Chapter 7
Migration and Chemical Transformation of Pollutants in the Marine Ecosystem

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Abstract Marine pollution is the most challenging and inadequately addressed global environmental issue. The rapid increase in industrial and agricultural growth coupled with technological advancements has introduced massive emissions and discharges of hazardous wastes in the biosphere. Over time humans have exploited the marine ecosystem as a major sink of pollution from both land and water sources. Ocean pollution is the mixture of heavy metals, organic pollutants, pharmaceutical residuals, plastics, and oil spills. This chapter investigates the migration and chemical transformation mechanisms of major marine pollutants including heavy metals, organic pollutants, pharmaceutical residuals, plastics, and oil spills. Metals mostly settle and adsorbed on sediments at the bottom which act as secondary source and may resuspend in marine environment through desorption. Chemical transformation of heavy metals is dependent on its chemical forms as metals in exchangeable fraction are highly active whereas residual fractions are observed to be relatively stable in marine environment. Deep-sea ecosystem acts as sinks for organic pollutants and biomagnification leads to build-up of pollutants in marine organisms. Microbial transformation of organic pollutants helps in the removal of organic pollutants in the deep sea through aerobic hydrocarbon degradation. The primary

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mechanism for the abiotic transformation of medicinal chemicals in the aquatic environment is photochemical degradation. Plastics in the marine environment may undergo both abiotic and biotic degradation processes while plastic additives are also released along with degradation mechanisms and likely to migrate into species through leaching, evaporation, abrasion, and ingestion. Oil droplets when released into marine environment go through complex biological, physical, and chemical transformations which include spreading, drifting, dispersion, stranding, and weathering. The transformation processes of pollutants in marine ecosystem help to further develop insights into the toxic effects produced by pollutants in the marine ecosystem.

Keywords Marine · Ecosystem · Pollutants · Migration · Chemical transformation

1 Introduction

The marine ecosystem is the most productive ecological community in the biosphere and plays an essential role in material circulation, energy flows, and regulating carbon and water cycles in the ecosphere. The environmental pollution of marine ecosystems has raised a global concern while getting worse pollution effects from both land and water sources. Environmental pollutants usually emerge from many activities of human settlements including construction, urbanization, tourism, agriculture, and the industrial sector which ultimately end up in the oceans (Williams 1996). Increasing pollution of marine ecosystems can be directly or indirectly linked to the world's growing human population. The data statistics reveal that >40% of world oceans have been affected by anthropogenic activities (Halpern et al. 2008). Coastal areas are particularly vulnerable and human activities have destroyed >65% of seagrass and wetlands and depleted >90% of important marine species (Lotze et al. 2006). In addition to that rising global temperatures can accelerate the acidification process and algal blooms in the marine environment (Albright 2011; Anlauf et al. 2011; Cooper et al. 2008; Mostofa et al. 2013). The major pollutants include heavy metals, organic pollutants, plastics, and oil spills (Dubois et al. 2018; Zhang et al. 2019b).

Heavy metals are produced by several natural processes, including comets, erosion, volcanic eruptions, and mineral weathering. These metals are usually found in forms that are insoluble, including complexes, precipitated forms, or mineral structures (Ayangbenro and Babalola 2017). Various heavy metals are emitted during mining activities, depending on the specific kind of mining. Metals originating from anthropogenic sources are usually highly bioavailable, as these elements are soluble and mobile in reactive forms (Ayangbenro and Babalola 2017). Organic pollutants such as persistent organic pollutants (POPs) are much more toxic regardless of being present in lower concentrations. Organic chemicals were extensively used during the industrialization period. Most of these compounds were found to be beneficial in pest control and other diseases, although they have an impact on humans

and other living organisms in the ecosystem. A vast array of synthetic or semisynthetic materials are known as plastics, and they are easily molded into a variety of products and shapes for a comprehensive variety of applications. The effects of plastic litter on marine biodiversity and ecosystems have been well documented, making it a worldwide environmental concern. Injuries to wildlife are often caused by ingestion of or entanglements in plastics found in the environment. The marine ecosystem is contaminated annually by three to four million tons of oil, according to the Maritime and Fisheries Research Centre (Purwendah et al. 2019). The majority of the world's environmental contaminants originate from hydrocarbons derived from crude oil (Ławniczak et al. 2020). Human activity results in the release of liquid petroleum hydrocarbons into the ocean or coastal areas, which is referred to as a "marine oil spill" (Li et al. 2016b). In addition to that pharmaceutical residues have been measured in several types of water bodies, including terrestrial, marine, fresh, and transitional waters, along with the organisms such as fauna and macroflora that reside inside them.

The migration and chemical fate of major pollutants in the marine ecosystem should be well documented to better understand the extent of ecological effects and to develop a mitigation plan for combating marine pollution.

2 Heavy Metals

Metal pollution related to human activities places the dominant position (Li et al. 2020; Wang et al. 2020b; Zhang et al. 2020) although many natural sources might also pose metal toxicities in the environment (Kang et al. 2017; Wang et al. 2020a). In the marine ecosystem, metals can enter either through rainfall, atmospheric deposition or through direct wastewater discharges from land sources (Godwin et al. 2019; Karageorgis et al. 2020). Heavy metals are naturally present in the crust of Earth in very small quantities (Mishra et al. 2023). In fact, these elements are present universally in all ecosystems (water, air, soil) in trace amounts (<10 ppm) (Shah 2021). Almost forty elements are classified as heavy metals (Sharma and Agrawal 2005). Some of them are essential, some are beneficial, and some are toxic (Ansari et al. 2004). Essential heavy metals, such as Cu and Zn, which serve as cofactors or activators of enzyme reactions (Mildvan 1970), have established biological functions and are hazardous if beyond specific concentrations (Shah 2021). Nonessential heavy metals, on the other hand, are very poisonous if they are allowed to accumulate in metabolically active locations, and these elements have no known biological function in marine invertebrates (Shah 2021). These heavy metals have the ability to accumulate in living organisms and are persistent and difficult to degrade in the environment, for instance, Hg, Ag, Pb, and Ni. The heavy metal pollution in marine environment has become an issue of major concern as they are non-biodegradable, highly persistent, toxic, and bioaccumulative in nature (Kostka and Leśniak 2020; Webb et al. 2020; Zhu et al. 2019).

2.1 Migration

Through atmospheric and hydrological processes, heavy metals may travel long distances (Guzmán and Jiménez 1992; Marx and McGowan 2010). These contaminants can infiltrate the marine environment through several pathways, including storm water runoff, dredging, agricultural practices, atmospheric deposition, and the discharge of sewage and industrial effluent (Shah 2021). These trace elements are transported to marine environments either as dissolved substances in water or in combination with suspended sediments (Al-Rousan 2012).

The homogenization distribution and dilution of the metal pollution in marine environment is largely determined by the hydrodynamics and flow of water currents (Makaoui et al. 2005; Orbi and Nemmaoui 1992; Zhang et al. 2018). Heavy metals tend to have low solubility, yet they get swiftly diluted and transported to large distances as soon as released into water body. Metals finally settled and absorbed on the sediments in the bottom (Varol et al. 2020; Zhang et al. 2018), which also act as the heavy metal sinks and significant pollution source in the marine ecosystem (Jafarabadi et al. 2018a, b, 2020a; Wang et al. 2018, 2020a, b).

In water bodies sediments not only act as the sinks but also play role in storage and transportation of heavy metals through strong binding forces with inorganic and organic ligands on their surfaces (Yu et al. 2001). Sediments also play a role of secondary source and can release heavy metals in marine environment through desorption and particle resuspension governed by bioturbation and hydrodynamic processes (Anderson and Hayes 2015; Xie et al. 2019). In particular fine-grained particles enriched with organic matter have high specific surface area and strong binding forces for metals (Buyang et al. 2019; Charriau et al. 2011; Hu et al. 2018). The transportation of heavy metals in estuarine regions is controlled by complex processes of sedimentation, remobilization processes and through sorption/desorption mechanisms (de Souza Machado et al. 2016). Other factors that can affect the mobility and bioavailability of heavy metals in marine ecosystem include geochemical properties of the sediments (i.e., redox potential, Fe-Mn oxides, sulfides, organic matter) (Zhang et al. 2014). With changes in environmental conditions of salinity, pH, and redox potential, the heavy metals bound in sediments get remobilized and may become bioavailable and highly toxic to benthic community (Calmano et al. 1993). In addition to that, extreme hydrodynamic events like floods, typhoons, and storms might also cause the sediment transportation and redistribution, thus affecting the transportation and mobility of heavy metals from sediments (Li et al. 2018; Tsai et al. 2016).

