



Marine Contaminants of Emerging Concern

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Acronyms and Abbreviations

AFFF	Aqueous film-forming firefighting foams
ATSDR	Agency for Toxic Substances and Disease Registry (USA)
BPA	Bisphenol A
C60	Fullerenes
CAS	Chemical abstracts service
CDC	Center for Disease Control and Prevention (USA)
CEC	Contaminant of emerging concern
CFC	Chlorofluorocarbon
CNT	Carbon nanotube
DDT	Dichlorodiphenyltrichloroethane, a shortened version of a former name used for 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene)
EDC	Endocrine disrupting chemical
EEA	European Environment Agency
FOSA	Perfluorooctane sulfonamide
Gr	Graphene, an allotrope of carbon
HCF	Hydrofluorocarbon
IMO	International Maritime Organization (a United Nations Intergovernmental Body)
IUPAC	International Union of Pure and Applied Chemistry
NOAA	National Oceanic and Atmospheric Administration (USA)
NORMAN	An international network of reference laboratories, research centres and related organizations for monitoring of emerging environmental substances
nZVI	Nanoscale zero-valent particulate iron
OECD	Organisation for Economic Co-operation and Development
PBB	Polybrominated biphenyl
PCB	Polychlorinated biphenyl
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substances
PFC	Perfluorinated chemical or perfluorocarbon. These are related but distinctly different groups of substances (see ► Box 13.6)
PFBA	Perfluorobutanoic acid or perfluorobutanoate (see ► Box 13.9)
PFCA	Perfluoroalkyl carboxylic acid
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS (or PFSA)	Perfluorooctane sulfonic acid
PFOSA	Perfluorooctane sulfonamide
PFSA	Perfluoroalkane sulfonic acid
POP	Persistent organic pollutant
POSF	Perfluorooctane sulfonyl fluoride
PPCP	Pharmaceutical and personal care product
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (a European Union Regulatory Organisation).
TBT	Tributyltin
UNESCO	United Nations Educational, Scientific and Cultural Organization
US EPA	United States Environmental Protection Agency

13.1 Introduction

Identifying and listing substances or materials as **contaminants of emerging concern (CECs)** is not a simple task, and for the marine environment specifically is a challenge for environmental regulators, managers and researchers worldwide (► Box 13.1) (Tornero and Hanke 2017). Some of these agencies have widely different definitions of what a CEC actually is (Halden 2015).

The meaning of the term **contaminant** is relatively well understood and is discussed in ► Chapter 1 of this book. Although the text used by various authors and agencies to define contamination varies, it usually includes or implies the involvement of human-related activities and results in the production of an unnatural concentration of material in a specific environment leading to an associated adverse consequence or impairment to the natural condition for one or more at-

tributes of that environment. However, the terms **emerging** and **concern** are more subjective, and are subject to time scales and prevailing circumstances.

13.1.1 What is Meant by “Emerging”?

A meta-analysis of 143,000 publications about 12 prominent CECs ranging from the pesticide DDT to nanoparticles and microplastics (Halden 2015) showed a common time course of emergence and subsidence of concern spanning about 29 years. That study noted

that a number of factors can trigger and accelerate the **emergence** of new CECs, for example, new methods of detection and lowered detection limits, paradigm shifts in scientific understanding, breakthroughs in the design and manufacture of materials and changes in marketing and consumer behaviour leading to increased chemical consumption. Each of these factors can bring long-ignored environmental contaminants into the public eye and drive an increasing **level of concern**. This increase in the level of concern about a substance or material often triggers further research and publishing activity and the development of new regulations.

Box 13.1: Definitions of Contaminants of Emerging Concern

Despite the large number of papers published in recent years on the topic of **contaminants of emerging concern**, no commonly agreed definition exists (Nilsen et al. 2018). However, the following definition used by United Nations Educational, Scientific and Cultural Organization (UNESCO) and its refinement by the NORMAN network (► Box 13.2) capture the essence of the definitions in common usage:

The definition used by UNESCO (UNESCO 2019).

“Emerging pollutants can be understood in a broad sense as any synthetic or naturally-occurring chemical or any microorganism that is not commonly monitored or regulated in the environment with potentially known or suspected adverse ecological and human health effects. These contaminants include mainly chemicals found in pharmaceuticals, personal care products, pesticides, industrial and household products, metals, surfactants, industrial additives and solvents. Many of them are used and released continuously into the environment even in very low quantities and some may cause chronic toxicity, endocrine disruption in humans and aquatic wildlife and the development of bacterial pathogen resistance.”

The NORMAN network (► Box 13.2) defines the word **contaminant** as: “Any physical, chemical, biological, or radiological substance or matter that has an adverse effect on air, water, or soil” and includes the following additional criteria to define a “contaminant of emerging concern”:

- currently not included in routine environmental monitoring programmes and which may be a candidate for future legislation due to its adverse effects and/or persistency and
- a substance for which fate, behaviour and (eco)toxicological effects are not well understood.

Important Note

Contaminants of emerging concern are **not limited to newly developed chemicals**. Many are substances that have entered and been present in the environment for years, even decades. However, their presence has only recently raised concerns.

13.1.2 What is Meant by “Concern”?

The term **concern** in the CEC context is subject to interpretation and may mean different things such as interest, importance or cause of anxiety; all of these interpretations involve factors that are difficult to measure objectively. For a typical CEC, its associated **level of concern** progresses time-wise in a common pattern shown in ■ Figure 13.1. The level of concern associated with a particular contaminant tends to increase as potential threats and knowledge gaps are realized, and to decline as knowledge increases and risk management strategies relating to the contaminant, such as behavioural changes, exposure controls, voluntary phase-outs and as regulatory actions take effect. For some CECs, such a pattern of time-wise waxing and waning in level

of concern can be repeated if novel adverse effects are observed with the contaminant.

The long human experience with the element lead (Pb) provides an example of its **emergence** as a contaminant of concern. Several millennia ago, metallic lead was readily extracted from ores by early civilizations and the metal found a multitude of uses due to the ease with which it could be cast and shaped due to its softness and low melting point relative to other metals available at the time. For example, in ancient Roman times (approx. 500 BCE through 500 CE) there was widespread use of pipes made of metallic lead for potable water supply, in wine making, and also to line copper (Cu) cooking pots, together with the use of lead-containing compounds for a range of culinary, medicinal and decorative purposes, all of which be-

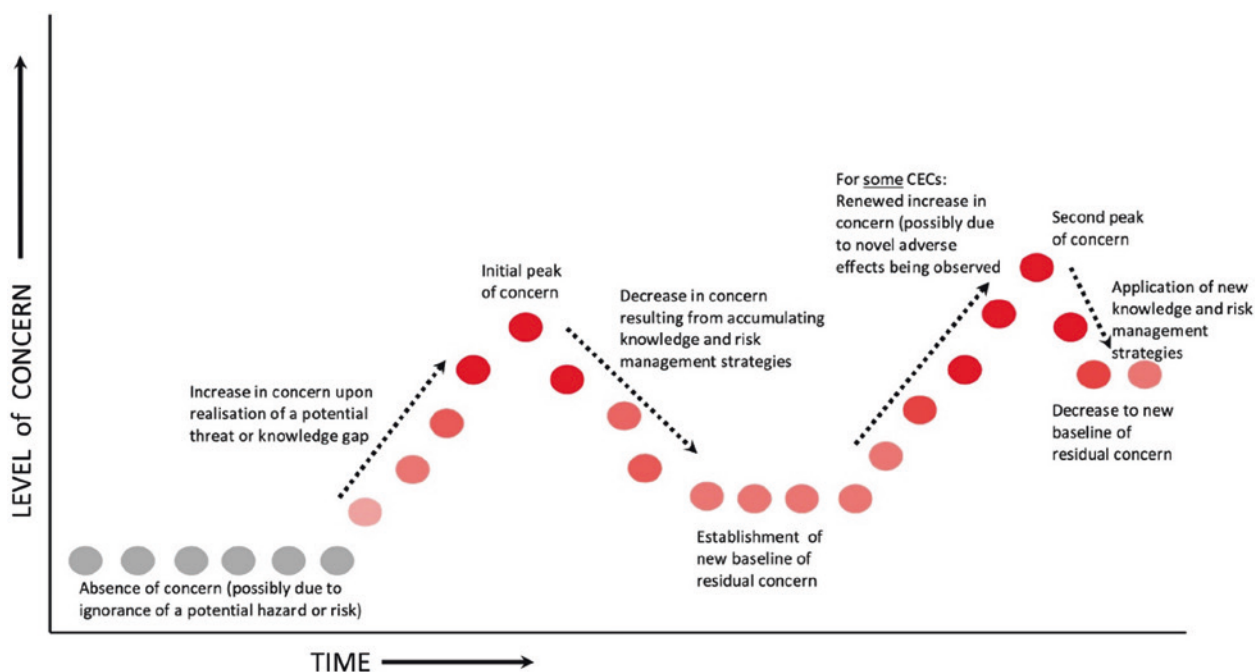


Figure 13.1 The common time-wise progression that develops for a contaminant of emerging concern (CEC). Adapted from Halden (2015) by M. Mortimer

came associated with lead poisoning (Cilliers and Re-tief 2019), thus making lead an **emerging contaminant of concern** in those long-gone times.

