Chapter 1
Introduction to Marine Pollution

Abstract The ocean plays a key role in cycles of carbon, nitrogen, phosphorus and a variety of other important chemicals. Ocean chemistry has been changing due to human activities, both regionally in coastal waters and in the open ocean. Some of the greatest impacts are on carbon, nitrogen, and dissolved oxygen, which affect biological productivity. The rate of primary production is determined primarily by light and nutrients. Decades of pollution of marine waters, along with coastal habitat destruction, overfishing and bottom trawling have had devastating impacts on biodiversity and habitats. The increasing demand for seafood worldwide has depleted fish populations and devastated the economic well-being of coastal communities. At the same time, climate change is altering the oceans in major ways that we are only beginning to understand.

Land-based sources pollute estuaries and coastal waters with nutrients, sediments, pathogens as well as many thousands of toxic chemicals, including metals, pesticides, industrial products, pharmaceuticals and more. Following the industrial revolution, increasing amounts of materials have been discharged into the environment from chemical industries, sewage treatment plants, and agriculture, eventually reaching marine ecosystems. Highly visible events such as the *Exxon Valdez*, and the Gulf of Mexico “gusher” have raised public awareness of marine pollution in recent decades. There is growing scientific evidence demonstrating serious, sometimes disastrous, impacts of pollution in the marine environment. Pollutants of major concern are those that are widespread and persistent in the environment, accumulate in biota, and induce effects at low concentrations. Toxic chemicals are varied and often difficult to detect. In recent years, attention is being devoted to new or newly recognized threats to the environment – contaminants of emerging concern (CEC), ocean acidification, and noise pollution.

Keywords Metal • Pesticide • Acidification • Eutrophication • Litter • Metal • Nitrogen • Noise • Nutrient • Sediment

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1.1 Sources and Fate in the Environment

Sources of contaminants in the marine environment are mostly based on land. While many pollutants come from industrial or residential areas, others come from agricultural areas. Factories and sewage treatment plants discharge into receiving waters through a pipe – this is referred to as a "point source" and it can be monitored and regulated by environmental protection agencies. Since passage of the Clean Water Act in the United States in 1972, much progress has been made in controlling pollution from point sources. However, the historic use of some chemicals no longer manufactured in the United States (e.g., DDT, PCBs) has left a legacy of contamination. Sediments remain contaminated with these persistent chemicals, which continue to affect marine life long after their inputs have ceased. In recent decades attention has moved from end-of-pipe discharges to diffuse pathways of runoff and atmospheric deposition. Sources of contaminants that wash into the water during rainfall are diffuse and enter water bodies in many places, as do pollutants from the atmosphere that come down in precipitation. This diffuse pollution is referred to as "non-point source," and is not so easily regulated. Non-point sources, such as farms, roadways, and urban or suburban landscapes remain largely uncontrolled, and are major sources of continuing pollution inputs. The few sources that are not land-based include oil spills from tankers and drilling platforms, leaching of antifouling paints and discharge of wastes from vessels. Point sources of pollution from industrial discharges and oil spills are highly destructive to local areas where they occur, but lower concentrations of these chemicals are widespread in the global oceans. Elevated levels of persistent organic pollutants and methylmercury are widespread and of concern since these chemicals build up in food chains and pose a threat to humans from eating contaminated fish and other seafood.

1.1.1 Metals

Metals released from mining and industrial processes are among the major contaminants of concern in coastal environments. Many studies have shown their accumulation in sediments and coastal organisms. Mercury, cadmium, copper, zinc, and silver are major contaminants from industrial processes including power plants. Since mercury is present in coal, when it is burned the mercury enters the atmosphere, where it can be transported long distances before being deposited far from its source. While some metals (copper and zinc) are essential for life at low concentrations, other metals play no normal biological role. While most metal contaminants originate from land-based industrial sources, metals also are used in anti-fouling paints for ships. Since fouling organisms can accumulate on ship bottoms (reducing streamlining, thus increasing fuel consumption), antifoulant coatings have been developed. For thousands of years ship hulls have been treated with various substances to reduce fouling. Paints containing copper have been used for many years. Starting in the 1940s organotin compounds were developed for this purpose and one of the most effective and long-lasting is tributyltin, which is one of the most toxic to other non-target organisms.

In aquatic environments, copper exists in particulate, colloidal and soluble states, predominantly as metallic (Cu^0) and cupric copper (Cu^{2+}). It forms complexes with both inorganic and organic ligands. The toxicity of copper is directly associated with the free ion, as is the toxicity of Cd, so measurements of total Cu or total Cd in the water overestimate the amount the is bioavailable (Sunda et al. 1978; Sunda and Lewis 1978).

Mercury is a highly toxic element that is found both naturally and as a contaminant. Although its potential for toxicity in highly contaminated areas such as Minamata Bay, Japan, in the 1950s and 1960s, is well documented, mercury can also be a threat to the health of people and wildlife in environments that are not obviously polluted. The risk is determined by the form of mercury present and the geochemical and biological factors that influence how it moves and changes form in the environment. Mercury can exist in three oxidation states in natural waters: Hg^0, Hg^{1+} and Hg^{2+}. The distribution of the forms depends on the pH, redox potential, and availability of anions to form complexes with the mercury. In the environment, inorganic mercury can be transformed into organic mercury compounds. Methylmercury (meHg) is a highly toxic form, and inorganic Hg can be converted to meHg by bacteria in marine sediments (Fig. 1.1). Bacteria capable of methylating Hg^{2+} have been isolated from sediment, water, soil and fish tissue. However, little is known about the physiology and the mechanisms controlling methylation. MeHg, in addition to being far more toxic than inorganic forms of the metal, also is biomagnified up the food chain, so tissue concentrations increase as it passes up the food chain. People are exposed to meHg primarily by eating fish that are high on aquatic food chains.

The other organometal of concern is tributyltin, which was formerly used in antifouling paints for vessels, but unlike Hg, tributyltin (TBT) breaks down in the environment, losing its butyl groups over time, reducing its toxicity as it eventually becomes inorganic tin, which is not toxic. However, the breakdown is not as rapid as initially thought, so effects can persist for some years.

Metals tend to bind to sediments, from which they are available to varying degrees to marine organisms, particularly benthic ones, from which the metals can be moved up the food chain. Bioavailability of sediment-bound metals is a critical issue for their toxicity.

Acid volatile sulfide (AVS) has been used to predict the toxicity in sediments of divalent metals, including copper (Cu), cadmium (Cd), nickel (Ni), lead (Pb) and zinc (Zn) (Ankley et al. 1996; Berry et al. 1996). The rationale is that the AVS in sediment reacts with the simultaneously extracted metal (SEM), the reactive metal

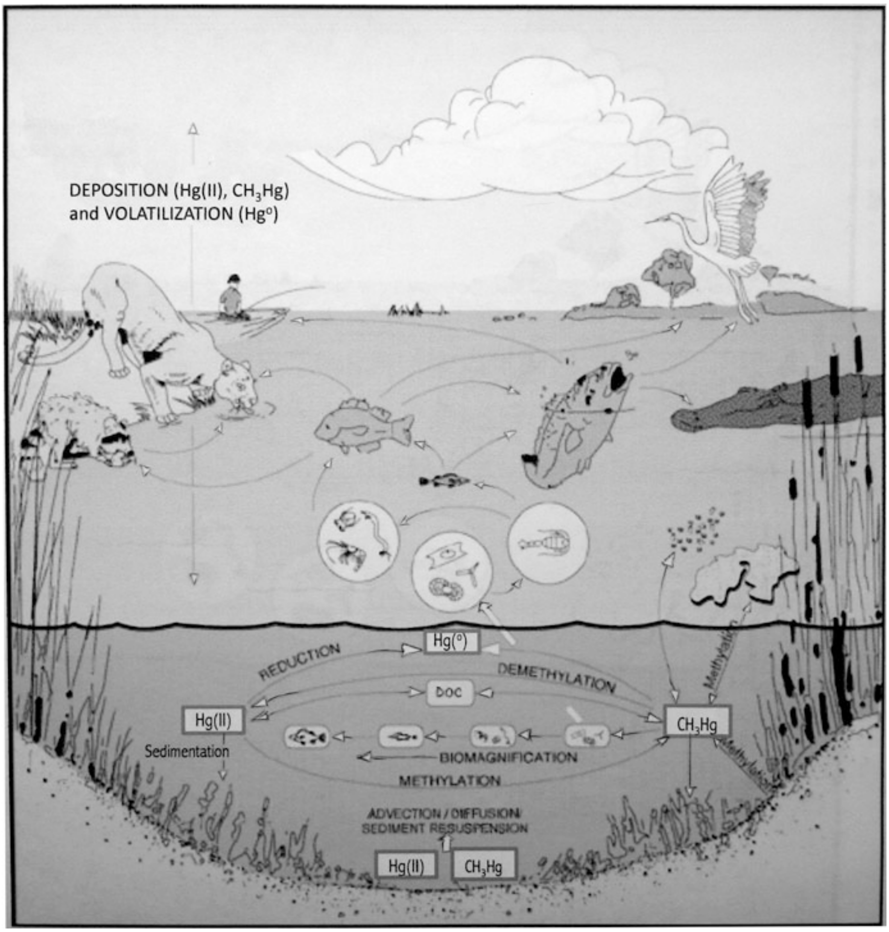


Fig. 1.1 Mercury cycle (From USGS)

fraction that is measured in the cold acid extract. This reaction forms an insoluble metal sulfide that is relatively non-available for uptake. Estuarine sediments tend to have high levels of sulfide, and thus relatively low bioavailability of sediment-bound metals. Ironically, elevating the oxygen in overlying water increases the redox potential in the sediment while decreasing AVS, thus increasing metal availability in the sediment's pore water. Thus, increased oxygen from water quality improvements can increase the mobility of trace metals and may cause sediment-bound metals to leach into the overlying surface water. In contrast, prolonged hypoxia promotes the release of iron and manganese from contaminated estuarine sediments (Banks et al. 2012).

