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REVIEW ARTICLE

Hydrocarbons in seawater: Sources, fate, impacts, and remediation strategies

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Abstract: Hydrocarbon contamination in marine environments poses a significant global environmental challenge, impacting ecosystems, human health, and economic activities. The present review provides a comprehensive overview of hydrocarbons in seawater, addressing their diverse sources, complex fate and transport mechanisms, ecological and toxicological impacts, and various remediation strategies. Both natural seepages from geological formations and a wide array of anthropogenic inputs are discussed as primary contributors to marine hydrocarbon burdens. Anthropogenic carbon inputs include large-scale accidental oil spills, chronic operational discharges from shipping and offshore platforms, industrial effluents, and diffuse urban runoff carrying petrogenic and pyrogenic hydrocarbons, during the past 50 years. In the sea, hydrocarbons undergo a series of interconnected physical, chemical, and biological transformations that mediate their persistence, bioavailability, and spatial distribution. The specific environmental conditions, such as temperature, nutrient availability, and microbial community composition, significantly influence the rate and extent of these natural attenuation processes. The ecological consequences range from acute lethal impacts causing immediate mortality in marine organisms to chronic sublethal effects on reproduction, growth, immune response, and behavior across a wide range of taxa, from plankton to marine mammals. Furthermore, long-term ecosystem disruptions, including habitat degradation of vital coastal areas, such as mangroves and coral reefs, and bioaccumulation within the food web, pose serious threats to ecosystem health and biodiversity. To mitigate these adverse effects, a range of remediation strategies has been developed and implemented; their mechanisms, effectiveness in various scenarios, inherent limitations, and potential secondary environmental considerations are explored in this review. Emphasis is placed on the importance of integrated approaches that combine rigorous prevention measures, rapid and effective response protocols during spill events, and sustainable, environmentally sound long-term remediation techniques. Understanding the intricate interplay between the sources, transformations, impacts, and potential solutions for hydrocarbon contamination is crucial for developing robust management plans and safeguarding the long-term health and resilience of marine ecosystems.

Keywords: Hydrocarbons; Marine environment; Natural source; Anthropogenic pollution; Monitoring programs; Remediation strategy

1. Introduction

The oceans represent vast and dynamic reservoirs of life. They are constantly exposed to various chemical compounds, among which aliphatic hydrocarbon mixtures are significant substances with profound natural origins and widespread anthropogenic influences.[1-3] Fundamentally, hydrocarbons are organic compounds composed of hydrogen and carbon atoms, existing in a broad spectrum of physical states, from volatile gases, such as methane to heavy, viscous liquids, and solid tars.[4] Their presence in the marine environment is not recent, considering that natural geological processes have continuously introduced these compounds into the oceans for millions of years, shaping unique ecosystems around several localized inputs.[1,5-7] However, the advent of the industrial age and the escalating global reliance on fossil fuels have dramatically altered the magnitude, frequency, and composition of hydrocarbon inputs, transforming what were once isolated natural seepage into widespread contamination events.[8-10]

The ecological and economic significance of marine ecosystems necessitates a comprehensive understanding of hydrocarbon dynamics. These environments, ranging from surface waters enriched with phytoplankton at the base of the aquatic food webs to deep-sea hosting chemosynthetic communities and an intricate benthic ecosystem, are all potentially susceptible to hydrocarbon exposure of both natural and anthropogenic origins.[11-13] Hydrocarbons can exert deleterious effects at every trophic level, impacting organisms from unicellular species to apex predators, such as marine mammals and seabirds.[14,15] Furthermore, the recreational and economic value of coastal areas, including vital fisheries, aquaculture operations, and thriving tourism industries, is directly threatened by hydrocarbon pollution, leading to significant financial losses and long-term environmental damage.[8,9] The inherent toxicity and bioaccumulation potential of many hydrocarbon compounds pose a multifaceted threat, prompting extensive scientific inquiry into their fate and effects in marine systems.[1,8,11,14,15]

Natural hydrocarbon sources in the marine environment primarily include geological seeps and biogenic production.[12,13,16,17] Deep-sea seeps found along continental margins worldwide (e.g., Gulf of Mexico, Santa Barbara Channel) continuously release oil and gas from subsurface reservoirs through fissures and faults in the seabed.[5,6,18] These natural inputs have sculpted unique chemosynthetic ecosystems, where specialized microbial communities thrive on hydrocarbons and sulfur compounds, forming the base of unique food webs. At the same time, volcanic activity and hydrothermal vents also contribute a minor amount of hydrocarbons.[19-21] Submarine pockmarks are seabed depressions or craters that typically form through episodic or continuous expulsion of subsurface fluids, such as methane gas and other hydrocarbons. They act as geological pathways for hydrocarbons stored deep within the Earth's crust to migrate and escape into the marine environment. These deep-sea features are therefore considered natural sources of hydrocarbons in the ocean.[22,23] Moreover, aquatic organisms, including phytoplankton, bacteria, and algae, naturally produce small quantities of diverse hydrocarbons, which contribute to the background levels in seawater.[24] Although these natural processes are constant, a continuous degradation of hydrocarbons is operated by specialized endemic microbial populations, demonstrating the ocean's inherent capacity for natural attenuation.[25]

In contrast, anthropogenic sources introduce hydrocarbons into the marine environment with significantly greater magnitude and frequency, often in concentrated, acute events.[8,9] The primary anthropogenic contributor is the petroleum industry, encompassing exploration, production, transport, and refining activities. Major oil spills from accidents (e.g., Exxon Valdez, Prestige), offshore drilling blowouts (e.g., Deepwater Horizon), and pipeline ruptures represent catastrophic point source inputs that release vast quantities of crude oil over short periods, overwhelming natural degradation processes.[26-28] Beyond these high-profile incidents, chronic operational discharges from shipping (e.g., ballast water, engine room effluence) and discharges of produced water from offshore oil and gas platforms may increase the background level of global pollution.[29-31] Moreover, land-based sources, such as urban and industrial runoff carrying hydrocarbons from road spills, industrial effluents, and atmospheric deposition of combustion byproducts from vehicles and industries, also represent significant and diffuse inputs to water bodies.[32,33] Notably, the chemical composition of anthropogenic hydrocarbons, particularly refined products, often markedly differs from that of natural seeps, containing elevated concentrations of more toxic and bioavailable compounds, exacerbating the ecological impacts.[34]

In the marine environment, aliphatic hydrocarbon mixtures can undergo a complex series of physical, chemical, and biological transformations that govern their distribution, persistence, and ultimate fate.[1,2,35-37] Processes, such as spreading, evaporation of volatile components, dissolution into the water column, wave dispersion, and emulsification can rapidly alter oil physical characteristics.[1,36,37] In surface waters, chemical transformations include photo-oxidation by sunlight, which can lead to the formation of more polar and sometimes more toxic compounds.[38-40] However, microbial degradation represents the most critical natural attenuation pathway, where diverse marine bacteria and archaea metabolize hydrocarbons, breaking them into less harmful byproducts, and eventually carbon dioxide and water.[22,25,41] Other processes include sedimentation of dense oil components and the formation of aerosols that can transport hydrocarbons over long distances.[42] Understanding these intricate processes is fundamental to predicting the relevance and impact of hydrocarbon spills and developing effective response strategies.

The environmental and human health impacts of hydrocarbons in seawater are profound and multifaceted. For example, seabirds are particularly vulnerable to dense oil pollution, which affects their feather insulation, leading to hypothermia, mobility issues, and buoyancy issues. At the same time, marine mammals can suffer from ingestion, aspiration, and organ damage.[11,43] Chronic, sublethal effects are equally concerning, including impaired growth, reproduction, immune suppression, developmental abnormalities, and behavioral changes in fish and invertebrates.[1,44] Besides direct toxicological effects, hydrocarbon mixtures can also degrade critical habitats, such as coral reefs, seagrass beds, and mangrove forests, leading to long-term ecosystem damage and loss of biodiversity and ecosystem services.[45,46]

Considering the relevant threats posed by hydrocarbon pollution, various containment measures, monitoring programs, and remediation strategies have been developed and continuously refined. Generally, initial responses to accidental spill events focus on containment using booms and mechanical recovery through skimmers to physically remove oil from the water surface.[47] Chemical dispersants are sometimes used to break down oil slicks into smaller droplets, enhancing natural dispersion and microbial degradation. However, their use remains controversial due to potential toxicity to marine life.[48] Monitoring the contamination caused by aliphatic hydrocarbon mixtures may involve various techniques, from remote sensing for large-scale tracking to chemical analyses of water, sediment, and biota samples, alongside biomonitoring programs.[49,50] Remediation strategies aim to restore affected environments, with bioremediation a prominent approach. This involves enhancing the activity of native oil-degrading microorganisms through nutrient addition (biostimulation) or introducing specialized microbial strains (bioaugmentation).[51] Other methods include *in situ* burning, shoreline cleaning, and natural attenuation, where the environment can recover over time. The selection of the most appropriate strategy depends on factors, such as oil type, environmental conditions, and the sensitivity of the affected ecosystem.

Given the great relevance of hydrocarbon mixtures in the oceans, the present review aims to consolidate current scientific knowledge about the origin and fate of these compounds in seawater, exploring the complex interplay of processes governing their distribution and transformation, the impact on marine biota and human health, and the evolving strategies employed for their containment, monitoring, and remediation. Although in-depth knowledge of each specific topic discussed here is available, scientific literature does not always provide a comprehensive and coherent synthesis of various issues concerning hydrocarbons in the sea, which is the primary focus of the present systematic review. By integrating geochemistry, oceanography, marine biology, and environmental sciences insights, this review provides a holistic overview of the critical environmental issue associated with hydrocarbon mixtures and highlights areas for future research perspectives.

2. Natural origins of hydrocarbons in seawater

Hydrocarbon mixtures are intrinsically linked to the Earth's geological and biological cycles; their presence in the marine environment is a fundamental and ancient phenomenon, pre-dating human civilization by millions of years. Natural processes contribute to introducing various hydrocarbons into the oceans, influencing background levels, shaping unique chemosynthetic ecosystems, and playing a role in the global carbon cycle.[52-54] Understanding these natural origins is crucial for distinguishing between background levels and pollution events and appreciating the inherent capacity of marine systems to process these compounds.[1,2,50]

Among the primary natural pathways of hydrocarbon input into seawater, geological seepage represents one of the primary continuous sources of emissions, being the most significant and well-studied natural hydrocarbon emission processes.[5,12,17,34,50] These occur when deeply buried petroleum and natural gas, formed from the thermogenic alteration of organic matter in sedimentary basins, migrate upward through faults, fractures, and porous rock formations in the seafloor to reach the water column and eventually the surface.[5,12,17] Seeps are commonly found globally along continental margins, in active tectonic regions, and within sedimentary basins.[12,17]

The Gulf of Mexico, which hosts one of the world's most extensive and active deep-sea seep areas, is characterized by thousands of individual seeps releasing variable quantities of oil and gas, from small, chronic trickles to larger, more episodic bursts.[5,55] These seeps create distinct ecological communities characterized by chemosynthetic organisms (i.e., tube worms, mussels, bacterial mats) that utilize methane and sulfide as energy sources, forming the base of complex food webs independent of sunlight.[55] The Santa Barbara Channel off the coast of California is another well-known example, mainly characterized by a prolific shallow-water oil seep system, such as Coal Oil Point.[5,56] These seeps have been active for millennia, releasing crude oil that frequently washes to the shoreline as a form of spherical aggregates, a natural phenomenon long recognized by indigenous populations.[56] Other significant seep areas include the Caspian Sea, the North Sea, and various regions along the Atlantic and Pacific continental slopes.[5] Partly similar phenomena to submarine seepages are represented by pockmarks; these are depressions or craters found on the seabed, typically formed by the episodic or continuous expulsion of fluids, such as methane gas and other hydrocarbons, from the subsurface.[22,23,57,58] Unlike seepages, pockmarks have also been found in areas with relatively shallow water and are not directly related to fractures in the Earth's crust, but rather to geological formations with hydrocarbons close enough to the surface of the seabed to produce slow and episodic upwelling.[23,57] Although the hydrocarbon contribution from pockmarks is lower than that of natural seepages, their presence may help shape the characteristics of relatively shallow ecosystems, such as some regions of the Mediterranean.[22,57,58]

