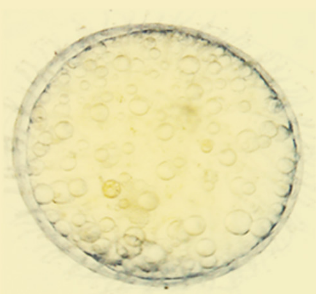
VOLUME 1

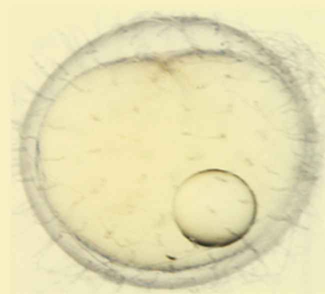
MARINE ECOLOGY:
CURRENT AND FUTURE DEVELOPMENTS

MARINE POLLUTION: CURRENT STATUS, IMPACTS, AND REMEDIES



Activated egg stage
3 min

Early morula stage
4 h



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6 somite stage
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34 somite stage
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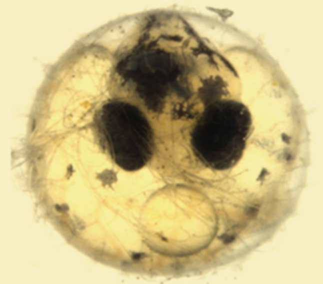

Heart development stage
145 h

Editors:
De-Sheng Pei
Muhammad Junaid

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Marine Ecology: Current and Future Developments

(*Volume 1*)

Marine Pollution: Current Status, Impacts, and Remedies

Edited by

De-Sheng Pei & Muhammad Junaid

Research Center for Environment and Health,
Chongqing Institute of Green and Intelligent Technology,
Chinese Academy of Sciences, Chongqing, China

Marine Ecology: Current and Future Developments

Volume # 1

Marine Pollution: Current Status, Impacts, and Remedies

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CONTENTS

FOREWORD

This book, edited by De-Sheng Pei and Muhammad Junaid, emphasizes that the oceans are a vast but fragile resource that must be protected if we want to protect our livelihoods and our planet. Although marine pollution is a topic of concern for a long period of time, it has recently attracted the significant attention of scientific and non-scientific debate circles, including environmentalists, economists, and politicians. The chapters on methods to assess pollution provide important information for identifying, measuring, and remediating various pollutants, while the chapters on known pollutants and their management point out how widespread the problems are and how intense international effort is required to resolve the problems.

Besides providing food, transportation and lifestyle resources, the oceans serve as a vast sink to absorb increases in global heat, mitigating at least temporarily more extreme changes in global climate. But in doing so, oceans also present a threat to coastal communities by altering local weather patterns and disrupting local livelihoods with changes in acidity and temperature.

This book will prove to be a useful resource for students, researchers, and policymakers, who are working on the management and protection of the world's valuable marine resources and environment.

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PREFACE

There are increasing environmental concerns about the current status of the world's oceans. The rapid development of industrial zones and growth of human population in coastal areas have led to exploitation of marine resources resulting in chemical pollution from industry, domestic wastewater intrusion, invasion of non-native species, toxic algal bloom, and microbial pathogens. On the other hand, earth's oceans offer abundant food resources, easy shipping, and coastal living. In this book, the experts from different countries in Asia, Europe, and America give their overviews and opinions about the current status of marine pollution, environmental impacts, and possible remedies.

Introductory Chapter 1 highlights the overall theme of this book: the importance of oceans in the 21st century. This chapter orderly presents an overview of pollution dynamics including inorganic pollutants (heavy metals, metalloids), organic pollutants (POPs-persistent organic pollutants, PAHs-polycyclic aromatic hydrocarbons, and PCBs-polychlorinated biphenyls), microplastics, and algal blooms in the marine environment. The second section specifically introduces the negative impacts of marine pollution and assessment methods to highlight the toxicity of marine pollutants. The last section of Chapter 1 is an overview of various remedial techniques, such as bioremediation, phytoremediation, and the challenges related to marine pollution. Chapter 2 describes common sampling procedures for the most diverse and abundant marine organisms that comprise ecosystem components under the Essential Ocean Variables (EOVs), such as phytoplankton, zooplankton, and fish. In this framework, biodiversity is assessed based on the status of ecosystem components, including phytoplankton biomass and diversity, zooplankton biomass and diversity, fish abundance and distribution, as well as marine turtle, bird and mammal abundance and distribution.

Chapters 3 & 4 highlight the important reactions of metals and non-metals with inorganic and organic constituents in marine water and sediments. In addition to these reactions, Chapter 3 also covers biokinetic aspects of two major marine environmental problems: eutrophication and the release of organotin compounds and copper from antifouling paints used on ships' hulls, as an example of the effects of uncontrolled introductions of metals and non-metals on marine ecosystems. Chapter 4 highlights natural and anthropogenic sources of metals and non-metals, as well as their toxicity and accumulation in different marine organisms. Chapter 5 discusses pollution dynamics of organic contaminants and associated impacts in marine ecosystems. These contaminants include persistent organic pollutants (POPs), such as pesticides, brominated flame retardants, perfluoroalkyl compounds, fluorotelomer alcohols, perfluoroalkyl sulfonic acids (PFSAs), perfluorocarboxylic acids (PFCAs), fluorotelomer carboxylic acids, fluorotelomer sulfonic acids, and fluorinated polymers. Apart from POPs, microplastics and accidental oil spills are also highlighted in terms of their growing concern in oceanic gyres. Chapter 6 explores monitoring of organic pollutants in the marine ecosystem, including fate, distribution, and behavior of PCBs, as well as uptake of organic contaminants/PCBs by marine organisms.

Chapter 7 describes pollution dynamics along the Pakistan coast with special reference of nutrient pollution. In this Chapter, the magnitude of pollution (organic and inorganic) in coastal environments of Pakistan is discussed including plastic pollution, and enrichment of macro-nutrients in coastal waters leading to the explosion in frequency of harmful algal blooms. Chapter 8 explores ecotoxicology of heavy metals in marine fish. The authors review the occurrence and chemistry of heavy metals in the marine environment, as well as the bioaccumulation and toxicity of heavy metals in marine fish. Chapter 8 also summarizes the public health risks due to the consumption of heavy metals' contaminated fish. Chapter 9 highlights the effects of microplastic on the marine ecosystem. Further, several aspects related to research gaps for the management of microplastic waste are proposed. Chapter 10 explores methods to measure toxicity in flora and fauna exposed to different categories of marine pollutants, their sources, various exposure routes, and associated toxicological impacts on marine organisms. Chapter 11 covers the topic of chemical toxicity screening by using marine medaka (*O. melastigma*) as a model system. This chapter provides the recent research progress in the toxicological impacts and responsive biomarker of *O. melastigma* caused by various marine pollutants, such as heavy metals, endocrine disruptors, and organic pollutants.

Chapter 12 reviews the problems of invasive species in Andaman and Nicobar Islands, Andaman Sea, India. Chapter 13 highlights the problems of dispersal of invasive species through marine ecosystems with a special focus on the case study of five invasive species and associated problems. Chapter 14 describes the effects of the disturbing unique island biodiversity of marine protected areas linked with the environmental changes influenced by anthropogenic activities, overexploitation of resources, and the habitat loss due to developmental activities and natural change in climate. Chapter 15 presents information on monitoring environmental indicators and bacterial pathogens in aquaculture practices impacted the Muthupettai Mangrove Ecosystem, Tamil Nadu, India. This chapter, a research article instead of a review, reports on the vulnerability of the mangrove ecosystems after continuous discharges of untreated aquaculture effluents have caused water quality to deteriorate so far that physiochemical parameters and bacterial pathogens highly exceed WHO, EU, and CPCB standard permissible limits.

Chapter 16 highlights the vast potential of marine microbes (bacteria and fungi) for their application in bioremediation of heavy metals. This chapter also discusses the specific factors influencing heavy metal bioremediation including biotic and abiotic factors. Chapter 17 focuses on bioremediation of low and high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) in the marine environment through bacterial and fungal strains (lignolytic fungi and non-lignolytic fungi). Further, recent advancements in applications of genomics, proteomics and metabolomics technologies for in-depth investigation of microbial communities involved in PAHs remediation are summarized. Chapter 18 provides final thoughts and concluding remarks.

This book contains the latest progress in the theoretical background of marine pollutants, occurrence, distribution, risk assessment, and the bioremediation in the marine environment, which will be of specific interests for academic scientists, students, and government officials to develop background knowledge of marine pollution based multidisciplinary research.

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DEDICATION

This book is in the memory of my mother, Ms. Jinhua Wang, who passed away on February 14, 2014. This book is dedicated to all the researchers around the globe, who are working effectively and finding novel ways to protect the environment.

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I would like to dedicate this book to my father, Mr. Muhammad Yahya (Late, January 30, 1992) and my beloved mother, Ms. Najma Jalil.

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CHAPTER 1

An Introduction to the Recent Perspectives of Marine Pollution

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Abstract: Marine ecosystem covers two-thirds of the earth's surface, and is characterized by its rich biodiversity and endemism of marine life. However, like many other ecosystems, it has been subject to diverse anthropogenic pressures, such as climate change, pollution, and biodiversity losses. In the first part of the book, we discussed the pollution dynamics of the inorganic pollutants (heavy metals, metalloids) and organic pollutants including persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), microplastics, nutrients, and algal blooms in the marine environment. Marine pollutants can have a wide range of pollution sources that are able to cause deleterious effects on marine flora and fauna. The second section of the book specifically elucidates the toxicity assessment by using marine model organisms. It provides extensive new insight into screening biomarker genes combined with advanced gene editing applications. In the last section of the book, various remedial techniques, such as bioremediation and phytoremediation, were discussed whether it could be beneficial to deal with the challenges of marine pollution.

Keywords: Marine Ecosystem, Pollution Dynamics, Remedial Measures, Toxicity Assessment.

According to the United Nations Convention on the Law of the Sea (UNCLOS), the marine pollution is defined as "the introduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, which results or is likely to result in such deleterious effects as harm to living resources and marine life, also hazardous to human health" (Williams, 1996). The driving factors for emissions of marine pollutants include infrastructure development, human settlements, anthropogenic interventions, resource utilization, agriculture

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activities, industrialization, and tourism (Derraik, 2002). The prominent marine pollutants of major concern include inorganic elements, persistent organic pollutants, microplastics, radionuclides, and oil spills. Most of these pollutants are interlinked in terms of their sources, jeopardizing the marine environment, and ecological resources. However, the existing classification of marine pollutants needs to be redefined (Islam & Tanaka, 2004). Due to the marine fisheries and commercial exploitation of coasts, most of the coastal areas in the world have been severely affected by marine pollution. Therefore, control of marine pollution is critically important and immensely needed for the conservation of marine ecology and sustainable management of resources. In addition, there is a scientific knowledge gap about marine pollution, which is also a constraint for controlling marine pollution.

The problem of marine pollution is dated back to the history of human civilization due to the anthropogenic interventions (Islam & Tanaka, 2004). However, this issue failed to receive considerable attention until recently when the consequences of marine pollution reached a threshold level and resulted in adverse impacts on the ecosystem and climate change. Now, marine pollution and associated hazards have become major environmental concerns around the globe. Among marine pollutants, persistent organic pollutants (POPs) are carbon-based legacy organic pollutants, which exhibit a high environmental persistence and toxicity (Tieyu *et al*., 2005). POPs have attained a considerable global attention due to their potentials for long-range transport, persistence behavior, lipophilic nature, bio-accumulation, and biomagnification in the ecosystems, as well as their pronounced adverse effects on the environment and human health (Harrad, 2009). POPs usually include polychlorinated biphenyls (PCB), organochlorine pesticides (OCPs), brominated flame retardants (FBRs), polyfluorinated sulfonamides (FSAs), and other industrial chemicals, such as unintentional by-products of many industrial processes, especially polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD), commonly known as 'dioxins' (Tieyu *et al*., 2005). In 2001, the Stockholm Convention under the umbrella of United Nations Environment Programme (UNEP) enlisted the sources, behavior, fate, and effects of POPs. This Convention was enacted in 2004. In 2008, 180 parties had accredited the Stockholm Convention in order to cope with POPs mediated hazardous impacts on human health and the environment. Initially, the Convention had listed 12 POPs for eradication and named them as “dirty dozen” that included DDT, aldrin, dieldrin, chlordane, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and toxaphene (Xu *et al*., 2013).

A comprehensive study reported the contamination of POPs (organochlorine compounds) in the coastal water samples collected from 30 beaches of 17 countries, and the highest concentration was found at the coasts of USA, followed by Western Europe and Japan; while the lowest levels of POPs were reported at the coasts of tropical Asia, Australia, and Southern Africa (Ogata *et al*., 2009). POPs also include polycyclic aromatic hydrocarbons (PAHs) as the priority class of organic pollutants, which are primarily emitted from incomplete combustion of petroleum products in automobiles, industries and also through the pyrolysis of organic materials. In the marine environment, several processes, such as deposition through the atmosphere, industrial sewage, transport (marine ships), oil spills, and terrestrial runoff, are the potential sources of PAHs (Hamid *et al*., 2016). POPs exhibit exceptionally long retention time in the living bodies, pass through different stages of the food chain, and result in biomagnification at higher trophic levels. Further, persistent compounds can be bio accumulated and bio concentrated at the low trophic levels (Hamid *et al*., 2016).

PCBs, organochlorines, organometallics, polychlorinated dibenzodioxin (PCDDs), and polychlorinated dibenzofurans (PCDFs) are compounds, which are usually present in elevated concentrations in the tissues of the exposed animals at higher trophic levels (Pérez-Carrera *et al*., 2007). Bioaccumulation and bioconcentration may be the consequences of biomagnification process along the food chain in the marine ecosystem. The vertebrates and invertebrates in the aquatic ecosystem absorb different pollutants that can cause acute and chronic toxicity after magnification (Islam & Tanaka, 2004). Although many studies are available on the levels of pollutants in the marine ecosystems and their consequences, the precise and conclusive review of those studies is still elusive, which has been summarized in this book. This issue of organic contamination in the marine pollution is alarming to the extent that the Scientific Committee of International Whaling Commission (IWC) devised and launched a comprehensive program "Pollution 2000+" to elucidate the cause-and-effect relationship in cetaceans (Helmerhorst *et al*., 1999). The objective of this program was to develop a predictive model that can link the concentration of the pollutants in the tissues with its effects at the population level. Pollution 2000+ specifically focused on PCBs as model organic pollutants to determined effects for organochlorine pesticides (OCs) pollution (Helmerhorst *et al*., 1999).

Inorganic components include inorganic nutritive ions such as phosphates and nitrates, sulfur, arsenic, aluminum, cadmium, lead, mercury, and nickel, gases like carbon dioxide and metals. All of these inorganic ions are essential for maintaining ecological balance (Islam & Tanaka, 2004). Nevertheless, when these ions occur in higher concentrations, they affect the natural ecological harmony also affect the aquatic organisms. For example, Nitrogen and Phosphorous act as a stimulus to increase the algal production. If the biomass production remained increased, then the algal layer becomes thick that prevent the sunlight and oxygen

CHAPTER 2

Sampling Pelagic Marine Organisms

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Abstract: Marine life remains far less well documented than terrestrial biodiversity. The main reason resides in the vastness of the ocean. Ocean waters, with an average depth of ≈3,800 m, cover 71% of the world's surface. The difficult access, the complexity of the logistics (any study below the top few meters of the ocean requires large means, specialized personnel, and equipment), and the high cost of research have determined the majority of studies being performed in the terrestrial environment. However, in recent times, this severe imbalance has started to reverse. This is mainly due to the implementation of supra-governmental cooperation programs. Due to human-driven ecosystems alteration, over-fishing, ocean acidification, and chemical pollution (together with other threats), multiple marine species are endangered, so this effort is more than ever relevant and eminently urgent. Recently, the Global Ocean Observing System (GOOS) has proposed, the development of an integrated framework for continued and systematic ocean observation. This framework is based on Essential Ocean Variables (EOVs) aiming to provide a credible response to scientific and societal issues, a high feasibility for sustained observation, and cost-effectiveness. Ecosystem EOVs have been developed. In this framework, biodiversity will be assessed based on the status of ecosystem components, nominate phytoplankton biomass and diversity, zooplankton biomass and diversity, fish abundance and distribution (as well as marine turtle, bird and mammal abundance and distribution). Recommendations for each EOV, including what measurements are to be made, but up to this point those recommendations do not exist. This chapter will try to identify common sampling procedures for the most diverse and abundant marine organisms considered as ecosystem components under the EOVs, *i.e.*, phytoplankton, zooplankton, and fish.

