and other bivalves, including oysters.

Other researchers have examined the effects of MPs on invertebrates. Larval ascidians, *Ciona robusta* and sea urchins *Paracentrotus lividus* ingested microbeads, which slowed metamorphosis of the ascidian and altered development of the sea urchin larvae (Messenitti *et al.* 2017). The isopod, *Idotea emerginata* ingests MPs but is not impaired at the concentrations tested (Hamer *et al.* 2014) whereas other crustaceans such as the Norway lobster *Nephrops norvegicus* do not distinguish between MPs and food and retain them for prolonged periods (Hale *et al.* 2020). Invertebrates that live in sediments ingest plastic particles and sediments when burrowing. When exposed to MPs, the polychaete *Arenicola marina* exhibited lower weights, decreased feeding activity, reduced energy reserves, and altered engineering behavior in burrowing (Wright *et al.* 2013).

In the field samples, the proportion of invertebrates with MPs ranges from 40% to nearly 100% depending on the species and the proximity to high concentrations. While MPs were found in tissues and organs, including hemolymph of some invertebrate species, the specific impacts are poorly documented (Zhang *et al.* 2020). It is not surprising that different experimental approaches lead to different research results. Some European studies report no response for some invertebrates (OSPAR 2017) whereas others report negative impacts to larval shape, growth rate, reproduction, and behavior and in some cases mortality (Wright *et al.* 2013; Egbeocha *et al.* 2018; Prinz and Korez 2018; Hale *et al.* 2020). The lack of standard approaches for identifying and analyzing MPs and determining health impacts makes it difficult to compare the results of marine invertebrate exposure studies.

Vertebrates

Microplastics are found in marine vertebrates (fish, seabirds, turtles, and mammals). As discussed throughout the paper for all organisms, the challenges have been to demonstrate what, if any, impacts may be attributed to MPs and their additives and to ensure that samples are not contaminated by omnipresent MPs, *i.e.* results are valid with appropriate quality assurance/quality control (QA/QC) (Wesch *et al.* 2016). Field studies have examined MPs in gastrointestinal tracts of pelagic and benthic fish with varying results. Pelagic fish may or may not have more MPs than benthic fish but in general omnivorous fish ingest more plastics than herbivorous and carnivorous fish (Mizraji *et al.* 2017). Laboratory studies on fish that used microbeads with pollutants sorbed from the marine environment have demonstrated liver toxicity and pathology and some effects have been shown with microbeads alone (Rochman *et al.* 2013a). At the cellular level, MPs appear to cause hepatic stress, metabolic changes, reproductive anomalies, endocrine changes and altered larval development (Rochman *et al.* 2013a, b; Egbeocha *et al.* 2018).

Seabirds ingest MPs but a lack of standardized methodologies makes it difficult to assess impacts (Lusher *et al.* 2015; Amélineau *et al.* 2016). Current data suggest that ingestion of surficial contaminants on MPs may not impact seabirds, (Tanaka *et al.* 2015; Bang *et al.* 2021). Long-lived northern fulmars (*Fulmarus glacialis*) ingest MPs and are used as indicators in Europe (Provencher *et al.* 2018). Persistent organic pollutants were found in muscles and other tissues, however it was determined that these chemicals were accumulated by ingesting prey rather than from MPs (Herzke *et al.* 2016). Other studies have found that an Arctic sea bird, the little auk (*Alle alle*) had a ten-fold increase in MPs compared to concentrations in seawater and that the MPs are transferred to the young (Amélineau *et al.* 2016). In the North and South Atlantic great shearwaters (*Ardenna gravis*) ingest and retain MPs in their gastrointestinal tract, which come from pelagic sources rather than their primary prey, sand lance (*Ammodytes* spp.) that retain no MPs (Robuck *et al.* 2021).

