

## Chapter 3

# THE AMAZING WORLD OF ANTHROPOGENIC ORGANIC CHEMICALS

- 3.1 Introduction**
- 3.2 A Lasting Global Problem: Persistent Organic Pollutants (POPs)**
- 3.3 Natural but Nevertheless Problematic: Petroleum Hydrocarbons**
- 3.4 Notorious Air and Groundwater Pollutants: Organic Solvents**
  - BTEX Compounds
  - Tertiary Dialkyl Ethers
  - Polychlorinated C<sub>1</sub>- and C<sub>2</sub>-Hydrocarbons
  - Volatile Methylsiloxanes (VMS)
- 3.5 Safety First: Flame Retardants All Around Us**
- 3.6 How to Make Materials “Repellent”: Polyfluorinated Chemicals (PFCs)**
- 3.7 From Washing Machines to Surface Waters: Complexing Agents, Surfactants, Whitening Agents, and Corrosion Inhibitors**

### **3.8 Health, Well-Being, and Water Pollution: Pharmaceuticals and Personal Care Products**

Pharmaceuticals

Ingredients of Personal Care Products

### **3.9 Fighting Pests: Herbicides, Insecticides, and Fungicides**

### **3.10 Our Companion Compounds: Representative Model Chemicals**

### **3.11 Questions**

### **3.12 Bibliography**

### 3.1 Introduction

In this chapter, we take a closer look at the vast world of “anthropogenic organic chemicals,” defined in Chapter 1 as organic compounds that are of interest in terms of their distribution in and effect on the environment. We also take a first glimpse at how the characteristics and properties required to make a chemical suitable for a particular purpose are related to its chemical structure and influence its environmental behavior. Obviously, anthropogenic chemicals serve certain purposes in our daily lives, and are therefore designed to persist long enough to fulfill their task. In fact, for many applications, chemicals need to be resistant to degradation even under harsh conditions. Thus, a conflict of interest often exists between the usefulness of a chemical in human society and the concern about its potential to persist in the environment. The challenge is to replace chemicals of particular concern, above all compounds that are persistent, bioaccumulative, and toxic, so-called PBT Chemicals (see Strempel et al., 2012), with more environmentally benign compounds. This undertaking is anything but trivial and requires not only profound knowledge on the use patterns and environmental behavior of chemicals, but also incorporation of economic and political constraints.

The aim of this chapter is to discuss representatives of important groups of chemicals used for specific purposes in our daily lives rather than to overwhelm the reader with an endless collection of chemical structures. Key references that serve as entry points into the vast literature on the various groups of compounds are also supplied. At the end of the chapter, we choose some representative model compounds from each of these groups as our “companion compounds” throughout the book. These compounds are of interest because of their occurrence in the environment as well as their distinct properties and reactivities. They are called our companions because we frequently meet them throughout the book as we introduce new topics and concepts, and they will appear in examples and problems. But for now, let us look at some of the numerous organic chemicals that surround us.

### 3.2 A Lasting Global Problem: Persistent Organic Pollutants (POPs)

We begin by looking at the persistent organic pollutants (POPs), a group of diverse chemicals that are not categorized by their use or structure but by their fate characteristics, which make them of particular environmental concern. POPs include high production volume chemicals that are commercially produced as well as chemicals that are primarily formed as by-products of various combustion processes. As of 2004, this group of chemicals was defined and sanctioned by the United Nations Environment Programme (UNEP) Stockholm Convention on Persistent Organic Pollutants (Secretariat of the Stockholm Convention, 2015). The goal of the Stockholm Convention is to assess the global presence of POPs (see Lohmann et al., 2007; Nizzetto et al., 2010) and to minimize, if possible, their use and release. According to this convention, all POPs share certain characteristics: (i) they persist in the environment, which means that neither abiotic nor biological transformation leads to significant removal of the chemical in any environmental compartment; (ii) they are prone to long-range transport and, thus, to global distribution, even to remote regions where the chemical

has not been used or disposed; (iii) they bioaccumulate in the food web; and (iv) they are toxic to living organisms, including humans and wildlife.

The chemical properties that favor bioaccumulation from air or water include low volatility, significant hydrophobicity (they are “water hating,” see Chapter 9), and persistence. For example, apolar compounds, such as the polychlorinated and polybrominated pollutants, travel long distances and bioaccumulate. Such compounds have also been shown to be toxic in that they may disrupt the endocrine, reproductive, or immune system or cause neurobehavioral and developmental disorders and cancer (see Li et al., 2006).

Initially, the chemicals listed and regulated were the so-called “legacy POPs” or the “dirty dozen.” The legacy POPs include nine polychlorinated pesticides, such as hexachlorobenzene (HCB), DDT, aldrin, and chlordane; polychlorinated biphenyls (PCBs) used in numerous industrial and consumer applications; and the unintentionally produced polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). As illustrated in Fig. 3.1, some of these chemicals are not single compounds but rather complex mixtures of isomers and congeners, which are related by origin, structure, or function.

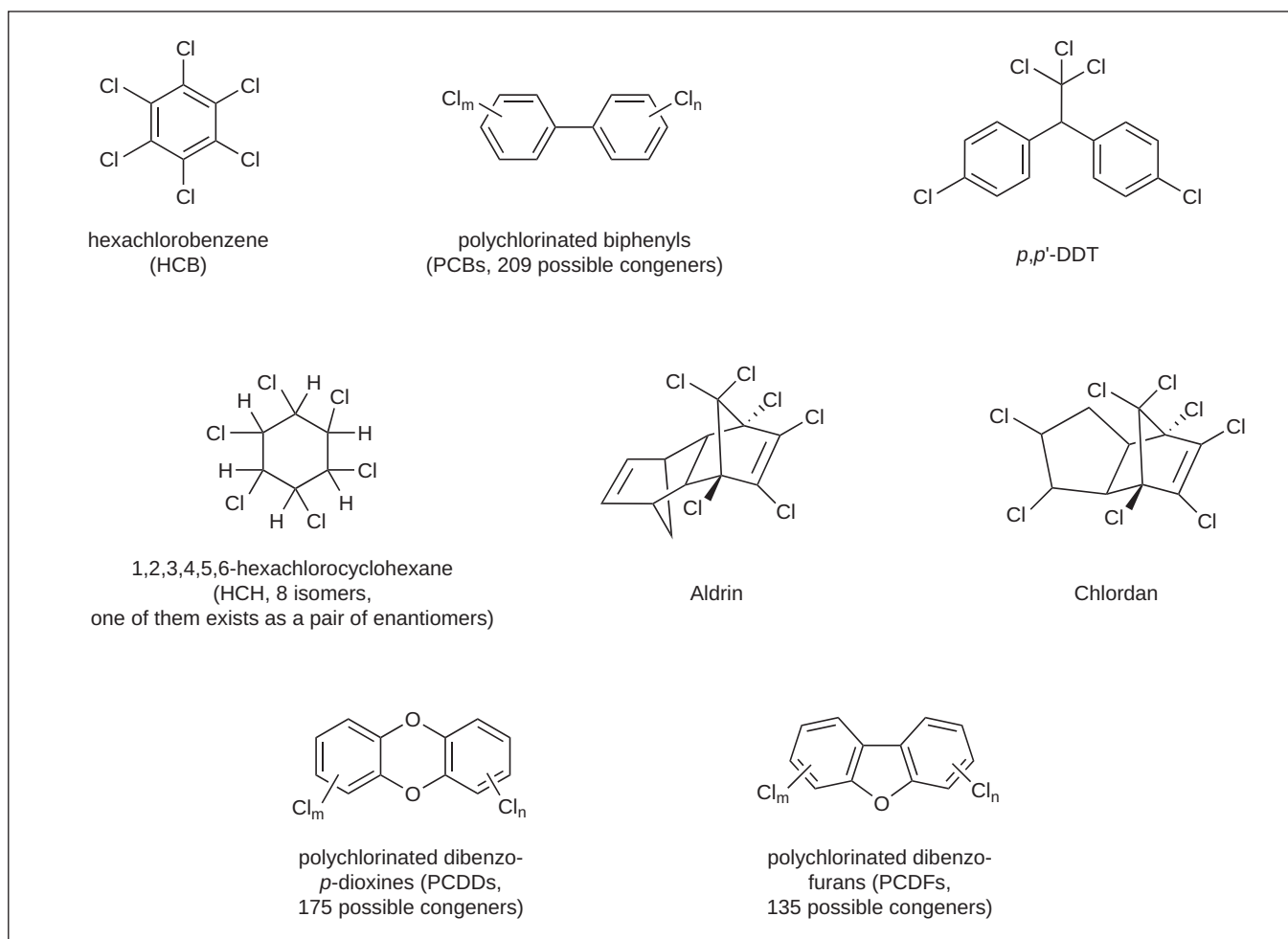
The Stockholm Convention also allows addition of new high production volume chemicals to the list. Chemicals already added or being considered since 2004 include alpha-, beta-, and gamma-hexachlorocyclohexane (see stereochemistry in Chapter 2); pentachlorobenzene and hexabromobiphenyl; as well as a series of other polyhalogenated, polybrominated, and polyfluorinated compounds, which we encounter in Sections 3.5 and 3.6. Although not listed in the Stockholm Convention, an additional group of compounds of considerable global concern that are commonly included in the POP category are the polycyclic aromatic hydrocarbons (PAHs). We address PAHs in Section 3.3 on petroleum hydrocarbons.

