Chapter 20
Pollution with Hazardous Substances

Katja Broeg and Norbert Theobald

Abstract This chapter provides a short overview on the historical background of marine environmental pollution by hazardous substances and the measures implemented to minimize its amount and impact. In order to better understand the problems involved with contaminants in the marine environment, the basic common principles, e.g. their physico-chemical properties, persistency, behavior, and environmental impacts are described. Sources and fate of chemicals as well as their way into the environment also belong to the factors which are needed to know in order to assess the environmental risks of contaminants and protect the environment from its exposure and effects.

Examples are given for selected contaminants synthetized and used during different periods, starting in the mid of 1900 until the first decade of 2000, representing different classes of compounds: organochlorines (PCBs), organometals (TBT), and pharmaceuticals. For those examples, also information about the current status in areas of the Northeast Atlantic or the Baltic Sea is provided together with references and sources for further reading. The chapter ends with a summary on challenges and future perspectives.

Keywords Environmental pollution • Contaminants • Marine environment • Properties of chemicals • Sources • Fate • Biological effects • Monitoring and assessment • TBT • PCB • Pharmaceuticals

20.1 Introduction

Our seas and oceans constitute a final sink for many chemical compounds used and intentionally or unintentionally released into the environment. During the early phase of chemical industrialization with a limited knowledge on the effects and toxicity of

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the produced chemicals, the common opinion had been that the high amount of water would dilute any of these substances to a level where no toxic effects can be expected: "the solution to pollution is dilution" was a common concept.

These expectations turned out to be wrong. In the early 1960s, causal links between the production and use of organochlorine pesticides, dead birds and failed reproduction were established by Rachel Carson ("The silent spring" 1962).The response was political and legislative regulation of the responsible substances, starting with DDT and PCBs, and a rising awareness concerning the potential environmental risks of chemical substances in general. HELCOM and OSPAR, regional marine conventions for the protection of the seas from chemical pollution and other man-made threats were founded.

Even though regulation of these substances led to their significant reduction over time (e.g. Bignert and Helander 2015) these responses didn't provide enough sustainable protection and precaution. Historic and present cases show that the story continues: substances like Tributyltin (TBT), per- and polyflourinated compounds (PFAS, e.g. PFOS), and brominated flame retardants (BFR), just to name a few, entered the environment decade after decade and displayed their toxic potential to marine animals and people as the end-user of fish and shellfish (HELCOM 2010). Response time between the use and release of hazardous substances, and their final regulation and ban is still long since response doesn't start until considerable harm has occurred and scientifically proved. Still, it has not to be demonstrated in all cases that a newly synthetized compound doesn't pose an environmental risk before it is put on the market. In fact, banned chemical compounds are often replaced by others with unknown behavior and toxicity as seen in case of PFOS and BFRs (Blum et al. 2015; EFSA 2012).

Hazardous substances have seldom been developed, produced and released into the environment in order to harm the environment on purpose. In fact, these compounds have been developed to obtain a positive effect to people, e.g. to gain energy, enhance crop production, ease technical processes, make life easier or more agreeable or to heal human or animal diseases. However, often it turned out that because of the huge amounts produced and/or because of their great persistency or toxicity, some compounds show negative effects in the environment which had not been considered before. Chemical industry constitutes a main "problem solver" in modern society. Wherever a problem arises, new industrial chemicals and pesticides are developed in order to overcome problems: repellents, smoothers, plasticizers, flame retardants, biocides, and many others. Remarkably, human and veterinary pharmaceuticals which are prescribed for health benefit are meanwhile measured in so called "effect concentrations" in the aquatic environment which means that negative health effects for fish and other marine organisms cannot be excluded (Brodin et al. 2013). Experience from the last years clearly demonstrate, that environmental behavior, persistency, and toxic effects of these substances are still not sufficiently understood before chemicals are used in products and production processes (Blum et al. 2015). Many substances from consumer products enter the aquatic environment as so-called "micropollutants" from sewage treatment plants where they are not sufficiently retained (Luo et al. 2014). It is suspected that even the implementation of the European Union Water Framework Directive (WFD) and the European regulation on Registration, Evaluation; Authorization, and Restriction of Chemicals (REACH) might fail in thoroughly safeguarding the marine environment from the impact of contaminants (for PFAS see Blum et al. 2015) (see also Gilek and Karlsson, Chap. 37). Most recently, the European Marine Strategy Framework Directive (MSFD), aimed at reaching the good environmental status (GES) of the marine environment by 2020, has been implemented. It also includes hazardous substances under its descriptor 8 with the target to reach “concentrations of contaminants that are at levels not giving rise to pollution effects”.

Beside the industrial chemicals and pesticides, heavy metals still give rise to concern in the marine environment (HELCOM 2010). Like already described above for the synthetic compounds, metals and their use have partly been regulated, e.g. mercury, cadmium, and lead. But after a phase of decrease of concentrations, some of them remain at their levels or are even increasing in recent times.