The hydrocarbons released from geological seeps exhibit a wide range of geochemical characteristics depending on their source rock, thermal maturity, and migration pathways. Naturally seeping oil often contains a complex mixture of alkanes (saturated hydrocarbons), cycloalkanes, and polycyclic aromatic hydrocarbons (PAHs), along with non-hydrocarbon compounds, such as sulfur, nitrogen, and oxygen-containing molecules.[1,2,34,50] Notably, crude oils from natural seeps often contain distinct compounds, hopanes, steranes, and terpanes that are resistant to degradation and reflect the original organic matter from which the oil was produced.[59,60] These hydrocarbons constitute fingerprint compounds, allowing them to differentiate natural seepage oil from anthropogenically sourced oil in environmental samples.[60] The gaseous components of natural seeps are predominantly methane, with the presence of small amounts of heavier gaseous hydrocarbons (ethane, propane, butane) and trace quantities of non-hydrocarbon gases, such as carbon dioxide and hydrogen sulfide.[61,62] The stable isotopic composition of methane ($\delta^{13}C$ and δD) is often used to distinguish between thermogenic (geological) and biogenic (microbial) methane sources.[61]

In addition to typical cold seeps, hydrothermal vents, which are found predominantly along mid-ocean ridges and back-arc basins, also release hydrocarbons into the deep ocean.[19-21,60] These systems involve seawater circulation through hot, fractured oceanic crust, leading to chemical reactions and the discharge of superheated, chemically rich fluids.[63] While the primary constituents of hydrothermal fluids are typically trace elements and sulfur compounds, significant amounts of hydrocarbons, including methane and heavier alkanes and aromatics, have been detected in various vent systems globally.[63] The origin of these hydrocarbons in hydrothermal systems can be varied. Some are abiogenic, meaning they are formed by inorganic chemical reactions involving carbon dioxide, hydrogen, and minerals at high temperatures and pressures within the Earth's crust, such as serpentinization reactions.[60,63] The "Lost City" hydrothermal field in the Atlantic, for instance, is known for its abiogenic methane and light hydrocarbon production.[63] Other hydrocarbons found in vent fluids can have a thermogenic origin, such as conventional petroleum, formed by heating deeply buried organic matter in sediments that are subsequently incorporated into the hydrothermal circulation.[60] A third potential source is biogenic methane produced by thermophilic and hyper-thermophilic microorganisms residing in the subsurface or within the vent structures.[19,20,63] The relative contribution of each origin varies among different fields, but the presence of hydrocarbons in these extreme environments underscores the diverse geological and chemical processes that can generate them.[19,20,60,63]

Beyond geological processes, marine organisms themselves represent a continuous and diffuse source of a wide range of hydrocarbons to seawater. These biogenic hydrocarbons are fundamentally different in their genesis and often in their chemical structure compared to fossil fuels.[64,65] Algae, particularly phytoplankton, are prolific producers of hydrocarbons. Many species of green algae (*Chlorophyta*) and cyanobacteria produce short-chain volatile hydrocarbons, such as isoprene and longer-chain alkanes (e.g., n-heptadecane, n-octadecane).[24] These compounds are typically synthesized as metabolic byproducts, signaling molecules, or components of cell membranes. For instance, n-alkanes are commonly found in the waxes and cuticles of many organisms. The large biomass and rapid phytoplankton turnover in surface waters imply that the collective contribution of these biogenic hydrocarbons may be substantial, especially in productive regions.[24,64,65]

Marine bacteria and archaea also play a crucial role in producing and transforming hydrocarbons. Some marine bacteria are known to synthesize long-chain hydrocarbons, including branched and cyclic compounds, as components of their cell membranes (e.g., hopanoids) or as storage products.[66] Moreover, methanogenic archaea, prevalent in anaerobic marine sediments and anoxic water columns, produce vast quantities of biogenic methane through the anaerobic decomposition of organic matter.[67] This biogenic methane can diffuse out of sediments, forming methane plumes in the water column, or be oxidized by methanotrophic bacteria. While methane is a potent greenhouse gas, its natural production and consumption by marine microbes are integral to the global carbon cycle.

Zooplankton and other marine invertebrates can contribute to the hydrocarbon pool by accumulating and transforming lipids and hydrocarbons from their diet. For example, some copepod species produce certain hydrocarbons, and their fecal pellets contribute to the downward flux of organic matter, including associated hydrocarbons, to deeper waters and sediments.[68,69] On the other hand, the degradation of deceased macroalgae and marine plants represents a fascinating and environmentally significant natural process with the potential to generate hydrocarbons.[41] When these organisms die, their organic matter, rich in lipids, carbohydrates, and proteins, sinks to the seabed. Under specific anoxic conditions, microbial communities play a crucial role in breaking down this complex organic material. Anaerobic decomposition prevents complete oxidation, leading to the formation of various intermediate compounds. Over geological timescales, these organic molecules undergo further transformation through diagenesis and catagenesis, and the original biomass is rearranged and cracked, eventually forming liquid and gaseous hydrocarbons.[70]

An additional natural source of hydrocarbons in the sea is atmospheric deposition of biogenic compounds. Terrestrial vegetation and soils are primary global sources of biogenic volatile organic compounds, including isoprene and monoterpenes.[71] These compounds, once emitted into the atmosphere, can undergo chemical reactions, forming aerosols, and be transported long distances before being deposited onto the ocean surface through wet or dry deposition.[72] Although difficult to quantify, the atmospheric deposition of biogenic hydrocarbons may contribute to the background levels in surface seawater, where they can then be subjected to microbial degradation or photo-oxidation processes,[36,37,41,48] a pathway representing a continuous, widespread, and often diffuse input contribution to the overall natural hydrocarbon budget of the ocean.[1,2]

3. Anthropogenic origins of hydrocarbons in seawater

While sometimes attributed to natural phenomena, the pervasive presence of hydrocarbons in seawater is overwhelmingly dominated by anthropogenic activities. From catastrophic oil spills to insidious chronic discharges, human interaction with petroleum products has profoundly altered the marine environment.[1,2] Understanding the sources, quantifying their inputs, and distinguishing between types of hydrocarbons are crucial steps in mitigating their ecological impact. Regional variability profoundly shapes hydrocarbon dynamics in marine environments, influencing spill impacts, response efficacy, and remediation success. In colder climates, such as the Arctic, low temperatures slow oil weathering, biodegradation rates, and natural dispersion, leading to prolonged oil persistence and enhanced bioaccumulation in the food web. Conversely, warmer temperate and tropical waters facilitate faster degradation, but may promote rapid evaporation of volatile compounds, altering oil composition and toxicity.[1,2]

Catastrophic oil spills leave an indelible mark on public consciousness and the environment. These incidents typically involve large-scale release of crude oil or refined products, often with devastating immediate consequences. Tanker accidents have historically been a significant source of large-scale oil spills.[2,8,10,26] The past 50 years have been marked by numerous nautical accidents that have mainly involved large oil tankers or ships, with spillage of large quantities of mixtures of crude oil or refined hydrocarbons. In 1978, the huge crude carrier Amoco Cadiz, following the breakage of a rudder, ran aground near the coast of Portsall, Brittany, France. About 223,000 tons of light crude oil and fuel are spilled into the sea, covering a significant ocean area and affecting about 360 km of the Brittany coastline, including sandy beaches, rocky shores, salt marshes, and estuaries.[73] The spill is estimated to have caused the mortality of approximately 9,000 tons of oysters, drastically affecting the region's economy around the farming and trade of these organisms. Nearly 20,000 seabirds were recovered dead, and significant impacts were observed on benthic fauna and various fish species.[1,2,73]

In 1979, the huge carrier Atlantic Empress collided with the tanker Aegean Captain during a tropical storm, followed by fire and explosion, approximately 300 nautical miles east of Tobago in the Caribbean Sea. A massive spill of about 287,000 tons of light crude oil occurred due to strong currents, high water temperatures, and the light nature of the spilled oil, which led to rapid dispersion on the ocean. Considering the relatively long distance from the coast, no significant impact or long-term environmental damage was officially reported on nearby islands. No specific widespread marine species involvement or threat was documented due to the rapid dispersion and lack of comprehensive studies at the time; therefore, the real adverse effects on living species remain unknown.[1,2,74]

The tanker Castillo de Bellver broke in half and sank following a fire in the engine rooms in 1983, about 70 nautical miles north-west of Cape Town, South Africa. Approximately 252,000 tons of light crude oil spilled into the ocean. Most oil drifted offshore due to prevailing winds, resulting in little coastal pollution. Some “black rain” fell on agricultural land by atmospheric transport and deposition, but no long-term damage was recorded. About 1,500 Cape Gannets were oiled and threatened, while the impacts on fishing grounds and fish stocks were considered negligible due to the rapid dispersion of light hydrocarbon mixtures.[1,2,75]

In 1988, the tanker Odyssey broke in half during a severe storm in the North Atlantic, approximately 700 nautical miles off Nova Scotia, Canada, causing a spill of approximately 132,000 tons of North Sea Brent crude oil. The oil slick initially extended over 80 km^2, drifted eastward, but, due to the remote location and rough seas, it never reached shore and dispersed naturally. However, it significantly harmed the local krill population, disrupting the food chain. No additional large-scale impact on coastal species was reported.[1,2,76]

The Exxon Valdez disaster in 1989 is considered one of the most significant of the modern era. The ship, bound for Long Beach, California, struck the Bligh Reef in Prince William Sound, Alaska. Approximately 37,000 tons of crude oil spilled into Alaska’s Prince William Sound. Although this event reported the smallest volume of crude oil spilled, it represents one of the most impactful historical events to have caused long-term ecological damage, which affected over 1,900 km of coast.[26] It has been estimated that the immediate effects included the deaths of many seabirds (between 100,000 and 250,000), almost 3,000 marine mammals, and an indeterminable number of salmon and herring.[26] Several years after the disaster, evidence of adverse effects on marine birds was found in various species, including cormorants, ducks, and guillemots.[26,76] As mentioned above, low temperatures have significantly altered the natural dispersion and degradation dynamics of hydrocarbons, and this, combined with the difficulty of reaching the site located in a relatively inaccessible environment, has favored the chronicity of the adverse effects.[1,2,26,76]

The National Marine Fisheries Service, National Oceanic and Atmospheric Administration, in Juneau, has determined that in 2001, approximately 90 tons of oil remained in the sandy soil of the contaminated shoreline, estimating a slow decrease in impact of about 4% per year from 2001 onward.[77] The chronic oil impact, lasting longer than anticipated, has resulted in more long-term species losses. It has also been estimated that many marine species directly affected by oil contamination may require over 30 years for recovery.[26,76,77] The Exxon Valdez disaster, due to its severity and extension, is considered the first accident to have had a significant impact on a large geographical and temporal scale.