Global control strategies, such as the Stockholm Convention, aim to reduce the production and use of POPs. However, as evident from the lasting ubiquitous global presence of many legacy POPs in the environment, particularly in the Arctic’s cold regions (Lohmann et al., 2009; Ruggirello et al., 2010), such strategies do not necessarily lead to an immediate reduction of detection in the environment. The presence of various old sources plus the characteristics of POPs leads to continuing emissions and lasting detection. To identify and design optimal future mitigation strategies, further developments in emission inventories, as attempted for PCBs (Breivik et al., 2007), as well as more refined chemical fate and effect models for identification and assessment of old and new POPs are necessary (Scheringer, 2009; Swackhamer et al., 2009; Stempel et al., 2012).

### 3.3

## Natural but Nevertheless Problematic: Petroleum Hydrocarbons

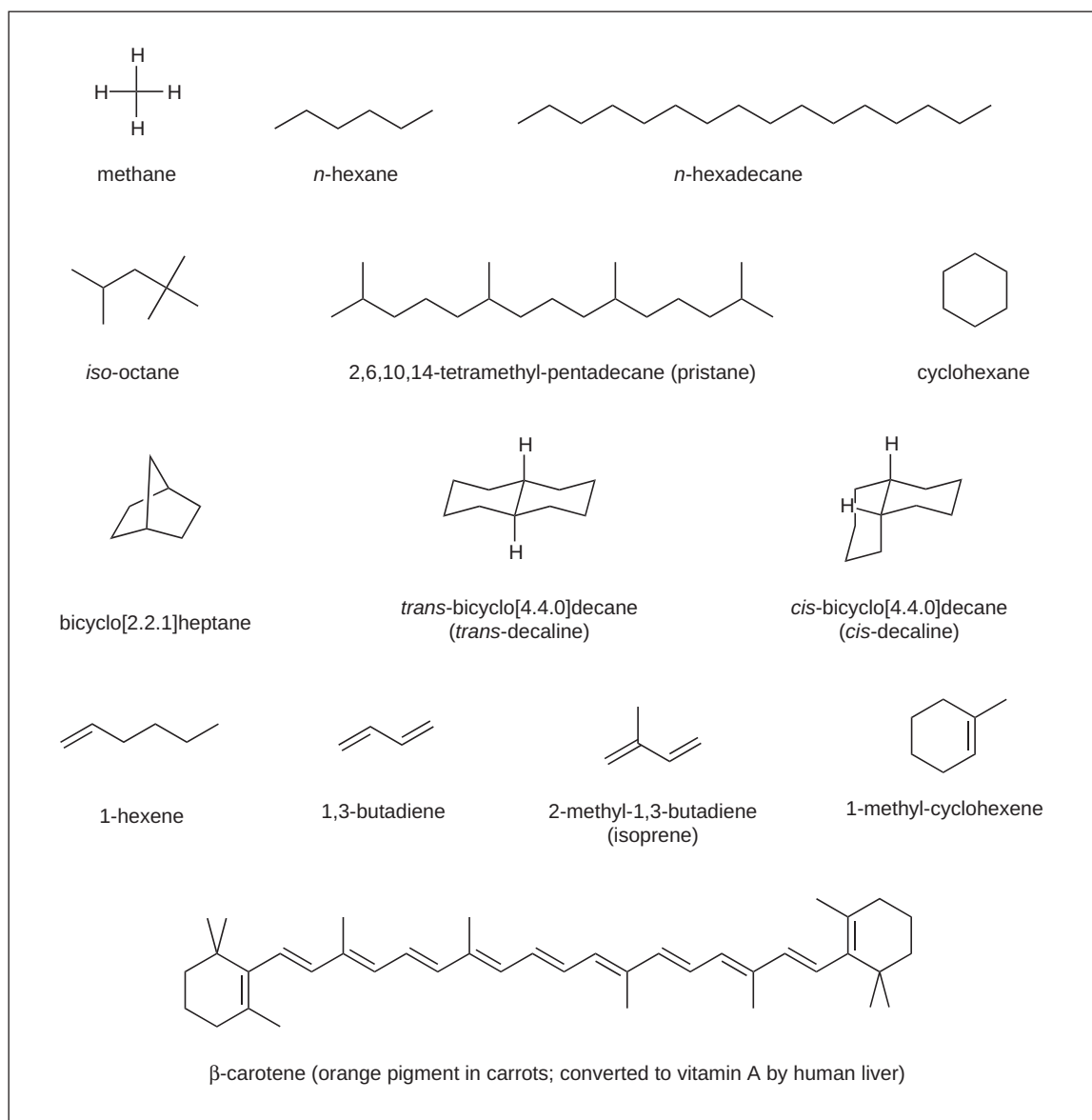
We now encounter another group of “classical” organic contaminants, the petroleum hydrocarbons. These compounds are everywhere in the environment. Natural



**Figure 3.1** Some members of the so-called “legacy POPs,” the “dirty dozen.”

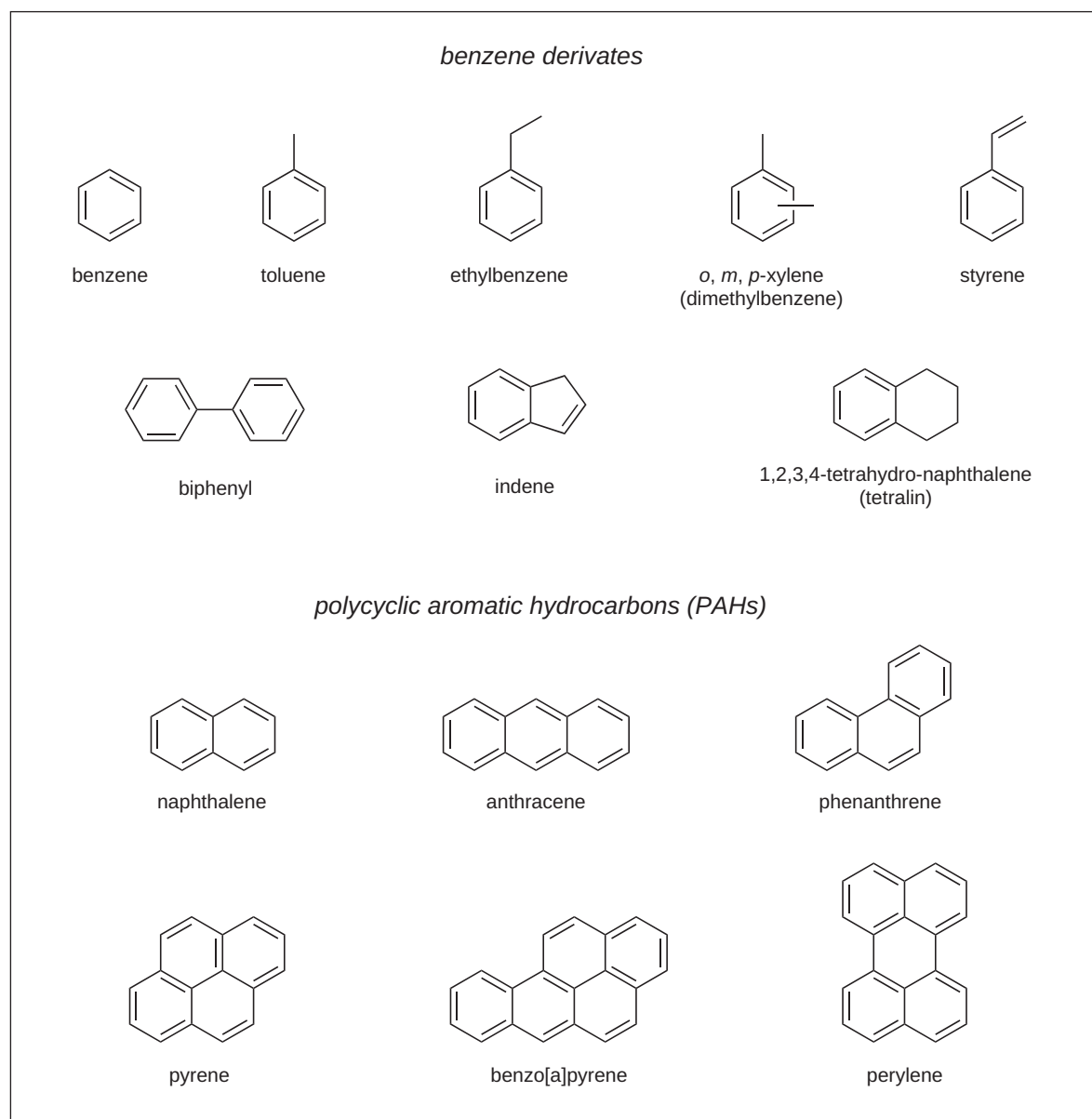
hydrocarbons (Fig. 3.2) range widely in size from methane ( $16 \text{ g mol}^{-1}$ ) to  $\beta$ -carotene ( $537 \text{ g mol}^{-1}$ ). Diverse branched, olefinic, cyclic, and aromatic hydrocarbons exist in fossil fuels or are derived from commercial processing of these fuels (Fig. 3.3). The global annual production of liquid petroleum products, including gasoline, kerosene, and heating oils, is more than 3 billion metric tons, so it is no surprise that processing and use of these hydrocarbons create major environmental problems. Petroleum hydrocarbons are released to the atmosphere when we pump gasoline into our cars and incompletely combust them in our engines. They are also introduced to street surfaces when our cars slowly leak engine oil. They contaminate our groundwaters from leaky gasoline underground storage tanks or heating oil tanks. Thus, not only through large oil spills, such as the wreck of the *Exxon Valdez*, the Gulf War oil spill, or the Deepwater Horizon disaster, do petroleum hydrocarbons pollute the environment.

