

ENVIRONMENTAL POLLUTANTS IN THE MEDITERRANEAN SEA: RECENT TRENDS AND REMEDIATION APPROACHES

Editor:
Tamer El-Sayed Ali

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Environmental Pollutants in the Mediterranean Sea: Recent Trends and Remediation Approaches

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PREFACE

Pollution of the aquatic environment is a real threat across the globe. It is becoming a topic of intense study for researchers. It has been updated and almost completely revised. The Mediterranean Sea has been recognized as a target hotspot of the world as the pollutants' concentration in this region is greater than other vast oceans.

The book summarizes the basic pollutants in the Mediterranean Sea, focusing on microplastics, rare earth elements and biotoxins. The impacts of pollutants on the aquatic environment and health have received greater attention in this edition, and there are more case descriptions that cover some countries in the Mediterranean region. This edition has a simple emphasis on pollution problems in the Mediterranean region. The present book is an attempt to put together, to a certain level, the scientific publications on the referred topic for the benefit of the target audience. In addition, more references are included at the end of the chapters, including many websites.

A framework: Chapters 1 through 5 provide basic information on pollutants in the Mediterranean Sea with a special focus on some countries in the region and how humans are affecting the environment. They also discuss important concepts of the pollutant's hazards. Chapter 1 demonstrates the impact of Biotoxins in Lebanon as a case study. Chapter 2 discusses the bio-monitoring of effluents. Chapter 3 introduces basic concepts in microplastic pollution and its effect on fish while Chapter 4 explains the impact of microplastics on the Moroccan Mediterranean. Chapter 5 delves into the ecological impacts of rare earth elements influx into the Mediterranean Sea.

I hope readers who are interested in environmental pollution in general, or involved in aquatic science in particular, can find this book useful and objective achievable. Finally, I would very much welcome any feedback from readers.

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CHAPTER 1

Biotoxins in the Mediterranean Sea: Lebanon as a Case Study

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Abstract: Marine biotoxins are naturally occurring chemicals produced by toxic algae. They can be found in seawater and can accumulate in various marine organisms, such as commercial seafood. When contaminated seafood is consumed, these biotoxins can cause poisoning in humans, with varying health consequences depending on the type and amount of toxins. The proliferation of biotoxin-producing algae in the marine environment has dire socio-economic and environmental consequences due to the contamination of water and seafood. Due to the number of factors related to human pressures and climate change impacts, the frequency of marine biotoxins' occurrence is increasing significantly globally, and in regional seas such as the Mediterranean Sea. In this chapter, we highlight Lebanon in the Eastern Mediterranean Sea, where marine biotoxins were recently studied. The results show for the first time the presence of lipophilic toxins and cyclic imines in marine biota, with values for okadaic acid, dinophysistoxin 1 and 2, pectenotoxin 1 and 2, yessotoxins and azaspiracids below the detection limit (LOD). Levels above LOD were detected for domoic acid (DA), gymnodimine (GYMb), and spirolides (SPXs) in some species/areas. Maximum levels of DA, GYM, and SPXs (3.88 mg DA kg⁻¹, 102.9 µg GYM kg⁻¹, 15.07 µg SPX kg⁻¹) were found in the spiny oyster (*Spondylus spinosus*) in agreement with the occurrence of *Pseudo-nitzschia* spp, *Gymnodinium* spp, and *Alexandrium* spp. DA was below the EU limit but above the lowest observed adverse effect level (0.9 µg g⁻¹) for neurotoxicity in humans and below the acute reference dose (30 µg kg⁻¹ body weight), both established by EFSA. Considering the lowest lethal dose (LD50) after administration of GYM and SPXs to mice, it is unlikely that there is a health risk due to exposure to these toxins from seafood consumption in Lebanon. Nevertheless, the chronic toxicity of DA, GYMs, and SPXs remains unclear, and the effects of repeated

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consumption of contaminated seafood need to be investigated. Because biotoxins have been detected in bivalves and commercial species, as well as other organisms in the marine trophic chain, it is evident that species other than bivalves should be monitored, and the spiny oyster (*S. spinosus*) may play the role of a sentinel species in biotoxin studies. A regular monitoring program is needed to provide reliable, accurate estimates of bloom toxicity and to investigate their potential impact on marine species and human health in Lebanon.

Keywords: Cyclic imines, Emergent pollutants, Lipophilic toxins, Lebanon, Mediterranean sea, Marine biotoxins, Marine biota, Public health, Seafood.

