

# **Pesticides and Biocides**

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#### **Acronyms and Abbreviations**

2,4-D	2,4-Dichlorophenoxyacetic acid
2,4,3-1	2,4,5-11chiorophenoxyacetic acid
AChR	Acetyl cholinesterase receptor
ATPase	A group of enzymes that catalyse the hydrolysis of a phosphate bond in ATP to form adenosine di-
	phosphate (ADP)
ATP	Adenosine triphosphate
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BMF	Biomagnification factor
BSAF	Biota-sediment accumulation factor
CAT	Catalase activity
CCA	Copper, chrome and arsenic wood treatment
DDD	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethane
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene
DDT	1-Chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene
EC50	Effective concentration to cause a sublethal effect to 50% of the test population
EQY	Effective quantum yield
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FOA	Food and Agriculture Organisation of the United Nations

- GST Glutathion-S-transferase
- HCH Hexachlorocyclohexane
- IMI Imidacloprid
- IMO International maritime organisation
- Koa Octanol-water partition coefficient
- Koc Organic carbon–water partition coefficient
- Kow Octanol-water partition coefficient
- LC50 Lethal concentration to cause 50% mortality to a test population
- LPO Lipid oxidation levels
- MCPA 2-Methyl-4-chlorophenoxyacetic acid
- MoA Modes of action
- nAChR Nicotinic acetylcholine receptor
- OC Organochlorine
- OP Organophosphate
- OTCs Organotin compounds
- PBT Persistent, bioaccumulative, toxic chemical
- POPs Persistent organic pollutants
- PSII Photosystem II inhibiting
- QB Plastoquinone B protein binding site on the D1 protein in Photosystem II
- REACH Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (a European Union regulation)
- ROS Reactive oxygen species
- TBT Tributyltin
- TSCA Toxic Substances Control Act
- vBvP Very bioacculumative very persistent chemical
- USA United States of America
- US EPA United States Environmental Protection Agency

# 7.1 Introduction

**Pesticides** are chemicals that have been specifically synthesised to "*kill pests, including insects, rodents, fungi and unwanted plants*" (WHO 2020). They are generally used with the aim of protecting plants or plant products and this is why they are referred to in European Union legis-

lation as Plant Protection Products. **Biocides** are chemicals that are also designed to have the same properties as pesticides but they are not used to protect plants or plant products. Examples of biocides include: wood preservatives, repellents, antifouling paint for boats and chemicals used to prevent biofouling on underwater structures such as discharge pipes. While pesticides and biocides are technically different types of chemicals they will be discussed collectively in this chapter as they are both designed to kill or inhibit organisms.

Pesticides are predominantly **organic chemicals**, the vast majority of which are synthetic. They are produced by chemists in large-scale industrial plants and almost always have a carbon basis derived from petroleum hydrocarbons. There are no natural background concentrations of synthetic pesticides; however, many pesticides are now found virtually in all biological and environmental samples that have been analysed. For example, organochlorine pesticides including DDT and its breakdown products DDD and DDE have been found globally in water, soil, sediment, animal tissue (e.g. Mansouri et al. 2017) and human tissue (Jaga and Dharmani 2003). These, usually low, concentrations of pesticides are termed ambient concentrations.

In this chapter, we introduce the history of pesticide use; discuss types of pesticides and those of most concern to the marine environment in terms of exposure, environmental fate, behaviour and toxicity.

## 7.2 A Brief History of Pesticide Use

We often think that pesticides are recent inventions, but humans have been using pesticides based on arsenic, copper, mercury and sulphur as well as plant derivatives for over 3000 years. For example, sulphur was burned to fumigate homes in Greece around 1000 B.C. (Baird and Cann 2012) as well as to purify temples. Matthews (2018) refers to some early methods used around 1600–1800s to manage pests on plants using vinegar, salt, cow urine, boiled herbs, and tobacco that were first reported by Lodeman in 1896.

In 1885, copper in the form of the Bordeaux mixture (a copper sulfate pentahydrate and lime mixture) became the first large-scale fungicide applied to plants. In fact, pesticides based on copper and mercury are still used in agriculture today. Bordeaux mixture and copper hydroxide are two fungicide/s permitted to be applied to organic farms in many regions while mercury (as methoxy ethyl mercury chloride) is also still used in some countries as a fungicide.

Plant-derived insecticides such as pyrethrins are reported to have been used around 400 B.C. in Persia (modern day Iran) becoming popular in Europe in the early 1800s, and today there are over 2000 globally registered products containing pyrethrin (Mathews 2018).

One of the first (produced as early as 1874) and most well-known synthetically produced insecticides is DDT. Even though the compound had been synthesised earlier, its insecticidal activities were only discovered in 1939, by chemist Paul Hermann Müller, for which he was awarded the Nobel Prize for Medicine in 1948. It has been reported that DDT has saved millions of lives when used to control malaria, a dis-

**Figure 7.1** Rachel Carson, the author of *Silent Spring* (1962), the book that highlighted the toll of pesticides on the environment. She began her career with the US Fish and Wildlife Service (CC BY 2.0)

ease transmitted by mosquitoes in many tropical regions. It became a common agricultural pesticide along with other organochlorine pesticides such as dieldrin, lindane, endrin and chlordane. DDT is infamous for its ability to biomagnify (concentrations are passed from prey to predator and increase as food chains are ascended) and to cause egg-shell thinning in birds of prey as described in the 1962 *Silent Spring* by Rachel Carson (**•** Figure 7.1). Because of its dramatic adverse effects on non-target organisms, DDT was included in the Stockholm Convention that aimed to reduce and ultimately ban Persistent Organic Pollutants (POPs). However, it can still be used for disease vector control (e.g. malarial mosquitoes).

Organophosphate pesticides such as malathion and trichlorfon were developed alongside organochlorine pesticides in the 1930s and 1940 s but ultimately replaced organochlorines as they were less toxic to mammals and were less persistent. Another class of pesticides known as carbamates were introduced around 1958 (Matthews 2018).

As the chemical control of weeds was also becoming a necessity, due to the industrial revolution, the growth of the **herbicide** industry began in the 1940s. This included the development of synthetic herbicides such as MCAP, 2,4-D and 2,4,5-T (a component of agent orange the powerful defoliant used extensively in the Vietnam War), atrazine, amitrole, and diuron. Glyphosate was first registered in the USA in 1974 and is one of the most commonly used herbicides today. The first synthetic fungicide was thiram that was used as a seed treatment and its success led to the development of other fungicide such as fentin and ferbam.

Within six years of the patenting and use of DDT concerns about its impacts on non-target species were



being raised (e.g. Coburn and Treichler 1946; Mitchell 1946). Rachel Carson's book Silent Spring highlighted the detrimental environmental effects of some pesticides and created a groundswell of public awareness associated with the impacts of pesticides on the environment and to humans. Prior to 1962, the US government mainly regulated pesticides to ensure the efficacy of chemical preparations (e.g. the Insecticide Act of 1910 and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1947). In 1952, an amendment to the Food, Drug, and Cosmetic Act established an approach for setting tolerances for chemical residues in food, feed, and fibre. The Toxic Substances Control Act (TSCA) of 1976 required the United States Environmental Protection Agency (US EPA) to prevent "unreasonable risk of injury to health or the environment". Because of this, the US EPA banned or severely restricted aldrin, chlordane, DDT, dieldrin, endrin and heptachlor and assumed responsibility for assessing the risk posed by new chemicals. Similar regulatory changes occurred in many countries and the pesticides mentioned above and additional persistent organic pollutants (POPs) have now been banned or are to be phased out by signatories of the Stockholm Convention 2001 (for further detail see Chapter 8).

When Silent Spring was published in 1962 over 500 new pesticides were entering the market annually. In more recent times, the process of registering a pesticide has required rigorous environmental and human health assessment. This has dramatically increased the cost and time for bringing a pesticide to market. The estimated cost of discovery, development and registration for bringing a new pesticide to market in 2006 was US\$180 million requiring a timeframe of 8-10 years (Whitford et al. 2006). In addition, Bayer CropScience (► https://cropscience.bayer.co.uk/tools-and-services/stewardship-food-and-environment/bringing-products-to-market) estimate that only 1 in every 139,000 potential active ingredients makes it to commercial markets. Associated with this has been a decrease in the number of active ingredients introduced into the commercial market from approximately 19 per year in 1997 to approximately 8 per year in 2018 (Phillips 2020). It is likely that the stringent and costly, but necessary, processes for registration of new pesticides have limited more new products being approved for use.

Neonicotinoids (e.g. acetamiprid, clothianidin, imidacloprid and thiamethoxam) are a relatively new group of insecticides, which were commercialised in the 1990s. The structure of neonicotinoids is based on nicotine, which is a natural chemical synthesised by a range of plants that has powerful insecticidal properties. Neonicotinoids are the most extensively used group of insecticides globally (Jeschke et al. 2011; Simon-Delso et al. 2015). Originally thought to act specifically on target organisms (i.e. insects), there is growing evidence that negative impacts are occurring on non-target estuarine and marine species including crustaceans (prawns/ shrimps) and molluscs (oysters) (e.g. Hook et al. 2018; Butcherine et al. 2019; Ewere et al. 2019).

## 7.3 Types of Pesticides

Pesticides are classed in different ways for different reasons but all are designed to target specific groups of pest organisms. The chemical structure is a driver of the mode of action (MoA-the means by which pesticides exert their toxic effects) and these characteristics influence what the target organisms are. Most commercial pesticides are synthetic but as noted earlier some are derived from natural products. In the constant battle for survival many plants synthesise a range of chemicals that kill, repel or inhibit bacteria, fungi and insects (i.e. they produce natural pesticides). For example, pyrethrins are secondary metabolite terpenoids produced by sunflowers and other plants, azadiractin is a compound found in the neem tree and Sero-X is based on cyclotides (a group of circular mini-proteins) that are naturally produced by the butterfly pea plant (Clitoria ternatea). Sometimes, the structure of natural pesticides provides precursors or inspiration to develop similar but synthetic pesticides (e.g. pyrethroids were inspired by the molecular structure of naturally found pyrethrins).