Although they share a common source, the various hydrocarbons in the exceedingly complex mixture that is oil certainly do not behave in the same way once released into the environment. Some constituents tend to vaporize while others clearly prefer to bind to solids. Some oil hydrocarbons are rather unreactive whereas



**Figure 3.2** Examples of aliphatic, alicyclic, and olefinic hydrocarbons.

others are easily biodegraded or interact with light; some are quite nontoxic while others are renowned for their carcinogenicity. We highlight two groups of compounds that are of particular interest to many environmental chemists, engineers, and toxicologists: the BTEX compounds (benzene, toluene, ethylbenzene, and the three xylene isomers; Fig. 3.3) and the polycyclic aromatic hydrocarbons (PAHs; Fig. 3.3). The BTEX components are important gasoline constituents and are also widely used as solvents (see Section 3.4). They are very common soil and groundwater pollutants with contamination typically occurring near petroleum and natural gas production sites, gasoline stations, and other areas with storage tanks containing gasoline or other petroleum-related products. A total of about 600,000 regulated underground storage tanks are currently operated in the United States (U.S. EPA, 2013). As a consequence of leaks or spills from storage tanks, the liquid gasoline or oil phase,



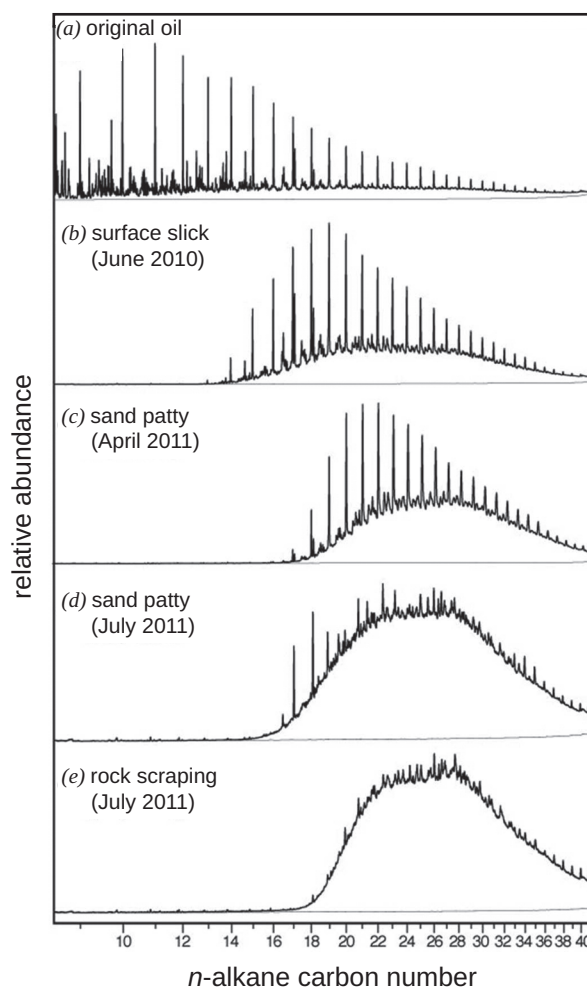
**Figure 3.3** Examples of aromatic hydrocarbons.

commonly referred to as NAPL (non-aqueous phase liquid), spreads in the soil. When exposed to infiltrating rainwater, the various NAPL components are dissolved according to their water solubility (Chapter 9) and may then be transported into groundwater, contaminating drinking water resources. Since the BTEX compounds are appreciably soluble in water, particularly toxic benzene, such soil and groundwater contamination often triggers monitoring programs and remediation actions (e.g., Farhadian et al., 2008).

The major sources of PAHs in the environment include the combustion of fossil fuels (gasoline, oil, coal), application of asphalts and coal tars, and use of creosotes as wood preservatives. PAHs are also produced and consumed when barbecuing food

(see Bansal and Kim, 2015). From a human health perspective, PAHs have drawn considerable interest primarily because some of them are potent carcinogens (e.g., benzo(a)pyrene; Fig. 3.3). This toxicity is the main reason why PAHs are considered to be among the most important air pollutants (see Barro et al., 2009; Kim et al., 2013). Furthermore, because of their high tendency to bioaccumulate, PAHs are of great ecotoxicological concern (see Logan, 2007) and thus are commonly considered as POPs or PBTs.

Oil is a complex mixture and Fig. 3.4 illustrates how after a spill its composition may change over time due to the weathering processes. For example, between April and mid July 2010, the Deepwater Horizon disaster released about  $2 \times 10^5$  metric tons of gases ( $C_1$  to  $C_5$  hydrocarbons) and  $5 \times 10^5$  metric tons of oil into the Gulf of Mexico, making it the largest spill in U.S. history (Reddy et al., 2012). By comparing the gas chromatograms of the original oil with the subsequent surface slick (Fig. 3.4a and b), one sees that the more volatile fraction of the oil encompassing the molecules with less than 13 carbon atoms was almost completely lost after a relatively short time. These losses are primarily attributable to volatilization and, to a lesser extent,



**Figure 3.4** Gas chromatograms of (a) the original oil from the Macondo Well; (b) a surface slick taken a two months after the blow up; (c,d,e) weathered oil samples collected one year later. On the *x*-axes, retention times are given in *n*-alkane units (retention time of the sharp peaks corresponding to the elution of the respective linear alkane). The *y*-axes provide the relative abundances of the components within the sample analyzed. The different chromatograms cannot be compared quantitatively. Figure from Aeppli et al. (2012).



dissolution of the more water-soluble aromatic compounds, including the BTEX compounds (Aeppli et al., 2012). An important feature of the weathering process is the increasing fraction of compounds making up what is called the unresolved complex mixture (UCM) or “hump” in the gas chromatogram (Fig. 3.6c, d, and e). In addition, we emphasize that a large number of polar compounds that are not amenable to gas chromatographic analysis, and therefore not visible in Fig. 3.4, are present in crude oil or are produced during weathering by biological and photochemical transformation reactions (McKenna et al., 2013).

### 3.4 Notorious Air and Groundwater Pollutants: Organic Solvents

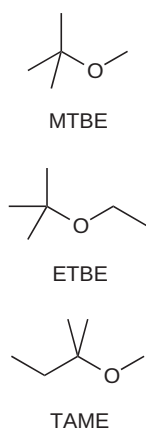
In a chemistry laboratory, solvents are needed to dissolve substances without chemically changing them. In society, we find solvents to be another group of high production volume chemicals used in industrial processes and consumer products that are released into the environment. A large variety of solvents exist on the market, with demand in the millions of metric tons in the United States alone, as different properties are necessary for different applications (Wildes, 2007). A solvent must be able to dissolve certain other compounds, but it also must exhibit advantageous properties such as viscosity, volatility, surface wetting, as well as thermal and chemical stability.

Large emissions of solvents into the environment lead to exposures that may be harmful to living organisms, including humans. Of particular concern are the solvents classified as *volatile organic compounds* (VOCs). The term “volatile” is used because these chemicals have relatively high vapor pressures and thus evaporate quite easily under ambient conditions (see Chapter 8). Exposure to VOCs in indoor environments is more concentrated than outdoors and may lead to a variety of adverse health effects in humans, ranging from local irritation to organ damage (Wallace et al., 1986). Other VOCs are of environmental concern because they are involved in the formation of ground-level ozone (Jenkin and Clemitshaw, 2000).