1.1.2 Organics

Oil

Petroleum hydrocarbons (including both linear alkanes and polyaromatic hydrocarbons, PAHs) in the marine environment have been a long-standing problem. There is great public concern about oil spills and the resultant shoreline fouling and mortality of large numbers of marine birds and mammals. Major oil disasters in recent years include the *Exxon Valdez* in Alaska, and the blow out of the mile-deep BP well *Deepwater Horizon* in the Gulf of Mexico.

Many of the major spills had long-term consequences, associated mainly with estuaries and marshes, due to the persistence of oil or petroleum fractions in these low-energy environments. The bioavailability of residual oil to benthic infauna is influenced by several factors, such as water solubility, weathering rate and sediment grain size. These effects may last for decades on processes including behavior, development, genetics, growth, feeding, and reproduction. Long-term effects have been studied after spills, and they vary depending on the nature of the oil, the temperature, and the nature of the area of the spill. After a spill, most of the oil undergoes a weathering process. However, oil in marshes or sandy beaches can sink down to depths where it persists for decades in the absence of oxygen.

The number of spills from tanker ships has decreased over the past three decades. There were about three times as many spills in the 1970s as in the 1990s. However, the number of spills does not consider the volume of oil; the frequency of large spills has decreased as well as the frequency of small ones.

The *Exxon Valdez* Oil Spill

The *Exxon Valdez* oil spill occurred in Prince William Sound, Alaska, on March 24, 1989, when *Exxon Valdez,* an oil tanker struck Prince William Sound's Bligh Reef and spilled 260,000–750,000 barrels (41,000–119,000 m^3) of crude oil. It is considered to be one of the most devastating human-caused environmental disasters. Within 6 h of the grounding, the *Exxon Valdez* spilled approximately 10.9 million gallons of its 53 million gallon cargo of Prudhoe Bay crude oil. The *Valdez* spill was the largest ever in U.S. waters until the 2010 *Deepwater Horizon* oil spill, in terms of volume released. However, the remote location, which could be reached only by helicopter, plane, and boat, made government and industry response efforts very difficult. The oil eventually covered 1,300 miles (2,100 km) of coastline, and 11,000 square miles (28,000 km^2) of ocean. After the spill, the subsurface oil persisted, and chronic exposures continued to affect biota for over a decade. The region is a habitat for salmon, sea otters, seals and seabirds, many of which were obvious victims of the spill, which involved 1,500 miles of oiled shoreline, several hundred thousand dead birds and marine mammals. Three years after the spill, most of the remaining oil was sequestered in places where degradation was inhibited, such as intertidal subsurface sediments or under mussel beds. Heavily oiled coarse sediments protected oil reservoirs beneath the surface, preventing it from weathering in intertidal sites. These sites often contained fish eggs and other vulnerable biota (Peterson et al. 2003).

Various reasons for the spill include the following: Exxon Shipping Company failed to supervise and provide a rested and sufficient crew. The third mate failed to properly maneuver the vessel, possibly due to fatigue or excessive workload. (The 1989 tanker crew was half the size of the 1977 crew, worked 12–14 h shifts, plus overtime.) *Exxon Valdez* was sailing outside the normal sea lane to avoid small icebergs thought to be in the area. Exxon failed to properly maintain the Collision Avoidance System (RAYCAS) radar, which should have indicated to the third mate an impending collision with the Bligh Reef. The captain was asleep when the ship crashed, having had too much to drink. At the helm, the third mate did not look at the radar, because it was not turned on, having been broken and disabled for over a year. Coast Guard tanker inspections in Valdez were not done, and the number of staff was reduced (National Transportation Safety Board 1990).

Lack of available equipment and personnel hampered the spill cleanup, which was delayed during a few days of relatively calm weather because of confusion over which entity (Exxon, the EPA, the State of Alaska) was in charge. Many cleanup techniques were tried with only moderate success. One trial burning was conducted during the early stages of the spill to burn the oil, in a region of the spill isolated from the rest by another explosion. The test reduced 113,400 l of oil to 1,134 l of removable residue, but because of unfavorable weather no additional burning was attempted. The dispersant Corexit® 9580 was tried as part of the cleanup. Corexit has been found to be effective but toxic to wildlife. The primary means of open water oil recovery was with skimmers, but the skimmers were not readily available during the first 24 h following the spill. In general, most skimmers became less effective once the oil had spread, emulsified and mixed with debris. Thick oil tended to clog the equipment. Sorbents were used to recover oil in cases where mechanical means were less practical. The drawback to sorbents was that they were labor intensive and generated additional solid waste. In 1989, hoses spraying seawater were used to flush oil from shorelines. The released oil was then trapped with offshore boom, and removed using skimmers, vacuum trucks (useful for thick layers of oil) and boom (e.g., sorbents). Because there were rocky coves where the oil collected, the decision was made to displace it with high-pressure hot water. However, this also displaced and destroyed the microbial and meiofaunal populations on the shoreline; many of these organisms are important ecologically and/or capable of biodegradation of oil. At the time, both scientific advice and public pressure was to clean everything, but since then greater understanding of bioremediation processes has developed. The general opinion is that the high pressure hot water treatment did more harm than good. Beach applications of dispersants were also tried in several locations. Corexit® 7664 was applied on Ingot Island, followed by a warm water wash. No significant change in oil cover or the physical state of the oil was observed after the treatment, but some ecological impacts were found in the treated areas. It appeared that the effects were due more to the intensive washing than to the use of dispersant, and were evident in intertidal epibenthic macrobiota. Despite the extensive cleanup attempts, less than 10 % of the oil was recovered. An important observation that resulted from the *Exxon Valdez* oil spill was that natural cleaning processes (bioremediation), on both sheltered and exposed beaches, could be very effective at degrading oil. It took longer for some areas of shoreline to recover from invasive cleaning methods (hot water flushing) than from the oil itself. NOAA determined that as of early 2007 more than 26,000 gallons (98 m^3) of oil remained in the sandy soil of the contaminated shoreline, declining at a rate of less than 4 % per year (Cleveland et al. 2010).

The Gulf Oil Spill and Dispersants

On April 20, 2010, the Macondo well blowout occurred approximately 5,000 ft below the surface of the Gulf of Mexico, causing the BP-Transocean drilling platform *Deepwater Horizon* to explode, killing 11 workers and injuring others. About five million barrels of crude oil were released into the sea; on average, 60,000 barrels a day (about 11,350 t of gas and oil per day) before the gusher was capped on July 15. Over 630 miles of Gulf Coast shoreline were oiled, mostly in Louisiana. There were over 400 controlled burns, which killed hundreds of sea turtles and unknown numbers of dolphins. To protect marshes from incoming oil, booms were set around islands and shorelines, and two million gallons of the dispersant Corexit® were applied on and beneath the surface of the sea to break up the oil. After extensive use, oil was no longer visible on the surface of the water, and some claimed it was "gone" and degraded by microbes. The use of the dispersants was highly controversial. By enhancing the amount of oil that physically mixes into the water column, dispersants reduce the amount of oil that reaches shoreline habitats, but dispersants are controversial because of the toxicity of dispersed mixtures. Also, once oil is dispersed in deep water, it cannot be recovered. Oil, when combined with dispersants in the water is usually more toxic than either the oil or the dispersant alone. Most studies found that the combination of oil and dispersant increased toxic effects. Two dispersants, Corexit® 9500 and 9527A, were used, which are complex mixtures of chemicals that have surfactant (wetting) properties, which allows them to act as emulsifiers (USEPA 2010). Although these two are EPA-approved, they are more toxic and less effective than other approved dispersants (Scarlett et al. 2005).

EPA performed short-term tests on mysid shrimp and inland silverside fish stated that JD-2000® and Corexit® 9500 were generally less toxic to small fish and JD-2000 and SAF-RON GOLD® were least toxic to mysid shrimp. However, on May 20, EPA gave BP 24 h to find a less toxic alternative, which BP ignored. On May 25, the EPA gave BP a directive to reduce dispersant use, but the Coast Guard granted exemptions, allowing continued use of Corexit®. The goal of the EPA was to decrease toxicity, while that of the Coast Guard was to protect the coastline from being oiled.

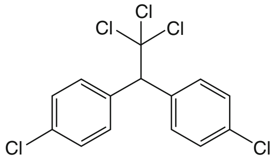
The blowout occurred in deep water, where a turbulent discharge of hot pressurized oil and gas mixed with seawater and dispersed by itself into droplets and gas hydrates without the use of chemicals. This mixture did not rise to float on the surface but stayed in a subsurface plume. Amid reports of the oil being nearly gone, a plume of hydrocarbons about 22 miles long in deep water over 3,000 ft below the surface was discovered. Camilli et al. (2010) found a continuous plume of oil, which persisted for months without substantial biodegradation. Samples collected from the plume had monoaromatic petroleum hydrocarbon concentrations $>50\ u\text{g}\ \text{l}^{-1}$. Dissolved oxygen concentrations suggest that microbial respiration in the plume was not more than 1 uM oxygen per day. The high pressures and low temperatures made the mixture of oil, dispersants, sea water and methane neutrally buoyant.

Subsequently, Kujawinski et al. (2011) reported that a major component of the dispersant was contained in the plume in the deep ocean and had still not degraded after 3 months. They measured one of Corexit® 9500A's main ingredients in May and June and again in September, 2 months after the well was capped. The results raise questions about what impact the oil and dispersant might have had on the environment. The toxicity of this mixture on deep sea corals and cold seep communities is unknown, as are the impacts on planktonic filter feeders and fish eggs/larvae in the water column. Eventually intense microbial activity degraded the oil (Kessler et al. 2011).

