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Oceans in Peril: Grand Challenges in Applied Water Quality Research for the 21st Century

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Abstract

Oceans cover most of the planet and 60% of the world's population lives near the coast. Anthropogenic activities along coastlines and in the open ocean have placed the oceans in peril. According to a Pew Oceans Commission Report, among the greatest threats to the ocean are land-based runoff from coastal development, nutrient pollution, overfishing, and invasive species. Here, we describe threats due to microbial, nutrient, chemical, and plastic pollution in addition to declining biodiversity and describe fundamental and applied research needed to mitigate the threats. While the research needs are diverse, we identify several research foci that transcend individual threats: monitoring, fate and transport studies, modeling, innovative natural and engineered treatment systems, and toxicity and health studies. Research within the environmental engineering and science community that addresses these needs will contribute to improving ocean health.

Key words: environmental monitoring; coastal pollution; declining biodiversity; nutrients; chemicals; fecal indication bacteria

Introduction

Oceans cover over two-thirds of the planet and 60% percent of Earth's population lives within 100 km of the coasts (Vitousek *et al.*, 1997). They provide immense benefits to society including ecosystem services, fisheries, and recreation (Table 1). The oceans, like much of the world's natural resources, are in peril from a variety of anthropogenic stressors. The Pew Oceans Commission report on the state of the world's oceans proclaims that the oceans are in crisis (Pew Oceans Commission, 2003). According to the report, the most serious threats to the ocean are pollutants derived from land-based runoff from coastal development, nutrient pollution, overfishing, and invasive species (Pew Oceans Commission, 2003). Yet, a recent effort to quantify human impacts on the marine environment found significant uncertainty around the effects from land-based pollution due to lack of quantitative data globally (Halpern *et al.*, 2008). Limited spatial and temporal data have hindered our understanding of both the causes of and potential resolutions to the threats facing the world's vast oceans. In this article, we discuss threats outlined in the Pew Oceans Commission's report and grand challenges to understanding and addressing the threats. With regard to pollutants, we give particular attention to microbial, chemical, and nutrient pollution, in addition to ocean acidification (OA) and marine debris (e.g., plastics). We also describe applied, interdisciplinary environmental research that can inform the problems of declining biodiversity and invasive species.

Pollution

Microbial pollution

Microbial pollution of coastal waters occurs when enteric microbes enter waters used for recreation or aquaculture. Enteric microbes include pathogenic viruses, bacteria, and protozoa that are transmitted via the fecal-oral route, and fecal indicator organisms like *Escherichia coli* and enterococci typically used to assess microbial water quality. Sources of these organisms to coastal waters include land-based runoff, spilled sewage, animal (including human) feces, and treated wastewater. Microbial pollutants are routinely monitored in coastal waters of developed countries, but are not monitored in most developing countries. Shuval (2003) estimated that globally there are 120 million cases of gastrointestinal illness and 50 million cases of severe respiratory illness per year caused by swimming in microbe-polluted coastal waters. In Southern California alone it is estimated that 1.5 million cases of excess gastrointestinal illness at a cost of

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Table 1. Examples of Benefits Provided by Oceans

Benefit	*Value (Costanza et al., 1999)*	*Notes*
Fisheries and shellfisheries	\$902 billion per year	Globally, 16% of population rely of fish for protein (Tidwell and Allan, 2001)
Recreation	\$3077 billion per year	Nearly 4 in 10 U.S. households visit the beach each year (NOAA, 2006); tourism and recreation industry the largest sector of the ocean economy (Kildow *et al.*, 2014)
Ecosystem services	\$1272 billion per year for nutrient cycling/ waste treatment; \$16432 billion per year for climate regulation	

\$50 million occur each year (Given *et al.*, 2006). Illnesses caused by consuming filter-feeding shellfish that can accumulate pathogens are not included in the estimates. Microbial pollution in the marine environment has been detected in areas as remote as Antarctica (Delille and Delille, 2000).

In the United States and other developed regions, national regulations aim to reduce incidence of thalassogenic disease by dictating allowable levels of microbial pollution at recreational beaches (Bartram and Rees, 2000). The BEACH Act (2000) mandates that U.S. beaches be monitored for microbial pollution to protect swimmers from unacceptable levels of gastroenteritis risk. Routine monitoring resulted in 20120 beach advisories and closures in 2012 as a result of elevated levels of microbial pollutants. This number is up from 6200 in 1999 (Dorfman and Haren, 2013). Of the advisories and closures in 2012, 63% were due to unknown sources of contamination (Dorfman and Haren, 2013). At the same time, nearly one-third of the shellfish harvesting waters in the United States are classified as being ''fecal impaired'' by the National Shellfish Registry (NOAA, 1998). There is a clear need to identify the sources of contamination and remediate microbial pollution in coastal waters.

The USEPA recently refined its beach water quality criteria (USEPA, 2012), allowing beach managers to develop their own ''site-specific'' water quality criteria. Beach managers can develop site-specific criteria by showing that their beaches would be better managed using different fecal indicator organisms (USEPA, 2014) from those recommended by USEPA (*E. coli* and enterococci) or showing that the source of microbial pollution at the beach is different from the source assumed by USEPA (disinfected wastewater treatment plant discharge mixed with some raw sewage) in developing their water quality criteria (Soller *et al.*, 2014). At the same time, USEPA will allow managers to use models to predict when a beach should be under a microbial pollution advisory (USEPA, 2012). There are a number of applied research needs related to microbial source tracking (MST) and modeling that can inform the implementation of these new provisions allowed by USEPA.