INTRODUCTION

Phytoplankton blooms have been known since the earliest human records (Boni, 1992; Zheng and Klemas, 2018). The global increase in these events has been notable since the 1980s (Smayda, 1990; Boni 1992, Vlamis and Katikou, 2015; Vilariño *et al.*, 2018) and has been attributed to favorable external conditions such as nitrogen/phosphorus resources, pH, and temperature (Stauffer *et al.*, 2020; Zhang *et al.*, 2020). More recently, these blooms have been attributed in part to the effects of ocean warming, marine heat waves, oxygen depletion, eutrophication, and pollution (Gobler *et al.*, 2017; Gobler *et al.*, 2021).

Of more than 70,000 phytoplankton species worldwide (Guiry, 2012), about 300 species can cause “red tides” (Hallegraeff *et al.*, 1995; Lindahl, 1998), and of these, more than 100 are producers of natural toxins that generate toxic episodes, known as Harmful Algal Blooms (HABs), that can be dangerous to humans and other organisms (Berdalet *et al.*, 2016).

According to Karlson *et al.* (2021), HABs can be divided into six main categories based on their adverse effects on the environment and/or human health: 1. Those that produce phytotoxins that accumulate in suspension feeders (bivalves); 2. Those that cause damage to respiratory mechanisms (fish gills) and/or feeding responses through toxin transfer, leading to mortality of fish and other marine life; 3. Blooms with high biomass that cause nuisance effects and/or lead to oxygen depletion; 4. Blooms disrupt the ecosystem and have multiple cascading effects on species interactions; 5. Those that produce aerosolized toxins that affect human respiratory health; and 6. Localized blooms of harmful benthic or epiphytic microalgae differ from planktonic HABs in habitat, mechanisms, and magnitude of adverse effects.

Phytoplankton cells form the base of the marine food chain and are an important food for filter-feeding bivalves and larval fish and crustaceans (Powell *et al.*, 1995; Cloern and Dufford, 2005). Consequently, HABs’ toxins can be bio-

accumulated and biomagnified in the marine trophic chain (Orellana *et al.*, 2017), and may be detrimental to plants, animals, people, and ecosystems (Harrison, 2005; Costa *et al.*, 2017). Thus, HABs can generate several socio-economic implications (Visciano *et al.*, 2016; Nwankwegu *et al.*, 2019; Zhongming *et al.*, 2021; Corriere *et al.*, 2021) which often depend on the size, severity, timing, and duration of the event (Qiao and Saha, 2021).

Biotoxins can be divided into hydrophilic and lipophilic molecules that can cause different symptoms: water-soluble toxins that cause Paralytic (PSP) and Amnesic Shellfish Poisoning (ASP), while liposoluble toxins cause Diarrhetic (DSP) and Neurotoxic Shellfish Poisoning (NSP) (FAO/IOC/WHO, 2004; Visciano *et al.*, 2016). Skin contact with contaminated water, inhalation of aerosolized biotoxins, or direct consumption of contaminated seafood can result in the effects of HABs on human health (Visciano *et al.*, 2016; Sonaka *et al.*, 2018).

Lipophilic Toxins (LTs)

Based on their polarity, marine biotoxins can be classified as hydrophilic, lipophilic (LTs), or amphiphilic (Alarcon *et al.*, 2018).

LTs are toxic metabolites from phytoplankton (*dinoflagellates*) isolated from different bivalve species (Draisci *et al.*, 1996) and classified into different classes (Liu *et al.*, 2019): Okadaic acid (OA), Dinophysistoxins (DTXs) and Azaspiracids (AZAs) which cause Diarrhetic shellfish poisoning (DSP) (Vale and Sampayo, 2002) and are considered tumor promoters (Fujiki and Suganuma, 1993). These also can cause pathological changes in the liver, pancreas, thymus, and spleen of mice (Ito *et al.*, 2000); while Pectenotoxins (PTXs) and Yessotoxins (YTXs) have not been shown to cause diarrhetic symptoms following intoxication (EFSA, 2008, 2009; Vlavis and Katikou, 2015; Ferron *et al.*, 2016), but Domoic Acid (DA) is a potent neurotoxin responsible for Amnesic shellfish poisoning (ASP) that causes damage to the central nervous system (Gago-Martínez and Rodríguez-Vázquez, 2000; Diogène, 2017).