However in the present time, with our better understanding of the health risks associated with lead and its uses, and the availability of non-toxic materials for potable water distribution networks, lead is no longer a CEC so far as potable water, water used for irrigation, and stock watering, or for cooking pots, is concerned. However, lead in airborne dusts is now a CEC in localities potentially impacted by lead ore processing, with recent media reporting of lead levels in children in Mount Isa in Queensland, Australia (Forbes and Taylor 2015). In addition, lead contamination of the marine environment near lead smelters, for example, at Port Pirie in South Australia is an ongoing issue relating to both toxic impacts on the marine ecosystem and adverse impacts on human health related to contamination of seafood (Lafratta et al. 2019; EPASA 2005). Likewise, in the past, many of the Persistent Organic Pollutants (POPs) (see ► Chapter 8) were once CECs (e.g. DDT and other organochlorine pesticides in the 1960s and 1970s).

Although most, if not all, of the POPs are still **contaminants of concern**, for many of them the term **emerging** is no longer applicable. There are many more historical examples of contaminants that have **emerged**, but subsequently have been managed through the acquisition of better knowledge to the stage that the reasons for **concern** are addressed and reduced or elimi-

nated and the title **contaminant of emerging concern** is no longer applicable.

13.2 Contaminants of Emerging Concern in the Marine Environment

The list of potential candidate substances to be CECs in the marine environment is very large. In excess of 100 million chemical substances are currently registered in the Chemical Abstracts Service (CAS) and about 4000 new ones are registered every day. The number of registered and pre-registered substances in REACH (the European Union legislation for the Registration, Evaluation, Authorisation and Restriction of Chemicals) lists 30,000–50,000 industrial chemicals present in daily-use products, all of which are potentially ultimately released into the environment (Dulio et al. 2018). However, not all of these chemicals are **of concern** once released to the environment, and many are unlikely to become CECs. Numerous international environmental agencies and regulators have compiled individual lists of chemicals and substances they regard as being **of concern** but there is no common list accepted by all the relevant organizations.

The European Commission Joint Research Centre has compiled a “*comprehensive list of chemical substances considered relevant*” under European Union legislation and by international organizations (Tornero and Hanke 2017). Although not all of the listed contaminants are of concern for the marine environment, this

list is invaluable in presenting in one table the total of approximately 2700 **of concern** substances (or groups of substances) identified under relevant global conventions (e.g. the Stockholm Convention on POPs), European legislation (e.g. REACH), government agen-

cies (e.g. the United States Environmental Protection Agency (US EPA) Priority Pollutants legislation) and international research groups (e.g. the NORMAN Network), together with the status of each contaminant on its source list.

Box 13.2: The NORMAN Network

The NORMAN Network is an international “*network of reference laboratories, research centres and related organisations for the monitoring of emerging environmental substances*”. It was established by the European Union in 2005 and seeks to promote and to benefit from the synergies between research teams from different countries in the field of emerging substances.

The stated purpose of the NORMAN Network is to:

- enhance the exchange of information on emerging environmental substances;
- encourage the validation and harmonization of common measurement;
- encourage the validation and harmonization of common measurement methods and monitoring tools so that the requirements of risk assessors and risk managers can be better met; and
- ensure that knowledge of emerging pollutants is maintained and developed by stimulating coordinated, interdisciplinary projects on problem-oriented research and knowledge transfer to address identified needs.

The NORMAN Network has developed a methodology for prioritization of emerging contaminants, based on citations in the scientific literature. Examples of contaminants covered include surfactants, flame retardants, pharmaceuticals and personal care products, fuel additives and their degradation products, biocides, polar pesticides and their degradation products and various proven or suspected endocrine disrupting compounds.

The NORMAN Network systematically collects monitoring data and information on effects and hazardous properties for these substances and, on the basis of this information, allocates them to pre-defined categories (substances for which there is not yet sufficient toxicity information, substances with evidence of hazard but not yet satisfactory analytical performance, etc.). Currently the NORMAN Network website (► <https://www.norman-network.net>) lists almost 1000 substances as **emerging contaminants of concern** and provides substance fact sheets and related databases. The list is regularly updated, with particular emphasis on metabolites and transformation products that appear as relevant emerging substances but are not yet part of regular monitoring programmes.

A review of the operations of the NORMAN Network since its establishment, its organization and working groups structure is provided in Dulio et al. (2018).

Several large-scale monitoring programs in the marine environment have focused on detecting and monitoring **emerging contaminants of concern**. The most well known (and possibly the largest, longest lasting and best resourced) of these programmes is the Mussel Watch Program conducted by the National Oceanic and Atmospheric Administration (NOAA) in North America since 1986 (NOAA 2008). (See also ► Chapter 2, ► Box 2.1).

In the marine environment, a good example of an **emerging contaminant** of worldwide concern at the time (some 50 years before the present) is provided by the emergence of concern over the use of tributyltin (TBT) as an active ingredient in anti-fouling coatings applied to the hulls of ships. The published scientific material on the TBT issue is very extensive, but an overview published by the European Environment Agency (EEA) is succinct and comprehensive (Santillo et al. 2002) (see also ► Chapter 7). In summary, the use of antifoulant protection on the submerged por-

tion of ship hulls is essential to minimize the growth of marine life (fouling) that causes hull damage to timber vessels and reduces speed and increases fuel consumption in all affected vessels regardless of the material from which they are constructed. Initially, wooden ships were protected with metallic copper sheathing. In later times, copper-containing paints were used on vessels of all types, and in the late 1960s, organotin compounds (in particular, TBT) were found to be a very effective ingredient in anti-fouling paints and these compounds rapidly became the active ingredient of choice in hull paints and use was widespread by the early 1970s.

However, the widespread use of TBT-based anti-foulant paints by commercial shipping, including fishing fleets, and by leisure craft became associated with a marked decline in many commercially important marine mollusc fisheries (for example, mussels and oysters), characterized by declining populations of many



■ **Figure 13.2** Stripping TBT-based antifoulant paint from a ship hull during drydocking for maintenance and repaint in the Port of Brisbane, Australia during the 1990s. After work completion the drydock was re-flooded, and paint debris accumulated on the dock floor was flushed into the river. *Photo: M. Mortimer*

resource species especially where there was a high density of boat traffic. Research demonstrated the toxic consequence of the exposure of marine molluscs to low (ng/litre) concentrations of water-borne TBT was primarily imposex (the development of male sexual structures in females—leading to reproductive failure), but also shell deformities, failure of larval settlement and bioaccumulation of TBT. (See also ► Box 7.2).

Subsequently, TBT was found to be environmentally persistent, particularly in sediments (a half-life of 4 years) but much less so in waters (half-life of 6 days), and increasing concentrations were found in the tissues of a wide range of marine life including fish and marine mammals. The sources of TBT to the marine environment were not only its release from vessel coatings, but also from poorly or non-regulated disposal of TBT-containing paint residues stripped from vessels when hulls were repaired and when regularly scheduled repainting was carried out (■ Figure 13.2).