MST is the tracking of microbial pollution in the environment to its sources (Santo Domingo *et al.*, 2007). Fecal indicator organisms can come from a variety of fecal (Layton *et al.*, 2010) and nonfecal sources (Yamahara *et al.*, 2007; Russell *et al.*, 2013). Understanding the source of contamination can allow remedial actions to be taken, total maximum daily loads (TMDLs) to be established, health risk to be inferred, and site-specific water quality criteria to be developed (USEPA, 2012). A number of diverse MST targets have been developed. Most of these are genetic markers from bacteria that are unique to the intestinal tract of specific animals. For example, there are MST markers for humans (Shanks *et al.*, 2009, 2010; Layton *et al.*, 2013), dogs (Schriewer *et al.*, 2013), birds (Lu *et al.*, 2008; Lee *et al.*, 2013; Sinigalliano *et al.*, 2013), and ruminants (Shanks *et al.*, 2008). The specificity and sensitivity of these markers appear to vary by geographic region in some cases, but they can be very high (Boehm *et al.*, 2013).

The challenge is interpreting the concentrations of MST markers in the environment for microbial source allocation and health risk assessment. The number of MST markers relative to fecal indicator organisms varies by fecal source (Ervin *et al.*, 2013), so the relative concentration of, for example, human and gull-associated markers cannot be used to infer which source contributes more fecal indicator organisms to a waterbody. Additionally, the decay of the MST markers relative to each other and fecal indicator organisms varies, adding additional complexity to interpreting their concentrations in water samples (Wang *et al.*, 2013). Although microbial pollution from human feces is likely to present the greatest health risk to swimmers (Soller *et al.*, 2014), there has been limited research to relate MST marker concentration to health risk (Harwood *et al.*, 2014; Boehm *et al.*, 2015). Levels of human-associated markers close to assay detection limits have been observed at urban beaches or beaches with known sewage inputs (Santoro and Boehm, 2007; Boehm *et al.*, 2009b; Russell *et al.*, 2013). The presence of low levels of markers has been useful for source attribution, but it is unclear whether the low level of markers might indicate a significant health risk. Research is needed to understand how concentrations of the MST targets relate to a health risk. This could be achieved with quantitative microbial risk assessments (Boehm *et al.*, 2009a, 2015; Viau *et al.*, 2011; Soller *et al.*, 2014) or epidemiology studies (Colford *et al.*, 2007, 2012; Boehm and Soller, 2011).

Research on fate and transport of microbial pollutants including pathogens, MST markers, and indicator organisms is needed. Understanding various fate and transport processes can inform the creation of models both for beach management (these tend to be statistical models (Francy, 2009; Thoe *et al.*, 2015)) and for source allocation and TMDL development (these tend to be deterministic models) (Liu *et al.*, 2006; Boehm *et al.*, 2009b; Nevers and Boehm, 2010). Sunlight appears to be one of the most important factors affecting microbial pollutant concentrations in clear water (Boehm *et al.*, 2009b), but most research has been done with indicator organisms, and very little on actual pathogens and MST markers. The roles of grazing (Boehm *et al.*, 2005) and particle-microbe interactions in attenuating concentrations in the environment are not particularly well understood (Nevers and Boehm, 2010). A major challenge in modeling microbial pollutants in environmental waters is dealing with the inherent uncertainty (Gronewold and Wolpert, 2008), and short-period (Boehm, 2007) and small-spatial variability (Boehm *et al.*, 2002) that has been documented in their concentrations. An open question: how precise can models really be given these measurement uncertainties?

Finally, low impact development (LID) is gaining popularity as a means for reducing the impact of microbial pollution from stormwater and urban runoff discharges on coastal waters. According to the National Resources Defense Council (Dorfman and Haren, 2013), untreated stormwater is the most frequently cited cause of beach advisories and closures in the United States. LID for pollutant reduction typically consists of passive structures, as recommended through best management practices (BMPs), such as wetlands or biofilters that treat runoff via natural processes (sunlight or passage through soil or other permeable media). Leisenring *et al.* (2012) reviewed the performance of BMPs around the world and found that most of them were not capable of removing fecal indicator bacteria efficiently. However, there has been very limited or no work to examine removal of indicator organisms, pathogens, or MST markers from runoff (Li *et al.*, 2012; Mohanty *et al.*, 2014) using BMPs. Innovations in natural and engineered treatment systems for treating stormwater or urban runoff before it discharges to the coast are needed to control inputs of microbial pollutants (Fletcher *et al.*, 2008; Jiang *et al.*, 2015).

Nutrient pollution

Excess nutrient inputs to coastal waters can lead to eutrophication that can dramatically affect marine food webs and ecosystem health. Sources of nutrients to coastal waters include wastewater discharges, agricultural, urban and stormwater runoff, atmospheric deposition, and groundwater. Primary and secondary changes in coastal waters characteristic of eutrophication include the following: increases in algal blooms, shifts in the dominant phytoplankton including the emergence of harmful algae, reduction in the abundance of vascular plants, benthic organisms, and pelagic fish, reduction in dissolved oxygen concentrations, and decreases in pH (Cloern, 2001; Sunda and Cai, 2012). The effects of excess nutrient inputs can be observed throughout the world, on all continents except Antarctica (Cloern, 2001; Sunda and Cai, 2012). A national assessment of estuarine waters in the United States indicates 65% of U.S. estuaries are moderately to severely eutrophic (Bricker *et al.*, 1999). The hypoxic ‘‘dead zone’’ in the Gulf of Mexico is one of the most striking examples of the adverse effects of eutrophication in marine waters (Rabalais *et al.*, 2002).