The Cyclic Imines (CIs)

With the discovery of new detection methods, the toxin groups are constantly updated and new toxins are identified and classified as “emerging toxins”. Cyclic Imines (CIs), Palytoxin (PITX), and Ciguatoxin (CTX) are examples whose appearance in the environment may be due to climate change affecting the distribution of phytoplankton species (EFSA, 2009, 2010a, 2010b). CIs, discovered in Canada in 1991 (Munday, 2008), are associated with algal blooms and shellfish contamination and are neurotoxins, antagonists of nicotinic receptors that affect the central nervous system (Otero *et al.*, 2011). CIs are macrocyclic

Short-Term Bioassay Tests for Toxicity Effluents Estimation and Bio-Monitoring Uses in Aquatic Ecosystems

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Abstract: Bioassays are defined as the measurement of toxic responses upon exposure to chemicals under controlled conditions in the laboratory using cultured organisms and represent powerful tools for the assessment of environmental quality. These biological tests were pointed out as the most common methods used to assess the environmental risk, mainly in marine ecosystems besides biomarkers and biosensors. The list of different toxicity bioassays is still increasing and a large battery of different aquatic organisms is available for the measurement of organic and inorganic chemical toxicity.

The species selected for the available battery of bioassays differ taxonomically and play different roles in aquatic ecosystems. Else, they have different routes of exposure to bio-potential.

Although many bioassays provide information about the overall toxicity induced, new test systems are developed and used for the determination of specific toxicity in a number of biological pathways disrupted by contaminants.

Hereby, the list of bioassay tests used in aquatic ecosystems assessment is updated besides specific toxicity pathways for almost invertebrate and vertebrate aquatic species used to determine organic and inorganic pollutants effects.

Keywords: Aquatic ecosystems, Accute toxicity, Bioassays, Biomonitoring, Bioindicator organisms, Biochemical reponses, Chronic toxicity, Effluents, *In vivo*, Inorganic pollution, Invertebrates, Marine Pollution, Microbiological test, Organic pollution, Physiological reponses, Toxicity, Tests, Toxicity, Vertebrates.

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INTRODUCTION

Recent data highlighted the consequences caused by the number of pollutants in aquatic environment organisms, which may remain recessive for several generations and exhibit major effects on the population (Arslan 2017). Multiple damages caused by these pollutants at the level of population and ecosystem, as in organ function (reproductive stages and biological diversity) are still increasing (Minguez *et al.* 2017, Di Paolo *et al.* 2015) and signs of alterations specifically detected in different levels (Amara *et al.* 2012, Zaaboub *et al.* 2015, Minguez *et al.* 2014, Martinez-Gomez *et al.* 2010). The evaluation of the complex actions and bioavailability of contaminants and the determination of their biological effects for almost unidentified substances have been realized by means of bioassays using live organisms (AL Shackleton *et al.* 2002, Almeida *et al.* 2012, Amara *et al.* 2012). Thus, all aquatic organisms exposed to many xenobiotics during their lives both from water, aquatic food chain, or sediments, and the degree of contamination appraised by chemical analyses is still insufficient to provide or estimate the deleterious effects on the biota despite the increasing number of recent studies related to chemical contamination of the environment and their toxic effects (Meijome *et al.* 2006, Mânzatu *et al.* 2012).

The major sources of these chemical substances are industrial and agricultural activities and almost all of these sources have ultimate contact with aquatic ecosystems, causing organic alteration and stress (Schintu *et al.* 2015). Since the last decencies, chemical analyses have been complemented with biological criteria from bioassays to design a more comprehensive approach to aquatic pollution assessment (Minguez *et al.*, 2014a, b). The bio-tests were previously recognized as tools of indication for potential toxicity of a certain effluent to the biological communities inhabiting the receiving waters and used to evaluate the status of natural environments against the impact of anthropogenic activities (MacDonald *et al.* 1997, Wells *et al.* 1998).

Thus, acute toxicity tests became routinely used to evaluate the quality of waters in aquatic coastal areas and to assess the toxicity of pollutants, mainly heavy metals, polyaromatic hydrocarbons, pharmaceutical compounds, or pesticides (Meinguez *et al.* 2017, Bao *et al.* 2013, Mottier *et al.* 2013, Mai *et al.* 2012).