The progressive introduction from 1982 by countries and international organizations (see timeline in Santillo et al. 2002) of restrictions on the use of TBT-based antifoulants, culminating in their effective phase-out by the International Maritime Organization (IMO), a specialized agency of the United Nations responsible for regulating shipping in its adoption of the International Convention on the Control of Harmful Antifouling Systems on Ships (IMO 2001). This convention imposed a global prohibition of the application of organotin compounds which act as biocides in anti-fouling systems on ships by 1 January 2003 and a complete prohibition of the presence of organotin compounds which act as biocides in anti-fouling sys-

tems on ships by 1 January 2008 and has succeeded in successfully managing the TBT contamination problem.

13.3 The Relationship Between CECs and Endocrine Disrupting Chemicals

Since the late 1980s, there has been growing evidence of the feminization of male fish in waters receiving sewage treatment plant discharges (e.g. Jobling et al. 1996, 1998) and this triggered concern in the general community and the attention of regulatory agencies and researchers concerning the presence of estrogenic chemicals in outfalls and receiving waters.

Common usage of the term **endocrine disruption** in the context of chemical pollution originated in 1991 as a consensus statement at a conference workshop series publication in Wisconsin, USA (Colborn and Clement 1992). The convenor of that conference, Theo Colborn along with others, subsequently published the book *Our Stolen Future* (Colborn et al. 1997), a landmark publication in raising public attention to the issues relating to endocrine disruption in wildlife and potentially humans.

The growing attention, given to **endocrine disrupting chemicals (EDCs)** phenomenon (► Box 13.3), raised the **concern** levels about contaminants in aquatic environments, and in particular chemicals that are EDCs, and as a consequence numerous chemicals and substances became CECs. However, it is important to note that the EDC phenomenon is an expression of toxic effect, and although many CECs are associated with the EDC phenomenon, many are regarded as CECs for other reasons.

Box 13.3: Endocrine Disrupting Chemicals (EDCs)

The endocrine system comprises glands that produce chemical substances (hormones) that regulate the activity of cells or organs. Thus, the endocrine system regulates the body's growth, metabolism, and sexual development and function.

EDCs interfere with the endocrine system in several ways:

- mimicking or antagonizing the action of endogenous hormones;
- interfering with the synthesis, metabolism, transport and excretion of natural hormones and
- altering the hormone receptor levels.

Pollution of marine waters by EDCs may pose adverse health effects, reproductive abnormalities and impaired development in marine life. Evidence of endocrine disruption has been reported in bivalves, crustaceans, fish, reptiles, birds and mammals (Godfray et al. 2019).

Major sources of EDC pollutants to the marine environment include sewage treatment plant discharges and runoff from intensive animal husbandry. EDCs from these sources include endogenous hormones such as estrogens, progesterone and testosterone produced in mammals, as well as synthetic hormones and industrial chemicals. Synthetic hormones are used as oral contraceptives, in hormone replacement treatment and as animal feed additives. Many industrial chemicals including phenols, halogenated substances including organochlorine pesticides and PCBs, and phthalates have EDC properties. Those of most concern have long half-lives in the marine environment. EDC effects of most concern are those at the population, community and ecosystem level, but there is limited knowledge of these effects as yet (Windsor et al. 2017), and assessing a causal link between EDCs and population-level effects in the marine environment is not an easy task because of the uncertainty generated by the (still) largely undescribed endocrinology of most marine invertebrates (Katsiadaki 2019).

A comprehensive overview of current knowledge in the field of EDCs is provided in Godfray et al. (2019).

Examples of estrogenic chemicals include dichlorodiphenyltrichloroethane (DDT), dioxins, polychlorinated biphenyls (PCBs), bisphenol A (BPA), nonylphenol, polybrominated biphenyls (PBB), phthalate esters, perfluoroalkyl and polyfluoroalkyl substances (PFAS), polybrominated diphenyl ethers, endosulfan, atrazine and triclosan (NIEHS 2022).

13.4 Pharmaceuticals and Personal Care Products (PPCPs) as CECs

The group of chemicals and substances collectively known as PPCPs includes both **pharmaceuticals and personal care products** used for personal health/well-being or for cosmetic purposes (see ► Chapter 12). The common usage of the term PPCPs also includes non-medicinal/non-cosmetic household products or their ingredients such as disinfectants (e.g. triclosan) and antiseptics, soaps, detergents and other cleaning products, synthetic musks and fragrances cosmetics, lotions, preservatives and sunscreen agents (e.g. oxybenzone). A recent overview of the global extent of discharges of PPCPs was provided in Dey et al. (2019).

Pharmaceuticals are defined as prescription, over-the-counter and veterinary therapeutic drugs used to prevent or treat human and animal diseases, while personal care products are used mainly to improve the quality of daily life (Boxall et al. 2012).

Pharmaceuticals can be classified by their therapeutic uses. The common uses being: anti-diabetics (e.g. alpha-glucosidase inhibitor), β -blockers (e.g. atenolol, metoprolol), antibiotics (e.g. trimethoprim), lipid regulators (e.g. gemfibrozil), anti-epileptic (e.g. acetazolamide), tranquilizers (e.g. diazepam), anti-microbials (e.g. penicillins), anti-ulcer and anti-histamine drugs (e.g. cimetidine, famotidine), anti-anxiety or hypnotic agents (e.g. diazepam), anti-inflammatories and analgesics (e.g. ibuprofen, paracetamol, diclofenac), anti-depressants (e.g. benzodiazepines), anti-cancer drugs (e.g. cyclophosphamide, ifosfamide), anti-pyretics and stimulants (e.g. dexamphetamine, methylphenidate, modafinil), and estrogens and hormonal compounds (e.g. estriol, estradiol, estrone).

Currently more than 5000 manufactured pharmaceutical medicines are consumed by humans and/or domesticated animals, with an estimated total annual worldwide consumption in the range of 90,000–180,000 tonnes with the largest national consumptions being Russia, China, South Africa, India and Brazil (Van Boeckel et al. 2015; Tijani et al. 2016). A comprehensive overview of the current understanding of the extent and potential impact of contamination of the marine environment by pharmaceuticals is provided in the recent review by Ojemaye and Petrik (2019).

A large portion of medications that are ingested orally or by infusion are excreted through urine and/or faeces due to their incomplete absorption (metabo-

lism) in humans and animals, these ultimately end up in wastewater treatment plants. Subsequently, municipal sewage treatment plants are major points of release of pharmaceuticals into the marine environment because wastewater treatment plants are not designed to decompose the vast majority of pharmaceutical compounds, which are by intent stable and robust, polar and non-volatile in nature. The most frequent and widespread pharmaceuticals in sewage and the discharge from marine outfalls are antibiotics and non-steroidal anti-inflammatory drugs (Ojemaye and Petrik 2019). Other pathways for pharmaceuticals to be delivered into the marine system are via landfill sites, septic tanks, urban wastewater, showering and bathing, industrial effluent and agricultural runoff.

Measured concentrations of pharmaceuticals from worldwide coastal environment locations in seawater, sediments and organisms (Ojemaye and Petrik, 2019) range from 0.21 to 5000 ng/L (seawater), 0.0402 ng/g dry weight to 208 ng/g wet weight (biota) and 0.2 µg/kg dry weight to 466 µg/kg wet weight (sediments). However, despite evidence of their increasing presence, little attention has been directed towards understanding the release of pharmaceuticals into coastal-marine environments and their potential negative impact on marine ecosystems. This qualifies many pharmaceuticals as CECs in the marine environment.

Since the active ingredients in pharmaceuticals are chosen on the basis that their physicochemical and biological properties can produce specific biological effects in humans and animals, they have a high potential to trigger negative impacts on non-target organisms. In addition, anti-infection agents could create an ecological hazard by advancing the spread of resistant genes in the environment (Costanzo et al. 2005).

