Persistent Organic Pollutants (POPs)

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Abbreviations

AAS	Australian Academy of Science
ACS	American Chemical Society
BDE	Bromodiphenyl ether
BHC	An acronym for “benzene hexachloride”—a name sometimes used inappropriately for lindane (gamma-hexachlorocyclohexane). Using the acronym BHC for lindane is misleading because the 6 carbon ring chemical structure in the lindane molecule is cyclohexane, not a benzene ring. A more appropriate acronym for lindane is gamma HCH (HexaChlorocycloHexane).
CB	Chlorinated biphenyl
CDD	Chlorinated dibenzodioxin
CDF	Chlorinated dibenzofuran
DDD	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethane
DDE	1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethylene
DDT	DichloroDiphenylTrichloroethane, a shortened version of a former name used for 1,1′-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene)
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HBCDD	Hexabromocyclododecane
HCBD	Hexachlorobutadiene
HCH	Hexachlorocyclohexane
NDP	National Dioxin Program
OCDD	Octachlorodibenzodioxin
OCDF	Octochlorodibenzofuran
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-*p*-dioxin
PCDF	Polychlorinated dibenzofuran
PCN	Polychlorinated naphthalene
PCP	Pentachlorophenol
PeCB	Pentachlorobenzene
PFOA	Perfluorooctanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFOS	Perflurooctanoic acid
POP	Persistent Organic Pollutant
POPRC	Persistent Organic Pollutants Review Committee
SCCP	Short-chain chlorinated paraffin
TCDD	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin
TEF	Toxic equivalent factor
TEQ	Toxic equivalent
UNEP	United Nations Environment Programme
USA	United States of America (USA)
WHO	World Health Organization
WHO-TEF	A TEF (toxic equivalent factor) published by the World Health Organisation

8.1 Introduction

Anyone interested in the history of environmental chemistry, and in particular the management and remediation of pollution, soon encounters the term **POP** along with the **Stockholm Convention** and **the dirty dozen**. This chapter gives an overview of this topic. It provides an important expansion of ▸ Chapter 7 on pesticides and biocides further addressing those pesticides that are also classified as POPs along with POPs that are derived from other sources.

The acronym **POP** is used for each member of a group of compounds called Persistent **Organic Pollutants**. The Stockholm Convention is an international agreement endorsed by most nations with the intent of managing (limiting the generation and usage, and where possible eliminating) further environmental contamination by this problematic group of chemicals. Some countries have not yet ratified (officially adopted) the terms of the Convention, (for example, the United States of America (USA)), or only partly ratified. The term **the dirty dozen** (a common descriptor for a group comprising 12 individuals of ill-repute) was used for the original 12 POPs listed in the Stockholm Convention in 2001.

The POPs are of concern because not only are they toxic contaminants but they also have a strong potential to bioaccumulate and persist (▶ Box 8.1). This aspect of their environmental fate and impact is related to their physicochemical properties.

Box 8.1: Definition of POPs and Their Problematic Properties

As defined by the United Nations Environmental Programme (UNEP) Stockholm Convention (UNEP 2018), Persistent Organic Pollutants (POPs) are organic (i.e. carbon-based) compounds possessing a particular combination of physical and chemical properties such that, once released into the environment, they:

- remain intact for exceptionally long periods of time (many years);
- become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air;
- accumulate in the fatty tissue of living organisms including humans, and are found at higher concentrations at higher levels in the food chain; and
- are toxic to both humans and wildlife.

8.2 History of POPs

As highlighted in ▶ Chapter 7, the problems of bioaccumulation and toxic effects associated with pesticides that are POPs became widely recognised with the publication of *Silent Spring* (Carson, 1962), which publicised the unintended environmental consequences associated with the use of organochlorine insecticides including DDT(◘ Figure 8.1), lindane (also known as BHC), heptachlor, and chlordane introduced during the 1940s and in widespread use by the 1950s. *Silent Spring* and the media publicity and public debate sent a

◘ **Figure 8.1** Spraying DDT in 1955 to manage western spruce budworm control, Powder River control unit, Oregon, United States of America (USA). *Source*: Wikimedia commons, *Photo*: R. B. Pope Date: July 1955 *Credit*: USDA Forest Service, Pacific Northwest Region, State and Private Forestry, Forest Health Protection. Collection: Portland Station Collection; La Grande, Oregon. *Image*: PS-1428 strong message to the community, and to governments and chemical regulators on a global scale (note: this happened before the internet or real-time social media communication was even conceived!).

Although the environmental impacts associated with POPs are now recognised by scientists and governments, the claims made in *Silent Spring* were hotly debated for many years following publication (ACS 2012). For example, in Australia in 1972 (a decade after the book was published), an enquiry established by the Australian Parliament was still reviewing and debating whether ongoing DDT use was problematic for wildlife and human health (Parliament of Australia, 1972). In 1972, the use of DDT in Australia and New Zealand was estimated as 900 tonnes per year (AAS 1972) despite restrictions introduced during the 1960s.

8.3 The Stockholm Convention

The focused attention by government agencies at an international scale on the environmental issues associated with POPs led to the establishment in 2001 of a global treaty among nations, formally known as the *United Nations Environment Programme (UNEP) Stockholm Convention on Persistent Organic Pollutants*. The convention, with the objective to "*protect human health and the environment from persistent organic pollutants*" came into force in 2004 and was ratified by 152 UN member states. By mid-2018, the number of ratifying states (including the European Union) had increased to 182 (◘ Figure 8.2).

The history, scope, amendments, and signatories can be found online at the United Nations Treaties website:

► https://treaties.un.org/Pages/ViewDetails.aspx?src=TREATY&mtdsg_no=XXVII-15&chapter=27&clang=_en

Full details of all aspects of the convention are available at the website of the Secretariat of the Stockholm Convention:

► http://www.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx

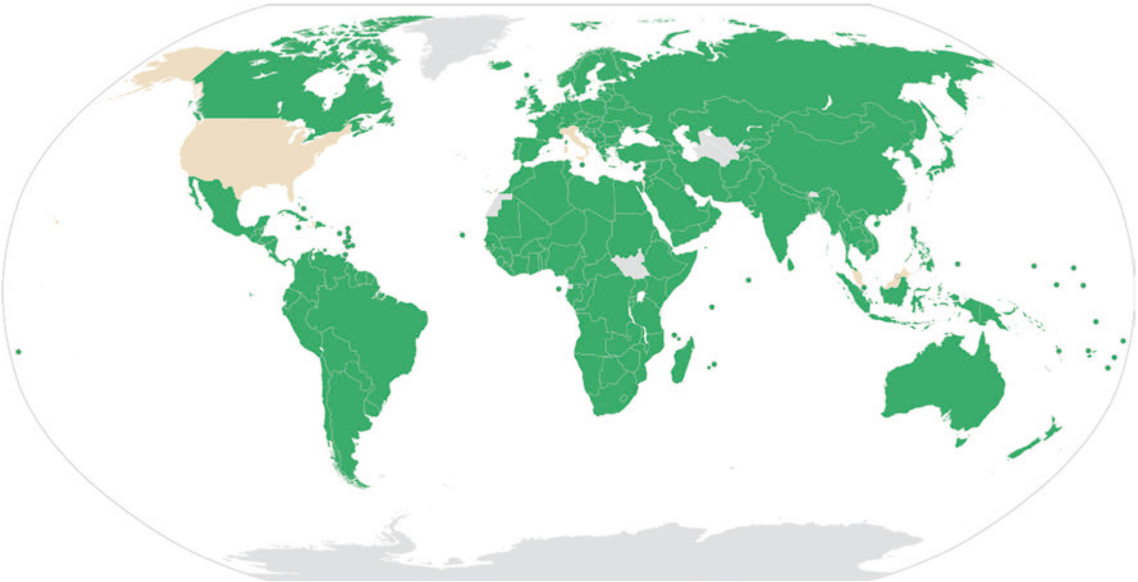
8.3.1 Overview of the Convention

The initial version of the convention covered 12 POP compounds known as **the dirty dozen**. The signatories to the original version of the convention agreed to:

- outlaw nine intentionally-manufactured POP chemicals;
- limit the use of DDT for malaria control; and
- reduce inadvertent production of dioxins and furans.

The convention committed developed countries to provide financial resources and measures to eliminate production and use of intentionally-produced POPs, eliminate unintentionally produced POPs where feasible, and manage and dispose of POP waste in an environmentally sound manner.