The major guidelines provided for the use of biological effects techniques mainly for oil spill pollution monitoring were those of European, Mediterranean, or American regions (UNEP/MAP/MED POL 2004, Martinez-Gomez *et al.* 2010) and applied biological-effects techniques (bioassays and biomarkers) were used as tools to assist in determining the damage to health in marine ecosystems.

In addition, it has been largely reported that bioassays provide an integrative response for the combined effect of all pollutants present in effluents or waste discharges, with potential synergistic or antagonistic interactions. Therefore, the integrative assessment of aquatic pollution nowadays includes both chemical and biological monitoring (Fernández Méijome *et al.*, 2006, Gunjan *et al.*, 2015, Di Paolo *et al.* 2015).

Due to the importance of bioassays in aquatic monitoring, here we provide the bioassays' definition and present the most reported bioassays, mainly regarding the vertebrate and invertebrate species used.

DEFINITION OF BIOASSAY

Several definitions have been proposed for the bioassay as it responds only to the biologically available fraction and identifies toxicity in relevant marine organisms (Fernández Méijome *et al.* 2006). The most suitable definition is provided by the Water Framework Directive (Environment Agency 2002a), as a bioassay is the measurement of the toxic response upon exposure to a chemical under controlled conditions in the laboratory using cultured organisms. Thus, the ideal bioassay remains simple to emulate, regularly inter-calibrated, sensitive to a wide range of pollutants, able to utilize organisms from reliable stock, practicable, relevant, readily understood, and able to yield statistically robust data (Environment Agency 2002b). It is important to specify that a bioassay can provide predictions of environmental impacts, whereas ecological community measures only impacts after they occur, and thus, the use of bioassays for investigative monitoring is probably their most important role related to the requirements of the Directive of Environment Agency (2002a) and those recently published (Hunting *et al.* 2017).

DIFFERENT TYPES OF BIOASSAYS

Different bioassays using different species representative of the ecosystem have been used to obtain relevant information on potential ecological risks in polluted environments. Species selected for the different proposals differ by taxonomy, their roles in ecosystems, route of exposure, availability, and easy culture in the laboratory (Zovkol, 2015). Bioanalytical bioassays as biomarkers and biosensors represent suitable detection systems signaling potential damage in the environment and a wide variety of biological bioassays have been developed to evaluate different endpoints, such as sub-lethal effects, and biochemical responses (Stekenburg *et al.* 2007). In recent decades, toxicity biotesting has grown steadily as a useful tool in environmental risk assessment, including the most used direct

The Challenge of Microplastics in Aquatic Ecosystem: A Review of Current Consensus and Future Trends of the Effect on the Fish

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Abstract: In recent decades, the prevalence of plastics in the marine environment has increased and is amongst the most pervasive problems affecting the marine environment globally. Numerous studies have documented microplastic ingestion by marine species with more recent investigations focusing on the secondary impacts of microplastic ingestion on ecosystem processes. However, few studies so far have examined microplastic ingestion by mesopelagic fish which are one of the most abundant pelagic groups in the oceans and their vertical migrations are known to contribute significantly to the rapid transport of carbon and nutrients to the deep sea. Therefore, any ingestion of microplastics by mesopelagic fish may adversely affect this cycling and may aid in the transport of microplastics from surface waters to the deep-sea benthos.

Microplastics are ubiquitous in the marine environment and are increasingly contaminating species in the marine ecosystem and the food chain, including food stuffs intended for human consumption. The effects of microplastics on aquatic organisms are currently the subject of intense research. Here, we provide a critical perspective on published studies of microplastic ingestion by aquatic biota. We summarize the available research on Microplastic presence, behavior, and effects on aquatic organisms monitored in the field and laboratory studies of the ecotoxicological consequences of microplastic ingestion.

Finally, researchers plan further studies to learn more about how these fish are ingesting and spreading microplastics. It will be particularly interesting to see whether the fish ingest these microplastics directly as mistaken prey items, or whether they ingest them through eating prey species, which have previously ingested the microplastics. Also, there is a need to understand the mechanism of action and ecotoxicological effects of environmentally relevant concentrations of microplastics on aquatic organism health.

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Keywords: Biota, Ecotoxicology, Marine ecosystem, Microplastics.