The *Deepwater Horizon* blowout was unprecedented because of the use of dispersants at the wellhead, retention of oil as finely dispersed droplets and emulsions and deepwater retention of plumes of natural gas that underwent rapid microbial degradation. Subsurface effects of oil had not been seen before. According to the government's "oil budget," released by NOAA in November 2010, one fourth of the oil evaporated or dissolved into the water, and 13 % was blown into fine droplets as it rushed from the broken pipe. Corexit® 9500 sprayed at the wellhead dispersed another 16 % into fine droplets, which joined the plume. Natural oil-degrading Proteobacteria then worked on the plumes (Hazen et al. 2010). Rapid degradation was seen at 5 °C. Thus, intrinsic bioremediation of the plume took place in the deep water, as a result of the geography of the Gulf of Mexico, which is fairly enclosed. When the hydrocarbons were released from the well, bacteria bloomed, and then swirled around and often came back repeatedly over the leaking well. Water with a bacterial community got a second input of hydrocarbons and the organisms attacked and degraded the new oil (Valentine et al. 2012). In addition to the oil that was degraded, the Unified Command, led by the U.S. Coast Guard, physically removed about a third of it, and burning at the surface removed another 5 %. However, the budget was criticized as incomplete. Samantha Joye of the University of Georgia said her data showed that oil and gas at depth remained much longer than the oil budget suggested. There was also the "residual" oil unaccounted for, which is still out there, on or under beaches, in marshes, sunk to the bottom, or floating as tarballs.

If dispersants had not been used, the surface oil would have been weathered (tar balls) by the time it reached the coast. This would have created a public relations nightmare on beaches and affected the socio-economic activities of residents and tourists. The dispersed oil below the ocean surface appears to have killed benthic animals in intertidal and shallow subtidal regions on and near sandy beaches. In the wetlands only the fringe-edge marsh plants were damaged by the toxic

Fig. 1.2 DDT molecule



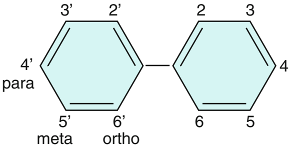
oil/dispersants in the surface water, since the plants appear to have absorbed these chemicals which caused the death of shoots. At the time this book is being written, in 2011 and 2012, there have been relatively few published reports on effects, as many scientists are not permitted to publish their findings yet, and it is too early to say anything about long-term effects on the Gulf ecosystems.

Pesticides

Halogenated hydrocarbons (mostly DDT-related pesticides, PCBs, and dioxins) have been studied intensively for decades. DDT (dichlorodiphenyltrichloroethane) (Fig. 1.2), the most powerful pesticide the world had ever known, could kill hundreds of different kinds of insects.

Synthesized in 1874, its insecticidal ability was identified in 1939 by the chemist Paul Hermann Müller. It was used in World War II, clearing South Pacific islands of malaria-causing insects, and was used as a de-lousing powder in Europe. When it became available for civilian use, few people expressed concern about this miracle compound. In 1948, Müller won the Nobel Prize for Physiology and Medicine. Related pesticides included aldrin, dieldrin, chlordane, heptachlor, and toxaphene, which caused fish kills when applied near the water. These chemicals are lipophilic and highly persistent. Rachel Carson's writing about the dangers of DDT was stimulated by bird kills that occurred as the result of DDT sprayings. Having already collected a large amount of research on the subject, she decided to write a book. *Silent Spring* described how DDT entered the food chain and accumulated in the fatty tissues of animals, including humans, and caused cancer and genetic damage. A single application on a crop, she wrote, killed insects for weeks and months (not only the targeted insects but many others) and remained toxic even after dilution by rainwater. She concluded that DDT and related pesticides had harmed birds and other animals and had contaminated the world food supply. The book alarmed readers and triggered an indignant response from the chemical industry. "If man were to faithfully follow the teachings of Miss Carson," complained an executive of the American Cyanamid Company, "we would return to the Dark Ages, and the insects and diseases and vermin would once again inherit the earth." Anticipating such a reaction, Carson had written *Silent Spring* with numerous scientific citations and a list of expert scientists who had approved it. Many eminent scientists supported it, and President Kennedy's Science Advisory Committee vindicated the book. As a result, DDT came under much closer government scrutiny and was eventually banned. Most other chlorinated hydrocarbons were also phased out

Fig. 1.3 PCB molecule, showing positions where Cl could be attached



Structure of Polychlorinated Biphenyl (PCB) Molecule

in subsequent decades. An important legacy of *Silent Spring* was a new public awareness that nature was vulnerable to human activities. The growth of the environmental movement was partly a response to this new awareness. Most uses of DDT and other chlorinated hydrocarbons were banned in the1970s. In the United States, the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) requires that adverse ecological effects be balanced against the economic costs of regulating pesticide use and benefits the pesticide provides.

The diversity of pesticides has increased greatly. Hundreds of chemicals are now in use, and they generally occur in mixtures, whose toxicity may be additive or synergistic or antagonistic. Newer chemicals are less persistent than the "legacy pesticides" and do not generally cause kills. However, they can produce sublethal effects such as endocrine disruption, altered development and behavior, reduced growth, and other effects that are the major focus of this book. "Second generation" pesticides such as organophosphates and carbamates are much less persistent in the environment. Nevertheless, if spraying coincides with the time of reproduction and early life stages of susceptible organisms, they can also have deleterious effects. "Third generation" pesticides such as insect growth inhibitors, chitin synthesis inhibitors, and juvenile hormone mimics such as methoprene are more narrowly focused on insect biology, but tend to have severe effects on crustaceans, especially early life stages.

Industrial Chemicals

PCBs

PCBs (polychlorinated biphenyls) are also chlorinated hydrocarbons, and were manufactured from 1929 until they were banned in the U.S. in 1979 (Fig. 1.3). They include over 200 congeners with differing numbers of chlorine on different locations on the biphenyl structure, have a range of toxicity, and vary in consistency from thin, light-colored liquids to yellow or black waxy solids. In terms of toxicity, there are two distinct categories – coplanar (or non-*ortho*-substituted) and non-coplanar (or *ortho*-substituted) congeners. Coplanar PCBs have a fairly rigid structure, with the two phenyl rings in the same plane, which gives the molecule a structure similar to polychlorinated dibenzo-p-dioxins (PCDDs) (see below), and allows them to act in the same way as these molecules. Non-coplanar PCBs, with chlorine atoms at the *ortho* positions, are not part of the dioxin group. Nevertheless they have some neurotoxic and immunotoxic effects, but at levels higher than normally associated with dioxins. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints and rubber products; in pigments, dyes, and carbonless copy paper; and many other industrial applications. PCBs entered the environment during their manufacture and use in the United States. They can still be released into the environment from poorly maintained hazardous waste sites that contain PCBs; illegal or improper dumping of PCB wastes; leaks or releases from electrical transformers containing PCBs; and disposal of PCB-containing products into landfills not designed to handle hazardous waste. PCBs may also be released into the environment by the burning of some wastes in municipal and industrial incinerators.

Because of their persistence in the environment and low water solubility, chlorinated hydrocarbons tend to accumulate in sediments and in tissues. Chlorinated hydrocarbons are highly persistent and remain in the environment (especially in sediments) for many decades, so they continue to be found long after they have been banned. Since PCBs are particularly resistant to microbial degradation, they may remain for long periods of time cycling between air, water, and soil. PCBs can be carried long distances and have been found in snow and sea water in areas far away from where they were released. As a consequence, PCBs are found all over the world. In general, the lighter the form of PCB (i.e., fewer chlorine atoms per molecule), the further it can be transported. PCBs accumulate in aquatic biota, including plankton and fish. Like chlorinated pesticides and methylmercury, PCBs biomagnify. Thus, larger fishes higher on the food chain are likely to have higher concentrations than smaller fishes (Fig. 1.4).

As a result, people who ingest fish may be exposed high concentrations. The highest environmental concentrations of PCB are usually found in soil and sediment, with much lower levels found in air and water. Fortunately, PCB levels have been declining in the past few decades and have been the subject of a number of federal and state regulations and clean-up actions in the U.S.

Dioxins

Dioxins and furans are some of the most toxic chemicals known. Dioxin is a general term that describes a group of hundreds of chemicals that are highly persistent in the environment. The most toxic compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin or TCDD (Fig. 1.5). Polychlorinated dibenzofurans are similar to dibenzodioxins, but with a single oxygen connecting the benzene rings instead of two.