# 7.3.1 Classification by Target Organism

The wide-ranging biology and life-cycle characteristics of different taxonomic groups influence the chemical characteristics of an effective pesticide. Yet the very similarities within taxonomic groups enable a pesticide to be effective on multiple species of that or similar types of organisms. For these reasons, the broad pesticide grouping of target organisms is influenced by the effectiveness of the mode of action on similar traits and characteristics within taxonomic groups. Table 7.1 shows the range of target organisms by which pesticides are classified into different types. Of course, not all these are directly relevant to the marine environment so some relevance has also been provided so you can focus your attention on those pesticides which are of most concern.

#### 7.3.2 Classification by Chemical Structure

Another way of classifying pesticides is based on their **chemical structure**. Pesticides with the same key chemical structures are grouped together. Usually, pesticides with the same chemical structure will have the same

• Table 7.1 Pesticides, their target organism and relevance to the marine environment						
Pesticide type	Target organisms	Relevance to the marine environment				
Acaricides	Mites/spiders	Usually applied very locally in terrestrial environments				
Algicides	Algae	Used to eradicate nuisance algae (most commonly in freshwater) and in marine aquariums, they are taxonomically relevant				
Avicides	Birds	Seagull and other nuisance marine bird control. They are taxonomically relevant				
Bactericides	Bacteria	Used in mariculture and are taxonomically relevant				
Disinfectant	Microorganisms	Usually applied locally in terrestrial environments. Pandemic situations such as COVID-19 dramatically increase usage which may enhance risk via sewage treatment plants				
Fungicides	Fungi	Catchment discharges, they are taxonomically relevant				
Herbicides	Plants	Catchment discharges, they are taxonomically relevant				
Insecticides	Insects	Catchment discharges, they are taxonomically relevant				
Larvicides	Insect larvae	Catchment discharges, they are taxonomically relevant				
Molluscicides	Molluscs	Discharge pipe management, they are taxonomically relevant				
Piscicides	Fish	Applied to eradicate invasive fish (most commonly in freshwater), they are taxonomically relevant				
Rodenticides	Rodents	Isolated irradiation programs on islands, transport accidents				
Termiticides	Termites	Usually very localised terrestrial application				
Marine applications						
Antifoulants	Broad spectrum	Fouling communities				
Parasiticides	Sea lice	Mariculture				
Nematicides	Nematodes	Mariculture				

mode of action and are therefore likely to affect the same type of organisms. There are seven main groups of pesticides including organochlorines, organophosphates, carbamates, pyrethrin and pyrethroids, neonicotinoids, phenylpyrazoles and triazines, along with some elemental-based inorganic pesticides (**1** Table 7.2).

# 7.3.3 Classification by Mode of Action (MoA)

MoA is operationally defined and a number of different MoA schemes have been developed. They generally describe the key biological changes that occur as part of the toxic response of an organism. However, for pesticides, the MoAs are generally defined in terms of the biological receptor that they interact with to cause toxicity (HRAC 2020; FRAC 2020; IRAC 2019). Some of the major groupings of pesticides based on their mode of action are: acetylcholinesterase inhibitors; photosystem II inhibiting herbicides; nicotinic acetylcholine receptor (nAChR) competitive modulators; and synthetic auxins. The mode of action of a pesticide is controlled by its chemical structure, specifically its three-dimensional shape and volume. This is because the toxic effect is caused by the pesticide having a shape similar to a natural protein or chemical that binds to a binding receptor and triggers a biochemical reaction. A pesticide can bind either reversibly to a receptor (e.g. it can be bound and then released from the receptor) or irreversibly (once bound it is not released from the receptor). Despite binding to a receptor, pesticides do not trigger the normal biochemical reaction, rather they typically prevent normal reactions from occurring. In such cases, the pesticides are competing with the correct protein to bind to the receptor.

If a pesticide inhibits a particular biochemical pathway then it is described as having a specific MoA. Examples of the classification of pesticides by target organism; chemical structure and mode of action are presented in **Table 7.2**. Whereas, some pesticides react with many different biological molecules and these are termed as having a non-specific MoA. It is possible for a pesticide to have both specific and non-specific MoAs. For example, pesticides such as ametryn, atrazine, diuron, hexazinone, simazine and tebuthiuron have a specific MoA in plants of binding to the plastoquinone B (QB) protein binding site on the D1 protein in Photosystem II) and hence are called Photosystem II inhibiting (PSII) herbicides. However, they also

	Mode of action		Most are neurotoxins, affecting the central nervous system DDT disrupts the transfer of nerve impulses by inhibiting the $K^+$ and $Ca^{2+}$ ATPase which controls the active transfer of ions through membranes	Acetyl cholinesterase receptor (AChR) inhibitors. These pes- ticides bind to acetyl cholinesterase that leads to the accu- mulation of acetyl choline in nerve cell synapses and uncon- trolled muscle contraction, depletion of cellular energy and death	Reversible inactivation of the enzyme AChR Similar to organophosphates but with different reactive properties	Affect the sodium channels and lead to paralysis of the or- ganism	Chemically related to nicotine and like nicotine these com- pounds act on receptors in the nerve synapse Nicotinic ace- tylcholine receptor (nAChR) competitive modulators	Block glutamate-activated chloride channels in insects
	Target purpose		Insecticide	Insecticide	Insecticide Herbicide	Insecticide	Insecticide	Insecticide
rganisms and mode of action	Characteristics/Behaviour		Chlorinated hydrocarbon compounds and known persistent organic pollutants (POPs) Likely to biomagnify Toxic to marine life, humans and other animals	Readily biodegrade Widely toxic to insects Identified human toxicity	Functional group: carbamate esters More degradable than organophosphates	Properties derived from ketoalcoholic es- ters of chrysanthemic and pyrethroic ac- ids isolated from flowers of pyrethrums	Many are water soluble, slower break- down in soil Absorbed by plants and provide protec- tion during growth Photodegrades, half-life minimum around 3 months	Characterised by a pyrazole ring and at- tached phenyl group
ure, behaviour, target o	Common examples		DDT 2,4,5-T dieldrin lindane chlordane heptachlor	Chlorpyrifos valathion diazion	Carbaryl aldicarb carbofuran oxamyl methomyl	Allethrin resme- thrin permethrin cyfluthrin esfen- valerate	Imidacloprid thiacloprid clothianidin	Fipronil pyriprole accoprole
pesticide groupings, struct	Characteristic structure or example		I O O O	R <sup>10</sup> -P-OR <sup>3</sup> R <sup>20</sup> -OR <sup>3</sup>	R <sup>1</sup> 0 C R <sup>3</sup>	COOH (1R,3R)- or (+)-trans- chrysanthemic acid.	HD HD N	N N N N N N N N N N N N N N N N N N N
• Table 7.2 The main	Chemical group	Organic	Organochlorines (or- ganic compounds of- ten with ring struc- tures (e.g. a benzene ring) and at least one but up to six covalently bonded chlorine atoms)	Organophosphates (the central structure is O = P(OR) <sub>3</sub> , with the P atom being central and having alkyl or aro- matic groups attached)	Carbamates (structures are similar to carbamic acid)	Pyrethroids and pyre- thrins	Neonicotinoids (structures are similar to nicotine)	Phenylpyrazoles

(continued)

	Mode of action	Photosystem II inhibiting herbicide preventing electron transfer between photosystem I and II. Photosynthetic en- ergy deviators compete for electron flow at the reducing end of photosystem I. They accept electrons that would usually have been passed on to iron-sulphur proteins that mediate electron transfer They are also inhibitors of chloroplast development and block carotenoid synthesis	Acts by mimicking the plant hormones such as auxins, cy- tokinins and abscisic acid, interfering with natural plant growth regulators		Mercury has a strong affinity for sulfhydryl groups (SH) in proteins, enzymes, haemoglobin and serum albumin. The central nervous system is affected by damage to the blood- brain barrier; transfer of metabolites such as amino acids are affected	Interference of complex homeostasis, for example stimulat- ing free radical production in cells which induces lipid perox- idation and disturbs antioxidant capacity	Coagulates proteins, forms complexes with coenzymes, in- hibits the production of ATP. Like cadmium and mercury, it can substitute for phosphorous in some biochemical pro- cesses	Multiple depending on species e.g endocrine disruption -inhibiting cytochrome P450, inhibit oxidative phosphorylation and alter mitochondrial structure and function Causes imposex and shell thickening in molluscs
	Target purpose	Herbicide	Herbicide		Fungicide	Algicide Fungicide Bactericide Biocide	Insecticide	Biocide
	Characteristics/Behaviour	Nitrogen containing hetrocycles. Soluble in water Considered as POPs resisting biological and chemical degradation. High affinity for soil organic matter and may be trans- ported through soil	High volatility Slightly soluble in water		Lipophilic and biomagnifies (organo-me- tallic forms) Does not readily biodegrade Species and forms vary in toxicity	Persistent Does not readily biodegrade	A metalloid Does not readily biodegrade As <sup>3+</sup> and As <sup>6+</sup> vary in toxicity	Slow degradation in reducing environ- ments
	Common examples	Atrazine cyanazine propazine simazine ametryn	2,4-D MCPA fenoprop		Methoxy ethyl mer- cury chloride	Copper sulphate, copper hydroxide, copper oxychloride	Copper arsenate, CCA (copper, chro- mium, arsenic) wood treatment herbicide	Organotin, TBT
d)	Characteristic structure or example	H N N N N N N N N N N N N N N N N N N N	HO HO HO		H <sub>3</sub> C H <sub>9</sub>	Cu <sup>2+</sup>	0, CH₃ Na⁺ 0 <sup>, AS,</sup> OH	Sar, CI
• Table 7.2 (continue	Chemical group	Triazines (a benzene ring with three carbon atoms re- placed by nitrogen at- oms)	Phenoxy (carboxylic acid)	Inorganic	Mercury	Copper	Arsenic	Tin

have a non-specific MoA in plants of indirectly increasing the concentration of reactive oxygen species (ROS) that can cause irreversible cell damage and ultimately lead to cell death (apoptosis) (Vass 2011). The MoA for a pesticide can also change depending on the organism being exposed. For example, PSII herbicides have a different MoA in amphibians where they cause endocrine-disrupting effects (Mnif et al. 2011; DEPA 2015) (See ► Chapter 13 for more detail on endocrine disruption). Thus, determining the MoA of pesticides is not straightforward.