A third, likely underestimated while understudied pollutant category is anthropogenic particles. These small particles can interact with biota not only by chemical but often by physical effects. In contrast to chemicals, where quantitative environmental risk assessments follow standardized procedures, there are at present no such procedures in place to analyze environmental risks of particles like micro/nanoplastics and engineered nanoparticles (Klaine et al. 2012).

Since the above mentioned compounds are all not appearing as single pollutants in the environment but constitute various complex mixtures, there is growing scientific concern that their impact in general is underestimated as their interaction might potentiate their toxicity (see Sect. 20.3) (Altenburger et al. 2015).

Impact of hazardous substances on the marine and coastal environment shows strong regional differences. The highest impact is measured or estimated in coastal areas, close to cities, harbors, marinas, estuaries, followed by shipping lanes and hot-spot areas like offshore oil and gas platforms, and dumping grounds of warfare agents and industrial chemicals (HELCOM 2010). This chapter will provide you with information on sources, behavior, fate, and effects of examples of different types of chemical compounds. We end it with a prospective outlook to challenges and problems which still have to be addressed and solved if we aim to reach a sustainable, environmentally friendly, and healthy use of chemical substances in the future, and thereby protect the marine environment.

20.2 Sources and Common Principles of Marine Pollution

20.2.1 Sources

Because of the wide uses of the man-made (or man-used) substances and applications, their potential sources are widespread and variable. The knowledge about the sources of pollutants is essential for possible regulation and reduction measures.

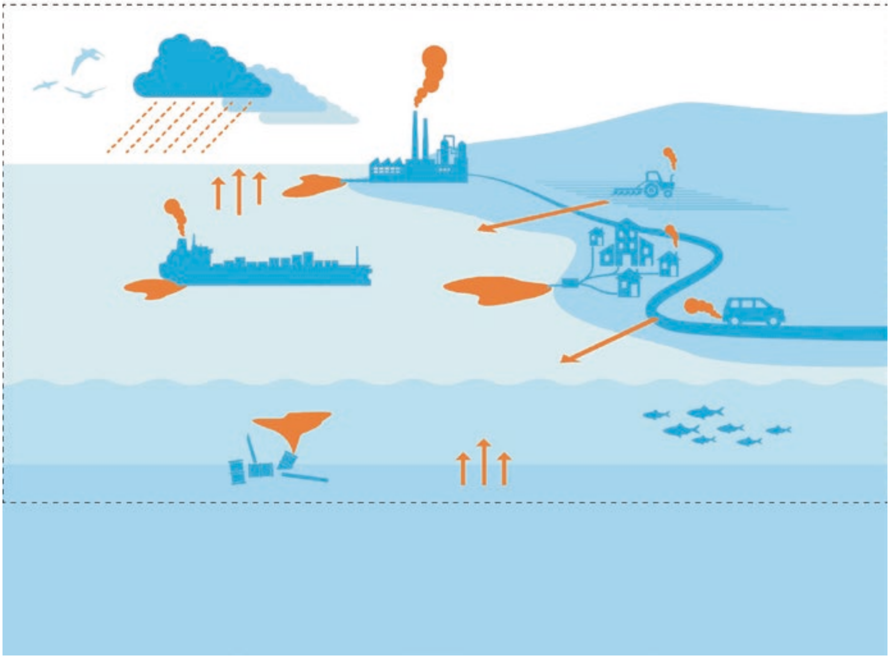


Fig. 20.1 Overview of sources of marine pollution by chemicals (source: Baltic Eye, Stockholm University)

Roughly, sources can be divided by geographic aspects into sea- and land-based sources as shown in Fig. 20.1.

The main chemical inputs from sea-based sources are coming from shipping (e.g. emissions by operation: exhaust fumes, tank washing, leaching from antifouling paints), offshore industry (oil-, gas-, ore-, sand exploration and exploitation), legacies like dumped munitions and industry waste, as well as dredging of contaminated sediments. Remarkably, even environmentally friendly techniques like offshore wind energy have to be considered for possible inputs of hazardous substances such as biocides, lubricating oils, anticorrosion paints, or sacrificial anodes.

Hazardous substances inputs from land-based sources are even more diverse and multifaceted:

Riverine inputs, inputs from point sources like industries (Schmid, Chap. 15), households, sewage treatment plants, and runoff from agriculture and traffic infrastructure, constitute the main land-based sources. Examples for substance groups released from the different sources are given in Table 20.1.

Another significant source is air-borne, via local traffic and combustion, or via atmospheric transport (see physical-chemical properties).