Here, we focus on a few solvents that are notorious such as air and groundwater pollutants, including the BTEX compounds, tertiary dialkyl ethers (methyl- and ethyl-*t*-butyl ether (MTBE, ETBE) and methyl-*t*-amyl ether (TAME)), along with some polychlorinated C<sub>1</sub>- and C<sub>2</sub>-hydrocarbons. In addition, we briefly address quite a different and perhaps less familiar group of emerging pollutants, the volatile methylsiloxanes (VMS), which are subject to long-range transport in the atmosphere, thus making them candidates for the POPs list.

#### BTEX Compounds

The BTEX compounds (benzene, toluene, ethylbenzene, and the three xylene isomers; Fig. 3.3) make up a significant fraction of gasoline, which is a major source for their emission into the environment (see Section 3.3). However, the individual BTEX compounds are also used in large quantities in industry as solvents and starting materials for the synthesis of numerous other chemicals (Moskowitz, 2010). Furthermore, except for benzene, they are used as cleaning agents and solvents for a variety of consumer-oriented applications. Hence, numerous pathways exist by which



**Figure 3.5** Structures of the gasoline additives methyl-t-butyl ether (MTBE), ethyl-t-butyl ether (ETBE), and methyl-t-amyl ether (TAME).

BTEX compounds are continuously introduced into all environmental compartments, with about 22,000 metric tons reported being directly emitted from industrial use, including about 11,000 metric tons of toluene, in the United States alone in 2011 (U.S. EPA, 2015a).

### Tertiary Dialkyl Ethers

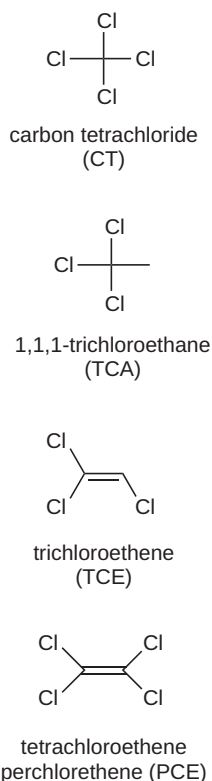
Although the tertiary dialkyl ethers MTBE, ETBE, and TAME (see Fig. 3.5) are also used as solvents in industry, they are of environmental concern primarily because they are “fuel ethers,” added in large quantities as oxygenates to gasoline in the low percentage range in some parts of the world. Oxygenates improve the combustion process and thus reduce emissions of carbon monoxide and hydrocarbons in exhaust. They are produced in millions of metric tons per year (Yee et al., 2013). Besides methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), MTBE has been and still is the most important global fuel additive.

The release of MTBE into the subsurface causes problems because of the chemical’s high water solubility, low biodegradability, and rather low odor and flavor thresholds (van Wezel et al., 2009). MTBE has a water solubility that is about 20 times higher than that of benzene. As a consequence, MTBE is transported much faster than the BTEX compounds in the subsurface and, therefore, can potentially contaminate groundwater at a much larger scale. It comes as no surprise that MTBE is frequently detected in public drinking water supplies using groundwater as their source (e.g., Williams and Pierce, 2009). Since 2000, the two other ethers, in particular ETBE, have been increasingly used as substitutes for MTBE because of economic reasons and because they are thought to be less problematic with respect to groundwater contamination. However, these alternative ethers have similar characteristics to MTBE, perhaps making them similarly potent pollutants (Shih et al., 2004; van Wezel et al., 2009).

### Polychlorinated $\text{C}_1$ - and $\text{C}_2$ -Hydrocarbons

As PCBs are referred to as legacy POPs, one could similarly term some chlorinated solvents as legacy groundwater pollutants because they are among the most frequently detected groundwater contaminants (Moran et al., 2006). The most common pollutants include carbon tetrachloride (CT), 1,1,1-trichloroethane (TCA), trichloroethene (TCE), and tetrachloroethene (or perchloroethene; PCE) (Fig. 3.6). Because they are nonflammable, these chemicals have long been used as solvents in the dry cleaning industry or as metal degreasing agents in the automotive and other metal working industries. Carbon tetrachloride was phased out of production in the 1990s because of its role in stratospheric ozone depletion, replaced almost exclusively by PCE (Doherty, 2000). Two other widely used chlorinated solvents are trichloromethane (chloroform;  $\text{CHCl}_3$ ) and dichloromethane (methylene chloride;  $\text{CH}_2\text{Cl}_2$ ).

Similar to gasoline and other petroleum products, chlorinated solvents are introduced into the subsurface by spills, leaky storage tanks, or even illegal disposal. Compared to gasoline or heating oil, they have several characteristics that make them even more pernicious groundwater pollutants. First, liquid polychlorinated hydrocarbons exhibit densities greater than water and thus form DNAPLs (dense non-aqueous phase



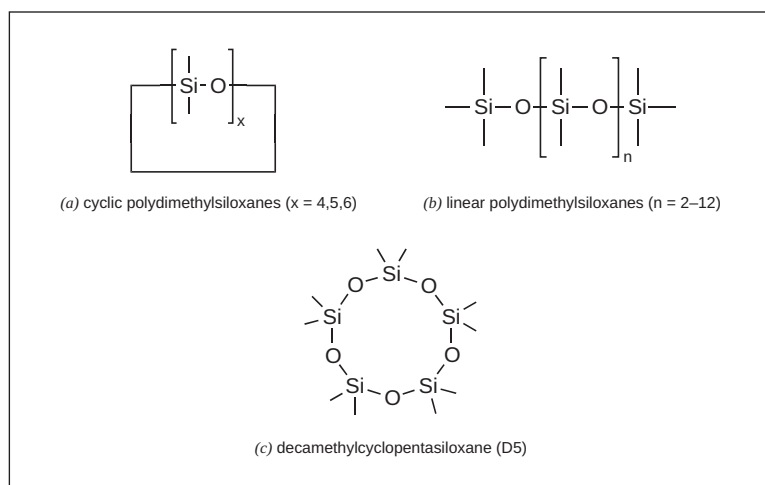
**Figure 3.6** Structures of some common polychlorinated solvents causing major groundwater contamination issues.

liquids) in the subsurface. DNAPLs tend to sink through aquifers until they reach impermeable bedrock, thus producing numerous “new” contamination sources that are difficult to locate and remediate. Furthermore, under oxic conditions, these solvent chemicals are persistent and, when dissolved in water, they are quite mobile in the subsurface, leading to long-lasting contamination of large groundwater areas. Finally, under anoxic conditions, they may be transformed into less halogenated products that are more toxic than the parent compound. A classical example is the formation of vinyl chloride ( $\text{CH}_2=\text{CHCl}$ ) by reductive dechlorination of PCE or TCA (see Chapters 23 and 27).

### Volatile Methylsiloxanes (VMS)

The volatile methylsiloxanes (VMS) are a group of structurally related solvents that include various linear and cyclic oligomeric structures (Fig. 3.7). Besides being widely used in industrial applications, these solvents are present in numerous personal care and household products, including skin lotions, body washes, shampoos, cosmetics, deodorants, fragrances, and cleaning products (Horii and Kanan, 2008; Wang et al., 2009). The properties that make VMS suitable for all these applications include low surface tension, low viscosity, high thermal stability, hydrophobicity, and relatively high volatility, the last being a result of their smaller vdW interactions as compared to other organic molecules of the same size (Rücker and Kümmerer, 2015). The desired properties for a specific application can be “fine-tuned” by choosing the appropriate number of dimethylsiloxane units or by using VSM mixtures. Generally, in many consumer products, the cyclic VMS (D4, D5, D6, see Fig. 3.7) are present in significantly higher quantities than the linear ones (L4 – L14) (Horii and Kanan, 2008; Wang et al., 2009).

Because of their volatilities and use patterns, a large fraction of VMS used in personal care products is emitted into the atmosphere. For example, the annual atmospheric emissions of D5, the most widely used VMS, to the Northern Hemisphere have been estimated to be 30,000 metric tons (McLachlan et al., 2010). Not surprisingly, the air



**Figure 3.7** General structures of (a) cyclic and (b) linear polydimethylsiloxanes. (c) D5 is the most common polydimethylsiloxane present in personal care and household products and is used as a dry cleaning solvent.

concentrations of D5 detected in the center of a city were found to be significantly higher than just outside of the city (Buser et al., 2013).