Other concerns are that the metabolites of many pharmaceuticals are potentially active and unsafe in the environment. For example, paracetamol and amitriptyline are mostly metabolized into highly reactive compounds (Graham et al. 2013). Also, of concern is that pharmaceuticals are discharged into the marine environment from sewage treatment plants as complex mixtures thus exposing marine life to potential synergistic environmental effects. For example, a synergistic antioxidant response in fish was demonstrated in a laboratory study involving co-exposure to a mixture of fluoxetine (an antidepressant medication) and roxithromycin (an antibiotic), and also with a mixture of fluoxetine and propranolol (a β-blocker used to treat a range of cardiac disease symptoms) (Ding et al. 2016).

Similarly, some ingredients of **non-medicinal/non-cosmetic** household products (e.g. triclosan—a widely used bactericide in healthcare products such as skin care ointments and lotions, mouthwashes and toothpastes, shower gels and shampoos) are not efficiently broken down in typical municipal sewage treat-

ment plants, so that the end-of-treatment discharges from these facilities are major point sources of release into the marine environment (Cui et al. 2019). Triclosan is persistent and bioaccumulative in the aquatic environment and triggers a number of toxic responses (Maulvault et al. 2019).

The array of PPCPs in sewage discharges is extensive, but the potential for adverse effects is largely unknown for most of the active ingredients present (Ojemaye and Petrik 2019). The NORMAN Network (► Box 13.2) currently lists almost 300 PPCPs substances as CECs.

13.5 Nanomaterials

The manufacture and use of nanoparticles and **nanos-structured materials** (also known as **nanomaterials**) is an expanding field of modern technology. As a consequence, the perceived risks associated with potentially toxic properties of these novel materials have resulted in their attracting attention as a new class of CECs.

By their nature, **nanoparticles** are units of particulate materials with a maximum dimension sized in nanometres (10^{-9} m). Although there is no single internationally accepted definition for **nanomaterials** (Jeevanandam et al. 2018), they are commonly defined as materials in which a single unit is sized in the range of 1–100 nm in at least one dimension. The term **aerosols** is often applied to nanoparticles when they are airborne, for example, in wind-borne dust or otherwise suspended in the atmosphere. The US EPA routinely uses the term **ultrafine particles** when discussing natural nanomaterials and aerosols. A summary of types and classifications of nanomaterials, and common technical descriptors is at ► Box 13.4.

Interestingly, the use and manufacture of nanomaterials are not an entirely modern phenomenon. The Ancient Egyptians used nanoparticulate lead sulfide as a hair dye some 4000 years ago (Walter et al., 2006) and more recently (400–100 BC) red enamels used by Ancient Celtic cultures were based on nanoparticulate copper oxides (Brun et al. 1991) and stained glass in medieval churches incorporated gold and silver nanoparticles (Schaming and Remita 2015).

The origin and source of nanoparticles and nanomaterials is diverse (► Box 13.5). Naturally occurring nanoparticles (colloids) and nanomaterials are widespread in both the living and inanimate world. In addition, nanoparticles and nanomaterials may be produced as an incidental by-product of an industrial process, or they may be manufactured explicitly by an engineered process to exploit specific features that stem from their small size.

The application of nanoparticulate and nanostructured materials has increased over the past decade be-

Box 13.4: Types and Classifications of Nanomaterials

Carbon-Based Nanomaterials: These comprise carbon and include morphologies such as hollow tubes, ellipsoids or spheres. Examples include fullerenes (C₆₀), carbon nanotubes (CNTs), carbon nanofibers, carbon black, graphene (Gr) and carbon union.

Inorganic-Based Nanomaterials: These comprise metal and metal oxides such as titanium dioxide (TiO₂), zinc oxide (ZnO) and zero-valent iron (nZVI).

Organic-Based Nanomaterials: These include nanomaterials made mostly from organic matter, excluding carbon-based or inorganic-based nanomaterials.

Composite-Based Nanomaterials with One Phase of Nanoscale Dimension: These include combinations of nanoparticles with other nanoparticles or nanoparticles combined with larger particles or with bulk-type materials (e.g. hybrid nanofibers), or more complicated structures, such as a metal–organic frameworks. Composites may be any combinations of carbon-based, metal-based or organic-based nanomaterials with any form of metal, ceramic or polymer bulk materials.

Nano-objects are often categorized as to how many of their external dimensions are at the nanoscale. For example, a nano-object with:

- all three external dimensions in the nanoscale is a **nanoparticle**;
- two external dimensions in the nanoscale is a **nanofibre** and optionally with the terms **nanorods** and **nanotubes** being used if they are solid or hollow, respectively; and
- one external dimension in the nanoscale is a **nanoplate** (if the other two dimensions are similar) or **nanoribbon** (if the other two dimensions are significantly different).

Nanostructures may be categorized by the phases of their components. For example, a nanostructure comprising:

- at least one physically or chemically distinct region at a nanoscale, or collection of regions with at least one at a nanoscale is a **nanocomposite**;
- a liquid or solid matrix with at least one at a nanoscale, filled with a gaseous phase is a **nanof foam**;
- a solid material containing pores or cavities with dimensions on the nanoscale is a **nanoporous material**; and
- a significant fraction of crystal grains at the nanoscale is a **nanocrystalline material**.

A comprehensive review of the different types of nanomaterials is provided in Jeevanandam et al. (2018).

cause they provide enhanced or unique physicochemical properties (e.g. melting point, wettability, electrical or thermal conductivity, catalytic activity, light absorbance or scattering) that are different from those of their bulk counterparts. Manufactured nanomaterials can significantly improve the characteristics of bulk materials, in terms of strength, conductivity, durability and lightness, and they can provide useful properties (e.g. self-healing, self-cleaning, anti-freezing and antibacterial) and can function as reinforcing materials for construction. By 2014, some 1814 nanotechnology-based consumer products were commercially available in over 20 countries (Vance et al. 2015). Examples of the incorporation of nanoparticles in consumer products include titanium oxide nanoparticles as a white pigment in paints, cosmetic creams and sunscreens, and silver nanoparticles used in numerous personal care products such as air sanitizers, wet wipes, shampoos and toothpastes, as well as in clothing and laundry fabric softeners (PEN 2019). Nanoscale zero-valent particulate iron (nZVI) is a widely used remediant for treating toxic wastes due to its large specific surface area and high reactivity (Stefaniuk et al. 2016).

Unfortunately, the highly sought physicochemical properties of nanomaterials that have led to their in-

creasing applications can also have an associated environmental downside. For example, nanoparticulate zinc oxide (ZnO) used in sunscreens is toxic to marine algae largely because of its dissolution as Zn²⁺ (Franklin et al. 2007), and nZVI use in contaminant remediation presents a range of potentially harmful environmental consequences that are not well understood (Stefaniuk et al. 2016). The enhanced toxic potential of nanosized materials may arise from their capacity to penetrate and disturb the cells and cellular systems of living tissues.

The challenge for regulators is to determine whether nanomaterials should be regulated in the same way as micron-sized particles. Among metal nanomaterials, cerium dioxide (used as a diesel fuel additive) and nanosilver are more toxic than their micron-sized forms, whereas because of their solubility there is no difference in toxicity for zinc oxide nano- and micron-sized particles in freshwaters (Batley et al. 2013). The enhanced surface area of nanosized materials can result in different cellular uptake rates, oxidative mechanisms and processes including translocation relative to that of exposure to the same material when it is not nanosized (Oberdörster et al. 2005). In the environment, aggregation is a common feature of nanomaterials, and

often coatings are used (e.g. citrate or polyvinylpyrrolidone (PVP)) to minimize this. Aggregation is greatest in marine waters due to their high ionic strength, leading to sizes > 100 nm and in many cases resulting in sedimentation (Klaine et al. 2008). The presence of organic particles such as those formed from extracellular polymeric substances can briefly stabilize nanomaterials (<48-h) (Gondikas et al. 2020). Seawater enhances the dissolution of silver from coated Ag nanomaterials,

largely through chloride complexation, which reduces silver toxicity (Angel et al. 2013).

Some nanoparticles and nanomaterials are released directly into the environment from the use of consumer products (e.g. silicon nanoparticles in car tyres are released by abrasion in normal vehicle use), or indirectly (e.g. nanoparticles in pharmaceuticals and cosmetics can end up in sewage, and then be discharged to the marine environment).