Not only are marine mammals less well-studied, there is no standardized or consistent approach to evaluate impacts (Zantis *et al.* 2021). Marine mammals at greatest risk are filter feeders such as humpback whales *Megaptera novaeangliae* and other baleen whales that are found in areas with high MPs in their habitats (Egbeocha *et al.* 2018). High levels of neoplasia (uncontrolled growth of cells and tissues) in marine life (*e.g.*, sea lions and turtles) occur in areas that are impacted by anthropogenic pollutants, however these are not directly related to MPs and many may be related to viral induced cell growth (McAloose *et al.* 2015). Contaminants are found in whale blubber and skin of whale sharks *Rhincodon typus* with MPs retained in digestive systems (Egbeocha *et al.* 2018); however, there is no direct evidence that MPs are a source or the only source of contaminants. In a study of whales, seals and dolphins, MPs were found in the digestive tract of all 50 animals examined, with higher concentrations in animals that died from infectious diseases. However, data were insufficient to implicate MPs as potential cause of deaths (Nelms *et al.* 2018).

Ecosystems

Prinz and Korez (2018) examined 236 scientific publications to better understand the impact of MPs on ecosystems and found that only about 4.4% of the publications extrapolated cellular impacts to ecosystem levels. They suggested the need for risk assessments relating organismal impact to ecosystem-level impacts and evaluation of sublethal effects related to microplastic pollution. In general, although uncertainties exist, meta-analysis of published studies indicates that there are four physiological and biological effects of MPs on marine organisms that could possibly lead to impacts at population and ecosystem levels: physical malfunctions, endocrine disruptions, alteration of gene expression and changes in metabolite composition. All of these can impact behavior, reproduction, growth, and development, and possibly impact populations (Foley *et al.* 2018; Erni-Casola *et al.* 2019).

Human Impacts

Microplastics are present in humans from inhaled dust (*e.g.*, MPs from insulation, furniture) and from food that contains particles. Micro- and nanoplastics have been found in the intestinal tract and other organs and excrement of human and wildlife (Galloway *et al.* 2016). Confirmation of nanoplastics (≥ 700 nm) in human serum has implications for translocation to other organs (Leslie *et al.* in press). Although problems may come from ingesting plastics themselves, concerns about the release of additives such as PBA, DEHP and other phthalates and possibly growth of microbes on the plastics have been postulated as issues of concern (vom Saal and Hughes 2005; Wright and Kelly 2017; Mammo *et al.* 2020). However, while bivalves and other marine biota ingest MPs and many invertebrates and fish have MPs in their tissues, consumption of marine biota is not deemed a major source of MPs in humans (Carberry *et al.* 2018). Currently, MPs in seafood are not quantified or regulated and there are no guidelines or standards for MPs applicable either to humans or wildlife.

Regulations

There are no regulations for MP discharges at the state or federal level for drinking water, fresh water, or marine waters or for MP levels in food. The EPA has a nascent program on method standardization and development for sediments and waters.

EPA's Office of Water publishes Trash Free Waters Monthly Update³⁵ that addresses a variety of issues affecting water quality, including plastics. There currently are no guidelines or regulations for consumption of MPs in seafood for humans or in prey for wildlife as Canadian Environmental Protection agency has developed for PFAS (ECCC 2018).

Local Research Projects

Woods Hole Oceanographic Institution (WHOI) oceanographers Scott Gallagher and James Churchill are examining release of MPs from WWTPs in the Massachusetts Bay/Buzzards Bay areas during storm events and will use the data to model the transport of MPs from point source releases.

³⁵ epa.gov/trash-free-waters

Summary Uncertainties and Recommendations

As a society we rely on plastics which are integrated into all aspects of our lives. Photos of plastic entangled around the necks of seabirds and seals and the formation of plastic-laden ocean gyres have raised awareness in the public, but it has not reduced our continued use and discard of plastics. The total amount of plastic in the environment has been increasing at a rate of 8.4% per year between 1950 and 2015 (Geyer *et al.* 2017) and its growth is unlikely to decrease in the near future (Amaral-Zettler *et al.* 2020). Plastics will continue to be a part of our society and inevitably escape into aquatic environments. We need to understand and set safe levels of plastics and particles in our environment for both aquatic life and human health. In addition, the role of plastic as a vector for transport of microbial colonies that harbor antibiotic resistant or hazardous microbes is not well understood (Amaral-Zettler *et al.* 2020). Plastics may adsorb contaminants and degradation and breakdown of particles can release additives, many of which are toxic (Amaral-Zettler *et al.* 2020). Very few studies extrapolate biotic effects to ecosystems (Prinz and Korez 2018).