Primary productivity in marine waters is typically nitrogen limited (Howarth, 1988; Cloern, 2001). The marine nitrogen cycle is complex and involves numerous microorganisms with diverse metabolisms (Gruber, 2008). Denitrification and anaerobic ammonium oxidation (anammox) are two microbial mediated processes capable of removing dissolved nitrogen from the water column (Devol, 2008) so these processes are key in controlling total nitrogen concentrations. Recent work has identified that phosphorous limitation can also occur in marine waters (Krom *et al.*, 1991; Rabalais *et al.*, 2002), and in some systems nutrient co-limitation occurs (Arrigo, 2005; Saito *et al.*, 2008). New insights regarding the marine nitrogen cycle are occurring all the time (Santoro *et al.*, 2011). Continued fundamental research to understand the organisms active in the nitrogen cycle, the conditions under which they are active, and how to accelerate nitrogen removal in systems with excess nitrogen is needed.

Unlike microbial pollutants, there are no nationwide criteria for nutrients in marine waters; however, there exists guidance on how site-specific nutrient criteria should be created (USEPA, 2001). National criteria for nutrients are inappropriate as marine waters have nonlinear responses to nutrient inputs and concentrations (Cloern, 2001). For example, Chesapeake Bay and San Francisco Bay have historically had the same mean annual nitrogen and phosphorous concentrations, yet Chesapeake Bay is eutrophic and San Francisco Bay is not (Cloern, 2001). This is attributed to the abundance of benthic filter feeders in San Francisco Bay that are able to clear the water column of phytoplankton (Cloern, 1996). In general, the response of marine waters to nutrient addition can be modulated by tide range, stratification, residence time, density of shellfish, and riverflow (Gilbert *et al.*, 2010). Efforts are underway in many states to develop numeric nutrient criteria for their marine waters that take into account these modulators (USEPA, 2015). Both fundamental and applied research is needed to inform the setting of numerical nutrient limits including a better understanding of how coastal waters respond to nutrient inputs. The current understanding is very site specific and the unique attributes of each estuary or coastal water appear to control its response to nutrient inputs. Widely applicable models for understanding nutrient effects in marine waters would be extremely useful.

It has been argued that eutrophic marine systems are more likely to experience blooms of harmful algae (Cloern, 2001). This is, in part, because a higher N:P or N:Si ratio in marine waters can favor dinoflagellates (Heisler *et al.*, 2008), and dinoflagellates represent a large majority of harmful algae. Harmful algae include dinoflagellates, diatoms, and cyanobacteria that produce toxins including saxitoxins, okadaic acid, venerupin, brevetoxin, domoic acid, ciguatoxin, pfisteria toxin, and β-N-methylamino-L-alanine (BMAA) (Boehm and Bischel, 2011). Some coastal waters and/or fish and shellfish growing in the waters are routinely monitored for the presence of these toxins (i.e., Puget Sound, WA) and safety thresholds are enforced in some states (i.e., Washington). However, there are no nationwide water quality criteria for harmful algae or their toxins at the present time. Monitoring for harmful algae and their toxins is not routine in U.S. coastal waters. Research efforts to simplify or automate these measurements could increase monitoring efforts. For example, Monterey Bay Aquarium Research Institute (MBARI) has developed an environmental sample processor (ESP) that can be deployed in the ocean and monitors water for harmful algae *in situ* (Scholin *et al.*, 2009; Yamahara *et al.*, 2015).

Eutrophication and resulting hypoxia, particularly in a stratified water column, can lead to a decrease in pH due to proton production during respiration and reduced buffering capacity (Sunda and Cai, 2012). There are concerns that the decrease in pH can locally exacerbate the effect of OA caused by rising global atmospheric CO_2 concentrations (Doney *et al.*, 2009). Coastal resource managers are increasingly interested in understanding whether reductions in nutrient discharges, from wastewater, for example, to coastal waters can alleviate problems of decreasing pH (Washington State Blue Ribbon Panel, 2012; Boehm *et al.*, 2015). Sunda and Cai (2012) showed that in the Gulf of Mexico and the South China Sea, discharge of nutrient-laden runoff from the Mississippi and Yellow rivers, respectively, contributes to local acidification by enhancing primary productivity in stratified waters. The importance of this process in other coastal regions needs to be evaluated to determine whether local management actions by water quality managers at the scale of counties and cities can reduce the potential for OA in local waters (Boehm *et al.*, 2015). Both monitoring and modeling efforts to assess the effects of nutrient and organic discharges, from anthropogenic waste streams and natural discharges like rivers and creeks, on local marine carbonate chemistry is needed. Advances in monitoring approaches are particularly important as glass electrodes typically used to measure pH in coastal seawater by dischargers for their monitoring programs are not precise enough to discern small changes in coastal pH (Boehm *et al.*, 2015). Newer sensors are becoming available to measure other relevant carbonate system parameters like pCO_2 and alkalinity (Byrne, 2014) and additional efforts to develop such sensors are needed.