Box 13.5: Origin and Sources of Nanomaterials

There are three main origins of nanomaterials—incidental, engineered and naturally produced.

Incidental Nanomaterials: These are produced as a by-product of industrial processes such as nanoparticles present in vehicle engine exhaust, welding fumes and other combustion processes.

Naturally Produced Nanomaterials: Dust from soil ablation by winds, volcanic eruptions and forest fires are events of natural origin that produce large quantities of nanoparticulate matter that significantly affect worldwide air quality.

Nanoparticles and nanostructures are present in living organisms ranging from microorganisms (e.g. bacteria, algae and viruses) to complex organisms, such as plants and animals. Plants accumulate nutrients extracted from the soil as biominerals in nanoform.

The natural transport of mineral aerosol particles to the oceans has an important role in supporting marine biological productivity. Iron, along with phosphorus and silica, is a limiting nutrient for most marine phytoplankton. Iron is needed for a multitude of enzymes and electron transfer proteins including those essential for photosynthesis (Bristow et al., 2017). The major source of iron input to oceanic waters far from land is deposition of wind-transported continental dust (Buseck and Posfai, 1999). Since phytoplankton form the basis of the marine food web and is responsible for approximately half of global carbon dioxide fixation, this natural transport of iron in mineral aerosol particles is an essential contributor to the removal of excess CO₂ and carbon sequestration by marine phytoplankton (Basu and Mackey, 2018).

Engineered Nanomaterials: A diverse range of nanomaterials is synthesized by both **bottom-up** (meaning the constructive build-up of material from atom to clusters to nanoparticles) and **bottom-down** (meaning the reduction of a bulk material to nanometric-scale particles) processes. These products have a multitude of applications including medical (e.g. targeted drug delivery in pharmacology), cosmetics and sunscreens, electronics, catalysis (e.g. automotive applications), food (production, processing and packaging), construction (e.g. new materials), renewable energy and environmental remediation.

A comprehensive review of the different types of engineered nanomaterials and their applications, together with methods of synthesis, is provided in Ealias and Saravanakumar (2017).

The fate and impacts of nanomaterials in the environment have been comprehensively reviewed (Klaine et al. 2008; Lead et al. 2018). It is generally agreed that the current environmental concentrations are orders of magnitude below those known to have toxic effects on aquatic biota (Batley et al. 2013).

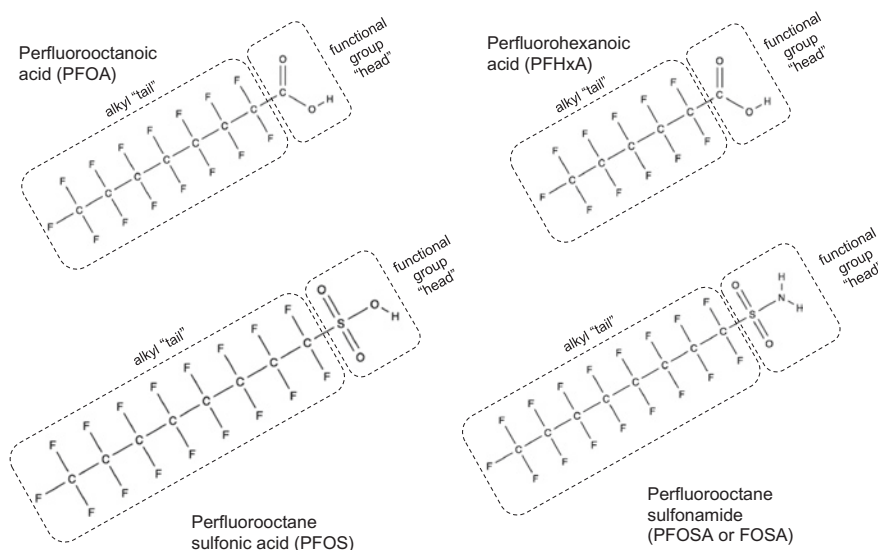
13.6 PFAS (Per- and Polyfluoroalkyl Substances)

The term PFAS (per- and polyfluoroalkyl substances) applies to the set of more than 4700 synthetic substances manufactured and used in a variety of industries since the 1940s (OECD 2019), and some have been classified as POPs (► Chapter 8). All PFAS constitute an array of highly persistent environmental CECs that

has triggered a global response by research and regulatory organizations over the past two decades.

PFAS comprise a set of compounds each of which has a molecular structure comprising an aliphatic moiety (i.e. a group of covalently bonded carbon atoms in a straight or branched chain, and in some cases including non-aromatic rings) that is highly fluorinated and linked to a functional group moiety. This PFAS molecular structure can be conceptualized as an alkyl tail of carbon atoms with fluorine atoms attached to a functional group head (► Figure 13.3). The degree of fluorination of the aliphatic moiety in a PFAS structure can be partial or total. In polyfluoroalkyl substances, fluorine atoms replace only some of the hydrogen atoms in the aliphatic chain, whereas in perfluoroalkyl substances, fluorine atoms replace all of the hydrogen atoms in the aliphatic chain. The general formula for

Figure 13.3 Typical perfluorinated PFAS molecules showing the basic structure comprising a perfluorinated alkyl tail attached to a functional group head. Structures here are the linear isomers. A mixture of linear and branched isomers may be present in an environmental sample. Adapted from Mueller and Yingling (2017) by M. Mortimer



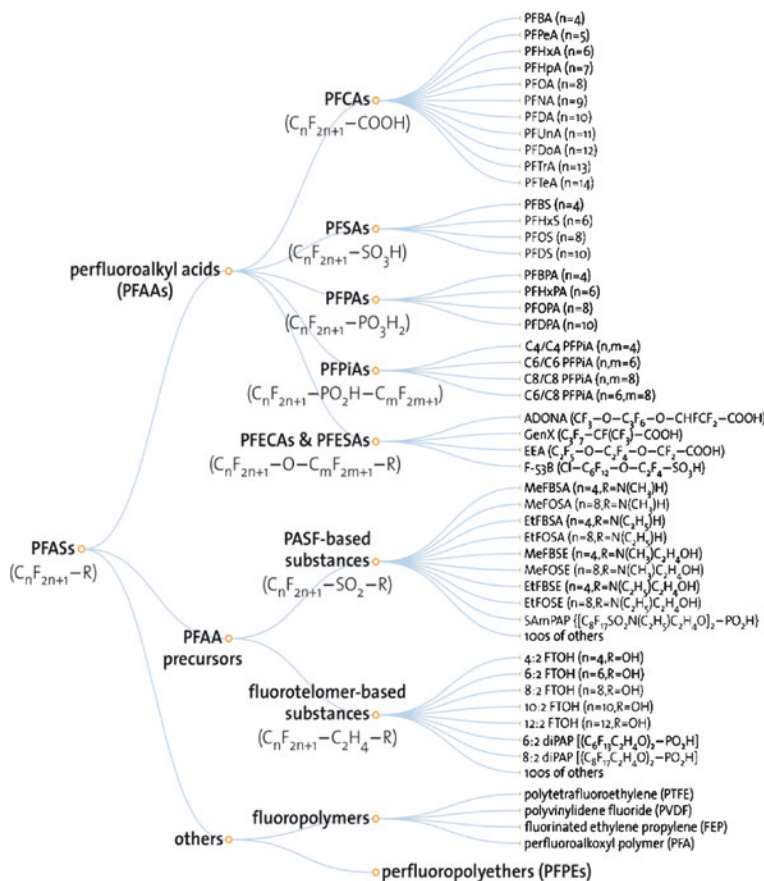
a perfluorinated PFAS is $C_nF_{2n+1}-R$ where n is 3 or greater and $-R$ is a functional group such as carboxylic acid (COOH), sulfonic acid (SO₃H) or sulfonamide (SO₂NH₂) (Figure 13.3).

Note that the term **PFAS** sometimes appears in print in the context of more than one fluorinated chemical, but the addition of the *s* is redundant since the acronym **PFAS** includes the plural (ATSDR 2017). Also, it is important to note that PFAS (per- and polyfluoroalkyl

substances) are sometimes called perfluorinated chemicals and the acronym **PFC** is then used. However, this use of the **PFC** acronym can be confusing since **PFC** is also commonly used for a related, but distinctly different group of substances: the *perfluorocarbons* (Box 13.6).