### 7.4 Quantities of Pesticides Used

A recent estimate of annual global pesticide usage by the Food and Agriculture Organisation of the United Nations (FAO) is 4.2 million tonnes for 2019 (FAO 2021). Pesticide usage has risen steadily since 1990 and nearly doubled in that time (FAO 2021) (• Figure 7.2). Despite a plateau being reached in recent years, total pesticides use increased in the 2010s by more than 50% compared to the 1990s, with pesticides use per area of cropland increasing from 1.8 to 2.7 kg/ha (FAO 2021). Asia is the largest user of pesticides accounting for on average 52.8% of global usage, followed by the Americas with 30.2% and Europe with 13.8%. The largest single country user of pesticides is China that uses an annual average of 1.77 million tonnes followed by 408,000 tonnes by the USA and 377,000 tonnes by Brazil (FAO 2021). Some countries such as Italy, Portugal, Austria, Czechoslovakia and Denmark have decreased their use of pesticides in recent times (Worldatlas 2018; Sharma et al. 2019).

The trends in pesticide usage over time are highly variable between countries ( Table 7.3). There are numerous factors that influence the amounts of pesticides used by any one country, some examples include amount of land dedicated to agriculture, type of crops



■ Figure 7.2 Global use of pesticides from 1990 to 2017. *Data* source: FAO ▶ http://www.fao.org/faostat/en/#data/RP

Table 7.3	Changes in the usage of all pesticides sir	ice 1990
in selected co	ountries	

Country	Trend in total pesticide usage between 1990 and 2018 (compared to 1990 usage, tonnes)
Denmark and Italy	Decreased to $\approx 50\%$
Australia	Increased to 350%
Austria	Decreased to 75% in 2014, Increased to 122% since 2014
India	Decreased to 20% in 2008, Increased to 75% since 2009
Germany	Increased to 166%
China	Increased to 200%
Brazil	Increased to 800%
Argentina	Increased to 1000% till 2010, Decreased to 665% since 2011

Data source: FAO ► http://www.fao.org/faostat/en/#data/RP

grown, population, trade regulations, climate, developments in integrated pest management, the extent of non-pesticide reliant forms of agriculture (e.g. organic farming and permaculture).

Global pesticide use is reported to have significantly increased with time during 1990 and 2007 (Zhang 2018). However, the trend changed in 2007 showing two phases, 1990–2007, and 2007–2014. Specifically, total global insecticide use has significantly declined since 2007 with the use of chlorinated hydrocarbons decreasing since 1990, carbamate use decreased since 2007 and organophosphates have generally decreased over time (Zhang 2018). Furthermore, Zang (2018) reports that plant growth regulators and other more novel pesticides have increased continuously since 1990, herbicide use has mostly increased since 1990 and fungicide and bactericide use have stabilised.

#### 7.5 Environmentally Relevant Properties

As with all chemicals, the **environmental fate** and effects of pesticides are determined by their chemical structure and physicochemical properties and the physicochemical properties of the media where the pesticide is located. Environmentally relevant physicochemical properties include: molecular weight; aqueous solubility and hydrophobicity; partition coefficients; bioaccumulation and bioconcentration factors; volatility; and degradability (or persistence). A brief description of each of these properties and how they affect environmental fate follows (See also > Box 7.1).

## 7.5.1 Molecular Weight

Typically, as the molecular weight of a chemical increases a range of other physicochemical properties change. For example, **as the molecular weight increases the chemical becomes less water soluble** (because it requires more energy to dissolve the chemical), becomes more soluble in plant and animal tissue, becomes less volatile (as it takes more energy to volatilise the chemical), and is more likely to bind to organic matter and particles.

#### 7.5.2 Aqueous Solubility and Hydrophobicity

The solubility of a pesticide is the maximum mass of the pesticide that can be dissolved in a solvent at a specified temperature and pressure. An important factor in determining the solubility of a pesticide is the polarity (charge) of the pesticide and the solvent. A general rule of thumb is that like dissolves like. So polar pesticides will dissolve in polar solvents and conversely non-pola chemicals will dissolve in non-pola solvents. Water is polar and thus the more polar the pesticide the greater it's aqueous solubility and the lower the pesticide solubility in a non-polar solvent such as animal tissue. In order for a pesticide to enter an animal it must pass a cell membrane that is composed of a nonpola lipid bilayer. The more non-pola a pesticide the greater its solubility in the cell membrane and its ability to enter the organism.

Chemicals that have high aqueous solubility are termed **hydrophilic** (water-loving) or conversely **lipophobic** (fat-hating). Chemicals that are highly soluble in tissue are termed **lipophilic** (fat-loving) or conversely **hydrophobic** (water-hating). Lipophilic pesticides, once ingested by organisms, are more likely to become stored in the fatty tissues. Here they will bioaccumulate, and if this organism, is prey for another, then the higher order predator receives an already accumulated dose, and so on up the food chain, this is known as biomagnification (see  $\triangleright$  Chapter 2). The potential for biomagnification is of great concern to regulatory agencies, and there are tests that are used to assess the potential of a chemical to biomagnify.

How hydrophobic or hydrophilic a pesticide is will affect its distribution in animals and plants. The more hydrophobic a pesticide the greater the proportion that will be found in the non-aqueous parts of animals and plants (e.g. cell walls, fat cells). Conversely, the more hydrophilic a pesticide the greater the proportion that will be found in aqueous parts of animals and plants (e.g. blood plasma, cytoplasm). It is important to note that irrespective of the aqueous solubility or hydrophobicity of a pesticide some will always be found in the less favoured phase (water or tissue). The aqueous solubility and hydrophobicity of pesticides also play a role in how pesticides are excreted from the animal or plant. Hydrophilic pesticides will mainly be excreted by urine and to a lesser degree sweat or any other process that leads to the loss of water. Conversely, hydrophobic pesticides will mainly be excreted by processes that remove solid material (e.g. such as faeces and loss of dead cells, eggs, leaves or branches). An exception to this is mammalian mothers milk which is high in fat and therefore likely to have related lipophilic contaminants.

## 7.5.3 Partition Coefficients

#### Octanol-water partition coefficient

A partition coefficient is the ratio of the concentration of a chemical in two different media once equilibrium has been reached. The magnitude of a partition coefficient depends on the solubility of a chemical in the two different media. Because partition coefficient values can be very small and very large they are usually expressed as a logarithm. A widely used partition coefficient in environmental science is the octanol–water partition coefficient (Kow or its logarithm, Log Kow). This partition coefficient is calculated using Eq. 7.1.

$$LogKow = log\left(\frac{concentration in octanol}{concentration in water}\right)$$
(7.1)

Box 7.1: Important Physicochemical Properties of Organic Pesticides That Control Their Environmental Behaviour

□ Table 7.4 ► Box 7.1: shows important physical and chemical properties of some common pesticides.

	*	*				
Pesticide	Pesticide type	Molecular weight (amu)	Aqueous solubility (mg/L)	Log octanol– water partition coefficient	Vapour pressure (mPa)	Log bioconcentration factor
Atrazine	PSII herbicide	215.7	35	1.59–2.34	0.038	0.63
Imidacloprid	Neonicotinoid insecticide	255.7	0.61	0.57	4×10	-0.21
Diuron	PSII herbicide	233.1	~35	2.87	$1.1 \times 10^{-3}$	0.98
Chlorothalonil	Fungicide	266	0.81	2.92–2.94	0.076	2.00
DDT	Organochlorine insecticide	354.5	0.006	6.91	0.025	3.50
Chlorpyrifos	Organophos- phate insecticide	350.6	~1.4	4.7	2.7	3.14
Cybutryne	PSII herbicidal biocide	253.4	7.0	3.95	0.09	2.20
Deltamethrin	Pyrethroid insecticide	505.2	0.0002	4.6	$1.2 \times 10^{-5}$	3.15
Dieldrin	Cyclodiene insecticide	380.9	0.14	3.7	0.024	4.54
Fipronil	Phenylpyrazole insecticide	437.2	1.9–2.4	4.0	$2 \times 10^{-3}$	2.50

Table 7.4	Box	7.1: Proj	perties of	common	pesticides	that in	fluence tl	heir envi	ironmental	behaviour
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<sup>1</sup>amu = atomic mass units. *Data sources*: MacBean (2012) and the Pesticide Property Database (University of Hertfordshire 2013)

An example calculation of the octanol-water partition coefficient (Kow) for a hypothetical pesticide (Q) is presented below:

Solubility (s) of Q in water = 0.1 mg/LSolubility of Q in octanol = 158,489 mg/L

Kow = solubility in octanol/aqueous solubility 158,489 mg/L

```
= 0.1 mg/L
```

```
= 1,584,890
```

Log Kow = 6.19

At its simplest, Kow is determined by mixing the chemical of interest in a flask containing water and octanol then letting the system stabilise until equilibrium is reached (i.e. the concentrations of the chemical in the octanol and water are stable over time). While this sounds quite easy there are challenges in obtaining accurate estimates as the Kow increases. With increasing Kow, the aqueous solubility becomes very small and thus small differences in the measured aqueous concentration can result in large differences in Kow. For example, if the aqueous solubility of pesticide Q was 10% smaller or larger than 0.1 mg/L ( $\triangleright$  Box 7.1) then the Kow values would be 1,760,000 or 1,440,000, respectively. Other difficulties in measuring Kow and other partition coefficients have been identified during their 40–50 years of application (Hermens et al. 2013).

The Kow is the main physicochemical property used to express the lipophilicity of a compound and it is widely used as a surrogate of the likelihood of a chemical to accumulate in fatty tissue. The relationship between Log Kow and accumulation into animal tissue is shaped like an upside-down U—a positive linear re-



**C** Figure 7.3 A typical relationship between the logarithm of the octanol–water partition coefficient (log Kow) and the logarithm of by uptake by tissue (log  $K_B$ ). Adapted from Connell and Hawker 1988 by M St. J. Warne

lationship up to Log Kow values of about 6 at which point it plateaus off and then above log Kow values of 7 accumulation decreases ( Figure 7.3). This could be due to decreased solubility in animal tissue because of the increased size of the pesticide molecule and there being so little dissolved in the water to accumulate into the tissue. Some argue that the decrease in accumulation is due to the fact that as log Kow increases the rate of accumulating decreases and that if the duration of the accumulation experiments was continued until equilibrium was reached that the relationship would remain linear beyond log Kow values of 6.