INTRODUCTION

Despite scientific concern and the increasing worldwide contamination of aquatic ecosystems with hundreds of natural and industrial chemical compounds, research on the pollution of marine environments from plastic is scarce. There is an enormous quantity of plastic litter in the aquatic environment. Approximately, 8.3 billion metric tons of plastic had been produced in 2017, and its production is being steadily increased yearly (Geyer *et al.*, 2017). Up to 10% of the plastic produced each year worldwide terminates in the aquatic environment, where it persists and accumulates (Jambeck *et al.*, 2015), thus being ubiquitous in the environment. By 2050, plastic stocks in the ocean will equal and may surpass fish stocks (Gallo *et al.*, 2018). Plastics do not last forever and the marine environment is suitable for their degradation, meaning fragmenting the original plastic pieces, turning the oceans into a soup of microplastics. With the time, the abundance of micro- and nano-plastic particles will be considerably higher than the number of plankton. Thus, it is one of the environmental problems facing humanity (Thompson *et al.*, 2009; Faggio *et al.*, 2018; Strungaru *et al.*, 2018; Savoca *et al.*, 2019a).

These particles may be accidentally and deliberately ingested by marine organisms. Therefore, they may cause significant impacts on these organisms, such as inflammation, mal-feeding, and weight loss. Microplastic contamination may also spread from one organism to another when prey are ingested by predators. As the fragments can bind to chemical pollutants, these associated toxins could accumulate in predators. Moreover, laboratory studies indicate that micro- and nano-plastics can cause various negative effects in fish such as physical damage, abnormal behavior, change in lipid metabolism, as well as cytotoxicity. Thus these pollutants are of high concern regarding the ecosystem, animal state, and human health (WHO, 2010). They are globally dispersed in marine, freshwater, and terrestrial ecosystems (Ng *et al.*, 2018). Additionally, they can be transported for long distances mainly through long-range air circulation, water currents, and contaminated biota. In general, animals and humans may be exposed to both substances through contaminated food, water, air, and soil (Horton *et al.*, 2017; Barboza *et al.*, 2018; Lehner *et al.*, 2019). Therefore, this review aims to raise awareness on the topic of the potential effects of micro-and nanoplastics ingestion by fish and investigate if microplastics can interact positively or negatively with the eco-toxicological effects of other contaminants. There may be synergistic effects of microplastics and other contaminants on organism health, or they may function as a transport vector for other

contaminants. Moreover, this review aims to increase overdue attention to such a class of chemicals, a topic that has not been sufficiently investigated.

SOURCES AND DISTRIBUTION

In the marine ecosystem, microplastics are a heterogeneous group of particles that vary in shape, size, and chemical composition. They are found in sediments/sea floor, on the sea surface, in the water column, and also in wildlife. The most commonly manufactured plastics are polyethylene and polypropylene (US EPA, 2018). Microplastics could be defined as tiny fragments (less than 5mm in size) of degraded plastic, synthetic fibers, and plastic beads that have accumulated in the marine environment following decades of pollution (Blair *et al.*, 2017). While nanoplastic particles are defined as plastic particles ranging from 1 to 100 nm in size (Weis *et al.*, 2015). Microplastics are often classified into primary and secondary types. Primary microplastics were originally produced to be < 5 mm in size, while secondary microplastics result from the breakdown of larger items. Microbeads which are used in personal care products, industrial abrasives, and pre-production plastic pellets used to make larger plastic items are the main sources of primary microplastics (Anderson *et al.*, 2016). Sources of secondary microplastics include microfibers from textiles, tire dust, and larger plastic items that degrade and consequently fragment into microplastic particles, mostly due to natural forces like sunlight and wave action (Duis and Coors, 2016). The extent of plastic degradation depends on factors including polymer type, age, and environmental conditions like weathering, temperature, irradiation, and pH (Akbar and Özdemir, 2016). Additionally, marine microplastics would continue to increase as larger plastic litter degrades into secondary microplastics (Anderson *et al.*, 2016).

PHYSICAL AND CHEMICAL PROPERTIES

Plastics are cheap, light in weight, strong, durable, and corrosion-resistant materials, with high electrical and thermal insulation properties. The diversity of polymers and the versatility of their properties are used to make a variety of products that bring technological advances, energy savings, and many other benefits (Andrady and Neal, 2009; Savoca *et al.* 2019b).

Microplastics in the marine environment are typically found as pellets, fragments, or fibers and are composed of diverse polymers. Such microplastics are commonly denser than seawater and are expected to sink to the seabed. These include polyester, polyamide, and polyvinyl chloride (PVC). Others are lighter than seawater and are often found floating on the water surface. These include polyethylene, polypropylene, and polystyrene (Smith *et al.*, 2018).