The toxicity of other dioxins and chemicals such as dioxin-like PCBs are measured in relation to TCDD. Dioxins and furans are formed as unintentional by-products of many industrial processes that use chlorine, such as chemical and pesticide manufacturing, pulp and paper mills that use chlorine bleach, the production of polyvinyl chloride (PVC) plastics, the production of chlorinated

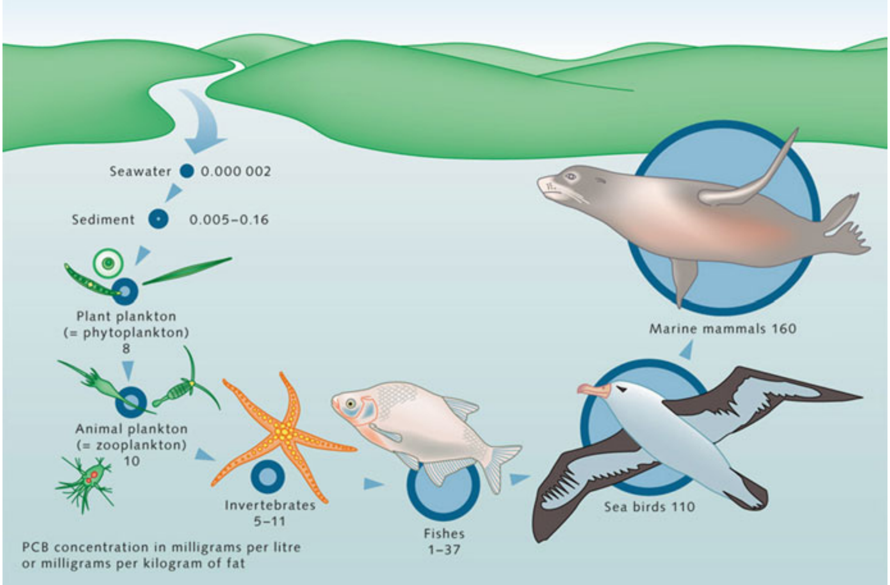
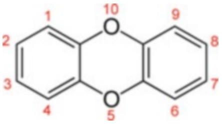


Fig. 1.4 Biomagnification of PCBs (From oceansoffun.org)

Fig. 1.5 Dioxin molecule, showing positions where Cl could be attached



chemicals, and incineration of waste including plastics,. Dioxin, a contaminant of Agent Orange, was found at Love Canal in Niagara Falls, NY and was the basis for evacuations at Times Beach, MO and Seveso, Italy. The industrial accident in Seveso led to many cases of Acquired Dioxin-Induced Skin Haematoma, or ADISH, in which the skin acquires disfiguring lumps. Perhaps the most famous case of ADISH was that of Viktor Yushchenko, who was poisoned while running for the presidency of Ukraine. The disfiguration led to the diagnosis. He went on to win the election, but had to undergo many surgical procedures to preserve his life. Like PCBs, dioxins are persistent in the environment and biomagnify in food chains.

1.1.3 Contaminants of Emerging Concern (CECs)

"Emerging contaminants" have been defined as any synthetic or naturally occurring chemical or microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological or human health effects. In some cases, release of these contaminants to the environment has occurred for a long time, but the chemicals have not previously been regarded as contaminants and are widespread in the environment. They are derived from municipal, agricultural, and industrial wastewater sources. Some examples are: alkylphenols, used as detergents and known to disrupt the reproductive system; pharmaceuticals, and triclosan (trichlorohydroxydiphenyl ether), an antibacterial agent found in many personal care products and which has been identified as posing risks to humans and the environment.

Microplastics are both abundant and widespread in the oceans, found in highest concentrations along coastlines and within mid-ocean gyres. Ingestion of microplastics has been demonstrated in a range of marine organisms, a process which may facilitate the transfer of chemical additives or hydrophobic waterborne pollutants to biota.

Halogenated Organics

Polybrominated diphenylethers (PBDEs) are used as flame retardants on many consumer products. PBDEs are chemically similar to chlorinated hydrocarbons, with bromine instead of chlorine, and cause long-term adverse effects in humans and wildlife. They move from consumer products to the outdoor environment, and have been found in tissues of marine mammals in the Arctic, very far from sites of use. Fluorinated compounds are also of concern. Perfluorinated compounds (PFCs) are a family of manmade chemicals that are used to make products that resist heat, oil, stains, grease and water. Common uses include nonstick cookware, stain-resistant carpets and fabrics, coatings on some food packaging (e.g., microwave popcorn bags and fast food wrappers), and in fire-fighting foam. These chemicals, such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are persistent and ubiquitous in the environment. PFCs are also likely to be toxic and have bioaccumulative properties. All of the chemicals listed above are, like DDT, PCBs and dioxin, halogenated – that is, include F, Cl or Br in their structure, which makes them resistant to microbial degradation.

Pharmaceuticals and Personal Care Products (PPCPs)

These contaminants are being discovered in our waters, as well as in fish tissue, at very low concentrations. Pharmaceuticals are prescription and over-the-counter therapeutic and veterinary drugs, including antibiotics, birth control pills, tranquilizers, etc., while personal care products include soaps, fragrances, sunscreen, and cosmetics. It is likely they have been present in the environment for as long as they have been in use. Many PPCPs remain in the environment because as they degrade, more are added, and their use is increasing. Because of increasing concentrations, effects in the environment are being noticed. When endocrine disruption was first being studied in aquatic biota in the early 1990s, people looked to the “usual suspects," the chlorinated hydrocarbons (which do have endocrine effects). Later it was noticed that estrogens themselves were in the water, coming from sewage treatment plants without being broken down, and it was realized that estrogens from birth control pills were playing a major role. Glucocorticoids are also found in the environment at concentrations higher than those of estrogens, which may be high enough to affect aquatic life. Even caffeine (found in many food and beverage products as well as some pharmaceuticals) has been found in coastal waters.

Nanoparticles

Nanomaterials or nanoparticles ($<$100 nm) are being used in many applications, including cosmetics, electronics, drug delivery, manufacturing, paints, and more. They may be composed of carbon (nanotubes, fullerenes), transition metals (gold, platinum, silver), metal oxides (titanium dioxide, zinc oxide), polystyrene, and silica, and are being manufactured in increasing amounts. Greater use of such products has led to their release into the environment in runoff and sewage effluent, and their accumulation in coastal environments. They have come under scrutiny as potential pollutants. For example, it was found that the nanoparticulate form of titanium dioxide (TiO2) exposed to ultraviolet radiation can be toxic to marine organisms (Miller et al. 2012).

While metal nanoparticles (NPs) may have fates similar to other forms of the same metal, metals in NPs may be tightly bound to the core material and not readily dissociate (Griffitt et al. 2008). However, Cleveland et al. (2012) studied fate of three nanosilver consumer products, two AgNP standards, and ionic silver (Ag^+) in estuarine mesocosms. The consumer product released significant amounts of Ag ($>$80 %) over 60 days, which moved from the water column into estuarine biota, including clams, grass shrimp, mud snails, cordgrass, biofilms, intertidal sediment, and sand. Ag was adsorbed from the water into the biofilms, sediment, and sand, then from the sand to the clams. Significant amounts were taken up by the organisms through trophic transfer.

Research is underway to develop analytical methods to measure these unregulated chemicals in water, sediment, and waste down to trace levels, determine their environmental occurrence, sources and pathways of release to the environment, their transport and fate, and potential ecological effects. There is a need to develop standardized analytical techniques and reliable extraction procedures, understand the role of wastewater treatment systems on the environmental fate of these contaminants, and characterize the mechanisms responsible for their transport and fate in the environment.

Noise Pollution

Though not fitting the definition of a "chemical," noise pollution in the ocean is another stress of emerging concern. For millions of years, the oceans have been filled with sounds from natural sources such as the clicks of whales and the snapping of shrimp. Many marine species have specialized hearing abilities, communication skills and echolocation abilities. However, humans generate a lot of sound. An increase in motorboats, primarily commercial shipping traffic, exploration and extraction of oil and minerals, air guns used for seismic exploration, sonar and even jet skis contribute to the increased level of underwater noise. Sound travels four times faster in water (1,230 m/s) than in air (340 m/s) so it travels farther under water. High intensity sound in the oceans can travel for thousands of miles. Since water is denser than air sound waves travel though water at higher energy levels and are hence louder. New sources of marine sound pollution have been added. One source having immediate and obvious negative effects has been the development and testing of "Low-frequency Active (LFA) Sonar" that has a potential worldwide deployment by the U.S. Navy. Several tests have resulted in large losses in marine life.

1.1.4 Nutrients and Sewage

Nutrient enrichment due to excessive amounts of nitrogen (N) is the primary cause of impaired coastal waters worldwide, while excessive phosphorus (P) tends to be associated with enrichment in fresh waters. Nitrogen occurs in several oxidized forms, collectively termed NO_x. N is an essential nutrient and a fertilizer that contributes to agricultural productivity but also a pollutant. It is a benefit or a hazard, depending on its form, location, and quantity. Human activities, primarily increased use of commercial fertilizers, have increased N inputs by ten-fold in many parts of the world. Another major source is burning of fossil fuels, which emit NO_x into the atmosphere, creating acid rain and air pollution as well as water pollution. Coastal oceans receive enormous inputs of nitrogen and phosphorus from sewage treatment plants, runoff of fertilizers and atmospheric deposition. Sewage, even after treatment, contains high levels of nutrients. Excess N flows from agricultural fields, suburban lawns, and stockyards, generally as ammonia and nitrate, entering freshwater and going down to estuaries via streams and rivers, altering water chemistry and ecological communities. It also is released from septic tanks and reaches coastal waters via groundwater, and comes down from the atmosphere in precipitation. These nutrients cause algal blooms, followed by hypoxia (low oxygen) in deeper waters (Fig. 1.6). The global rise in eutrophic and hypoxic events is due to increases in intensive agriculture, industrial activities, and population, which have increased N and P flows in the environment. There are variations in the importance of each source among regions. For example, in the U.S. and Europe, agricultural sources (animal manure and fertilizers) are generally the primary contributors, while sewage and industrial discharges (which usually receive treatment prior to discharge) are a secondary source. Atmospheric sources are also a significant contributor of N in coastal areas. N from fossil fuel combustion and volatilization from fertilizers and manure is released into the atmosphere and deposited on land