The amount of plastic particles (MPs, fibers, and nanoplastics) in the ocean is poorly documented. While MPs research in marine waters is increasing, the varied approaches to examining impacts to biota, humans, and ecosystems makes comparisons difficult among studies. Approved and standardized approaches to assess the types of MPs and their size, shape and behavior in the ocean are needed to provide insights and create a quantitative database. Appropriate QA/QC must be applied to all studies to have confidence in the results. Often overlooked is the need to ensure that airborne plastics, plastics on samplers' clothes and other plastic contamination are being excluded from samples.

Ongoing research is examining whether MP release is impacted by the changing precipitation experienced in the Northeast, and how this impacts their transport and fate in Massachusetts Bay (S. Gallagher, pers. comm. 2021). The relative contribution from WWTPs compared to other sources of MPs and fibers is also unknown. The scientific literature examining impacts on species is varied in part based on differences in species and experimental approaches: some studies report no effects while others report metabolic and physiological effects as well as kidney or other organ failures and pathologies. The following recommendations reflect the lack of clear agency guidance on acceptable levels and basic unknowns about concentrations, dispersion and impacts. These recommendations are related to MWRA's commitment to its AMP, which specifically focuses on safe consumption of seafood and the impacts to marine biota and the ecosystem.

Recommendations

- Conduct literature and database searches by EPA, MADEP and the Massachusetts Department of Public Health (MADPH) to provide guidance on acceptable MPs concentrations in drinking water and discharges to fresh and marine receiving waters. A framework for setting standards, identifying critical issues relevant to MPs in receiving waters, and identify the impacts of MPs on ecosystems is necessary to protect human health and the environment.
- Conduct literature review searches on WWTP influent and effluent removal rates for all microplastic particles, including microfibers that identifies MP release to the environment. These values should be compared to MWRA rates of release and presented to OMSAP. While nanoplastics are not included in this document, they may become a concern in the future.
- Agencies should develop standardized methodologies and approaches for measuring, quantifying and categorizing MPs in different matrices (*e.g.*, sediment, water column, and organisms).

- Special studies as collaborative efforts should focus on MP issues related to discharges to Massachusetts Bay and impacts on biota focusing on issues related to the AMP.
- Special studies as collaborative efforts should review MPs in selected marine invertebrates, fish and marine mammals and ecosystem impacts pertinent to Massachusetts Bay. It should include and the physical and chemical impacts of MPs, adsorbed chemicals and microbes, and the release of additives on both organisms and the ecosystem. The search should also include data on human consumption of MPs in seafood.
- A special study should monitor distribution of particles near and away from the outfall at depths and in sediments to understand the fate of particles and potential impacts on pelagic and benthic communities. Depending on the results, further monitoring may be required of WWTPs.

Recap

The lack of understanding in the current concentrations of MPs and their health effects, and the absence of regulations for MPs in drinking, fresh, and marine waters make it difficult to identify acceptable levels of release from WWTPs. The implications for biota include interfering with digestion, cellular disruption, impacts to the physiology and metabolism of organisms, and liver toxicity and pathology. Contaminants and pollutants may be sorbed from marine fibers and microplastic particles, but these processes are poorly understood and these effects may be species specific, further confounding understanding and regulation. Currently there are no standard methods for assessing impacts on individual species or at the ecosystem level. Additionally, different types of MPs, *e.g.*, PE, PP, PET, PVC and others adsorb chemicals differently and have different additives, many of which are toxic, which may also be released when ingested. As of this writing, data on MPs from MWRA effluent and their distribution throughout Massachusetts Bays are unknown, although current research and monitoring studies are underway. Federal and state agencies should examine what is known about increasing plastics in marine waters and develop a framework for addressing these issues to minimize impacts on marine biota, humans and ecosystems. Internationally accepted methods that are broad ranging enough to encompass different matrices and experimental objectives need to be developed. These methods must incorporate appropriate QA/ QC standards in order to have confidence in experimental results.