#### Organic Carbon–Water Partition Coefficient

The organic carbon–water partition coefficient (Koc or its logarithm, Log Koc) is a measure of how much of a chemical will bind to the organic carbon in soil or in sediment as opposed to being dissolved in soil or sediment pore water at equilibrium. The larger the Koc value the greater the proportion of the pesticide that will bind to the organic carbon and the less that is likely to be transported off-site dissolved in surface or groundwater. Conversely, the greater the Koc the more of the pesticide that can be transported bound to eroded soil particles or bound to suspended solids in water. This partition coefficient is calculated using Eq. 7.2.

$$LogKoc = log\left(\frac{concentration in organic carbon}{concentration in water}\right)$$
(7.2)

#### Octanol-Air Partition Coefficient

The octanol-air partition coefficient (Koa or its logarithm, Log Koa) is a measure of how much of an organic chemical will bind to air particles as opposed to the gaseous phase of air at equilibrium. The octanol is used as a surrogate for the organic component of air particles—which is what the organic chemical binds to. The larger the Koa value the greater the proportion of the pesticide that will bind to air particles and the less that will be in a gaseous form. This partition coefficient is calculated using Eq. 7.3.

$$LogKoa = log\left(\frac{concentration in octanol}{concentration in air}\right)$$
(7.3)

Bioaccumulation, Bioconcentration and Biomagnification Factors

These terms are sometimes used interchangeably by people. However, they are not the same. Bioconcentration is the process of a chemical moving from the surrounding ambient media into plants or animals. Thus, for aquatic organisms, bioconcentration is the movement of a chemical from water into the organism. For terrestrial organisms, it is the movement of a chemical from the air into the organism. The bioconcentration factor (BCF) is thus the ratio of the concentration of the chemical in the organism to that in the ambient Eq. 7.4 media.

$$BCF = \left(\frac{\text{concentration in the organism}}{\text{concentration in the ambient media}}\right) (7.4)$$

The size of the BCF depends on such properties as the aqueous solubility and Kow of the chemical being considered.

Biomagnification is the process of a chemical moving into an organism solely from the food that it eats. With biomagnification, there is an increase in the organism concentration in those organisms higher in food chains. A classic example of biomagnification is DDT where concentrations in algae were low but increased in zooplankton, herbivorous, carnivorous fish and finally in fish-eating birds of prey. The biomagnification factor (BMF) is the ratio of the chemical in the organism to that in its food Eq. 7.5.

$$BMF = \left(\frac{\text{concentration in the organism}}{\text{concentration in the eaten food}}\right)$$
(7.5)

Thus, the BMF will vary for different species in a single food chain.

Bioaccumulation is the process of a chemical moving from the ambient environment and/or from food into an organism. Bioaccumulation does not differentiate the source of the chemical, unlike bioconcentration and biomagnification. Bioconcentration and Biomagnification factors can be determined experimentally in laboratories using well-established protocols (e.g. OECD 2012). In contrast, bioaccumulation factors are usually measured in the field where it is not possible to determine the source of the chemical in the organism. Despite considering uptake from both the ambient environment and food, the bioaccumulation factor (BAF) is calculated using the same formula as the BCF (> https://www. epa.gov/pesticide-science-and-assessing-pesticide-risks/ kabam-version-10-users-guide-and-technical-3#:~:text=Bioaccumulation%20factors%20(BAF)%20are%20 calculated, which%20the%20pesticide%20was%20taken).

Another relevant factor for pesticides in marine ecosystems is the biota-sediment accumulation factor (BSAF). The BSAF is the ratio of the concentration of the chemical in the organism to that in the sediment Eq. 7.6.

$$BSAF = \left(\frac{\text{concentration in the organism}}{\text{concentration in the sediment}}\right)$$
(7.6)

Different species and types of organisms have different lipid contents and as lipid is where bioaccumulating chemicals are stored this will affect the magnitude of the BCF, BMF, BSAF and BAF values. Normalising the organism concentration data to the lipid content of the organism removes the effect of lipids and assists with inter-species comparisons. The lipid correction is done by expressing the organism concentration as mass per kg lipid. For example, a lipid corrected BCF is calculated using Eq. 7.7:

$$BCF(lipid) = \left(\frac{\text{concetration in the organism's lipid}}{\text{concentration in the ambient media}}\right) (7.7)$$

The same logic applies to BCF, BAF and BMF values for plants, except that they are corrected for the organic carbon content of the plant. For the BSAF, there are two normalisation steps—the correction for the lipid content of the organism and a correction for the organic carbon content of the sediment.

If the BCF, BAF, BMF and BSAF values are greater than one it means the chemical preferentially partitions into the organism. These factors can be very large and therefore are often expressed as log10 values (e.g. a BCF of 1,000,000 would have a log BCF of 6). At what BAF, BCF or BMF value a chemical is considered to accumulate varies amongst different organisations. However, in order for a chemical to be classed as a persistent, bioaccumulative, toxic chemical (PBT) or a very bioacculumative, very persistent chemical (vBvP), their BCF must be at least 2000 and 5000, respectively (> https:// reachonline.eu/reach/en/annex-xiii-1.html).

#### 7.5.4 Volatility

Volatility is a measure of the ease with which a chemical changes state from a solid or liquid phase into the gaseous phase. One measure of volatility is vapour pressure. It is the pressure exerted by a vapour when it is in equilibrium with its solid and/or liquid forms. The vapour pressure increases with increasing temperature and decreasing atmospheric pressure. The more volatile a pesticide the greater the amount that will be in the gaseous compartment of the environment under any set of environmental conditions (particularly temperature and pressure) as opposed to staying in the aqueous, soil, sediment, animal or plant compartments. The greater a pesticide's volatility the greater the probability that it will be transported by the mass movement of air.

## 7.5.5 Degradation and Persistence

There are various forms of degradation that are caused by biological (biotic) factors collectively called biodegradation and/or by non-biological (abiotic) factors collectively called chemical degradation. Biodegradation is generally caused by the metabolic activity of micro-organisms including bacteria, yeasts and fungi. However, most plants and animals also have various mechanisms for degrading or metabolising contaminants. Chemical degradation includes breakdown by water (hydrolysis) and by sunlight (photolysis). Typically, biological and chemical degradation break pesticides down into smaller chemicals with reduced toxicity and increased aqueous solubility compared to the original (parent) compound. The faster a pesticide is degraded to nontoxic chemicals the shorter the period that organisms are exposed to it and the lower its ability to cause toxic effects. The chemicals produced through degradation are called degradation products or degradates.

The word persistence (the opposite of degradability) was introduced into the scientific literature on pesticides to describe their continuing existence in the environment, and it was only after this that the term was applied to any organic chemical that is biologically active (Greenhalgh 1980). In a practical sense, a pesticide needs to have some persistence to ensure that it remains biologically active for sufficient time to act on target pests. However, the longer the persistence the greater the chance that the pesticide will be biologically active on or in the food grown for human consumption and the greater the chance of being transported from the site of application and exerting harmful effects to non-target organisms. This is why persistence is viewed as a key characteristic of pesticides in assessing their potential to cause environmental harm.

Persistence is a measurable property and represents a chemical resistance to change of its chemical structure and is a variable, which is a function of many interactions such as sunlight, heat and microbiological decay that result in oxidation, reduction, hydrolysis, photolysis and substitution (Grenhalgh 1980). The physical properties of a chemical inducing vapour pressure, solubility in water, dissociation constant, partition coefficient, sorption to soil and volatility will influence its persistence. Understanding these properties is essential for product registration today. Further to this, characteristics of the receiving environment including soil/ sediment particle size, soil moisture content, organic matter content, pH, microbial biomass and temperature play a role in environmental persistence. Hence, persistence is site and condition-specific. Persistence

7

<b>Table 7.5</b> Classification of the rate of degradation of pesticides in water				
Half-life (days)	Persistence			
<1	Fast degradation			
1–14	Moderately fast degradation			
14–30	Slow degradation			
>30	Stable in water			
Data source: University of Hertfordshire (2013)				

**Table 7.6** Pesticides must have one or more of the listed properties to be classified as either a persistent, bioaccumulative and toxic (PBT) chemical or as a very persistent and very bioaccumulative (vPvB) chemical 2021

PBT	vPvB
Half-life in marine water > 60 days	Half-life in marine water, fresh or estuarine water >60 days
Half-life in fresh or estuarine water >40 days	
Half-life in marine sediment > 180 days	Half-life in marine, fresh or estuarine water sediment > 180 days
Half-life in fresh or estuarine water sediment > 120 days	
Half-life in soil > 120 days	Half-life in soil > 180 days
Examples include: aldrin, chlordane, heptachlor, methoxychlor and toxaphene (all of which are organochlorine pesticides)	Examples: TBT
Adapted from REACH (2021) and US EPA (undated)	

is usually measured in the laboratory under standardised experimental conditions that are optimal for degradation. They should therefore be used cautiously as they may not reflect environmental degradation rates. For example, laboratory-based shake flask degradation studies of PSII herbicides in seawater have typically reported half-lives of one to three months (see references in Mercurio et al. 2015). Yet Mercurio et al. (2015) using field-based mesocosms in tropical marine waters found that the half-lives were all greater than 1 year.

Persistence is usually expressed in terms of the chemical's half-life  $(t_{1/2})$ —the period of time required for the concentration of the chemical to be halved. The  $t_{1/2}$  of a chemical can be measured in any abiotic environmental compartment (e.g. soil, water, sediment, air). A commonly used scheme for classifying the rate of degradation of pesticides is that of the Pesticide Property DataBase (PPDB) (University of Hertfordshire 2013) (• Table 7.5).

The European Union (REACH 2021) and the United States of America (USA) (US EPA, undated) have classifications for persistent chemicals called persistent, bioaccumulative and toxic (PBT) chemicals and very persistent, very bioaccumulative (vPvB) chemicals. The minimum persistence required to be classified as a PBT or vPvB chemical is presented in **I** Table 7.6. Some PBT and vPvB chemicals may also meet the requirements to be classed as a POP as their requirements partially overlap.