Table 20.1 Examples for pollutant groups from different sources

Shipping	Offshore industry	Aquaculture	Dumping	Household	Agriculture	Industry	Traffic
Antifouling	Process chemicals	Fertilizers	Industrial chemicals	Pharmaceuticals and personal care products	Fertilizers	Industrial chemicals	Waste (plastics)
Combustion gases and washwater	Combustion gases	Nutrients	Munition	Plasticizers	Pesticides	Wastewater	Combustion gases
Waste	Sacrificial anodes	Pharmaceuticals		Flame retardants	Pharmaceuticals	Combustion gases	Oil
Oil	Oil	Antifouling		Combustion gases			

20.2.2 Common Principles of Marine Pollution

Modern life in our highly industrialized and globalized world puts significant effects on the environment by removing natural resources, by changing the distribution of natural compounds, and by introducing new, man-made substances. The effects of these activities are complex and depend on a great number of both, quantitative and qualitative parameters. Qualitative, substance specific aspects which influence the behavior and impact of chemicals in the environment are e.g. their chemical stability, physical-chemical properties and their effects towards organisms (Sect. 20.3.2). Quantitative aspects are roughly dependent on the use or production amounts of the substances, their emission rates, and the proportion which enters the environment. For the evaluation of the ecological effects, the combination of both aspects have to be considered, as both influence the behavior and fate in the environment.

Chemical stability is dependent on the molecular structure of a specific compound. If the stability under environmental conditions (e.g. temperature less than 50 °C, UV-radiation by sunlight, presence of oxygen and water, pH range of 2–10) is high, there is a great potential that these compounds have a long life time and are persistent in the environment. Often the stability of compounds is characterized by their environmental half-life. Chemical reactivity can be fairly well estimated and predicted from the molecular structure of a chemical compound. A special form of degradation is the transformation of substances by biological organisms. This **biodegradation** is structure dependent as well. Often but not always the affinity to chemical and biological degradability are similar. Figure 20.2 presents a very general overview on the influence of the structure of organic substances on their chemical behavior: At the right side, the most simple substances containing only carbon and hydrogen atoms (hydrocarbons) are chemically fairly stable compounds and thus quite persistent in the environment. However, they can be biodegraded by specialized bacteria. Examples for these hydrocarbons are the major constituents of

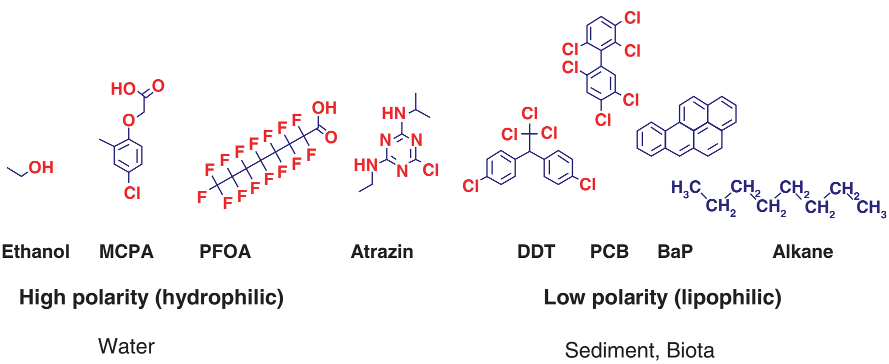


Fig. 20.2 Examples of chemicals of environmental concern demonstrating the wide range of chemical structures and their chemical and physical-chemical properties. The compounds are ordered by their polarity (*right side*: non polar, left side polar compounds). The chemical reactivity (degradation potential) increases from right to left

mineral oil. Even more stable are hydrocarbons with a ring structure like polycyclic aromatic hydrocarbons (PAHs) which are an important pollutant-class found ubiquitously in the environment. Replacing all hydrocarbons by halogen atoms (fluorine, chlorine, or bromine), leads to molecules with increased stability as well, because the C-halogen bonds are very strong and need high energy for degradation. Chlorinated hydrocarbons (CHC) like polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs, used as flame retardants) and polyfluorinated chemicals (PFAS, used as surface protection agents) are examples for pollutants being presently of environmental concern. Replacing hydrogen atoms by other functional groups like $-OH$, $-COOH$, $-SO_3H$, $-NH_2$, $-NO_2$ generally leads to substances which are more reactive and often more easily transformed and degraded. Many of the new chemicals of emerging concern (CECs) belong to these compounds (left part of Fig. 20.2). Metals cannot be degraded and are thus in principle persistent, however they can be transformed by speciation into different oxidation states, can be changed by complexation, or eliminated by sedimentation of insoluble forms. By this, their bioavailability and toxicity can be changed and thus, their environmental impact.

Physical-chemical properties determine the behavior of a substance in the environment. The most important parameters are the volatility and polarity of a substance.

The volatility determines how easy a compound can be eliminated from the liquid phase (rivers, oceans) or from the solid phase (soil). Being in the atmosphere, pollutants can be transported much faster and thus be distributed away from their primary sources and spread regionally and even globally (atmospheric transport). By this, even semi-volatile compounds like PCBs and PAHs (with boiling points above 300 °C) have been globally distributed and already found in the Arctic food chain in 1975 (Bowes and Jonkel 1975). In part, these pollutants are not transported in the gaseous state but attached to aerosols.