2.2 Chemical Transformation

The fate of heavy metals such as chemical interactions, mobility, toxicity, and bioavailability in marine ecosystem largely depends on their chemical fractions (Hu et al. 2018; Nemati et al. 2011; Sundaray et al. 2011; Xia et al. 2020). These chemical fractions include residual, oxidizable, reducible, and exchangeable forms (Kang et al. 2017; Nemati et al. 2011; Sundaray et al. 2011; Xia et al. 2020; Zaaboub et al. 2015). Of these forms exchangeable fraction is highly active whereas residual fraction is observed to be relatively stable (Hu et al. 2018). The other two forms become active or firmly bound based on physical and chemical properties of sediments (Palleiro et al. 2016; Xia et al. 2020; Yu et al. 2020). The bioavailability and mobility of heavy metals in the sediment is based on their solid phase form and total concentration (Filgueiras et al. 2002; Gao et al. 2008).

A study was conducted in assessing the accumulation and chemical forms of potentially toxic metals (PTMs) in core sediments (0–40 cm) collected from the ten coral ecosystems of the Persian Gulf, Iran (Jafarabadi et al. 2020b). The chemical forms of metals in sediments can strongly affect their mobility, toxicity, chemical interactions, and bioavailability (Kang et al. 2017). Most of the metals were found in the form of mobile bioavailable fractions in surficial sediment, the sediment layer at which the interaction with marine biota is maximum (Fig. 7.1).

Heavy metals in the state of reducible fractions are largely affected by oxidation, reduction conditions in the under water. The metals in acid soluble fraction are affected by pH change in sediments and oxidizable state on organic matter and oxidation-reduction potential (ORP) (Liu et al. 2019). The metals soluble in acid are retained on solid surface by weak interactions and can be released by ion-exchange processes. Lowering pH causes the change in ionic composition of sediments through adsorption-desorption reactions leading to metals remobilization (Filgueiras et al. 2002; Peng et al. 2009).

Cd has significantly different behavior from other metals. The enrichment and sedimentation processes of Cd do not get affected by adsorption mechanism due to its high content in acid soluble state (Liu et al. 2019). Cu metal is retained in sediment through specific adsorption and exchange along with precipitation (Filgueiras et al. 2002). A study was conducted (Sundaray et al. 2011) to evaluate the water quality, risk assessment, and mobility of heavy metals in sediment samples collected from Mahanadi River and estuarine systems (Sundaray et al. 2011), which receive major pollution load from agricultural and industrial areas of Orissa, India (Sundaray et al. 2006, 2009). The results suggested that Cr (58.9–86.1%), Pb (41.9–80.2%), and Fe (73.4–94.5%) dominated the residual fraction in the Mahanadi River estuarine sediments (Sundaray et al. 2011). The heavy metals like Pb, Ni, Zn, Cu, Co, Cd, and Mn were found in carbonate phase because of their high affinity for carbonate and may co-precipitate with it (Sundaray 2007).

Cr was found to have lower association degree (0.8–3.9%) in carbonate phase because of Cr^{3+} ions inability to form carbonates complex. The higher content of Mn in carbonate phase is mostly because of their ionic radii similarity with calcium,

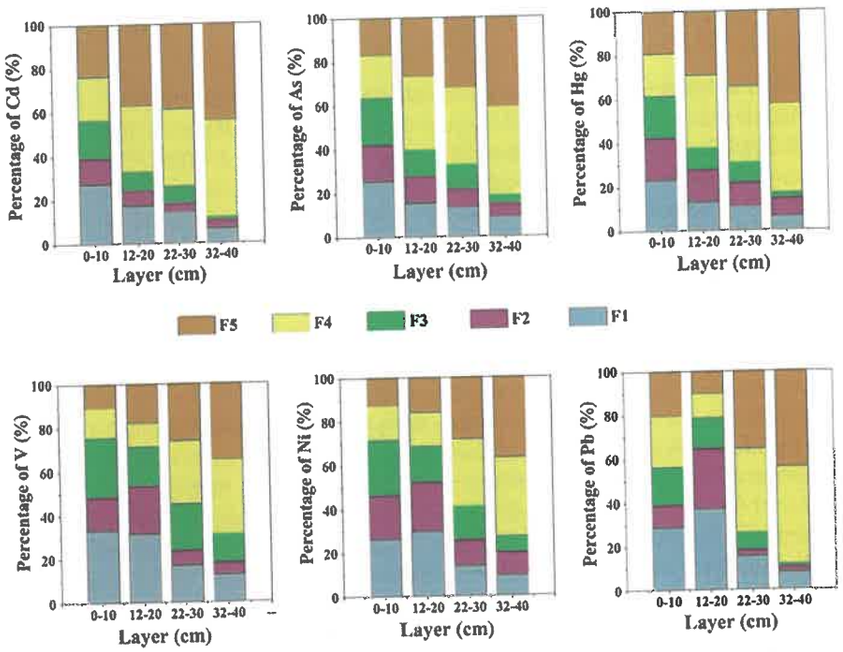


Fig. 7.1 Contribution of Cd, As, Hg, V, Ni, and Pb in the exchangeable (F1), carbonate (F2), reducible (F3), organic (F4), and residual (F5) fractions. Source: Jafarabadi et al. (2020b)

allowing the substitution of Ca with Mn in carbonate phase (Ansari et al. 2004; Marx and McGowan 2010; Mildvan 1970; Rath et al. 2009; Sundaray 2007; Zhang et al. 1988). The results also indicated that Fe–Mn oxy-hydroxide acts as the scavenger for all heavy metals except Cd and Cu due to the flocculation, adsorption, and co precipitation of heavy metals with Fe and Mn oxy-hydroxide colloids (de Andrade Passos et al. 2010; Iwegbue et al. 2007, 2009; Rath et al. 2009; Venkateswaran et al. 2007). Organic bound metals Fe, Ni, Cr, Co, and Pb were found to be the second most dominant fractions.

Hg is highly toxic and bio-accumulative neurotoxin metal (Streets et al. 2019) and is released in environment from natural (volcanoes and forest fires) as well as anthropogenic sources (coal-fired power stations, artisanal and small-scale gold mining, cement manufacture, waste incineration) releasing both forms Hg (0) and Hg (II) (Dastoor et al. 2015; Durnford et al. 2010). Hg (II) with its high affinity for organic matter and mineral surfaces in sediments acts as its sinks and also acts as important site for Hg methylation (MeHg). MeHg forms monomethyl mercury (MMHg) mostly exists in natural environment, whereas in sea water dimethylmercury (DMHg) is the dominant species. Both MeHg forms are lipophilic and toxic but only MMHg has been found to biomagnify in food webs (Lavoie et al. 2013). Hg methylation is a biotic process completed by some microorganisms carrying the genes (hgcAB genes) involved in the methylation process (Parks et al. 2013). These

organisms carrying hgcAB genes consist of a wide range of methanogens, some fermentative microorganisms, iron-reducing bacteria, and sulfate-reducing bacteria (Gilmour et al. 2013, 2018). Demethylation of MeHg can occur through biotic and abiotic means. Abiotic demethylation can occur through photochemical degradation in surface waters (Klapstein and O'Driscoll 2018; Krithiga et al. 2022; Lehnherr et al. 2012; Poste et al. 2015; Seller et al. 1996).

3 Organic Pollutants

Organic pollutants that exist for long periods in ecosystems due to their nonbiodegradability are known as persistent organic pollutants (POPs) (Alharbi et al. 2018; Krithiga et al. 2022). These compounds are much more toxic regardless of being present in lower concentrations. Organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), and endosulfan, as well as industrial chemicals and by-products such as polychlorinated biphenyls (PCBs) and certain polybrominated diphenyl ethers (PBDEs), are classified as POPs and regulated under the internationally binding Stockholm Convention (Dietz et al. 2013; Rigét et al. 2010). POPs contain a wide range of substances, including chemical compounds that are used in agricultural land, production processes, disease management, and any industrial procedures. These compounds are unintentionally produced as a result of the burning of medical waste, smoke-emitting manufacturing operations, or combustion (Kosek et al. 2018; Kosek and Ruman 2021).