## 7.6 Pesticide Distribution in the Marine Environment

Most pesticides measured in marine environments originate from terrestrial sources ( Table 7.1), with several notable exceptions such as antifoulants. Pesticides are transported from their source via water and sediment (• Figure 7.4 and  $\blacktriangleright$  Section 7.6.1) and via the atmosphere (> Section 7.6.2). Pesticides have been measured in waters, sediment and biota in marine environments throughout the world for many decades (• Tables 7.7, 7.8 and 7.9). Once pesticides are taken up by organisms ( Table 7.9), they too act as a transport pathway in a spatial sense and also through food chains.

## 7.6.1 Transport to Marine Environments via River Waters and Sediments

Most pesticides are applied to land, particularly in agriculture. For example, over 70% of pesticide use in Australia is applied to agricultural land (IbisWorld 2016). However, pesticides are quite extensively used in urban areas for the control of termites, insects and weeds in and around houses, for fleas and parasitic worms in domestic pets and to control weeds in parks and water-



■ Figure 7.4 Sources of pesticides to the marine environment. Adapted from ■ Figure 1.1>

• Table 7.7 Examples of the global distribution of pesticides in marine waters							
Location	Examples of pesticides measured						
Great Barrier Reef La- goon, Australia	ametryn, atrazine, diuron, hexazinone, tebuthiuron, bromacil, fluometuron, metribuzin, prometryn, propazine, simazine, terbuthylazine, terbutryn, desethyl atrazine, metolachlor, 2,4-D, MCPA, fluroxypyr, imazapic, imidacloprid, metsul- furon-methyl, tebuconazole, propiconazole, pendimethalin, chlorpyrifos, endosul- fan, malathion	Lewis et al. (2009) Thai et al. (2020)					
Mediterranean Sea	atrazine	Nödler et al. (2013)					
Baltic Sea	atrazine	Nödler et al. (2013)					
Caribbean and Pacific Surface water slicks	DDTs <sup>1</sup> , cyclodiene pesticides, chlordane-related compounds, hexachloro cyclo hexanes, chlorinated benzene	Menzies et al. (2013)					
Jiaozhou Bay, China	atrazine and acetochlor	Ouyang et al. (2019)					
Japan Sea, North Pacific and Arctic Oceans	α-HCH, β-HCH, Υ-HCH, δ-HCH, heptachlor, aldrin, heptachlor epoxide, α-endosulfan, dieldrin, endrin, β-endosulfan, p,p'-DDD, p,p'-DDE, endrin aldehyde, p,p'-DDT, methoxychlor and endosulfan sulfate	Minggang et al. (2010)					
North Pacific to Arctic oceans	chloroneb, simazine, atrazine, alachlor, dacthal, chlorobenzilate, methoxychlor, and permethrin	Gao et al. (2019)					
Cape Town, South Af- rica	atrazine, alachlor, simazine, metolachlor, and butachlor	Ojemaye et al. (2020)					
<sup>1</sup> DDTs=DDT, DDD, DDE							

<b>Table 7.8</b> Examples of the global distribution of pesticides in marine sediments						
Location	Types of pesticides measured	Source				
Singapore coastline	DDTs <sup>1</sup> , HCH, chlordane, Hheptachlor, aldrin, dieldrin, en- drin, endosulfan, mirex, methoxychlor	Wurl and Obbard (2005)				
Jiaozhou Bay, China	Atrazine and acetochlor	Ouyang et al. (2019)				
Osaka Bay, Japan	DDT, HCH, chlordane	Iwata et al. (1994)				
Aegean coast	DDT, DDE, lindane, heptachlor, aldrin, dieldrin, endrin	Muzyed et al. (2017)				
Australia	Organochlorines and PSII herbicides	Haynes et al. (2000)				
Hong Kong waters	DDT, HCH, chlordane	Richardson and Zheng (1999)				
Tyrrhenian Sea, Italy	HCH, DDTs, endosulfan, aldrin, dieldrin, endrin	Qu, et al. (2018)				
Mar Menor lagoon, eastern Spain	Organophosphorus and triazine pesticides	Moreno-González and León (2017)				
West coast of Tanzania	DDTs, HCH, endrin, dieldrin, naphthalene, acenaphthylene, anthracene, heptachlor, pyrene	Mwevura et al. (2020)				
San Blas Bay Multiple Use Nature Re- serve, Argentina	Endosulfan, heptachlors, DDT, chlordane, HCH	Commendatore et al. (2018)				
North coast of Vietnam	DDTs, HCH	Nhan et al. (1999)				
Antarctica	DDTs, HCB, HCH	Zhang et al. (2015)				
Bearing Sea, Chukchi Sea and adja- cent Arctic areas	DDTs, HCH	Jin et al. (2017)				
Gulf of Mexico	Organophosphate pesticides (e.g. chlorpyrifos, diazinon, di- methoate, ethion, malathion, parathion, terbufos)	Ponce-Vélez and de la Lan- za-Espino (2019)				
<sup>1</sup> DDTs=DDT, DDD, DDE						

ways. These urban pesticides are predominantly discharged to waterways via surface runoff, storm water drains and wastewater treatment plants.

The main means of off-site transport is surface water runoff and subsequent delivery to estuaries and marine waters. Groundwater also transports pesticides offsite but their contribution is generally much less than surface water, although in dry periods, the contribution may be significant. Pesticides are registered for use on certain crops or types of agriculture at a maximum application rate. Therefore, the types of crops or agriculture and the percentage of the catchment on which they occur will determine the type, mass and concentration of pesticides that are transported from agricultural land to marine waters. Recent work has also shown that land use controls the number of pesticides present (Warne et al. 2020a), the toxicity of pesticide mixtures and the risk that pesticides pose (Warne et al. 2020b) at the point where rivers discharge to marine waters. The distance from the point of pesticide application to the ocean influences how much and what types of pesticides actually end up in marine waters. Rainfall volume and intensity combined with environmental properties such as the soil moisture content, the amount of vegetative ground cover, slope of the ground and the extent of riparian vegetation are

key factors that control the amount and the rapidity with which surface runoff and eroded soil enters waterways. The same transport pathways occur in urban areas but in addition pesticides are transported to waterways via wastewater treatment plants (e.g. Bailey et al. 2000; Zhang et al. 2020) and stormwater drains (e.g. Chen et al. 2019).

Pesticides in runoff will either be dissolved in water (including being bound to dissolved organic carbon/ matter) or bound to suspended sediment particles. The proportion of dissolved and bound forms will vary depending on the physicochemical properties of the pesticides and of the water. For example, Davis et al. (2012) and Packett (2014) found that between 10% and approximately 33% of a range of pesticides were bound to suspended sediment in freshwaters. Bound pesticides are generally not available to water column dwelling organisms (e.g. fish and algae) but are available to benthic organisms or filter feeders. Not all the pesticides that enter a waterway will reach the ocean. There are numerous processes that remove pesticides. Dissolved pesticides can be biologically or chemically degraded, they may bind to suspended or bottom sediment, be absorbed by biota, or be volatilised. The distance that bound pesticides are transported depends on the size (diameter) of the particle they are bound to and the ve-

• Table 7.9 Examples of the global distribution of pesticides in marine o	rganisms	
Location and organisms	Types of pesticides measured	Source
India; commercial marine fishes, seaweeds	HCH, DDTs <sup>1</sup> , heptachlor, endosulfan, dieldrin	Muralidharan et al. (2009); Sundhar et al. (2020)
Northeastern Brazil; King mackerel	Organochlorines	Miranda and Yogui (2016)
Northern Florida Reef Tract, USA; coral, fish, sponge	DDTs, endrin, mirex, deildrin, aldrin, chlordane, nonachlor, heptachlor, BHC,	Glynn et al. (1995)
Cambodia, China, India, Indonesia, Japan, South Korea, Philippines, Malaysia, Russia, Singapore and Vietnam; mussels	Organochlorines	Monirith et al. (2003)
Mediterranean Sea; bluefin tuna	HCB, DDTs	Klinčić et al. (2020)
Australia; coral, dolphins, fish, invertebrates, molluscs, seagrass, turtles,	PSII herbicides, OCs, lindane, aldrin, atrazine, chlorpyrifos, endosulfan ( $\alpha$ , $\beta$ and endosulfan sulfate), dieldrin, DDTs, diuron, hexachlorobenzene, heptachlor, heptachlorepoxide, lindane	Klumpp and Von Westernhagen (1995); Heffernan et al. (2017); Vi- jayasarathy et al. (2019); Haynes et al. (2000); Cagnazzi et al. (2020)
Aegean Coast; fish	DDTs, lindane, heptachlor, aldrin, dieldrin, endrin	Muzyed et al. (2017)
Irish Sea (Liverpool Bay); molluscs, crustaceans, fish, sea stars	DDTs, dieldrin	Riley and Wahby (1977)
North Sea off Netherlands Mediterranean Sea, North Pacific and Bering Sea, Eastern Arabian Sea, North West Pacific, Gulf of Mexico, Atlantic Ocean, Caribbean; zooplankton	Depending on location: DDTs, HCH, chlordane, dieldrin, endrin	Day (1990) and citations therein
Incheon North Harbour and Kyeonggi, Republic of Korea; zooplank- ton, oyster, crab, goby	Organochlorines: HCHs, DDTs, chlordane	Kim (2020)
North Atlantic; killer whales	Organochlorine pesticides	Pedro et al. (2017)
Argentina; dolphins	Organochlorine pesticides (DDE, endosulfan, endosulfan sulfate, hepta- chlor) Organophosphate and pyrethroid pesticides	Romero et al. (2018)
Northwest Pacific; birds and marine mammals	Organochlorine pesticides	Tsygankov et al. (2018)
Antarctica; humpback whales	Organochlorine pesticides	Das et al. (2017)
Oregon/Washington coast; shrimp, molluscs, fish	DDT, DDE, dieldrin	Claeys, et al. (1975)
Arctic; beluga whale, fish, seal	Endosulfan	Weber et al. (2010)
<sup>1</sup> DDTs=DDT, DDD, DDE		

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locity of the water—with larger particles settling out of suspension at higher flow velocities while fine particles will remain in suspension until the flow velocities are low. This particle size and velocity related transport of pesticides can lead to pesticide bound sediments moving down a waterway in a number of steps over a number of flood events. Similarly, in flood plumes pesticides bound to larger particles will not be transported as far from the river mouth as those bound to finer particles or dissolved in the water. In addition, smaller particles have a much larger surface area to mass ratio and thus the same mass of smaller particles will have higher mass of pesticides bound than larger particles.