Since then, restrictions and regulations have been implemented globally, but significant accidents continue to occur. In 1991, an explosion on board the oil tanker ship “ABT Summer” caused a fire and the complete sinking of the vessel. The accident occurred approximately 700 nautical miles off the coast of Angola, where about 260,000 tons of crude oil spilled into the ocean. Due to its remote location and rough seas, the oil dispersed naturally, and no coastline was affected. In this case, no specific widespread marine species were directly involved or threatened, although the real pollution extension and adverse effects on living species remain unknown.[78]

In the same year (1991), an explosion and fire during offloading operations occurred, leading to the tanker Haven breaking apart and sinking off the coast of Genoa, Italy, in the Mediterranean Sea. About 144,000 tons of heavy crude oil spilled out in the sea, causing significant pollution along the shores of Italy (Liguria, Tuscany) and France (French Riviera, Corsica). Oil slicks covered large areas of the Ligurian Sea, directly impacting the local marine life, including fish, crustaceans, coastal birds, fish farms, and coastal ecosystems. The specific estimate of the marine species involved or threatened is unavailable, but recovery of some affected areas took over a decade.[1,2,79] Peculiar characteristics, such as enclosed basins and the Mediterranean Sea present unique challenges. Limited water circulation can trap pollutants, exacerbating their long-term impact on coastal ecosystems and delaying recovery compared to open oceans with more efficient dilution and dispersion mechanisms.[1,2,79]

The Prestige oil spill, which occurred in November 2002 off the coast of Galicia, Spain, remains one of Europe's worst environmental disasters. The single-hulled oil tanker suffered a structural failure in a storm and eventually broke in half and sank, unleashing an estimated 63,000 tons of viscous crude oil into the Atlantic.[27,80] Almost 3,000 km of coastline across Spain, Portugal, and France were heavily polluted; the thick, black crude smothered beaches and rocky shores, destroying sensitive habitats and severely impacting the rich marine ecosystem.[80-82] An estimated 115,000 to 230,000 seabirds, particularly diving species, such as guillemots, razorbills, and puffins, perished from hypothermia, starvation, and drowning after their feathers were matted with oil, compromising their waterproofing and ability to fly.[80] Marine mammals, including porpoises and dolphins, were also at risk from direct contact and consuming contaminated prey.[80-82] Shellfish, crustaceans, and various marine invertebrates suffered extensive mortality, and fishing grounds, vital to the local economy, were closed for extended periods.[29,80-82] The long-term effects on fish stocks, particularly those with benthic or demersal life habits, and the wider food chain are still being studied, with concerns about persistent contamination and shifts in trophic levels.[81,82]

Although oil spills resulting from nautical accidents have been numerous and frequent, other events related to oil exploration, extraction, and production have caused particularly significant environmental disasters. A clear example is the event on the offshore oil platform Ixtoc 1 in 1979, located in the Bay of Campeche, off the coast of Ciudad del Carmen, in the Gulf of Mexico. Due to a series of factors and rather complex dynamics, the extraction well collapsed, generating an explosion and a fire that caused the entire structure to sink. This caused a crude oil spill directly from the base of the well at about 3,200 meters of depth, among the largest in history, estimated at 476,000 tons. Due to the depth of the source of the leak and the limited technological means available at the time, the operations to close the leak were very complex and protracted for approximately 9 months, rising to one of the most significant ecological disasters known at that time.[83] Oil from the well reached Mexican coastal areas and extended north to Texas (United States), affecting approximately 270 km of the United States' beaches. Coastal lagoons and estuaries experienced persistent contamination. The spill caused a severe impact on various mollusk species and littoral crabs, with ghost crab populations almost eliminated. It also affected the breeding and growth of various fish species belonging to all trophic levels. The critically endangered Kemp's ridley sea turtles' nesting grounds were affected, impacting their population for decades.[84]

In 2010, in the Gulf of Mexico, approximately 41 nautical miles off the coast of Louisiana, the Deepwater Horizon offshore platform disaster occurred due to the blowout of an oil well, following the explosion and fire of the drilling rig. The source of the spill was located at great depth, over 1,500 meters below sea level, and it affected vast areas of the Gulf of Mexico, including deepwater ecosystems, surface waters, and over 1,770 km of coastline across five states in the United States (Louisiana, Mississippi, Alabama, Florida, and Texas). For almost 3 months, an estimated over 670,000 tons of crude oil spewed uncontrollably into the Gulf of Mexico, where the spill created an oil slick that, at its peak, covered over 28,000 km^2 and is ultimately considered the most significant ecological disaster to have occurred in the United States.[28,46] It caused the largest and longest marine mammal unusual mortality event in the Gulf, with thousands of dolphins and whales found stranded, many with lung disease, reproductive failure, and compromised immune systems. Over 167,000 sea turtles were estimated to have died, and Kemp's ridley sea turtle nests were significantly affected and decreased. The spill also led to a significant increase in strandings of marine mammals for years afterward. Widespread mortality was also observed at all trophic levels, from various bird species (e.g., pelicans) to fish, deep-sea corals, and larvae of both vertebrates and invertebrates. Over 6,800 dead animals were reported during the same year of the accident (2010). The fishing and tourism industries, vital to the Gulf states, suffered immense economic losses, and the long-term effects on fish stocks and coastal wetland ecosystems, which experienced accelerated erosion, continue to be monitored and addressed to this day.[1,2,28,46,84]

The Gulf War oil spill, which occurred in 1991 during the Gulf War, is considered the largest oil spill in history. It was caused by Iraqi forces intentionally releasing oil into the Persian Gulf to impede a potential United States military forces beach landing. The spill involved millions of barrels of oil from tankers, pipelines, and terminals, causing extensive environmental damage to the coastal habitats and marine wildlife of Kuwait and Saudi Arabia. Vast hydrocarbon mixtures were intentionally released into the Persian Gulf, igniting hundreds of oil wells in Kuwait. The spill primarily involved crude oil, with initial estimates ranging from approximately 270,000 to 1.5 million tons. The oil slick reached a maximum size of over 10,000 km^2 and was up to 13 cm thick in some areas. The disaster affected around 600–700 km of the Saudi Arabian coastline, including sandy beaches, gravel shores, wetlands, lagoons, and muddy tidal flats. Kuwait, Iran, Bahrain, and Qatar also experienced some oil contamination. The general extent of the disaster was significant, halting fishing and prawn industries in the Gulf due to contamination. Oil penetrated sediments to 10–50 cm depths, slowing natural degradation.[85] Widespread mortality among various marine species was registered. Nearly 30,000 seabirds, primarily grebes and cormorants, died from being coated in oil. The intertidal zones were severely impacted, causing the death of 50–90% of fauna, such as crabs, amphipods, and mollusks. Benthic ecosystems were heavily oiled, leading to decreased abundance and diversity of organisms, such as ostracods. Mangrove forests along the Saudi coast were also damaged, with nearly half affected and one-third killed, though some natural regeneration occurred. It has been estimated that the full recovery from the Gulf War oil pollution will take several decades, with some areas, such as salt marshes, showing slower recovery.[85] Although some areas, such as rocky beaches and mangroves, have fully recovered within a few years, the more sensitive ecosystems, due to their anaerobic nature and lack of physical action, will require a longer time, which is still difficult to quantify.[85,86]

The events here described can be considered the most significant in terms of volumes of hydrocarbon mixtures released into the marine environment and impact on living organisms. Figure 1 shows the geographical distribution and the origin of the spills, as well as those generated after nautical accidents, offshore platform accidents, or other events. Alongside these acute events of great magnitude and relevance, numerous smaller

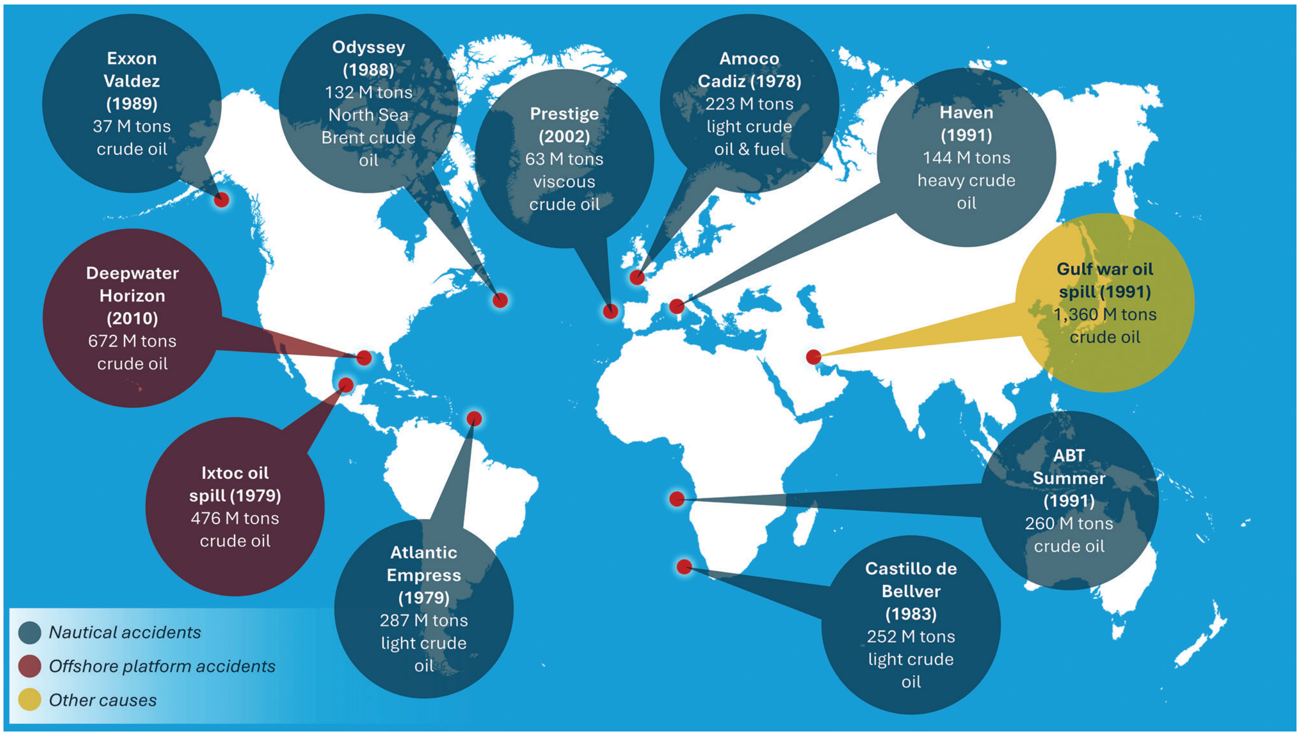

Figure 1. Main catastrophic oil and fuel accidentally spilled in the marine environment throughout the world in the last 50 years. Popup information includes the name of the accidental spill event, the year, the estimated quantity of discharged hydrocarbons, and the type of hydrocarbon mixtures. Dark blue pop-ups indicate nautical accidents, mainly caused by very large oil tankers, red ones indicate accidents generated at oil offshore platform installations, and the yellow pop-up is related to a deliberate crude oil spill during the Gulf War (1991), as well as other causes. M indicates million. Image created by Daniele Fattorini with Microsoft Office 365 enterprise, PowerPoint v.2504.

oil and fuel spills also occur, characterized by a higher frequency. Minor incidents, such as spills from fishing vessels or small commercial boats also contribute to chronic oil pollution. Other examples of accidental spills include offshore drilling blowouts and subsea pipeline ruptures. These events can occasionally be caused by corrosion, geological activity, or external damage.