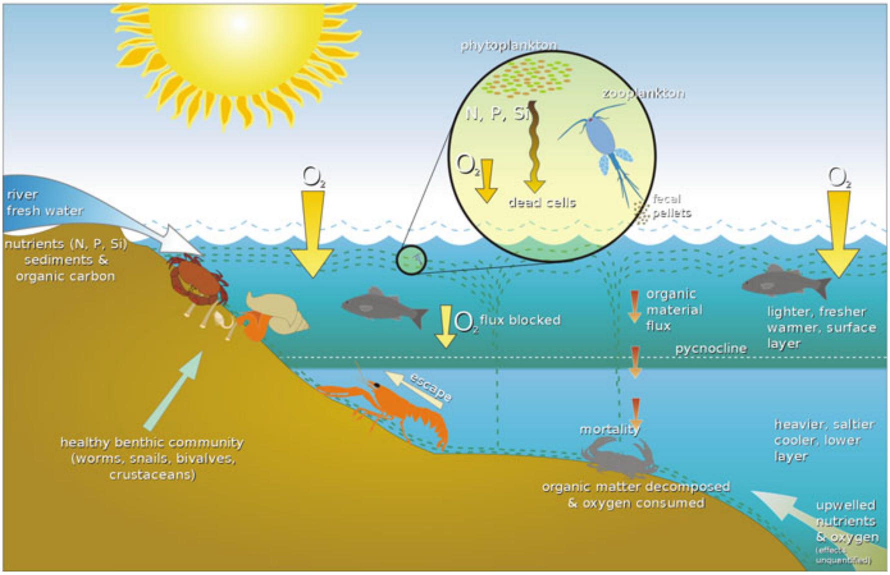


Fig. 1.6 Eutrophication diagram (Taken from Wikimedia (original source US EPA))

and water by wind and precipitation. In Chesapeake Bay, atmospheric sources account for a third of all controllable N that enters the bay. However, in Latin America, Asia, and Africa, wastewater from sewage and industry are often untreated and may be the primary contributors to eutrophication.

Nutrient enrichment of marine waters promotes excessive growth of algae, both attached multicellular forms (e.g., sea lettuce) and microscopic phytoplankton. Small increases in algal biomass can increase production in food webs sustaining fish and shellfish. However, over-stimulation of algal growth can severely degrade water quality and threaten human health and living resources. Some phytoplankton species, generally dinoflagellates, produce toxins that can impair respiratory, nervous, digestive and reproductive system function, and even cause death of fish, shellfish, seabirds, mammals, and humans. These harmful algal blooms (HABs) can cause fish kills, human illness through shellfish poisoning, and death of marine mammals and shore birds. HABs may be called "red tides" or "brown tides" because of water discoloration when these blooms occur. Their economic impacts can be severe, as shellfish harvest and fishing are closed. HABs have been increasing worldwide, and strong correlations have been shown between N input and phytoplankton production. There are examples in regions around the world such as Chesapeake Bay, the Inland Sea of Japan, the Black Sea, and Chinese coastal waters, where increases in nutrient loading have been linked with the development of large blooms, which can lead to toxic effects on ecosystems, fisheries resources, and human health (Anderson et al. 2002). Not only has the frequency of HABs been increasing, new toxin-producing species have been found to cause serious problems.

With species that do not produce toxins, algal blooms eventually die and sink and are degraded by bacteria, whose metabolism consumes oxygen. If the aeration of water by mixing is less than bacterial metabolism, the bottom waters will become hypoxic (low oxygen) or anoxic (devoid of oxygen), creating stressful or lethal conditions. This is a major problem in many estuaries, especially in late summer and early fall, and is termed eutrophication. Hypoxia has been increasing globally; increasing numbers of "dead zones" have been reported a result of fertilizer runoff and nitrogen deposition from fossil fuel burning. Eutrophication is especially harmful to coral reefs, where the nutrients cause benthic algae to proliferate and cover and smother the corals, eventually leading to the replacement of the coral community with an algal community, especially when grazers (e.g., parrot fish) are not plentiful (Bell 1992). Of the 415 areas around the world identified as experiencing some form of eutrophication, 169 are hypoxic and only 13 are classified as "in recovery." Seasonal occurrences of dead zones with no oxygen have expanded in the Gulf of Mexico (where the dead zone has approached the size of New Jersey) and many other regions worldwide. While trends show increases worldwide, some localized areas are improving (Diaz and Rosenberg 2008). Efforts to reduce the flow of fertilizers, animal waste and other pollutants into the Chesapeake Bay appear to be helping the bay's health. The size of mid- to late-summer "dead zones," in deep channels of the bay has been declining.

Sewage and nonpoint runoff also discharge microbes into the water. Microorganisms such as hepatitis A virus, and pathogenic bacteria (e.g., *Salmonella, Listeria monocytogenes, Vibrio cholerae* and *Vibrio parahaemolyticus*) have been reported in coastal waters. Coliform bacteria are a commonly used bacterial indicator of water pollution, although not an actual cause of disease. Microbiological contamination can occur in marine biota when sewage from humans or animals is discharged to coastal waters or arrives in river flow. High levels of pathogens may result from inadequately treated sewage, which may be from a sewage plant without secondary treatment. Older cities with aging systems may have leaky pipes, pumps, or valves, which can cause sanitary sewer overflows. Some older cities also have combined sewers (sanitary and storm sewers) which may discharge untreated sewage during rain storms when the volume of water exceeds the capacity of the system. Pathogens may be from animal feces, from poorly managed livestock operations or dense concentrations of wild animals. Bacteria and viruses from humans and animals, mainly attached to fine particulate matter, can affect bathing water quality and accumulate in filter feeding shellfish.

Microbial pollution by pathogens from sewage or animal waste is of concern for drinking water supplies, but is also a human health issue in coastal waters where swimmers may become ill after rain has washed bacterial pollution in from combined sewers or runoff from land. Infections and illness due to recreational water contact are generally mild and difficult to detect. Even when illness is more severe, it may still be difficult to attribute to water exposure. Epidemiological studies have shown gastrointestinal and respiratory infections associated with polluted recreational water. Bathing beaches may be closed by officials when they have excessive levels of bacterial pollution. Another concern is accumulation of pathogenic bacteria in edible shellfish. Since many estuaries are contaminated by municipal and agricultural wastes, bacteria and viruses can cause disease associated with shellfish consumption. Gastroenteritis and hepatitis A are the most important diseases transmitted to humans through shellfish, but cholera and typhoid fever were the first to be linked to consumption of contaminated shellfish. Viral outbreaks are also associated with eating contaminated shellfish. Initially, the analysis of outbreaks was based on epidemiological data but advances in molecular biology and the ability to detect low levels of enteric viruses in shellfish has provided more accurate assessment of shellfish as a path for disease transmission. Shellfish beds are closed when tests indicate elevated bacterial levels. Microbiological quality of coastal waters has been improving following better waste water treatment.

1.1.5 Carbon Dioxide, Climate Change and Ocean Acidification

The burning of fossil fuels emits carbon dioxide into the atmosphere, which results in the "greenhouse effect," raising the earth's temperature. Studies confirm that in the past century the oceans have warmed by about 1 °F to a depth of 200 ft, and the overwhelming scientific consensus is that increasing levels of human-caused greenhouse gases in the atmosphere are the principal cause. As surface water warms, vertical water movements (upwelling) which bring nutrients up to surface waters where most phytoplankton are found, are reduced and thermal stratification increases. There is a negative relationship between ocean temperatures in the tropics and subtropics and productivity of plankton, probably because of reduced upwelling and increased stratification. Much of the CO_2 is absorbed by the ocean where it is converted to carbonic acid, which releases hydrogen ions into the water, reducing its pH and making it more acidic. Since the industrial age began, the pH of the oceans has declined by 0.1 pH unit, which, because the pH scale is logarithmic, represents a 30 % increase in acidity. According to projections of the IPCC (Intergovernmental Panel on Climate Change), pH values will decrease another 0.2–0.3 units by 2100, thus doubling the current acidity.

The extent to which human activities have raised ocean acidity has been difficult to calculate because it varies naturally between seasons, from one year to the next, and between regions, and direct observations go back only 30 years. Combining computer modeling with observations, Friedrich and colleagues (2012) concluded that CO_2 emissions over the last 100–200 years have already raised ocean acidity far beyond the range of natural variations. The excess hydrogen ions reduce seawater concentrations of carbonate ions. They studied changes in the saturation level of aragonite (a form of calcium carbonate) typically used to measure of ocean acidification. As seawater becomes more acid, the saturation level of aragonite drops. Their models captured the current seasonal and annual variations of aragonite in coral reefs, where today's levels of aragonite saturation are already five times below the pre-industrial range. The saturation state, denoted by the Greek letter Ω, refers to the degree to which seawater is saturated with a carbonate mineral and is inversely proportional to the mineral's solubility. The saturation state is determined by the concentration of calcium and carbonate ions in relation to the solubility coefficient for the particular calcium carbonate mineral (aragonite, calcite). Aragonite saturation is very sensitive to acidity because it is more soluble. It is also the form most often used for mollusk shell formation, so this can affect the growth of these organisms. When the saturation state equals 1, there is an equal chance of dissolution or formation of calcium carbonate; when it is <1 dissolution is favored, and when it is >1 formation of calcium carbonate is favored. If the aragonite saturation state falls below 1 (undersaturation) already-formed shells will dissolve. If it falls below 1.5, some organisms are unable to build new shells. The saturation state is highest in shallow warm tropical waters and lowest in deep and cold high latitude waters (Feely et al. 2004). This suggests that effects of acidification will be more severe in cold high latitudes.

Acidification can interact with eutrophication. When nutrient-rich river water enters coastal waters, phytoplankton bloom. When the algae die, sink to the sea floor and decompose, carbon dioxide is released and oxygen depleted. The dissolved CO_2 reacts with water, forming carbonic acid. Ocean acidity also increases when excess carbon dioxide is absorbed from the air at the ocean's surface. The combination of these two sources of CO_2 increases acidity beyond what would be expected from the individual processes (Cai et al. 2011).