Keywords: Marine Environment, Essential Ocean Variables (EOVs), Phytoplankton, Zooplankton, Fish.

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INTRODUCTION

The most consensual agreed definition of biodiversity, "the variability among living organisms from all sources including, inter alia, terrestrial, marine and other aquatic ecosystems and the ecological complexes of which they are part; this includes diversity within species, between species and of ecosystems", can be found in article 2 of the Rio de Janeiro Convention on Biological Diversity (GBO, 2014). This binding agreement had the conservation of biodiversity at its core, and it makes clear that already by 1992 (when realities like global warming and climate change were just the concern of a few), biodiversity was recognizably facing accentuated alteration under the pressure of growing anthropogenic impact. Two and a half decades later, protection measures, either at species or ecosystems levels, are still infrequent. Moreover, a broad understanding of all of the components and functions of marine ecosystems as well as a thorough registry of marine biodiversity are lacking. Biological diversity has to be documented and understood before it can be totally preserved (Zampoukas *et al*., 2014).

Marine life remains far less well documented than terrestrial biodiversity. Considering the major taxa, current knowledge indicates that diversity is much greater in the sea as compared to freshwater or land. Thirty-two of the currently recognized 34 animal phyla occur in oceanic waters, being 16 exclusively marine. Other major animal phyla, including the cnidarians, sponges, as well as the non-metazoan brown (Phaeophyta) and red algae (Rhodophyta) are largely marine (Chapman, 2009). This reflects the ocean as the cradle of life. However, species diversity is far lower in the sea (≈250,000 species registered) than on land (1.4 - 1.7 million). The main reason possibly resides in the vastness of the ocean. Ocean waters, with an average depth of ≈3,800 m, cover 71% of the world's surface. As a result, the marine environment is physically much less variable in space and time than the terrestrial environment, lowering genetic connectivity and speciation rates (Paulay & Meyer, 2002). Additionally, the most diverse group within the animal kingdom, the insects, together with that in the plant kingdom, the angiosperms, is largely restricted to terrestrial and freshwater environments. The higher species richness of the terrestrial and freshwater habitats together with a comparatively higher easiness of access (any study below the top few meters of the ocean requires large means, specialized personnel and equipment being, thus, highly expensive) have determined the majority of studies being performed in the terrestrial environment. According to Hendriks and Duarte (2008), of the 13336 articles concerning biodiversity published between 1987 and 2005, 72% addressed terrestrial ecosystems. However, in recent times, this severe imbalance has started to reverse. This is mainly due to the implementation of supra-governmental international cooperation programs, such as the United Nations' The World Ocean Assessment, the Oslo and Paris Commissions (OSPAR and cooperating entities on data collection, *e.g.*, ICES), the HELCOM Monitoring and Assessment Strategy, the Convention on Protection of the Black Sea Against Pollution, and multiple EU funded projects.

Human-driven ecosystems alteration, over-fishing, ocean acidification and chemical pollution (together with other threats) endanger marine species. Many mammals, birds, reptiles, and fish are currently in danger of extinction (Mark J. Costello, 2015; Mark J. Costello & Scott Baker, 2011; Webb & Mindel, 2015). Global, regional, and local scale assessments need data collected by similar methods and procedures in order to produce variables that can be integrated for analyses (Pereira *et al.*, 2013). The EU Marine Strategy Framework Directive (2008/56/EC) requires that European marine waters achieve a Good Environmental Status (GES) by 2020 (Boero, Dupont, & Thorndyke, 2015). It links ecosystem components, anthropogenic pressures and impacts on the marine environment and it contains the explicit regulatory objective that "biodiversity is maintained by 2020", as the cornerstone for achieving GES. For this, an extensive system of measures of biodiversity and ecosystem functioning was determined. The European Commission produced a set of detailed criteria and methodological standards (Commission Decision 2017/848 of 17 May 2017) to obtain and report those measures in order to help Member States implement the Marine Directive at local and regional scales. Similarly, UN's World Ocean Assessment emphasizes the need for more standardized reporting of information (Inniss *et al.*, 2016).

The ocean environment is vast, the marine biosphere difficult to access. The remoteness, harshness, and depth of the ocean make them challenging to study and dramatically raise the cost involved in its observation. Duplication of efforts should be avoided. Cutting across observing platforms and networks, and the adoption of common standards for data collection and dissemination to maximize the utility of data are imperative. Recently, the Global Ocean Observing System (GOOS) has proposed, under the umbrella of the Intergovernmental Oceanographic Commission (IOC) of UNESCO, to develop an integrated framework for continued and systematic ocean observation. This framework is based on what was defined as Essential Ocean Variables (EOVs). By definition, an EOV should provide i) a credible response to scientific and societal issues; ii) a high feasibility for sustained observation, and; iii) cost-effectiveness. Among other domains, ecosystem EOVs have been developed in collaboration with the Group on Earth Observations (GEO BON) (Pereira *et al.*, 2013). Up to this point, the defined ecosystem component EOVs directly dealing with biodiversity consist of those related to the status of ecosystem components and those related to the extent and health of ecosystems. The former is phytoplankton biomass and diversity, zooplankton biomass and diversity, fish abundance and distribution, marine turtle, bird and mammal abundance and distribution; the latter, cover and

CHAPTER 3

Macroelements and Microelements in Marine Ecosystems: An Overview

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Abstract: In this chapter, aspects concerning the complexity of marine chemistry were discussed. In this scope, important reactions of metals and non-metals with inorganic and organic constituents of water and sediments were considered. In addition to these reactions, this chapter considers biokinetic aspects, which are responsible for very important regulations concerning the assimilation and biotransformation of many chemical elements. Finally, two major environmental problems (eutrophication due to the excessive supply of nitrogen and phosphorus, and release of organotin compounds and copper from antifouling paints used on ships' hulls) were presented with the intention of discussing some forms in which uncontrolled introductions of metals and non-metals can change negatively the quality of marine ecosystems.

Keywords: Bioaccumulation, Essentiality, pE X pH Diagrams, Toxicity.

INTRODUCTION

The oceans cover approximately 71% of the Earth's surface, thereby playing an important role in human activities, including the transportation of millions of tons of cargo, as well as fishing activities. Additionally, the oceans are an important source of commercial extraction of sodium, magnesium, chlorine, and bromine. A large part of the world's population conglomerates in coastal environments, and this situation is worrying because of the bulky discharges of domestic and industrial wastes. Approximately 40% of the world's population lives near

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coastlines (up to 100 km away), thereby offering many opportunities for pollutant loading, including nutrients (nitrogen and phosphorus) that are able to promote eutrophication, as discussed later in the text (Wallace *et al*., 2014). As early as 1977, serious environmental problems had already been reported in coastal environments, when wastewater discharges, in the vicinity of five domestic outfalls in southern California, were responsible for remarkable decreases in the biodiversity of benthic organisms (Reish *et al*., 1977). According to the authors, the population of benthic organisms decreased because of the presence of high concentrations of some elements (nitrogen, for example) in the marine water, which were able to cause severe biological damages upon pelagic larvae of benthic organisms. Nowadays, many underdeveloped and developing countries still have serious problems related to basic sanitation and, consequently, coastal pollution.

Besides the domestic wastewater discharges, several agrochemical and industrial pollutants are brought by the rivers, and this pollution has been responsible for severe degradation of estuarine ecosystems, as well as worrying decreases in the population of many species of fish and other marine organisms. Obviously, because of this estuarine pollution, fishing industries have been suffering economic losses for decades.

The oceans are also hugely important from a biogeochemical point of view, since marine environments play important roles in the planetary distribution of several chemical elements. This fact is very important, for example, for regulating the atmospheric levels of CO_2 and O_2 with imperative consequences for the maintenance of life on our planet.

Regardless of whether for economic purposes or for environmental regulation and preservation, the importance of the oceans is based on their biodiversity. In this regard, it is necessary to maintain satisfactory physical and chemical conditions in the oceans, including adequate concentrations of trace elements, such as cobalt, copper, iron, manganese, and zinc, in order to promote the development of life. At the same time, the contents of toxic elements, such as cadmium, lead, and mercury, should be very low. In this scenario, human activities are potential sources of harmful wastes capable of causing serious disequilibria in marine life and in its ability to control biogeochemical cycles over long periods of time. The next section deals with the capacity of marine life to regulate two of the most important of these cycles, namely the biogeochemical cycles of carbon and oxygen.

The Importance of Marine Life for Carbon and Oxygen Biogeochemical Cycles

The marine life has extreme importance concerning the regulation of the global climate. This control is realized by means of thermohaline currents, but the fluxes of CO_2 between marine water and the atmosphere also effectively contribute to the regulation of atmospheric levels of this gas (vanLoon & Duffy, 2005), which is accomplished mainly by means of photosynthesis and burial of $CaCO_3$ (in marine sediments). As discussed below, both situations need the participation of marine life.

Photosynthesis is one the most important mechanisms for keeping concentrations of CO_2 in Earth's atmosphere well below those found in the atmosphere of Venus, for example (Rothschild & Lister, 2003; Allègre & Dars, 2009). In marine environments, a large proportion of the photosynthesis is carried out by phytoplankton, so that this wide group of living organisms is considered the fuel that moves marine ecosystems (Boyce *et al.*, 2017). Photosynthesis uses atmospheric CO_2 that is dissolved in marine water with the consequent production of carbohydrate, whose minimum formula is $[CH_2O]$, and oxygen gas. As indicated in Equation 1, this vital biochemical process also needs water and sunlight, whose energy is given by hν, where h is the Planck constant (6.63×10^{-34} J s) and ν is the electromagnetic radiation frequency (Hz).

$$CO_{2(g)} + H_2O_{(l)} + h\nu \rightarrow [CH_2O]_{(s)} + O_{2(g)} \quad \textbf{(1)}$$

The marine photic zone, with an average depth of approximately 250 m, is considered a soup of living organisms, and many of them belong to phytoplankton and zooplankton. In this zone, zooplankton eats phytoplankton and both classes of organisms are consumed by bigger animals. All these organisms breathe aerobically, thus releasing CO_2 to marine water, the pH of which favors its conversion to bicarbonate (HCO_3^-). After the death of marine organisms, bacteria decompose their soft tissues, releasing organic molecules that are also dissolved in marine water. These bacteria continue decomposing the dissolved organic matter and more CO_2 is returned to the photic zone, where, as discussed above, the formation of HCO_3^- is favored. In this sense, marine life recycles both organic and inorganic carbon in the photic zone. A large part of the atmospheric CO_2 assimilated by the oceans tends to be returned to the atmosphere within days or months. However, carbon recycling is not 100% efficient, and approximately 4-5 x 10^{12} kg C $year^{-1}$ escapes from the superficial waters, a small part of which is deposited, buried, and accumulated in deep marine sediments. The buried carbon, which is not recycled by benthic and pelagic organisms, does not return to the

CHAPTER 4

Sulfur, Aluminum, Arsenic, Cadmium, Lead, Mercury, and Nickel in Marine Ecosystems: Accumulation, Distribution, and Environmental Effects

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Abstract: This chapter deals with aspects concerning the presence of sulfur, aluminum, arsenic, cadmium, lead, mercury, and nickel in marine environments. For each of these elements, information about their natural and anthropic sources, as well as their toxicity and accumulation in different organisms, was provided. It was shown that the total accumulation of aluminum, cadmium, lead, mercury, and nickel in physical marine compartments (water, particulate matter, and sediments) is not necessarily related to the bioaccumulation of these elements, since many aspects concerning the bioavailability (including chemical speciation) should be considered.

Keywords: Chemical Speciation, Bioaccumulation, Human Health.

INTRODUCTION

In this chapter, we discuss chemical and environmental aspects concerning the presence of some key elements in marine ecosystems, choosing the following elements: sulfur, arsenic, aluminum, cadmium, lead, mercury, and nickel. These elements were chosen because they belong to specific groups, so that sulfur is an essential element (a secondary macroelement), while arsenic is classified as a

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non-metallic toxic element, and a microelement. In turn, aluminum, cadmium, lead, and mercury represent the group of toxic metals, which are commonly found in marine environments as microelements. Finally, nickel is a metallic microelement with some essential functions associated with different forms of life. In the next sections, we discussed the ways in which these seven elements are distributed, transformed, and accumulated in the different marine environmental compartments, as well as their natural and anthropic sources. This chapter also discusses toxicological aspects concerning the assimilation of some of these elements by humans. Fig. (**1**) shows marine environments that can integrate many compartments, including coastal vegetation and giant aquatic animals such as whales. In this photo, we have an adult humpback whale (Praia do Forte Beach, Bahia State, Brazil), whose length can reach 16 m.

Fig. (1). Humpback whale (*Megaptera novaeangliae*) in the Brazilian coast (Personal archive).

Sulfur

Sulfur is an essential element because it is found in the composition of amino acids as cysteine ($C_3H_7NO_2S$), thus participating in the chemical composition of proteins and/or enzymes. Much of the sulfur that reaches the oceans comes from leaching of soils, rocks, and minerals. This contribution of continental sulfur is delivered almost exclusively by rivers (Cardoso & Pitombo, 1992). The marine chemistry of several elements, including cadmium, lead, mercury, and nickel, is controlled by species containing sulfur since these microelements form insoluble sulfides, thus exhibiting direct impact on their bioavailability. As sulfur can assume many oxidation states (-2 to +6), this element presents several chemical forms, as discussed in Chapter 3, entitled "*Macroelements and microelements in marine ecosystems: an overview*".

An important natural source of sulfur for marine water is the geological activities that occur in the oceanic floor (average depth of 4-5 km) where deep, cold marine water infiltrates through cracks in the rocks and is overheated by the proximity of hot rocks. This overheated water captures H_2S, which comes from magma, and becomes acidic, thus reacting with rocks and dissolving metals such as iron, copper, and zinc. Insoluble sulfides of these metals are formed, and their precipitation builds geological structures called fumaroles or smokers, the color of which tends to be black, due to the presence of iron sulfides, or white. Around these fumaroles, there is exuberant life for which chemosynthesis is the source of energy. Specialized bacteria promote the oxidation of H_2S, thus producing nutrients that sustain many forms of life (Martins and Nunes, 2009).

The transfer of sulfur from the atmosphere to the oceans occurs by means of the deposition of sulfate salts formed in atmospheric reactions in which H_2S is subsequently oxidized to SO_2, SO_3, and SO_4^{2-}. The average concentration of SO_4^{2-} in marine water is around 2.6 g L^{-1} (Garrison, 2006). The oceans also have elementary sulfur, but the occurrence of this species needs intermediate values of pE as well as small to intermediate values of pH, as discussed in Chapter 3 entitled "*Macroelements and microelements in marine ecosystems: an overview*".