The convention includes an agreement to follow procedures to identify additional POPs and outlines the



◘ **Figure 8.2** Countries that have ratified the Stockholm Convention (green) and those that have signed but not ratified the convention (tan). *Source*: Wikimedia commons. *Author*: Canuckguy criteria applied in doing so. Under the convention, reviews of chemicals as potential new POPs are led by a Persistent **Organic Pollutants Review Committee (POPRC)** comprising government-designated experts in chemical assessment and/or management. The members are nominated by and represent the signatory nations on a regional basis. The review process accounts for persistence, bioaccumulation, potential for long-range environmental transport, and toxicity of potential new POPs.

A series of review reports on individual POPs, published by the POPRC are available online, for example, UNEP (2015) in respect of the brominated flame retardant c-Decabromodiphenyl ether (c-decaBDE).

8.3.2 Annexes and Exemptions for Some POPs

Under the Stockholm Convention, each of the POPs is assigned an agreed **Annex** status. These are **A**—elimination, **B**—restriction, and **C**—unintended production:

- Annex A POPs (elimination) are prohibited from production and use (except for specific usage exemptions allowed only for convention parties that register for the exemption) and may be imported or exported only under specific restrictive conditions.
- Annex B POPs (restriction) are restricted from production and use (except for registered acceptable purposes) and imported and exported only under specific restrictive conditions. An example is that DDT use is still permitted for disease vector control for serious diseases such as malaria.
- Annex C POPs (unintentionally produced) are subject to release reduction and elimination, and the use of the best available techniques and best environmental practices for preventing releases of POPs into the environment are promoted.

Exemptions for some POPs and their uses are allowed in cases where replacement technologies do not yet exist, or viable replacement technologies are not readily available. This enables signatories to the Convention to take measures to reduce or eliminate releases from intentional production and use. Exemptions are limited to a specific time period.

In addition, the convention requires that signatory nations ensure stockpiles and wastes consisting of, containing, or contaminated with POPs, are managed safely and in an environmentally sound manner. This requires that such stockpiles and wastes be identified and managed to reduce or eliminate POPs releases from these sources, and that transport of wastes containing POPs across international boundaries is done according to international rules, standards and guidelines.

8.3.3 The Original Set of 12 POPs Covered by the Stockholm Convention

The original **dirty dozen** POPs are listed in ◘ Table 8.1 with their structures and historical main uses, along with some general characteristics and toxicity. It is useful to note that:

- all are **chlorinated hydrocarbons** (also known as organohalogens) and nine are pesticides;
- all are chemically stable and **highly lipophilic** compounds that do not degrade readily even under extreme environmental conditions; and
- **some partially degrade into compounds of similar stability and toxicity**.

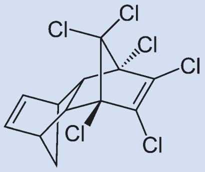
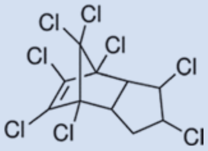
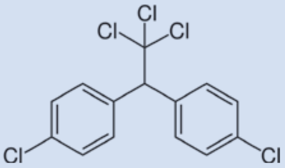
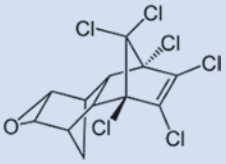
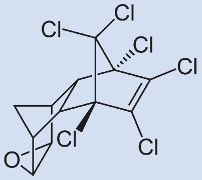
Furthermore, all have an established history of environmental persistence, bioaccumulation, and capacity for global distribution, and their use and release are associated with unintended adverse environmental consequences.

8.3.4 Additional POPs Now Covered by the Stockholm Convention

Since 2009, a further 16 compounds have been added to the listed Stockholm Convention POPs. In addition to several additional chlorinated hydrocarbons, the additions to the POPs list include several **polybrominated hydrocarbons** widely used as fire-retardants. The most recent **new POP** was added in 2015.

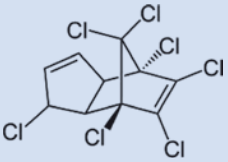
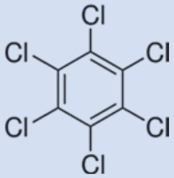
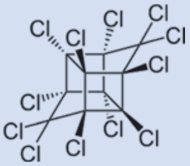
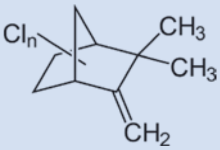
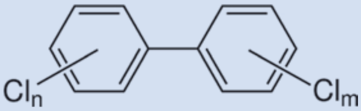
These new POPs are shown in ◘ Table 8.2 with their structures, uses, and general features of characteristics and toxicity. Like the original **dirty dozen** POPs, many of the additional POPs are chlorinated hydrocarbon pesticides, but also included are non-pesticide chlorinated hydrocarbons, several **brominated fire-retardant compounds**, and a **per-fluorinated compound** (known generally as a PFOS). Like the original POPs, these chemicals also have a demonstrated capacity for environmental persistence, for bioaccumulation, and for global distribution and most have been detected in the marine environment and various marine species. Studies of toxicity to marine species are limited for some POPs and consideration needs to be made about potential sources and risk to the marine environment. Atmospheric transport is an important pathway to the marine environment for some POPs. Their use and release are associated with unintended adverse environmental consequences.

Table 8.1 The original 12 POPs listed in the Stockholm Convention (the dirty dozen)

POP name	Structure, uses, characteristics and toxicity
Aldrin (listed in Annex A)	 Formerly used as a soil treatment to kill termites, grasshoppers, corn rootworm, and other insect pests. After release to the environment, aldrin rapidly converts to dieldrin (see below, this table) which is also toxic. Can cause sublethal and lethal effects on marine crustaceans, molluscs, fish and birds. Also toxic to humans. Half-life in soil: approximately 110 days.
Chlordane (listed in Annex A)	 Formerly used extensively to control termites and as a broad-spectrum insecticide on a range of agricultural crops. Can cause lethal and sublethal effects in marine crustaceans, molluscs, fish and birds. Impacts the immune system in humans and possible carcinogen. Half-life in soil: variable approximately 1–4 years.
DDT (listed in Annex B)	 Widely used during World War II to protect soldiers and civilians from malaria, typhus, and other diseases spread by insects. Subsequently, widespread use of DDT continued for disease control, and use increased rapidly for pest control on a variety of agricultural crops, especially cotton. DDT is still used against mosquitoes in several countries to control malaria. DDT degrades to DDD and DDE, both of which are extremely persistent and have similar toxicity as DDT. Potential for trophic transfer and also to offspring of suckling mammals established. Causes egg shell thinning in birds, particularly high trophic order birds. Toxic to marine crustaceans, molluscs and fish. Half-life in soil: 10–15 years.
Dieldrin (listed in Annex A)	 Degradation product of aldrin (see above, this table), consequently concentrations of dieldrin measured in the environment may in part reflect a history of both dieldrin and aldrin usage. Formerly used widely to control termites and textile pests, dieldrin was also used to control insect-borne diseases and insect pests living in agricultural soils. Highly toxic to fish and other aquatic animals. Half-life in soil: approximately 5 years.
Endrin (listed in Annex A)	 Formerly used to control pests on crops such as cotton and grains, and rodents such as mice and voles. Animals can metabolise endrin, so it does not accumulate in their fatty tissue to the extent as structurally similar chemicals. Toxic to marine fish, crustaceans, echinoderms and algae. Half-life in soil: up to 12 years.

(continued)

Table 8.1 (continued)

POP name	Structure, uses, characteristics and toxicity
Heptachlor (listed in Annex A)	 Formerly used to kill soil insects and termites including cotton insects, grasshoppers, other crop pests, and malaria-carrying mosquitoes. Believed to be responsible for the decline of wild bird populations including Canadian Geese and American Kestrels in the Columbia River basin in the USA. Toxic to amphipods, crustaceans, molluscs, and fish. Half-life in soil: 6–9 months.
Hexachlorobenzene (listed in Annex A) (listed in Annex C)	 First introduced in 1945 to treat seeds, HCB kills fungi that affect food crops. It is also a by-product of the manufacture of some industrial chemicals and exists as an impurity in several pesticide formulations. Potential for trophic transfer and also to offspring of suckling mammals established. Limited marine toxicity data available. Half-life in soil: Highly variable depending on climate 0.6–6.3 years.
Mirex (listed in Annex A)	 Used mainly to combat fire ants, and also against other types of ants and termites. One of the most stable and persistent pesticides. Also used as a fire retardant in plastics, rubber, and electrical goods. Limited marine toxicity data available. Half-life in soil: 10–12 years.
Toxaphene (listed in Annex A)	 Formerly used as a pesticide on cotton, cereal grains, fruits, nuts, and vegetables. It was also used to control ticks and mites in livestock. Toxic to marine crustaceans, molluscs, and fish. Long-term exposure highly toxic to fish, with effects including reduced reproductivity. Half-life in soil: Variable, from 3 months up to 12 years.
Polychlorinated biphenyls (PCBs) (listed in Annex A with exemptions) (listed in Annex C)	 These compounds were used in industry as heat exchange fluids, as fluids in electricity transformers and capacitors (Figure 8.3), and as additives in paint, carbonless copy paper, and plastics. Commercial mixtures of PCBs known as Aroclors were manufactured in large quantities (see ► Box 8.2). Of the 209 different types of PCBs, 13 exhibit a dioxin-like toxicity. Some studies show selected PCBs are toxic to marine crustaceans and molluscs, but research is limited. Half-life in soil: Their persistence in the environment corresponds to the degree of chlorination, and half-lives can vary from 10 days to 1.5 years.