Engineered and natural systems can be designed to remove nutrients from waste flows. Biological denitrification, anammox, and chemical or biological phosphorous unit processes can remove nutrients from wastewater flows (Tchobanoglous *et al.*, 2003). Upgrading wastewater treatment facilities to remove nutrients using these or other advanced treatments may be necessary to reduce nutrient fluxes to sensitive habitats, particularly once nutrient criteria are developed. Natural treatment systems such as biofilters (Bratieres *et al.*, 2008), wetlands (Jasper *et al.*, 2014), and grass swales can remove nutrients from urban and stormwater runoff, although their performance can be unreliable (Fletcher *et al.*, 2008; Leisenring *et al.*, 2012; Li and Davis, 2014). Work that informs the design of engineered and natural treatment systems that effectively and predictably remove nutrients from runoff in particular is needed to reduce nutrient inputs to coastal waters. For example, recent studies illustrated that addition of newspapers or woodchips to biofilters can enhance denitrification (Goh *et al.*, 2015; Peterson *et al.*, 2015).

Chemical contaminants

A variety of chemical contaminants have been extensively studied in the marine environment, including organochlorine compounds (i.e., polychlorinated biphyenls [PCBs] and pesticides), polyaromatic hydrocarbons (PAHs), heavy metals, and radionuclides. These contaminants are usually strongly associated with particulate matter and bioaccumulate in organisms, biomagnify in the foodweb, and negatively affect ecosystem health. Adverse health effects from exposure to these contaminants range from disruption of the endocrine system to cancer in a variety of organisms, including humans (Addison, 1996; Longnecker *et al.*, 1997; Gilbert *et al.*, 2002; Hoeve and Jacobson, 2012). While some of these chemicals can naturally occur in the environment, elevated concentrations are typically found in coastal areas due to anthropogenic inputs from agricultural, urban, and industrial activities. The contaminants enter the environment from both terrestrial runoff and atmospheric deposition and undergo environmental cycling (between sediment, air, and land), with concentrations found even in remote regions of the world such as the Arctic (Muir *et al.*, 1992; Ferm, 1996).

Regulation of the production, use, and discharge of organochlorine compounds, polyaromatic hydrocarbons, heavy metals, and radionuclides has reduced their input into the environment, but their persistence has continued to make it challenging to effectively remediate them. For example, approximately 6.1 million metric tons of petroleum products containing PAHs are annually released into the ocean primarily due to anthropogenic sources, and this number excludes single catastrophic events (Haynes and Johnson, 2000). While dispersants are used to cleanup petroleum products in marine systems to reduce immediate impacts to wildlife, the dispersants themselves alter the behavior of the hydrocarbons, resulting in increased water solubility and bioavailability, which can cause long-term delayed toxicological impacts to marine organisms from exposure (Wolfe *et al.*, 1998). Similar to PAHs, organochlorine, heavy metal, and radionuclide sorption and solubility behavior can change in different environmental conditions altering environmental fate and bioavailability over time (Waldichuk, 1985; Rainbow, 1995; Haynes and Johnson, 2000; Buesseler *et al.*, 2011; Yoshida and Kanda, 2012). Due to the behavior and persistence of these compounds, solutions to reduce their inputs into the environment are needed, as are techniques for cost-effective large-scale remediation after inadvertent inputs. Conventional engineering approaches that employ a single technology may be cost-intensive and less effective than combining multiple remediation strategies. For example, using electrobioremediaton, which combines electrokinetic remediation and bioremediation, accelerates degradation and improves removal efficiency of hydrophobic organic contaminants in comparison to using a single technology (Li *et al.*, 2010; Megharaj *et al.*, 2011). Further work to combine physical, chemical, and biological remediation strategies has significant potential to result in novel treatment approaches.

While the sources, fate, and health effects of the above compounds are relatively well known, a class of contaminants requiring further characterization is contaminants of emerging concern (CECs). CECs include a large number of compounds with a variety of uses and physicochemical properties. Common classes of CECs are pharmaceuticals, personal care products, pesticides, herbicides, perfluorinated compounds (PFCs), and flame-retardants. CECs found in coastal waters are from both point and nonpoint sources including wastewater effluent, industrial waste, stormwater, and runoff. Due to the large number of chemicals classified as CECs with different properties and the lack of established measurement methods for many of these compounds, the source, fate, transport, and effects of CECs in the marine environment are not well understood. Preliminary studies show that many CECs can be detected in coastal marine waters that are impacted by wastewater discharge, in sediment, and in fish (Maruya *et al.*, 2012; Vidal-Dorsch *et al.*, 2012). Toxicity studies have also shown that certain pharmaceuticals can lead to endocrine and physiological disruption in marine organisms, but the toxicities at environmentally relevant concentrations of many individual CECs, or mixtures of them that can have synergistic effects, have not been measured (Bay and Vidal-Dorsch, 2012; Scott *et al.*, 2012). A 2-year pilot study, focused on quantifying CECs in mussel tissue in coastal regions in California, prioritized further monitoring of four types of CECs due to the high frequency of detection and concentration of these contaminants (Maruya *et al.*, 2014). The CECs recommended for future monitoring efforts are PFCs, flame retardants, the additive 4-nonylphenol and its derivatives, and the pharmaceutical lomefloxacin (Maruya *et al.*, 2014). While the California-based CEC study provides initial guidance on monitoring priorities, additional studies are needed on a larger spatial and temporal scale to confirm its findings and determine priority CECs based on location and associated land use. With the exception of polybrominated flame retardants and PFCs, very limited information exists on CECs in the marine environment beyond the California coast. Table 2 summarizes findings from relevant studies on personal care products and pharmaceuticals (PPCPs) in the marine environment. Based on current review of available published literature, analysis of PPCPs in the marine environment is limited to coastal environments and does not include samples from remote regions.