Rainfall and related climatic conditions (such as monsoon seasons) influence the distance freshwater discharges (flood plumes) are transported in the marine waters. For example, flood plumes from rivers on the eastern coast of Queensland and adjacent to the Great Barrier Reef usually extend up to several kilometres off shore into the lagoon but under extreme conditions have been measured some 75 km offshore (Prekker 1992; see also Devlin et al. 2001). While the Amazon River, which discharges more freshwater than other river, affects the Atlantic Ocean's density and optical properties for more than 3500 km from the river mouth (Hellweger and Gordon 2002).

Pesticides bound to particles are in equilibrium with the concentration of pesticides in water—pesticides are continually binding to and being released from the particles. Therefore, if bound pesticides are deposited in areas with lower aqueous concentrations of pesticides, the particles can act as a source of pesticides to the water due to the release of pesticides from the particles. Similarly, if sediment contaminated with pesticides are resuspended either by natural causes (e.g. storms, strong tidal movement or wind) or by human causes (e.g. dredging), pesticides will desorb from the particles and increase the aqueous concentration. Such increased pesticide concentrations typically persist for a fairly short period of time as the pesticides rapidly resorb onto suspended solids and sediment.

The pattern of pesticide transported to marine waters varies depending on the size and geographical characteristics of the catchment and the rainfall pattern. Typically, waterways draining small catchments deliver pesticides in relatively short duration pulses, while those draining large catchments tend to have considerably longer periods of elevated pesticide concentrations. The proportion of a pesticide that is transported off agricultural land is largely controlled by the length of the period between pesticide application and the next rain event. The longer the period between application and rain the smaller the percentage of the applied pesticide that will be transported off-site. Another key feature of pesticides being transported to marine waters is that they almost always occur in mixtures ( $\triangleright$  Box 7.2).

#### Box 7.2: Aqueous Transport of Pesticides to the Great Barrier Reef, Australia

The Great Barrier Reef (GBR), located on the north-east coast of Australia, is the world's largest coral reef ecosystem and is a National Marine Park and a World Heritage Listed site. The reef is exposed to multiple stressors—one of which is the quality of water entering the reef from adjacent land (Waterhouse et al. 2017). This water has three main contaminants: suspended solids, nutrients (nitrogen and phosphorus) and pesticides (Waterhouse et al. 2017). In order to improve the health and resilience of the reef, the Australian and Queensland governments have developed a series of Reef Water Quality Improvement Plans that have set land use management and pollutant reduction targets. The pesticide reduction target is to protect at least 99% of aquatic species throughout the wet season (November to April) from the harmful effects of pesticide mixtures at the mouth of waterways that discharge to the GBR (Australian and Queensland governments 2018). Progress to achieving the pesticide target is determined by monitoring pesticide concentrations in rivers that discharge to the reef, wetlands, in flood plumes and in-shore waters of the reef itself. The number of sampling sites and the number of pesticides analysed for have varied over time. Currently, over 80 pesticides and degradates are monitored in 20 waterways from grab samples collected by automated samplers. In-shore sampling at sites is conducted at 11 sites, up to 50 km from the nearest river mouth, using passive samplers.

Flood plumes are monitored on an ad-hoc basis. Both in-shore and flood plume samples are analysed for 45 pesticides and degradates. Up to 50 pesticides have been detected in rivers. Of the approximately 2600 river samples collected between 2011 and 2015 over 99.8% contained more than one pesticide. The maximum, mean and median number of pesticides in each sample was 20, 5.1 and 4 respectively (Warne et al. 2020a). Similarly, 59 pesticides have been detected in 22 coastal wetlands and each wetland contained 12 to 30 pesticides with a mean of 21 (Vandergragt et al. 2020). At least 24 pesticides were detected in flood plumes while 27 pesticides were detected in in-shore samples in 2017/2018 and all flood plume and in-shore samples contained pesticide mixtures (**•** Figure 7.5). Pesticides are detected year-round in both the rivers and in-shore with higher concentrations occurring in the wet season.



■ Figure 7.5 ► Box 7.2: Marine pesticide monitoring sites in the Marine Pollution Monitoring Program (2017–2018) of the Great Barrier Reef Marine Park Authority. *Image*: A. Brushett with ARC GIS Pro from data in Gallen et al. 2019

## 7.6.2 Transport of Pesticides to Marine Waters via the Atmosphere

As long ago as 1975 Goldberg cited earlier work by Lloyd Jones who determined the evaporation rate of DDT to show that if the annual amount of DDT used was applied evenly over the Earth's land that all the DDT could evaporate (Goldberg 1975). He also coined the phrase **global distillation** to describe the volatilisation of pesticides, their mass movement by wind systems throughout the world and subsequent transfer to marine waters by precipitation. The term was later expanded to include the transport of pesticides from warm climates (particularly the tropics) to colder polar regions (**•** Figure 7.6).

In hot climates, a percentage of applied pesticides will evaporate from plants, soil and water. They are then moved by large-scale air movements north or south towards the colder polar regions. Once the air temperature at which condensation occurs is reached the pesticides will condense onto any surfaces including biota, ice, snow, soil and water. Thus, there is a spatial separation of pesticides with those with the lower condensation point being transported further towards the poles than pesticides with higher condensation points. This is called **global fractionation**. Air temperatures vary annually with the season. In winter, the condensation temperature for a pesticide may be reached leading to its condensation. In summer, the higher air temperature could again lead to the pesticide evaporating and being transported further towards the poles until its temperature of condensation is again reached. This annual evaporation, transport and condensation cycle is called the grasshopper effect ( Figure 7.5). The rate of degradation in the air also affects the distance that pesticides will be transported—with less persistent chemicals having a reduced likelihood of being transported long distances. Global distillation accounts for the exposure of Arctic wildlife to many POPs, including pesticides, and subsequent toxic effects (Sonne et al. 2017).

Wania (2003) divides pollutants into four groups based on their physicochemical properties (see earlier text) and likelihood of participating in global distillation:

- Fliers are so volatile they remain in the air and are not deposited on land or water even at the poles;
- Single hoppers are sufficiently volatile to be transported to and deposited at the poles in a single event;



**Figure 7.6** Global atmospheric transport of Persistent pesticides by global distillation with more volatile (lower condensation temperature) pesticides being transported further towards the poles (A to C) and annual movement of pesticides by the grasshopper effect. Adapted from Semeena 2005 by M St. J. Warne

- Multiple hoppers will be transported toward the poles by a series of evaporation and condensation cycles; and
- Swimmers have very low volatility but relatively higher aqueous solubility and are therefore transported by oceans currents.

This classification is helpful as it indicates the main mechanism(s) that are responsible for the transport of pesticides.

Interestingly, while there is considerable evidence for global distillation occurring in the northern hemisphere, the evidence is limited for the southern hemisphere (e.g. Iwata et al. 1994; Corsolini et al. 2002, 2003). Sadler and Connell (2012) argue that this is probably due to three reasons. First, the southern hemisphere contains much less land and more ocean than the northern hemisphere. Second, the two large land masses that could provide a means of transfer from tropical to near polar conditions (i.e. Africa and South America) are triangular in shape with less land closer to the poles. Third, the pesticides that are deposited in water are likely to bind to particulate matter and settle at depth onto the ocean floor.

## 7.6.3 Potential Impacts of Climate Change on Transport of Pesticides to and Within Marine Waters

The effects of climate change on the transport of pesticides have received relatively little attention and are far from conclusive. Nonetheless, some potential effects have been identified (e.g. Wang et al. 2016) and are discussed below (see also ► Chapter 14). Increased air temperatures will increase the volatility of pesticides so if the same amounts of pesticides are used a greater proportion will be subject to atmospheric transport. Increased air temperature will (and this has been shown to be occurring) decrease the amount of ice which is likely to lead to the release of pesticides present in melting ice increasing aqueous pesticide concentrations and the amount available to enter polar ecosystems. Also, as ice is a major site for the deposition of pesticides in polar regions, warmer air temperature could lead to less pesticides being deposited on ice. Increased air temperatures may result in the condensation temperatures of some pesticides not being reached and therefore not being deposited.

Climate change forecasts have also predicted increased frequency and intensity of extreme weather events such as droughts, storms, cyclones and hurricanes. The preceding years weather conditions play a role in determining the runoff of water from rain. For example, under conditions of less than normal rainfall, the soil moisture content will be lower, and this decreases the permeability of soil to water. Less than normal rainfall may also decrease ground cover resulting in increased water runoff and increased soil erosion. An increase in the frequency and/or intensity of extreme rainfall events is likely to lead to increased surface runoff and the transportation of soil-bound pesticides.

Global warming could also change oceanic currents and thus the spatial distribution of pesticides. Global warming could lead to changes in the type and intensity of pressure exerted by animal and plant pests to agriculture, and this could lead to increased or changed pesticide use (Noyes et al. 2009; Kattwinkel et al. 2011). Irrespective of how exactly climate change affects pesticide transport it is likely to have significant effects and is likely to cause many as yet unforeseen changes to pollutant transport.

Climate change could also affect the persistence and toxicity of pesticides (e.g. Noves et al. 2009). The Q10 rule states that for every 10 °C increase in temperature, the rate of biological and chemical reactions will increase by two-threefold. Thus, degradation rates of chemicals could increase leading to decreased persistence, and this in turn could lead to increased or decreased toxicity depending on whether the degradates are more or less toxic than the parent compound. Increased ambient temperature is likely to decrease the risk that volatile pesticides will cause harm to aquatic organisms due to increased volatilisation. Temperature is a stressor to organisms, and they all have a thermal tolerance range. Ambient temperature outside an organism's tolerance range places an additional stress on the organism and is likely to increase the toxicity of pesticides (e.g. Negri et al. 2011, 2019a).