(continued)

Table 8.1 (continued)

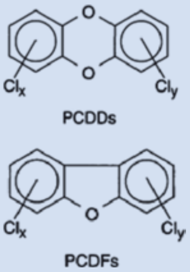
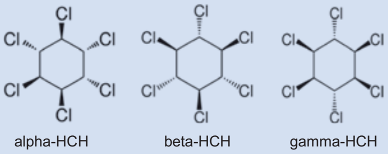
POP name	Structure, uses, characteristics and toxicity
Polychlorinated dibenzo-*p*-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs) (listed in Annex C)	 Produced unintentionally due to incomplete combustion, and also during the manufacture of pesticides and other chlorinated substances. Commonly emitted from the burning of hospital waste, municipal waste, and hazardous waste, and also from automobile emissions, peat, coal, and wood. There are 75 different dioxins, of which seven are considered to be of concern. Half-life in soil: Variable, 2.5–6.0 years.

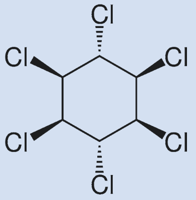
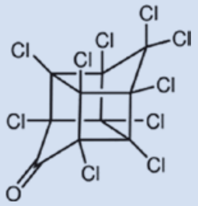
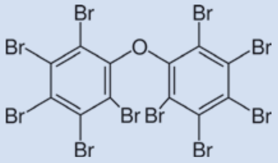
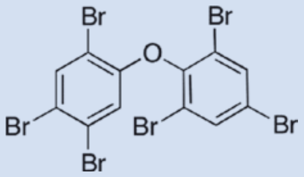
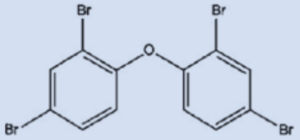
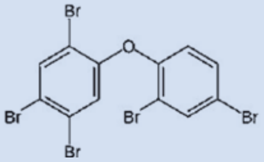
Figure 8.3 Liquid Aroclors (PCB mixtures) had worldwide use as dielectric fluid in transformers common throughout power supply grids. In practice, the dielectric is an oily liquid that surrounds the electricity-conducting copper wire coils inside the transformer. Its roles are cooling and electrical insulation, and both the transformer body and the cooling pipes visible on the outside of the transformer shown here are filled with dielectric fluid. The disposal of these PCB mixtures from obsolete and redundant equipment is an ongoing concern. Poor disposal practices in the past (e.g. to unlined landfill) caused serious widespread contamination of waterways and aquatic ecosystems. *Photo*: M. Mortimer

Table 8.2 Additional POPs listed in the Stockholm Convention since 2009

POP name	Structure, uses, properties and toxicity
Hexachlorocyclohexane (alpha-isomer HCH and beta-isomer HCH) (listed in Annex A without exemptions)	 The technical grade (meaning 'as manufactured') of hexachlorocyclohexane (HCH) contains five isomers, namely alpha-, beta-, gamma-, delta- and epsilon HCH. Use of alpha- and beta-HCH as insecticides was phased out years ago, but these chemicals were produced as by-products in the production of the gamma isomer (lindane). At many chemical plants an estimated 6–10 tons of alpha- and beta-HCH were produced for each ton of lindane manufactured (a ton is 0.9071 tonne). This resulted in large stockpiles of unwanted byproduct and site contamination (Fig. 8.4). Highly persistent in water, particularly in colder regions and may bioaccumulate and biomagnify in biota and arctic food webs, thus are often found in seals and polar bears. They are subject to long-range transport, classified as potentially carcinogenic to humans, and adversely affect wildlife and human health in contaminated regions. Half-life in soil: alpha-HCH 20 weeks; beta-HCH 7–10 years.

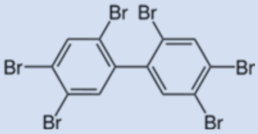
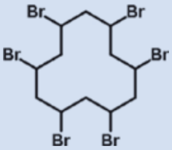
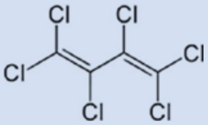
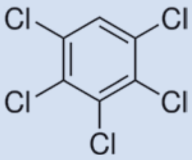
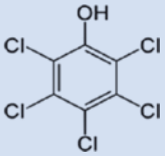
(continued)

Table 8.2 (continued)

POP name	Structure, uses, properties and toxicity
Lindane (gamma-isomer HCH) (listed in Annex A with exemptions)	 Gamma-hexachlorocyclohexane (lindane) formerly used as a broad-spectrum insecticide for seed and soil treatment, foliar applications, tree and wood treatment and against ectoparasites in both veterinary and human applications. Persistent, bioaccumulates easily in the food chain and bioconcentrates rapidly. Evidence of long-range transport and toxic effects (immunotoxic, reproductive and developmental effects) in laboratory animals and aquatic organisms. Toxic to marine rotifers, crustaceans, molluscs and fish. Half-life in soil: Variable, 3 months to over 3 years.
Chlordecone (listed in Annex A without exemptions)	 Similar compound to Mirex and used as an agricultural pesticide. Chlordecone (Kepone) was first produced in 1951 and commercially introduced in 1958. Currently, no use or production of the chemical is reported, as many countries have already banned its sale and use. Highly persistent, and with high potential for bioaccumulation and biomagnification. Physico-chemical properties and modelling data show that chlordecone can be transported for long distances. It is classified as a possible human carcinogen and is extremely toxic to aquatic organisms. Likely exposure pathway is via food. Limited study on toxicity to marine species. Half-life in soil: 1–2 years.
Decabromodiphenyl ether (Commercial mixture, c-decaBDE) (listed in Annex A with exemptions)	 Deca-BDE is used as an additive flame retardant, with many applications including in plastics/polymers/composites, textiles, adhesives, sealants, coatings and inks. DecaBDE-containing plastics are used in computer and TV casings, wires and cables, pipes and carpets. Commercially available decaBDE (c-decaBDE) contains small percentages of octa- and nona-BCE. Usage peaked in the early 2000s, but it is still extensively used worldwide. Adverse effects on fish and terrestrial species. Half-life in soil: Highly variable depending on conditions > 6 months up to 50 years.
Hexa- and hepta bromodiphenyl ether (Commercial octaBDE) (listed in Annex A with exemptions)	 Hexabromodiphenyl ether and heptabromodiphenyl ether are the main components of commercial octabromodiphenyl ether. The commercial mixture of octaBDE is highly persistent. The only degradation pathway is through debromination and producing other bromodiphenyl ethers. Many products and materials in use still contain these compounds. Highly persistent is highly bioaccumulative and has a high potential for long-range environmental transport. Marine toxicity poorly understood. Half-life in soil: Highly variably between compounds and environmental conditions, from several weeks up to a decade.
Tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE) (listed in Annex A with exemptions)	  Used as additive flame retardants. TetraBDE and pentaBDE are the main components of commercial pentabromodiphenyl ether. The commercial mixture of pentaBDE is highly persistent in the environment, bioaccumulative and has a potential for long-range environmental transport (it has been detected in humans throughout all regions). Considered toxic to fish and birds. Half-life in soil: Variable, aerobic soils 10 days to 1 year.