The range of structurally related compounds comprising more than 4700 member group of PFAS substances is illustrated in the **PFAS family tree** in Figure 13.4.

Figure 13.4 The PFAS family tree with examples. Adapted from Wang et al. (2017) by M. Mortimer. PFCAs=Perfluoroalkyl carboxylic acids; PFSAs=Perfluoroalkane sulfonic acids; PFPAs=Perfluoroalkyl phosphonic acids; PFPiAs=Perfluoroalkyl phosphinic acids; PFECA and PFESA=Perfluoroether carboxylic and sulfonic acids; PASF = Perfluoroalkane sulfonyl fluoride



Box 13.6: What are Perfluorocarbons (PFCs) and How do they Relate to Per- and Polyfluoroalkyl Substances (PFAS)?

The acronym **PFC** is widely used for two related but distinctly different groups of substances—(1) the **perfluorocarbons** and (2) the **perfluorinated chemicals**. Examples of organizations that have used the acronym **PFC** for both groups are the USEPA, the U.S. Center for Disease Control and Prevention (CDC), and the UN Organisation for Economic Co-operation and Development (OECD). However, the USEPA now states on its website that it is trying to consistently use the acronym **PFAS** rather than **PFC** when referring to perfluorooctane sulfonic acid (PFOS), PFOA and other substances in the per- and polyfluoroalkyl group (► <https://www.epa.gov/pfas/what-are-pfcs-and-how-do-they-relate-and-polyfluoroalkyl-substances-pfas>). Likewise, the United States Agency for Toxic Substances and Disease Registry (ATSDR) website fact sheet makes a similar comment (ATSDR 2017).

Another reason for avoiding use of the PFC acronym for PFAS is that the acronym PFC has been used in official Kyoto Protocol documents since its adoption in 1997, specifically to designate greenhouse gas perfluorocarbons (United Nations 1998).

Perfluorocarbons and PFAS are closely related, in that:

- the molecules of both contain fluorine and carbon atoms; and
- both persist in the environment for long periods but are not found naturally except for the perfluorocarbon, carbon tetrafluoride that occurs in association with fluorite minerals (Mühle et al. 2010).

However, perfluorocarbons and PFAS are quite different, in that:

- perfluorocarbon molecules contain only carbon and fluorine atoms, but PFAS molecules can include many other atoms including oxygen, hydrogen, sulfur and nitrogen; and
- perfluorocarbons are used in and emitted from different applications and industries than PFAS.

Other groups of fluorinated hydrocarbon compounds that are sometimes confused with the PFAS and PFC groups are the chlorofluorocarbon (CFC) group and the hydrofluorocarbon (HFC) group. The members of the CFC group are hydrocarbon chain structures with hydrogen atoms replaced with both chlorine and fluorine atoms. An example is dichlorotetrafluoroethane ($C_2Cl_2F_4$). The HFC group is hydrocarbons with only some hydrogens replaced by fluorine. An example is tetrafluoroethane ($C_2H_2F_4$). Both CFCs and HFCs are synthetic compounds (trade name Freons™) used as aerosol and refrigerant gases, but being phased out since CFCs are ozone-depleting substances, and HFCs are very potent greenhouse gases.

PFAS are highly valued in a wide range of industrial applications on account of their extreme resistance to degradation, thermal stability and other physico-chemical properties including unique surface tension that provides a remarkable aptitude to self-assemble into sturdy thin repellent protective films, in addition to having unique spreading, dispersing, emulsifying, anti-adhesive and levelling, dielectric, piezoelectric and optical properties (Krafft and Riess, 2015). It is the unique properties of the fluorine atom, in particular, the strong C–F bond (one of the strongest in organic chemistry), in addition to the bonds between fluorinated carbons being stronger than the bonds between hydrogenated carbons, that together give PFAS their highly valued attributes for industrial applications.

Since the development of PFAS in the 1940s, their applications have included surface coating of textiles, carpets, cardboard packaging products and papers where use is made of their unique surfactant properties (both water-repelling and oil/fat-repelling), and in aqueous film-forming firefighting foams (AFFF) where they are effective in extinguishing hydrocarbon-fuelled fires. Unfortunately, the extensive use of PFAS, in par-

ticular, the use of AFFF, together with their high solubility in water, low/moderate sorption to soils and sediments and a high resistance to biological and chemical degradation has led to the global emergence of PFAS as an array of highly environmental persistent contaminants of emerging concern (CECs). Their perfluorinated carbon chains form a helical structure, in which the carbon skeleton is completely covered by fluorine atoms. This cover shields the PFAS molecule from most chemical attacks and results in highly stable molecules. Because most PFAS compounds are anthropogenic creations, and also due to the presence of the multiple and very strong C–F bonds, there is a lack of naturally occurring microbes capable of breaking them down. Once released to the environment many PFAS can degrade to PFAAs, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), which are the two PFAS compounds most commonly found in the environment in high concentrations. Once waters and sediments are contaminated by PFAS, they present a considerable challenge to successful remediate.

Some PFAS, specifically PFOS, PFOS salts and POSF (perfluorooctane sulfonyl fluoride), are listed

POP substances in the Stockholm Convention (see ► Chapter 8). However, PFAS do not bioaccumulate in the same way as most other Stockholm Convention POPs such as the halogenated hydrocarbon pesticides and flame retardants that are lipophilic in nature and are preferentially accumulated in lipid-rich tissues (see ► Chapter 7). Notably, PFAS are not lipophilic since their alkyl tails make them both hydrophobic (water-repelling) and oleophobic/lipophobic (oil/fat-repelling)

in character. Many PFAS, including PFOA and PFOS, do have a high potential to bioconcentrate, bioaccumulate and biomagnify, and now have an ubiquitous and growing presence throughout the food chain. However, they bind to proteins and consequently bioaccumulate in blood and blood-rich tissues rather than lipid-rich tissues. The relationship between the carbon chain length of PFAS and environmental behaviour and fate is discussed in ► Box 13.7.

Box 13.7: The Role of PFAS Chain Length in Relation to Environmental Behaviour and Level of Concern

Sometimes carbon chain length is used to group PFAS which may behave similarly in the environment, particularly the perfluoroalkyl carboxylic acids and sulfonic acids (PFCA and PFSA), and the terms **long-chain PFAS** and **short-chain PFAS** used in relation to their potential environmental significance. For example, the Organisation for Economic Co-operation and Development (OECD 2013) uses these definitions:

Long chain refers to:

- perfluoroalkyl carboxylic acids with eight or more carbons (seven or more carbons are perfluorinated);
- perfluoroalkane sulfonates with six or more carbons (six or more carbons are perfluorinated); and
- substances with the potential to degrade to PFCA or PFSA (i.e. precursors).

Short chain refers to:

- perfluoroalkyl carboxylic acids with seven or fewer carbons (six or less carbons are perfluorinated); and
- perfluoroalkane sulfonates with five or fewer carbons (five or less carbons are perfluorinated).

However, caution should be applied in making generalizations about PFAS behaviour based only on chain length. Although in general terms, the potential toxicity of PFAS increases with the length of the carbon-carbon chain, as does the potential for bioconcentration, bioaccumulation and persistence in the environment, other factors besides chain length are involved, including the functional groups in the PFAS structure and the interactions involving PFAS-protein binding to form complexes (Ng and Hungerbuehler 2015). Studies also show that bioaccumulation factors reach a maximum at a carbon chain length of 11 (Ng and Hungerbuehler 2014).