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Disclaimer

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List of Acronyms Used in this Paper

AFM-IR	Atomic force microscopy–infrared spectroscopy
AMP	Ambient Monitoring Plan (for MWRA)
BPA	Bisphenol A
CEC	Contaminants of Environmental Concern
CO ₂	Carbon dioxide
deca-BDE	Decabromodiphenyl ether
DEHP	Bis (2)-ethyl hexyl phthalate
DVD	Digital video disk or digital virtual disk
ECCC	Environment Canada and Climate Change
ESEM-DDS	Environmental scanning electron microscopy–energy dispersive x-ray spectroscopy
EPA	U.S. Environmental Protection Agency
FDA	U.S. Federal Drug Administration
FPA-FTIR	Focal plane array-Fourier transform infrared spectroscopy)
FTIR	Fourier transform infrared spectroscopy
LDPE	Low density polyethylene
LOAEL	Lowest observed adverse effect level
LLPDE	Linear low density polyethylene
MP	Microplastic
MADEP	Massachusetts Department of Environmental Protection
MADPH	Massachusetts Department of Public Health
MWRA	Massachusetts Water Resources Authority
NPDES	National Pollutant Discharge Elimination System
OMSAP	Outfall Monitoring Science Advisory Panel
PA	Polyamide
PCA	Polycarbonate
PE	Polyethylene
PET/PETE	Polyethylene terephthalate
PFAS	Per- and polyfluoroalkyl substances
PLA	Polylactic acid
PP	Polypropylene
PPCP	Pharmaceuticals and other personal care product
PS	Polystyrene
PUR	Polyurethane
pyro-GC/MS	Pyrolysis-gas chromatography with mass spectrometry
PVC	Polyvinyl chloride
QA/QC	Quality assessment/quality control
TDS-GC/MS	Thermodesorption gas chromatography with mass spectrometric detection
TGA-GC	Thermogravimetry gas chromatograph
WHOI	Woods Hole Oceanographic Institute
WWTP	Wastewater treatment plant

Appendix A. Members of Panel and Committee

Outfall Monitoring Science Advisory Panel (OMSAP)

Judith Pederson, Massachusetts Institute of Technology Sea Grant
Bob Beardsley, Woods Hole Oceanographic Institution
Peter Burn, Suffolk University
Ginny Edgcomb, WHOI
Loretta Fernandez, Northeastern University
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Jeff Rosen, Corona Environmental Consulting
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Public Interest Advisory Committee

Bruce Berman, Save the Harbor/Save the Bay
Priscilla Brooks, Conservation Law Foundation
Robert Buchsbaum, Mass Audubon (retired)
Rich Delaney, Provincetown Center for Coastal Studies (retired)
Pam DiBona, Massachusetts Bays National Estuary Partnership
Andreae Downs, MWRA Wastewater Advisory Committee
Joe Favaloro, MWRA Advisory Board
Heather McElroy, Cape Cod Commission
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Interagency Advisory Committee

Todd Callaghan, Massachusetts Coastal Zone Management
Ben Haskell, Stellwagen Bank National Marine Sanctuary
Matthew Liebman, United States Environmental Protection Agency (retired)
Jeff Kennedy, Massachusetts Division of Marine Fisheries
Pam DiBona, Massachusetts Bays National Estuary Partnership
Cathy Vakalopoulos, Massachusetts Department of Environmental Protection
Steve Wolf, U. S. Army Corps of Engineers, currently at U.S. Environmental Protection Agency

Presentation at the Ad Hoc Microplastic Meetings

James Churchill, Woods Hole Oceanographic Institution (Emeritus)
Scott Gallagher, Woods Hole Oceanographic Institution (Visiting Investigator)