Polarity strongly influences the distribution of a substance in the water phase: Polar compounds (high polarity) show good water solubility (hydrophilic) and do not show a tendency to adsorb on solid particles. Thus, they can be easily transported over large distances by river or ocean currents. On the other side, non-polar compounds are only sparely soluble in water (hydrophobic or lipophilic) and show a high affinity to solid surfaces like suspended matter in the water, or sediments. By this affinity to solid particles, they are easily sedimented and thus, less mobile in the water phase. Concentration gradients often are much steeper than for water soluble compounds and riverine loads are reduced by more than 90% within the estuary by sedimentation. Lipophilic substances are also adsorbed to biological surfaces, taken-up by organisms, and can be accumulating in biologicals tissues. Thus, non-polar substances and their lipophilic property can lead to bioaccumulation (accumulation of a substance in various tissues of an organism) and, if they are stable, even biomagnification (process by which the concentration of a substance increases in each successive link in the food chain).

A frequently used parameter for quantifying the polarity of a substance is its partition coefficient between octanol (a lipophilic liquid) and water, expressed as a logarithmic value: log K_{OW}. Values of <4 mean relatively polar properties. These substances are found preferably in the water phase, whereas in sediments and biota, accumulation and concentrations are low. Substances with log K_{OW} values of >5 are lipophilic. They show higher concentrations in sediments and have a high potential for bioaccumulation. With very high log K_{OW} values (>7) bioaccumulation often decreases again, because these compounds are less easily transported through biomembranes (e.g. deca-PBDE) and therefore have a lower bioavailability.

Like chemical reactivity, the physical-chemical properties are dependent on the molecular structure of a specific compound. At present, volatility and polarity can be fairly well estimated and predicted from the molecular structure. In Fig. 20.2, the substances are arranged according to their polarity: at the right side, the most lipophilic (non-polar) compounds are found and at the left side the most polar (hydrophilic) ones.

Models and programmes checking the structural similarity of substances regarding their biological activity and mode of action are applied in order to predict the potential impact of new substances, e.g. QSAR (Quantitative structure–activity relationship).

20.3 Environmental Impact

20.3.1 Environmental Risk Assessment

One important parameter for estimating the potential impact of hazardous substances and conduct an environmental risk assessment is the amount that enters the environment, the so-called "predicted exposure concentration" (PEC). Because a direct measurement of concentration is not feasible in most cases, this value is often predicted on the basis of models. One example is the MAMPEC model for the prediction of the release of TBT from antifouling paints. The exposure determines the relevant concentrations in the different matrices which are then set into relation to ecotoxicological criteria and results from ecotoxicological laboratory studies and bioassays which determine the "predicted no effect concentration" (PNEC).

Anthropogenic substances can differ very much in their life cycles and these determine to which extend, how fast and under which conditions they enter the environment. The following examples demonstrate the wide range of possible scenarios:

Mineral oil, consisting of higher alkanes from mineral sources, is a product which is used in the largest amounts of man used goods. Its toxicity is moderate. In principle, no oil should enter the environment, as it is completely used. However, due accidental losses (during production, transport, or use) or non-optimal processing, a certain amount of the oil used in fact enters the environment. Because of the huge amount of oil used, even a small fraction of it is a large amount and can become an environmental problem. Therefore, because of the huge amounts of handlings, not because of its high intrinsic toxicity, oil has become a material of environmental concern.

Polychlorinated dibenzodioxines (PCDDs) can be considered as an example for the other extreme: These compounds exhibit an extremely high toxicity but have never been produced on purpose and have no commercial use. They are generated as by-products in certain technical processes in minute amounts. But because of their extremely high toxicity (together with their persistency and bioaccumulation potential), they are of high environmental concern. Dioxins got worldwide attention due to an industrial accident, the Seveso disaster in 1976, when it had been released into the environment. Within days more than 3300 animals, mostly poultry and rabbits, were found dead. People living in the vicinity of the plant suffered from skin inflammation and chloracne as immediate acute effects. A follow-up study in 2009 found an increase in lymphatic and hematopoietic tissue neoplasms and increased breast cancer rates (Pesatori et al. 2009).

Pesticides may act as an example for medium production amounts and definite toxic effects. These substances are deliberately emitted into the environment on local scales to prevent pests by plants and vermin in agriculture and gardening. At least when they leave their application range (e.g. by run-off or overdosage) and dedicated time period, they become substances at the wrong place or concentration and thus, to contaminants or pollutants.

Various factors influence the environmental impact of a substance. The more of them are critical, the larger the environmental concern becomes. For example: Compounds with a high chemical stability (persistency), showing in their physical-chemical properties a high lipophilicity with a high bioaccumulative potential and exhibit a high toxicity are called PBT (persistent, bioaccumulative and toxic) compounds and are regarded as highly hazardous pollutants and have become subject of international regulation, e.g. Stockholm Convention (Gilek and Karlsson, Chap. 37).

Other groups of special concern are substances of very high production volume (HPV) though with less high toxicity, and compounds with high impact on sensitive physiological processes e.g. hormone regulation (endocrine disrupters) or cell division/ DNA damage (carcinogenic compounds).

20.3.2 Biological Effects

The term "biological effects of contaminants" means the impact of substances, and their mixtures on physiology, fitness, reproduction, and health of marine organisms. Under environmental conditions, chemical substances always occur in combination, as mixtures, whereas risk assessments, chemical regulation, and chemical analysis are mainly performed at single substance level.