Anthropogenic activities, including shipping traffic, offshore drilling, and coastal development, dictate the frequency and type of hydrocarbon inputs. Regions with intensive human activity often face chronic pollution and a greater risk of large-scale spills. On the other hand, biodiversity plays a critical role, as diverse ecosystems often exhibit greater resilience and a wider array of microbial communities capable of hydrocarbon degradation. However, highly specialized or endemic species can be particularly vulnerable to oil exposure, leading to severe ecological disruption.

Offshore drilling blowouts and pipeline ruptures incidents can release substantial hydrocarbons over extended periods, often in less accessible deep-sea environments, making response efforts particularly challenging. Quantifying global inputs from these accidents may be complex due to the varying sizes and durations of such events, but they remain a consistent source of episodic, localized pollution. While large spills grab headlines, chronic discharges contribute a substantial, often unquantified, cumulative load of hydrocarbons to the marine environment. These continuous, smaller releases can have insidious long-term impacts on marine life and ecosystems.[29-33] In oil and gas production, “produced water” is a byproduct that emerges to the surface along with oil and gas. This water, often of geological origin, can be highly saline and contains various organic and inorganic compounds, including dissolved and dispersed hydrocarbons (e.g., aliphatic hydrocarbons, benzene, toluene, ethylbenzene, xylenes, and PAHs). The volume of produced water discharged globally is enormous, with estimates of millions of barrels daily. While there are treatment technologies to reduce hydrocarbon concentrations before discharge, even low concentrations released consistently can accumulate and have localized impacts, particularly in coastal and shelf environments.[30,62]

In addition, routine operations of the global shipping fleet contribute significantly to hydrocarbon pollution. These include ballast water discharges, tank cleaning residues, and engine room bilge water. Due to the continuous, point-based nature of this type of pollution, it is extremely difficult to estimate its true impact and overall volumetric contribution over time. Many activities that cause hydrocarbon pollution sometimes escape the control of the relevant authorities or public awareness, and therefore, the extent of the impact may be underestimated. However, several investigations suggest that operational discharges from shipping collectively release more oil into the oceans annually than catastrophic spills, probably representing the main source of chronic and widespread hydrocarbon contamination in the sea. Some estimates indicate that 90% of all oil discharged by ships is attributed to deliberate, illegal dumping of oily residues from routine operations, potentially accounting for hundreds of thousands to over 2.5 million tons of hydrocarbons annually.[29,30] Additional sources of hydrocarbons are characterized by urban runoff; stormwater runoff from urban areas is a diffuse but significant source of oil residues and fuel. Rain washes oil, grease, and other petroleum products from roads, parking lots, and other impervious surfaces into drainage systems that ultimately discharge into coastal waters. These hydrocarbons originate from vehicle emissions, leaky engines, spills at gas stations, and industrial activities. Urban runoff usually contains a complex mixture of petrogenic (petroleum-derived) and pyrogenic (combustion-derived) hydrocarbons. While difficult to quantify precisely on a global scale, studies of urban waterways consistently report the presence of total extractable and aromatic hydrocarbons in sediments and water, with concentrations varying depending on the level of urbanization and industrial activity.[31] Urban runoff varies significantly based on natural factors (precipitation intensity and duration, soil characteristics, land cover, slope) and anthropogenic factors (level of urbanization, type of impervious surfaces). Quantifying pollution from urban runoff on a global scale is inherently difficult. The most sophisticated models are based on simulating the accumulation of pollutants on urban surfaces during dry weather, followed by washing during storm events, but the uncertainty in such models is often very elevated. While some detailed studies are available at local and regional levels (e.g., in Europe or the United States), reliable global data are completely lacking.[31]

Atmospheric deposition of combustion products may also represent a significant source of hydrocarbons in the environment. The combustion of fossil fuels, whether from vehicles, industrial processes, or power generation, releases hydrocarbons and their derivatives directly into the atmosphere. These airborne pollutants can then be transported globally and deposited onto the ocean surface through wet deposition (rain, snow) and dry deposition (particulate matter). While often at low concentrations, the vastness of the ocean surface makes atmospheric deposition a significant contributor to the global hydrocarbon budget in seawater, especially for volatile and semi-volatile compounds.[42,71,72] Estimating the global annual volume of hydrocarbons released into the environment through atmospheric transfer and deposition is a complex task due to several factors, including the vast array of hydrocarbon compounds, their varying atmospheric lifetimes, diverse emission sources (both natural and anthropogenic), and the challenges of global monitoring and modeling. However, studies focusing on specific, environmentally significant groups, such as PAHs suggest that atmospheric deposition is a significant pathway to their ecosystem entry. The estimated global atmospheric input of PAHs to the ocean is over 1 million metric tons annually. This underscores that atmospheric deposition, encompassing both direct emissions and long-range transport, represents a substantial and continuous source of hydrocarbon pollution to the global environment.[42]

Despite regulations and increasing awareness, illegal dumping of oil and oily waste significantly contributes to marine hydrocarbon pollution. This includes the deliberate discharge of bilge water, tank cleaning residues, and even spent lubricating oils from smaller vessels or less regulated operations. Satellite surveillance has revealed the prevalence of illegal dumping, particularly in busy shipping lanes and areas with lax enforcement. Some reports suggest that thousands of cases of illegal dumping of hydrocarbons occur in European seas alone every year, collectively exceeding the inputs from major tanker accidents.[87] Figure 2 summarizes and outlines the main sources of chronic discharge of oil, fuel and related waste into the marine environment; all these "secondary" sources of release of hydrocarbon mixtures into the environment as a whole highlight that the severity of an oil spill is not solely determined by its size but also by the type of oil, the sensitivity of the affected environment, the effectiveness of the responses, and frequency of events.

Chronic pollution may often induce sublethal effects across many taxa, from plankton to marine mammals.

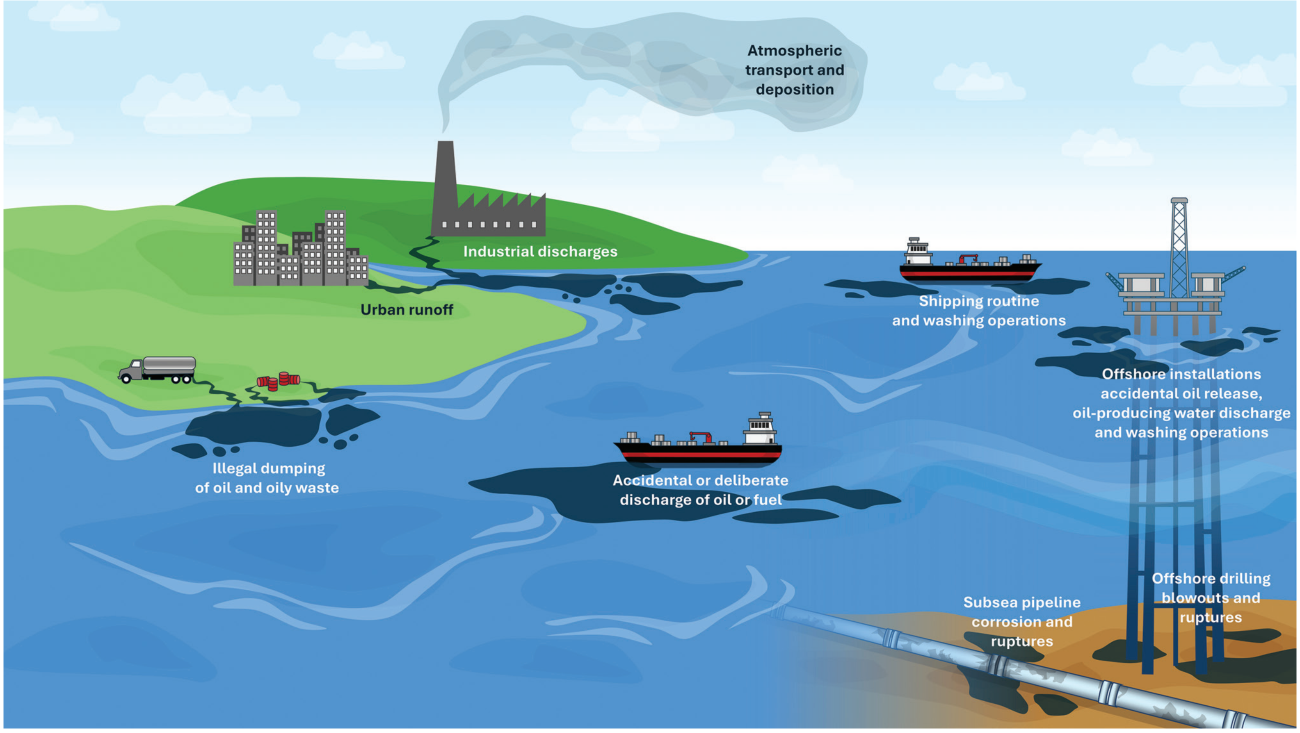

Figure 2. Main chronic hydrocarbon spill, release, or discharge events in the marine environment. Inputs may be characterized by shipping routine or washing operations, offshore drilling blowout and ruptures, accidental release of oil-produced waters, urban and industrial runoff and discharges, atmospheric transport and deposition of hydrocarbon derived from industrial activities, and a series of illegal dumping of oil, fuels, and oily waste products. Image created by Daniele Fattorini with Microsoft Office 365 enterprise, PowerPoint v.2504.

Affected species experience impaired growth and reproduction, immune suppression, developmental abnormalities, and behavioral changes. Long-term ecosystem disruption, including habitat degradation of vital coastal areas, such as mangroves and coral reefs, and bioaccumulation within the food web, severely threatens ecosystem health and biodiversity. Species, such as seabirds, marine mammals (e.g., dolphins, whales), sea turtles (e.g., Kemp's ridley), fish, deep-sea corals, and various invertebrates and their larvae are particularly vulnerable to these persistent effects.[11,44-46]

4. Fate of hydrocarbons in seawater

The fate of hydrocarbon mixtures in the sea, whether from natural or anthropogenic sources, is characterized by numerous and complex chemical–physical processes and interactions with living organisms. These processes are strongly influenced by the characteristics of the hydrocarbon mixtures, such as density, viscosity, volatility, and composition, but also by environmental conditions and variables, such as temperature, salinity, wave motion and currents, wind intensity, and proximity to the coast.[88-90] As mentioned above, regional variability significantly modulates hydrocarbon dynamics in marine environments, influencing oil density, dispersion, spreading, and emulsification. Based on this perspective, there is no unified fate of hydrocarbons in the oceans, as cold, temperate, or tropical environments can significantly alter the extent and speed of the chemical–physical and biological phenomena at play.[1,2] Considering the numerous variables in play, Figure 3 proposes a series of model mechanisms of the main processes triggered by the presence of hydrocarbons in the sea, considering that such phenomena may deviate from those described, depending on the existence of particular and peculiar environmental conditions and events.