## 7.7 Marine Biocides

Within hours of a structure's submergence, a fine biofilm, which is comprised of microorganisms (mainly bacteria), develops on its surface (Steinberg et al. 2002). This initial layer then facilitates the attachment of macro-organisms such as barnacles, serpulid worms, bryozoans, ascidians and algae by providing biochemical cues that trigger larval settlement (• Figure 7.7). These biofouling communities are natural but they interfere with marine structures and shipping. Marine and estuarine aquaculture facilities, uptake and discharge pipes, and boats and ships of all sizes are susceptible to biofouling that significantly increases fuel consumption and infrastructure maintenance (Sonak et al. 2015). As a general rule of thumb, each 10 µm of surface roughness increases fuel consumption by approximately 1% (Lackneby 1962 in Westergaard 2007). Antifoulants are reported to save hundreds of millions of dollars in fuel costs to the shipping industry and result in significant reductions of carbon dioxide emissions (Champ 1999; Sonak et al. 2015), but they can cause harmful environmental effects.

Antifoulant paints are applied directly to structures that are placed in the marine environment. The most widely known antifoulants are tributyltin (TBT), a class of organotin compounds (OGTCs). Copper is also a well-known antifoulant paint additive and has been used in various forms for many hundreds of years. Figure 7.8



b)

shows a historical use of copper sheeting to protect wooden pylons from attack by marine borers. The photo reveals that even though the coverage of copper sheeting is now far from complete it is still exerting its biocidal properties—as indicated by the state of the pylon.

As a function of its lipophilic character and low water solubility, up to 90% of TBT introduced into water readily adsorbs to particulate matter. The level of adsorption is dependent on the sediment characteristics, salinity, pH, oxygen levels, temperature and the presence of dissolved organic matter (e.g. Burton et al. 2004). It is also thought that the biocidal action of TBT may inhibit normal biodegrading processes. Estimates of the half-life of TBT in the environment vary significantly. The half-life of TBT in the water column ranges from a few days to weeks, whereas once deposited in benthic sediments, TBT can last unaltered for decades, particularly in anoxic conditions (Svavarrson 2001).

High concentrations of TBT are normally associated with commercial ports, dockyards and marinas



**Figure 7.8** Copper sheeting was used to protect pylons prior to the invention of antifouling paints. This metal remains a legacy pollutant (Richmond River, NSW, Australia 2020). *Photo*: A. Reichelt-Brushett

and along coastal shipping routes, particularly if these sites have fine silt-like sediment. TBT reservoirs in sediment create a long-term legacy, which extends decades past their actual use dates and their legal restrictions and/or ban. There is growing evidence that since the banning of TBT impacted ecosystems are recovering (Gibson and Wilson 2003; Kim et al. 2017). However, research in Arcachon Bay (one of the first TBT sites identified) showed that sediment contamination was still affecting non-target species after 20 years (Ruiz et al. 1996), and it is suggested that TBT will be a legacy problem into the future (Langston et al. 2015). A recent review by de Oliveira et al. (2020) also showed that the biological impacts of TBT continued to be reported globally between 2000 and 2019.

TBT reservoirs are particularly difficult to manage in areas such as ports and docks, where remobilisation of TBT is ongoing because of maritime traffic and/or dredging. To handle ever-larger vessels, dredging activities at ports are increasing worldwide. These dredging activities are responsible for frequent re-suspension, and re-loading of TBT from/to the sediment and through the disposal of dredge spoil can also impact sites previously unaffected by TBT (Svavarrson 2001).

## 7.7.1 Impacts of TBT Use and Regulation

Within two decades of the widespread use of TBT as antifouling agents, the toxicological problems associated with their use became clear, when the commercial oyster production in France almost completely collapsed in the late 1970s (Alzieu et al. 1989). Further established toxicological effects include imposex in gastropods (a phenomenon of masculinisation of females) (> Box 7.2) and immuno-suppression in seabirds and marine mammals, both of which result in significant population declines (Tester et al. 1996; Kannan et al. 1998; Tanabe et al. 1998). Frouin et al. (2010) provide a detailed review of the behaviour and toxicity of organotin compounds in marine environments and highlight the toxicological effects of extremely low concentrations (ng/L-µg/L range). The review by Frouin et al. (2010) is highly recommended for further reading if this topic interests you.

The detrimental effects of TBT have resulted in many legislative changes in developed countries and have culminated in the global ban of organotin compounds as antifouling agents since 2008. Countries in which the use of TBT had been regulated since the 1980s have shown a significant decrease in concentration in both waters and organisms (Evans et al. 1996; Tester et al. 1996). In July 1987, the UK Government banned the use of TBT-based antifouling paints for vessels under 25 m in length and also its use in aquaculture. Similarly, USA, Europe, Canada, South Africa restricted the use of TBT in antifouling boat bottom paints by vessel size (less than 25 m in length) and restricted the release rates of TBT from co-polymer paints. Japan and New Zealand banned TBT on all vessels. Most Australian States and Territories contributed to international efforts by banning the application to vessels less than 25 m in length (late 1980s-90 s). The IMO Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention) was adopted in 2001 and came into force in September 2008. A complete ban on the application of TBT on vessels under 25 m length came into force on 1 January 2003, with a complete global prohibition by 1 January 2008. After initial banning on small boats, the use of TBT on ocean-going vessels was still permitted on the grounds that these vessels do not sit for long periods of time in near-shore waters and are therefore unlikely to affect local shellfisheries. Legislation banning, the use of TBT on vessels over 25 m, is coming into effect in some countries.

#### Box 7.3: The Effects of TBT on Non-target Organisms

The main objective in the development of antifouling paints has been to inhibit the settlement of marine organisms and barnacles. TBT is toxic to a large range of organisms from plankton to marine mammals and potentially humans. There is considerable evidence that TBT is more toxic to marine organisms than freshwater species (Leung et al. 2007) and effects have been recorded in the ng/L range (Antizar-Ladislao 2008; Frouin et al. 2010). TBT exhibits the strongest (known) toxic effects to gastropods, with at least 200 species known to be susceptible to TBT-induced endocrine disruption. TBT interferes with the gastropod endocrine systems by inhibiting the P450 cytochrome system, which is linked to the conversion of male hormones (androgens) to female hormones (estrogens) in females. The ecological effect is a masculinisation of females, which is termed **imposex**. Affected females grow a vas deferens and in severe cases a penis which eventually blocks the oviducts. Although egg production continues during several gradual stages of penis growth, eventually the organism is unable to maintain a constant production of eggs (**a** Figure 7.9). Advanced stages of imposex result in sterility, premature death of the female and subsequent population decline.

TBT also reduces growth rates in adult oysters, thickens oyster shells and reduces the meat content. The shell thickening is caused by an enzyme disfunction in shell deposition and results in making the oysters unmarketable. Oysters affected in this way are often referred to as **golf-ball oysters**.

The ecotoxicological impact of TBT on fish, birds, seals and other marine mammals has been less well studied, although there is considerable evidence that TBT causes immuno-suppression in these taxonomic groups, thereby acting as a co-factor in causing increased mortality of, for example, sea otters (Kannan et al. 1998). Based on a significant association between TBT concentrations and parasitic infection rates of lung nematodes in porpoises, Nakayama et al. (2009) suggest that OGTCs are responsible for increasing susceptibility of infectious disease for this species. Likewise, mass mortality of coastal bottle-nose dolphins in the USA has been attributed to immune suppression in these inshore dolphins which have significantly higher TBT tissue levels than their offshore counterparts (Tanabe et al. 1998).



■ Figure 7.9 ► Box 7.2: An imposex impacted female conch (right) with normal male conch (left). *Images*: FWC Research CC BY-NC-ND 2.0

#### 7.7.2 Advancing Technologies

Initially, the antifoulant paints that included TBT were designed so that the TBT would passively leach from the paint. However, the release rate was unpredictable and inconsistent, and therefore its antifoulant properties were not optimal. Self-polishing co-polymer paints were introduced in the 1970s. The advantage of this technology is that the biocide is slowly released as a result of wave action or the forward motion of the ship. Once the outer surface is worn away, the next layer begins to release the biocide. Thus, the biocidal activity of the antifoulant paint is consistent throughout its 5-year lifespan, which is twice that of the first TBT paints. Since the ban on TBT, copper has again become the most widely used antifoulant, but because of its well-established toxicity to non-target organisms, it has also come under increasing scrutiny. It is subject to restrictions in a number of countries such as Denmark and Canada and is entirely banned for the use on small boats on the Baltic Coast of Sweden. The US EPA is currently reviewing its regulation, and it is expected that restrictions on the use of copper will result from this review in the future (Blossom et al. 2018).

Other widely used additives to antifoulant paints are cybutryne (commonly referred to as Irgarol 1051) and diuron—both Photosystem II inhibiting herbicides, and chlorothalonil (a fungicide). These additives diffuse out of the paint and have been detected in marine waters and sediment throughout Europe, North and Central America and Asia (Harino et al. 2009; Thomas and Langford 2009). Since around 1990, there has been considerable interest in developing natural antifoulants that are synthesised by marine organisms. These include many different types of chemicals: toxins, anaesthetics, surfactants, attachment and metamorphosis inhibitors and repellents. To date, no natural antifoulants have been commercially released.

Perhaps the search for better or safe biocides is fundamentally flawed because the very properties that are required to be an effective biocide (toxic to algae, crustaceans and molluscs and reasonable persistence) are also the properties that mean the biocide is likely to exert harmful effects on non-target organisms. It is also complicated by the fact that there are multiple organisms in biofilms. In spite of these challenges, many novel approaches are being researched. Non-stick foul-release coatings, such as Intersleek 700, Sealion and Bioclean, which incorporate silicone elastomers, waxes or silicone oils, and natural coatings that utilise secondary metabolites with biocidal properties derived from soft corals, sponges and microorganisms, present the two main lines of research into nontoxic alternatives (e.g. Michalek and Bowden 1997). Nonstick technology, while entirely non-toxic, has one major disadvantage, they only self-clean effectively at high velocity (Dafforn et al. 2011), and therefore they are only suitable for high speed vessels. Other examples of novel approaches to inhibit fouling include electrical currents (Hong et al. 2008) and intelligent paints that take up copper from seawater (Elmas et al. 2018).