Overview of Marine Plastic Pollution in the Moroccan Mediterranean

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Abstract: Plastic debris has become the main component of marine litter in the Moroccan Mediterranean due to the massive consumption of plastic and poor plastic waste management. In Morocco, plastic pollution has been a subject of increasing environmental concern in the last few years. This literature review was conducted to collect current data on plastic pollution in the Moroccan Mediterranean, considering the presence of marine debris as well as macroplastics and microplastics in different compartments. Our study shows that, until now, very few studies have been carried out and there is a lack of information, especially on the prevalence of plastic debris in the water environment, sea floor, and aquatic animals. In general, plastic is the most predominant waste on the beaches of the Moroccan Mediterranean, always contributing to more than 50% of the total composition of the waste encountered. Based on the records, tourism, recreational activities, and fishing are one of the main sources of plastic accumulation in the Moroccan Mediterranean. This was due to a lack of awareness among beach users. Awareness and behavior change is key to minimizing plastic waste on Morocco's beaches and coasts. In addition, all aspects of waste management must be improved. The beaches of the Moroccan Mediterranean have also been contaminated by microplastics. A significant positive correlation was also observed between human population density and industrial activity on microplastic abundance. Microplastic has only been found in a few commercial fish species and sea turtles, but more work will be needed in the future.

Keywords: Beach, Characterization, Coast, Debris, Ingestion, Macroplastics, Management, Marine debris, Marine fauna, Marine litter, Mediterranean, Microplastics, Mismanagement, Mitigation, Morocco, Pollution, Quantification, Recycling.

INTRODUCTION

Plastic pollution of the oceans has been identified as one of the major environmental challenges of the 21st century (De-la-Torre *et al.*, 2021). Each year,

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millions of tons of plastic litter are released into the sea with detrimental environmental implications. Tourism and recreation activities, agriculture, and poor management of municipal and industrial solid waste, and dumping of poorly treated/untreated wastewater are considered the major land-based sources of marine debris, while marine sources include fisheries, shipping, and aquaculture (Li *et al.*, 2016).

The Mediterranean Sea has been recognized as one of the most affected seas by plastic pollution in the world (Suaria *et al.*, 2016; Fossi *et al.*, 2018; Constantino *et al.*, 2019). The coasts of the Mediterranean are inhabited by about 10% of the global coastal population and the basin constitutes one of the world's major shipping routes. It receives water from densely populated basins. During the last decades, large research activity has been conducted on the study of plastic pollution in the Mediterranean Sea. These studies indicate the presence, quantity, sources, and to some degree, the impacts of marine debris on beaches (Vlachogianni, 2019; Mghili *et al.*, 2020), the seafloor (Fortibuoni *et al.*, 2019), the sea surface (Arcangeli *et al.*, 2018; Zeri *et al.*, 2018), and biota (Anastasopoulou *et al.*, 2018). In the Mediterranean, the ingestion of plastics by marine species is one of the most documented impacts (Fossi *et al.*, 2018). More than 40 articles on the incidence of marine debris ingestion in marine biota in the Mediterranean have been published in the last five years. Despite this mass of information, the overall knowledge of the plastic pollution issue in the Mediterranean Sea is still limited and fragmented. Most studies have been carried out in the western Mediterranean Sea, while the southwestern Mediterranean has been less studied.

The Moroccan Mediterranean coastline extends 512 km from Tangier in the west to Saidia in the east. It is recognized for its high marine biodiversity and a wide variety of coastal landscapes. In recent years, the population of the Moroccan Mediterranean coast has undergone a significant change. The population has doubled from 1.5 million in 1971 to more than 2.8 million in 2014 (RGPH, 2014). In parallel with the increase in the coastal population, economic activities such as industry, agriculture, fishing, aquaculture, and tourism are well developed. In the list of top 20 waste-producing countries (Jambeck *et al.*, 2015), Morocco is placed eighteenth on this list with 0.31 million metric tons of mismanaged plastic waste per year. According to the Ministry of Industry, 26 billion plastic bags are consumed annually in Morocco, or 800 bags per capita. The amount of plastic waste entering the sea from land in Morocco in 2010 was estimated to be between 0.05 and 0.12 million metric tons (Jambeck *et al.*, 2015). The majority of waste is deposited in landfills, while only 8% is recycled. Plastic pollution in the Moroccan Mediterranean has been demonstrated in several abiotic compartments, including beaches, sediments, sea floor, and biota. Despite this fact, information is

still limited. There are still several gaps in knowledge about plastic pollution in the Moroccan Mediterranean.