3.1 Migration

Organic contaminants are frequently carried in deep marine ecosystems through a complicated assemblage of biophysical mechanisms known as biological pump (Galbán-Malagón et al. 2012). The efficiency of biological pump is extremely affected by solar and climatic factors resulting in seasonal and regional variations (Lutz et al. 2007). The transportation of dissolved organic pollutants in the marine environment depends on many factors including settling particle properties, deep-water local environmental conditions, physicochemical properties of organic pollutants, seafloor geomorphology, biodiversity, and climate factors. As a result, knowing the biological pump's appropriation efficiencies and mechanisms is critical, as these activities affect the deep sea's "sink and source" role (Sanganyado et al. 2021). It was reported by Hatzianestis et al. (2020) that from Cretan Strait deep-water outflows were the source of PAHs in the Aegean Sea and hence its accumulation in sediments. Ocean currents through horizontal and vertical movements cause interaction between sea surface and seafloor (Jia et al. 2019). Oceanic current plays a vital role in flux of organic contaminants in the deep sea with the net flow affected by geophysical, seasonal, and climate conditions.

3.2 Chemical Transformation

Biomagnification' significantly occurs in aquatic organisms because of feeding actions that lead to high pollutant concentrations in the body than food sources (Walters et al. 2011; Yoshino et al. 2020). The biotransformation process of organic pollutants is similar in both deep sea and surface waters despite the fact that there is significant difference in the hydrostatic pressure and temperature (Louvado et al. 2015). Temperature plays a significant role in the degradation of organic pollutants as the enzymatic activity of organohalogen-degrading microorganisms declines at low temperature. Several studies have isolated bacteria from deep-sea hydrothermal vents which can degrade organohalogens and were found to readily degrade PAHs and n-alkanes (Ma et al. 2021). Further studies from Australia have discovered three genes associated with aerobic hydrocarbon degradation (alkB, c23o, and pmoA) using next-generation sequencing (van de Kamp et al. 2019). Research studies have demonstrated that lighter congeners such as di- and tri-PCBs have been more successfully degraded than heavier forms such as tri-PCBs (Scoma et al. 2019).

4 Pharmaceuticals

Pharmaceuticals are produced by the synthesis or extraction of natural inorganic or organic chemical substances and are effective for disease prevention and treatment. These chemicals are commonly utilized for diagnostic purposes in both human and animal subjects and for enhancing the overall quality of life. Additionally, they may be administered to animals to enhance their development rate and optimize their eating efficiency (Daghrir and Drogui 2013). These drugs can be categorized into various groups based on their therapeutic uses. These groups include anti-diabetics (such as alpha-glucosidase inhibitors), β-blockers (such as atenolol and metoprolol), antibiotics (such as trimethoprim), lipid regulators (such as gemfibrozil), antiepileptic drugs (such as acetazolamide), tranquilizers (such as diazepam), antimicrobials (such as penicillins), antiulcer and antihistamine drugs (such as cimetidine and famotidine), antianxiety/hypnotic agents (such as diazepam), anti-inflammatories and analgesics (such as ibuprofen, paracetamol, and diclofenac), antidepressants (such as benzodiazepines), anticancer drugs (such as cyclophosphamide and ifosfamide), antipyretics and stimulants (such as dexamphetamine, methylphenidate, and modafinil), and estrogens and hormonal compounds (such as estriol, estradiol, and estrone) (Bruce et al. 2010; Canonica and Blaiss 2011; Esplugas et al. 2007; Nussbaumer et al. 2011).

4.1 Migration

Following their use, pharmaceutical substances are released into the environment either as metabolites or as parent chemicals. This often occurs via the discharge of treated wastewater from wastewater treatment facilities (WWTPs), where their removal is generally inadequate. The environmental presence of secondary pharmaceutical sources encompasses several factors, such as manufacturing facilities, the agricultural practice of land application of sewage sludge, aquaculture activities, and veterinary treatments (Vieno et al. 2017). Because of their intrinsic biological activity and "pseudopersistence," these chemicals have been identified as a potential danger to aquatic environments. Despite being the final recipient of continental pollution, their existence in the marine environment has received little attention.

Antibiotics are among the most often observed classes in sediments and marine waters (Arpin-Pont et al. 2016). Particular concern arises when an outbreak of antibiotic-resistant bacteria results from overall contamination (Marti et al. 2014). The effluent from sewage treatment facilities (STPs) and riverine inputs account for a significant portion of the pollution that has been released into marine habitats. Despite the fact that the amount of antibiotic residues will drop significantly as a result of the attenuation process (which may include dilution, adsorption, hydrolysis, photolysis, and/or biodegradation), the risks associated with antibiotic usage still remain (Zhang et al. 2013). Because of their bio-accumulative capacity, they may still threaten aquatic life (Chen et al. 2015). Aquatic pollution poses significant challenges because aquatic creatures are subjected to continuous exposure throughout their life cycles and over several generations (Daughton and Ternes 1999).

4.2 Chemical Transformation

In the aquatic environment, compounds may undergo several processes, including photochemical depletion, sorption onto solid matrices, dilution, and movement throughout the water column. Additionally, these compounds may be taken up by biological species present in the aquatic system. The primary mechanism for the abiotic transformation of medicinal chemicals in the aquatic environment is photochemical degradation. Photolytic reactions might manifest themselves via two distinct mechanisms: The compound undergoes significant photodecomposition, resulting in the formation of several photoproducts, hence rendering the two reactions unstable (Ojemaye and Petrik 2019). Primary photolysis is accomplished through the direct consumption of sunlight, whereas indirect photolysis requires the use of natural photosensitizers (Nikolaou et al. 2007). Pharmaceuticals have the capacity to undergo three primary prospective fates:

(i) The substance dissolves in carbon dioxide and water via mineralization (Klaminder et al. 2014).

(ii) The substance's lipophilic properties hinder its degradation, resulting in a portion of it being retained in the sludge.
(iii) The lipophilic precursor undergoes metabolic transformation into a more hydrophilic derivative, which retains stability and persistence, enabling its passage via the effluent treatment facility and subsequent discharge into recipient aquatic environments (Richardson and Bowron 1985).

In direct photolysis, a molecule takes in energy from the sun and breaks apart. In indirect photolysis, naturally occurring molecules such as nitrates create strong reactive species such as singlet oxygen (O_2), hydroxyl radicals (OH) or alkyl peroxyl radicals (OOR), and "aqueous" electrons. However, carbonate radicals are formed when hydroxyl groups react with carbonate/bicarbonate ions. This radical can scavenge HO and slow down or even stop degradation. Photosensitization is another type of indirect photolysis that occurs when a species that absorbs light, such as colored dissolved organic matter in its triplet state, moves energy to an organic species that is in its ground state. This energy transfer induces excitation in the organic species, enabling it to participate in photolytic reactions. Humic acids have the ability to impede the pace of photo transformation via their light absorption properties and function as internal filters. Consequently, this impedes the flow of energy to other substances, including medicinal chemicals (Prabhakaran et al. 2009). Conversely, several investigations have shown the crucial role of inherent chromophores found in dispersed organic material as the primary photosensitizer in the indirect photo transformation of medicinal compounds in natural environments, particularly in situations of limited energy availability (Peuravuori and Pihlaja 2009).

The significance of photochemical degradation in determining the fate of pharmaceuticals in the environment is supported by a number of indicators. A considerable number of these compounds are equipped with functional chromophore groups, aromatic rings, and heteroatoms, which enable them to either absorb solar radiation or engage in reactions with photogenerated transient species present in natural waters, such as reactive oxygen species and photoexcited natural organic matter (NOM). Moreover, certain compounds in question possess structural moieties, including phenol, nitro, and napthoxyl groups, which bear resemblance to those identified in pesticides known to experience photodegradation (Boreen et al. 2003). There has not been enough research on how pharmaceuticals are separated from sediment in marine environments, but these results show that sediment processes might have an effect on where pharmaceuticals end up in aquatic ecosystems. Sediments can potentially serve as a secondary source of contamination, facilitating the release of pharmaceuticals in response to fluctuations in pH and environmental salinity, storm activity, or tidal movements (Liang et al. 2013). Biotic processes can only cause limited degree of transformation because of the biopersistence of many organic compounds (Fatta-Kassinos et al. 2011; Kümmerer et al. 2004). Whether through biotic or abiotic processes, the partial breakdown of medicines and/or their by-products during wastewater treatment may result in transformation products (TPs). These TPs are characterized by distinct features compared to the original compounds (Kern et al. 2010). After being released into aquatic ecosystems,

medicines and their metabolites possess the capacity to undergo metabolic transformations, both biotic and abiotic, leading to their breakdown. Additionally, they may bind to particulate matter that is suspended (SPM) and sediments and, in some instances, accumulate inside the tissues of aquatic species (Ramirez et al. 2009). The applicability of existing data on the ecological fate of medicines in freshwater settings to marine environments is not guaranteed. The variances in physico-chemical parameters such as salinity, pH, and organic matter content between freshwater and saltwater have the potential to influence the environmental destiny of medicinal compounds (Weigel et al. 2002).