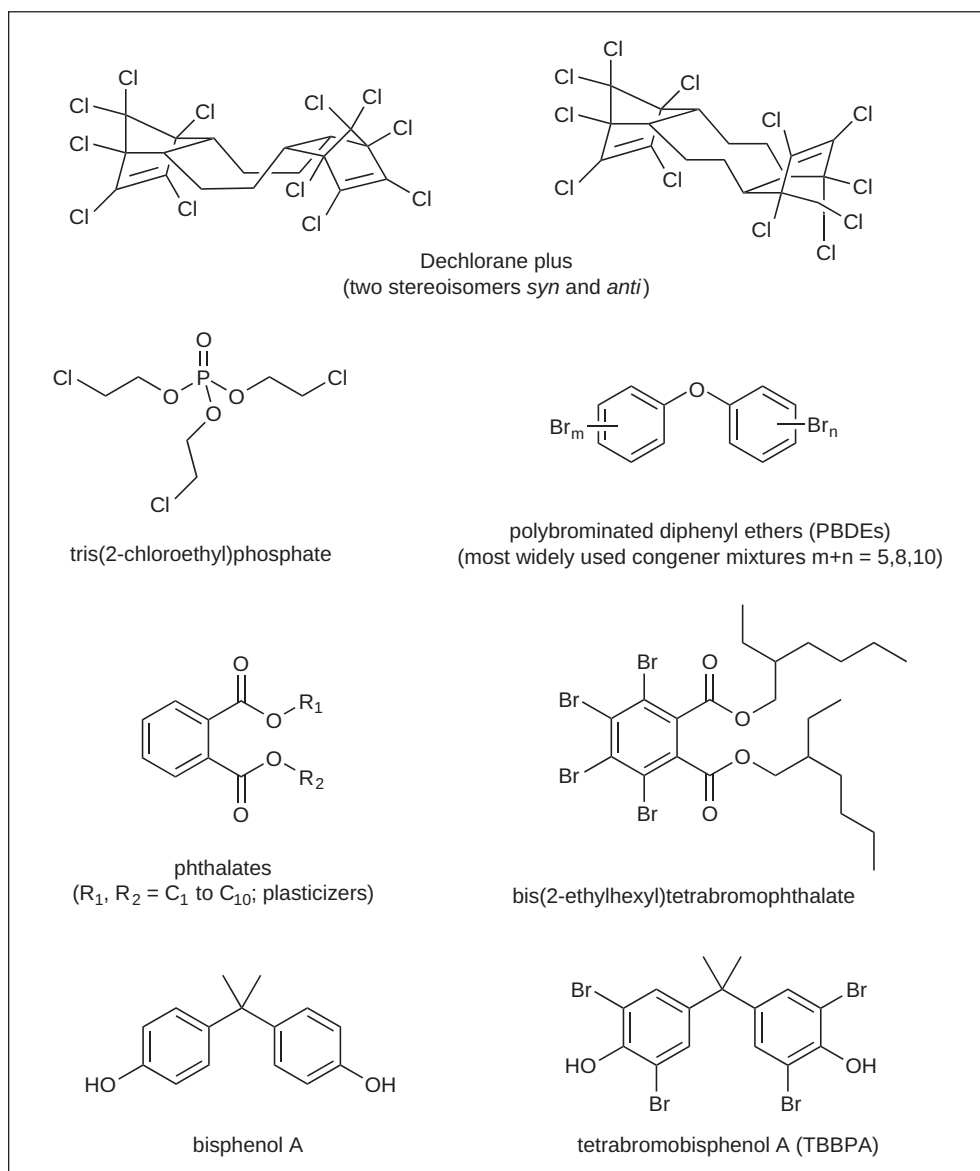
Although VMS react with hydroxyl radicals in the atmosphere at appreciable rates, their half-lives in the atmosphere are long enough to permit long-range transport. Therefore, VMS have not only been detected in air near sources in highly populated areas but also in remote areas, including the Arctic (Genualdi et al., 2011; Krogseth et al., 2013). Because of their hydrophobicity and persistence in water, VMS have also been shown to bioaccumulate in aquatic organisms and aquatic food webs (Warner et al., 2010; Kierkegaard et al., 2011; Borga et al., 2012). Although the available toxicity data indicates that acceptable exposure thresholds are significantly higher than the concentration levels presently detected in environmental compartments, VMS remain a group of compounds that need to be further assessed (see Wang et al., 2013), as exemplified by the inclusion of cyclotetrasiloxane (D4) on the EU's Priority List of Suspected Endocrine Disruptors (European Commission, 2007).

### 3.5 Safety First: Flame Retardants All Around Us

Looking further into the world of anthropogenic organic chemicals, we encounter chemical groups commonly used and emitted from consumer products. An outbreak of fire is a scary thought, whether it be in our home or office, while traveling in cars, trains or airplanes, or while out in restaurants or theaters. In all these places, we are exposed to materials that may catch fire. In order to retard and even prevent the combustion process, "flame retardants" are added to almost every material we touch in our daily lives from furniture, textiles, electronic devices, and toys, to plastics, coatings, and foams. The amount of flame retardant added to any material is based on the desired level of fire safety, often regulated by governmental ignition test standards. Loadings in materials range from less than 1 percent by weight for organic flame retardants to more than 60 percent for inorganic compounds, such as aluminium trihydroxide (Beard, 2007). Therefore, flame retardants represent the most important group of polymer additives with a rising global consumption, estimated at about 2 million metric tons in 2008, of which about 1/3 are organic chemicals.

Since a wide range of materials are loaded with flame retardants, quite a structural variety of retardant compounds are available on the market (see Beard, 2007; EFRA, 2010). These flame retardants interfere with the combustion process in different chemical and physical ways, depending on their chemical nature. Most organic flame retardants are polychlorinated or polybrominated aliphatic or aromatic compounds, some containing a phosphate ester group such as tris(2-chloroethyl)phosphate (see Fig. 3.8). In addition, as alternatives, a number of halogen-free phosphorus flame retardants are widely used (van der Veen and de Boer, 2012).

Polyhalogenated compounds effectively inhibit combustion via two pathways. First, halogenated radicals formed when the flame retardant is heated, trap other highly reactive radicals formed when materials catch fire. This interrupts the gas phase



**Figure 3.8** Some prominent flame retardants, plasticizers, and related compounds.

radical reactions generating heat that promote continued combustion. Brominated compounds are more effective at combustion suppression than chlorinated ones because the carbon-bromine bond is more easily cleaved than the carbon-chlorine bond (see bond energies in Table 2.4). Secondly, upon combustion, polyhalogenated compounds do not burn completely, thus building a char layer that shields the material from oxygen and the flame.

In most cases, these retardants are only physically mixed into materials. Therefore, they are defined as additives and may diffuse out and enter the environment. Considering that many of the retardants are structurally similar to the halogenated legacy pollutants previously discussed, it comes as no surprise that they are

ubiquitously found in the environment, just like the legacy pollutants. In fact, many that replaced polybrominated biphenyls (PBBs) in the 1970s, including polybrominated diphenyl ethers (PBDEs) (see Hites, 2004; Frederiksen et al., 2009), Dechlorane Plus, and related compounds (see Sverko et al., 2011), have already been banned or added to lists of high priority chemicals with persistence and bioaccumulation potential (e.g., Muir and Howard, 2006; Howard and Muir, 2010). Unfortunately, burning, dismantling, and recycling electronic waste results in further contamination (Eguchi et al., 2013) and formation of brominated and chlorinated dioxins and furans (see Weber and Kuch, 2003; Tue et al., 2013), especially in developing countries. The PBDEs are examples of compounds for which their accumulation in the environment and bioaccumulation in food webs could have been anticipated before they were brought onto the market because PBDEs have characteristics similar to PCBs and PBBs (see Section 3.2). New polyhalogenated aromatic compounds have emerged as substitutes for PBDEs, and many are also persistent, bioaccumulative, and already detected in the environment. Examples are a series of brominated benzenes (Venier et al., 2012), decabromodiphenyl ethane (DBDPE) (Egeback et al., 2012), brominated benzoic acid and brominated phthalic acid esters (Fig. 3.8), and tribromophenoxy compounds (Ma et al., 2012a and b).

Flame retardants are often applied in combinations. Some of them also serve as plasticizers, additives that increase the plasticity or fluidity of a given material. From an environmental point of view, the most prominent plasticizers are the phthalates (phthalic acid esters, see Fig. 3.8 and Net et al., 2015). For example, by incorporating bromine atoms into the structure, an effective flame retardant is obtained, such as bis(2-ethylhexyl)tetrabromophthalate (Fig. 3.8). Other examples of compounds that serve dual purposes are the polychlorinated paraffins (see Houde et al., 2008; Friden et al., 2011) and some phosphate esters such as triphenyl phosphate.