The flux of sulfur from the oceans to the atmosphere is by marine spray and production of $(CH_3)_2S$ by phytoplankton (Manham, 1994). Except for deep marine waters, in which there are large emissions of H_2S from geological activities, this weak acid is not found in large amounts in shallow water. However, it remains very important because of its dissociation, whose equilibria are indicated in the following Equations 1 and 2 with the respective constants (K_{a1} and K_{a2}) of 9.6 x 10^{-8} and 1.3 x 10^{-14}.

$$H_2S_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + HS^-_{(aq)} \quad \textbf{(1)}$$

$$HS^-_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + S^{2-}_{(aq)} \quad \textbf{(2)}$$

Equations 3 and 4 represent, respectively, the mass action law of the reactions indicated in Equations 1 and 2.

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CHAPTER 5

Pollution Dynamics of Organic Contaminants in Marine Ecosystems

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Abstract: While the biomass of marine ecosystems is only about 1% of their terrestrial counterparts, their productivity rivals that of all land-based ecosystems taken together. The structure and performance of these ecosystems are strongly affected by environmental factors, such as temperature, nutrients, transparency, solar visible and UV radiation. Increasing pollution, not only of coastal habitats but also of open ocean waters, results in changes in productivity and species composition. Persistent organic pollutants (POPs) are organic chemicals that are not degraded for long periods and include brominated flame retardants, perfluoroalkyl compounds, fluorotelomer alcohols, perfluoroalkylsulfonic acids (FPSAs), perfluorocarboxylic acids (PFCAs), fluorotelomer carboxylic acids, fluorotelomer sulfonic acids, and fluorinated polymers. Pesticides enter the aquatic ecosystems with terrestrial run-off, but are distributed not only in coastal areas and estuaries. Microplastics are of growing concern since they are concentrated in oceanic gyres. They are ingested by plankton and accumulated in the food chain. Accidental oil spills and catastrophic events are the reason for the pollution by crude oil and its products. Mineral oil pollution has been found to affect all the biota from plankton, *via* invertebrates to vertebrates.

Keywords: Organic Pollutants, Persistent Organic Pollutants, Pesticides, Microplastics, Mineral Oil, Coastal Ecosystems, Open Ocean Habitats.

INTRODUCTION

Marine ecosystems are major biomass producers. Prokaryotic and eukaryotic photosynthetic organisms generate about the same amount of biomass as all terrestrial ecosystems taken together and constitute important sinks for atmospheric CO_2 (Field, Behrenfeld, Randerson, & Falkowski, 1998). The biological pump in the oceans is a key element (Honjo *et al*., 2014) mitigating fix dissolved CO_2 to produce organic biomass. This material in the form of dead

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organisms and fecal pellets sinks to the deep sea sediment in the form of 'oceanic snow' and increases the largest carbon reservoir on Earth (IPCC, 2014).

Marine ecosystems are affected by a plethora of environmental stress factors threatening the sustainable development of resources for the rapidly increasing human population (2012). The primary producers are photosynthetic prokaryotes, such as cyanobacteria, eukaryotic phytoplankton, and macroalgae. In addition, many non-photosynthetic organisms are found in the water column ranging from viruses, heterotrophic bacteria to zooplankton and higher zoological taxa. The primary producers form the basis of the intricate food webs and therefore any disturbance at the basis is relayed to the primary and secondary consumers culminating in fish, birds and even humans for which the marine ecosystems contribute major resources for food production and technology.

Commencing in the 1970s, stratospheric ozone depletion by anthropogenic production and emission of chlorinated fluorocarbons (CFCs) and other trace gases resulted in an increase in the solar UV-B radiation (defined as 280-315 nm). Exposure to excessive solar UV-B radiation is detrimental for many organisms since it causes damage to the DNA (Sinha & Häder, 2002), reduces photosynthetic productivity (Jin, Duarte, & Agustí, 2017) and affects many other physiological and biochemical processes in the cell (Rastogi *et al*., 2014). In addition to the damage of cellular targets, solar UV radiation produces reactive oxygen species (ROS) both inside the cell as well as outside *via* excitation of dissolved organic matter (DOM) in the water, which in turn impair cellular functions (Maraccini, Wenk, & Boehm, 2016).

Despite of the implementation of the Montreal Protocol and its amendments detrimental enhanced UV-B still persists because of the long lifetime of the CFCs in the stratosphere (Bais *et al*., 2015; McKenzie *et al*., 2011; Newman & McKenzie, 2011; Solomon *et al*., 2016). Therefore, the ecophysiological effects of solar UV-B radiation are still a topic of increased interest (Häder & Gao, 2015).

Increasing temperatures due to global climate change (IPCC, 2014) are another stress factor for marine ecosystems. Fossil fuel burning, tropical deforestation, and altered land usage result in the increasing release of carbon dioxide into the atmosphere. The mean global temperature of the oceans has increased by ~1°C since 1900 (Fischetti, 2013), but the error bars are considerable. The temperature increase in Arctic and Antarctic waters are much higher than the mean values and amount to about 4°C depending on the region (Pithan & Mauritsen, 2014). One consequence of this ocean warming is an enhanced stratification and shoaling of the upper mixed layer (UML) (Boyce, Lewis, & Worm, 2010; G. Wang, Xie, Huang, & Chen, 2015), which confines the organisms dwelling in this layer to a thinner water column and exposes them to higher solar visible and UV radiation (Gao *et al*., 2012). In addition, the stronger thermocline, which defines the lower limit of the UML and separates it from the cooler deeper water, hinders the transport of dissolved macronutrients from below into the UML (Behrenfeld *et al*., 2006).

Increasing pollution from a multitude of sources is a major problem for marine ecosystems, which affects primary producers, consumers and the intricate food webs (Gerlach, 2013; C. H. Walker & Livingstone, 2013). This has resulted in massive destruction of native populations and enhancing extinction of species in all taxa (Ceballos *et al*., 2015). Organic pollutants include pesticides, detergents and surfactants, solvents and residues of oil spills. Many of the toxic materials are persistent organic pollutants (POPs). Pollution is more pronounced in coastal habitats than in the open ocean (Gómez & O'Farrell, 2014; Munir, Zaib-un-nisa Burhan, Morton, & Siddiqui, 2015). In contrast, the latter is affected by the accumulation of plastic materials, which amounts to about 250,000 tonnes collected in the oceanic gyres (Eriksen *et al*., 2014). Coastal ecosystems accumulate pollutants from terrestrial run-off, which include heavy metals, industrial wastes, agricultural fertilizers, and pesticides, as well as surfactants and cleansing products from households (Nemerow, 1991; S.-L. Wang, Xu, Sun, Liu, & Li, 2013; Zaghden *et al*., 2014).

This review provides an overview of the types and sources of organic pollutants in the oceans as well as on bioindicators and potential methods of remediation in order to preserve or restore the ecological integrity and providing the numerous services marine ecosystems offer.

PERSISTENT ORGANIC POLLUTANTS

Persistent organic pollutants (POPs) are organic chemicals that stay in the environment and are not degraded for long periods (Harrad, 2009). These pollutants include brominated flame retardants, perfluoroalkyl compounds, such as polyfluorinated sulfonamides (FSAs), fluorotelomer alcohols (FTOHs), perfluoroalkylsulfonic acids (FPSAs), perfluorocarboxylic acids (PFCAs), fluorotelomer carboxylic acids, fluorotelomer sulfonic acids, and fluorinated polymers. They are toxic wastes and are found in air, soil, water, and sediments. The United Nations Environment Programme (UNEP) listed the sources, behavior, fate and effects of POPs in the Stockholm Convention on 22 May 2001, which entered into force in 2004 when 50 countries had ratified it; in late 2008 180 parties had ratified it in order to protect human health and the environment from POPs. The Convention lists aldrin, chlordane, DDT, dieldrin, heptachlor,

CHAPTER 6

Monitoring of Organic Pollutants: PCBs in Marine Ecosystem

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Abstract: Marine ecosystem is rich and diverse, and plays a vital role in maintaining the natural balance of the planet. Though, the chemical revolution brought many benefits to human civilization but it also affected natural ecosystem due to chemical pollution. Unfortunately, oceans are one of environmental compartments that is at the most receiving end of the chemical pollution. There is a need to monitor chemical pollution in oceans for its normal functioning and providing a healthy habitat to marine biota. The chemical pollution of polychlorinated biphenyls (PCBs) is one of the most prominent types of organic contamination in the oceans. PCBs, comprising of 207 congeners, are considered legacy contaminants. PCBs are banned because of persistent, bioaccumulative and toxic attributes. Being hydrophobic in nature, they tend to bio-accumulate and bio-magnify, causing human health concerns that many of the sea organisms serve as food to human beings and other living organisms through food chain. Monitoring of PCBs in oceans can be done through various methods/techniques involving bio-indicators, biological monitoring, chemical monitoring, biomarkers and through isotopic analysis. The use of any single technique may not help in achieving the maximum control and monitoring of PCBs; so a use of combined approach is recommended to ensure proper monitoring of PCBs in the marine environment.

Keywords: Marine Ecosystem, PCBs Monitoring, Bioindicators, Control Measures, Isotopic analysis

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INTRODUCTION

Marine ecosystem is a complex system that is rich in biodiversity. The organisms in the marine environment are affected by variations in pH, temperature, dissolved oxygen, water circulations, and light. These changes can be natural but anthropogenic pollution load in the marine ecosystem is also contributing. The uptake of pollutants by the organisms is dependent upon the properties of pollutants such as partition coefficient, hydrophobicity, *etc*. The serious threat posed to the marine ecosystem is by pollutants, which are persistent/recalcitrant. PCBs are amongst these and are of major concern while dealing with the toxicities and disruption of living organisms functions. It is very important to continuously monitor the marine ecosystem for any toxic chemical or pollutant. The monitoring can be achieved through different mechanisms such as bioindicators, chemical monitoring, biological monitoring and through isotopes and biomarkers.

Marine pollution started when humans opened the doors of oceans for transport and from the industrialized era. Since the oceans are continually facing the disposal of wastes and pollution level increases day by day. Even if today we stop polluting oceans, persistent pollutants are already there in the ocean environment. Earth contains 70% of the water in oceans, therefore, everything ends up into oceans. Due to anthropogenic activities, hundreds of thousands of pollutants are introduced into the marine environment. Most of them are organic in nature and some are inorganics as well.

ORGANIC POLLUTANTS

Organic pollutants that have sufficiently long retention time in living organisms, pass through food chains and undergo the process of biomagnification and reach higher trophic levels. Less persistent compounds can be bioconcentrated or bioaccumulated at lower trophic levels, for example, polycyclic aromatic hydrocarbons (PAHs) (Potters, 2013). Organochlorines (dieldrin) and the PCBs, are those compounds that are present in high concentrations within the tissues of the highest trophic levels. Polychlorinated dibenzodioxin (PCDDs), polychlorinated dibenzofurans (PCDFs), and some organometallic compounds also fall in the same category (Gioia, *et al*., 2011; Potters, 2013). The types and sources of various organic pollutants are listed in Table **1**.

Biomagnifcation along terrestrial food chains is principally due to bioaccumulation from food, the principal source of most of the pollutants. In a few instances, the major route of uptake may be from the air, from contact with contaminated surfaces, or from drinking water. Biomagnifcation along aquatic food chains may be the consequence of bioconcentration as well as bioaccumulation. Aquatic vertebrates and invertebrates can absorb pollutants from ambient water; bottom feeders can take up pollutants from sediments.

Urbanized runoff or wastewater discharge through point or non-point sources are the main cause of the presence of organochloride in water. In the ocean, organochlorine contaminants bound to marine sediments and are being continuously restored into the ecosystem by means of physical or biological disturbance (Sawyna, *et al*., 2017). Benthic organisms are mostly exposed to organochlorine because of deposited organochlorine into sediments. Thus benthic organisms especially fish species can be a good indicator of the presence of organochlorine in marine ecosystems (Hinojosa-Garro, *et al*., 2016). DDT, an organochlorine compound, is recognized as the pesticide, and known for its negative impacts on animals and humans. DDT is banned due to its several health and social issues such as accumulation and biomagnifcation properties in organisms (Rossi, *et al*., 2017).

Table 1. Types and Sources of Organic Pollutants.

Compounds	Source	Available in the Marine Environment	Examples
Organometallic Compounds	Antifouling biocides for ships and fishing nets, agricultural fungicides, and rodent repellents	Bound to marine sediments and, bioaccumulated	Diethyl magnesium organolithium *e.g* butyllithium
Polycyclic Aromatic Hydrocarbons	Heating, burning, and pyrolysis of organic substances, *e.g* gas, coal, oil, garbage, wood, and *etc*.	Bioaccumulated, biomagnified	Pyrene, benzopyrene,
Polybrominated Compounds	Electronics, airplanes, motor vehicles, textiles, foams, and plastics	Bioaccumulated, biomagnified	decabromodiphenyl ethers and its isomers *etc*.
Plastics	Cosmetics, personal care products, packaging products *e.g* Plastic bags, storage containers, Rope, bottle caps, and *etc*.	Bioaccumulated, present in water and sediments	Polyethylene, polypropylene
Organochloride compounds	Industrial and wastewater	Bound to marine sediments	DDT

Organometallic compounds are being used in industry and agriculture. They are toxic for the marine environment. Their toxicity not only depends on the nature of the metallic atom, but also on the organic compounds bound to the metal. Phenylsilatrane is a very toxic example of organometallic compounds (Egorochkin, *et al*., 2013). The toxicity of metal (mercury, vanadium, chromium, iron, rhodium, cobalt, iridium, phosphorus, boron, selenium, molybdenum,

CHAPTER 7

An Overview of Pollution Dynamics along the Pakistan Coast with Special Reference of Nutrient Pollution

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Abstract: Pollution in coastal waters is quickly becoming a conspicuous problem throughout the world and the coastal areas of Pakistan are also included in severely affected and therefore no exception. Anthropogenic activities are generally accountable for the deprivation of the marine environment along with their resources across the ocean bodies. The oceans economy not only offers significant development opportunities but also raise some challenges. Not only marine sources, the land-based sources are the prominent contributor of pollution as add in the pollution through direct and indirect wastes discharge as well as effluents in the adjacent coastal waters from untreated domestic and industrial sources. In this chapter, the magnitude of pollution (organic and inorganic) in coastal environments of Pakistan was discussed including plastic pollution as in recent days, it's a hot issue and a detailed topic itself. The weathering material, river runoff, industrial and domestic waste water enter through different channels and take part in coastal pollution. Most of the pollutants like pesticides, herbicides, heavy metals and macro-nutrients, presented intensification in a marine environment. Nutrient dynamics and their cycling influence the process of eutrophication in the adjacent coastal waters and an enrichment of macro-nutrients in coastal waters reveals an increment in the explosion frequency of harmful algal blooms were reported. The animal manure, sewage treatment, runoff of fertilizers, storm water runoff, plant discharges, and power plant emissions, and failing septic tanks are the primary sources of nutrient pollution. The algal blooms are responsible to produce algal toxins or red-tide toxins and these naturally-derived toxins harm the organisms, including humans. These bloom toxins initially contaminated the fish or seafood species, then responsible for significant loss of fish and shellfish species and ultimately economy damage.

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Keywords: Marine Environment, Coastal Pollution, Nutrient Dynamics, Heavy metal Contamination, Pollution Impacts.