(continued)

Table 8.2 (continued)

POP name	Structure, uses, properties and toxicity
Hexabromobiphenyl (HBB) (listed in Annex A without exemptions)	 Formerly used as a flame retardant, mainly in the 1970s. No longer produced or used in most countries due to restrictions under national and international regulations. Highly persistent in the environment, highly bioaccumulative and with a high potential for long-range environmental transport. Half-life in soil: Variable.
Hexabromocyclododecane (HBCD or HBCDD) (listed in Annex A with exemptions)	 Formerly used as a flame retardant additive to polystyrene materials in the 1980s as a part of safety regulation for articles, vehicles, and buildings. Highly toxic to marine diatoms and considered very toxic to other marine biota. Half-life in soil: ~8 months.
Hexachlorobutadiene (HCBD) (listed in Annex A without exemptions) (Also listed in Annex C)	 Hexachlorobutadiene is commonly used as a solvent for other chlorine-containing compounds. It is no longer intentionally produced but is a by-product in the manufacture of chlorinated aliphatic compounds such as carbon tetrachloride and tetrachloroethene (both produced on a large scale). Highly persistent in the environment, highly bioaccumulative and with a strong potential to bioaccumulate and biomagnify, and has a potential for long-range environmental transport. It is extremely toxic to aquatic organisms. Toxic to marine invertebrates and fish. Half-life in soil: 4–26 weeks.
Pentachlorobenzene (PeCB) (listed in Annex A without exemptions) (Also listed in Annex C)	 Formerly used in PCB products, in dyestuff carriers, as a fungicide and a flame retardant. May still be used as a chemical intermediate (e.g. for the production of quintozene). Also produced unintentionally during combustion, thermal and industrial processes, and present as an impurity in products such as solvents or pesticides. Persistent in the environment, highly bioaccumulative and has a potential for long-range environmental transport. It is moderately toxic to humans and very toxic to aquatic organisms. Toxic to marine molluscs, crustaceans and fish. Half-life in soil: 45 days.
Pentachlorophenol and its salts and esters (PCP) (listed in Annex A with exemptions)	 Former uses as herbicide, insecticide, fungicide, algaecide, disinfectant and in antifouling paint. Applications included agricultural seeds, leather, wood preservation, cooling tower water, rope and in paper manufacture. Contaminants can include other polychlorinated phenols, PCDDs, and PCDFs. Toxic to algae, invertebrates and fish. Half-life in soil: weeks to months~45 days.

(continued)

Table 8.2 (continued)

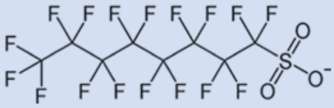
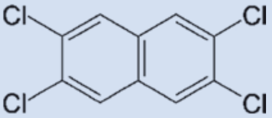
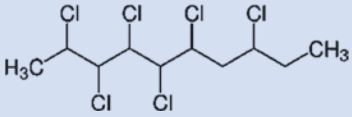
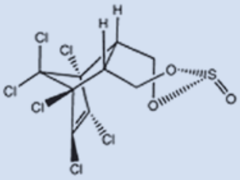
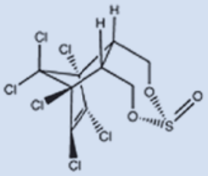
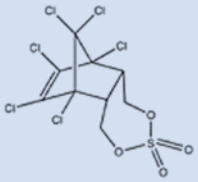
POP name	**Structure, uses, properties and toxicity**
Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS) (listed in Annex B with exemptions)	 PFOS is both intentionally produced and is a degradation product of related anthropogenic chemicals. The current intentional use of PFOS is widespread and includes: electric and electronic parts, fire-fighting foam, photo imaging, hydraulic fluids and textiles. PFOS is still produced in several countries. PFOS is extremely persistent and has bioaccumulation and biomagnifying properties. However, PFOS does not follow the classic pattern of other POPs by partitioning into fatty tissues, but instead binds to proteins in the blood and the liver. It has a capacity to undergo long-range transport and also meets the toxicity criteria of the Stockholm Convention. Limited study of toxicity to marine species, impacts measure on molluscs and fish. Half-life in soil: Highly variable: years to decades.
Polychlorinated naphthalenes (PCNs) (listed in Annex A with exemptions) (also listed Annex C)	 Commercial PCNs are mixtures of up to 75 chlorinated naphthalene congeners plus byproducts, used for insulated coatings on electrical wires, and as wood preservatives, rubber and plastic additives, for capacitor dielectrics and in lubricants. PCNs are unintentionally generated during high-temperature industrial processes in the presence of chlorine. While some PCNs can be broken down by sunlight and, at slow rates, by certain microorganisms, many PCNs persist in the environment. Bioaccumulation is confirmed for tetra- to hepta- CNs. Toxic to marine algae and crustaceans. Limited studies. Half-life in soil: >1 year.
Short-chain chlorinated paraffins (SCCPs) (listed in Annex A with exemptions)	 Used as a plasticiser in rubber, paints, adhesives, flame retardants for plastics as well as an extreme pressure lubricant in metal working fluids. SCCPs are produced by chlorination of straight-chained paraffin fractions. Appear to be hydrolytically stable and sufficiently persistent in air for long-range transport to occur and lead to significant adverse environmental and human health effects. Many SCCPs bioaccumulate. Toxic to marine algae, invertebrates but limited other studies. Half-life in soil: Variable.
Technical endosulfan and its related isomers (listed in Annex A with exemptions)	 α-Endosulfan (Endosulfan-I)  β-Endosulfan (Endosulfan-II)  Endosulfan Sulfate Used as an insecticide/acaricide since the 1950s to control crop pests, tsetse flies and ectoparasites of cattle, and as a wood preservative. Currently used as a broadspectrum insecticide to control a wide range of pests on a variety of crops including coffee, cotton, rice, sorghum and soy. Endosulfan occurs as two isomers: alpha (α)- and beta (β)-endosulfan. Technical endosulfan is found as a mixture of conformational stereoisomers, typically in a roughly 70:30 mix of -: β- isomers. The α- isomer, or endosulfan-I, is more thermally stable, and the β- isomer, endosulfan-II, will irreversibly convert to the α- isomer, though the process is slow. The primary degradation product of endosulfan is endosulfan sulfate. Endosulfan bioaccumulate has the potential for long-range transport and is toxic to humans and a wide range of aquatic and terrestrial organisms. Toxic to marine algae, annelids, echnioderms, crustaceans, molluscs and fish. Half-life in soil: 2 months to 2.5 years.

Figure 8.4 Dumping of residual HCH isomers at a former lindane factory in the 1950s. *Source*: Vijgen (2006)

The addition of new POPs to the convention is a dynamic process, with an established protocol for expert review of changes (see ▶ Section 8.3.1). Very recently, in June 2022, the Conference of the Parties to the Stockholm Convention amended Annex A to list "*perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds in Annex A without specific exemptions (decision SC-10/13)*". For specific details see ▶ http://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx. The pesticide Methoxychlor, the flame retardant Declorane Plus, and a plastic stabiliser UV-238 are being reviewed for listing as POPs.

Box 8.2: Aroclors and Other Commercially Manufactured PCB Mixtures

PCBs were produced on a commercial scale as specific PCB congener mixtures formulated to obtain chemical properties desired for specific industrial applications. Most of these mixtures were produced for use as dielectric fluid in electrical transformers and capacitors, with other uses including hydraulic fluids, printing inks, and carbonless copy paper.

PCBs were produced commercially in the USA from 1929 through to 1977 by the Monsanto Chemical Company and marketed as mixtures called Aroclors. Monsanto reportedly produced from 500,000 to 600,000 tonnes of PCBs (about half the worldwide total) during its almost 50 years of production. PCB mixtures manufactured outside the USA by others had trade names such as Clophen (Germany), Prodolec (France), and Phenoclor (Japan). Although such PCB mixtures are no longer used, large quantities of Aroclors are present in old equipment still in use and as a legacy of poor disposal practices (e.g. into landfills) and potentially available for release to the environment.

The Aroclors manufactured in the USA each have a four-digit identification number. The last two digits (e.g. 60 in Aroclor 1260) indicate the average percentage of chlorine by weight in the mixture. Most Aroclor names have 12 as the first two digits, but this is not related to chemical structure. Aroclors 1016, 1242, 1254, and 1260 together comprised more than 90% of the PCBs that were produced in the USA. Note that **Aroclor** (a registered trade name of the Monsanto Company) is the correct spelling. However, it often appears **misspelt as Arochlor**.

8.4 Naming Conventions for Individual PCCD, PCDF, and PCB Compounds

The naming of the individual structural congeners is based on the number and positions of the chlorine atoms (▶ Box 8.3). The general formulae for PCCD (dioxins), PCDF (furans) and PCBs (polychlorinated biphenyls), along with two example structures are illustrated at ◘ Figure 8.5. For PCCD and PCDF, the numbers 1–9 indicate the possible positions of the chlorine atoms. For PCB, the numbers 2–6 (2′–6′) indicate the possible positions of the chlorine atoms at ortho(o), meta(m), and para(p) positions, respectively.