For CECs, an integrated approach of preventing and characterizing chemical inputs into the environment is necessary. Studies have shown that marine sampling locations impacted by stormwater discharge had higher detection frequency and concentrations of target CECs than those impacted primarily by wastewater discharge from publicly owned treatment works (POTWs) (Maruya *et al.*, 2012, 2014; Alvarez *et al.*, 2014). Thus, managing stormwater and urban runoff using LID, such as bioretention ponds (Hsieh and Davis, 2005) as well as improving conventional wastewater treatment through advanced treatment, such as ozonation and wetlands (Oulton *et al.*, 2010), can reduce the inputs of CECs to coastal waters. The types of CECs discharged from POTW effluent and runoff can vary based on regional and industrial activities, which will impact the effectiveness of advanced treatment or LID. Monitoring of CECs is needed to develop a better understanding of the sources and behavior of these contaminants undergoing treatment.

Developing cost-effective analytical tools and methods to measure mixtures of CECs in different matrices is needed to better characterize environmental concentrations. Better detection methods to measure trace levels of these contaminants will allow study of fate and transport and of ecotoxicological and human health effects at environmentally relevant concentrations. Analytical tools that expedite detection of these contaminants in a variety of organisms at environmentally relevant concentrations can facilitate toxicity studies to increase understanding of the synergistic and chronic health effects of these contaminants and develop appropriate sublethal toxicological parameters (Fent *et al.*, 2006). Advances in analytical equipment such as ultra-high-performance liquid chromatography has resulted in significant progress in detecting CECs, but shortcomings include high cost and lack of validation procedures for different analytical methods and environmental samples (Wille *et al.*, 2012). Biosensors, which can provide real-time data on the concentrations and biological effects of CECs, are a potential alternative to conventional techniques of liquid chromatography and bioassays, but most CEC biosensors are still in developmental stages in the laboratory and have not been deployed in the field and are not commercially available (Rodriguez-Mozaz *et al.*, 2005). Sampling studies have excluded certain CECs, such as phalates and alkylphenols, due to lack of confidence in performance and reliability of current analytical methods (Bay and Vidal-Dorsch, 2012; Maruya *et al.*, 2012; Scott *et al.*, 2012). Due to the lack of studies quantifying CECs in the marine environment it is not yet possible to determine the environmental risk associated with most of these contaminants (Scott *et al.*, 2012). Combining advanced analytical tools with improved biomarker monitoring can result in cost- and time-effective characterization of these CECs in water, sediment, and biota, which in turn can lead to risk assessments that better inform policy.

Marine debris (plastics)

Marine debris, defined as anthropogenic material such as plastic that enters and persists in the marine environment, represents a growing problem (Cole *et al.*, 2011; Engler,

Table 2. Summary of Environmental Analysis of Pharmaceuticals and Personal Care Products (PPCPs), a Class of CECs, in the Marine Environment

Study location	*Environmental sample type*	*Number of PPCPs analyzed*	*Most detected compounds*	*Detection frequency*	*Reference*
Southern California USA	Seawater	56	Gemifibrizol	90%	Vidal-Dorsch *et al.* (2012)
			Atenolol	90%	
California Coast USA	Tissue	88	Lomefloxacin	62%	Dodder *et al.* (2014)
			Sulfamethazine	36%	
Victoria Harbor Hong Kong, China	Seawater	10	Oxfloxacin	~35%	Xu *et al.* (2007)
Todos Os Santos Bay Brazil	Sediment	9	Caffeine, Ibuprofen, Galaxoline, Tonaline, Atenolol	100%	Beretta *et al.* (2014)
Puget Sound and Bellingham Bay, Washington, USA	Sediment	119	Diphenhydramine	87.5%	Long *et al.* (2013)
			Triclocarban	35%	

CEC, contaminants of emerging concern.

2012; Wright *et al.*, 2013). Marine plastics are just one type of internationally recognized highly persistent pollutant that may have a significant effect on the ecological integrity of the ocean and ultimately affect human health (Gregory, 2009; Lozano and Mouat, 2009). Marine plastics of varying sizes are globally yet heterogeneously distributed, and it is estimated that up to 10% of the 265 million tons of plastics produced annually eventually enter the marine environment (Cole *et al.*, 2011; Gouin *et al.*, 2011; Bakir *et al.*, 2014). Plastics enter oceans via a variety of sources, with 80% of marine plastics generated from land-based sources, such as beach litter and surface runoff (Andrady, 2011; Cole *et al.*, 2011). Plastic debris ranges in size from discarded fishing nets to tiny pieces of plastics from air-blasting or scrubbing soaps. While plastics are persistent in the environment, they can break down over time into smaller fragments due to chemical, physical, and biological weathering (Cole *et al.*, 2011; Koelmans *et al.*, 2013). Once in the ocean, plastic debris can be detrimental to marine life in various ways. Large plastic debris such as fishing lines and nets pose a threat to marine life entanglement, while smaller plastic debris often referred to as microplastics, can be ingested by marine organisms.