The increasing pH of saltwater may affect the environmental destiny of ionizable medicines. Due to light attenuation, photodegradation may be a less relevant removal process in coastal waters than in more shallow freshwater habitats. Because of changes in water composition, indirect photodegradation pathways may vary from those seen in freshwater (Ge et al. 2010; Mei Fun Choong et al. 2006). There is some information indicating that the environmental destiny of medicinal substances may exhibit variations between freshwater and saltwater settings.

The observed transformation characteristics of ibuprofen exhibited variations when exposed to freshwater and marine environments (Weigel et al. 2004). Furthermore, it was observed that prochlorperazine exhibited greater stability in saltwater than in freshwater (Mei Fun Choong et al. 2006). Both aerobic and anaerobic biodegradation are effective approaches for the removal of pharmaceuticals from contaminated water sources (Wellington et al. 2013). Subsequent investigations have shown that diclofenac, as an illustrative example, undergoes biodegradation during a period of 10 days subsequent to its absorption into sludge. Drug transformations may occur in wastewater or water treatment facilities and, in rare cases, in surface water via sedimentation, hydrolysis, and photolysis (Van Doorslaer et al. 2014).

5 Plastics

Plastic is a man-made material and serves many benefits to human society because of its low price, ease of production, light weight, and durability (Andrady and Neal 2009; Luo et al. 2021). According to estimates in the year 2018 the global plastic production has reached to 359 million tons (Bridson et al. 2021). Most commonly used plastic polymers in industrial applications include polyvinylchloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), and polyethylene (PE) (Andrady 2011; Hidalgo-Ruz et al. 2012). Plastics can be classified based on particle size into Macro-plastics (>20 mm), Meso-plastics (5–20 mm), Micro-plastics (MPs, <5 mm) down to Nano-plastics (from 1 μm to 1 nm) (Franzellitti et al. 2019; Gunaalan et al. 2020). Plastic polymers are not only used for consumer products but are also widely used to make foams, adhesives, sealants, coatings, and synthetic fibers which have industrial applications (Engelhart 2010). According to data in Europe the plastic use is mostly dominated by (38%)

packaging, (21%) building and construction, (7%) automotive, (6%) electronics, and (28%) in other areas as medical and leisure activities.

But the diverse consumption of plastics is associated with high plastic waste generation on land and finally disposed into oceans. Most of the plastic products have short life span with estimates that 40% of plastic products with service life of less than 1 month (Achilias et al. 2007). Plastics properties such as durability and stability make them more resistant to degradation and tend to accumulate in the nature (Barnes et al. 2009). Plastics can persist in the environment for hundreds or thousands of years but as plastics ages in the marine environment its degradation leads to release of potentially harmful chemical compounds (Deanin 1975). Plastic pollution in the marine ecosystem is currently recognized as a significant environmental issue with studies reporting plastic debris accumulating all over the seabed and water column (Table 7.1).

5.1 *Migration*

Although the accurate amount of plastic waste entering the marine environment is not known, according to rough estimates 4.8–12.7 Mt/year of land-based plastic waste makes its way into oceans (Gregory 2009; Jambeck et al. 2015). The wind and water currents in marine environment transport the plastic fragments as it ages (Noone et al. 2013). Plastic particles with size range of >5 mm are called macro- and meso-plastics, while micro-plastics have diameter less than 5 mm (Cole et al. 2011). Depending on their density, shape, and composition, plastics can be buoyant, neutrally buoyant, sinking, or spread both horizontally and vertically in the water column and on the bottom (Cole et al. 2011). For example, foams made of polyethylene, propylene, and many types of polystyrene are less dense than sea water and float, whereas vinyl chloride and polyethylene terephthalate sink (Andrady 2015). Furthermore, the distribution is influenced by physical elements such as winds, currents, and coastline topography as well as human factors such as metropolitan centers, tourists, and trade routes (Li et al. 2016a).

Synthetic polymers such as polypropylene and polyethylene are buoyant and can be transported in sea water (Andrady 2011). Even polyvinylchloride polymer which is heavier than saltwater can be transported by underlying water currents (Engler 2012). A study conducted by Collignon et al. (2012) found that in the Northwestern Mediterranean Sea particle concentrations were five times higher before the occasion of strong breeze which increased the fraternization and perpendicular redistribution of plastics in the water in the North Atlantic Subtropical Gyre. Also, an inverse relation was found between ocean side plastic particle intensity and storm velocity. The tides and tsunamis can also increase migration of plastics in marine water (Sadri and Thompson 2014). MPs have high concentrations in sediment compared to surrounding water in oceans (Alomar et al. 2016; Suaria and Aliani 2014; Woodall et al. 2014) accounting for up to 3.3% of the sediment mass on contaminated beaches (Boucher et al. 2016; Van Cauwenberghe et al. 2015a, b). As a result

Table 7.1 Micro-plastics abundance in marine environment worldwide

Country	Area/location	Concentration of MPs		Seasons/ year of study	References
		In water	In sediments		
China	Buqu River, Tibet Plateau	967 ± 141 particles/m^3	130 ± 71 particles/kg	March 2019	Jiang et al. (2019)
	Naqu River, Tibet Plateau	817 ± 589 particles/m^3	50 ± 7 particles/kg		
	Lhasa river, Tibet Plateau	683 ± 354 particles/m^3	180 ± 42 particles/kg		
	Downstream Lhasa, Tibet Plateau	700 ± 94 particles/m^3	195 ± 64 particles/kg		
	Upstream Nyingchi, Tibet Plateau	483 ± 118 particles/m^3	65 ± 21 particles/kg		
	Nyingchi, Tibet Plateau	517 ± 24 particles/m^3	90 ± 14 particles/kg		
North America	Lake Michigan	–	524/g	210	Cheng et al. (2022)
United Kingdom	Southern coast, Bristol Channel	51,144 particles km^2	1446 particles/ kg	2020	Wilson et al. (2021)
Western Australia	Stormwater drainage	–	3500 particles/ kg	2021	Lutz et al. (2021)
Sri Lanka	Bundala National Park (BNP)	0.276 ± 0.077 particles km^2 in BNP	102 ± 16 particles/kg in BNP	2020	Dharmadasa et al. (2021)
	Hikkaduwa Marine National Park (HNP)	0.515 ± 0.054 particles km^2 in HNP	111 ± 29 particles/kg in HNP		
Ireland	Coastline of Ireland	–	553 particles/kg	2016	Mendes et al. (2021)
Mauritius	Coastal sites around Mauritius Island	–	196 ± 2.84 particles/kg	2019	Mattan-Moorgawa et al. (2021)
USA and Mexico	Wider Caribbean sea	270 ± 55 particles km^2	–	2018	Aranda et al. (2022)
Spain	Harbor of Cartagena	–	19.37 ± 2.43 particles/kg	2019	Bayo et al. (2022)
Kenya	Marine nearshore surface waters	0.58 ± 1.29 particles m^3	–	2021	Kosore et al. (2022)

(continued)

Table 7.1 (continued)

Country	Area/location	Concentration of MPs		Seasons/ year of study	References
		In water	In sediments		
China	Northern South China Sea	–	130.56 ± 40.48	2019	Ding et al. (2022)
Chile	Southeast coast	–	146.67 ± 14.67 particles/kg	2021	Jorquera et al. (2022)
	Northeast coast		133.33 ± 13.33 particles/kg		
	Northeast sector of the inner sea		78.58 ± 0.85 particles/kg		
Poland and Sweden	Gdansk harbor	161 ± 75 m^3	–	2021	Ferrero et al. (2022)
	Baltic Sea	24 ± 9 m^3			
	Gotland Island	45 ± 20 m^3			
Antarctica	Ross Sea surface water	0.10 ± 0.14 m^3	–	2017, 2018	Zhang et al. (2022)
	Dumont d'Urville Sea subsurface water	1.66 ± 1.20 m^3			
Portugal	Coastal area between Setúbal city and Sesimbra village	0.45 ± 0.52 m^3	–	2018	Rodrigues et al. (2020)
Northwestern Florida	Winter season	–	12.41 ± 3.56 particles/kg	2022	Ridall and Ingels (2022)
	Spring season		2.17 ± 0.63 particles/kg		
Argentina	Luna Azul	–	496/kg	2019	Jaubet et al. (2021)
	Aguirre		792/kg		
	Constituci'on		1061/kg		
	Popular		826/kg		
	Bristol		513/kg		
	Corrientes		666/kg		
	Luna Roja		247/kg		
	Playita		184/kg		
	Brusquitas		295/kg		
Vietnam Tien Giang Province	Estuary	–	42.5 particles/kg	2020	Hien et al. (2020)
South Georgia	King Edward Point Research Station	1.75 ± 5.17	–	2019	Buckingham et al. (2022)
	Gull Lake	2.67 ± 3.05			
Greece	Mediterranean coastal Antinioti lagoon	40–50 particles/L/ month	–	2020, 2021	Simantiris et al. (2022)

(continued)

Table 7.1 (continued)

Country	Area/location	Concentration of MPs		Seasons/ year of study	References
		In water	In sediments		
China	Yellow Sea, the East, China Sea, and South China Sea	800–15,600 m^3 (average)	20–700 m^3	2019	Yin et al. (2022)
United Arab Emirates	Coastline of the UAE	–	225.0 ± 90.1	2021	Al Hammadi et al. (2022)
	Sharjah		191.7 ± 125.8		
	Ajman		216.7 ± 146.5		
	Umm Al Quwain coastal waters		91.7 ± 52.0		

Source: Nawab et al. (2023)

of biofouling and interactions with marine organisms, microplastics accumulation in the ocean can lead to their sinking, with more plastic thickness as biofouling occurs, leading to high concentration of microplastics in the seabed sediments than in the surrounding seawater (Andrady 2011; Jorissen 2014; Reisser et al. 2013). MPs can accumulate in ocean sediments for very long time period.