The present study aimed to collect and analyze scientific papers that have studied plastic pollution in the Moroccan Mediterranean, to obtain an overview of the state of the art of studies carried out on plastic pollution in the Moroccan Mediterranean, and to define the possible gaps in this knowledge.

MATERIALS AND METHOD

Using the keywords “plastic”, “marine litter”, “marine debris”, “marine environment”, “coastal environments” and their respective French translations, all combined with “Morocco/Moroccan”, we have performed a literature review in the search databases Google Scholar, Scopus and Web of Science. In this study, we retrieved book chapters and papers published in national and international journals. The conference papers were also included in this analysis as data because these papers are also considered important. Searches were also conducted on the references mentioned in the retrieved articles.

All articles (n = 18) treating plastic pollution in the Moroccan Mediterranean were included in this study. First, we analyze and report data on plastics on beaches, in the sediment, and on the seafloor. Then, we concentrate our attention on microplastics in the marine environment, including marine biota.

In this review, we aim to respond to the following questions: 1) How has scientific research on plastic pollution evolved in the Moroccan Mediterranean in recent years? 2) What are the themes covered? 3) What are the main types of debris in the Moroccan Mediterranean? 4) What are the sources of this debris 5) and What are the main gaps in scientific knowledge to guide future work?

RESULTS AND DISCUSSION

Scientific Production

Over the last few years, scientific production about marine debris has increased in the Moroccan Mediterranean (Fig. 1). From this review, we retrieved 18 articles. Despite this, we have observed that the number of papers about plastic pollution in Morocco is low (X=3 papers/year). The total number of papers remains exceedingly low when compared to the global publication rate, reflecting a lack of studies on plastic pollution in the Moroccan Mediterranean.

Of the 18 studies identified in the Moroccan Mediterranean, the most common type of publication was scientific articles (n = 11; 61.13%), followed by

CHAPTER 5

Potential Ecological Impacts of Rare Earth Elements in the Marine Environment: A Baseline for Future Research**Ahmed Mandour^{1,*}**¹ *Department of Oceanography, Faculty of Science, Alexandria University, Baghdad St., Moharem Bek, 21511, Alexandria, Egypt*

Abstract: Rare earth elements (REE) have become a strategic commodity of contemporary economies due to their various uses in the technological, smart, and renewable energy industries. The boom of their uses resulted in an increased influx to the marine environment either as a result of mining or industrial discharges, or from the disposal of solid wastes, atmospheric fallout for military tests of smart weapons, and remobilization from the sediments. Although sediments are the main reservoir of REE in the marine environment, and their auspicious normalization patterns are useful geochemical tracers, it has been found that anthropogenic contributions influence REE's natural occurrence. This indeed has raised concerns about the potential ecological impacts of REE on the marine biota and in turn on human health. The chapter gives some insights into the sources and potential ecological impacts of REE while revealing the need for future research and the knowledge gap about the REE and their ecological impacts as a group and as individual elements, as well as some potential solutions to the increased anthropogenic influx of REE to the marine environment. The potential ecological impacts of REE influx to the marine environment constitute both their bioavailability and their toxicity. Predicted ecological impacts on the marine biota may be similar to other trace metals, sharing analogous chemical characteristics. Nevertheless, whether LREE or HREE are more toxic is debatable, and their physiological and cytological effects on different organisms are still under investigation. This prompts the need for a new understanding of REE's ecological impacts by focusing on influx rates, ecotoxicity, and mitigation of ecological impacts.

Keywords: Aquatic, Anthropogenic contribution, Aquatic, Biota, Bioavailability, Bioconcentration, Ecological impacts, Ecotoxicity, Health, Lanthanides, Nano-oxides marine, Pollution, Pollution mitigation, Remobilization, Rare earth elements, Sediments.

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INTRODUCTION

The preservation of the marine environment is vital to the livelihood and well-being of humanity as a whole. The marine living and non-living resources and ecosystem services are invaluable to the current global economy and the sustainability of socio-economic development. As the need for economic expansion and technological development increased, the exerted pressures on the marine environment exponentially grew in response to a multitude of threats elicited by the interference between natural and man-made pressures.