Microplastics, defined as plastics having a particle size less than 5 mm, have recently been identified as CECs, and are considered a leading global environmental issue (Browne *et al.*, 2007; Sutherland *et al.*, 2010; Andrady, 2011; Cole *et al.*, 2011; Wagner *et al.*, 2014). Microplastic abundance has increased by two orders of magnitude over the past 40 years in the North Pacific, and the abundance of microplastics in all marine environments is projected to continue to increase (Wright *et al.*, 2013). Microplastics can cycle through the food web and enter the human food chain (Wright *et al.*, 2013). They are transported long distances, reaching remote regions of the globe, are ingested by aquatic organisms, and then transferred between trophic levels (Andrady, 2011; Cole *et al.*, 2011; Wright *et al.*, 2013). Microplastic ingestion and retention occurs in a wide range of marine aquatic organisms at varying trophic levels from zooplankton to fish, and trophic transfer has also been shown to occur among different organisms (Browne *et al.*, 2007; Graham and Thompson, 2009; Murray and Cowie, 2011; Cole *et al.*, 2013; Farrell and Nelson, 2013; Chua *et al.*, 2014; Setälä *et al.*, 2014; Van Cauwenberghe and Janssen, 2014). Accumulated microplastics in bivalves (Van Cauwenberghe and Janssen, 2014) and decapod crustaceans (Murray and Cowie, 2011) used for human consumption have been documented, indicating the potential for human intake of microplastics through dietary exposure.

In addition to the microplastic itself acting as a potentially harmful contaminant, microplastics act as a source and sink of both organic chemicals and trace metal contaminants (Andrady, 2011; Engler, 2012). Hydrophobic organic contaminants and trace metals sorb onto microplastics in the environment and concentrate to higher levels than the ambient seawater. Sorption of these contaminants can increase over time as the plastic ages. Marine plastics that undergo aging exhibit changes in porosity, which facilitates subsequent organic matter fouling, thereby altering the pellets' surface area and polarity, potentially leading to increased sorption (Rios *et al.*, 2007; Ashton *et al.*, 2010; Mato *et al.*, 2014; Rochman *et al.*, 2014). Studies have also shown these contaminants can then be transferred to marine species once ingested, but the extent to which the contaminants affect the ecosystem has yet to be fully understood, with conflicting assessments of environmental exposure (Teuten *et al.*, 2007; Bakir *et al.*, 2014).

A better understanding of the fate, transport, and impacts of marine plastics, and specifically microplastics, is necessary when considering the most effective approaches to take to remediate and prevent these pollutants. Although reported values from decades of sea surface samples provide an initial estimate of the abundance and distribution trends of microplastics in the open ocean and gyres, more extensive research on microplastic abundance and distribution in coastal systems is needed because initial studies indicate that coastal areas near industrial and urban centers can be hotspots (Browne *et al.*, 2011; Norén and Naustvoll, 2011; Wright *et al.*, 2013). Unfortunately, given the current available technologies, global removal of plastics currently in the environment is an insurmountable undertaking. Various ocean ''garbage patches'' in the subtropical gyres, such as the Great Pacific Garbage patch, have concentrations of marine plastics orders of magnitude higher than the rest of the open ocean (Law *et al.*, 2010). Attempting to clean up only plastic in the Great Pacific Garbage Patch would not only require use of numerous ships and large amounts of fuel, but also would need to account for spatial variability and heterogeneity of the Garbage Patch, and minimize inadvertent disturbance to marine life and removal of pelagic organisms (Moore *et al.*, 2001; Goldstein *et al.*, 2013). While new techniques to sample, detect, and analyze microplastics in the marine environment have been developed (Hidalgo-Ruz *et al.*, 2012; Nuelle *et al.*, 2014), published research on remediation techniques for plastics is lacking. To combat the projected increase in marine plastic pollution, innovative technologies to prevent plastics from entering the marine environment and to degrade plastics already in the environment need to be developed. Calculations completed by Jambeck *et al.* (2015) show that mismanaged waste is a major source of land-based input of microplastics in the marine environment and that top contributors are countries with fast economic growth with lagging waste management infrastructure. Potential approaches include development of technologies that implement BMPs that employ physical barriers to prevent inputs into the marine environment and the use of microbial populations capable of degrading microplastics (Shah *et al.*, 2008). In addition, implementation of biodegradable plastics on a large scale to replace current plastics used in industry is needed. The use of biodegradable plastics such as polyhydroxyalkanoates (PHA) is currently limited by high production cost using the traditional processing of PHA from cultivated feedstocks from corn and sugar cane (Rostkowski *et al.*, 2012). Research examining the production of PHAs using the waste biogas methane and methanotrophic bacteria as an alternative to the traditional approach of PHA production, shows promise of reduced economic and environmental costs (Pieja *et al.*, 2011; Rostkowski *et al.*, 2012). Continuation of research in innovative production and application of biodegradable plastic can lead to cost-effective replacement of traditional plastics.

Declining Biodiversity

Declining biodiversity is one of the major environmental challenges of the 21st century (Pew Oceans Commission, 2003; Bollman *et al.*, 2010; Butchart *et al.*, 2010). Despite a commitment from global leaders at the Convention on Biological Diversity in 2002 and a few local successes, biodiversity continues to decline due to overfishing, invasive species, climate change, habitat loss or fragmentation, human population growth, and nitrogen pollution (Butchart *et al.*, 2010). There is also ample evidence of the demise of individual species. The National Oceanic and Atmospheric Administration (NOAA) currently lists 2215 marine species as endangered or threatened under the Endangered Species Act (NOAA, 2015b), with 14 candidate species under review and 30 proposed for listing. (NOAA, 2015a). Simultaneously, the spread of invasive species in estuaries and coastal habitats is a major concern for both native and economically relevant species. NOAA estimates costs to control and eradicate invasive species in the United States at $137 billion annually, in addition to severe and often permanent species and habitat loss (NOAA, 2015c).