Organic chemical compounds, such as additives in plastic, migrate at varying rates depending on their size. Smaller molecules tend to travel more quickly, such as monomers with lower boiling temperatures (Hahladakis et al. 2018). Even at room temperature, monomers, including vinyl chloride, ethylene, butadiene, and formaldehyde, will travel more quickly. Solubility, on the other hand, refers to the transfer of chemical compounds from a fluid phase such as water or air to a solid phase such as plastics.

5.2 Chemical Transformation

Once in the ocean water plastics are subject to wave action which stimulates physical breakdown from macro size to micro or even nano-plastics (Andrady and Neal 2009; Cózar et al. 2014) which cause an increase in particle surface area and additives leaching from plastics. Degradation of plastic polymers in the marine environment causes chemical changes in plastics through biotic and abiotic interactions (Strlic and Kolar 2005). Degradation involves series of chemical actions on plastic polymer that breaks the polymer as a result of different weathering processes including thermo-oxidative degradation, photo deprivation, thermal deprivation, and biodegradation resulting in the release of MPs in marine environment from macroscopic plastics (Fig. 7.2). The process of degradation causes shifts in physical and chemical properties of plastic polymers like surface morphology, density, particle size, color, and crystallinity (Rincon-Rubio et al. 2001).

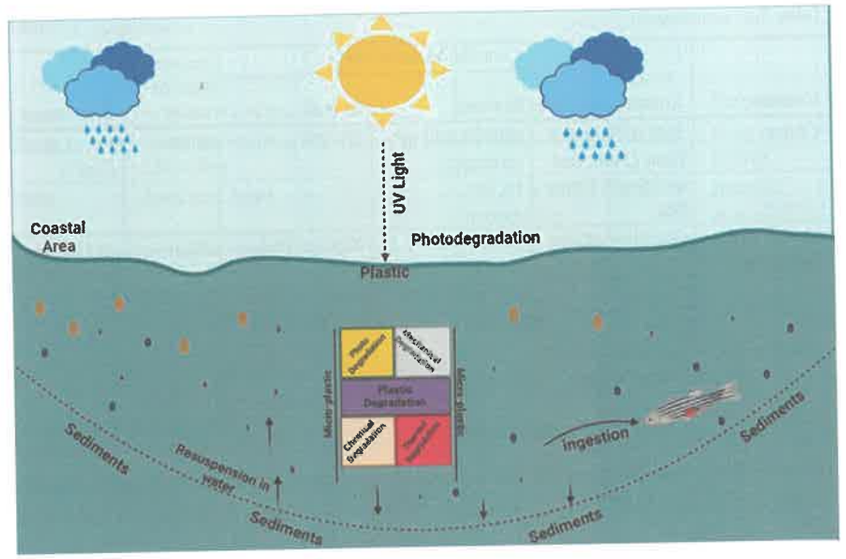


Fig. 7.2 Chemical transformation of plastics in marine ecosystem through mechanical, chemical, thermal, and photodegradation processes (created using BioRender: https://www.biorender.com/)

Abiotic degradation of plastics occurs through hydrolytic, thermal, and UV light interactions (Andrady 2011). Abiotic factors which trigger the plastics degradation on the ocean surface are moderate temperatures, sunlight with 300 nm and longer wavelengths, reaction with oxygen and hydrolysis (Pritchard 1998). Abiotic degradation is generally subdivided into three important steps, i.e., initiation, propagation, and termination (Pritchard 1998). In the first step of initiation chemical bonds (C-H) are broken in the main polymer chain through light or heat action which produces free radicals (Gijsman et al. 1999; Pearce 1975; Yousif and Haddad 2013). Propagation is the step in which reaction between polymer radical and oxygen forms hyperoxides and complex reactions may lead to autooxidation (Pritchard 1998; Rabek 2012; Singh and Sharma 2008). Oxidation thus leads to branching, crosslinking, random chain scission and produces oxygen-containing functional groups (Chiellini et al. 2002; Pritchard 1998). Termination of reaction occurs when combination of two radicals produces inert products (Grassie and Scott 1988). Ketones, aldehydes, and olefins are mostly produced as a result of termination reactions which are also susceptible to photo-initiated degradation because of unsaturated double bonds. This reduces the molecular weight of polymers and makes them brittle (Summers and Rabinovitch 1999) and more susceptible to fragmentation by increase in surface area for further reactions.

Plastics are generally divided into two groups while discussing their degradation pathways: plastics with carbon-carbon backbone and plastics with heteroatoms in the main chain. PVC, PS, PP, and PE belong to the first category, whereas PU and PET plastics contain heteroatoms in their C-chain (Gewert et al. 2015).

The degradation of plastics with a carbon–carbon backbone is detailed below.

- *Poly(vinyl chloride) (PVC)*
- PVC is the least stable with highest photodegradation rates with exposure to UV light (Feldman 2014). Exposure to sunlight causes dichlorination of PVC, leading to the formation of conjugated double bonds in polyene polymers and hydrochloric acid, along with smaller amounts of other by-products (Nagy et al. 1980; Pielichowski et al. 2022). Discoloration of the polymer is the visual sign of degradation (Feldman 2014). PVC has been found to have high resistance toward biodegradation (Summers and Rabinovitch 1999) because of the presence of halogens especially chlorines which increase the resistance to aerobic biodegradation (Summers and Rabinovitch 1999).
- *Polystyrene (PS)*
- UV light when absorbed by the PS polymer leads to the excitation of phenyl rings with energy causing the cleavage of nearest C-H bond resulting in the formation of polymer radical (Yousif and Haddad 2013). This forms cross-linking and chain scission with the formation of olefins and ketones (Singh and Sharma 2008; Mishra and Yagci 2016). The main products of degradation are volatile styrene monomers (Mishra and Yagci 2016). In contrast to abiotic pathways, the PS polymer is most durable thermoplastic toward biodegradation (Mor and Sivan 2008).
- *Polypropylene (PP)*
- PP polymer is less stable because of tertiary carbon atoms in the backbone which is more susceptible to be degraded through abiotic factors (Grassie and Scott 1988; Mishra and Yagci 2016). Along with molecular weight reduction new functional groups especially hyperoxides and carbonyl groups are formed (Mishra and Yagci 2016). Microbial degradation is decreased due to tertiary carbon atoms in the structure (Singh and Dwivedi 2004).
- *Polyethylene (PE)*
- Abiotic oxidation of polyethylene (PE) from exposure to UV light leads to the formation of oxygenated low-molecular-weight fragments including ketones, aldehydes, alcohols, and aliphatic carboxylic acids (Vasile 2006) during the propagation phase in which autoxidation by complex radical reactions takes place (Tolinski 2009). The range of degradation products includes ethane, ethene, propane, propene, hexane, and butene (Mishra and Yagci 2016). Biodegradation may start at any terminal methyl group in PE and is faster if the molecular weight of polymer fragment is less than 500 Da (Vasile 2006). Small polymer fragments are further biodegraded to acids and esters (Vasile 2006) with ultimate products of humus, CO2, and H2O as a result of enzymatic action.
- Plastics with carbon and hetero atoms in the main chain have high thermal stability with potential susceptibility to hydrolytic cleavage (Müller et al. 2001). Degradation of plastics with heteroatoms in the main chain is discussed below:
- *Poly(ethylene terephthalate) (PET)*
- In marine environment hydrolytic degradation and photo-oxidation are important pathways for PET degradation. The cleavage of ester bond by photodegradation

results in the products of carboxylic acid end group and vinyl end group either directly or through radicals. The hydrolytic degradation of PET (Summers and Rabinovitch 1999) in water is higher under acidic or basic conditions (Allen et al. 1991) with end products of carboxylic acid alcohol functional groups. PET polymer is highly resistant to biodegradation because of compact structure but a study has also reported weak degradation of PET by microbes and lipase (Zhang et al. 2004).