One of the top concerns of such pressures is pollution by anthropogenic materials due to its ecological impacts as well as its impacts on human health and the economic viability of an ecosystem (UNEP, 2012). A substance can be considered a pollutant when it exceeds its natural background levels in a specific ecosystem either due to a deliberate or an accidental process. Trace metals are widely common inorganic pollutants, reported to be in contingency with industrial/agricultural hubs, densely populated urban centers, and areas with dense maritime activities (Forstner & Wittman, 1983; Berias, 2018). Consequently, trace metals belonging to the transitional elements such as V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg, and As became the focus of research and were taken into consideration during designing pollution mitigation policies by states due to their common use in industry, agriculture, and domestic products.

In the past three decades, rare earth elements (REE) became widely used in technological industries. This prompted an increase in the demand for REE and increased the economic and strategic value of REE. During this period, limited attention was given to the ecological impacts of REE on the marine environment, with the aforementioned metals still the main focus of research and policymaking. In the 80s and the 90s, most research focused on the chemistry and geochemistry of REE in the marine environment. However, the exponential increase of reliability REE in modern industries which in turn resulted in an increase in their influx to the marine environment has started to grasp the attention of both researchers and policymakers as it holds potential ecological risks and threatens human health.

The present chapter probes the issue of increased REE influx to the marine environment as a form of pollution and explores the associated potential ecological risks while aiming also to shed the light on the relative mitigation options concerning mitigating those risks and points out the research gaps in such perspective.

RARE EARTH ELEMENTS AND THEIR SOURCES IN THE MARINE ENVIRONMENT

Rare earth elements (REE) are a chemically coherent group of metals. They comprise 17 elements including the 15 elements of lanthanides plus the other two elements (Scandium (Sc) & yttrium (Y)) that share similar chemical properties with Lanthanides (Lucas *et al.*, 2015). Lanthanides are classified according to their atomic weight into two groups (Fig. 1): Light (LREE) includes the elements Lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) samarium (Sm), and europium (Eu) as well as scandium (Sc); while heavy (HREE) includes gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (Gonzalez *et al.*, 2014). Some authors refer to Eu, Gd, Tb, and Dy as medium (MREE).

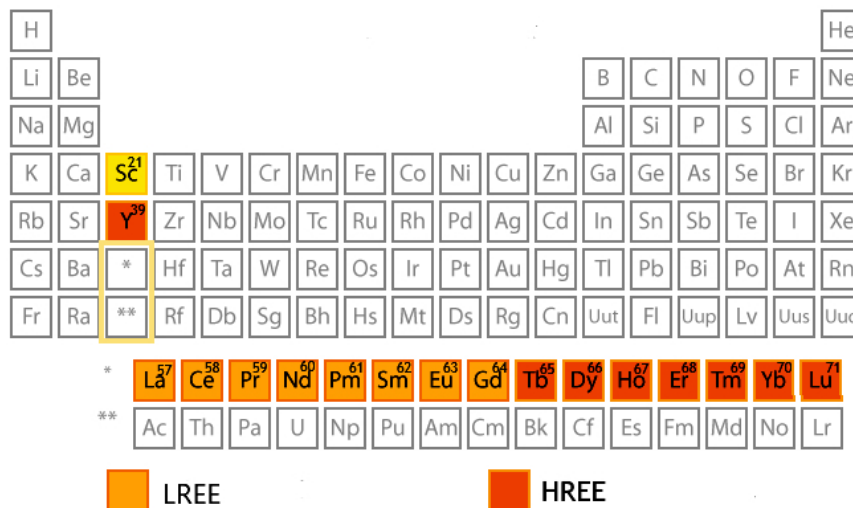


Fig. (1). The disposition of REE (LREE & HREE) in the periodic table.

REE occur naturally in the upper Earth's crust with Ce being the most abundant (60 ppm) ranking 25th of the 78 common elements in the Earth's crust millions, and Tm and Lu being the least abundant at about 0.5 part per million (Taylor & McLennan, 1995). REE occurs either in economic ore deposits or in accessory minerals such as monazite. Economically viable REE deposits are abundant in Central Asia, specifically in China and Mongolia, however, the export restrictions imposed by China have drawn attention to other source countries such as Australia, Brazil, Canada, South Africa, Tanzania, Denmark (Greenland), and the United States (Fathollahzadeh *et al.*, 2019; Kennedy, 2016).

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