Rising temperatures due to increases in greenhouse gases are also warming the surface water of the oceans. Thermal expansion as well as increased meltwater and discharged ice from terrestrial glaciers and ice sheets are causing sea level to rise. Warmer ocean currents also can move migrating fish and invasive species to areas they previously didn't previously inhabit, and alter timing of reproduction or migration. Warm water holds less oxygen, and tends to amplify the threats of toxic pollution.

1.1.6 Litter, Marine Debris

Marine debris is any man-made object discarded, disposed of, or abandoned that enters the coastal or marine environment. It may enter directly from a ship, or indirectly when washed out to sea. Materials can be dumped, swept, or blown off vessels and platforms at sea. Sources of the debris are littering, dumping in rivers and streams, and industrial losses, e.g. spillage of materials during production, transportation, and processing. It is estimated that about 14 billion pounds (6.4×10^9 kg) of trash end up in the oceans every year. Plastics comprise a large proportion of the debris, and the variety and quantity of plastic items has increased dramatically, including domestic material (shopping bags, cups, bottles,

Fig. 1.7 Marine litter (From NOAA)

bottle caps, food wrappers, balloons) (Fig. 1.7), industrial products (strapping bands, plastic sheeting, hard hats, resin pellets), and lost or discarded fishing gear (nets, buoys, traps, lines).

Glass, metal, styrofoam, and rubber are used for a wide range of products. While they can be worn away – broken down into smaller and smaller fragments, they generally do not biodegrade entirely. As these materials are used commonly, they are common in marine debris. Derelict fishing gear includes nets, lines, crab/shrimp pots, and other recreational or commercial fishing equipment that has been lost, abandoned, or discarded in the marine environment. Modern gear is generally made of synthetic materials and metal, so lost gear can persist for a very long time.

Marine debris accumulates along shorelines and in coastal waters, estuaries, and oceans throughout the world. It can be blown by the wind, or follow the flow of ocean currents, often ending up in the middle of oceanic gyres where currents are weakest. The Great Pacific Garbage Patch is one such example; comprising a vast region of the North Pacific Ocean. Estimated to be double the size of Texas, the area contains over 3 million tons of plastic, mostly in very small pieces. Islands within gyres frequently have their coastlines covered by litter that washes ashore; prime examples being Midway and Hawaii, where plankton tows sometimes come up with more plastic pieces than plankton. The next biggest known marine garbage patch is the North Atlantic Garbage Patch, estimated to be some hundreds of km across. All estimates of the amount of litter are underestimates. Wind pushes the lightweight plastic particles below the surface, suggesting that research into how much plastic litter is in the ocean conducted by skimming the surface may vastly underestimate the true amount (Kukulka et al. 2012).

In addition to the visible litter that washes up on beaches, microscopic plastic debris from washing clothes is accumulating in the marine environment and could be entering the food chain. Researchers traced the “microplastic” back to synthetic clothes, which release up to 1,900 tiny fibers per garment every time they are washed (Browne et al. 2011). Earlier research showed plastic smaller than 1mm was being eaten by animals and getting into the food chain. In order to identify how widespread the presence of microplastic was on shorelines, the team took samples from 18 beaches around the globe, and found that samples contained pieces of microplastic. Polyester, acrylic and polyamides (nylon) were the major ones, and their concentration was greatest near large urban areas. They found exactly the same proportion of plastics in sewage, which led them to conclude that sewage was the source of the fibers.

1.2 Measuring Effects on Biota

Toxic effects, both lethal and sublethal, have been documented extensively in laboratory experiments. There have been fewer field studies of effects on populations of marine organisms. Early work on pollutant effects relied on tests that measured lethality. The LC_{50} – the concentration of a toxicant that produced 50 % mortality – was the benchmark. Regulations under FIFRA (the U.S. Federal Insecticide Fungicide and Rodenticide Act) for developing criteria for pesticides for the protection of aquatic life require standard endpoints, the LC_{50}, which is of little ecological relevance. Toxicity tests are required for a few species: rainbow trout, bluegill, and daphnids – one cold-water fish, one warm water fish and one crustacean – all freshwater. Unfortunately, even today, over half a century later, many studies still rely on this approach – acute toxicity tests – that are still considered most useful in a regulatory context. These tests do not consider sublethal toxicity or toxicity that is delayed in time, or differences in life history among species. Knowing sublethal effects of chronic lower dose exposures on physiology, behavior, development, etc., is essential for understanding ecological impacts of pollutants in nature and is the focus of this book.

Extensive research has shown that toxicants can disrupt the metabolic, regulatory, or disease defense systems, eventually compromising survival or reproduction. Sublethal effects can lead to understanding of mechanisms and also to understanding of ecological effects in the “real world.” Another insight is that early life stages – gametes, fertilization, embryonic and larval development – are most sensitive to stresses including contaminants. The hormonal control of reproduction can be affected by many contaminants, now called “endocrine disruptors.” Exposures during early life stages may cause effects that appear later, sometimes many years later. Thus, long-term delayed effects and indirect effects are important to evaluate. There has been a trend towards greater ecological realism in ecotoxicology, but advances have been mainly in freshwater ecosystems.

1.2.1 Hormesis

In toxicological investigations, whatever the endpoint, the degree of response typically goes up with the dose, a fundamental principle of toxicology. However, this is not always the case; there are cases in which low levels of a toxicant produce "positive" effects, while higher concentrations produce "negative" effects (e.g., increased growth vs. reduced growth). In these cases, the dose response curve is J-shaped, or inverted U- shaped. Some of the early reports of this phenomenon, termed "hormesis", were made with marine organisms. Laughlin et al. (1981) reported that crab zoeae (*Rhithropanopeus harrisii*) exposed to low concentrations of jet fuel oil had increased weight above that of controls. Stebbing (1981) similarly found increased growth in colonies of the hydroid *Campanularia flexuosa* in low concentrations of cadmium and copper. Many studies on different organisms with different toxicants have shown a similar pattern, which led Calabrese and Baldwin (1997) to conclude that hormesis is generalizable with respect to organism, endpoint, and chemical class, though this has not been universally agreed upon.

1.2.2 Mechanistic Approaches

A dominant approach of ecotoxicology focuses on discovering mechanisms of action at the biochemical level. There is considerable effort and an enormous literature devoted to development of biochemical biomarkers, which are measured in tissues and body fluids of organisms exposed to environmental chemicals. These responses presumably occur prior to effects at higher levels of organization and can be early warning signals. This reductionistic approach is useful for learning molecular mechanisms, but it cannot predict effects on whole organisms, populations, communities, or ecosystems. Many are biomarkers of exposure, rather than of effects, and do not necessarily link to impairment of growth, reproduction, energy utilization, etc. However, in some cases such connections are made. For example, Sanders et al. (1991) related changes in stress proteins to scope-for-growth measurements in Cu-exposed mussels, which relates to fitness and could have consequences at the population level. Integrated measures have been developed, such as scope-for-growth, which is an indication of energy status based on the concept that energy needed for detoxification will reduce the amount available for growth. The vast literature on biochemical biomarkers is the subject of many books but is barely covered here, where the focus is on organism-level responses. These processes, including respiration, osmoregulation, energy metabolism, excretion, growth, reproduction, behavior, etc., must function appropriately for individuals and populations to thrive. While most studies have been in laboratory organisms (which may be exposed to far higher concentrations of chemicals than occur naturally) some studies have measured these processes in organisms from contaminated sites. Automated monitoring systems have been developed to measure rates of physiological processes and certain types of behavior (Depledge et al. 1995).

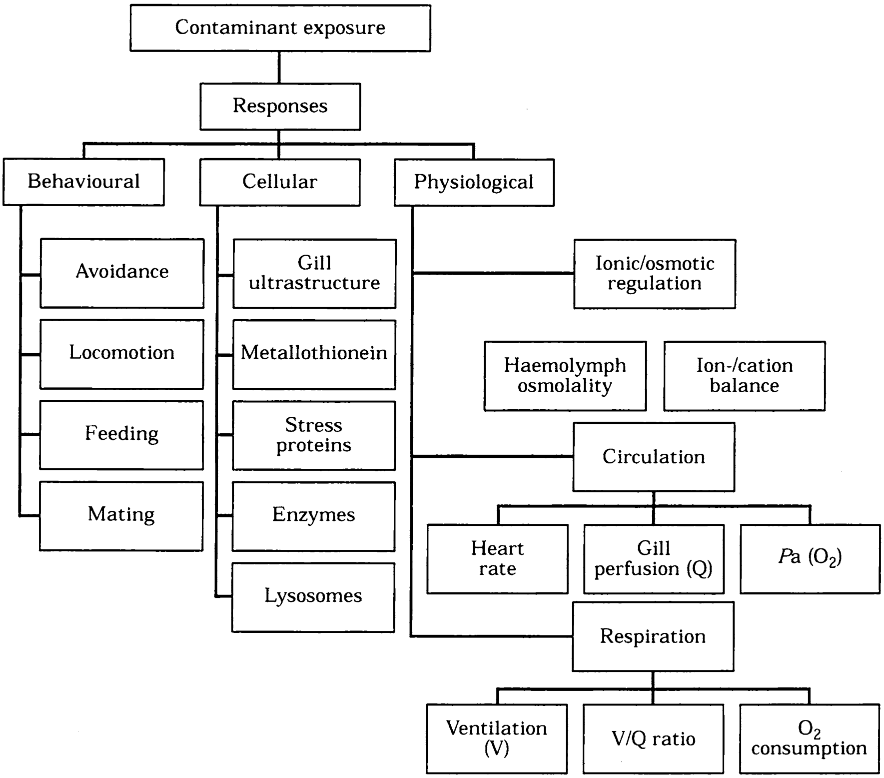


Fig. 1.8 Compensatory responses of *Carcinus maenas* following exposure to copper (Reprinted from: Hebel et al. 1997: 178, courtesy Elsevier Publishing Company)

1.2.3 Linked Responses – Metals

Comprehensive linked responses of many systems to the same stressor can be found. For example, Hebel et al. (1997) examined in a holistic way the responses of the crab *Carcinus maenas* to copper, including behavioral (locomotion, feeding, mating), physiological (osmoregulation, circulation, respiration), and cellular responses (lysosomal changes, induction of metallothioneins (MT) and stress proteins, and altered enzyme activity) (Fig. 1.8). A proposed sequence of responses is as follows: when the contaminant is first detected, the crab may attempt to avoid it and leave the area. If the chemical interferes with chemoreception, other behaviors such as reduced feeding will follow. Copper enters the crab via the gills, causing changes in cardiac and ventilatory activity. Effects on osmoregulation may follow, and some days later gill structural damage will occur, further impairing osmoregulation. The crab may increase its ventilation to compensate, but oxygen uptake will probably decline nevertheless. Detoxification mechanisms will be activated such as formation of granules to excrete excess metal. At the molecular level MT synthesis and stress proteins will be increased, which may or may not allow repair of damage and restoration of normal function.