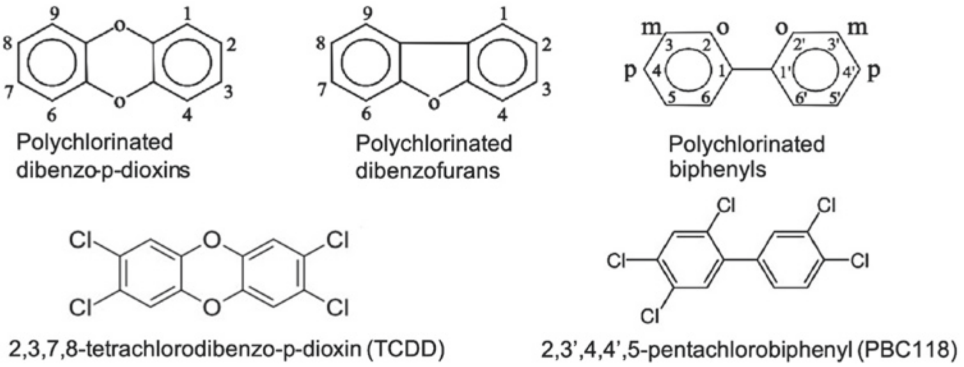


Figure 8.5 Chemical structures and naming conventions for PCDDs, PCDFs and PCBs

Box 8.3: The Meaning and Use of the Terms 'Congener', 'Congener Number', 'Homologue', and 'Homologous Series'

In chemistry, **congeners** are chemical substances **related to each other by origin, structure, or function**, and a **homologous series** is a set of compounds with the same functional group and similar chemical properties in which the members differ by the number of repeating units they contain. An example is the homologous series of straight-chained alkanes: i.e. methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), etc. In that series, each successive member differs in structure by the addition of an extra methylene bridge (the -CH_2- unit) inserted in the carbon chain.

A **homologue** (alternative spelling: homolog) is a compound belonging to a homologous series.

In the context of PCBs, polychlorinated dibenzo-*p*-dioxins (dioxins), and furans, the term **congener** is used to refer to an individual PCB, or dioxin, or furan compound within the series. Each of the different possible PBC structures is a **congener**, and PCBs occur in 209 congeners, with each structure unique in terms of the location of chlorine atoms within the PCB molecule. For example, the single chlorine atom in chlorobiphenyl can be in one of three locations, and the two chlorine atoms in dichlorobiphenyl can be located in any two of 12 locations in the PCB molecule.

The 209 possible PCB congeners can be named by their IUPAC or **BZ congener number** (for example, 2,3′,4,4′,5-penta polychlorinated biphenyl is **PCB 118** on the list of 1 through 209 possible congeners). The **BZ** is an acronym for the names of the authors (Ballschmiter and Zell) who proposed this identification system in 1980.

See ▶ https://www.epa.gov/sites/production/files/2015-09/documents/congenertable.pdf for the list and structure of all 209 PCB congeners.

Similarly, there are also 209 possible congeners of both PBBs (Polybrominated biphenyls) and PBDEs (polybrominated diphenyl ethers) (since like PCB, they are based on a double benzene structure), whereas CDDs (chlorinated dibenzodioxins) and CDFs (chlorinated dibenzofurans) have 75 and 135, possible congeners, respectively. BZ congener numbers are also assigned to each series.

In the context of polychlorinated dibenzo-*p*-dioxins (dioxins), the term **homologous series** means a group of dioxins with the same degree of chlorination (that is, with the same number of chlorine atoms in their structure, regardless of the positions of the chlorines in the dioxin structure). For example, the set of dioxins with five chlorines (the penta-CDDs) together comprise a homologous series, and the set of dioxins with six chlorines (the hexa-CDDs) is together another homologous series. Similarly, with the PCBs, PBBs and PBDEs and with the furans—the group of PCBs (or group of PBBs, PBDEs and furans) with the same number of chlorines (or bromines for PBBs and PBDEs) is a **homologous series**.

8.5 Assessment of Toxicity and Quantifying Exposure Risks for POPS

The toxicity of POPs can be expressed in standard terms such as LC50, EC50, etc. (see ▶ Chapter 3). However, POPs are commonly present in an environmental sample as a mixture of related compounds (see ▶ Chapter 14), for which the individual concentrations are measured and reported. Such **mixtures** may comprise both the parent compound and its breakdown products and metabolites—each with their own specific toxicities (e.g. DDT is commonly found with its breakdown products DDE and DDD). Some POPs are found and measured in the environment in one or more isometric forms (for example, hexachlorocyclohexane—HCH). Other examples are heptachlor (mostly found as heptachlor epoxide), and endosulfan (both parent isomers and endosulfan sulphate).

Where toxicities of parent material and breakdown product are similar, the concentrations present are often listed and assessed as totals (e.g. total DDTs). However, for some POPS such as PCDDs, PCDFs, and PCBs assessments of toxicity and exposure risks are more complex, as these POPS typically occur in the environment as mixtures of congeners with a wide range of potential toxicities.

8.5.1 Assessment of Toxicity and Exposure Risks for Dioxins, Furans, and Dioxin-Like PCBs

Dioxins, and furans have similar chemical structures, properties, and toxicities. By convention, when discussing toxicity and exposure risks, the term **dioxins** or **total dioxins** is generally taken to include PCDDs, PCDFs and **dioxin-like PCBs**. The **dioxin-like PCBs** are those PCB compounds exhibiting similar toxicity to dioxins, with toxic responses expressed including dermal toxicity, immunotoxicity, reproductive deficits, teratogenicity, endocrine toxicity and carcinogenicity/tumour promotion similar to those observed for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

8.5.2 The Meaning and Use of the Terms TEF and TEQ

In the environment, PCDDs, PCDFs, and **dioxin-like PCBs** are usually present in complex mixtures. For example, with PCBs, the proportion of congeners present in environmental samples is often related to the composition of the commercial formulation that is the source of contamination (e.g. Aroclor).

The World Health Organization (WHO) identifies 29 closely-related PCDD, PCDF, and **dioxin-like PCB** congeners as having a common mechanism of toxicity to PCBs. However, since their toxicities differ, WHO has adopted a **toxic equivalent factor** (**TEF**) for each of the 29 congeners to calculate a human risk assessment for individual components of the chemical mixture. TEFs are weighting factors assigned to specific congeners to reflect their toxicity relative to that of the most toxic dioxin, TCDD with $\text{TEF}=1$.

The WHO-adopted TEFs are listed in Table 8.3. The original set of TEFs was adopted in 1998, but new TEF values were adopted following a review in 2005. The rationale and methods used in the TEF review process are reported in Van den Berg et al. (2006).

The toxicity of a mixture of PCDDs, PCDFs, and dioxin-like PCBs is quantified as its **Total TEQ**. To calculate Total TEQ, the concentration of each congener present is multiplied by that congener's TEF to determine a **weighted** concentration or **toxic equivalent** (TEQ), and the total toxicity of the mixture is the sum of the individual congener TEQs as shown in Eq. 8.1.

$$\begin{aligned}\text{Total TEQ} &= ([\text{PCDD}_i] \times \text{TEF}_i)_n \\ &+ ([\text{PCDF}_i] \times \text{TEF}_i)n + ([\text{PCB}_i] \times \text{TEF}_i)_n\end{aligned} \tag{8.1}$$

where:

$i=$ a unique number assigned to each individual chemical applied iteratively starting at 1 and proceeding sequentially.

$n=$ the total number of unique pollutants.

Such results are expressed in concentration units such as picogram TEQ per gram.

It is important when comparing contamination assessments between sites, and/or for assessing historical changes in POP concentrations and distribution, that TEQ assessment dates are checked to ensure that all TEQs and conclusions are based on the current (2005) WHO-TEQs, and to recalculate any Total TEQs that are based on out-of-date TEQs (e.g. assessments dated earlier than 2005).

8.5.3 Use of Homologues and Congener Profiles in Forensic Investigations

Knowledge of the contaminant constituents in a sample containing a mixture of dioxins, furans, PCBs and/or PBBs, and PBDEs can be useful in developing a characteristic profile of contaminants present. For example, patterns of similarity in the presence and relative concentrations of members of a homologue set can be used to describe similarities and differences in contamination patterns between sites or across environmental media (e.g. EPHC 2005).

Frequently, similarities in **homologue and congener profiles** can be used as a **fingerprint** to make associations between PCDD/PCDF/PCB and/or PBB and PBDE contamination at a site and historical activities associated with the site. Similarly, PCDD/PCDF/PCB and/or PBB and PBDE profiles in samples from exposed persons/fish/livestock/food can be compared with profiles in samples taken from potential sources of the contamination. However, congener composition in a mixture released to the environment can change over time, making **fingerprinting** a complex task (Saba and Boehm, 2011).