- *Polyurethane (PU)*
- PU polymers are large and complex chains with carbon, oxygen, and nitrogen atoms (Szycher 2013). The degradation process starts with cleavage of ester bond. The degradation process of PU polymer is through hydrolysis, photo-oxidation, and biodegradation in the marine environment. The most prevalent chemical reaction is the hydrolytic degradation reaction (Nakajima-Kambe et al. 1999; Szycher 2013) of ester bond accelerated under acidic conditions. PU is known for its susceptibility to fungal (Nakajima-Kambe et al. 1999) and bacterial biodegradation as well as biodegradation by poly-urethanase enzymes (Szycher 2013; Zhang et al. 2004). Microbial attack is more prevalent on polyster segments of PU, whereas polyether segments are more resistant (Chanda and Roy 2007; Szycher 2013).

Biotic degradation of plastic polymers is followed by abiotic pathways as smaller fragments produced as a result of abiotic degradation can pass through cellular membranes and undergo biodegradation by cellular enzymes, while some microbes biodegrade plastic fragments by producing extracellular enzymes (Shah et al. 2008). Abiotic degradation also produces carbonyl groups which make the polymer more hydrophilic and enhance its availability for biodegradation (Mishra and Yagci 2016). In biodegradation polymer is transformed into its monomer units followed by mineralization (Shah et al. 2008). These abiotic and biotic degradation processes in the marine environment may take the time period of up to decades or even longer. Plastics have lengthy ecological life span of up to thousands of years and in the marine environment the complete conversion of breakdown products by photo-oxidative degradation into inorganic molecules, water, and carbon dioxide is a very slow process (Lithner et al. 2011) and particularly becomes very slow by deprivation of UV-B rays in sunshine (Andrady 2005).

During the processing of plastic products additives are added in certain ratios to enhance the service life and improve the polymer performance (Hahladakis et al. 2018). Different plastic additives can be classified based on its use and functions such as stabilizers, antistatic agents, antioxidants, colorants, flame retardants, and plasticizers (Groh et al. 2019). The additives in plastic polymers can easily leach out in the marine environment during degradation as additives are not usually covalently bonded to the polymer. Another problem is sorption of persistent organic pollutants (POPs) such as PCBs, DDTs, and PAHs on the plastic surface resulting in magnification of their concentrations compared to surrounding water (Andrady 2011). Plastic particles in the range of micro and nano size ranges are more prone to sorb contaminants in water due to high surface-to-volume ratio (Cole et al. 2011).

According to estimates >8 million tons of plastics are discharged into marine environment every year accounting for 80% of marine litter (Andrady 2011). The plastic additives have increasingly been detected in global marine waters (Bergé et al. 2013) with PAEs and polybrominated diphenyl ethers (PBDEs) most frequently found in concentration range of 2.2–23.4 μg/L and 0.1–23.2 ng/L, respectively. The most concerning for the biologists is that not only additives have been detected in seawater and seafloor sediments but increasing concentrations found in biological tissues of marine organisms including fish, invertebrates, marine mammals, and sea birds (Cheng et al. 2013; Johansson et al. 2006; Peng et al. 2007) proving that plastic additives are likely to migrate into species through leaching, evaporation, abrasion, and ingestion (Ryan 2019). Many studies have been conducted to study the impacts of additives leaching from plastic polymers during plastic aging (Chen et al. 2019; Khaled et al. 2018; Luo et al. 2020; Paluselli et al. 2018; Rani et al. 2017) (Fig. 7.3).

A study was conducted on two common plastic materials plastic garbage bags and insulation layer of plastic cables under light conditions. The results analyzed

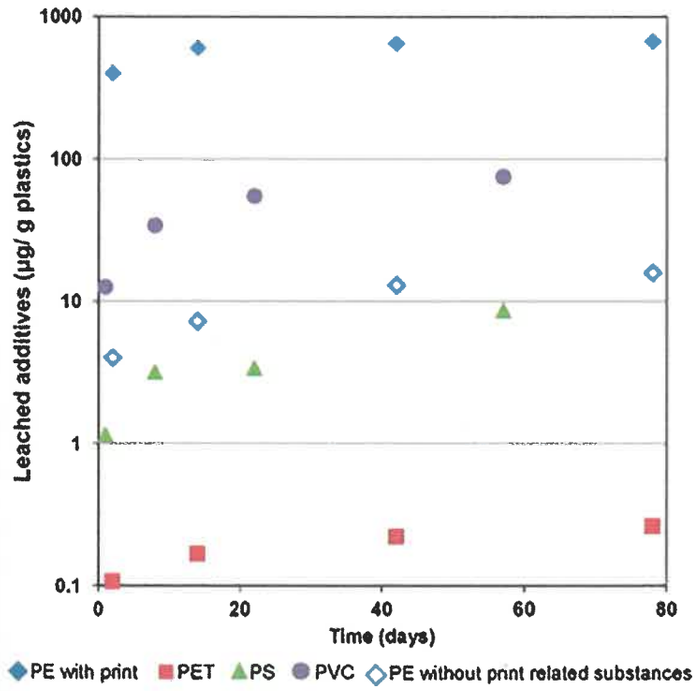


Fig. 7.3 Summary of selected additives leached from different plastic polymers into salt water (SW condition) illustrated as leached additives per gram plastic versus leaching time. *PE* polyethylene, *PET* polyethylene terephthalate, *PS* polystyrene, *PVC* polyvinylchloride. Adapted from Suhrhoff and Scholz-Böttcher (2016)

that after 90 days most significant additives released were PAEs and with aging there was increase in the amount of PAEs by a factor of 5 (Paluselli et al. 2018). It was also found that increase in surface roughness and cracks after aging promoted the leaching of additives especially under acidic conditions. Increase in aging time also led to the release of lead chromate causing high toxicity (Luo et al. 2020). Adsorption of contaminants in water on plastic polymer occurs not only through physical processes but also through chemical interactions. While physical adsorption is based on large surface area and force of Van-der-Waals, chemical adsorption is due to the attractive forces between organic chemicals and aquaphobic plastic exterior. Chemical sorption depends on various factors such as sorbent's physical and chemical properties, crystallinity (Karapanagioti and Klontza 2008; Mato et al. 2001), surface area, (Teuten et al. 2009), and diffusion (Karapanagioti and Klontza 2008; Pascall et al. 2005). It is reported that polyethylene has large surface area than PP and PVC and attraction for range of hydrophobic organic compounds. A study reported the decreasing order of hydrophobicity in the organic pollutants such as HCHs, < PCBs, < DDTs, < PAHs (Wang and Wang 2018).

6 Oil Spills

Annually it has been estimated that over one million metric tons of petroleum products are released into marine environment through accidental oil spills, marine transport, natural oil seeps, and from municipal and industrial sources (Boehmer-Christiansen 2008). The massive marine oil spill of 2010 Deepwater Horizon (DWH) released 4.9 million barrels of crude oil into the Gulf of Mexico and is the second largest oil spill in the USA after first Gulf War oil spill from Kuwait (Abbriano et al. 2011; Graham et al. 2010; Hemmer et al. 2011). Crude oil is a mixture of complex fluid with thousands of hydrocarbons (containing only H and C), non-hydrocarbons containing N (0.1–2%), O (0.1–1.5%) and S (0.5–6% of the oil), and metals in trace amounts (Wise et al. 2023). The structure of hydrocarbon and non-hydrocarbon components in crude oil is best summarized by Overton et al. (2016) which include saturated hydrocarbons (i.e., alkanes, cycloalkanes); polycyclic aromatic sulfur heterocycles (PASH), aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic oxygen heterocycles (PAOH); polycyclic aromatic nitrogen heterocycles (PANH), alkylated PASHs, PAHs, PAOHs and PANHs, asphaltenes; resins and biomarkers (e.g., hopanes and steranes).