PFAS have been globally detected in lakes, rivers, oceans and even in precipitation water at ng/L concentrations. PFAS are significantly transported in aquatic ecosystems, including transport to remote polar regions in aerosols. Not only is PFAS contamination of marine waters occurring on a global scale, but evidence is mounting of accumulation in wildlife even at locations remote from any direct source, for example, Antarctica (Llorca et al. 2012), particularly PFAS with alkyl chain lengths of less than 10 carbon atoms, but the ecotoxicological impacts of this in the short or long term are unclear. For example, Wei et al. (2007) reported PFOS and PFOA concentrations of 21.1 and 7 pg/L, respectively, in oceanic waters hundreds of kilometres south of Tasmania, Australia. These concentrations are comparable to the range reported for the mid to southern Pacific Ocean of up to 8 and 20 pg/L in Ahrens (2011). Toxicity data obtained to date suggest that a guideline value for PFOS in freshwaters for 99% species protection is near 30 ng/L and orders of magnitude higher in marine waters (G. Batley, personal communication).

PFAS have been found at ng/kg concentrations in deep sea sediments, and at hundreds of ng/g in fish. In the absence of effective rapid breakdown of many PFAS in the environment due to their chemical structure, the global fate of most discharged PFAS is dispersal and burial in the deep ocean sediments (Ahrens 2011). However, the future impacts on wildlife from exposure to the persistently dissolved fraction of PFAS are unknown. Simpson et al. (2021) demonstrated that for PFOS, a screening value of 60 µg/kg (for 1% organic carbon) would be protective of organisms in estuarine and marine sediments.

13.6.1 Naming Conventions Used for PFAS

In common with other compounds, all PFAS have chemical names consistent with the International Union of Pure and Applied Chemistry (IUPAC) system (Favre and Powell 2013). However, many of these IUPAC names are long and somewhat impractical to use

in reporting, and a simplified nomenclature and abbreviation system for PFAS has been developed in the scientific literature (Lehmler 2005). This simplified nam-

ing system for PFAS in reports and journal papers is explained further in Boxes 13.8 through 13.10 and in Tables 13.1 and 13.2.

Table 13.1 Examples of simplified naming of perfluoroalkyl carboxylates and acids

X	Y	Name and (acronym)	Formula
But-(4 Carbon Chain)	Carboxylate	Perfluorobutanoate (PFBA)	$\text{CF}_3(\text{CF}_2)_2\text{CO}_2^-$
	Carboxylic acid	Perfluorobutanoic acid (PFBA)	$\text{CF}_3(\text{CF}_2)_2\text{CO}_2\text{H}$
	Sulfonate	Perfluorobutane sulfonate (PFBS)	$\text{CF}_3(\text{CF}_2)_2\text{SO}_3^-$
	Sulfonic acid	Perfluorobutane sulfonic acid (PFBS)	$\text{CF}_3(\text{CF}_2)_2\text{SO}_3\text{H}$
Pent-(5 Carbon Chain)	Carboxylate	Perfluoropentanoate (PFPeA)	$\text{CF}_3(\text{CF}_2)_3\text{CO}_2^-$
	Carboxylic acid	Perfluoropentanoic acid (PFPeA)	$\text{CF}_3(\text{CF}_2)_3\text{CO}_2\text{H}$
	Sulfonate	Perfluoropentane sulfonate (PFPeS)	$\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$
	Sulfonic acid	Perfluoropentane sulfonic acid (PFPeS)	$\text{CF}_3(\text{CF}_2)_3\text{SO}_3\text{H}$
Hex-(6 Carbon Chain)	Carboxylate	Perfluorohexanoate (PFHxA)	$\text{CF}_3(\text{CF}_2)_4\text{CO}_2^-$
	Carboxylic acid	Perfluorohexanoic acid (PFHxA)	$\text{CF}_3(\text{CF}_2)_4\text{CO}_2\text{H}$
	Sulfonate	Perfluorohexane sulfonate (PFHxS)	$\text{CF}_3(\text{CF}_2)_4\text{SO}_3^-$
	Sulfonic acid	Perfluorohexane sulfonic acid (PFHxS)	$\text{CF}_3(\text{CF}_2)_4\text{SO}_3\text{H}$
Hept-(7 Carbon Chain)	Carboxylate	Perfluoroheptanoate (PFHpA)	$\text{CF}_3(\text{CF}_2)_5\text{CO}_2^-$
	Carboxylic acid	Perfluoroheptanoic acid (PFHpA)	$\text{CF}_3(\text{CF}_2)_5\text{CO}_2\text{H}$
	Sulfonate	Perfluoroheptane sulfonate (PFHpS)	$\text{CF}_3(\text{CF}_2)_5\text{SO}_3^-$
	Sulfonic acid	Perfluoroheptane sulfonic acid (PFHpS)	$\text{CF}_3(\text{CF}_2)_5\text{SO}_3\text{H}$
Oct-(8 Carbon Chain)	Carboxylate	Perfluorooctanoate (PFOA)	$\text{CF}_3(\text{CF}_2)_6\text{CO}_2^-$
	Carboxylic acid	Perfluorooctanoic acid (PFOA)	$\text{CF}_3(\text{CF}_2)_6\text{CO}_2\text{H}$
	Sulfonate	Perfluorooctane sulfonate (PFOS)	$\text{CF}_3(\text{CF}_2)_6\text{SO}_3^-$
	Sulfonic acid	Perfluorooctane sulfonic acid (PFOS)	$\text{CF}_3(\text{CF}_2)_6\text{SO}_3\text{H}$
– continues stepwise with additions to carbon chain... non (9), dec (10), undec (11), dodec (12), tridec (13) etc			
Tetradec-(14 Carbon Chain)	Carboxylate	Perfluorotetradecanoate (PFTeDA)	$\text{CF}_3(\text{CF}_2)_{12}\text{CO}_2^-$
	Carboxylic acid	Perfluorotetradecanoic acid (PFTeDA)	$\text{CF}_3(\text{CF}_2)_{12}\text{CO}_2\text{H}$
	Sulfonate	Perfluorotetradecane sulfonate (PFTeDS)	$\text{CF}_3(\text{CF}_2)_{13}\text{SO}_3^-$
	Sulfonic acid	Perfluorotetradecane sulfonic acid (PFTeDS)	$\text{CF}_3(\text{CF}_2)_{13}\text{SO}_3\text{H}$
– continues stepwise with additions to carbon chain... pentadec- (15), hexadec- (16), heptadec- (17) etc			
X = the name of the alkyl chain tail based on number of linked carbon atoms and Y = the functional group head			

Table 13.2 Examples of simplified naming for fluorotelomer-based polyfluoroalkyl substances

X	Y	Functional group	Name and (acronym)	Formula
4	2	Hydroxyl	4:2 fluorotelomer alcohol (4:2 FTOH)	$\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{OH}$
		Carboxyl	4:2 fluorotelomer carboxylic acid (4:2 FTCA)	$\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CO}_2\text{H}$
		Sulfonyl	4:2 fluorotelomer sulfonic acid (4:2 FTSA)	$\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{SO}_3\text{H}$
6	2	Hydroxyl	6:2 fluorotelomer alcohol (6:2 FTOH)	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{OH}$
		Carboxyl	6:2 fluorotelomer carboxylic acid (6:2 FTCA)	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{CO}_2\text{H}$
		Sulfonyl	6:2 fluorotelomer sulfonic acid (6:2 FTSA)	$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SO}_3\text{H}$
8	2	Hydroxyl	8:2 fluorotelomer alcohol (8:2 FTOH)	$\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$
		Carboxyl	8:2 fluorotelomer carboxylic acid (8:2 FTCA)	$\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{CO}_2\text{H}$
		Sulfonyl	8:2 fluorotelomer sulfonic acid (8:2 FTSA)	$\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SO}_3\text{H}$

X = fully fluorinated carbon atoms and Y = not fully fluorinated carbon atoms

Box 13.8: Simplified Naming System for Per- and Polyfluoroalkyl Substances (PFAS)

Many of the IUPAC names for PFAS are long and somewhat impractical to use in reporting, and a simplified nomenclature and abbreviation system for PFAS has been developed in the scientific literature (Lehmler, 2005). This practice of adopting simplified **literature names** for PFAS makes the writing (and reading) of reports and journal papers much easier. An example of this simplified naming is the use of the name **perfluorooctane sulfonate** (abbreviated as PFOS) rather than the IUPAC name for that compound, which is:

- 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro-1-octanesulfonate.

Most of the IUPAC name for this compound, including the string of numbers, describes the location of the fluorine atoms along the perfluorinated alkyl tail of carbon atoms in its molecular structure.