Thus, in order to obtain more comprehensive information about the actual status concerning the realistic impact of the respective pollution situation on marine organisms, the so-called biomarkers were developed. These tests are conducted on sentinels/indicator organisms like specific mussel and fish species, caught at study field sites in coastal and open sea areas. This is often done in parallel to the analysis of chemical burden in the same organisms, sediment and/or water within the framework of marine monitoring programmes for example of the regional conventions for the protection of the seas (e.g. Helsinki Commission: HELCOM (Baltic Sea), Oslo-Paris convention: OSPAR (North-East Atlantic); Barcelona Convention (Mediterranean Sea)). In fact, the combination of chemical and biological monitoring is a major step towards an early detection of potential risks posed by various pollution types, e.g. point-sources, chronic pollution situation, and pollution events (Viarengo et al. 2007; Wernersson et al. 2015; HELCOM 2010).

Various biomarkers are currently standardized and partly taken up into common regional monitoring programmes:

Biomarkers for general acute or chronic toxic effects (general toxicity): These biomarkers integrate effects of different contaminants by responding to various contaminant classes. They can be applied at different levels of biological organization. Examples are e.g. (1) at the cellular level such as lysosomal membrane stability; (2) at the individual level: fitness, growth, health; (3) at the population level: reproductive disorders.

In addition, there are biomarkers available for testing the level of e.g. mutagenicity, carcinogenicity, immunotoxicity, and endocrine disruption.

Some compounds cause very specific biological effects in sentinel organisms. These can be used to identify the presence and even concentration of a specific compound (e.g. imposex caused by TBT, see Fig. 20.4b). More detailed information concerning biomarkers, biotests, and bioassays and their potential use in environmental monitoring is summarized by Wernersson et al. (2015).

20.4 Examples for the Current Status of Contaminants

The status of marine environmental pollution by chemical substances is subject to numerous environmental monitoring programmes world-wide. Examples are the HELCOM Cooperative Monitoring in the Baltic Marine Environment (COMBINE), the OSPAR Coordinated Environmental Monitoring Programme (CEMP), and the US National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Program (NS&T). In most cases, assessments of the environmental status are conducted within 6-years periods (e.g. HELCOM Holistic Assessment (HOLAS 2010, 2017), OSPAR Quality Status Report). Major objectives concerning hazardous substances are to describe and evaluate the spatial distribution of contaminants and to investigate temporal changes of the burdens. Here we provide some examples from the North-East Atlantic and Baltic Sea for substances which are of environmental concern due to their demonstrated potential to have substantial impact on marine organisms.

The temporal courses of environmental concentrations differ between the various chemicals and are dependent on their start of production, amount, use, and spread in the environment. Figure 20.3 shows an example of a sediment core which had been analyzed for the concentration of selected environmental pollutants. It can

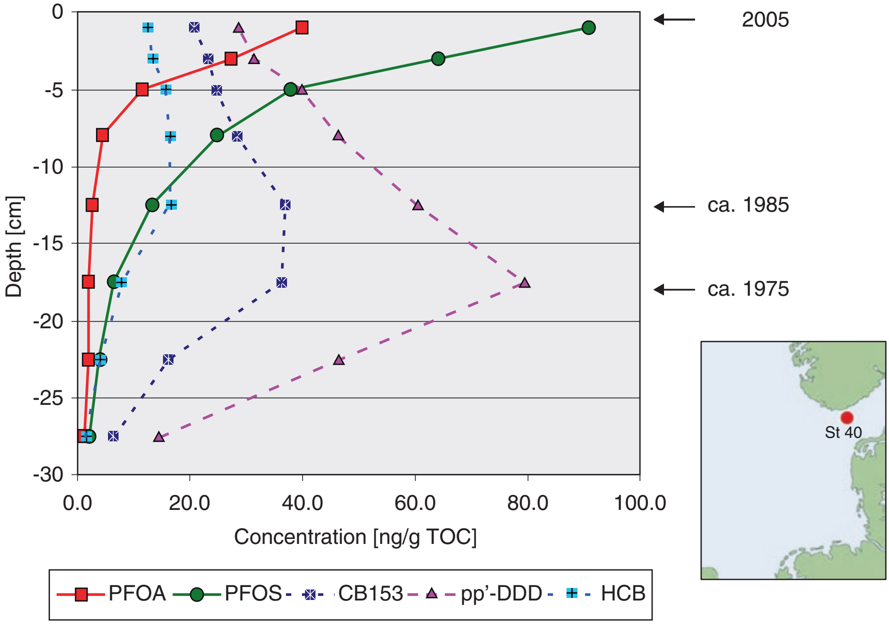


Fig. 20.3 Sediment concentrations (ng/g TOC) of selected contaminants in a sediment core from the Skagerrak (57°48N, 8°00E, Aug. 2005, water depth 700 m)

be seen from the graph, in which time periods the concentrations started to increase for new, emerging compounds like PFOA and PFOS. In case of the regulated contaminants DDD, PCB153, and HCB, concentrations decreased after regulation.