In some applications, flame retardants are covalently bound to polymer materials to minimize loss to the environment. Such compounds must exhibit functional groups that react with polymer constituents, such as, for example, the phenolic groups in tetrabromobisphenol A (TBBPA, Fig. 3.8), the most widely used brominated flame retardant. However, TBBPA is also applied as an additive and thus may be released into the environment (Howard and Muir, 2010). Looking at the structure of TBBPA, we see that it is similar to bisphenol A (Fig. 3.8), a high production volume chemical primarily used as a starting material for polymers. Bisphenol A is of considerable environmental concern because it has been shown to exhibit endocrine-disrupting effects in a variety of organisms (see Flint et al., 2012)

### 3.6

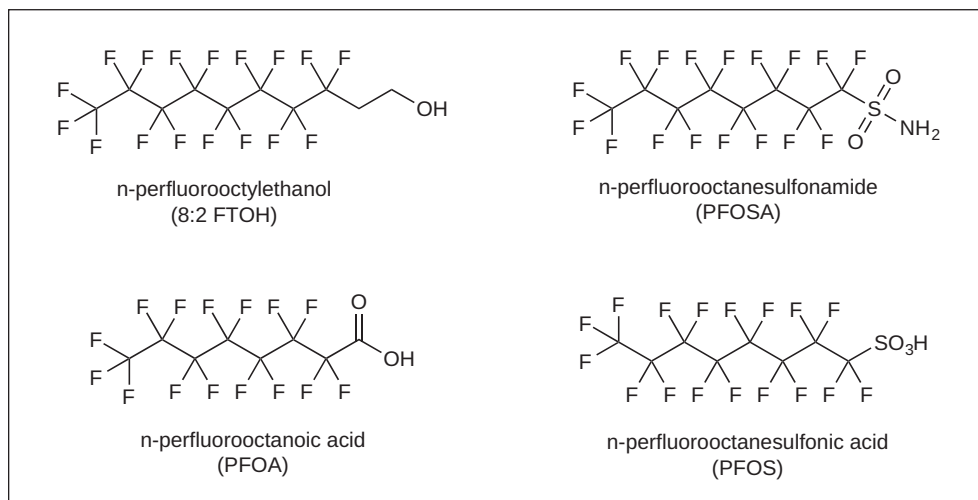
## How to Make Materials “Repellent”: Polyfluorinated Chemicals (PFCs)

All of us have probably experienced the water “repellency” of pans coated with Teflon® or textiles containing Gore-Tex®. Such products contain polytetrafluoroethylene, a widely used perfluorinated (completely fluorinated) polymer. Perfluorinated as well as other highly fluorinated compounds, all denoted as PFCs, make products



water-, and to a somewhat lesser extent, oil-, and fat-“repellent.” The term “repellent” is somewhat misleading, because on a molecular level, vdW forces always exist between water molecules and, for example, a Teflon<sup>®</sup> surface. However, the very high electronegativity of fluorine induces significantly smaller vdW interactions as compared to other organic molecules of the same size (Goss and Bronner, 2006; see also Chapter 7). Also, these forces are minor compared to the surface tension of water, thus minimizing the wetting of the surface and, therefore, leading macroscopically to the formation of water droplets. Therefore, a greasy Teflon<sup>®</sup> pan is easy to wipe clean after its use.

The previously mentioned PFC polymers are not those of primary environmental concern. Instead, the thousands of lower molecular weight PFCs with four to 14 carbon atoms, mostly aliphatic, are much more notable environmental pollutants. These compounds are used in numerous industrial and consumer applications because of their “repelling” characteristics, extreme stability, and surfactant properties (Lindstrom et al., 2011; Oliaei et al., 2013). Chemically, PFCs exhibit various chain lengths and can be divided into two categories of compounds, neutral and charged (see examples in Fig. 3.9). Neutral PFCs include the fluorotelomer alcohols (FTOHs), such as 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH denoting (per)fluoro hexyl, octyl, and decyl ethanol, respectively. The term telomer indicates that the chemical is a small polymer made from only two to five monomers. Another group of neutral PFCs are the perfluorosulfamides such as perfluorooctanesulfonamide (PFOSA). The most prominent strongly acidic PFCs, present as anions in water, include the perfluorocarboxylic acid (PFOAs, e.g., perfluorooctanoic acid (PFOA)) and the perfluorosulfonic acids (PFSA, e.g., perfluorooctanesulfonic acid (PFOS)). Evidence suggests that the acidic compounds PFOA and PFOS may be formed from precursor compounds, including FTOHs, via reactions in the atmosphere (Schenker et al., 2008) and by metabolic transformations in organisms, including humans (Vestergren et al., 2008; Martin et al., 2010; Yeung et al., 2013). All of the examples that we have chosen are linear carbon chain compounds because they are the most abundant PFCs produced, although numerous isomers exist for each of these compounds. For example, 89 branched isomers are theoretically possible for PFOS. However, only a few of these have been



**Figure 3.9** Some prominent perfluorinated compounds.

detected in technical PFOS products at a total mass fraction of 20 to 35%, the rest being linear compounds (Houde et al., 2006; Greaves and Letcher, 2013).

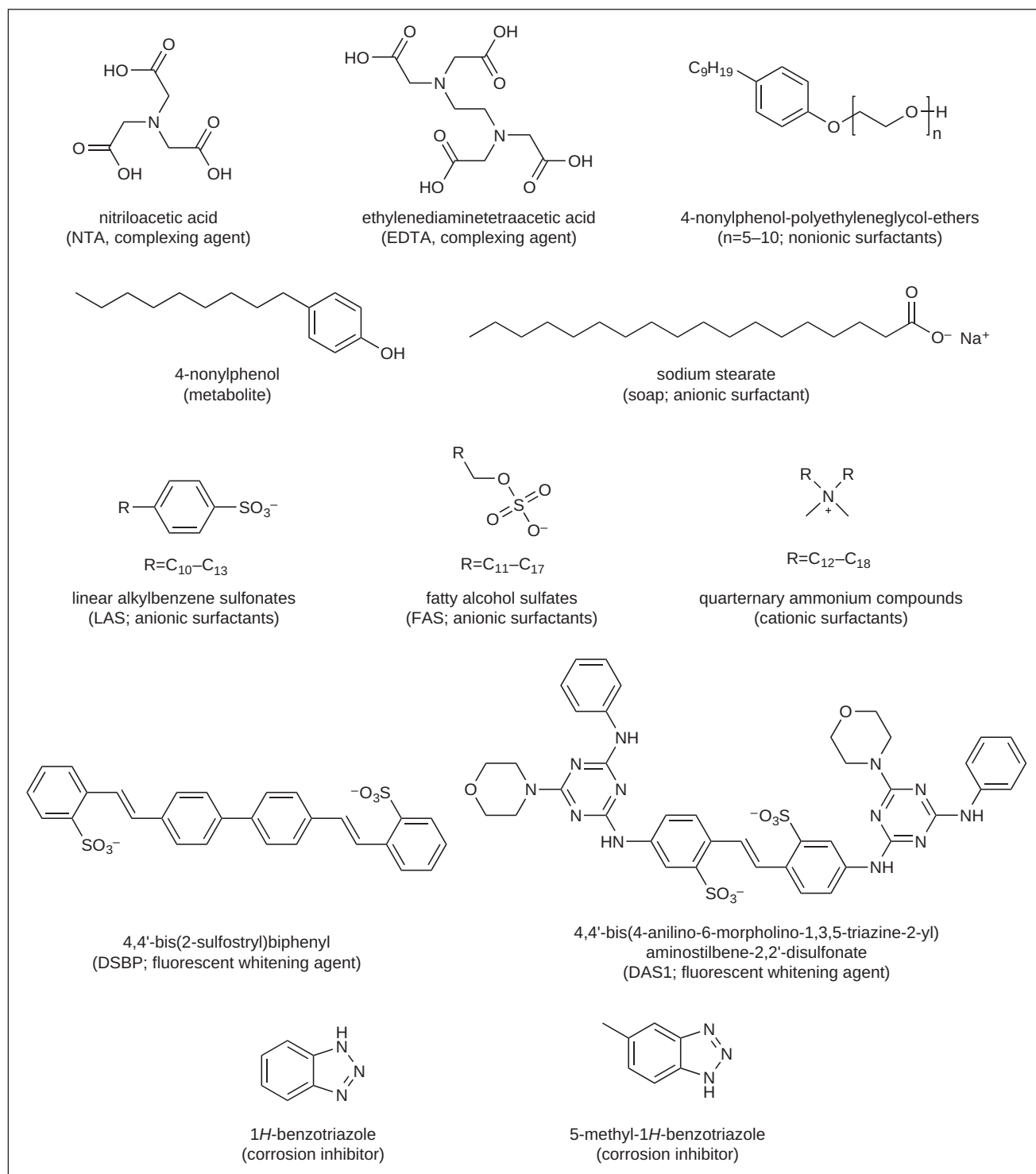
Although PFCs have been manufactured for more than 50 years, their occurrence in the environment was widely recognized only at the beginning of this millennium (Giesy and Kannan, 2001). The challenge of quantitative analysis of such compounds in environmental matrices, including biological samples (see Ahrens, 2011; Houde et al., 2011; Valsecchi et al., 2013), and the assumption that these compounds were not of toxicological concern contributed to delays in environmental detection. However, numerous recent studies reveal that PFCs are ubiquitous in the environment (see Ahrens, 2011; Benskin et al., 2012a and b; Zareitalabad et al., 2013) and in humans (Lindstrom et al., 2011), and accumulate in aquatic and terrestrial food chains (see Houde et al., 2006 and 2011). To date, the most widely investigated PFCs are PFOA and PFOS. These anionic PFCs strongly associate to proteins because of their charged nature and surfactant properties and, therefore, are found in the blood and liver of mammals, including humans, rather than in fatty tissue (see Chapter 16). Indoor sources, such as home furnishings and carpets, may significantly contribute to the accumulation of PFCs in humans, where some of these compounds exhibit half-lives of several years (Olsen et al., 2007; Beesoon et al., 2011; Shoeib et al., 2011). As evidence has also shown that PFCs are toxic, they are considered PBT chemicals (Lindstrom et al., 2011; Krafft and Riess, 2015).