6.1 Migration

The oil droplets get dispersed after its release in marine environment, whereas benzene and alkyl-substituted benzenes (monocyclic compounds) and low-molecular-weight 2–3 ring polycyclic aromatic hydrocarbons (PAHs) will go through partial dissolution (Wise et al. 2023). Naturally dispersed oil droplets readily aggregate with organic matter or clay minerals to form oil suspended particulate material (SPM) aggregates (OSAs), also called as oil–mineral aggregation, oil–clay flocculation, and oil–SPM interactions (Khelifa et al. 2002, 2005) (Fig. 7.4) (Omotoso et al. 2002; Owens 1999; Payne et al. 2003). In water oil droplets may be present either in dissolved oil components or dispersed oil droplets and the characteristics of oil droplets, in particular viscosity is an important parameter which affects the formation of OSAs (Bragg and Owens 1994; Khelifa et al. 2002; Le Floch et al. 2002; Omotoso et al. 2002). Oil droplets with low viscosity easily form OSAs (Khelifa et al. 2002), whereas oil droplets with high viscosity disperse less and hardly form aggregates with solids (Le Floch et al. 2002).

The water-soluble oil fractions and their derivative products include mixtures of monoaromatic hydrocarbons, PAHs generally called as BTEX (benzene, toluene, ethylbenzene, and xylenes), nitrogen- and sulfur-containing heterocyclic compounds, heavy metals, and phenols (Rodrigues et al. 2010; Saeed and Al-Mutairi 1999). Although dissolved oil fractions are relatively less common (<1% of crude

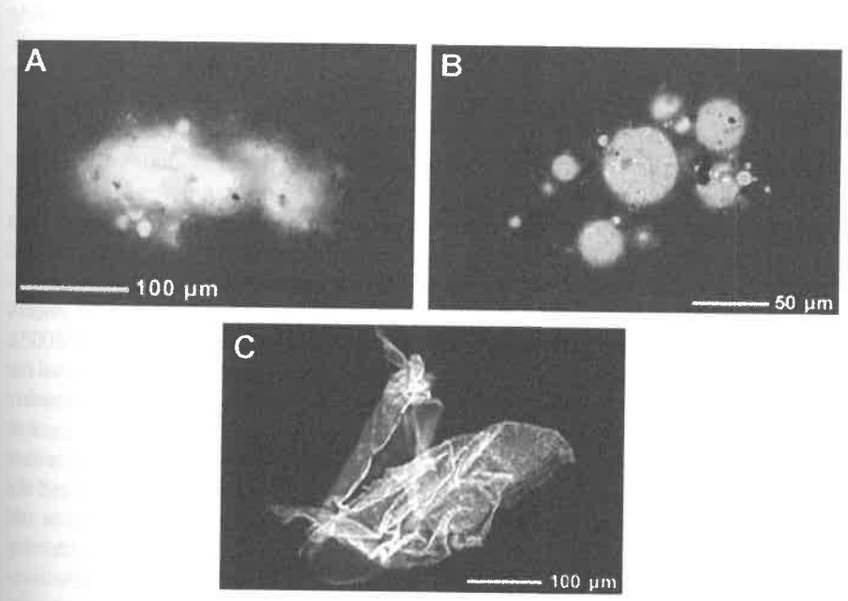


Fig. 7.4 Three distinct types of OSAs: (**a**) multiple droplets, (**b**) solid, and (**c**) flake aggregates as seen by combined bright-field and UV epi-fluorescence. Oil appears as bright areas and the mineral particles are dark in these microscopic images. Source: Gong et al. (2014)

oil), they are a major environmental concern (Saeed and Al-Mutairi 1999). The transportation of water-soluble oil compounds in marine environment is influenced by the process of biodegradation, solubilization, sorption on, and desorption from the sediments and SPM, and dilution into the water column. During the vertical transportation of SPM combined with deep-sea blowout, dissolved oil components can become incorporated into sediments in the bottom and may remain locked in place for long time (Gearing et al. 1980; Yamada et al. 2003). PAHs having mutagenic, toxic, persistent, and carcinogenic properties pose a serious threat to marine ecosystem associated with oil spills (Nam et al. 2008).

A study was conducted by Guo et al. (2007) to survey the spatial distribution of PAHs in surface waters, sediments, and SPM in some rivers polluted with industrial discharges in China. He concluded that more concentration of PAHs was observed in surface water and SPM with 2–3 rings PAHs dominated than in sediments where with 4–6 rings PAHs were found. Sediments act as vectors in the marine environment for oil droplets transportation and interactions between sediments and oil droplets determine its dispersion and degradation (Muschenheim and Lee 2002). Sediments in marine environment are either in the form of suspended particulate material (SPM) and settled aggregates. Oil droplets can interact with sediments in two ways either through direct aggregation forming OSAS or adsorption in sediment phase (Lee 2002; Sterling Jr et al. 2005), thus affecting the fate and transportation of oil particles in water (Bandara et al. 2011). The aggregates of oil with suspended particles (OSAs) cause stabilization of oil droplets and prevent re-coalescing, thus reducing the size of oil droplets and enhancing surface area leading to high rates of biodegradation (Ajijolaiya et al. 2006).

6.2 *Chemical Transformation*

Oil when released into marine environment go through complex transformations (biological, physical, and chemical), which include spreading, drifting, dispersion, stranding, and weathering. Weathering of hydrocarbons consists of evaporation, dissolution, biodegradation, emulsification (i.e., "mouse" formation), and photo-oxidation (Transportation Research Board and National Research Council 2003). An oil slick forms when oil spills into the ocean and quickly spreads across the surface (Garrett et al. 1998). The oil may be dispersed over hundreds of kilometers as dispersed droplets of oil within the water column or as thin films, oil slicks, formulations, and tar balls ranging in thickness from tens of micrometers to a few centimeters at the sea surface, depending upon the parameters of the ocean and the characteristics of the oil (Novelli et al. 2020). Weathering of oil droplets in the marine water alters the chemical composition of oil fractions (Fig. 7.5). Weathering processes cause the transformations in chemical composition of oil droplets compared to migration processes that move oil without altering its chemistry or composition. The events of spreading, evaporating and spraying, photo-oxidation, and emulsification are among the first steps in weathering to begin at the surface (Fingas

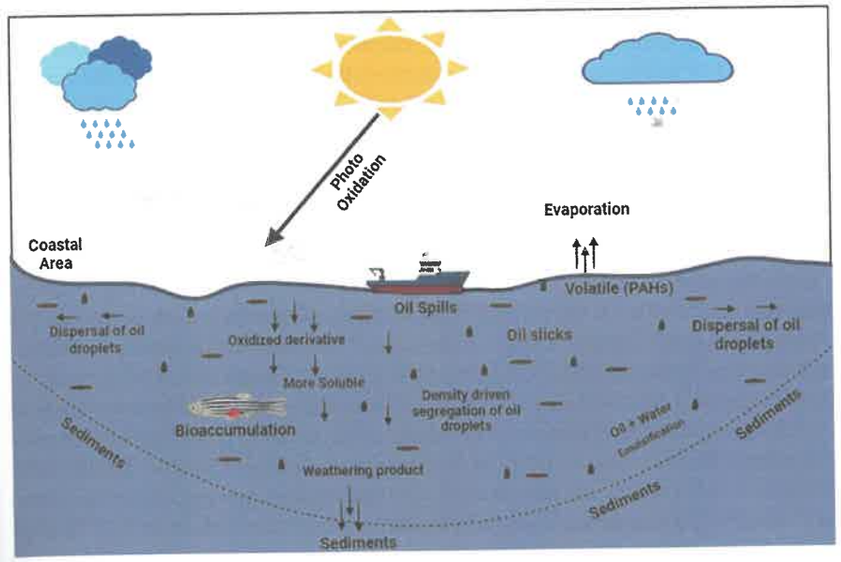


Fig. 7.5 Main processes in chemical transformation of oil droplets in marine ecosystem through photo-oxidation, evaporation, weathering & bioaccumulation (created on BioRender: https://www.biorender.com/)

2016; Tarr et al. 2016). The transfer of surface oil extends away from the splash or spill area during spreading, which is regulated by a density gradient and forms a thin layer of film (Zhang et al. 2019a).

The evaporation of volatile compounds from the water surface into atmosphere may occur within seconds to days and is based on environmental conditions, characteristics of compounds, and oil droplet physical form. Rising oil droplets stretch into a thin film at sea surface and highly volatile compounds evaporate quickly. Lighter fuels and medium crude oils, which have more volatile hydrocarbon contents typically becoming saturated with less than C15, monoaromatics, and lighter polyaromatic hydrocarbons (PAHs), show significant evaporation and aerosolization (Weitkamp et al. 2007). If rising oil droplets get trapped in established oil slick, it slows down the evaporation (Stout et al. 2016). In the atmosphere oxidation of volatile hydrocarbons forms secondary volatiles and smog. Chemical transformations of oil droplets lead to alteration in their molecular structure through the processes of either biological activity or complete/partial oxidation reactions. Photochemical reactions mostly cause partial oxidation (Ward et al. 2018), whereas the result of biodegradation may produce biomass, metabolites, or CO_2 as by-product (full oxidation).