INTRODUCTION

Coastal and estuarine ecosystems always remain sturdily subjective by the activities of mankind through pollution and habitat loss throughout the world. The environmental degradation, climate change, over-exploitation, pollution, poverty and lack of basic (health, water as well as education) facilities are the conspicuous issues for the coastal areas including the associated population. Pollution, now become one of the most significant challenges to the health of coastal ecology and systems. The pollution sources mainly include the land affected by agricultural or industrial activities, livestock or domestic waste discharge and also from coastal waters by aquaculture as well as other anthropogenic activities. The direct and untreated discharge of industrial and agricultural effluents and domestic sewage are the main contributor of pollution for the 990 km long coastline of Pakistan. The impacts of coastal pollution appeared as a consequence of various environmental issues mainly includes; the enrichment of organic matter leading to eutrophication, pollution through chemicals (metals and oil), sea level rise due to the global climate change and sedimentation as a result of land-based activities. According to preliminary estimation, the fisheries and allied resources are the primary livelihood for 80% of the coastal population of Pakistan as fishery-related exports acquiesce per year on average sum of PKR 8.8 billion (US$ 838 million) for the country. but this trade benefits are significantly dependent on the sustainable utilization of these marine resources. Over 75% of all marine pollution originates from land-based sources, which are primarily industrial, agricultural and urban. Point and non-point source pollutions continue globally, resulting in the steady degradation of coastal and marine ecosystems. There are various means of pollution incorporated through various human activities, including offshore oil and gas production and marine oil transportation. Other contaminants produced either naturally or anthropogenically ultimately flow into marine waters. Pharmaceuticals are also an important pollution source, mostly due to overproduction and incorrect disposal. Ship breaking and recycling industries (SBRIs) also releases various pollutants and substantially deteriorates habitats and marine biodiversity of adjacent coastal areas of Sindh and Balochistan coast.

AN OVERVIEW OF POLLUTION AND POLLUTANTS IN MARINE ECOSYSTEM OF PAKISTAN

In Pakistan, marine pollution is primarily restricted to the areas, which receive waste from the industrial, municipal, agriculture and oil spill sources. The coast of Pakistan faces semi-diurnal tides, therefore, washed twice a day and taking away the pollutants, however inside the harbours or creeks; the pollutants are oscillating for several days until they dispersed, washed or settle down at the bottom (Rizvi *et al*., 1988; Sayied, 2007; Saher and Siddiqui, 2016). The 800 Km coastline of Balochistan is almost free from marine pollution from land-based activities as it is sparingly populated. Sonmiani Bay is one of the most populated city along the Balochistan coast, located about 90 km away from Karachi (Saifullah and Rasool, 1995; Gondal *et al*., 2012; Saher and Siddiqui, 2016). The sources of fresh water are the seasonal runoff of the Porali and Windor Rivers (Rasool *et al*., 2002). These rivers receive effluents of around 122 industries, functioning at the Hub and Windor Industrial Trading Estate, which include textile weaving, plastic, chemical, food preservation, engineering, paper and paper product industries, *etc*., and mainly contribute to coastal contamination (LGB, 2008; Saleem *et al*., 2013; Saher and Siddiqui, 2016). The close adjoining area is from industrial sites of Karachi city and the few locations at the Hub industrial areas of Balochistan are the major waste receiving areas. Karachi is the most urbanized and industrialized city along the coast of Pakistan that has about 167 km long shoreline along the Sindh coast. By the virtue of the biggest city of Pakistan, it has the highest risk towards the environmental pollution, which insert from the diverse point and non-point sources (Rizvi *et al*., 1988; Saher and Siddiqui, 2016). Solid waste discharged into the marine environment is also a conspicuous serious threat to marine life. A substantially large quantity of solid waste from the coastal towns enters the sea on a regular basis, which is accumulated on beaches as well as in the shallow coastal waters, making the coastal area polluted (MFF, 2016). It is estimated that Karachi produces approximately 8000 tons of solid waste per day and a substantial portion, *i.e.* around 60% of uncollected solid waste mixes up with wastewater and enter in the sea at Karachi Harbour. It along with the ships, jetties, and inlets, thus compound the existing problem. The entered amount of solid wastes spreads in the harbour and accumulates in different points of the harbour and is expected to substantially increase with the rapid growth of population and economic activity. According to an estimation by the year 2020, solid waste generation in Karachi may come up to 16,000 to 18,000 tons each day and therefore, there is a need to improve present solid waste management practices and make them more effective and modernized according to acquired demand (MFF, 2016).

There are four main (Karachi harbour, located on the Lyari River, Port Qasim on the Indus deltaic region, Gizri creek near the Malir River and a Cape Monze area a side of Hub River) coastal areas of Karachi which continuously receive the land-based pollution. More than six thousand functional industries present in six different industrial estates and their untreated effluent along with 300 MGD municipal wastewater continuously discharged into coastal waters of Karachi (WWF, 2002; Mashiatullah *et al*., 2016). Two rivers (Malir and Lyari) are the

CHAPTER 8

Ecotoxicology of Heavy Metals in Marine Fish

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Abstract: Heavy metal pollution in the marine environment has been realized and developed to an important environmental problem since the 1950's. In the polluted areas, marine organisms are exposed to high level of heavy metals *via* different routes, accumulate them in the body, and may have harmful effects from molecular level to population level. Heavy metals in marine fish have been taken much attention due to human consumption and health. Marine fish accumulate heavy metals depending on the concentration and species of metals in water and food, and trophic level, ionic physiology, feeding habits (carnivorous, herbivorous or omnivorous), habitats (demersal, pelagic, or bento-pelagic), growing of fish, and other factors. Consequently, the concentrations of heavy metals in marine fish vary considerably among species and different sites, which can be well explained by the biokinetic model. High levels of heavy metals in marine fish can induce various acute and chronic toxic effects, including behavioral changes, organ pathological changes, biochemical and physiological changes, hematological changes, and so on. Heavy metal-contaminated fish consumption will pose threats to organisms at higher trophic level and humans. Here, we review the occurrence and chemistry of heavy metals in the marine environment, bioaccumulation, and toxicity of heavy metals in marine fish, and the general risk assessment of heavy metal in fish to human health.

Keywords: Heavy Metals, Bioaccumulation, Toxicology, Risk Assessment.

OCCURRENCE AND CHEMISTRY OF HEAVY METALS

Heavy metals are elements having atomic weights between 63.5 and 201, and a specific gravity greater than 5.0 (Fu and Wang, 2011). They include copper (Cu), zinc (Zn), iron (Fe), nickel (Ni), cobalt (Co), selenium (Se), silver (Ag), aluminum (Al), chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As) and so on. Among multitudinous classifications proposed, heavy metals are popularly divided into essential and non-essential metals for life by aquatic toxicologists (Wood *et al.*, 2011, Wood *et al.*, 2012). Indeed, the small quantities

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of these heavy metals, like Cu, Fe, Co, Mo, Zn, Ni, Mn, and Cr, are essential for organisms of proteins owing to their participation in metabolic reactions as cofactors or integral parts especially enzymes, but above the permissible limit, they can be hazardous to organisms. Some other heavy metals including Al, Cd, Pb, As, and Hg are not essential but toxic to organisms due to their interaction with biomolecules and interfere with corresponding functions. Heavy metals in the environment come from both natural and anthropogenic sources (Morel and Price, 2003). For many metals, anthropogenic inputs have exceeded the natural inputs currently. Heavy metals enter the seawater *via* river runoff, wind-blown dust, diffusion from sediments, hydrothermal vent inputs, and many anthropogenic activities (Fu and Wang, 2011). With large-scale industrial activities and fast urbanization processes, anthropogenic activities have released very substantial amounts of heavy metal into seawater and exerted tremendous pressure on marine ecosystems. Metal pollution in estuaries, bays, and coastal areas is often considered as a “traditional” environmental problem, but with such rapid industrialization and often “uncontrolled” releases of industrial wastes, it has led to further deterioration in marine environments and become a new challenge (Li *et al.*, 2012, Pan and Wang, 2012).

The concentrations of heavy metals vary both horizontally and vertically through the world’s oceans, determined by the relative rates of supply and removal (Donat and Dryden, 2001, Morel and Price, 2003). Beside concentrations, the chemical speciation of heavy metals is vital for physiology and toxicology (Donat and Dryden, 2001, Fu and Wang, 2011). The metals in seawater are mainly in the dissolved or particulate forms. It is generally recognized that the particulate metals exhibit negligible toxicity and bioavailability to aquatic organism relative to the dissolved metals. Dissolved metals can exist in different oxidation states, such as Fe(II)/Fe(III), Mn(II)/Mn(IV), Cr(III)/Cr(VI), Cu(I)/Cu(II), and As(III)/As(V), and chemical forms, such as free ions, organometallic compounds, organic complexes (*e.g.* metals bound to proteins or humic substances), and inorganic complexes (*e.g.*, metals bound to Cl^-, OH^-, HCO_3^-, SO_4^{2-}, *etc.*), depending on redox potential, pH and biological processes (Wood *et al.*, 2011, Wood *et al.*, 2012). The toxicity and bioavailability of heavy metals have been found to be proportional to the concentrations of their free metal ions but not their total concentrations. Complexation of metals by organic ligands will decrease the concentration of the free ion, thereby decreasing its toxicity or bioavailability. Seawater contains high levels of major ions, such as Na^+, Ca^{2+}, Cl^-, and HCO_3^-. For many metals, complexation with Cl^- and dissolved organic matters (DOMs) and the protective effects of competition by high concentrations of Na^+, Mg^{2+}, and Ca^{2+} lower the toxicity and availability of heavy metals in seawater (Grosell *et al.*, 2007).

Marine animals can accumulate, retain, and transform heavy metals inside their bodies when exposed to them through different routes/sources, such as diet, water, sediments, particles, and *etc*. Therefore, marine organisms are mostly good bioindicators for long-term monitoring of metal accumulation (Zhou *et al.*, 2008). Fish are usually considered as an organism of choice for assessing the effects of heavy metal pollution on aquatic ecosystems (van der Oost *et al.*, 2003). They are continuously exposed to heavy metals through their gills, skin, and intestine, resulting in high bioaccumulation and potential toxicity due to acute and chronic effects. The high bioaccumulation of heavy metals can affect biochemical and physiological systems, including behavior, organ histopathology, material/energy metabolism, enzyme activities, immune function, and gene expression. Fish also appear to have evolved different mechanisms for detoxification of heavy metals to counter the ambient heavy metal contamination. Heavy metal contaminated fish consumption could result in heavy metal exposure to humans and lead to an adverse health effect. Therefore, fish are good bioindicators of heavy metal toxicity and can be used as sentinels for biomonitoring of food safety.

BIOACCUMULATION MECHANISMS

Bioaccumulation is typically defined as the increase of concentrations of contaminants in aquatic organisms following uptake from the ambient environmental medium. Bioaccumulation is usually considered as a good integrative indicator of the chemical exposures of organisms in polluted ecosystems (Wang, 2016). Fish are at the high trophic levels of the aquatic food chains. Their metabolic activities allow them to accumulate the major, essential, and non-essential elements from water, food, or sediment (Castro-Gonzalez and Mendez-Armenta, 2008). Given the importance of fish both as food and bio-monitors, numerous studies have therefore determined the bioaccumulation of heavy metals in various fish over the past few decades. Several reviews have summarized metal accumulation in fish and concluded that the accumulation of heavy metals in fish is mostly depending on different feeding habits (carnivorous, herbivorous or omnivorous), differences in the aquatic environmental lives (demersal, pelagic, or bento-pelagic), growing rates of the species, types of tissues analyzed, and other factors (Neff, 2002, Varjani *et al.*, 2018, Yilmaz *et al.*, 2017, Yilmaz *et al.*, 2018).

Table **1** summarizes the concentration range of some essential metals (Cu, Zn, Fe, Cr, Mn, Mo, Ni) and non-essential metals (Al, As, Cd, Pb) in different fish species collected from different regions of the world. Among these data, metal concentrations were either quantified based on tissue dry weights or wet weights which were specified in the table and text. Typically, the wet weight to dry weight ratio of the fish would be in the range of 4-5 (Neff, 2002, Onsanit *et al.*, 2010);

CHAPTER 9

Effects of Microplastics in Marine Ecosystem

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Abstract: The increasing global production and widespread use of plastic have led to an accumulation of large amounts of plastic debris in the ocean. Microplastic exists in the marine environment on a global scale and can harm a great variety of marine organisms. Pollution caused by microplastic and associated pollutants, such as organic chemicals and heavy metals, threatens the survival of marine organisms. In this chapter, the following contents are summarized: (i) the distribution of microplastic in marine environment; (ii) the presence of microplastic in marine environment and organisms; (iii) the effects of microplastic on marine ecology, including the toxic effects on marine organisms, the effects on distribution of pollutants, and the combined pollution caused by microplastic and associated pollutants; and (iv) several aspects to work on the management and research of microplastic are proposed. Extensive research on microplastic pollution is going on.

Keywords: Marine Plastic Debris, Microplastics, Persistent Organic Pollutants, Heavy Metals, Ecological Effect, Combined Pollution.

INTRODUCTION

The current human history has been referred to as the plastic age. Plastic is being used in industry, agriculture and everywhere in our daily life due to its special properties, such as low density, good malleability, durability, low cost, *etc*. The global production of plastics reached 348 million tons in 2017 (Fig. **1**) (PlasticEurope, 2018). Unfortunately, a vast majority of the produced plastics are for single use. The very properties that make plastic so useful (*e.g.* low density, durability) also make them problematic in the environment. Due to the high disposal rate, low recycle percentage, and indiscriminate mismanagement, a large number of plastic litters enter into the sea and accumulate on shorelines, floating in the oceans and becoming the most numerous and ubiquitous component of marine litter on a global scale.

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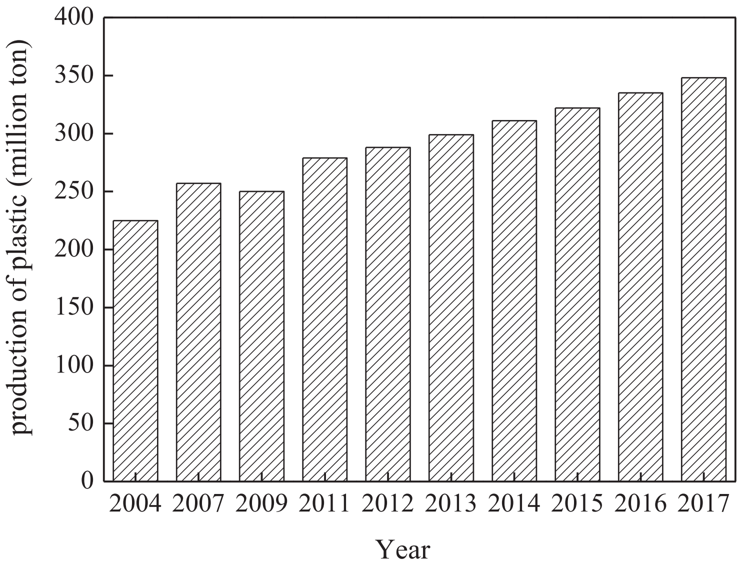

Fig. (1). The global production of plastic (PlasticEurope, 2018).

Plastic can potentially last several hundred to thousand years in the environment. There is a rising concern regarding the accumulation of floating plastic debris. United Nations Environment Programme (UNEP) began to focus on the plastic debris in the marine environment from 2011. It was reported in the first United Nations conference on the environment that the economic losses and costs caused by the generous plastic debris to the marine ecosystems might exceed US $13 billion per year. Marine plastic debris was ranked one of the ten most noteworthy urgent environmental problems in the annals of UNEP in June 2014 (UNEP, 2014). It was estimated that about 480 to 1279 tons of plastic debris was entered into the ocean in 2010 (Jambeck *et al.*, 2015).

Microplastics (MPs) are defined as small particles of plastic debris less than 5 mm in diameter by the National Oceanic and Atmospheric Administration (Wright *et al.*, 2013). They enter into the marine environment from the direct sources or primary sources, such as industrial accidental spillages during the processes of transportation and usage or the release of microbeads used in cosmetics through wastewaters (Browne *et al.*, 2015). Degradation and fragmentation of larger plastic items into small plastic fragments under the action of ultraviolet light, heat, wind, and waves represent an indirect source or “secondary source” of MPs input to the environment (Barnes *et al.*, 2009, Andrady, 2015).