Air, sediment, biota, and water samples are the most likely to have had their congener composition changed by environmental conditions. For example, composition changes can occur because PCDD/PCDF/PCB congeners with fewer chlorine atoms tend to partition into air and water more readily than those with more chlorine atoms. The relative partitioning potentials can be assessed from the partition coefficients

Table 8.3 Summary of WHO 1998 and WHO 2005 TEF values. Bold values show changes from 1998 to 2005. Adapted from Van den Berg, et al. 2006; see also ► https://www.who.int/ipcs/assessment/tef_values.pdf

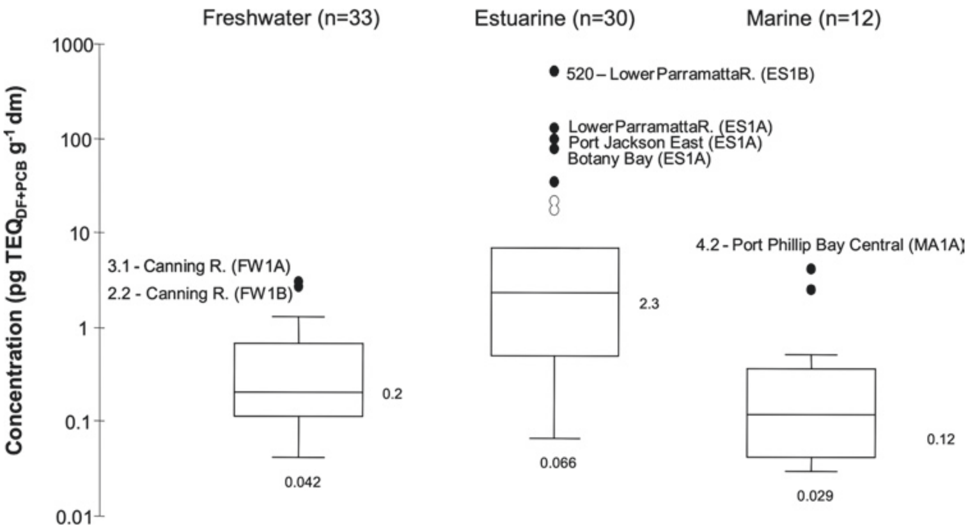
Compound	WHO 1998 TEF	WHO 2005 TEF
Chlorinated dibenzo-*p*-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	**0.0003**
Chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	**0.0003**
Non-*ortho*-substituted PCBs		
3,3′,4,4′-tetraCB (PCB 77)	0.0001	0.0001
3,4,4′,5-tetraCB (PCB 81)	0.0001	**0.0003**
3,3′,4,4′,5-pentaCB (PCB 126)	0.1	0.1
3,3′,4,4′,5,5′-hexaCB (PCB 169)	0.01	**0.03**
Mono-*ortho*-substituted PCBs		
2,3,3′,4,4′-pentaCB (PCB 105)	0.0001	**0.00003**
2,3,4,4′,5-pentaCB (PCB 114)	0.0005	**0.00003**
2,3′,4,4′,5-pentaCB (PCB 118)	0.0001	**0.00003**
2′,3,4,4′,5-pentaCB (PCB 123)	0.0001	**0.00003**
2,3,3′,4,4′,5-hexaCB (PCB 156)	0.0005	**0.00003**
2,3,3′,4,4′,5′-hexaCB (PCB 157)	0.0005	**0.00003**
2,3′,4,4′,5,5′-hexaCB (PCB 167)	0.00001	**0.00003**
2,3,3′,4,4′,5,5′-heptaCB (PCB 189)	0.0001	**0.00003**

of the individual compounds. For this reason, air and water samples are likely to be **enriched** with congeners with fewer chlorine atoms. In addition, the concentrations of individual congeners present in biota samples can also be altered through bio-degradation, with some congeners being selectively reduced and others remaining constant. Similar biodegradation involving debromination can occur with brominated contaminants, in fact more readily since the carbon-bromine bond is weaker than the carbon-chlorine bond.

8.6 Case Studies

8.6.1 Case Study 1—Dioxins, Furans, and Dioxin-Like PCBs in the Australian Aquatic Environment.

A comprehensive overview of dioxins, furans, and dioxin-like PCBs in Australia is provided in the series of studies comprising the National Dioxin Program



▣ **Figure 8.6** Concentrations of dioxin-like chemicals in aquatic sediments in Australia. *Source*: Müller et al. (2004)

(NDP) (EPHC 2005). The distributions of these POPs in the Australian aquatic environment are covered in Technical Report No. 6 (Müller et al. 2004). This study of Australian aquatic sediments showed that dioxins, furans, and dioxin-like PCBs were found in all samples, with middle-bound concentrations ranging from 0.002 to 520 pg TEQ g/dm (calculated using 1998 WHO-TEFs).

Aquatic sediments from urban/industrial sampling locations had significantly greater concentrations of dioxin-like chemicals than samples from remote and agricultural locations. The greatest concentrations occurred in sediments from the Parramatta River estuary (100 and 520 pg TEQ g/dm, ▣ Figure 8.6).

This pattern of POP distribution was similar in the case of bivalves and fish (▣ Figures 8.7 and 8.8). However, concentrations in the aquatic environment (sediments, bivalves and fish) were in most cases less than published levels for other industrialised countries.

Homologue and congener profiles for PCDD/PCDF were strongly dominated by OCDD, with the 1,2,3,4,6,7,8-heptachloro dibenzodioxin usually the congener with the second-highest concentration (▣ Figure 8.9).

8.6.2 Case Study 2—Spatial and Temporal Trends in Concentrations of Brominated Fire-Retardant POPs in Arctic Marine Mammal Tissues

Why are Arctic Marine Mammals at a High Risk of Bioaccumulating POPs?

Long-term **global transport pathways** for POPs result in the seas and **oceans being the ultimate sink for most of the** POPs released to the environment. In particular, the major processes for global transport of POPs tend to accumulate them in the colder waters of the polar regions—for example, the Arctic is well recognised as a sink for many POPs due to their repeated deposition and remobilisation (Breivik et al. 2007; Burkow and Kallenborn, 2000) (see also Chapter 7, ► Section 7.6.2). As a consequence, marine animal life is exposed to the hazard of bioaccumulating POPs, and particularly marine mammals (seals, walruses, sea otters, polar bears, and whales) since they are relatively long-lived, air-breathing animals and are relatively high in the marine food chain—especially polar bears.

The major route of uptake of lipophilic POPs by air-breathing aquatic animals is through diet. This is in contrast to the importance of lipophilic POP uptake from the water column through gill membranes in aquatic animals such as fish and aquatic invertebrates.

Potential routes of excretion of accumulated lipophilic POPs in air-breathing aquatic animals are also different from the routes of excretion for lipophilic POPs available to marine fish and crustaceans. In marine fish and crustaceans, the membranes of gills or equivalent organs, provide an important route for excretion of lipophilic POP contaminants to the surrounding water. The availability of this important excretion route in marine fish and crustaceans tends to limit the accumulation of persistent lipophilic compounds to an equilibrium concentration in the tissue lipids that is mediated by the partition coefficients for the POPs between blood lipid and water. However, air-breathing aquatic animals lack this excretion pathway for lipophilic contaminants to the surrounding water. Instead of excreting lipophilic compounds across