Photo-oxidation is a crucial stage in the degradation of crude oil spilled at sea, affecting mainly the aromatic contents of oil (Ward et al. 2018). PAHs and aromatic N, S, and O heterocycles are commonly photo-oxidized when exposed to sun radiation; these compounds react with oxygen to generate oxidized derivatives that are

more soluble in water and less susceptible to biological degradation than their parent compounds (Marty and Potter 2014). The study on Deepwater Horizon oil spill (DwH) in US waters had reported that almost half of the floating sea surface oil slick was photo-oxidized by mass (Ward et al. 2018) into alkanes and PAHs oxidized derivatives (Stout et al. 2016). After 10 years of DwH oil spill accident it was analyzed that some amount was still found in the environment. It was reported that concentration of hydrocarbons fell below the detection limits just within weeks but the material collected from sediments had shown the trapped fossil carbon which took several years to pre-spill values (Chanton et al. 2018; Giering et al. 2018)

Oxidation of oil compounds through microbes in marine environment need bioavailable substrates, i.e. oil compounds, trace elements, and nutrient availability (Sun and Kostka 2019) and excess oxygen, although under anoxic conditions hydrocarbon degradation may also occur but at slow rates (Head et al. 2006; Joye et al. 2016). Specific microbes may interact with individual hydrocarbon compounds or metabolites specializing in specific metabolic steps, creating collaborative networks that allow the joint utilization of complex organics such as oil (McGenity et al. 2012) which is not only formed on solid but also found on oil–water interface (Burd et al. 2020). Low-molecular-weight hydrocarbons have the highest rates of biodegradation, whereas if suitable conditions are available two- to three-ringed PAHs and low- and medium-weight straight-chain alkanes (up to n-C25) also undergo degradation in the marine environment (Joye et al. 2016). Those hydrocarbons with chains >n-C25 class such as resins, asphaltenes, and oil-soluble photo-oxidation products degrade very slowly. Emulsification occurs when water and oil are combined by the addition of water (60-80%); completely changing the properties and characteristics of oil spills expanding its volume from two to five times the original volume. The resulting emulsion density can be as great as 1.01 g/mL compared to the previous density 0.80 g/mL (Fingas and Fieldhouse 2004) increases the viscosity of the oil by an aspect of up to 1000 272 (Fingas and Fieldhouse 2004).

Weathering process may also be characterized by two types: mixture separation and transformation. Mixture separation involves the following steps: evaporation, dissolution, or sorption. Dissolution of oil fractions in oil slick or droplets separates the soluble from insoluble components. Alkanes with low molecular weight solubilize easily although other factors such as temperature, pressure, and the physical form of oil (such as thick slick, thin film, or dispersed droplets) also matter (Passow and Overton 2021). Sorption is a very compound-specific process but many soluble compounds sorb to surfaces (e.g., marine particles or algae cells) and remain associated with them (Kowalewska and Konat 1997; Larson et al. 2018; Parsons et al. 2014) converting them from the dissolved to the particulate phase in water. Coating and oil droplets trappings in aggregates will change the fate of oil compounds as particles may sink or be trapped by filter feeders, may be retained by filters or coagulate, whereas dissolved substances move with the water.

Different weathering procedures occur at various rates and durations, resulting in alterations to the content and behavior of oil spills through progressive weathering and differentiation procedures. For instance, evaporation happens just after the spill and works best right away; additional effects, such as settling, biodegradation, and emulsification, take place over much longer periods, often months or years. (Fingas

2016). The mechanism of transport influences the physical and chemical characteristics of spilled oil that ultimately reach the coast and affect shorelines. An oil slick forms when oil spills into the ocean and quickly spreads across the surface (Garrett et al. 1998). The oil may be dispersed over hundreds of kilometers as dispersed droplets of oil within the water column or as thin films, oil slicks, formulations, and tar balls ranging in thickness from tens of micrometers to a few centimeters at the sea surface, depending upon the parameters of the ocean and the characteristics of the oil (Novelli et al. 2020). Different weathering procedures occur at various rates and durations, resulting in alterations to the content and behavior of oil spills through progressive weathering and differentiation procedures. The transfer of surface oil extends away from the splash or spill area during spreading, which is regulated by a density gradient and forms a thin layer of film (Zhang et al. 2019a). Lighter fuels and medium crude oils with more volatile hydrocarbon contents typically becoming saturated with less than C15, monoaromatics, and lighter polyaromatic hydrocarbons (PAHs) show significant evaporation and aerosolization (Weitkamp et al. 2007). Photo-oxidation is a crucial stage in the degradation of crude oil spilled at sea, affecting mainly the aromatic contents of oil (Ward et al. 2018). PAHs and aromatic N, S, and O heterocycles are commonly photo-oxidized when exposed to sun radiation; these compounds react with oxygen to generate oxidized derivatives that are more soluble in water and less susceptible to biological degradation than their parent compounds (Marty and Potter 2014). Biodegradation might occur at the surface or in the water column depending upon a number of factors, including temperature, nutrient availability, chemical makeup, physical state of the oil, and the ability to participate in redox reactions (aerobic vs. anaerobic) (Atlas and Hazen 2011).

Marine pollution is a matter of great concern around the global; therefore, it is important to highlight some of the mitigation plans or actions taken by the world community to combat marine pollution (Table 7.2).

7 Conclusion

Over time, humans have exploited the marine ecosystem as a major sink for pollution from both land and water sources. Ocean pollution consists of a mixture of heavy metals, organic pollutants, pharmaceutical residues, plastics, and oil spills. Heavy metals predominantly settle and adsorb on sediments at the bottom, acting as secondary sources that may resuspend in the marine environment through desorption. The chemical transformation of heavy metals depends on their chemical forms, with metals in the exchangeable fraction being highly active, whereas residual fractions are relatively stable in the marine environment. The deep-sea ecosystem acts as a sink for organic pollutants, and biomagnification leads to the build-up of pollutants in marine organisms. Microbial transformation of organic pollutants aids in their removal through aerobic hydrocarbon degradation. The primary mechanism for the abiotic transformation of pharmaceutical chemicals in the aquatic

Table 7.2 Mitigation plans to combat marine pollution

Mitigation plans	References
The United Nations Sustainable Development Goals (SDG 14-Life Under Water) with target 14.1 defined as "prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution" by 2025	UN (2015)
Future Seas project	www.FutureSeas2030.org
Proposed addition of microbeads to Canadian Environmental Protection Act (CEPA) 1999	Pettipas et al. (2016)
Malaysia Roadmap toward Zero Single-use Plastics 2018–2030	https://www.mestecc.gov.my/web/wp-content/uploads/2019/03/Malaysia-Roadmap-Towards-Zero-Single-Use-Plastics-2018-20302.pdf (2018)
Abatement of marine litter and micro-plastics through the enactment of the Marine Strategy Framework Directive or MSFD	Gago et al. (2016); Galgani et al. (2013)
Europe's EMODNet Chemistry and Marine LitterWatch	Ave (2017); Jack et al. (2019)
Zero waste to Philippine waters by 2040 National Plan of Action for the Prevention, Reduction, and Management of Marine Litter (NPOA-ML) in 2021	Bueta (2022)
The Bangkok Declaration on Combating Marine Debris in ASEAN Region (ASEAN, 2019)	Hermawan and Astuti (2021)
The Ocean Clean-up	https://theoceancleanup.com/
Guidelines issued by the Ministry of Agriculture and Forestry in New Zealand for using 50-μm filtration for treating hull cleaning wastewater	Scianni and Georgiades (2019)
EU persistent organic pollutants (POPs) Regulation EU, 2019/1012)	http://chm.pops.int/Countries/StatusofRatifications/PartiesandSignatoires/tabid/4500/Default.aspx
EU Strategy for the Baltic Sea Region (EUSBSR) in 2009	https://www.eusbsr.eu/
The Interreg project NonHazCity (2016–2019)	https://projects.interreg-baltic.eu/projects/nonhazcity-7.html

environment is photochemical degradation. Plastics in the marine environment may undergo both abiotic and biotic degradation processes, while plastic additives are released along with degradation mechanisms, likely migrating into species through leaching, evaporation, abrasion, and ingestion. Understanding these transformation processes of pollutants in the marine ecosystem helps to develop further insights into the toxic effects produced by pollutants, ultimately contributing to more effective pollution management and mitigation strategies.

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Consent for PublicationNot applicable

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