According to the shape and morphotype, MPs are usually classified into the fiber, fragment, pellet or granule, and flake or film. Fiber mainly comes from clothing, disposable diapers, and fishery gears. The Fragment is usually as irregular shapes and from larger plastic items that have been broken by UV light, physical and chemical actions. Pellet or granule is mainly from preproduction plastic and daily cosmetics, such as toothpaste, shampoo, facial cleanser, *etc*. Flake or film is a thin sheet from plastic bags or other packaging materials. With respect to the polymer type, there are some common kinds of materials, including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyethylene terephthalate (PET), polyester, nylon, polyamide, acrylic, polystyrene butadiene styrene, polyurethane, *etc*.

MPs are considered as a new emerging pollutant and concerned researchers have started to study their effects and risks in the marine environment (for reviews, see Marris, 2014; Perkins, 2014). MPs pollution has been listed as the second major scientific problems in the field of environmental and ecological science in 2015. The plastic (including MPs) pollution of the marine environment was also considered as the major global environmental problems together with ocean acidification, de-oxygenation, ocean warming (Williamson *et al.*, 2016). Fig. (**2**) lists the number of publications on MPs during the year 2004 to February, 2019, showing the rapid increasing concern for plastic pollution. Jamieson *et al* (2017) reported that the persistent organic pollutants were detected in the organism collected from Mariana Trench, and MPs were considered as carriers of these pollutants. The results indicated that the impact of MPs on marine ecosystem might be far beyond what the human expect.

MICROPLASTICS IN THE MARINE ENVIRONMENT

As a new emerging pollutant, MPs have been found in high numbers in seawater and sediments. There are numerous reports about the distribution and characteristics of MPs in the marine environment. Here we briefly summarize their distribution in seawater and sediments.

The distribution of MPs in the sea is greatly influenced by currents. They distribute widespread in everywhere of the ocean, and high abundance is observed in certain regions (Law, *et al.,* 2010). MPs are universally found in the nearshore area, bay, strait, and around the area of islands, with their abundance varies significantly (Dubaish and Liebezeit, 2013; Collignon *et al.*, 2014; Desforges *et al.*, 2014; Song *et al.*, 2014; Zhao *et al.*, 2014). The abundances of MPs were 4137±2461 and 0.167±0.138 items m^{-3}, respectively, in samples from the Yangtze Estuarine and East China Sea (Zhao *et al.*, 2014). More than 90% of MPs were from 0.5 to 5 mm in size by the number of items, and the most frequent geometries were fibers, followed by granules and films (Zhao *et al.*, 2014). The

CHAPTER 10

Toxicity Evaluation in Flora and Fauna Exposed to Marine Pollution

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Abstract: Evaluating the toxicity in flora and fauna due to marine pollutants has attracted immense scientific, regulatory and public attention over the past years. In recent years, types and levels of contaminants in the marine environment have increased as a result of anthropogenic activities worldwide. These chemical substances are accumulated in the tissues of marine organisms and exerting harmful impacts on marine flora and fauna. Published literature on the biological effects of marine pollution revealed that the effects and distribution of marine pollutants have been increased significantly. This chapter focuses on better understanding of the toxicity evaluation of marine biota and has been divided into four main sections: (i) categories of marine pollutants affecting marine flora and fauna (ii) pollutant sources, routes of exposure and toxicological impacts on marine organisms (iii) impacts of pollutants specifically on marine flora (iv) bioassay studies at the organism level discussing marine toxicity.

Keywords: Marine Pollution, Toxicological Impacts, Plastics, Oil Spills, Bioassays, Bioaccumulation, Biomarkers.

INTRODUCTION

According to the United Nations Convention on the Law of the Sea, pollution is defined as the introduction of substances or energy directly or indirectly into the marine environment, which is likely to result in toxic impacts, for instance, harm to living resources and marine life, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of the

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sea water. Williams (1996) declared that there is only one type of pollution exists that is marine pollution, because every pollutant, whether in the air or on land ultimately sinks up in the ocean. The main sources of pollutant emissions in marine are human settlements and resource use, such as industrial development, urbanization, agricultural activities, tourism and infrastructural development and construction, Contaminants that pose major threats to marine flora and fauna are anticipated as oil spills and plastic debris (Islam and Tanaka, 2004).

Marine environment is considered as the dynamic and diverse network of habitat for a number of species, consequently many complex physical and ecological processes take place that interact with humans and their activities at many levels (Islam and Tanaka, 2004). Marine habitats with associated communities are classified into diverse ecosystems, for instance, salt marshes, open ocean, coral reefs, deep sea and shores, *etc.* Albeit, they are all linked with each other and the impacts on one ecosystem can affect others. Evaluating the impacts of pollutants in the marine environment, the function and structure of ecosystem are considered as important components. The profit human gains from different ecosystems are known as ecosystem services that include, fish, shellfish and other seafood's we consume. The other ecosystem services include recreational, economic and aesthetic benefits we derive from the sea (Barbier *et al.*, 2011).

The marine planktons of open oceans contribute a lot in the preservation of environment by transferring carbon to the deep sea, thus help in the maintenance of our atmosphere. Apart from this, open oceans and deep seas are also habitat to many fish that are being caught for food. Furthermore, marine planktons are the main source of food for young fish and many other marine species and capture sediments and organic waste that runs off the land (Raven *et al.*, 2005). A few decades back, anthropogenic activities have severely affected marine life, for instance, mining activities *i.e.* copper and gold mining. These all pollutants interact with the life cycles of many marine organisms and severely affect their life cycle (Harley *et al.*, 2006).

The list of flora and fauna exposed to marine pollution and severely affected are outlined in Table **1**.

Table 1. Fauna and Flora of marine biome exposed to marine pollutants.

Fauna		**Flora**
Green Sea Turtles	Tiger Shark	Dead Man's Fingers
Manatees	Fish	Green Feather
Parrotfish	Sailfish	Halimeda
Hermit crabs	Mahi-mahi	Leafy Flat-Blade

CATEGORIES OF MAJOR MARINE POLLUTANTS

Over the past few decades, marine pollution has become a major concern around the globe (Griffit *et al.*, 2008). Contaminants, such as oil-based products, pesticides, fertilizers, heavy metals, accidental oil spills, and plastic materials, have made survival of marine organisms difficult. Table **2** summarize a range of marine pollutants along with their sources and effects on marine life. Additionally, the percentage of pollutants entering the oceans annually is illustrated in Fig. (**1**).

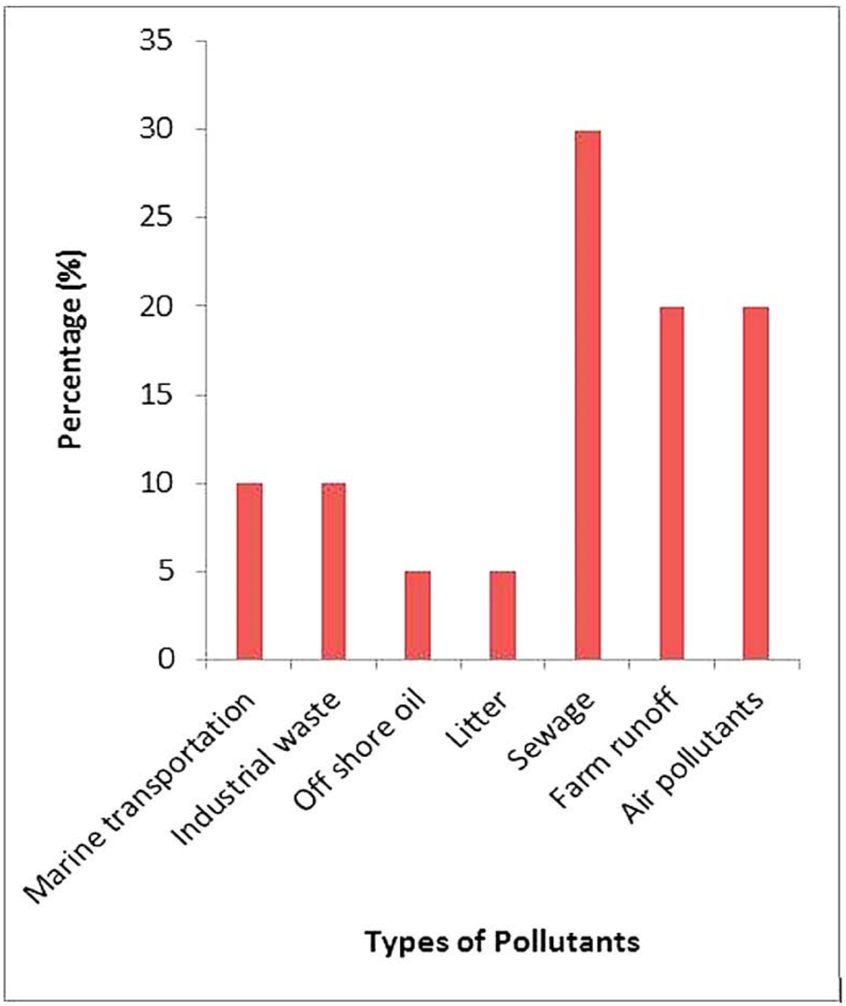

Fig. (1). Percentage of the total number of pollutants entering the oceans annually. This figure is developed by extracting information from the international report of the coastal cleanup (The Ring Leaders Programme, International Coastal Cleanup 2015).

CHAPTER 11

Marine Medaka (*Oryzias melastigma*) as a Model System to Study Marine Toxicology

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Abstract: Marine medaka (*Oryzias melastigma*) has been recognized as an ideal marine model fish widely used in the estuary and marine toxicological studies because of multiple favorable attributes, such as small size, short generation cycle, transparent embryos, sexual dimorphism, ease of maintenance, and wide range of salinity and temperature adaptations. Many studies have been conducted on both wild-type and transgenic fish *O. melastigma* model to evaluate the adverse effects by selecting specific biomarkers of the estuary and marine environmental pollutants. This review provides a recent research progress of the physiological effects and responsive biomarker of *O. melastigma* caused by various marine pollutants, including heavy metals, endocrine disruptors, and organic pollutants. Of note, this chapter summarizes the progress on whole-genome sequencing of *O. melastigma*, and promotes novel insights into the use of *O. melastigma* in future toxicity screening studies, targeting genetic biomarkers that highly activated by marine chemical pollutants using cutting-edge gene editing technique and bioinformatics system.

Keywords: Endocrine Disrupting Cmpounds (EDCs), Environmental Xenobiotics, Heavy Metals, Organic Pollutants, Transgenic Fish, Toxicology.

INTRODUCTION

In the past few decades, due to the rapidly increasing pollution in the marine ecosystem, several aquatic organisms have been chosen as suitable environmentally relevant models for ecotoxicity research. Zebrafish (Danio rerio) and Japanese medaka (*Oryzias latipes*) have been commonly used as fish models for eco-toxicological studies in the freshwater environment (Dodd, Curtis, Williams, & Love, 2000; Wittbrodt, Shima, & Schartl, 2002). However, a scarcity is existing related to the fish models that can be used for marine toxicological ass-

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essment, and marine medaka (*Oryzias melastigma*) is one of the best available options. In classification, marine medaka (*O. melastigma*) and Japanese medaka (*O. latipes*) belong to the Beloniformes order, Adrianichthyidae family, and *Oryzias* genus. *O. melastigma*, also known as *O. dancena* or Indian medaka, generally live on the coasts of China, Korea, Japan, and India. They provide many advantages: 1) small size of adults (2-3 cm); 2) short generation cycle (3-4 months); 3) transparent embryos; 4) distinct sexual dimorphism; 5) ability of spawn daily; 6) a wide range of salinity and temperature adaptation. These advantages make them easy to breed in the laboratory and sensitively respond to diverse chemicals. Therefore, *O. melastigma* is considered a promising model organism for marine and estuarine ecotoxicological study (Kim *et al.*, 2016).

Recently, many ecotoxicological studies have been conducted using *O. melastigma* as a fish model due to their bioavailability and sensitive toxic response, such as neurotoxicity, embryotoxicity, cardiac toxicity, immunotoxicity, endocrine disruptive effect, and metabolism alteration after exposure to contaminants and other environmental stressors. It is well known that the first transgenic fish were produced in China in 1985 (Zhu, He, & Chen, 1985). For the ecotoxicological risk assessment, transgenic fish have been applied to screen and monitor aquatic contaminants, because they can offer more advanced and integrated systems for the study of toxic mechanisms (Lele & Krone, 1996; Nerbert, 2002). Similarly, fluorescent protein reporter (*e.g.* GFP, RFP) are able to monitor pollutants by emitting the real-time fluorescence signal in live embryos and organisms. Furthermore, the expression levels of heat-shock protein, *cyp1a*, and vitellogenin (Vtg) can be used to monitor the exposure risk of heavy metal, persistent organic pollutants, and estrogen or estrogen-like pollutants, respectively. Taken together, this review summarizes the finding of the wild-type and transgenic marine medaka (*O. melastigma*) that used for marine toxicological studies, and highlights the health effects after exposure to various marine pollutants, such as heavy metals, endocrine disruptors, and organic pollutants.

Embryonic Development of *O. Melastigma*

Commonly, the developmental stage of the embryos is determined by hour post fertilization (hpf) or days post fertilization (dpf). The embryonic development of medaka *O. latipes* was divided into 45 stages as described by Iwamatsu (Iwamatsu, 2004). Chen *et al.* divided the embryonic development of *O. melastigma* into 8 stages and 33 substages on the basis of the development of medaka *O. latipes* (Bo, Cai, Xu, Wang, & Au, 2011). Darve *et al.* described 24 developmental stages of *O. melastigma* according to the morphological differences (Darve, Wani, Indulkar, & Sawant, 2013). Chen *et al.* investigated the embryonic development of *O. melastigma,* and particularly observed the brain, eye, heart, pectoral fin, and the trunk muscle by using *in situ* hybridization and immunostaining technique (Chen X *et al.*, 2011). As shown in Fig. (**1**), at the initial egg stage, the egg is surrounded by a thick chorion. There is a narrow space between chorion and vitellus. Short villi are seen over the whole surface of the chorion. Oil droplets are embedded at random in the cortical cytoplasm. At the early morula stage (4 hpf), blastomeres are appeared at the animal pole of the egg. At the late gastrula stage (21 hpf), the enveloping layer entirely covers the yolk sphere. At 6 somite stage (35 hpf), the small otic vesicles can be observed, and three regions of the brain (fore-brain, mid-brain, and hindbrain) are well defined. At 34 somite stage (80 hpf), about 3/4 of the yolk sphere is encircled by the embryonic body, and the pigmentation of the melanophores preliminarily appears in the eyes. At heart development stage (145 hpf), melanophores are distributed on the whole eyes, and the heart is developed.