# 7.8 Effects of Pesticides in Marine Environments

Early investigations of pesticides in the marine environment focused on the biomagnifying persistent organic compounds and their transfer through food chains into higher order species including cetaceans, sharks and large fish such as tuna and marlin. The health of sea birds, particularly large species such as pelicans and sea eagles, which are at the top of the food chain, was also of early concern. Research on the effects of pesticide on marine organisms is growing, yet many national guideline values for single pesticides in marine waters are considered to be of only limited reliability for ensuring the protection of marine ecosystems. In essence, marine ecotoxicological data are insufficient to determine reliable guideline values for many pesticides and of the guideline values that have been determined they are generally lower for marine waters compared to freshwaters.

The effects of pesticides can be measured according to responses of organisms from the subcellular level to whole organism level to the ecosystem level. Table 7.8 shows the examples of the current literature of a range of pesticides on their toxicity to marine species. Most studies have been completed on commercially important species. Other studies have shown the effects of atrazine on corals, seagrass, macro algae, algae, coralline algae, diatoms, phytoplankton and cyanobacteria (e.g. Howe et al. 2017 and citations therein). Negri et al. (2019b) recently conducted a large study that determined the toxicity of 21 pesticides on 16 tropical aquatic species. Table 7.10 highlights the lack of sublethal EC50 data and highly variable exposure times for different studies. More ecotoxicological research needs to be conducted on pesticides relevant to the marine environment.

Very few studies have investigated the effects of multiple concurrent pesticide exposures nor has much research been completed on effects of pulse exposure that are more consistent with natural environmental flows to the ocean. The study of the toxicity of mixtures is essential to understanding the actual risk that pesticides pose to marine organisms. The multiple stressors that organisms may need to respond to may reduce their overall fitness which further reduces the resilience of the population and long-term intergenerational survivorship. A combination of pesticides, like those that are present in catchment runoff (Brodie and Landos 2019; Warne et al. 2020a; Spilsbury et al. 2020), may each only need to be present at low concentrations in order to see measurable responses. This is illustrated in work by Thai et al. (2020) who monitored the Great Barrier Reef in-shore marine waters at nine sites for 30 pesticides. As the Great Barrier Reef lagoon is a National Marine Park and a World Heritage Site, it is recommended that at least 99% of species should be protected (Australian Government and Queensland Government 2018). In monitoring for 2018/2019, they reported that no individual pesticide exceeded their corresponding Australian and New Zealand water quality guideline values (Thai et al. 2020). However, when the combined toxicity of pesticide mixtures was accounted for using the method developed by Warne et al. (2020b), it was estimated that between  $\sim$ 2 and 10% of aquatic species would experience adverse sub-lethal effects at three of the nine monitoring sites. Research continues to develop guideline approaches that include the consideration of mixtures, their varying concentrations, mode of actions and relative toxicity for a range of representative organisms and keystone species.

## 7.9 Summary

This chapter introduced you to the various types of pesticides and biocides, how they are transported to marine waters and the risks they pose to the marine

• Table 7.10 Examples of e been discussed earlier)	cotoxicological studies on the e	ffects of a range of pesticides on marine organisms ( <i>Note</i> TBT and $\varepsilon$	antifouling products are not include	d in this table as they have
Pesticide	Species affected	Exposure effect	Endpoint	Source
Azamethiphos (organo- phosphate) used for the control of sea lice	<i>Homarus Gammarus</i> European lobster	1-h LC50 8.5-75.7 μg/L 1-h EC50 9.2-15.5 μg/L	Larval survival Immobility	Parsons et al. (2020)
	<i>Metacarcinus edwardsii</i> crab	30-min exposure caused significant mortality at 10–500 $\mu g/L$	Larval survival	Gebauer et al. (2017)
Chlorpyrifos (organophosphate)	Litopenaeus vannamei prawn	4-day LC50 2.1 μg/L Elevated catalase activity (CAT) and Lipid oxidation levels (LPO) in muscle, hepatopancreas and gills. Decreased acetyl- cholinesterase (AChE) activity in the brain and an increased glutathion-S-transferase (GST) activity in the hepatopancreas	Adult survival and biochemical function	Duarte-Restrepo et al. (2020) See also review by Huang et al. (2020)
Diazinon (organophosphate)	Acropora tenuis scleractinian coral	48-h EC50 54.7 µg/L	Larval metamorphosis	Flores et al. (2020)
Deltamethrin (pyrethroid) insecticide used for the con- trol of sea lice	<i>Homarus Gammarus</i> European lobster	1-h LC50 2.6-2.9 ng/L 1-h EC50 0.4-0.6 ng/L	Larval survival Immobility	Parsons et al. (2020)
Imidacloprid (IMI) (neonicotinoid) insecticide	<i>Metapenaeus macleaya</i> Eastern school prawn	8-day exposure $1-4  \mu g/L$ alterations in metabolic homeostasis and more frequent moulting	Juvenile metabolic homeosta- sis and moulting	McLuckie et al. (2020)
	Acropora tenuis scleractinian coral	48-h EC50 347 μg/L	Larval metamorphosis	Flores et al. (2020)
	Saccostrea glomerate Sydney rock oyster	1 mg/L significant effect on gill AChE activity 4-day exposure to 2 mg/L resulted in significant changes in gene expression and 14 gene ontology terms overexpressed	Adult biochemical function Genotoxicity	Ewere et al. (2019)
Calypso 480 SC (neonicotinoid) insecticide	Mytilus galloprovincialis Bivalve mollusc	96-h LC30 7.77 g/L LC30	Adult survival	Stara et al. (2020)
Chlorothalonil fungicide	Acropora tenuis scleractinian coral	48-h EC50 6.0 μg/L	Larval metamorphosis	Flores et al. (2020)
Fipronil (phenylpyrazole) insecticide	Acropora tenuis scleractinian coral	48-h EC50 29.1 µg/L	Larval metamorphosis	Flores et al. (2020)
Propiconazole fungicide	Acropora tenuis scleractinian coral	48-h EC50 1008 μg/L	Larval metamorphosis	Flores et al. (2020)
DDT (organochlorine)	<i>Mercenaria mercenaria</i> hard clam	24-h LC50 0.61 mg/L	Juvenile survival	Chung et al. (2007)

(continued)

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	Source	Lawton et al. (2010)	Bouilly et al. (2003)	Anguiano et al. (2006)	Bouilly et al. (2007)	Howe et al. (2017)	Negri et al. (2011)	Wessel et al. (2007)	
	Endpoint	Juvenile survival	Juvenile and adult (genotoxic- ity: abnormal number of chro- mosomes)	Adult survival Cytotoxicity	Adult (genotoxicity: abnormal number of chromosomes)	Adult Photosynthesis reduction in ef- fective quantum yield (EQY)	Adult (EQY)	Embryos	
	Exposure effect	96-h LC50 5608 μg/L	Significant differences in aneuploidy after treatments of 46.5 nM and 465 nM in comparison to control	12-day LC50 2.22 mg/L 1.9 mg/L cell viability significantly decreased	Induction of aneuploidy after treatments of 300 and 3000 ng/L Significant aneuploidy in offspring	48-h EC50 8 μg/L	24-h EC50 2.98 μg/L	DNA strand breaks at 150 and 300 nM	
	Species affected	<i>Mercenaria mercenaria</i> Hard clam	Crassostrea gigas Pacific oyster	Crassostrea gigas Pacific oyster	Crassostrea gigas Pacific oyster	<i>Exaiptasia pallida</i> and in-hospite <sup>a</sup> <i>Symbiodinium</i> spp. anemone	Acropora millepora scleractinain coral	Crassostrea gigas Pacific oyster	un a host cell
• Table 7.10 (continued)	Pesticide	A trazine (triazine) herbicide		Lindane (gamma-HCH)	Diuron (organochlorine) herbicide			Endosulfan (organochlorine) pesticide	<sup>a</sup> In-hospite means living with

Pesticides and Biocides

environment. Because of their very purpose, pesticides are toxic to target organisms but sometimes also to non-target organisms and occupational exposure mainly of agricultural workers. There are further concerns about potential impacts on human health in relation to the consumption of contaminated food. The most common source of pesticides in marine ecosystems is application on land although some pesticides are used in marine situations (e.g. anti-fouling agents). Transport of pesticides to the ocean is predominantly via the atmosphere and surface waters. The physicochemical properties of the pesticides and the physicochemical conditions and biochemical processes in air and fresh and estuarine systems influence the pathway of pesticides to the marine environment.

Pesticide solubility in water can vary according to their chemical characteristics, and this, in turn, affects the exposure to organisms via water. Once in water, pesticides are distributed (via a process called partitioning) into various compartments of the environment (e.g. water, suspended particles, sediment, plant and animal tissue and the air). For example, pesticides will bind, in varying degrees, to organic and inorganic particles and/or dissolved forms of organic matter. Binding to particles leads to a decrease in exposure of water column dwelling organisms but increased exposure to sediment-dwelling organisms (meiobenthos). Binding to dissolved organic matter influences solubility and subsequent distribution and availability to biota. Different types of pesticides have different rates of degradation or half-lives and this defines how long they may persist in the environment and pose a toxic threat. There are relatively few studies that investigate the toxic effects of pesticides to marine organisms but measurable responses at environmental relevant concentrations have been reported.

### 7.10 Study Questions and Activities

- 1. Determine the logKow of a new pesticide 'A' that has solubility in water of 0.67 mg/L and a solubility in octanol of 576,850 mg/L. Is this pesticide likely to accumulate in fatty tissue, explain your answer?
- 2. If the concentration of pesticide 'B' in fish tissue was 15 mg/kg and water concentration is 0.0028 mg/L, what is the BCF?
- 3. If the concentration of Pesticide 'C' in polychaete tissue was 12 mg/kg and the sediment concentration is 43 mg/kg, what is the BSAF?
- 4. Describe 'global distillation' in your own words.
- Look up the FAO website: ► http://www.fao.org/faostat/en/#data/RP find the country you live in and using the FAOSTAT tool report the data available on organophosphate pesticide use in the country you live. Explore the website and the FAOSTAT tool.

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