Declining biodiversity is best addressed proactively. Changes in biodiversity must be anticipated through knowledge of food webs, species habitats, fishing pressures, fecundity, and responses to environmental stressors. There is a lack of data on spatial and temporal distributions of marine organisms and furthermore a lack of coordinated monitoring of biodiversity along with environmental stressors. This is due to inherent challenges collecting data in the marine environment. Traditional methods for monitoring biodiversity rely on the physical identification of species that requires resources and time (e.g., taxonomic expertise, ship time, or diver time) and can be disruptive to marine ecosystems. New complementary and efficient methods are needed to anticipate and monitor biodiversity changes on large spatial and temporal scales (Thomsen and Willerslev, 2015).

Recent advances in molecular methods, particularly metagenomics, have facilitated biodiversity monitoring by enabling the identification of aquatic vertebrates and invertebrates by measuring the presence or concentration of their environmental DNA (eDNA) in water samples (Foote *et al.*, 2012; Taberlet *et al.*, 2012; Thomsen and Willerslev, 2015). eDNA is extraorganismal genetic material found in feces, mucus, sloughed cells, or other particles and can be either intracellular or extracellular (e.g., free DNA or particle bound DNA) (Thomsen *et al.*, 2011, 2012; Barnes and Turner, 2015). Species-specific primers are used to detect eDNA from a target species via QPCR. Primers targeting a group of organisms (e.g., vertebrates) are used to amplify eDNA for next generation sequencing (NGS) to identify all species present. eDNA techniques could potentially identify and quantify macroorganisms by analyzing a very small volume of water from the ocean (Thomsen *et al.*, 2012; Kelly *et al.*, 2014; Port *et al.*, 2015). Thus far, eDNA has primarily been used to investigate the presence and abundance of species in terrestrial (e.g., soil) and freshwater environments, but it has recently been applied to marine environments (Thomsen and Willerslev, 2015). Current research is exploring the validity of using QPCR and NGS to study invasive species, endangered species, and biodiversity of eukaryotic communities, respectively, in terrestrial sediments, aquatic sediments, ice, soil, freshwater, and seawater (see Thomsen and Willerslev (2015) for a review).

Preliminary research on the applicability of eDNA for biodiversity monitoring in the marine environment appears promising. In a comparison between traditional monitoring methods for marine fish and sequencing of eDNA from seawater samples, Thomsen *et al.* (2012) demonstrated that eDNA methods estimated fish diversity and, if not better than, traditional methods in a marine ecosystem. In a large seawater mesocosm, Kelly *et al.* (2014) showed that the relative abundance of eDNA correlated with biomass for the species present. In a study targeting harbor porpoises, Foote *et al.* (2012) showed that eDNA has the potential to detect marine mammals in controlled and natural marine waters.

Despite promising comparisons between eDNA molecular techniques and traditional monitoring, the evidence for the usefulness of eDNA for macroorganism monitoring is empirical and observational. Information on the fate and transport of eDNA in the marine environment is needed to fully grasp the power of this technology. It is necessary to understand how long eDNA persists in the environment to interpret how old a detected eDNA signal is, and thus, in combination with information on physical transport processes, the spatial domain in which it was shed from the macroorganism. Yet, there is limited work on eDNA persistence (Barnes *et al.*, 2014; Strickler *et al.*, 2015). There is a need to understand how environmental processes (sunlight, interaction with particles, salinity, and biological grazing) degrade eDNA from different macroorganisms. Additional work is needed to understand the shedding rates of eDNA from macroorganisms so that the concentration of eDNA can be related to the number of individuals or biomass of a particular species. A mass balance approach that considers sources (i.e., shedding) and sinks (i.e., decay) can contribute to an understanding of how to interpret and model concentrations of macroorganism eDNA in the environment.

Discussion

Fundamental and applied research are needed to mitigate the threats of pollution and declining biodiversity (Table 3) to the ocean. While the research needs are diverse, we identified several research foci that transcend the individual threats: monitoring, fate and transport studies, modeling, innovative natural and engineered treatment systems, and toxicity and health studies.

Efforts to monitor the marine environment at appropriate spatial and temporal scales are needed to inform coastal management and the development of scientific models. The oceans and coasts of the world are vast, and there are thousands of estuaries. Pollutant concentrations and biodiversity are monitored in only a small subset of the marine environment. Despite expert reports that cite the problem of marine pollution and declining biodiversity being the greatest threats to the oceans (Pew Oceans Commission, 2003; Center for Ocean Solutions, 2009; Bollman *et al.*, 2010), there is a dearth of quantitative information on the magnitude of the problem. A recent study by Halpern *et al.* (2008) quantified threats to the global ocean. The authors considered the threat of pollution, but had to rely on a number of weakly supported assumptions to obtain an impact estimate for each section of the global coast owing to a lack of quantitative information on concentrations and fluxes of pollutants.