In the open ocean, the oil on the water surface undergoes spreading, a rapid process driven by gravity and surface tension, forming thin films known as slicks. Large oil slicks can float and move on the surface waters. Wave motion and currents significantly affect the mobility, transport, and dispersion of such oil slicks, promoting rapid spread and drifting.[90] The simultaneous action of the waves and the wind plays

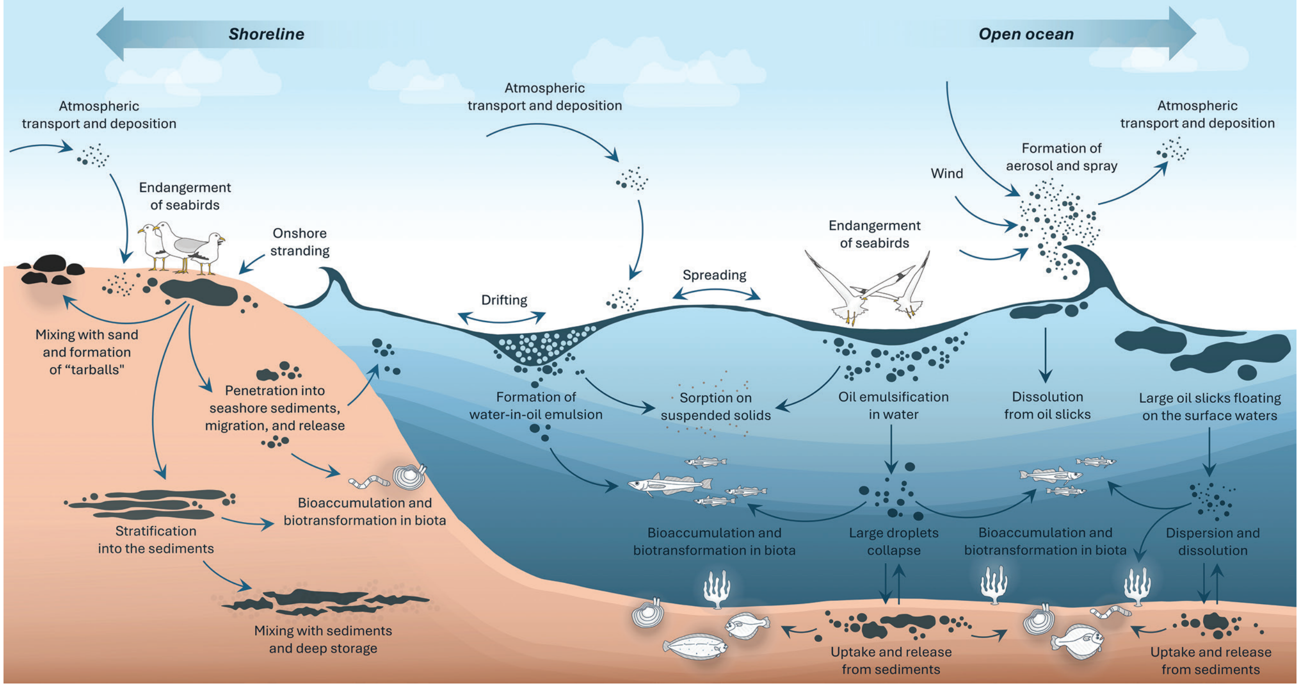

Figure 3. Fate of hydrocarbons in the sea. A range of potential phenomena associated with the presence of hydrocarbons in marine ecosystems, including transport and spread of oil slicks at the water surface, aerosol formation and atmospheric transport and deposition, dissolution and collapse in the water column, interaction and compartmentalization in sediments, and threats to various marine species, including invertebrates, vertebrates, and seabirds. Image created by Daniele Fattorini with Microsoft Office 365 enterprise, PowerPoint v.2504.

a significant role in the atmospheric transport and deposition of volatile oil components and the formation of aerosol and spray. This can lead to the widespread dispersal of oil hydrocarbons into the atmosphere.[88-90] Hydrocarbons transported through the atmosphere can move to destinations very far from the primary emission sources, reaching the surface of the water, beaches, or other emerged areas, through wet or dry deposition.[88,90]

Oil on the water surface or transported in the atmosphere can directly threaten seabirds, which are particularly vulnerable to this contamination. The more viscous components adhere to the plumage of these animals, causing movement and flight difficulties, thermoregulation disorders, impairment of various abilities, including catching food, and toxicity and death.[11,27,62,82]

Further interactions occur within the water column. Dissolution from oil slicks may occur when water-soluble components of the oil dissolve directly into the seawater. The sudden mixing of oil slicks and surface water favors the formation of emulsions (oil emulsification in waters or waters in oil emulsion), where small oil droplets are dispersed within the water column, often stabilized by natural surfactants. The heavier components tend to slowly disperse deep into the water column, while the lighter ones return to the surface, re-aggregating with the oil slicks and thus promoting a cycle.[90]

Simultaneously, oil can undergo sorption on suspended solids, where oil molecules adhere to particulate matter, increasing their density and potentially leading to sedimentation.[88,90] Within the water column, large oil droplets collapse, and dispersion and dissolution continue, breaking down the oil into smaller components. These processes facilitate the uptake and release from sediments. Once oil settles, it can be re-released into the water column, initiating a recurring cycle. All these transports and migrations contribute to bioaccumulation and biotransformation in biota, with various marine vertebrates (benthic or pelagic fish) and invertebrates (i.e., mollusks, polychaetes, and algae) taking up oil compounds, which are then metabolized and accumulated within their tissues, with significant toxicological effects on marine life.[11,62]

As oil drifts toward the coast, driven by currents and winds, it can lead to onshore stranding. Once on the shoreline, the interactions become more complex, largely dependent on the characteristics of the beach, the presence of rocks, and the type of sediments and sands.[90] Oil mixed with sand and the formation of "tarballs" is a common phenomenon, where oil adheres to sand particles, forming persistent, resistant oil-sand agglomerates. These tarballs and other oil residues can penetrate seashore sediments, migrate, and be released. This infiltration can lead to long-term contamination of the intertidal and subtidal zones.[88,90] Stratification can occasionally occur within the sediments, with oil burying itself at various depths. This buried oil can continue to undergo mixing with sediments and deep storage, making its remediation challenging. Like in the open ocean, bioaccumulation and biotransformation in biota may occur within the shoreline ecosystem, affecting benthic organisms and potentially their consumers.[11,27,62,82] In addition, the seabirds can be directly endangered due to contact with oiled shorelines, emphasizing the vulnerability of avian species to coastal oiling.[62,82]

Hydrocarbon mixtures in the sea can undergo various physicochemical and biological degradation processes at multiple stages. Although these processes determine a natural mitigation of hydrocarbon contamination, they can potentially lead to the formation of different compounds often characterized by a greater solubility in water and potentially a greater toxicity in living organisms.[35-40,89] Microbial biodegradation represents the primary natural attenuation mechanism for hydrocarbons in marine environments. This complex process involves diverse microbial communities, primarily bacteria and fungi, breaking down hydrocarbons into less harmful substances, ultimately leading to mineralization into carbon dioxide or methane. The efficacy and specific pathways of this degradation are critically dependent on oxygen availability, leading to distinct aerobic and anaerobic processes.[36,37,89]

Aerobic biodegradation is the dominant and generally more rapid process in oxygen-rich marine waters, such as the surface layers and oxic sediments. A series of specialized microorganisms possess enzymatic systems, particularly alkane hydroxylase complexes, that initiate the degradation of hydrocarbons.[36,37,41,89,91] The primary mechanism involves the incorporation of molecular oxygen into the hydrocarbon molecule by monooxygenases, forming an alcohol. This alcohol is then oxidized to a fatty acid, which undergoes successive β-oxidation cycles, progressively shortening the carbon chain and finally forming acetyl-CoA. Acetyl-CoA then enters the tricarboxylic acid cycle for complete mineralization to carbon monoxide and water, generating energy for microbial growth.[41,91] Biosurfactant production by certain aerobic microorganisms enhances the bioavailability of hydrophobic hydrocarbons by emulsification, making them more accessible for enzymatic reactions. Factors, such as temperature, nutrient availability (nitrogen and phosphorus being crucial, limiting nutrients), and the physical state of the oil (e.g., dispersion) significantly influence aerobic degradation timing, rates, and success.[36,37,91] The obligate hydrocarbonoclastic bacteria, mainly belonging to the class of Gammaproteobacteria, are considered the most important hydrocarbon degraders under aerobic conditions. These bacteria can use hydrocarbons as the sole source of carbon and energy and are ubiquitous in the oceans. Some relevant examples include *Alcanivorax* (e.g., *A. borkumensis, A. dieselolei, A. pacificus*), representing the most studied and important genus of obligate hydrocarbonoclastic bacteria, specializing in the degradation of n-alkanes (straight-chain hydrocarbons) and *Cycloclasticus* (e.g., *C. pugetii*), a genus known for its ability to degrade PAHs, which are more complex and thermodynamically stable compounds. The genus *Pseudomonas* represents an additional notable group of bacteria capable of aerobic biodegradation; several species, such as *P. putida* and *P. aeruginosa*, are known for their ability to degrade a wide range of petroleum hydrocarbons and are often employed in remediation and cleanup practices after oil spills.[91]

Anaerobic biodegradation becomes critical in anoxic marine environments, such as deep sediments, sub-seafloor oil reservoirs, and oxygen-depleted zones. While generally slower than aerobic processes, it plays a vital role in the fate of hydrocarbons in these environments.[91,92] Anaerobic microorganisms utilize alternative electron acceptors in the absence of oxygen, including nitrate, sulfate, ferric iron, or carbon dioxide. The initial activation of hydrocarbons under anaerobic conditions is a key step, as the lack of oxygen prevents direct monooxygenase activity. One of the most well-described mechanisms for alkane activation is fumarate addition, catalyzed by enzymes, such as alkyl succinate synthase.[92] This reaction involves the anoxic addition of fumarate to the alkane chain, forming 1-methylalkyl-succinate. This product then undergoes transformations and β-oxidation-like steps, eventually forming short-chain fatty acids, methane (methanogenesis), and carbon dioxide. Diverse anaerobic consortia are often involved, with specific microbes specializing in different steps of the degradation pathway. The presence of certain metal ions, such as iron, can also influence anaerobic degradation rates by acting as electron acceptors or mediating electron transfer.[91,92] Some examples of bacterial communities operating under anoxic conditions are denitrifying and sulfate-reducing bacteria, respectively, utilizing nitrate or sulfate as final electron acceptors to degrade hydrocarbons. Examples include species, such as *Aromatoleum* sp. (denitrifying) and *Desulfoglaeba* sp. (sulfate-reducing), which have been studied for their ability to activate alkanes by adding fumarate. In addition, under highly reducing conditions, methanogenic bacteria can degrade hydrocarbons to produce methane. Although the process is complex and often mediated by microbial consortia, species, such as *Smithella* sp. and *Anaerolinea* sp. have been associated with anaerobic degradation of hydrocarbons.[91,92]

Aside from these biodegradative phenomena, a series of chemical–physical processes may largely contribute to the degradation of hydrocarbon mixtures in the sea, especially at the surface level. It has recently been highlighted that complex mixtures of hydrocarbons in contact with water can undergo photo-oxidation, forming soluble organic compounds, such as aldehydes, ketones, and alcohols.[36-40] Most studies have focused on the physical and chemical alterations of hydrocarbons. Characterizing the involved photochemical processes and the molecules produced is complex, mainly due to the difficulty of observing these phenomena in natural conditions. The dissolved fraction of aliphatic hydrocarbons in seawater is essentially transparent to sunlight,[93] unlike the aromatic component, which is easily photo-oxidized with the formation of "sensitizing" substances. These sensitizers, in turn, make the aliphatic hydrocarbons photo-oxidizable.[38] For instance, anthracene easily absorbs sunlight and is photo-oxidized to 9,10-endoperoxide and anthraquinone (Figure 4). The same phenomenon has been observed for other PAHs, including benzo(a)pyrene.[38,93] In this sense, a mixture of aliphatic and aromatic hydrocarbons exposed to sunlight can lead to the initial production of sensitizers derived from the oxidation of some PAHs, which then facilitates the photo-oxidation of the aliphatic components, with the formation of more soluble organic compounds, including aldehydes, ketones, and alcohols.[36-40,93]