### 3.7 From Washing Machines to Surface Waters: Complexing Agents, Surfactants, Whitening Agents, and Corrosion Inhibitors

Expanding on the groups of chemicals found in consumer products, we now introduce laundry and dish detergents. These products include several classes of chemicals, all serving different purposes during the washing process. Because of their direct application into water, the various detergent components are introduced into wastewaters and thus enter the environment via effluents of wastewater treatment plants (WWTPs). Several of these chemicals are of concern with respect to water pollution. Among these are the builders that complex or precipitate metal ions, in particular calcium and magnesium, since these metals may interfere with the washing process by forming precipitates with soaps or surfactants. Detergents also contain surfactants or tensides, which lower the surface tension of water, thus changing its wetting properties and as a consequence improve the cleaning process at surfaces. At higher concentrations, surfactants form aggregates, called *micelles*, capable of keeping otherwise insoluble compounds in the aqueous phase. Other organic components present in laundry and dish detergents that should be mentioned include whitening agents, corrosion inhibitors, and fragrances.

Historically, the most widely used builders, i.e., complexing agents, were phosphates and phosphonates. Because phosphorus is a key nutrient in natural waters and can cause eutrophication problems, particularly in small lakes, phosphorus salts have been replaced in many countries by other chemicals including zeolites or





**Figure 3.10** Examples of laundry and dish detergent components, including complexing agents, surfactants, whitening agents, and corrosion inhibitors.

organic complexing agents such as NTA or EDTA (Fig. 3.10) (see Glennie et al., 2002). NTA and EDTA are also used in numerous other applications, such as pulp bleaching, textile processing, and scale removal. Whereas NTA is significantly eliminated in WWTPs, EDTA is persistent and one of the most abundant organic

contaminants in surface waters (Reemtsma et al., 2006; Barber et al., 2013). Both NTA and EDTA are of environmental concern because of their ability to (re)mobilize heavy metals in WWTPs and in the aquatic environment (Alder et al., 1990; Nowack, 2002).

Surfactants represent a group of diverse chemicals that are all built in the same general way: they contain both a hydrophobic and a hydrophilic part, thus giving them an *amphiphilic* character. This means, at interfaces, their hydrophilic “head” stays in aqueous solutions, whereas the hydrophobic “tail” tries to stay away. The hydrophilic head can be anionic, cationic, or neutral, whereas the hydrophobic tail usually consists of a long chain hydrocarbon moiety or, as encountered earlier, a perfluorinated alkyl chain (e.g., PFOA, PFOS, see Fig. 3.9). Surfactants are classified as high production volume chemicals with fabrication rates estimated at 15 millions metric tons per year (Reznik et al., 2010). They are not only used in detergents but also as soaps, wetting agents, dispersants, foaming agents, and emulsifiers in consumer and industrial applications. Some examples of important classes of surfactants are given in Fig. 3.10. An impressive use of surfactants that drew considerable attention was the application of about 8,000 m<sup>3</sup> of dispersants during the Deepwater Horizon oil spill with the goal to decrease the size of oil droplets and prevent the formation of large oil emulsions or oil slicks (Kujawinski et al., 2011). A historically interesting case of surfactants as water pollutants involves 4-nonylphenol-polyethyleneglycol ethers, which are only partially biodegradable in WWTPs and transform into quite persistent endocrine disrupting products, including the potent 4-nonylphenol (Ahel et al., 1994; Sumpter and Johnson, 2008).

Prominent fluorescent whitening or brightening agents include the two stilbene compounds 4,4'-bis(2-sulfostryl)biphenyl (DSBP) and 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazine-2-yl)aminostilbene-2,2'-disulfonate (DAS1). These fluorescent compounds absorb sunlight in the UV-region and re-emit light in the visible part of the spectrum. Whitening agents adsorb to textile surfaces, making them appear more white or bright. They are also used in many other applications, such as in paper manufacturing. DSBP and DAS1 are not significantly eliminated in WWTPs because they are quite water soluble and resistant to biodegradation (Poiger et al., 1998). As a consequence, they are introduced in significant quantities into surface waters, where they are often used as markers to trace the discharge and transport of domestic wastewaters in rivers and lakes (Stoll et al., 1998; Yamaji et al., 2010). Since DSBP and DAS1 have also been shown to interact with human and rainbow trout estrogen receptors, they are of concern as water pollutants (Simmons et al., 2008).

The final detergent components presented here are corrosion inhibitors, used in dishwashing for silver protection but also in many other products, including anti-icing fluids, cooling liquids, brake fluids, and additives in fracking wells. Typical inhibitors include the high production volume chemicals 1*H*-benzotriazole and 4- and 5-methyl-1*H*-triazoles. As these inhibitors are widely detected in natural waters, quite persistent, and potentially toxic, they are considered important emerging water pollutants (Janna et al., 2011; Seeland et al., 2012).

### 3.8 Health, Well-Being, and Water Pollution: Pharmaceuticals and Personal Care Products

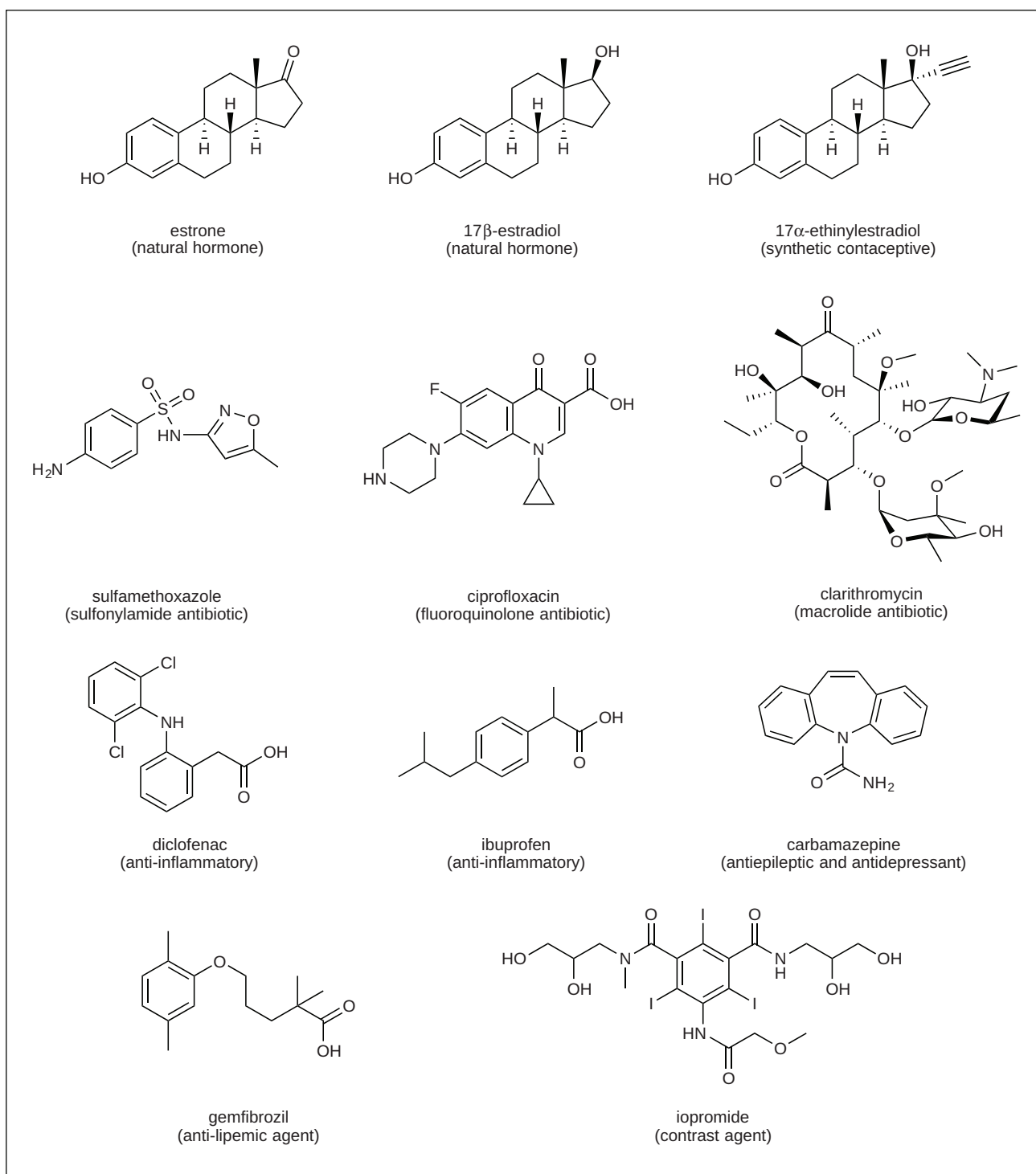
Thousands of chemicals are available on the market that support our health or help us to generally improve our well-being. Pharmaceuticals, including anti-inflammatories, antibiotics, beta-blockers, contraceptives, lipid regulators, antiepileptics, and antidepressants, are consumed daily in large amounts, as are personal care products such as soaps, shampoos, moisturizers, cosmetics, deodorants, fragrances, and sunscreens. Pharmaceuticals and ingredients of personal care products enter the environment primarily via municipal, industrial, and hospital wastewaters. Therefore, they are of primary concern as water pollutants (Hughes et al., 2013; Kaplan, 2013; Liu and Wong, 2013; Orias and Perrodin, 2013). In recent years, more wastewater and drinking water treatment plants have introduced advanced oxidation steps aimed at removing such compounds because traditional treatment plants provide insufficient removal. Sources other than WWTP outflows include runoff from agricultural fields fertilized with sewage sludge or animal manure, the latter commonly containing a variety of veterinary products including antibiotics and hormones (Metcalf et al., 2008).