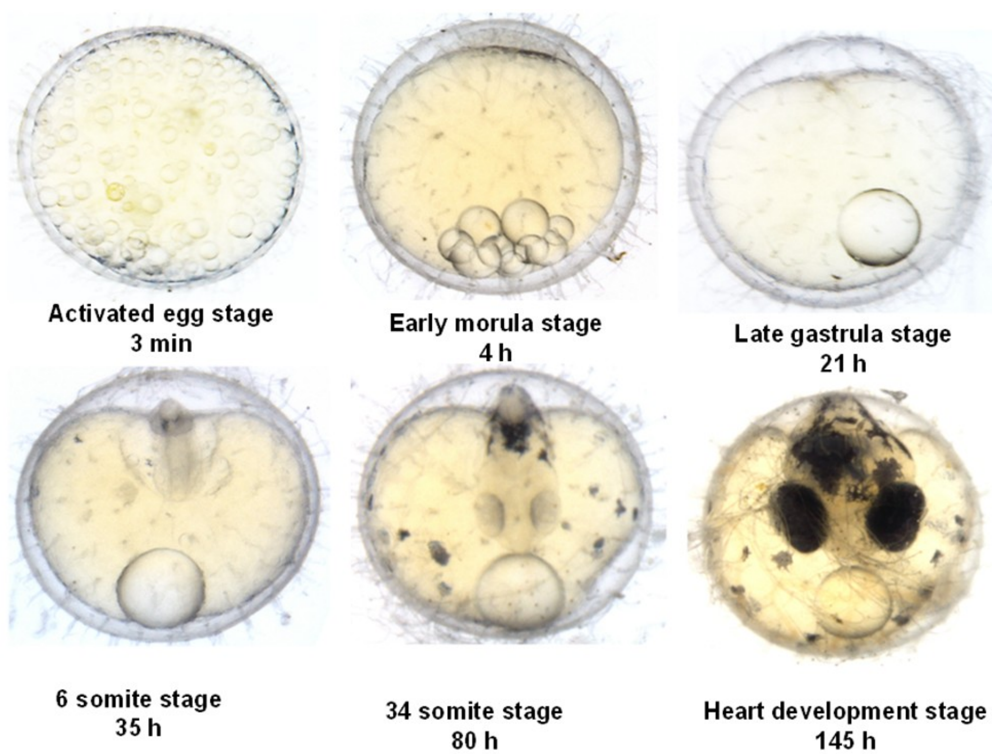

Fig. (1). Embryonic development of marine medaka *O. melastigma.*

Whole Genome Sequencing of *O. Melastigma*

Since the embryos of medaka *O. latipes* at early development stage are extremely sensitive to pollutants or stressors of seawater (Tian *et al.*, 2014; Tseng *et al.*, CHAPTER 12

Problems of Invasive Species: A Case Study from Andaman and Nicobar Islands, Andaman Sea, India

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Abstract: A fauna or flora that was not native to the particular environment and caused harm by its proliferation was considered an invasive species. This is one among the major concern for protecting the biodiversity as well as economic loss. However, in the marine environment, this problem is further complicated due to less barrier and other common factors, such as movement of the vessels, the release of ballast waters by the tankers, and water currents. The marine Island environment concern has gain significance due to the larger distribution of benthic faunal community and its biodiversity. A study was carried out to understand the status of this problem with reference to Andaman island environment and a probable mechanism to be implemented and their status was discussed in this article.

Keywords: Invasive Species, Marine Environment, Andaman and Nicobar Islands, Andaman Sea, India.

INTRODUCTION

An invasive species has been defined as a life form, which is not native to the particular environment, but proliferates and causes harm to the native species. This problem has been considered one of the major threats to any ecosystem with reference to the environment, economy, or to human health or combination of above. Colautti *et al*., (2004) very widely discussed the terminology "Invasive" species and its use of different organisms. However, in general terms, it is mostly accepted that an invasive species is a species that is introduced intentionally or unintentionally in an environment and proliferates causing damage to the introduced environment in all the aspects. The intentional introduction may happen through the imported live species in fisheries or aquaculture practices or

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aquarium that have been introduced into the natural system due to a certain purpose or improper management or deliberate actions. However, in the case of unintentional introduction, it is concerned with the ships or boat hull carry as biofoulers, ballast waters release or connecting major water masses by artificial means leading to the species migration from their original location to new locations. The United States estimated that out of 750,000 species around 50,000 species of plants, animals and microbes have been introduced as reported by Pimentel *et al.,* (2000). The estimated cost of loss due to this invading species was about USD 120 billion per year (Pimentel, 2005). The invasive alien species study in India was far behind with reference to its intensity, scale, and scope, due to its high taxonomic diversity and large distribution area (Khuroo *et al.,* 2007; Peh, 2010; Adhikari *et al.,* 2015). The invasive or alien species are introduced into the coastal or marine area by many different ways, such as shipping, mariculture, oil and gas exploitation, tourism, and aquarium trade. The present article deals with the status of invasive species in the tropical island coastal or marine area, specific to off Andaman and Nicobar Islands.

STATUS OF INVASIVE SPECIES IN ANDAMAN AND NICOBAR ISLANDS

Marine environment has the potential to invade by different species by the process of movement of current, migration of strong swimmers, external hull fouling, holes or crevices in the wooden hull of a ship, ballast tank waters, catastrophic events such as tsunamis, storm surges, *etc*., translocate the macro-fauna larvae, cysts, eggs, including fauna or flora itself to the alien environment. Even though the introductory environment is alien, the introduced species survive and thrive to become a threat to the native species. This review work identified different species as an invasive species and tabulated (Table **1**). Overall 182 species have the potential to invade into the alien environment by different means and survived to cause a threat to the native species. The marine algae *Monostroma oxysperma* from the Phylum Chlorophyta is the most potential species in this group of flora. The dominant alien species reported from Phylum Cnidaria has around 65 species from the reported one. The Class Scyphozoa and Hydrozoa reported as highest influenced among these phyla and these two Classes alone represented 60 species as invasive in nature. Over and above two more classes also had this trait, *i.e.* Class Cubozoa and Staurozoa. Between these Classes, 4 Orders once again represent the highest species showing invasive nature. They are Order Rhizostomeae (21 Nos.), Semaeostomea (10 Nos.) belonging to the Class Scyphozoa and the Order Leptothecata (15 Nos.) and Order Anthoethecata (7 Nos.) belonging to the Class Hydrozoa were found dominant in the total species identified in this Phylum. The Class Anthozoa has three Orders: Alcyonacea (1 No.), Scleractinia (1 No.), and Actiniaria (1 No.) with a representation of one species each under this trait.

Next to Phylum Cnidaria, the Phylum Chordata was identified having maximum invasive characteristic among the reported invasive species. Under the Phylum Chordata, the Class Ascidicea represented 39 species belonging to different Families. Out of these Families the Family Styclidae (9 Nos.) and Didemnidae (8 Nos.) were found dominant and remaining 4 Families Ascididae, Pyuridae, Perophoridae, and Polycitoridae have their own contribution to this activity.

The Phylum Arthropoda comes next to Phylum Chordata, which show 36 species having the invasive characters. This Phylum is represented by two Classes Malacostraca and Hexanauplia with three Orders each for their species distribution with invasive characters. The Orders are as follows: Isopoda (6 Nos.), Amphipoda (10 Nos.) and Decapoda (6 Nos.) from the Class Malacostraca and Sessilia (7 Nos.), Calanoida (6 Nos.), and Harpacticoida (1 No.) from the Class Hexanauplia.

Other than the above Phyla, there are other five Phyla, which also provide their share in the category of invasive species. They are Phylum Annelida (16 Nos.), Mollusca (8 Nos.), Ctenophora (4 Nos.), Bryozoa (6 Nos.) and Entoprocta (1 No.). Phylum Annelida represented five Orders: Sabellida (3 Nos.), Phyllodocida (4 Nos.), Terebellida (1 No.), Eunice (4Nos.), and Spionida (4 Nos.). In Phylum Mollusca, species belong to two Classes and three Orders. They are Class Gastropoda with Order Nudibranchia (1 No.) and Class Bivalvia with Orders Myida (6 Nos.) and Mytilidae (1 No.). The species identified under Phylum Bryozoa consists of one Class Gymnolaematidae and two Orders: Ctenostomatidae (1 No.) and Cheilostomatidae (5 Nos.). The Phylum Entoprocta is represented by only one Family, *i.e.* Barentisiidae with *Barentia ramosa* as the only invasive species.

INVASIVE SPECIES THREAT

Invasive species are the second largest threat to biodiversity next to environmental degradation. The anthropogenic trans-national and domestic movement leads to introduce inadvertently as well as deliberately in an environment for vanity or profit. Pimentel (2007) reported that 480,000 alien species were introduced all over the world, and these countries, such as UK, USA, South Africa, Australia, India, and Brazil, have three-fourths of these species.

The invasive species science is limited, so understanding of their impact on the environment is also limited. How a new species invades into a new habitat? It is well known that a species introduced in an environment should cross the barriers such as survival, establish its base population, reproduction and explosion then

CHAPTER 13

Problems of Invasive Species

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Abstract: As indicated by the World Conservation Union, obtrusive invasive species are the second most critical danger to biodiversity, after natural disasters. In their new environments, invasive alien species move to become predators, contenders, parasites, hybridizers, and affect native plants and creatures. Higher rates of multiplication, less normal predators and capacity to flourish in various conditions are some basic qualities, which can make them hard to control. Marine environments are among the most important ecosystems both from a monetary and ecological point of view. The complexity of marine biological communities and their area postures challenges for administration, valuation, and the foundation of sound strategy to defend them for these invaders. Different procedures, for example, aquarium exchange, aquaculture, channel development, dispatching, and live fish exchange have achieved the dispersal of creatures. These dispersal systems result generally in the modification of biodiversity and achieve monetary misfortunes on fisheries. Starting with a short prologue to intrusive species, this section investigates a couple of vital life forms that represent a genuine risk to the earth and the mode by which they spread. This section additionally clarifies the different effects caused by these species and the courses by which they could be controlled.

Keywords: Alien Species, Biodiversity, Invasive Species, Marine Ecosystem.

WHAT IS AN INVASIVE SPECIES?

A greater part of the earth is covered by water in which oceans and seas contribute 70% and coastline covers up to 1.6 million kilometers. The resources provided by oceans and coasts are essential for the survival and well-being of humankind in many ways. Many people not only utilize seafood as a food but seaweed provides livelihoods through sustainable harvesting. Some marine organisms, such as corals, kelp, mangroves and sea grasses, have the ability to reshape the marine environment that promotes further habitation for other organisms. Marine organisms have a chance of moving around the world with ocean currents or by attaching themselves to driftwoods (De Poorter, 2009). Development in trade and shipping has opened gate for speedy transport of the organisms too. A large

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volume of these organisms move around the world rapidly. It is estimated that 10 billion tons of ballast water carries 7,000 species every day, which are transferred worldwide every year (Ruiz *et al*.,1997). The term “invasive” means tending to spread very quickly and undesirably or harmfully. An invasive species is an introduced or alien species that is not an inhabitant of a precise location (Carlton, 1999). It can be a plant, fungus, or animal species that spreads to an extent supposed to cause damage to the environment (Pimentel *et al*., 2001). Around the world, a total of 480,000 invasive species have been recorded. The primary characteristic of invasive species is that it is rapidly reproducible and it spreads antagonistically. In North America, nearly 500 species have been transported around the world every day (Carlton, 1999; Fofonoff *et al*.,2003).

The most destructive of these invaders can displace native species, alter the community structure, food webs, and modify nutrient cycling and sedimentation processes. Alien invasive species have harmed economies by lessening fisheries, fouling ships structures, and blocking intake pipes. A couple of animal varieties also influence human being by causing infection (Ruiz *et al*.,1997). Invasive species expand frequently and cause allelopathy, by contaminating or causing illness to native species by acting as vectors, or hybridize them. These invasive species can change entire biological communities by adjusting hydrology, supplement cycling, and other environment forms. Regularly similar species that undermine biodiversity likewise make grave harm different characteristic asset businesses. Not all invasive species are detrimental. In numerous territories, many species are introduced for food and nourishment.

Causes of the Dispersal of Marine Organisms

Multiple processes influence the dispersal of marine organisms. Aquarium trade, aquaculture, canal construction, shipping, and live seafood trade may be the primary reasons for the dispersal of organisms. These dispersal strategies result mostly in alteration of biodiversity and bring about economic losses on fisheries.

The construction of canals came into existence in the late 1800s and early 1900s to give ships easier way around land obstacles. The Panama canal and Suez canal are the two major canal that play a major role in providing pathway for the exchange of marine invasive species The Panama Canal, which connects the Atlantic and Pacific Oceans in 1914, provides a chiefly significant model system for marine invasions in the tropics (Ruiz *et al*., 2009). The other one, the Suez canal connects the Mediterranean sea to the Red sea. This canal has paved way for the highly noxious jellyfish *Rhopilema nomadica*, to reach the Mediterranean Sea in the 1980s. Artificial canals provide a link to connect two drainages that have been blocked by natural barriers to prevent the exchange of organisms.

Construction of the Erie Canal has modified the scenery of New York State altering its social and economic stature. Within the canal and the water it connects, it has brought many species that are not indigenous. Eurasian watermill foil, a fast-growing aquatic plant forms a thick mat growth, which leads to the suffocation of the native plant species. Zebra mussels, Asian clam, Round goby, Sea lamprey, and water chestnut are few species that are found to be invasive in these areas.

Thus, they act as a key reason for the introduction of alien species through drainages. A few examples of organisms that bypassed natural barriers through the construction of canals include *Petromyzon marinus* in the upper great lakes *via* the Welland canal. The round goby, *Neogobius melanostomus* made its way through the Chicago Shipping and Sanitary canal to the Mississippi basin and spread throughout the country. "The shipjack herring, *Alosa chrysochloris* probably gained way into Lake Michigan *via* the Chicago Shipping Canal (Fago, 1993). The river darters, *Percina shumardi* (Becker, 1983), the gizzard shad, *Dorosoma cepedianum* (Miller, 1957) are also the best example that followed this route of invasion to inflate their ranges.

Since people started to cruise the oceans, different species have been going the world over with them. These are not constrained to valuable plants and creatures, nor to bugs, for example, pathogenic operators or rats, yet additionally incorporate critical quantities of marine living beings. Authentic records and archeological discovers demonstrate that the cruising boats of the early travelers were colonized by up to 150 distinctive marine life forms that lived on or in the wooden frames, or utilized the metal parts, for example, stay chains as a substrate. On the off chance that the development turned into an irritation, the life forms were scratched off while adrift.

In different cases, the creatures stayed on the decaying frame of a ship when it was rejected and could never again be repaired. It is not really astonishing then that numerous wood-exhausting species, for example, the shipworm *Teredo navalis* are found far and wide today. Be that as it may, it is not any more conceivable to decide if these species were at that point cosmopolitan before the European voyages of revelation. Expanding quantities of marine life forms are currently transported over the seas because of globalization, exchange, and tourism. It is evaluated that the water in counterweight tanks used to balance out vessels is separated from everyone else in charge of transporting a huge number of various species between topographically inaccessible locales. The vast majority of these exotics pass on amid the outing or at the goal, while just a little portion can effectively duplicate and shape another populace. In any case, an investigation of six harbors in North America, Australia, and New Zealand has demonstrated

CHAPTER 14

Disturbance and Biodiversity of Marine Protected Areas

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Abstract: The conservation of biological diversity and the sustainable use of its components are the major objectives of the Convention on Biological Diversity (CBD). To achieve these objectives, many marine protected areas (MPAs) were identified and developed. The success of these protected areas depends upon several factors of local concern. The failure of coastal and marine biodiversity protection was mainly caused by the environmental changes influenced by anthropogenic activities, overexploitation of resources, habitat loss because of developmental activities, and natural change in climate. This chapter highlights the status of these activities in the island environment and provides potential strategies for its protection by mainstreaming biodiversity with people's participation.

Keywords: Marine Protected Areas, Mainstreaming, Biodiversity, Andaman and Nicobar Islands, India.