Buoy networks along coastlines monitor physical variables using fixed sensors, both oceanic (e.g., temperature, salinity, density, and currents) and meteorological (e.g., wind speed

Table 3. Summary of Research Needs by Ocean Threat Category

Threat	*Research needs*
Microbial pollution	improved monitoring microbial source allocation fate and transport modeling - prediction for beach advisories BMPs for removal from land-based flow health risks associated with different microbial pollutant sources
Nutrient pollution	fundamental research on N cycle fundamental research on nutrient (co-)limitation models of coastal water ecosystem response to nutrient inputs monitoring of nutrients, toxins, and ocean acidification parameters modeling of nutrient impacts on ocean acidification parameters BMPs for removal from land-based flows
Chemical pollution	remediation technologies for legacy contaminants and CECs fate, transport, and measurement of CECs monitoring of CECs toxicity/risk assessments for CECs BMPs for removal from land-based flow
Marine debris	fate and transport studies of microplastics impacts of microplastics on ecosystem health biodegrabable plastics BMPs to remove from terrestrial and aquatic inputs to ocean
Declining biodiversity	shedding rates/sources of eDNA fate and transport of eDNA models of eDNA

BMP, best management practice; eDNA, environmental DNA.

and direction), but very few fixed buoys currently monitor chemical variables (Chapin *et al.*, 2004) and no fixed buoys measure biological variables. Chemical and biological variables have traditionally been measured ship-board or in the laboratory using grab samples. New, robust sensors and biosensors capable of measuring chemical parameters like alkalinity (Byrne, 2014) and nitrate (Chapin *et al.*, 2004) in seawater have been developed but are not widely deployed while sensors to measure other chemicals of interest in seawater have yet to be developed. The ESP (Scholin *et al.*, 2009; Yamahara *et al.*, 2015) is one of the few instruments currently capable of making remote, *in situ* biological measurements. Using microfluidics, it collects water samples, concentrates microorganisms and cells, and runs molecular probe-based and QPCR assays to detect organisms. Continued work is needed to develop (bio)sensors to effectively measure and determine effects of chemicals, nutrients, and microbial pollutants, and detect eDNA in the marine environment. Importantly, either through the use of sensors or grab samples, monitoring of pollutants and biodiversity together with physical variables at appropriate temporal and spatial scales is needed to gain insight into the occurrence and dynamics of these targets in the ocean. These data are also essential for putting pollution and loss of biodiversity in context of other problems facing the oceans, and defining the magnitude of the problems, especially in the face of climate change that is affecting the oceanic environment through, for example, temperature and pH changes.

An understanding of pollutant and eDNA fate and transport in the ocean in conjunction with process-based models is essential for interpreting their observed concentrations. Chemical and biological processes can influence the persistence and fate of pollutants and eDNA. For example, the persistence of microbial pollutants and macroorganism eDNA can be influenced by environmental variables such as pH, dissolved oxygen, biological activity, and sunlight (Barnes *et al.*, 2014). Physical processes control advection, dispersion, and interactions between water column and sediments. An understanding of the most important processes controlling pollutant and eDNA concentrations is needed to inform models that can aid in source identification and predictions under future scenarios. For example, in the case of nutrient pollution, a generalized model that allows prediction of when nutrient inputs to an embayment or estuary will result in increased primary productivity and eutrophication would simplify the development of numerical nutrient criteria. A process-based model of anchovy eDNA would allow managers to predict the area in which anchovies of different densities may be present and how recently the anchovies were present. These types of models would have great ecological and economic value.

Innovative treatment technologies are needed to control the input of pollutants from the land to the sea. POTW discharges to the ocean are well regulated for many legacy pollutants. However, treatment technologies may need to be altered or improved to remove unregulated contaminants such as CECs and human viruses, for example. Additionally, nutrient removal is typically not required for oceanic dischargers. This could change as the link between nutrient inputs and eutrophication and declining pH is further elucidated. Stormwater, urban, and agricultural runoff are important pollutant sources to the ocean. Most BMPs for removing runoff contaminants are unreliable and their performance unpredictable. Innovations to develop dependable natural (i.e., wetlands and biofilters) and engineered (i.e., ''pocket'' runoff treatment plants) treatment systems for reducing the contaminant loads in runoff are needed.

More studies to elucidate the relationship between the pollutant levels observed in the ocean and ecosystem and human health are needed. Understanding this relationship will ultimately allow researchers and managers to allocate resources to problems that are the most severe. Ecological risk assessment (ERA) can be used to predict the effects of stressors, including chemical pollutants, harmful algal blooms, and invasive species, on the marine ecosystem (USEPA, 2015). Biomarkers in sentinel species such as mussels and fish have been used to determine the health effects of exposure to persistent chemical pollutants and can be integrated into ERAs (van der Oost *et al.*, 2003; Galloway, 2006). Contaminant loads and effects of contaminants in marine mammals, while more difficult to assess than in mussels and fish, can provide insight to risk expected in high trophic level organisms and provide more robust ERAs (Ross, 2000). ERAs for emerging contaminants such as CECs and microplastics are needed and extending the use of biomarkers in various biota for these contaminants may be beneficial in developing ERAs. Integrated risk assessments, which include ecological and human risks, have been completed for legacy organic contaminants and show the importance of linking adverse effects between different trophic levels (Ross and Birnbaum, 2003). Human health effects from exposure to pollutants can be assessed through epidemiology studies and quantitative risk (microbial) assessment modeling. Human health effects are the main concern for microbial pollution. Work is needed to understand health effects from exposure to microbial pollutants from different fecal sources, and the health risks associated with exposure to newer indicators, like those used for MST.

The research activities identified here require an interdisciplinary approach. To conduct research that will have an impact, collaborative research between engineers and scientists with different expertise is needed. In addition, researchers must interact frequently with natural resource managers to ensure that the work is relevant to policy. Scientists should educate managers about their findings and managers should educate scientists about the management levers available and how science can better inform their use of the levers.

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