1.2.4 Field Studies

Integrated field approaches focused on ecological effects are essential complements to laboratory studies and can produce insights into effects at the population and community level. Field experiments can investigate contaminated environments, but only under very restricted conditions can scientists release known amounts of chemicals in the field to observe effects in a controlled experimental way. Attempts to bring the field closer to the lab include studies on multiple species in microcosms or mesocosms, which can be used to reveal community effects of contaminants. They allow for replication, so dose-response relationships under controlled conditions can be ascertained. They can account for differential sensitivity of different species, and biological interactions. There is much to be learned from such approaches. However, dosing of complicated mesocosms with known concentrations of specific chemicals does not really replicate the natural environment in which organisms are subjected to many different pollutants at different concentrations, and where some biota may have evolved increased resistance to some contaminants. Thus, there remains uncertainty with ecological risk assessments and with upscaling mesocosm studies to be consistent with field situations.

It is generally difficult to attribute problems seen in the field to particular contaminants since field sites generally have multiple contaminants. In some rare cases initial observations on natural populations in the field called attention to toxic effects of certain chemicals. This was the case with tributyltin (TBT) effects on oysters in Europe (see Chap. 8). Since abnormalities produced by TBT are unlike those produced by other chemicals, making the connection between effects observed (abnormal shells in oysters, imposex in snails) and the particular chemical (TBT) was easier (Alzieu et al. 1986).

At the level of the organism, life history strategies are related to the severity of effects of contaminants. Differential sensitivity can be related to physiological differences, generation time, and life cycle characteristics, which can all affect initial effects and the ability to recovery from the effects. Species that are “r-selected,” that tend to be opportunistic, short-lived, and produce large numbers of offspring, can exploit changing environments, including contaminated ones. High metabolic rates can lead to more rapid biotransformation. In contrast, “k-selected” species, which are long-lived, slow to mature, and have relatively few offspring, are suited to stable environments and less likely to be resistant to or to evolve resistance to contaminants. Long-lived species tend to be at higher trophic levels and accumulate greater body burdens of persistent contaminants over a long period of time. Their slow reproduction makes population recovery from declines very slow. Slow reproduction, combined with high bioaccumulation of contaminants makes them particularly vulnerable to reproductive effects. Maternal transfer of lipophilic contaminants (e.g., PCBs, DDT) into the yolk of developing oocytes, exposes the next generation even before they are hatched (Rowe 2008).

1.2.5 Oil

Early studies after oil spills focused on short-term monitoring and tests of acute toxicity in the laboratory. Approaches to studying sublethal effects in the laboratory include the use of the water-soluble fraction of oil or of particular PAHs. However, after the *Exxon Valdez* spill in Alaska it became clear that long-term impacts at the population level, as well as interactions among species and abiotic variables, need to be considered (Peterson et al. 2003).

Since the 1970s, it has been known that application of dispersants increases toxicity by increasing hydrocarbon exposure to water column species. Many scientists are concerned about the likelihood of severe, acute impacts on Gulf species exposed to Corexit® and oil in the water column. For vulnerable species such as seagrass, corals, plankton, shrimp, crabs, and small fish, acute effects can be lethal, particularly during the spring spawning season (Rhoton et al. 1998; Bhattacharyya et al. 2003; Chapman et al. 2007; Anderson et al. 2009; Couillard et al. 2005; Ramachandran et al. 2004; Fisher and Foss 1993). Coral larvae are extremely sensitive to the combined effects, with 0 % fertilization in the presence of dispersant and dispersed oil, compared with 98 % fertilization in the presence of oil alone (Negri and Heyward 2000; Shafir et al. 2007; Epstein et al. 2000).

1.2.6 CECs

Nanoparticles are likely to have enhanced toxicity due to their size, which facilitates movement across cellular membranes and into organelles. Inside cells, NPs can stimulate the formation of reactive oxygen species (ROS) that interfere with structural integrity of DNA, proteins, and cell membranes (Moore 2006). Studies on fish and invertebrates reveal that uptake and harmful effects are possible (Gagné et al. 2008; Griffitt et al. 2008). Fullerenes and nanotubes produced adverse effects on adult fish (Smith et al. 2007), and metal NPs caused deleterious effects in several fish species (Asharani et al. 2008) and invertebrates (Griffitt et al. 2008; Gagné et al. 2008). Most nanoparticle types present in the aquatic environment, such as titanium dioxide, have low acute toxicity, but display sublethal effects (Jovanovic and Palic 2012).

Noise pollution can cause lethal and sublethal effects. Most animals are alarmed by the sounds, which may damage internal organs especially ears, and cause a panic response. Normal communication between marine animals can be disrupted by noise. Scientists are working on the question of which frequencies and at what levels noise negatively effects marine life. The death of animals, especially cetaceans, often occurs hours after exposure to extreme underwater noise. For example, whales die after beaching themselves shortly after a tactical sonar exercise; this is a rather common occurrence. Such beachings have been reported in Greece, Madeira, Hawaii, Spain and the coastal US- areas where sonar exercises are common. In March 2000, at least 17 whales stranded themselves in the Bahamas, and a federal investigation identified testing of a U.S. Navy active sonar system as the cause. Other taxa are also sensitive. Giant squid were found dead along the shores of Spain in 2001 and 2003 following the use of air guns by offshore vessels; examinations indicated that the deaths were related to excessive sound exposure. André et al. (2011) examined the effects of low frequency sound exposure – similar to what the giant squid would have experienced – in four cephalopod species, and found that all of the exposed squid, octopus and cuttlefish exhibited massive acoustic trauma in the form of severe lesions in their auditory structures.

1.2.7 Nutrients

The two major symptoms of eutrophication are hypoxia and harmful algal blooms, both of which can destroy aquatic life in affected areas. Hypoxia occurs after algae die, sink to the bottom, and are decomposed by bacteria, using up the available dissolved oxygen. Salinity and temperature differences between surface and deep waters lead to stratification, limiting the ability to replenish oxygen from surface waters and creating conditions that lead to formation of a hypoxic or “dead” zone. Hypoxia is a chronic stress for organisms in or near the bottom, and there have been numerous studies of this stress alone and combined with effects of chemical contaminants. Hypoxia occurs when the dissolved oxygen (DO) falls below ≤ 2 ml of O_2/l, which may cause benthic species to abandon burrows for the sediment-water interface, eventually dying when DO falls below 0.5 ml/l. Dead zones in the coastal oceans have increased greatly since the 1960s, including continental seas, such as the Baltic Sea, Kattegat, Black Sea, and East China Sea, as well as the Gulf of Mexico.

Pelagic species experience habitat compression when hypoxia makes deeper, cooler water unavailable in the summer or overlaps with nursery habitat. Blue marlin, other billfish and tropical tuna are rapid swimmers that need high dissolved oxygen, and the expansion of dead zones shrinks the useable habitat for these valuable pelagic fishes. Ecosystems exposed to long periods of hypoxia have low secondary production and little or no benthic fauna. Factors determining the degree of degradation are the duration of exposure and DO concentration. It may take years to recover from severe hypoxia and the species that establish during recovery will likely not be the same as the pattern of species loss during DO depletion (Diaz and Rosenberg 2008). Hypoxia can interact with chemical contaminants to increase stress. Particularly sensitive ecosystems include submerged aquatic vegetation (e.g., eel grass), which dies as excessive algal growth reduces light penetration. Coral reefs are another particularly sensitive ecosystem, where excess nutrients alter the normal balance between corals and algae. Eutrophication and herbivore overfishing promote seaweed overgrowth and reef degradation. Harmful algal blooms (HAB) of species that produce toxins, can cause fish kills, human illness through shellfish poisoning, and death of marine mammals and birds.

1.2.8 Climate Change

The warming of the ocean will have numerous effects on all organisms, most basically elevating their metabolic rates, which ultimately determine life history traits, population growth, and ecosystem processes. Elevated metabolic rates create increased demand for oxygen at the same time that the warmer water can hold less oxygen. Variation in temperature can also affect biological processes such as the abundance and distribution of plankton. As the ocean surface warms, it becomes more stratified or confined to layers that mix less than they did in the past, which will reduce overall ocean productivity, because nutrients in surface water get depleted and plankton productivity depends on upwelling of deeper water to replenish nutrients. The annual primary production of the world has decreased since the 1980s (Hoegh-Guldberg and Bruno 2010). Studies suggest that increasing acidity reduces the availability of iron, an element crucial to phytoplankton production. Because iron already is limited in marine waters, increased acidity may have serious implications (Shi et al. 2010).