INTRODUCTION

Marine Protected Areas (MPAs) are regarded as one of the global thrust that has emerged towards a holistic management approach that takes the entire ecosystems into account with essential tools for implementation (Currie *et al.*, 2008). As per IUCN (2008), the definition of MPA is "A clearly defined geographical space, recognized, dedicated and managed, through legal or other effective means, to achieve the long-term conservation of nature with associated ecosystem services and cultural values". MPAs are an effective way of protecting and conserving the marine biodiversity and maintaining the productivity of the oceans with their cultural and historical heritage for today and future generations (Laxmilatha, 2015 and Brander *et al.*, 2015). MPAs provide necessary insights with several threats and consequences, of which some may be prevented or some may be unavoidable

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with concern to tourism influx and coastal urbanization (Gray, 2010). Although conservation fact is important for MPA, there are severe impacts on the coastline and marine environment with direct antagonism with traditional small-scale fishing and other recent activities like recreational fishing and aquaculture farm due to the above said factors.

The FAO (2011) technical guidelines for Responsible Fisheries defined MPA as: “any marine geographical area that is afforded greater protection than the surrounding waters for biodiversity, conservation or fisheries management purposes will be considered an MPA". The marine ecosystem is extremely diverse and attributed to the geomorphology and climatic variations along the coast, leading to recognition of the role of MPAs as one of the important step towards increasing the effectiveness of MPAs under the CBD 2020 agenda (Simard *et al.*, 2016), as Oceanic climatological changes can lead to a profound change in marine ecosystems. Molenaar and Elferink (2009) provided a short overview on the global regime with reference to the designation, identification and the regional cooperation on the protection of the marine environment of MPAs, including recent developments in the worldwide scenario. Reker (2015) discussed how best to evaluate the effectiveness of MPAs and regulate their effectiveness in protecting biodiversity across Europe's seas. Alino (2018) mentioned about marine passages that are also considered as a strategic zone, facilitating the exchange of materials and connectivity of various marine biogeographic regions.

Dorel *et al.,* (2015) worked on the PANACHE (Protected Area Network Across the Channel Ecosystem) project, which aimed for a coherent approach for a marine protected area (MPA) on both sides of the Channel, involving two nations - France and the United Kingdom, with their management judgments but also with the common desire to address MPAs in a genuine and effective way. The review work done by Jones *et al.,* (2011) outlined the policy agenda with regards to the main components of the emerging UK marine protected area (MPA) for creating a marine conservation zones (MCZs) and marine special areas of conservation (SACs), leading to increase in 27% of MPAs in English waters. Sink (2016), studied the key aspects of the initiative to explore and unlock the economic potential of South Africa’s marine and coastal environment. As agreed at the Rio ‘Earth’ Summit in 1992, marine sites, together with terrestrial and freshwater sites, form a part of the European Natura 2000 network of protected areas. The Marine Strategy Framework Directive (2008/56/EC) requires Member States to include in their programs in the establishment of MPAs, thus contributing to one of the key objectives of the Convention on Biological Diversity (CBD 2016). The review work was done by the European Commission in 2015, where they found that MPAs covered 6% of the European Seas by 2012, with an aim to reach 10% by 2020, even the economy and other benefits of the Natura 2000 network were also discussed (Jones and Burgess, 2005).

A contrast to the merits of MPAs, Rajagopalan (2008), came up with work saying that, though MPAs have become a tool that limits, prohibits and regulates the use-pattern and human action through certain frameworks of rights and rules, where essentiality of social components is needed to be considered for a long-term benefit of coastal communities. The existing studies say that least importance was given to the social aspect than the ecological and biological factors. Many times, in the past, over-exploitation of the world's fishery resources has been observed with regards to traditional communities. UK fishers fear that MPA restrictions beyond six nautical miles might be unilaterally imposed on them, a concern with the recent banning on pair trawling by English vessels to protect cetaceans in the south-west approaches (De Santo and Jones, 2007). Most of the MPAs in the Philippines have been established for the purpose of sustaining fisheries utilization in the adjacent fishing areas hampering the livelihood of the prevailing communities and other stakeholders in that area. The first empirical analysis was studied by Leisher *et al.,* (2007) with regards to the link between biodiversity conservation initiatives and poverty reduction. The procedure and outcome of the 2014 World Parks Congresses (WPC), which emphasized on the role of people (in particular, fishery folks) in marine conservation was studied by Charles *et al.*, (2016). This article clearly mentioned that inclusion of the human dimension in any evaluation of management practices, without this factor the MPA activities affect the local livelihoods of fishing communities (Lester and Halpern, 2008), Jones (2008, 2009). Many conservation NGOs had campaigned for the implementation of the Marine Act of a statutory, practicing no-take MPA setting ban on extractive and disturbing activities involving 30% of the national marine area, in keeping with previous recommendations (RCEP - Royal Commission on Environmental Pollution, 2004). Highly protected MPAs produce results rapidly, but benefits build up for decades. A good MPA should give protection to a broad spectrum of biodiversity, not just a handful of species. Therefore, documenting and analyzing the experiences and views of local communities, particularly fishing communities, with respect to various aspects of MPA design and implementation would help in integrating the MPA programme (Sanchirico, 2000; Fraga and Jesus, 2008). The Marine Act does not include a no-take MPA target, nor does it require any no-take MPAs, but it maintains the flexibility to ensure the right level of protection in each case, based on the evidence available (Appleby and Jones, 2012).

Chuenpagdee *et al.,* (2012) did a case study stating that MPA is not a simple management tool or an easy technical fix because of complexities existing within the process, which may surpass the expectations of promoters and stakeholders. The exponential increase in MPAs and its complexity involved within the marine

CHAPTER 15

Monitoring of Environmental Indicators and Bacterial Pathogens in the Muthupettai Mangrove Ecosystem, Tamil Nadu, India

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Abstract: Aim of this study focused on monitoring the environmental indicators and bacterial pathogens level based on the aquaculture practices that impacted on the Muthupettai mangrove ecosystem. Water samples were collected at five stations during the pre-monsoon season, and samples were analyzed by standard methods. The results of environmental parameters were shown as follows: temperature (31.4-33.2 °C), pH (7.9-8.6), EC (12-14 mS/cm), TSS (4650-5500 mg/l), TDS (36400-41650 mg/l), TS (41250-46450 mg/l) and DO (2.2-4.1 mg/l); total heterotrophic bacteria (72-294 102 cfu/mL), total coliform bacteria (9-150 101 cfu/mL), fecal coliform bacteria (4-135 101 cfu/mL), total *Enterococcus bacteria* (1-10 101 cfu/mL) and *E.coli* (2-46 101 cfu/mL); and the Pathogens: total *Vibrio* species (1-6 101 cfu/mL), total *Salmonella* species (1-3 101 cfu/mL), total *Shigella* species (1-2 101 cfu/mL), and total *Klebsiella* species (1-39 101 cfu/mL). These results were more vulnerable to the ecosystems and highly exceeded the standard permissible limits of the WHO, EU, and CPCB. Continuously discharges of untreated aquaculture effluents deteriorated the mangrove ecosystem qualities. Therefore, there is a need for a regular monitoring and systematic waste management from aquaculture, which can develop sustainable aquaculture and strictly follow the recommended management rules and regulations of aquaculture practices at national or regional level. Further research needs to improve the ecosystems qualities and maintain the rich biological diversity in the Muthupettai mangrove ecosystem.

Keywords: Physico-Chemical, Indicators, Pathogens, Shrimp Culture, Mangrove Ecosystem.

INTRODUCTION

Mangrove forests are most productive ecosystems, and covered with the 15 million hectares of forests at the interface between terrestrial, estuarine and mar-

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ine systems in the tropical and subtropical regions of 123 countries (Food and Agriculture Organization, 2007; Queiroz, 2017). Mangrove forests are the group of vascular plants, having special morphological, physiological and non-visible adaptations and support diverse groups of the ideal nursery and breeding ground to rich biodiversity, ranging from bacteria, fungi and algae through to invertebrates, birds, and mammals (Kantharajan *et al.*, 2017). They are provided the services for the supporting coastal livelihoods of communities with raw material and foods, coastal protection, soil erosion control, water purification, fisheries maintenance, and carbon sequestration, as well as recreation, education and research in globally (Barbier et al, 2011). The mangrove ecosystems services economical cost rate was at least US $1.6 billion and carbon sequestration rate 1.15-1.39 t/ha (6.5 billion tons) every year in around the world (Nellemann and Corcoran, 2009).

Over the past few decades, unregulated human development activities of the construction of ports, marinas, housing, and shrimp farms were the rapid level of the mangrove forests clearance in around the world (Bernardino *et al.*, 2017). The recent estimation report was (26%) 3.6 million ha mangrove forests loss (Food and Agriculture Organization, 2007, 2010; Queiroz *et al.*, 2013; Guzmán *et al.*, 2003; Ahmed *et al.*, 2017). 38% of mangrove areas were degraded and transformed the coastal aquaculture practices (1.4 million ha), shrimp culture 0.49 million ha (14%) and other forms of aquaculture in worldwide (Queiroz, *et al.*, 2017; Kauffman *et al.*, 2014). The unplanned and unregulated shrimp farming is strongly widespread destruction of mangroves in coastline countries, particularly Bangladesh, Brazil, China, India, Indonesia, Malaysia, Mexico, Myanmar, Sri Lanka, the Philippines, Thailand, and Vietnam losses more significant (Joffre and Schmitt, 2010; Ahmed and Glaser, 2016; Barraza-Guardado, 2013).

The shrimp industry is one of the most important factors to degrade the mangroves, discharging of effluents and water exchanges are multifarious impacts faced in the coastal ecosystem qualities (Kauffman *et al.*, 2014; Barraza-Guardado *et al.*, 2013). The effluent enter into the ocean can increase the continuously organic and inorganic matter, suspended solids and pathogens (Barraza-Guardado *et al.*, 2013; Cardoso-Mohedano *et al.*, 2018). Shrimp cultured wastewater directly affects the oxygen depletion, reduction of transparency, and eutrophication, which alters the benthic organisms of macrofauna populations and seawater qualities (Gengmao *et al.*, 2010; Ferreira *et al.*, 2011). The seawater contamination directly affected the rich biodiversity levels of the mangrove ecosystems, particularly more concentered the bivalves, crustaceans, fish, and birds (Sara *et al.*, 2011).

The seawater microbial contamination is a huge amount of the pathogens accumulation in filter feeding organisms of the bivalves vigorously affected the several infectious diseases to humans (Almeida and Soares, 2012). As the consumption of contaminated shellfish constitutes a potential risk to public health their hygiene-sanitary control is extremely important and legislated (Almeida and Soares, 2012; World Health Organization, 2010). Adequate legislation for safeguarding consumers can minimize the probability of shellfish microbial contamination. In Europe, the Directives 2006/113/CE (Anonymous, 2006) and 2004/41/CE (Anonymous, 2004) are guidelines to control the levels of microbiological indicators for both shellfish and overlying waters (Almeida and Soares, 2012; Anonymous, 2006). In India, mangroves occur on the West Coast, on the East Coast and on Andaman and Nicobar Islands (6,749 km^2), the fourth largest mangrove area in the world. According to the Government of India survey 40% (22 400 ha) was degraded conditions. Shrimp aquaculture is responsible for about 80 percent of the conversion of mangrove and this impact surrounded the seawater highly contaminated the coastal ecosystems (Mandal and Naskar, 2008). The Muthupettai mangrove ecosystem is a one of most productive environment in Tamil Nadu, but recent years rapidly increased the shrimp industries generated the untreated wastewater discharges was highly polluted the mangrove ecosystem natural behaviors and along with the seawater qualities. Here, very few studies only monitored seawater quality level in the coastal environment. Therefore, we are focused on the mangrove ecosystem near build the number of the shrimp culture pond wastewater discharges zone of the seawater and along with the towards different zone seawater physicochemical, microbiological indicators and pathogens level estimated in the Mutthpettai mangrove ecosystems.

MATERIALS AND METHODS

Study Area

Muthupettai mangrove ecosystems are situated at the southernmost end of the Cauvery delta connected to Palk Strait, which opens to the Bay of Bengal (Lat. 10° 23' 44.52”N: Long. 79° 29' 42” E) (Fig. **1**). The mangrove ecosystem covered with the 6800 ha, which the water spread area covers approximately 2720 ha. The mangrove ecosystem was declared as reserve forest since 1937. The mangrove environment is receiving a large amount of the freshwater from the river of Cauvery tributaries of the Paminiyar, Koraiyar, Kilaithangiyar, Kandankurichanar and Marakkakoraiyar rivers. Anthropogenic activities of aquaculture practices of 134 ha (1.75 h shrimp culture) major environmental issues of the Muthupet mangrove ecosystems (Jayanthi, 2010).

CHAPTER 16

Marine Microbial Mettle for Heavy Metal Bioremediation: A Perception

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Abstract: Marine environment gets polluted due to a range of contaminants including heavy metals. Various physicochemical methods available conventionally for heavy metal remediation suffer from one or the other limitation. Bioremediation is an encouraging solution to heavy metal pollution. Microbes are endowed with diverse potentials to combat heavy metal stress. In this chapter, major sources and effects of heavy metals, factors influencing heavy metal bioremediation, the microbial mechanism for heavy metal detoxification and transformation and involvement of marine microorganisms in heavy metal bioremediation have been discussed.

Keywords: Heavy Metal Pollution, Bioremediation, Marine Environment.

INTRODUCTION

Oceans provide food, recreation, and transportation, which sustain a substantial portion of world's economy (Ansari *et al.*, 2004). Over-population, urbanization and increased industrialization have significantly impacted this largest ecosystem as waste from any source ultimately finds its way to sea or ocean, besides this, pollution arises due to offshore drilling and related activities also (Gosai *et al.*, 2017; Gosai *et al.*, 2018a, b). Pollution of the marine environment poses ecological and economic pressures, because the marine environment holds fundamental importance owing to its biological productivity, geochemical cycling, and human utility (Dudhagara *et al.*, 2016 a, b; Gosai *et al.*, 2018 a, b). According to Article 1 (4) of the 1982 United Nations Convention on the Law of the Seas (UNCLOS), "pollution of the marine environment" is defined as "the int-

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roduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, which results or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of sea water and reduction of amenities" (UNCLOS,1982).

Domestic waste, agricultural waste, and industrial wastes are among the major marine pollutants. By and large the domestic and agricultural wastes are of similar composition worldwide, however, the composition of industrial waste varies significantly depending on the type of industry. A range of pollutants including polycyclic aromatic hydrocarbons (PAHs), heavy metals, other persistent organic pollutants (POPs), radioactive wastes and plastics *etc*. are contaminating the marine environment (Gosai *et al.*, 2017; Dudhagara *et al.*, 2016a, b).

In the sediments, the heavy metals are more persistent compared to organic contaminants such as petroleum hydrocarbons and pesticides. Moreover, they are mobile in sediments subjected to change in the pH and their speciation. So a fraction of the total mass can leach to aquifer or can become bioavailable to living organisms (Alloway, 1990; Santona *et al.*, 2006). Heavy metal poisoning can result from drinking-water contamination (*e.g*. Pb pipes, industrial and consumer wastes), intake *via* the food chain or high ambient air concentrations near emission sources (Lenntech 2004). In the past decade, Love Canal tragedy in the City of Niagara, USA demonstrated the devastating effect of soil and groundwater contamination on human population (Fletcher, 2002). The diffusion phenomenon of contaminants through soil layers and the change in mobility of heavy metals in aquifers with the intrusion of organic pollutants are being studied in more details in recent years (Cuevas *et al.*, 2011).

A range of physicochemical methods have been employed conventionally for removal of pollutants. However, these methods could not be a permanent solution, as they suffer from one or the other limitations. In this case, the involvement of microorganisms has been given tremendous importance to tackle this problem and microbial bioremediation has been in focus recently (Vala and Dave, 2017; Vala, 2018).

A combined pollution due to heavy metals and PAHs is also a matter of increasing concern these days (Liu *et al.*, 2017). Hence, the discussions in the present chapter are confined to microbial remediation of pollution arising due to some heavy metals as well as combined effects of heavy metals and PAHs as pollutants.