Specifically, it is known that experimental irradiation of alkylbenzenes in the presence of anthraquinone determines the formation of 1-phenylalkanone, alcohols, and benzaldehyde. These same compounds have been isolated from seawater in contact with petroleum mixtures under natural conditions, thus suggesting a photochemical origin.[38,94] Controlled photo-oxidation of the water-soluble fraction of gasoline in the presence of anthraquinone produced the same reaction products,[94] suggesting that the phenomenon does not concern only a few experimentally chosen model compounds, but rather involves all complex and heterogeneous

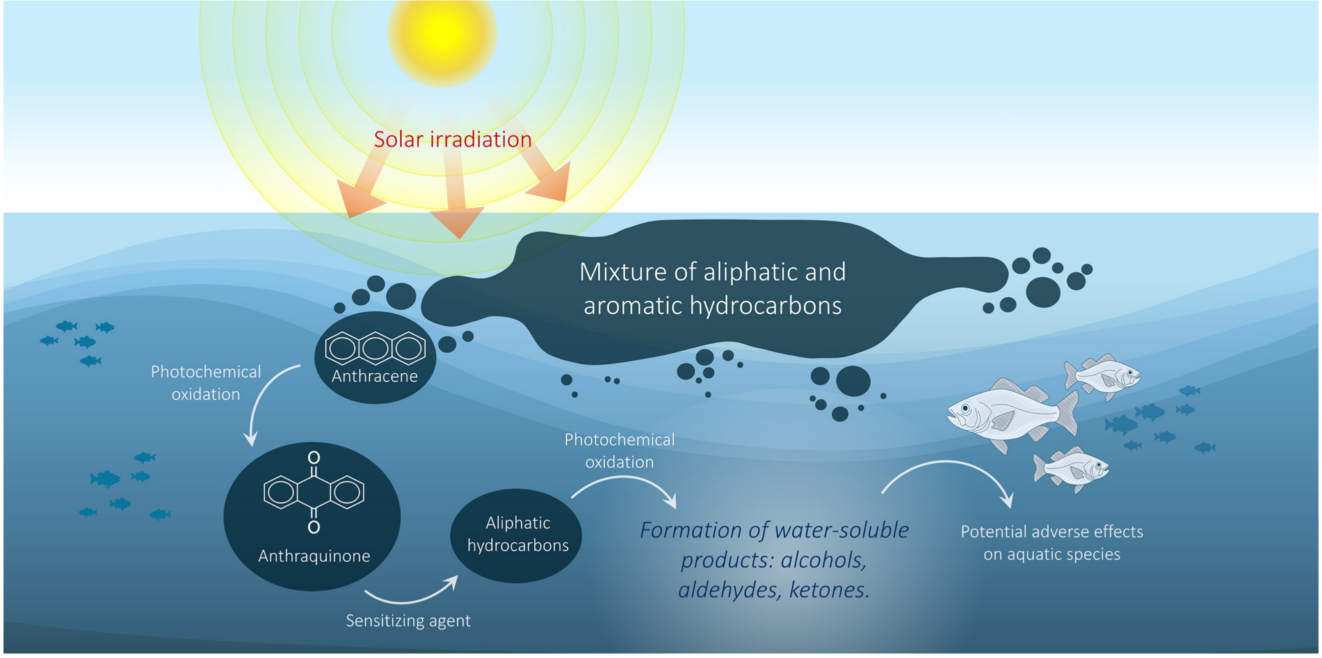

Figure 4. Photo-oxidation of hydrocarbons in the surface waters. Solar irradiation may produce photochemical oxidation of aromatic hydrocarbons with the formation of sensitizing agents, which in turn promote the photo-oxidation of the aliphatic components with the formation of aldehydes, ketones, and alcohols, that are more soluble and potentially dangerous for fish species. Image created by Daniele Fattorini with Microsoft Office 365 enterprise, PowerPoint v.2504.

mixtures, such as crude oil. Similarly, irradiation of alkylnaphthalenes in the presence of oil or the soluble fraction of gasoline in seawater formed photo-oxidation polar compounds, such as alcohols, aldehydes, acids, and quinones.[38,93,94]

Biodegradation and photo-oxidation processes, while seemingly beneficial in breaking down pollutants, can yield byproducts that pose significant adverse effects on marine organisms. Aerobic biodegradation can produce various oxidized intermediates. While some are less harmful, others, such as certain organic acids or partially oxidized PAHs, being more soluble than the original compounds, can potentially enter biological compartments more easily and exert greater toxicity, altering various physiological functions, including reproduction, growth, and immune response.[95] Under anaerobic conditions, degradation pathways can generate hydrogen sulfide, which is highly toxic to many marine species, particularly those in benthic environments. Other byproducts might include aromatic and aliphatic compounds that can bioaccumulate in the food chain, leading to long-term chronic toxicity in higher trophic levels. Photo-oxidation may also generate oxygenated PAHs, which exhibit enhanced toxicity compared to their parent compounds. They may cause DNA damage, oxidative stress, and endocrine disruption in marine organisms, affecting their development, behavior, and survival. Furthermore, some of these compounds can be highly persistent, prolonging their detrimental impact on marine ecosystems. The combined effects of these degradation byproducts contribute to altered community structures, reduced biodiversity, and overall ecosystem degradation.[95]

A highly relevant and timely aspect is the significant influence of climate change on marine hydrocarbon dynamics. Ocean warming can increase the temperature and dispersion of oil, potentially speeding up evaporation and natural dispersion and increasing the toxicity of some oil components. Ocean acidification, resulting from increased carbon dioxide absorption, might also affect the efficiency of oil-degrading microorganisms. Furthermore, extreme weather events, such as stronger storms and hurricanes, amplified by climate change, pose a greater risk of damage to offshore oil and gas infrastructure, increasing the likelihood of spills. Changes in ocean currents and sea level rise can also influence the transport and fate of spilled oil, making prediction and cleanup efforts more challenging.[96]

5. Effects of hydrocarbon pollution

Large quantities of hydrocarbons in the sea, whether from heavy crude oil, light oil, or refined products, such as fuels or other mixtures, always cause harmful effects.[11,32,52] The complexity of the mixtures and the variety of products potentially involved often make it difficult to predict the extent and severity of contamination and the possible short- and long-term effects. Furthermore, as previously described, the specific characteristics of the area affected by the contamination and various environmental variables can drastically influence the severity and persistence of the disturbances caused by the presence of hydrocarbons in the sea.[1,2]

In crude oil contamination, especially if characterized by high viscosity and density, the most immediately noticeable and significant damage is predominantly physical. Seabirds and marine mammals can become covered in oil, which adheres to their skin or plumage, forming a barrier and causing suffocation, inability to move or fly, impairment of various physiological functions, and compromising the ability to forage and reproduce. Animals relying on fur or feathers for insulation also suffer severe hypothermia when their protective layers are matted by oil, compromising their ability to regulate their body temperature, and causing fatigue, starvation, and even death.[97] In intertidal areas, the stranding of crude oil slicks can also cover the surfaces of numerous species of mollusks (mussels, oysters, gastropods,), crustaceans (crabs, hermit crabs, barnacles,), echinoderms (sea urchins), and other benthic invertebrates, compromising many of their vital functions and the capability to move, impeding respiration, feeding, and waste elimination.[11,32,52,97]

These physical effects are accompanied by toxicological damage. One primary mechanism is narcosis, particularly by low molecular weight aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, xylenes, naphthalene, and derivatives), which are highly soluble and volatile. These compounds can rapidly penetrate biological membranes, interfering with cellular processes, disrupting nerve impulse transmission, and causing central nervous system depression. This leads to disorientation, paralysis, and ultimately death in affected marine life.[97] Even at sublethal concentrations, hydrocarbons may inflict profound chronic sublethal effects, impairing the health and viability of marine populations. Physiological stress is a common response, characterized by elevated metabolic rates, disrupted osmoregulation, and altered energy allocation, as organisms expend energy on detoxification and repair rather than essential life processes. Reproductive impairment is a particularly concerning effect, with hydrocarbons interfering with hormone regulation, gamete development, fertilization success, and larval viability across a wide range of taxa.[43,82] This can lead to reduced spawning success, decreased fertility, and compromised recruitment, threatening population stability. Developmental abnormalities, such as fish larvae and invertebrate embryos, are frequently observed in early life stages, manifesting as skeletal deformities, cardiovascular dysfunction, and impaired organ development.[11,32] The aryl hydrocarbon receptor pathway, involved in xenobiotic metabolism, is often implicated in these developmental toxicities.[98] Furthermore, hydrocarbons can induce immune suppression, making organisms more susceptible to diseases, parasites, and environmental stressors, weakening population resilience.[11]

Hydrocarbons, especially persistent and lipophilic compounds, such as PAHs, exhibit tendencies for bioaccumulation in various vertebrate and invertebrate aquatic species.[15,62] Higher organisms generally possess the enzymatic pathways capable of metabolizing aliphatic and aromatic hydrocarbons; therefore, it is not uncommon to find higher levels of bioaccumulation in benthic invertebrate organisms from contaminated areas rather than in fish. On the other hand, it is known that some multienzyme systems capable of transforming specific xenobiotics (i.e., cytochrome P450) often produce products that express greater toxicity. Consequently, vertebrate organisms in contaminated areas may manifest notable adverse effects even without high levels of bioaccumulation.[15] As a result of these mechanisms, and given that hydrocarbon mixtures can undergo biodegradation, their bioaccumulation can be transferred into food chains, although biomagnification is generally not observed.[15] Given the high lipophilicity of the hydrocarbon mixtures, higher animals, such as marine mammals can be subject to an elevated bioaccumulation rate in tissues rich in body fat.[15,62]

Hydrocarbon pollution may disrupt entire marine ecosystems. Habitat degradation occurs when sensitive environments, such as coral reefs, mangrove forests, and salt marshes are directly contaminated, leading to structural complexity and functionality loss. For example, corals are highly sensitive to oil, which can cause bleaching, necrosis, reduced growth rates, impaired reproduction, and altered larval settlement. Chronic exposure can decrease their resilience to environmental stressors, such as ocean acidification and warming. Given the close ecological relationship between species, the entire coral reef ecosystem could be compromised in a cascade. Mangroves are also critically important coastal habitats that are highly susceptible to oiling. Oil can coat their roots (pneumatophores), affect gas exchange, leading to suffocation and death, especially in younger trees. Contamination of the anaerobic sediments further slows oil weathering. Oil can also cause defoliation, stunted growth, and deformities, compromising their vital role in coastal protection and as nursery grounds for various marine species.[45,46,85,86] This, in turn, diminishes biodiversity and the ecosystem services these habitats provide. Food web disruption results from the mortality of primary producers and consumers, and the bioaccumulation of toxic substances.[45,46] This can lead to trophic cascades, altering predator-prey relationships, competitive dynamics, and overall energy flow within the ecosystem, impacting the abundance and distribution of species across multiple trophic levels. Long-term impacts on ecosystem resilience and recovery are often observed.[85,86]

The socioeconomic consequences of hydrocarbon pollution are far-reaching. Industries heavily relying on healthy marine environments, such as fisheries and aquaculture, suffer significant economic losses due to contaminated stocks, fishing bans, fouled gear, and reduced market confidence in seafood safety.[1,2,8] Tourism and related businesses are also severely impacted, as oiled beaches and affected marine life deter visitors. Coastal communities, particularly those dependent on marine resources for livelihoods and cultural practices, often bear a disproportionate burden. Cleanup operations are expensive, and long-term environmental monitoring and restoration efforts add further economic strain.[1,2,8,9,28]