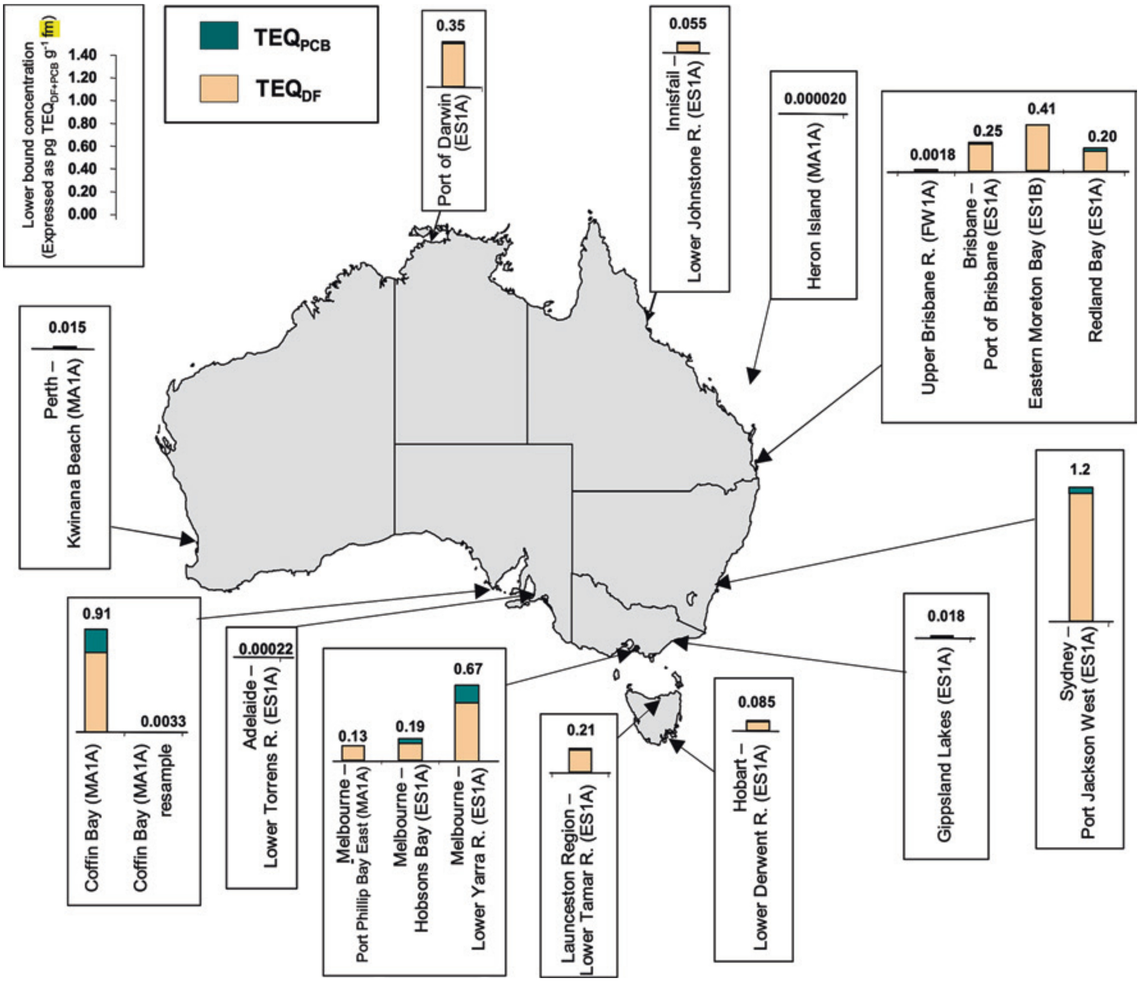


Figure 8.7 Geographical distribution of dioxin-like chemicals in Australian bivalve samples as TEQ values (from WHO 1998 TEFs) on a fresh mass basis. *Source*: Müller et al. (2004)

gill membranes to the surrounding water, air-breathing mammals are able to excrete such contaminants to air subsequently exhaled from the lungs. However, partitioning of lipophilic POPs from the blood plasma lipids across lung membranes to air subsequently exhaled from the lungs is much less efficient due to the orders of magnitude differences between typical POPs partition coefficients between lipid and water (Kow) versus lipid and air (Koa). The octanol-water coefficient (Kow) is a recognised surrogate for the partition coefficient between biotic lipid and water (Gobas and Mackay 1987) (see also ▶ Section 7.5.3, Chapter 7). Since Kow values for POPs typically range from 10^4 to 10^7, but Koa values range from 10^6 to 10^{12} (Wania and Mackay 1999), it is likely that rates for POPs partitioning from blood lipid into air via lungs in air-breathing are 1 to 3 magnitudes lower than for partitioning from blood lipid to water via gills. This leads to the expectation that because marine mammals are air-breathers, dietary acquired lipophilic POPs will inexorably accumulate in their tissue lipids.

Confounding Factors Involved When Assessing Spatial and Temporal Trends in POP Concentrations in Arctic Marine Mammals.

Although many studies have measured POPs concentrations in Arctic marine mammals, valid spatial or temporal comparisons are challenged by several confounding factors—for example that historical measurement data may not specify proximity of sampled animals to human populations and also biological factors such as species, age, health, and sex. In addition, sampling and analytical methodology for many organic contaminants was not standardised, making the results not easily comparable between studies (Green and Larson 2016).

For all mammals, transfer of lipophilic contaminants from mother to offspring is likely during lactation, resulting in increased body burden of contaminant in offspring and reduced burden in lactating females, thus sampling may show a pattern of greater contaminant concentrations in males than in females. However, this may be confounded in sampling data by

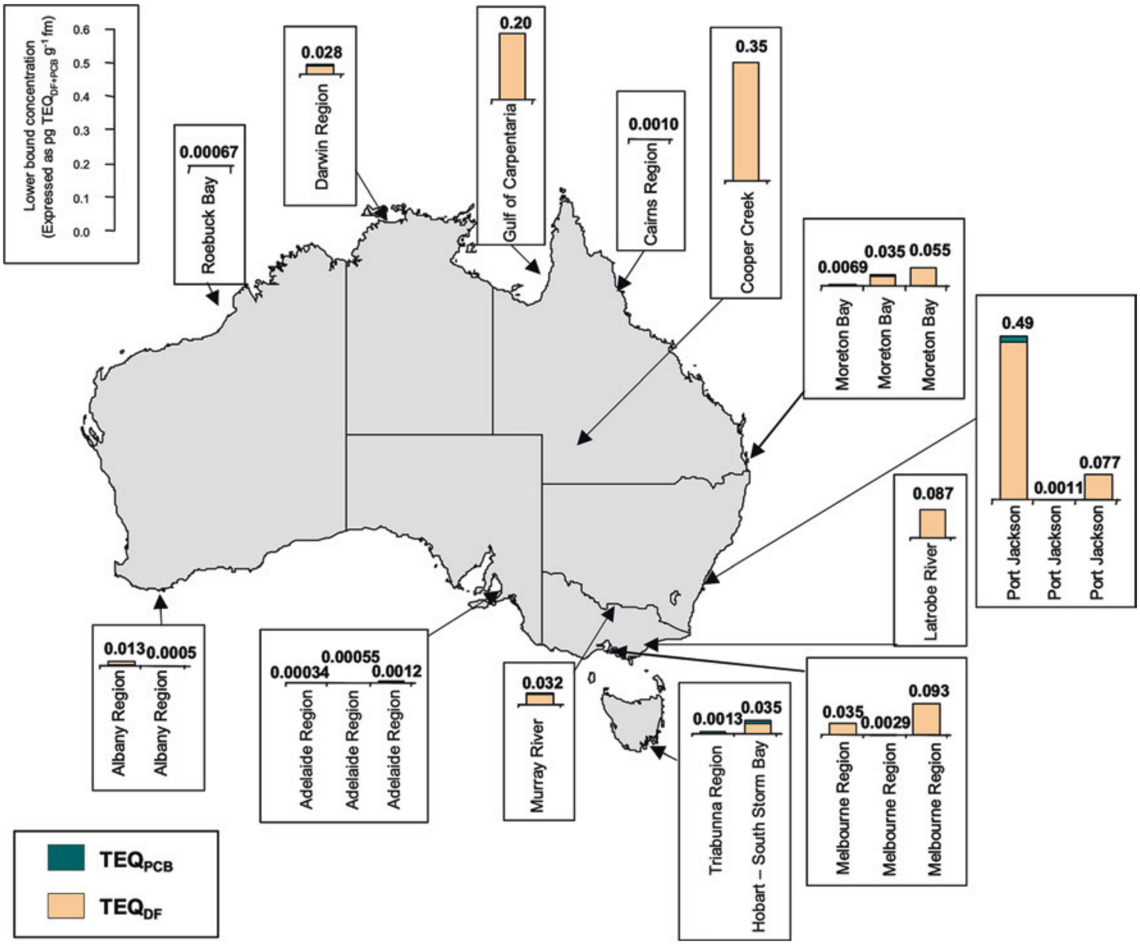


Figure 8.8 Geographical distribution of dioxin-like chemicals in Australian fish samples as TEQ values (from WHO 1998 TEFs) on a fresh mass basis. *Source*: Müller et al. (2004)

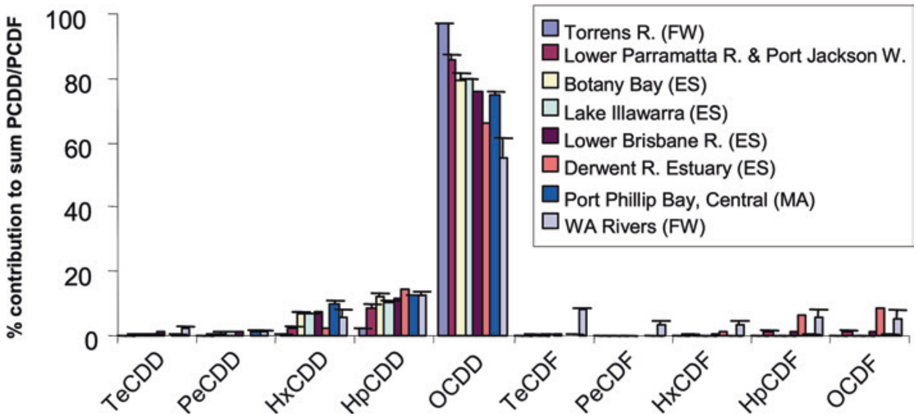


Figure 8.9 PCCD/PCDF homologue profile for sediments sampled from various locations in Australia. *Source*: Müller et al. (2004)

other factors such as differences in diet and body condition at the time of sampling, for example, in polar bears (Lippold et al. 2019; Tartu et al. 2017). In respect to the influence of diet, it is suggested (Letcher et al. 2009) that changes in contaminant body burden of POPs can occur in polar bears in western Hudson Bay as a consequence of the dietary shifts by these animals over the past several decades (Bentzen et al. 2007; Thiemann et al. 2008) from ice-associated to open-water-associated prey species when these animals responded to changes in sea ice cover. Regarding body condition, concentrations of lipophilic compounds in plasma and fat were 4–9 times higher in the thinnest compared to the fattest polar bears, whereas they were only 1.5–1.8 times higher in the individuals feeding at highest versus lowest trophic levels (Tartu et al. 2017). This means that in general, tissue concentrations of lipophilic POPs are highest when polar bears are at their thinnest from approximately November to April–May, depending on local sea ice conditions and food availability.