In the following section, developments for three important contaminant classes and groups: TBT, PCBs, and pharmaceuticals, are presented in more detail.

20.4.1 Tributyltin (TBT)

Organotin compounds have been used as efficient and cost-effective antifouling component from the 1960s on, starting in the USA. Antifouling means protecting ship hulls and underwater constructions from biofouling, the unwanted attachment and coverage with marine organisms. The most effective organotin compound proved to be based on tributyltin (TBT).

Relatively soon after the start of using TBT in antifouling paints and thus, deliberately releasing it to the marine environment by contact leaching, first indications of its negative environmental impacts emerged. In response, Canada recommended that TBT should not be used near shellfish farms already in the late 1960s.

From the 1970s on, indications for links between TBT and adverse effects on non-target organisms increased. Larval disorders and imposex (superimposition of male features in females), a condition where female snails developed penises and became sterile, were reported.

By the time that TBT antifouling paints were readily available in the US, Canada, and EU, it was apparent that there were associated problems. Despite this, the efficiency of TBT antifoulings and their wide applicability resulted in prevalent use worldwide.

Even though more and more studies continued to show that even at extremely low organotin concentrations, impact on non-target species occur, restrictions and regulation were not put in place until it was confirmed that commercial shellfish stocks were being affected. The commercial oyster (*Crassostrea gigas*) industry in Arcachon Bay, France, declined at the same time as growers of *C. gigas* along the east coast of England reported abnormal shell forms in the late 1980s. After several national and regional regulations, the IMO adopted the AFS Convention in 2001, which entered into force in 2008. No application of TBT should be performed on ships.

TBT is one example for a substance with extreme endocrine-disrupting potential and has been one starting point for the broad discussion on the use and regulation of endocrine disruptors.

Even though concentrations of TBT declined considerably following to regulation, there are still effect-concentrations measured in harbors in marinas due to release from old paint layers, sediments are still contaminated (HELCOM 2010). Figure 20.4a gives an example for the development of TBT concentrations and

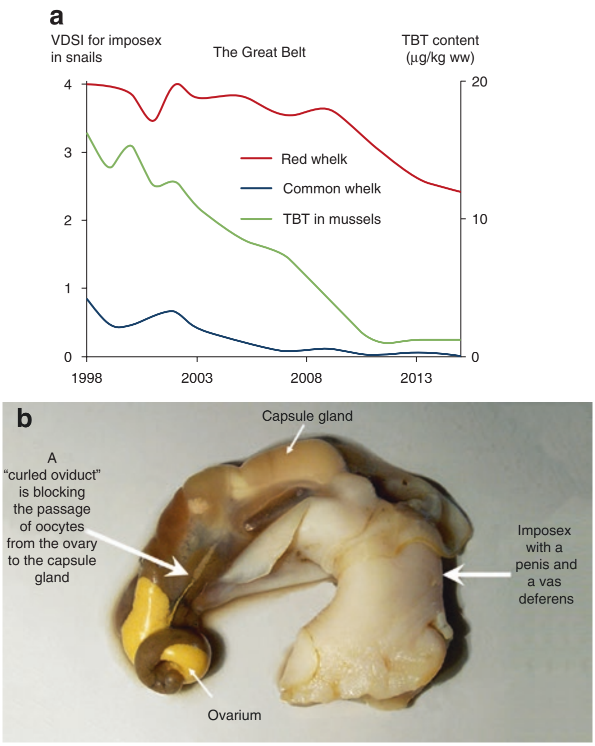


Fig. 20.4 (**a**) Development of imposex levels (expressed as Vas Deference Sequence Index, VDSI with maximum level of 4) in the marine snails red whelk (*Neptunea antiqua*) and common whelk (*Buccinum undatum*) compared to TBT levels measured in blue mussels in the Danish Great belt. Data comes from National monitoring data in the NOVA program in Denmark (provided by Jakob Strand, Aarhus University, Denmark). (**b**) Severe TBT effects lead to imposex and can cause sterile females in snails due to blockage of the oviduct. About 10% of red whelk females in the Great Belt had developed a "curled oviduct" in 2005 (Jakob Strand, Aarhus University, Denmark)

imposex conditions for stations in the Danish Belt Sea. Instead of measuring the TBT concentration, imposex can also be measured as indicator for exposure to TBT (see Sect. 20.3.2). Figure 20.4b shows an example for the highest level of imposex (Vas Deference Sequence Index VDSI 4) in a Red Welk.

20.4.2 Polychlorinated Biphenyls (PCBs)

PCBs are a substance group constituted by 209 possible congeners which are differing by the quantity and the position of chlorine atoms in the biphenyl structure.

PCBs were first synthetized in 1881. They entered the US market in 1929. Due to their very stable, chemically inert characteristics, they show low inflammability, resist heat and degradation, and are electrical insulting. These properties formed the basis for their widespread application as e.g. insulating fluids in transformers, hydraulic fluids, heat transfer fluids, but also as additives in pesticides, paints, inks, copy paper, plastics, and many more.