These dynamics can also have a direct impact on human communities. Humans consuming seafood (fish, shellfish, crustaceans) from oil-affected areas can be exposed to hydrocarbons, especially PAHs, which are known carcinogens and can cause other adverse health effects.[27,99,100] While depuration periods can reduce contaminant levels, the risk remains, particularly with chronic consumption of subtly contaminated seafood. In addition, individuals involved in cleanup operations or near spilled oil can experience direct exposure through dermal contact, inhalation of volatile organic compounds, or accidental ingestion. This can lead to a range of health issues, including respiratory problems, skin irritation, neurological symptoms, and potential long-term risks, such as increased cancer incidence. The physical and psychological stress on affected communities and cleanup workers also represents a significant health burden.[99,100]

Marine oil and hydrocarbon contamination extends beyond immediate environmental damage, deeply affecting human communities. For instance, the mental health of residents, especially those whose livelihoods depend on the sea, can significantly deteriorate. Witnessing the destruction of ecosystems and fearing for their future can lead to chronic stress, anxiety, depression, and even post-traumatic stress disorder. Studies after major spills have shown these psychological impacts can persist for years. Furthermore, oil spills exacerbate socioeconomic disparities in vulnerable populations. Fishing communities, indigenous groups, and those reliant on coastal tourism often face severe income loss and job displacement. This economic hardship can deepen existing poverty, disrupt traditional ways of life, and lead to food insecurity. The slow recovery of marine resources further prolongs these challenges, creating cycles of vulnerability and hindering equitable development.[101]

6. Containment, monitoring, and remediation strategies of hydrocarbons in seawater

In the wake of marine hydrocarbon contamination, a rapid and coordinated response is fundamental to mitigate environmental damage. This involves a comprehensive series of containment, monitoring, and remediation strategies, each with strengths and limitations. The selection of appropriate techniques hinges on factors, such as the type and volume of the spill, prevailing environmental conditions, and available resources. Containment techniques are designed to limit the spread of hydrocarbons, preventing further ecological harm and facilitating subsequent cleanup efforts.

Among these, the booming techniques involve deploying physical barriers on the water surface to encircle and concentrate the spilled material. Booms can be absorbent and designed to soak up oil, such as containment booms, which physically block its spread; they can also be fire-resistant and used in conjunction with *in situ* burning. Booming has been proven to be highly effective for preventing the spread of oil in calm waters, is relatively straightforward to deploy, and can be used to divert oil away from sensitive areas, such as coastlines or wildlife habitats. In addition, this technique aids in the efficiency of oil recovery operations by concentrating the slick. Booms' effectiveness significantly diminishes in rough seas, strong currents, or high winds, where oil can easily escape underneath or overtop the barriers. Large spills can overwhelm boom capacity, and their deployment and retrieval require substantial logistical support and personnel. Booms can also become saturated with oil, necessitating careful disposal.[47] During the Deepwater Horizon oil spill (2010), thousands of miles of booms were deployed to protect the intricate marshlands and coastlines of the Gulf of Mexico. While effective in localized, calmer areas, their overall impact was limited by the sheer scale of the offshore spill and prevailing weather conditions.[28,46]

In recent years, innovative technologies have been developed to remediate hydrocarbon contamination in the marine environment. Among these, nanomaterials offer a promising solution for crude oil absorption from the sea. Their exceptionally high surface area-to-volume ratio enables efficient capture of oil molecules. Materials, such as graphene, carbon nanotubes, and various metal-organic frameworks can be engineered to be superhydrophobic and oleophilic, meaning they repel water while attracting oil. When deployed, these nanomaterials can rapidly absorb significant quantities of spilled oil, forming stable aggregates that are easier to recover from the water surface. This aids in rapid cleanup and minimizes the environmental impact by preventing the spread and long-term consequences of oil contamination on marine ecosystems.[102]

Once contained, or when containment is challenging, various techniques are employed to remove or disperse the oil. Skimming involves using specialized vessels or skimmers to physically remove oil from the water surface. Skimmers operate through various principles, including weir skimmers, which allow oil to flow over a weir into a collection tank, oleophilic skimmers, where oil adheres to a rotating surface and is then scraped off, and vacuum skimmers.[47] Skimming usually consists of directly recovering the oil, making it available for potential recycling or proper disposal, thus reducing the total volume of contaminants in the environment. It is most effective in calm waters with relatively thick oil. The efficiency of such a technique may be compromised in rough seas, as wave action can break up the slick and mix the oil with the water column. Debris mixed with the oil can clog skimmer mechanisms, and the process often collects significant volumes of water along with the oil, requiring further separation.[47]

A controversial containment method is represented by *in situ* burning, which involves the controlled ignition and burning of oil on the water surface. It is often used with fire-resistant booms to concentrate the oil into a thick layer before ignition. This approach offers a rapid way to remove large quantities of oil, significantly reducing the volume that needs to be physically recovered and disposed of. It can be particularly effective in remote areas where logistical challenges make other recovery methods difficult. However, *in situ* burning causes air pollution, including the production of particulate matter, volatile organic compounds, and other combustion byproducts, raising concerns about air quality and potential health impacts. Public perception is not usually positive due to visible smoke plumes and the generation of atmospheric pollution. *In situ* burning was a key component of the Deepwater Horizon oil spill response. Over 400 controlled burns were conducted, removing an estimated amount of approximately 35,000 tons of crude oil, demonstrating its capacity for rapid oil removal in large-scale offshore incidents, when the vast extent of the contamination and adverse environmental conditions do not allow the adoption of different techniques.[28,46]

Another debated and controversial practice is the use of substances called dispersants. These are chemical agents sprayed onto oil slicks to break the oil into tiny droplets, allowing it to mix with the water column. This process facilitates dilution and degradation through natural processes and prevents the oil from rapidly spreading. Dispersants can quickly break up large, widespread slicks, preventing them from impacting coastlines, wetlands, and surface-dwelling wildlife. They can be applied efficiently from aircraft or vessels, rapidly responding to large-scale spills. The increased surface area of dispersed oil can accelerate natural biodegradation by marine microbial communities.[48] However, the use of these substances is not without risks. A primary concern is the potential toxicity to marine life from the dispersant chemicals and dispersed oil, which can become more bioavailable to organisms in the water column.[48] Dispersants do not remove oil from the environment; they merely change its physical state and location, often driving it deeper into the water column. Their effectiveness varies with oil type, water temperature, and salinity. The large-scale use of dispersants, particularly subsea applications, has been highly controversial.[48,103]

Chemical dispersants are complex mixtures, typically composed of surfactants and solvents. Surfactants are the key molecules that reduce the interfacial tension between oil and water, facilitating droplet formation. Surfactants are amphiphilic molecules with both oleophilic and hydrophilic components. This duality allows them to position themselves at the oil-water interface, lowering the surface tension and fragmenting the oil into small droplets. The most common surfactants are sorbitan esters (e.g., sorbitan monooleate), a non-ionic substance derived from sugars, often used for their emulsifying properties and relatively low toxicity. Other surfactants include ethoxylated fatty acid esters (nonionic surfactants that provide emulsion stability), sulfosuccinates (e.g., sodium dioctyl sulfosuccinate, an anionic surfactant with emulsifying properties), organic sulfonic acids and their salts (anionic surfactants aiding wide oil dispersion), and alkoxylated alcohols or ethoxylated alkylamine (nonionic surfactants).[48]

As additional components, solvents help transport and distribute the surfactants, keeping them in the solution and facilitating their penetration within the oil slick. Dispersant solvents usually consist of hydrotreated light oil distillates and hydrocarbon-based substances with low or absent aromatics to reduce toxicity. Other common solvents are glycols (e.g., propylene glycol, propylene glycol ethoxylate, and 2-butoxyethanol) that are less volatile and potentially less toxic than the aromatic solvents used in early generations of dispersants. However, the use of selected glycol ethers and 2-butoxyethanol has recently been the subject of concern for their potential adverse effects.[48]

The first massive use of dispersants dates to the accident of the supertanker Torrey Canyon in 1967, which caused the spill of approximately 120,000 tons of crude oil off the coast of Cornwall, United Kingdom. The chemical dispersants were used extensively and unprecedentedly; over 10,000 tons of these substances, such as BP 1002 containing non-ionic surfactant detergents, were sprayed on floating oil and contaminated beaches. These "first-generation" dispersants were highly toxic and contained aromatic solvents, such as benzene and xylene. Studies have determined that the oil/dispersant mixture was more harmful to the environment than the oil alone. Numerous seabirds died from lungs clogged by detergent foam, leading to increased awareness of the risks of dispersants and the development of less toxic formulations.[103]

During the Exxon Valdez Disaster in 1989, Corexit chemical dispersants were tested on a limited scale immediately after the spill. Although the composition of Corexit is not publicly available, it may contain substances, such as butoxyethanol bisulfonate, an additional organic sulfonate, and small concentrations of propylene glycol. Weather conditions and the viscosity of the oil did not favor significant dispersion, and the quantities of dispersant available and applied were insufficient to address the scale of the disaster. Some studies suggested dispersants may have formed chemically enhanced, potentially more toxic oil particles. Much of the cleanup subsequently focused on physical methods and biostimulation.[26,48,77,103]

Corexit dispersants were also used after the Deepwater Horizon disaster (2010). This event saw unprecedented use of dispersants, both on the surface and, for the 1st time, on a large scale, directly at the source of the release at depth. Nearly seven million liters of dispersants were applied, primarily Corexit 9500A and Corexit 9527A. This practice helped reduce the amount of oil at the surface, mitigating the impact on seabirds, marine mammals, and shorelines. Underwater dispersal was intended to prevent large quantities of oil from reaching the surface, but significant concerns were raised. Although dispersants reduced the visibility of oil at the surface, they introduced oil (and the dispersants themselves) into the deep-water column, where their persistence, fate, and effects on marine life were less understood and remain the subject of intense research.[28,46] The combined toxicity of oil and dispersant, the formation of "marine oil snow" that carried oil to the seafloor, and the health effects of cleanup workers were critical debate points. Some studies have suggested that underwater dispersal did not significantly reduce the overall amount of oil reaching the surface but altered its distribution.[28,46,48,103]

During the Prestige oil tanker spill (2022), given the type of oil and the adverse weather conditions that characterized the initial stages of the accident, the use of chemical dispersants was controversial and ultimately limited, deemed ineffective in containing the crude oil spill. For instance, dispersants work best on low viscosity, lighter oils, which can be easily emulsified. In contrast, the Prestige's heavy oil was inherently difficult to disperse chemically, due to its elevated viscosity. In addition to adverse weather conditions, rough seas and strong winds further complicate any attempts to effectively apply dispersants. While rough seas can promote some natural dispersion, they also hinder the targeted application and effectiveness of dispersants, which require a certain amount of contact and mixing time to work. In practice, the dispersants failed to fulfill the desired role of containing and dispersing the spill. The oil largely reached the coasts of Galicia and subsequently France and Portugal, causing devastating environmental and economic damage.[48,80-82,103] The Prestige accident and other spills have elicited international debate on the efficacy and potential ecotoxicological impacts of dispersants. Concerns include their effectiveness in the field and the combined toxicity of the dispersant and the dispersed oil on marine life. For the Prestige oil, which contained high levels of PAHs, dispersion could have carried these toxic compounds deep into the water column, potentially exposing benthic organisms and other species.[80-82]

Commonly used dispersants sometimes have complex formulations, for which details on the involved chemical species and their concentrations are not always available. Furthermore, over the years, various substances have been progressively abandoned and replaced with new products, making it difficult to compare their efficiency, benefits, and adverse effects, especially considering that the contexts of use often represent unique conditions. The regulatory framework on a global scale is therefore extremely diverse and subject to change over time. Further in-depth analysis of this topic is necessary.