An additional factor affecting concentrations of brominated fire-retardant POPs in polar bears is their demonstrated capability to biotransform these compounds (McKinney et al. 2011; Krieger et al. 2015; Vetter et al. 2015).

Temporal Trends for Brominated Fire-retardant POPs in Polar Bears.

Temporal trends for body burden of brominated fire retardants have been studied in polar bear subpopulations in the Barents Sea, East Greenland and Hudson Bay.

In the Barents Sea, tetraBDE concentrations decreased by 3% per year in female polar bears from 1997 to 2017 (Lippold et al. 2019). However the same study showed that hexaBDE concentrations were stable.

A study of subadult polar bears in East Greenland (Dietz et al. 2013) showed that between 1983 and 2010 both tetraBDE and 2 congeners of pentaBDE body burdens increased by 6–8% per year until 2000–2004, after which tetraBDE declined by 31% per year, along with a non-significant decline in pentaBDE concentrations. In addition, this study showed that both hexaBDE and HBCDD concentrations increased by 3% per year from 1983 to 2010, although hexabromobiphenyl (HBB) body burdens did not change.

In Western Hudson Bay polar bears, there are reported (McKinney et al. 2011) increases in ΣPBDE (mostly tetra-, penta- and hexaBDE) of 13% per year from 1991 to 2007, but with HBCDD only detected since 2000, and no change in hexabromobiphenyl (HBB) concentrations, which is similar to the results in the East Greenland study (Dietz et al. 2013).

It is suggested (Routti et al. 2019) that the above-noted declines in tetraBDE concentrations in Barents Sea and East Greenland polar bears reflect the phase out of the production of the commercial pentaBDE mixture (a listed POP comprising both tetra- and pentaBDE as the main components) in Europe in the late 1990s, and in the USA in the mid-2000s. It is also suggested (Routti et al. 2019) that the stability of hexaBDE concentrations in all polar bear subpopulations may result from the biodegradation (debromination) of recent emissions of decaBDE, noting that although production (but not import) was phased out firstly in Europe (1999) and later in USA, in China—the largest producer of decaBDE mixtures (c-decaBDE) output remains constant.

The increase in PBDE concentrations in polar bear tissues from the 1970s to mid-1990s, followed by reductions in some PBDEs since the late 1990s is similar to trends in marine mammals all over the world (Guo et al. 2012).

Recent (2012–2016) Spatial Trends for Brominated Fire-retardant POPs in Polar Bears.

A review (Routti et al. 2019) of available data on contaminant body burdens in polar bears (covering the period 2012–2016) shows that for brominated fire retardants, relative ΣPBDE concentrations for southern Hudson Bay > Barents Sea > East Greenland > western Hudson Bay > Chutki Sea and Kara Sea subpopulations (▣ Figure 8.10), and notes that this is consistent with a previous study that sampled bears in the period 1996–2002 (Muir et al. 2016). It is suggested (Routti et al. 2019) that this pattern of PBDE contamination reflects proximity to the sites of production, noting that in earlier years PBDE mixtures were produced in greater quantities in the USA than in Europe or Asia.

In respect of HBCDD, a recent review (Routti et al. 2019) shows that East Greenland and Barents Sea polar bear subpopulations carried greater concentrations than Hudson Bay bears (▣ Figure 8.10), and notes that is consistent with the higher use of HBCDD in Europe relative to the rest of the world.

8.7 Summary

POPS are organic compounds that are problematic for humans and the environment for many reasons. These compounds (and many of their degradation products) are highly toxic, accumulate in the fatty tissue of living organisms including humans, are found at higher concentrations at higher levels in the food chain, remain intact for exceptionally long periods of time, and become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air. Due to the high risks posed by POPs, the Stockholm Convention on Persistent Organic Pollutants was established in 2001 and by 2018 had been ratified by 182 nations. The original **dirty dozen** POPS were identified as posing significant risks to the humans and the environment. Since 2001 an additional 16 POPs have been added to the list of priority compounds in the Stockholm Convention and more are under consideration for listing.

POPs are often present in marine environments in complex mixtures of compounds and degradation products, and because many POPs (e.g. dioxins and furans) have similar chemical structures, properties, and toxicities, Toxicity Equivalent Factors (TEFs) and Toxic Equivalents (TEQs) are used to predict the toxicity of environmental samples.

The oceans are the ultimate sink for POPs after they are released into the environment. Because of the long-

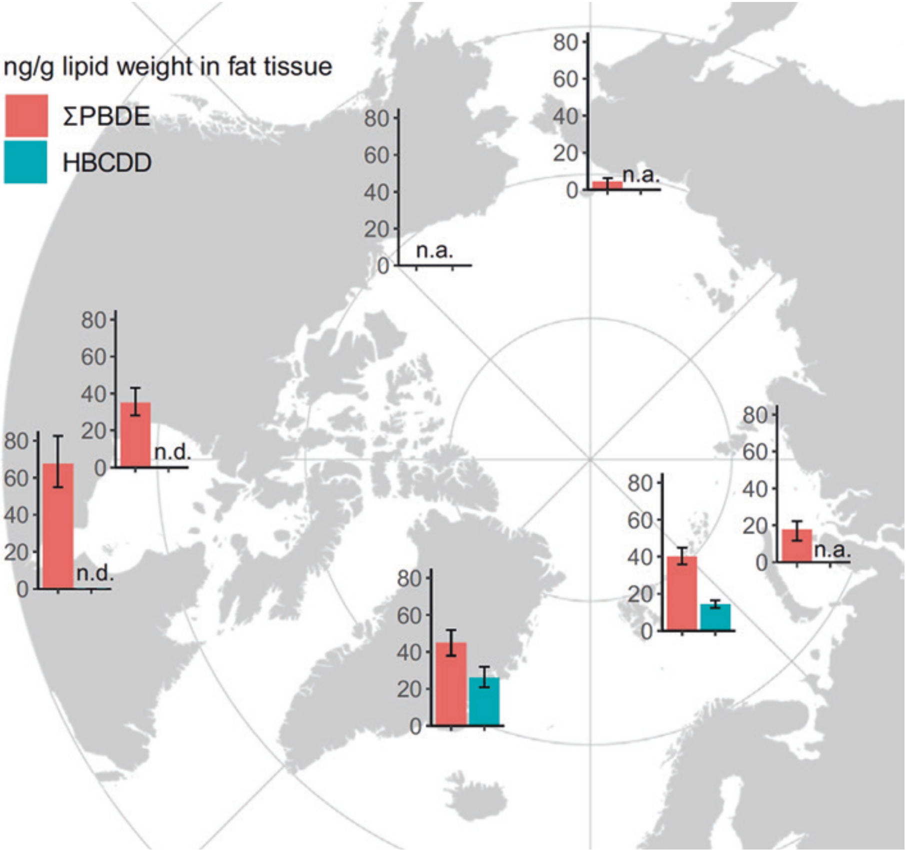


Figure 8.10 Concentrations of brominated fire retardants measured in polar bear fat tissues between 2012 and 2016. The abbreviations n.a. and n.d. signify not analysed or not detected, respectively. *Source*: Routti et al. (2019)

range global transport of POPs, their persistence and tendency to bioaccumulate and biomagnify, marine organisms high in the food chain (e.g. large mammals) are exposed to high POP concentrations. POPs can be passed from mother to offspring, which often results in higher concentrations in males than in females.

8.8 Study Questions and Activities

1. Briefly explain the three different annexes placed on POPs in the Stockholm convention.
2. Explain why different types of POPs tend to be present in the tissues of large marine mammals, and why the concentrations may differ depending on an organism's age and sex.
3. Select three POPs that are still intentionally produced and do some research to determine their current levels of production, uses, distribution in the environment, and the potential threats they pose to marine ecosystems.
4. Define TEQs and TEFs and explain why they are used for predicting the toxicity of POPs.

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