This long name can be simplified for reporting purposes by replacing the string of numbers with the term **perfluorooctane** (in this example **octane** becomes part of the name because the alkyl tail is 8 carbons in length), followed by the name of the functional group head which in this example is **sulfonate**.

Similarly, a simplified name for a PFAS with a perfluorinated alkyl tail 10 carbons in length would use **perfluorodecane** followed by the name of the functional group (e.g. **perfluorodecane sulfonate** [abbreviated as PFDS]) if the functional group is sulfonate.

- See ► Box 13.9 for more examples of the use of the simplified naming system for **perfluoroalkyl substances**, and ► Box 13.10 in the case of **polyfluoroalkyl substances**.

Box 13.9: Applying the Simplified Naming System to Perfluoroalkyl Substances

The use of the simplified naming system for **perfluoroalkyl** substances is illustrated in ► Table 13.1 using the perfluoroalkyl carboxylates and acids as examples.

In this system, the structure name is written in the form PFX_Y where:

- PF = perfluoro-
- X = the name of the alkyl carbon chain structure appropriate to the number of linked carbon atoms (for example, **but** for 4 carbons, **pent** for 5 carbons, etc.)
- Y = the name of the attached functional group **head**

For example, a perfluorinated (all hydrogens replaced by fluorine atoms) 4-carbon (butan-) chain, bonded to a carboxylic acid functional group is named **perfluorobutanoic acid** which can be abbreviated to the acronym **PFBA**.

However, beware that the usage of acronyms for PFAS is not standardized and many are ambiguous (for example, PFBA is used for both **perfluorobutanoic acid** and its anion **perfluorobutanoate**). Accordingly, authors and readers of reports concerning PFAS need to ensure that to avoid ambiguity, the compounds referred to using acronyms are clearly identified in the text (for example, by the CAS number and/or IUPAC name).

Note that there are both anionic (negative charged) and acid forms associated with functional groups such as carboxylate and carboxylic acid. However, except under conditions of extremely low pH, it is the anionic form that is found in the environment since the acid or salt form dissociates in solution (Buck et al. 2011).

Box 13.10: Applying the Simplified Naming System to Polyfluoroalkyl Substances

The **fluorotelomers** are a series of polyfluoroalkyl substances synthesized on an industrial scale and used in a wide range of commercial products. Two major industrial processes are used for the commercial manufacture of PFAS. These are the telomerization process and electrochemical fluorination (ECF) process. Both are described in Buck et al. (2011).

A widely used simplified naming system for fluorotelomer-based polyfluoroalkyl substances is illustrated in ► Table 13.2. In this system, the fluorotelomer polyfluoroalkyl structure name is written in the form of a ratio X:Y where:

- X = the number of fully fluorinated carbon atoms and
- Y = the number of carbon atoms not fully fluorinated

Thus, a fluorotelomer alcohol (FTOH) with 6 fully fluorinated carbons and 2 not fully fluorinated carbons is given the name **6:2 fluorotelomer alcohol** (abbreviated 6:2 FTOH), and similarly a fluorotelomer sulfonic acid (FTSA) with 8 fully fluorinated carbons and 2 not fully fluorinated carbons is given the name **8:2 fluorotelomer sulfonic acid** (abbreviated 8:2 FTSA or FtS 8:2).

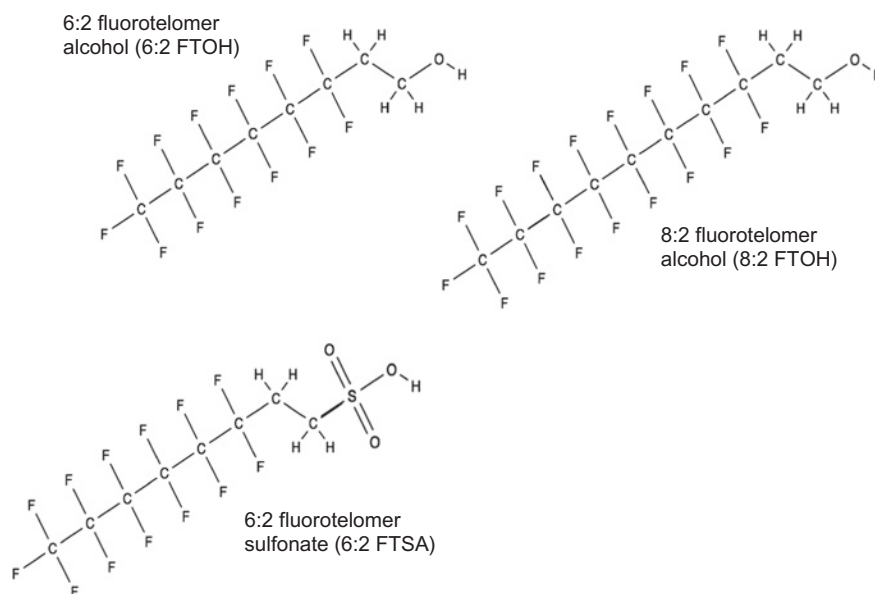
13.6.2 PFAS and Precursors

The concept of a **precursor** is important in the PFAS contamination context. There is a wide range of polyfluorinated PFAS comprising fluorinated structures capable of natural transformation to other more persistent fluorinated structures. Typically, such degradations follow a stepwise process ending with a perfluorinated PFAS, often PFOA or PFOS (thus sometimes termed **terminal PFAS**).

In an environment subject to PFAS contamination (for example, sites associated with PFAS manufacture, the use of AFFF, waste disposal by land-

fill or wastewater treatment), there are many **precursors** of PFOA and PFOS present. This conversion of precursors enables an increase in the relative quantities of PFOA and PFOS present after wastes are released, providing an explanation for the dominance of PFOA and PFOS in the global inventory of residual PFAS in the natural environment including the seas and oceans.

Polyfluorinated PFAS structures such as the fluorotelomers are typical **precursors** since the non-fluorinated portion of the carbon chain is open to biotic degradation and modification by abiotic processes such as oxidation (■ Figure 13.5).



■ **Figure 13.5** Example structures of polyfluorinated precursors. The sections of the molecule with a not fully fluorinated carbon are exposed to modification by both abiotic and biotic processes. Adapted from Mueller and Yingling (2017) by M. Mortimer

13.7 Summary

There is a large body of research papers and reports concerning the topic of **Contaminants of Emerging Concern (CECs)** but the term itself is not definitive since both **emerging** and **concern** may be subjective, and the list of materials identified as CECs changes over time and in response to community perceptions of risks to health and the environment. The NORMAN Network is a key organization in identifying such materials and coordinating meaningful related research.

In the marine environment, since the late 1900s the priority focus has moved from concern over unintended impacts from the widespread use of organic tin-based antifoulants used on the hulls of sea-going vessels to

impacts relating to a wide range of material types including EDCs, PPCPs, nanomaterials, PFAS compounds as well as environmental contamination by polymer and plastic debris.

Each of these current CECs covers a large number of chemical identities. Overall this is a wide-ranging and dynamic area of risk assessment, priority setting and ongoing scientific research.

13.8 Study Questions and Activities

1. In the context of the marine environment draw up a short list of up to five contaminants of emerging concern that are highlighted in recent media pub-

lications (noting that the media *may not* use the term **contaminant of emerging concern** as a descriptor) and compare this short list with contaminants which are popular topics in the programmes of recent conference presentations and journal publications. What do you suggest are reasons for similarities and differences between these two sets of CECs?

2. Identify two CECs in the marine environment that have been receiving frequent attention for a period longer than two or three years. Why are they still considered **emerging** (for example, has the baseline of residual concern changed)?
3. In this chapter, lead in the marine environment near Port Pirie, South Australia is used as an example. What other locations in Australia and other countries with territorial waters in the Pacific Ocean also have an emerging problem associated with lead mining and processing?
4. Which metallic contaminants are CECs in European marine waters?
5. What potential contaminants of marine waters are likely to become CECs as a consequence of the shift from fossil-fuel-based energy sources to renewables? What are some geographic locations where these may first emerge as CECs—explain why?

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