Among the most sensitive groups of organisms are organisms such as sea grasses, mangroves, salt marsh grasses, oysters, and corals, which form the habitat for thousands of other species. Intertidal mangroves and salt marshes are threatened by rising sea levels, and will have to migrate inland or elevate in order to prevent themselves from being submerged. Current and future CO_2 levels will result in changes in ocean temperature and chemistry beyond those that corals have experienced. Some scientists suggest that conditions have already reached a “tipping point” for coral survival, and corals now are less able to recover from additional change (Eakin et al. 2009; Anthony et al. 2008). They are considered one of the most sensitive ecosystems to climate change and can be likened to the canary in the coal mine. Coral reefs have been in existence for over 500 million years, but their continued persistence is in doubt. With increases in ocean temperature, corals begin to bleach (Fig. 1.9). Bleaching occurs when the corals lose their symbiotic relationship with single-celled photosynthetic algae, zooxanthellae, which provide corals with food and receive protection and nutrients needed for photosynthesis. Zooxanthellae are sensitive to temperature changes, and when they die or leave, bleached corals are generally unable to meet their energy requirements. Coral death by bleaching and diseases due to increased heat and irradiation, as well as the decline in calcification caused by ocean acidification are the most important large-

Fig. 1.9 Normal and bleached areas of coral (From NOAA)

scale threats. Since the 1980s, major bleaching events have increasingly occurred across the globe – for example, in 1998, 80 % of the coral reefs in the Indian Ocean bleached, causing 20 % mortality.

Unlike rising temperature, research on ocean acidification is relatively recent. However, changing pH levels can cause dissolution of a coral's calcium carbonate skeleton and impair calcification. Increasing CO_2 may be an additional stress driving a shift from corals to seaweeds on reefs. Coral (*Acropora intermedia*) mortality in contact with a common coral-reef seaweed (*Lobophora papenfussii*) increased two- to threefold between background CO_2 (400 ppm) and a level projected for late twenty-first century (1,140 ppm). The interaction between CO_2 and seaweeds on coral mortality was attributed to a chemical competitive mechanism. Thus, coral reefs may become more susceptible to seaweed proliferation under ocean acidification (Diaz-Pulido et al. 2011).

Polar ecosystems are also vulnerable to effects of climate change. Their temperatures are increasing more rapidly than elsewhere (>5 times the global average). Researchers have documented that warming ocean currents have accelerated melting of the Arctic sea ice sheet and the decline and breakup of Antarctic ice shelves. Greenland is now losing an estimated 100 billion tons of ice annually as a result of accelerated melting. Sea levels are now projected to rise much faster than predicted by the Intergovernmental Panel on Climate Change in 2007, because of this acceleration, further threatening coastal habitats (Schofield et al. 2010). As the temperature has risen, plankton blooms, typical of the region, have decreased, and the plankton community has shifted from large species to smaller ones. The shift in phytoplankton biomass and size has affected the zooplankton. Krill, which are inefficient at grazing on small phytoplankton, are declining, while salps, which are efficient, are increasing. Krill also depend on sea ice for their reproduction. Furthermore, other species that depend on the ice, like Adelie penguins, are also decreasing, while other penguin species have increased (Schofield et al. 2010).

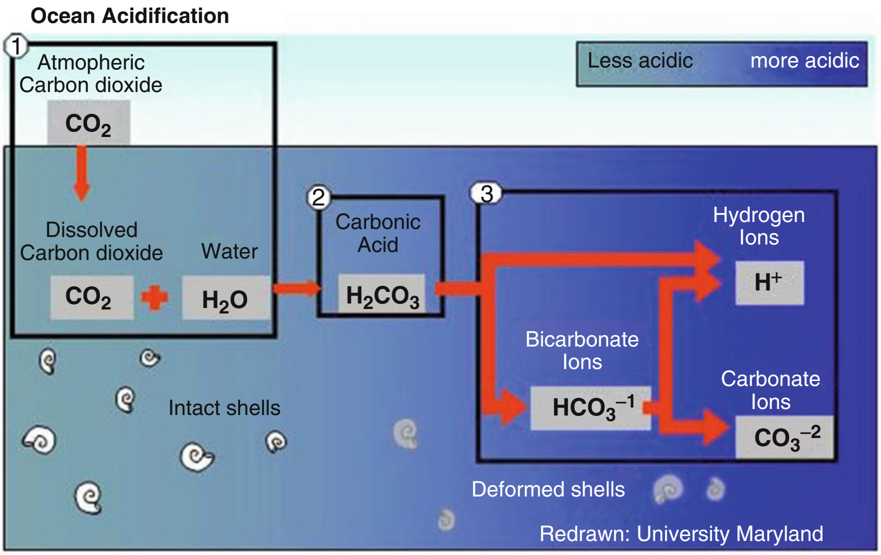


Fig. 1.10 Ocean acidification (Taken from Chesapeake Quarterly, Maryland Sea Grant College Program)

Along with physiological effects on organisms, temperature stress affects predator/prey interactions. Many intertidal organisms already live very close to their thermal tolerance limits. At cooler sites, mussels and rocky shore barnacles were able to live high on the shore, well beyond the range of their aquatic predators. However, as temperatures rose, they were forced to live at lower shore levels, placing them at the same level as predatory sea stars (Harley 2011). Daily high temperatures during the summer months have increased by almost 3.5º C in the last 60 years, causing the upper limits of the habitats to retreat 50 cm down the shore, while effects of predators, and the position of the lower limit, have remained constant.

The increased acidity of the oceans is expected to harm a wide range of ocean life – particularly those with shells (Fig. 1.10). Many organisms use calcium and carbonate ions from seawater to produce calcium carbonate for shells.

Some acidity is natural in some regions, even without added CO_2 from human activities. Water off the Pacific coast of the United States already has a low carbonate saturation state. When surface winds blow the top layer of water out from coastal regions, deeper water with high acidity (“corrosive water”) can upwell, and produce deleterious effects. The common mineral forms of calcium carbonate are aragonite and calcite. Aragonite calcifiers (corals, pteropods, bivalves) are expected to be more strongly affected than calcite calcifiers (coralline algae, sea urchins) because of differences in the solubility of the mineral: aragonite is more soluble than calcite. The resulting disruption to the ocean ecosystem could have widespread effects and further deplete already struggling fisheries worldwide. Research suggests that larval mollusks and other calcifying organisms are already experiencing these effects.

Delicate corals may face an even greater risk than shellfish because they require very high levels of carbonate to build their skeletons. Acidity slows reef-building, which could lower the resiliency of corals and lead to their erosion. Coral reefs are home for many other forms of ocean life, so their loss would reverberate throughout the marine environment and have profound social impacts in the tropics – especially on fishing and tourism. The loss of coral reefs would also reduce the protection that they offer coastal communities against storms surges and hurricanes, which might become more severe with warmer air and sea surface temperatures.

1.2.9 Marine Debris/Litter

Effects of marine litter are primarily physical rather than chemical. Marine debris takes a toll on the marine environment by affecting animals through ingestion or entanglement; it is estimated that up to 100,000 marine mammals, including endangered species, are killed each year by marine debris. Many marine animals consume flotsam by mistake, as it often looks similar to their natural prey. Sea turtles, for example, may mistake plastic bags or balloons for jellyfish. Marine debris is ingested by marine animals, including fishes, birds, sea turtles and marine mammals. Avery-Gomm et al. (2012) quantified the stomach contents of 67 Northern fulmars (*Fulmarus glacialis*) from beaches in the eastern North Pacific in 2009–2010 and found that 92.5 % of the birds had ingested an average of 36.8 pieces, or 0.385 g of plastic. Plastic ingestion in these fulmars is among the highest recorded globally. Compared to earlier studies in the North Pacific, these findings indicate an increase in plastic ingestion over the past 40 or so years. Plastic debris may become lodged in digestive tracts, blocking the passage of food and causing death through starvation. Tiny floating particles also resemble zooplankton, which can lead filter feeders to consume them and cause them to enter the food chain. In addition, hydrophobic pollutants collect on the surface of plastic debris, thus making plastic a source of toxicity, by transferring chemicals such as PCBs into the food web. Worldwide efforts are underway to monitor and remove marine debris, as well as to prevent further pollution by controlling litter or trash at its source. One unexpected finding was that the litter provided a habitat for the marine insect *Halobates sericeus*. These sea skaters, relatives of pond water skaters, inhabit water surfaces and lay eggs on flotsam (floating objects). Goldstein et al. (2012) found that they have exploited the plastic garbage as new surfaces for their eggs, leading to a rise in egg densities in the North Pacific Subtropical Gyre.

1.2.10 Survival in Contaminated Environments

The combined effects of many anthropogenic stressors pose major challenges to organisms in estuaries, and reduces biological diversity in contaminated environments.

The species that remain have some degree of inherent resistance to the contaminants they are subject to, and have developed adaptive strategies to reduce pollution impacts – such as increased resistance via plasticity or via selection over many generations. Numerous studies have been done examining the processes by which organisms detoxify metals (e.g., metallothioneins) and organic contaminants (CYP, or cytochrome P-450 system). The CYP system is important in metabolizing organic contaminants such as PAHs (Stegeman and Lech 1991). Other resistance mechanisms include reducing uptake of contaminants by being less permeable, and mucus production – excess mucus is shed from an organism, taking with it whatever was irritating the organism. Changing the energy budget is another common strategy – since they must spend more energy on detoxification, animals generally reduce their respiration and activity rates to maintain their energy balance.

While some organisms are able to develop tolerance to pollutants in their environment, this comes at a cost. A reduction of marine pollution in estuaries and oceans should be a long-term goal of policy-makers in order to protect the health of the oceans, their inhabitants, and humans.

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