In the environment, PCBs were first discovered in the late 1960s. After increasing awareness of their hazardous effects on environment and people, a ban of the commercial production of PCBs was implemented in North America in 1977.

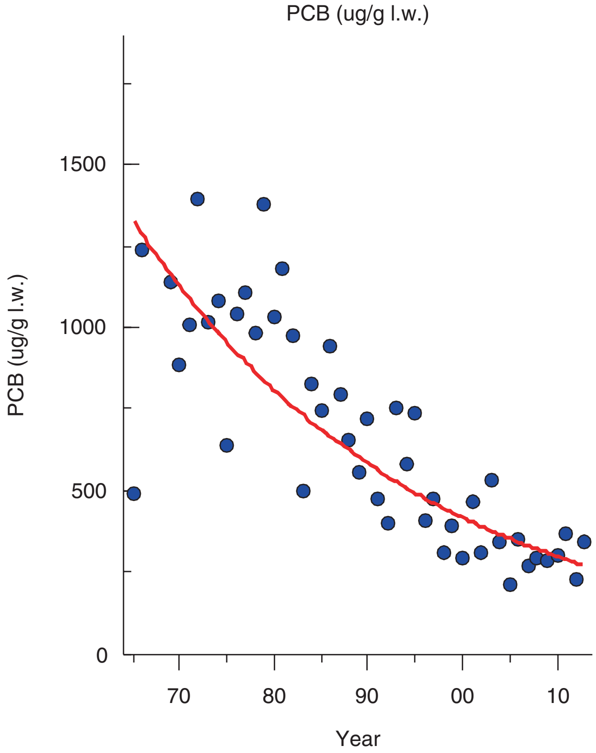
As two-third of the total amount of produced PCB (1.8 million tons estimated) is used in completely enclosed systems. It is estimated that only 30% of it has been released so far. The remaining part is most probably still in use until the serviceable lives of the machines and facilities end.

Environmental effects caused by PCBs are numerous. In marine mammals, population effects, immunosuppression, developmental disorders and abnormalities, carcinogenicity, endocrine disruption, skin disorders, tumors and lipid degeneration are reported in the scientific literature (Dedrick et al. 2012).

PCBs fall under the term "POPs", persistent organic pollutants, a group of synthetic organic chemicals that share similar properties, are highly toxic, and are able to directly and indirectly affect the health of animals and humans. Once they are released to the environment, they will stay there for an unpredictable time period and display their toxic potential. Even though, the "dirty dozen" POPs are regulated by the Stockholm Convention (see Gilek and Karlsson, Chap. 37), PCBs are still measured in the marine environment. Due to their persistency, marine sediments are still acting as a "reservoir", releasing PCBs, and making them available for organisms. Re-suspending occurs e.g. due to dredging activities and riverbed deepening (Sturve et al. 2005; Broeg et al. 2002), but also due to high prevalence of burrowing invertebrates. Increased re-suspending of PCBs caused by bioturbation of the non-indigenous species *Marenzelleria* and the prevalent amphipod *Monoporeia* has been shown in experiments (Hedman et al. 2009; Granberg et al. 2008).

The lipophilic PCBs biomagnify in the food web and are therefore still found in fatty fish and top predators (Fig. 20.5) but the concentrations decreased significantly during the last decades, accompanied by a significant improvement of the reproduc-

Fig. 20.5 Temporal changes in concentrations of PCB in eggs of the white-tailed sea eagles of the Swedish Baltic Sea coast, 1965–2013 (Bignert and Helander 2015)



tive success of the white-tailed sea eagle for example (Bignert and Helander 2015). Accordingly, water concentration is not a primary indicator for the levels of PCBs in the marine environments—highest concentrations are found in sediments and organisms. Due to the fact that PCBs are semi-volatile compounds, they have reached all areas in the world, even the most remote ones. Especially the Polar Regions are at risk as atmospheric transport of PCBs often ends there by condensation of the compound (global distillation).

20.4.3 Pharmaceuticals and Personal Care Products (PPCP)

Pharmaceuticals and personal care products are compounds with a great variety of molecular structures which makes their analysis quite complex. The fact that pharmaceuticals which are essential for human and farm animal welfare might pose a risk for the marine environment has been addressed only recently. Pharmaceuticals reach the environment by effluents from households and hospitals, run-off from fields as well as from wastewater treatment plans which in most cases are not able to successfully retain them (Köster, Chap. 16).

One of the most persistent pharmaceuticals known in the aquatic environment is carbamazepine, an antiepileptic drug. Its extreme persistency results in ever increasing concentrations in the coastal and marine environment. Figure 20.6 shows the concentration of selected pharmaceuticals in the German Bight in 2007. Remarkably, the observed concentrations are often well above those of "classical" contaminants such as HCH, DDT, PCB or PAK. Moreover they are in a concentration range observed for e.g. herbicides.