Major Sources of Heavy Metals

Industrial Effluents

Effluents released due to increased industrial growth are one of the major sources of heavy metal pollution. The coastal and marine environments receiving heavy metal-laden effluents have been the 'hotspots' for heavy metal contamination (Naser, 2013).

Sewage

The huge amount of sewage is discharged into the coastal and marine environment. Besides high suspended solids and the heavy load of nutrients, sewage discharges may contain heavy metals also and hence, affects life (Al-Muzaini *et al.*, 1999; Shatti and Abdullah, 1999; Singh *et al.*, 2004; Naser, 2013).

Dredging and Reclamation Activities

Dredging and reclamation activities diminish biodiversity, richness, abundance, and biomass of marine biota (Smith and Rule, 2001). Further, such activities mobilize increased levels of heavy metals leading them to enter foodweb components and hence posing threats to human health (Guerra *et al.*, 2009; Hedge *et al.*, 2009; Naser, 2013).

Toes *et al.*, (2008) carried out microcosm experiments with a view to simulating the influence of dredging in heavy metal-polluted sediments and observed that transient exposure to Cu and Cd resulted in prolonged modification of the indigenous bacterial community.

Desalination Plants

To meet the need for fresh water, desalinated seawater is harnessed especially in Arabian Gulf countries due to low precipitation and high aridity (Hashim and Hajjaj, 2005; Nazer 2013). Due to the discharge of reject waters from desalination plants on a daily basis to coastal and subtidal areas, increased levels of heavy metals have been observed in the vicinities of desalination plants along the Arabian Gulf coastline (Sadiq, 2002; Naser, 2010; 2012; 2013).

Oil Pollution

Activities pertaining to oil exploration, production, and transport contribute significantly to oil pollution (MEMAC, 2003). It has been reported that major oil spill during 1991 Gulf war has led to elevated levels of heavy metals (Al-Arfaj and Alam, 1993; Naser 2013). Table **1** shows sources of various heavy metals and

CHAPTER 17

Polycyclic Aromatic Hydrocarbons (PAHs): Occurrence and Bioremediation in the Marine Environment

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Abstract: Contamination by various hazardous compounds released due to sea-related activities has received great concern about the pollution of the marine ecosystem. Nowadays, polycyclic aromatic hydrocarbons (PAHs) are immerging as critical pollutant with context to the marine environment due to some distinctive properties, which makes them persistent organic pollutants (POPs) posing threat to the environment. PAHs make their way in marine environment through various natural and anthropogenic sources. Marine microorganisms have reported to be leading candidates for PAHs degradation. Recent advancements in genomics, proteomics, and metabolomics technologies have gathered significant increment in the knowledge of ecology, physiology and regulatory mechanisms of microbial communities involved in PAHs remediation. Morden technologies will be a vital approach to reveal the mechanisms involved in the bioremediation of pollutants and will offer more insights as yet more uncultivable microbial diversity attached with pollutant degradation.

Keywords: Bioremediation, Marine Environment, Polycyclic Aromatic Hydrocarbons.

INTRODUCTION

Over the preceding 60-50 years, marine environment has changed more hastily than in any other time period of the history by the human to comply with the vigorously growing demand for food, energy, fuel, and transportation. These changes have contributed to economic development and well-being but at the

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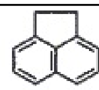
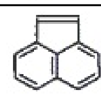
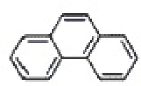
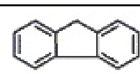
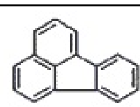
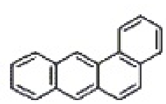
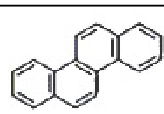
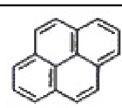
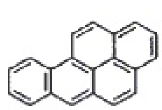
same time have made some unalterable loss to ecosystem diversity. Some common sources contributing in marine pollution are uncontrolled spew of untreated industrial wastes, various sea-based petroleum-related activities, agricultural and municipality run-offs, ship-breaking/recycling activities and spills/accidents during transportation (Dudhagara *et al.*, 2016a, Gosai *et al.*, 2018a). Majority of these sources contributes organic pollutants in the marine environment, amongst which polycyclic aromatic hydrocarbons (PAHs) these days are immerging as a critical pollutant of marine environment damaging the vital division of marine as well as terrestrial biota. Over the past decade, biodegradation has definitely immerged as the major acceptance for remediating PAHs contaminated environment (Dave *et al.*, 2014; Bhatt *et al.*, 2014). Potential marine organisms from the contaminated sites have proven to be the leading candidates for bioremediation of PAHs contaminated marine sites (Gosai *et al.*, 2018a, b; Sachaniya *et al.*, 2018).

Polycyclic or polynuclear aromatic hydrocarbons constitute a group of heterogeneous organic compounds comprising two or more fused benzene rings as their nuclei, which are arranged in linear, angular or cluster spatial configurations. As their name suggests, PAHs generally contain hydrogen and carbon as their atomic composition, but sometimes these atoms are substituted with oxygen, nitrogen, sulphur or sometimes a whole chemical reactive group in the benzene ring to form heterocyclic PAHs. Around 660 parent PAHs compounds solely consisting of conjoined benzene rings have been listed in the literature (Sander and Wise, 1997). These compounds can also be found occurring naturally not only on earth but also in the space, which are meant to be the indicator of possibilities of life throughout the universe.

These compounds hence have received great economic as well as the scientific concern due to their various deleterious structural and physicochemical properties. PAHs generally can be divided into two major groups. Those, having three or less than three aromatic rings are considered to be low molecular weight (LMW) PAHs and those having four or more than four aromatic rings are considered to be high molecular weight (HMW) PAHs. Diversity in the spatial configuration and size of these compounds result in a considerable discrepancy in their physicochemical properties. Different physical, solvation and molecular properties of some selected known PAHs are listed in Table **1**.

Generally, PAHs are lipophilic or hydrophobic in nature. Some of the LMW PAHs are partly soluble in the aqueous solvent. PAHs are highly photosensitive *i.e.*, they get decomposed when exposed to UV light as well as visible light. They are semi-volatile or have low volatility (Mackay and Callcott, 1998). Hydrophobicity or lipophilicity increases with the increase in the molecular weight as reflected by the increase in a number of aromatic rings (Ferreira, 2001). As a consequence of high hydrophobicity, HMW PAHs have higher tendency to

Table 1. Physical, solvation and molecular properties of 16 US EPA priority PAHs. Adapted and modified from [a]Larsson, 2013 and Ghosal *et al.*, 2016.

PAHs	Structure	Molecular Formula	Molecular Weight	B. Pt. (°C)	M.Pt (°C)	V.P. (mmHg at 25°C)	log Kow Value [a]	IARC [b]	EPA [c]
Naphthalene		$C_{10}H_8$	128.17	218	80.2	8.5×10^{-2}	3.36	2B	C
Acenaphthene		$C_{12}H_{10}$	154.21	279	93.4	2.5×10^{-3}	3.98	3	D
Acenaphthylene		$C_{12}H_8$	152.20	280	91.8	6.68×10^{-3}	4.07	n.c.	D
Anthracene		$C_{14}H_{10}$	178.23	342	216.4	6.53×10^{-6}	4.45	3	D
Phenanthrene		$C_{14}H_{10}$	178.23	340	100.5	1.2×10^{-4}	4.45	3	D
Fluorene		$C_{13}H_{10}$	166.22	295	116.7	6.0×10^{-4}	4.18	3	D
Fluoranthene		$C_{16}H_{10}$	202.26	375	108.8	9.22×10^{-6}	4.90	3	D
Benzo[a]anthracene		$C_{18}H_{12}$	228.29	438	158	4.11×10^{-3}	5.61	2B	B2
Chrysene		$C_{18}H_{12}$	228.29	448	254	6.23×10^{-9}	5.16	2B	B2
Pyrene		$C_{16}H_{10}$	202.26	150.4	393	4.5×10^{-6}	4.88	3	D
Benzo(a)pyrene		$C_{20}H_{12}$	252.32	495	179	5.49×10^{-9}	6.06	1	B2

CHAPTER 18

Tackling Marine Pollution: Final Thoughts and Concluding Remarks

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Abstract: This chapter encompasses the final words and summarized the current status of marine pollution globally in terms of the distribution, potential sources, associated hazardous impacts, and possible bio-remedial measures. This chapter is divided into two sections and highlighted the viewpoints about different topics discussed in this book and the concluding remarks.

Keywords: Marine Ecosystem, Pollution Control, Public Awareness, Remedial measures, Toxicity Assessment.

SUMMARIZED VIEWPOINT

Due to the anthrophonic interventions and exploitation of resources, marine ecosystems are facing significant challenges (Lu *et al.*, 2018). The marine ecosystem is complex in nature and rich in biodiversity, where non-native species from another environment can cause significant harms in terms of its proliferation and competition for the available resources. This is one of the major problems in the marine ecosystem that needs to be addressed for protecting the innate biodiversity and to avoid economic loss. This problem has become worse due to the factors, such as the release of the blast waters by the tankers, frequent movement of the vessels, and irregular water currents. There are other natural factors, such as dissolved oxygen, temperature, pH, water circulations, and light, also affect the marine organism, but the contribution of anthropogenic pollution is most significant. Recently, the plastic pollution, including plastic debris, microplastic, and nanoplastic, is becoming a global concern that is threatening the marine ecological environment (Auta *et al.*, 2017; Rezania *et al.*, 2018).

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The plastic debris may enhance the distribution and transportation of other pollutants, negatively affect the growth and survival of the organisms, and can also transfer along the food chain. Besides plastics, the other organic and inorganic pollutants that are persistent and recalcitrant in nature also induce deleterious effects on the marine ecosystem (Axel *et al.*, 2011; Lammel *et al.*, 2016; Wolska *et al.*, 2012). The intake of pollutants in the marine environment by the organism depends on different properties of the pollutants, such as partition coefficient, hydrophobicity, *etc*. Therefore, the continuous monitoring of different classes of pollutants is critically important to devise abating strategies for protecting biodiversity and reducing the burden of pollution on marine organisms. The monitoring of marine pollution can be performed through various methods, such as the use of bioindicators, biological monitoring, chemical monitoring, and isotopic analysis (Cunha *et al.*, 2017; Jr *et al.*, 2017; Wang *et al.*, 2014). However, the monitoring of real-time toxicity of pollutants to the marine life across a large spectrum is still challenging.

Recently, the integrated use of analytical, chemical, ecological, and toxicological assessment techniques is recommended for a more precise and efficient evaluation of the status and associated impacts of marine pollution. For biomonitoring and toxicology assessment, marine medaka (*O. melastigma*) has been proposed as a feasible and ideal model to investigate the estuarine and marine eco-toxicology (Kim *et al.*, 2016). *O. melastigma* possesses obvious advantages in comparison to other model animals, such as high fecundity, small size, transparent embryos, short generation cycle, the wide range of salinity adaptations, and sexual dimorphism (Bo *et al.*, 2011; Won *et al.*, 2011). Many of the previous eco-toxicological studies have employed wild-type and transgenic species of these models to elucidate the toxicogenetics endpoints and biomonitoring of organic pollutants, heavy metals, and endocrine disruptors (Huang *et al.*, 2015; Mu *et al.*, 2016). Therefore, *O. melastigma* can be used as an excellent to screen the biomarker of marine contaminants and to track the distribution of pollutants in the marine environment. In addition, the advance gene editing techniques, such as CRISPR/Cas9, can also be employed to investigate the changes in the genetic makeup of the marine organism and associated molecular pathways in response to the environmental stressors (Mu *et al.*, 2016; Xie *et al.*, 2017). This could be coupled with other genome information assessment strategies, *i.e.* transcriptome, proteome, and metabolome analysis through a feasible bioinformatics platform. The nexus of advance gene editing techniques and high throughput bioinformatic systems will provide a better understanding of molecular mechanisms and complex biological processes associated with the ecotoxicological effects of pollutants on marine species.

As far as the abatement strategies for marine pollution are concerned, bioremediation considered as the most useful and encouraging solution to control the pace of increasing marine pollution (Catania *et al.*, 2015). Microbes exhibit excellent potential to combat the stress of organic and inorganic pollutants through bioremediation (Marques, 2016; Mohanrasu *et al.*, 2018; Sakthipriya *et al.*, 2015). Despite the improvement in bioremediation efficiency for various classes of pollutants, such as PAHs, PCBs, and heavy metals, there is still room for further research in this field. Screening and isolation of microbes from diverse habitats may be useful and can assist to discover more efficient microbial strains. Apart from devising the new bioremediation techniques, there should be certain methods to enhance the bioavailability of the pollutants for assisting the microbial detoxification of the pollutants. The application of bioremediation can become commercial and profitable at large scale by genetically modifying the microbial strains for their metabolic potential.

CONCLUSION

The conservation of marine biodiversity and its biogeochemical implications are critically important for the continuation of the life cycle on planet earth. Hence, it is immensely important to devise strategies based on multidisciplinary efforts for in-depth understanding of the interaction of organic and inorganic pollutants and their different chemical species with different compartments of the marine ecosystem. Therefore, the continuous research, public awareness, outreach programs, policies making, and implementation, could prove as the building blocks for the abatement and prevention of marine pollution. In addition, the sustainable practices should be introduced regarding the treatments of agriculture, domestic, and industrial wastes to avoid the emissions of pollutants to the environment that ultimately sink in the marine resources. The industrial emissions could significantly control or reduce through making industrial and manufacturing processes much more efficient, educating the workers, and use of mitigation technologies. More international collaboration and agreements are needed in near future to combat marine pollution and preserve the endangered coastal and estuarine habitats. There is a dire need to educate the masses about the detrimental effects of marine pollution and its regional and global consequences in terms of climate change. Proactive forums also need to be established to present the novel and feasible solutions to decrease the number of pollutants entering the marine ecosystem. Lastly, scientific research must continue to elucidate the current status, toxic impacts, and available remedies for marine pollution.

CONSENT FOR PUBLICATION

Not applicable.

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Desheng Pei

Professor. Dr. Pei obtained his Ph.D. degree from the Institute of Hydrobiology (IHB), Chinese Academy of Sciences (CAS) in 2003. From Jun 2006 to Feb 2009, Dr. Pei worked at IHB. From Feb. 2009 to Feb. 2011, Dr. Pei concentrated his study on the mechanisms of DNA damage and repair in Northeastern University (USA). Thereafter, Dr. Pei worked at Dana-Farber Cancer Institute/Harvard Medical School to study the mechanism of carcinogenesis of neuroblastoma from Feb. 2011 to Feb. 2013. In August 2012, Dr Pei was promoted to the post of the professor at Chongqing Institute of Green and Intelligent Technology (CIGIT), CAS, and was selected by the Hundred Talents Program of Chinese Academy of Sciences. His discoveries have been published on more than 80 journals, including PLOS Genetics, Nucleic Acids Research, Biomaterials, etc. His research interests mainly focus on studying toxicological effects, mechanisms and ecological risk assessment of classic environmental pollutants.

Muhammad Junaid

Dr. Junaid received his Ph.D. degree from the University of Chinese Academy of Sciences (UCAS), Beijing in 2018. Currently, he is working as a Research Fellow at the School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, China. His research work is focused on understanding the ecological risks and toxicogenetic impacts of emerging and legacy organic and inorganic pollutants in the aquatic environment, model organisms and human cell lines. Further, based on research contributions, Dr. Junaid has been selected for the International Excellent Student Award by UCAS consecutively for two years 2017/2018 and also nominated for China Scholarship Council (CSC) Research Award (2018). His work has been published in Environmental Pollution, Science of the Total Environment, Chemosphere, Aquatic Toxicology, Biomaterials, the Journal of Hazardous Material, etc.