Following the initial containment works, effective spill response relies on robust monitoring to track the spill's trajectory, assess its environmental impact, and guide remediation efforts. Using airborne or satellite-based sensors to detect, map, and track oil spills, remote sensing may provide a broad, synoptic overview of the spill's extent, movement, and changes over time, crucial for large-scale incidents. Among the remote sensing technologies, synthetic aperture radar can penetrate cloud cover, offering data in adverse weather conditions, while conventional optical sensors are ineffective in darkness or limited lighting scenarios. In general, remote sensing enables rapid assessment and strategic planning of response operations. However, resolution can be restricted, making detecting very thin slicks or detailed features difficult. Interpretation of data requires specialized expertise, and remote sensing primarily provides surface-level information, not real-time subsurface dynamics. Satellite imagery and aerial surveillance were valuable during the Deepwater Horizon oil spill for tracking the massive oil slick, predicting its movement, and directing response vessels and booming operations to critical areas.[104]

Chemical analysis of environmental samples (water, sediment, biota) is a fundamental and central key to environmental monitoring plans, identifying specific hydrocarbon compounds, determining their concentrations, and assessing their degradation products and potential toxicity. Chemical determinations may provide precise and accurate quantitative and qualitative data related to pollutant characteristics, concentrations, and spatial distribution, which are essential for risk assessment, pollutant fate comprehension, and long-term monitoring of environmental recovery. The possibility of periodically monitoring over time and integrating data relating to abiotic matrices (water and sediments) and the tissues of bioindicator organisms can provide an integrated picture of the degree of contamination and related temporal trends.[49,50,105] Chemical analysis is time-consuming and requires specialized laboratory equipment and highly trained personnel for sample analysis and results interpretation. Following the Exxon Valdez oil spill (1989), extensive chemical analysis of hydrocarbon levels in water, sediments, and marine organisms was conducted for decades to track the persistence and spread of contaminants, providing critical data for understanding long-term ecological damage and recovery rates.[26,77] This data type also constitutes a fundamental scientific reference for planning monitoring plans and subsequent environmental investigations.[105]

In addition to chemical characterization, biomonitoring plays an immediate and central role. This approach uses living organisms as indicators of environmental health and pollutant exposure. It assesses physiological changes, bioaccumulation of pollutants in tissues, or impacts on population dynamics and community structure.[49,50,102,106] Biomonitoring provides an integrated measure of contaminant effects over time, reflecting the bioavailability of pollutants to organisms rather than just their environmental concentration. Biomonitoring can identify subtle ecological impacts that are not immediately apparent through chemical analysis alone. Given that the response of biological indicators can be slow to manifest, biomonitoring often requires long-term planning. Establishing causality between observed biological effects and specific contaminants can be complex, requiring a thorough understanding of baseline biological conditions. Thus, the success of a biomonitoring plan depends on a robust and solid scientific reference base regarding the stress-related biological effects of sentinel organisms and in-depth knowledge related to their sensitivity and responsiveness.[105,106] After the Prestige oil spill (2002) off the coast of Spain, biomonitoring studies on commercially important shellfish and fish populations, which continued for many years, have been fundamental for understanding the bioaccumulation trends in organisms' tissues, demonstrating the long-term impacts on marine food webs and the fishing industry.[27,80-82]

Various remediation strategies aim to clean up the spilled material and restore the affected environment to pristine conditions. Natural attenuation includes a series of intrinsic physical, chemical, and biological processes that reduce pollution over time without direct human intervention. These processes include dispersion, dissolution, volatilization, photo-oxidation, and biodegradation by naturally occurring microorganisms.[25] Natural attenuation is highly cost-effective and minimally invasive, as it avoids introducing additional chemicals or disturbances to the ecosystem; however, it can be a very slow process, potentially taking years or decades to exhibit a significant reduction of the contamination levels and extension. Natural attenuation is generally unsuitable for highly toxic or very large spills where immediate intervention may be required.[25]

Bioremediation represents the primary active strategy to mitigate the effects of oil spills. This approach leverages microorganisms (bacteria and fungi) to break down hydrocarbon contaminants into less harmful substances, such as carbon dioxide and water. Among the commonly used techniques, bioaugmentation involves the introduction of specific, pre-selected microorganisms, often specialized for degrading particular hydrocarbons, to the contaminated site to enhance biodegradation rates. On the contrary, the biostimulation approach focuses on adding nutrients (e.g., nitrogen, phosphorus) or oxygen to the contaminated environment to stimulate the growth and activity of indigenous, naturally occurring, hydrocarbon-degrading microorganisms.[51] Bioremediation practice is an environmentally friendly approach as it utilizes natural processes and can potentially lead to the complete degradation of pollutants rather than just their transfer. However, the process can be slow, and its effectiveness highly depends on environmental conditions, such as temperature, pH, salinity, and nutrient availability. In addition, the success of bioaugmentation can be limited by the ability of introduced microorganisms to compete with native populations.[51] Biostimulation was applied extensively after the Exxon Valdez oil spill in Alaska. Fertilizers were sprayed on oiled beaches to provide essential nutrients (nitrogen and phosphorus) to naturally occurring hydrocarbon-degrading bacteria, significantly accelerating the breakdown and removal of residual oil from the affected shorelines.[26,27]

Among the bioremediation techniques, promising attempts have recently been investigated using engineered microorganisms. This practice can represent an improved approach to cleaning up marine oil spills. Modified bacteria and fungi can accelerate their oil-degrading pathways, making them more efficient at breaking down complex hydrocarbons into harmless substances, such as carbon dioxide and water. These designed microbes can be optimized for specific oil components or environmental conditions, such as temperature and salinity. When deployed, they rapidly proliferate and consume the oil, significantly reducing the environmental impact of spills and offering a sustainable alternative to chemical dispersants, representing a promising practice for more effective and less invasive marine ecosystem recovery.[107]

Physical removal, involving the direct mechanical removal of spilled material from the environment, represents the ultimate available means where other systems cannot completely remove hydrocarbons from marine ecosystems. Physical removal techniques include manual cleanup of shorelines (using shovels, rakes, absorbent materials), use of absorbents on water, and large-scale mechanical recovery operations. These practices can quickly remove large quantities of oils, substantially reduce pollution, and prevent further spread. However, they are highly labor-intensive and costly, generating significant volumes of waste that require specialized disposal. It can disrupt sensitive habitats during cleanup operations and potentially harm workers exposed to toxic substances through contact or inhalation.[43,82]

Responding to marine hydrocarbon contamination requires a dynamic and adaptable approach. No single technique provides a universal solution; instead, a combination of containment, monitoring, and remediation strategies is typically employed, tailored to the specific characteristics of each spill. Ongoing research and technological advancements continue to refine these methods, striving for more effective, efficient, and environmentally sound responses to safeguard marine ecosystems.

7. Challenges, recommendations, and future research prospects

Hydrocarbon contamination in the marine environment represents a significant global threat, affecting ecosystems, human health, and economic activities. A key challenge lies in accurately quantifying the pervasive and often underestimated cumulative load of hydrocarbons from chronic sources, such as shipping discharges, urban runoff, and atmospheric deposition, which can have insidious long-term impacts beyond acute spill events. Furthermore, the efficacy and potential toxicity of chemical dispersants, particularly with viscous oils or in deep-water applications, remain debated. Future research could include a systematic review of the different types of chemicals used and their short- and long-term effects on marine ecosystems. Remediation efforts, such as bioremediation, face limitations in speed and effectiveness due to environmental variability and competitive microbial dynamics. The long-term recovery of affected ecosystems can also span decades, especially for sensitive habitats. In these terms, additional challenges and recommendations include the possibility of addressing these complex issues by adopting integrated approaches that combine rigorous prevention measures with rapid, effective response protocols and sustainable, environmentally affordable long-term remediation techniques. Future research should therefore continue to refine methods and approaches to define dynamic and adaptable strategies involving containment, monitoring, and tailored remediation practices. Ongoing studies are also vital to assess the long-term impacts on fish stocks and food chains, underscoring the continuous need for technological advancements to safeguard marine ecosystems comprehensively. Further investigations could also include a more in-depth study on how climate change can significantly alter marine hydrocarbon dynamics, considering that studies in this direction are still limited.

8. Conclusion

The pervasive presence of hydrocarbon mixtures in marine environments stems from continuous natural processes and significant anthropogenic activities, each with distinct characteristics and environmental implications. Natural sources, primarily geological seeps and biogenic production from marine organisms, have historically introduced hydrocarbons, contributing to background levels and fostering unique chemosynthetic ecosystems. However, the industrial age has dramatically escalated the magnitude and frequency of hydrocarbon inputs, transforming localized natural seepage into widespread contamination events. Anthropogenic contributions overwhelmingly dominate current hydrocarbon pollution. Harmful events, such as major oil spills from tanker accidents (e.g., Amoco Cadiz, Exxon Valdez, Prestige) and offshore drilling blowouts (e.g., Ixtoc 1, Deepwater Horizon), release vast quantities of crude oil, overwhelming natural degradation processes and causing relevant immediate and long-term ecological and economic impacts. These incidents lead to widespread mortality of marine fauna, habitat degradation, and significant financial losses in vital industries, such as fisheries and tourism. Beyond these acute disasters, chronic discharges from shipping operations, produced water from oil and gas platforms, urban runoff, and atmospheric deposition of combustion byproducts contribute to a substantial, often unquantified, cumulative load of hydrocarbons, leading to insidious long-term impacts. The chemical composition of anthropogenic hydrocarbons, particularly refined products, often contains more toxic and bioavailable compounds than natural seeps, exacerbating their ecological impacts.

Once in the marine environment, hydrocarbons undergo a complex series of physical, chemical, and biological transformations that dictate their distribution, persistence, and fate. Processes, such as spreading, evaporation, dissolution, dispersion, emulsification, and sedimentation alter their physical characteristics and movement. Crucially, microbial biodegradation, involving diverse communities of bacteria and archaea, and chemical transformations, such as photo-oxidation, represent the primary natural attenuation pathways, breaking down hydrocarbons into less harmful byproducts. These transformations can, however, also lead to the formation of compounds with increased water solubility and toxicity. Hydrocarbons may also be subjected to bioaccumulation and biotransformation in marine organisms, leading to significant toxicological effects across trophic levels.

In response to the significant threats posed by hydrocarbon pollution, a range of containment, monitoring, and remediation strategies has been developed and continuously refined. Initial responses to spills often involve physical containment using booms and mechanical recovery through skimmers. Chemical dispersants are sometimes used to break down slicks, enhancing natural dispersion and microbial degradation. However, their efficacy and potential toxicity remain controversial, particularly with viscous oils or deep-water applications. Monitoring efforts utilize remote sensing for large-scale tracking and chemical analyses of water, sediment, and biota samples for precise qualitative and quantitative data on contaminant levels and distribution. Biomonitoring programs further assess environmental health and pollutant exposure through living organisms. Remediation strategies aim to restore affected environments, with bioremediation being a prominent approach that enhances the activity of native or introduced oil-degrading microorganisms. The selection of the most appropriate strategy depends on factors, such as oil type, environmental conditions, and ecosystem sensitivity. The long-term recovery of affected marine ecosystems can span decades, especially for more sensitive habitats.

Overall, the present review consolidates current scientific knowledge regarding the origin, fate, impacts, and remediation of hydrocarbon mixtures in seawater. By integrating insights from geochemistry, oceanography, marine biology, and environmental sciences, it provides an overview of this critical environmental issue and underscores the dynamic and adaptive approach required for effective response, highlighting the ongoing need for research and technological advancements to safeguard marine ecosystems.

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Author contributions

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Availability of data

The original artwork of the figures is available from the corresponding author upon reasonable request.

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