There are numerous scientific publications on biological effects of pharmaceuticals which e.g. report about behavioral changes in invertebrates and fish (e.g. Brodin et al. 2013; Guler and Ford 2010). Small crustaceans which hide under stones to avoid being eaten by predators start swimming into the light after exposure to antidepressants (Guler and Ford 2010). Other substances found in considerable concentrations already in the environment are pain killers (diclofenac) and hormones (estradiol), just to name a few.

The discussion started whether to include some of them into the routine monitoring programmes and into the list of priority substances under the EU Water Framework Directive (WFD). A special analytical challenge arises by the great number of different classes of compounds which have to be monitored. For taking measures, there is a certain dilemma as for pharmaceuticals, regulation of use and production is—because of ethical reasons—not a primary measure to stop environmental exposure.

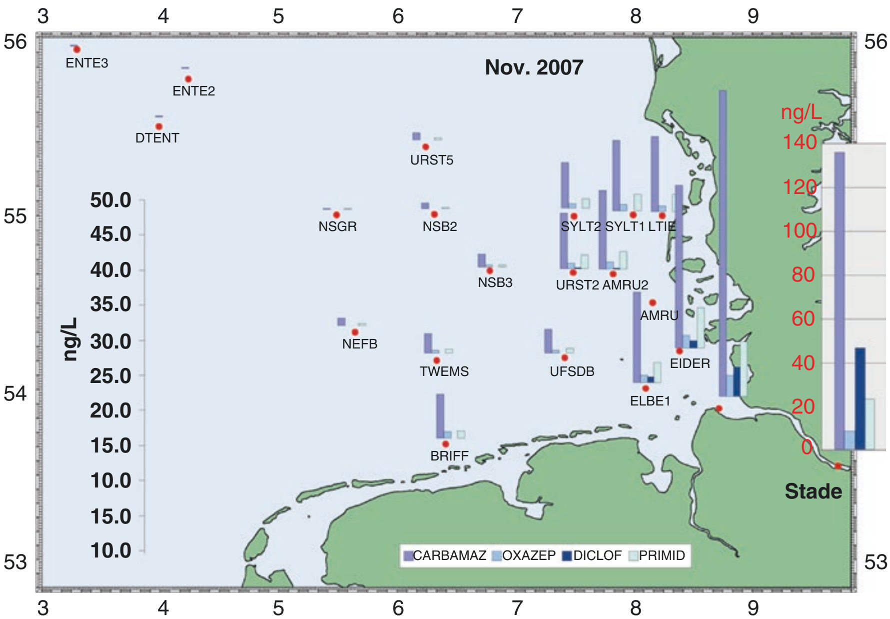


Fig. 20.6 Spatial distribution of the selected pharmaceuticals, carbamazepine, oxazepam, diclofenac, primidone (ng/L) in the surface water (5 m) of the German Bight in November 2007

20.5 Challenges and Future Perspectives

Substances with high persistency, toxicity, and the potential to bioaccumulate and biomagnify (PBT, vPvB) constitute a high environmental risk. Many substances with known PBT characteristics are subject to regulation and environmental monitoring (WFD, MSFD, REACH, Stockholm convention, national regulation, etc.; Gilek and Karlsson, Chap. 37). The problem is that properties and environmental behavior of a high number of chemicals of emerging concern (CECs) are unknown even though these substances are already in use. Another problem is posed by substances which do not necessarily have PBT properties but act hormone disruptive in low concentrations (EDCs), especially on sensitive live stages. Here it is nearly impossible to recapitulate the causative substance since concentrations are low and effects are often seen with a long time delay.

Hazardous substances and pollutants appear as cocktails in the environment. In addition, they may interact with each other and provoke mixture toxicity. Contaminants bind to particles, and particles release contaminants. Within all seas, strong regional differences are observed which have to be considered when solutions and measures for hazardous substances-related problems are elaborated. The combination of chemical and biological monitoring could be one step forward to get early information about potential pollution. As soon as toxic responses at lower organizational level (e.g. cellular responses, health, etc.) are detected in the environment, detailed chemical analyses can help to identify the causal agents, and mitigation measures can be initiated.

Nevertheless, there are also general aspects which have to be addressed:

These are e.g. the implementation of the precautionary principle and a considerable shortening of the political response time to contaminants of high environmental risk. In its report on "*Late lessons from early warnings: the precautionary principle*" the European Environment Agency (EEA 2001) presented e.g. the history of environmental hazards together with the question whether taking action early enough would have prevented harm. Lessons for better decision-making were drawn from cases where clear evidence of hazards to the environment had been ignored.

Due to the fact that the lessons from the 2001 report still remained highly pertinent, a second report has been published in 2013 (EEA 2013). The aim was to consider both kinds of examples, long-known issues with broad societal implications such as lead in petrol, mercury, environmental tobacco smoke and DDT, and issues which have emerged more recently such as the effects of the contraceptive pill on feminisation of fish and the impacts of insecticides on honeybees. The main lesson, people can learn from the reports is that the process of learning must continue to improve the protection of the marine environment from the impact of hazardous substances.

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