The flurry of research focusing on these chemicals in the past fifteen years started primarily from the debate on endocrine disruptors. To date, although various other adverse effects are possible, they are not well understood (Corcoran et al., 2010). A compound is termed an endocrine disruptor if it imitates a natural hormone in an organism that is responsible for the maintenance of homeostasis, reproduction, development, or behavior. Possible negative effects include reproductive disorders, various cancers, and feminization, for example, as observed in fish (Tyler et al., 1998; Sumpter and Johnson, 2008). As pharmaceuticals and certain ingredients of personal care products are biologically active chemicals that are often designed to alter physiological function, they may also be biologically active in wildlife species, even at low concentrations. Because of their manner of use, these chemicals are continuously emitted, and organisms in receiving waters may be exposed throughout their lifetime to a large number of such compounds simultaneously.

Here, we introduce some representative chemicals from the vast structural variety of pharmaceuticals and personal care products. We have selected them primarily based on their importance as environmental pollutants both with respect to exposure and effects (Benotti et al., 2009; Brausch and Rand, 2011; Howard and Muir, 2011). We also want to broaden the structural diversity of organic chemicals so far introduced. As we will see, these compounds are generally more polar than the chemicals we have already encountered. They exhibit various functional groups capable of hydrogen bonding, including acid and base functionalities. As a note, the common names are used for most of these chemicals instead of their lengthy systematic names.

#### Pharmaceuticals

We start with the most prominent and potent endocrine disruptors detected in wastewater and natural waters: natural estrogens, estrone and 17 $\beta$ -estradiol, as well



**Figure 3.11** Some prominent pharmaceuticals of environmental concern, particularly with respect to water pollution.

as the synthetic contraceptive 17 $\alpha$ -ethinylestradiol (Fig. 3.11). Historically, these hormones were the chemicals primarily blamed for the observed endocrine disruptive effects observed in aquatic organisms, particularly in fish (Corcoran, 2010). For example, exposure to 17 $\alpha$ -ethinylestradiol at environmentally relevant

concentrations was shown to induce feminization in fish (Tyler, 1998). Later, a variety of industrial chemicals and their transformation products were shown to also exhibit similar effects, though at much higher concentrations (Sumpter and Johnson, 2008). Such chemicals include many that we have already encountered in this chapter, such as certain POPs and bisphenol A. For example, Rutishauser et al. (2004) found that 4-nonylphenol, the surfactant transformation product, has a relative potency of  $2.5 \times 10^{-5}$  as compared to  $17\beta$ -estradiol in yeast cells and is cytotoxic to rainbow trout hepatocytes at concentrations above 50  $\mu\text{M}$ .

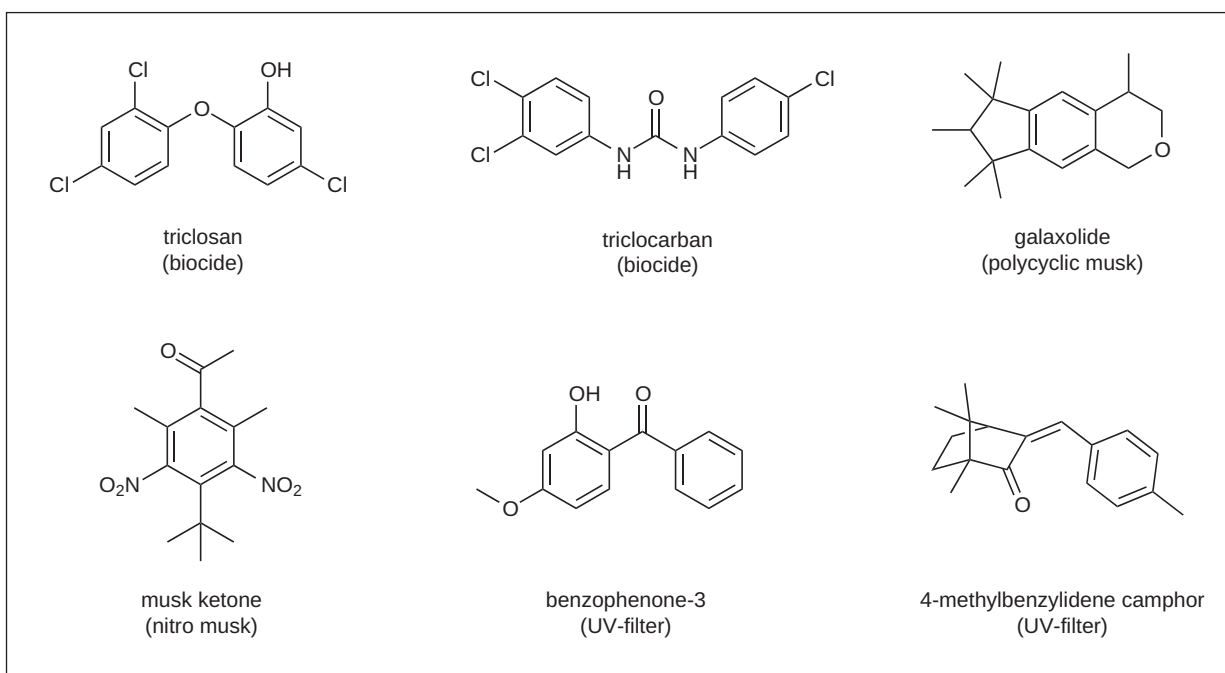
Another group of chemicals of considerable concern are antibiotics, also often referred to as antimicrobials, which are used in large quantities in human and veterinary medicine. The toxicity of antibiotics in addition to their potential to induce bacterial resistance are issues of growing concern (Knapp et al., 2010). The vast variety of antibiotics available act by different biochemical mechanisms and can be selectively applied to optimally cure or prevent specific human or animal diseases. Consequently, antibiotics represent a group of compounds exhibiting quite different and complex chemical structures, as illustrated by sulfamethoxazole, ciprofloxacin, and clarithromycin (Fig. 3.11). We complete our short list of pharmaceuticals frequently detected in wastewater and the aquatic environment with some representative compounds that are widely consumed for a variety of ailments: non-steroidal, anti-inflammatory drugs diclofenac and ibuprofen; antiepileptic and antidepressant carbamazepine; lipid-regulating medication gemfibrozil; and the X-ray contrast agent iopromide (Fig. 3.11).

### Ingredients of Personal Care Products

Besides solvents (see Section 3.4), personal care products contain several chemicals of environmental concern. Some prominent representatives frequently detected in surface waters (Brausch and Rand, 2011) include the biocides triclosan and triclocarban, the musks galaxolide and ketone, and the UV-filters benzophenone-3 and 4-methylbenzylidene camphor (4-MCB) (see Fig. 3.12). Pharmaceuticals and ingredients of personal care products are groups of very structurally diverse compounds (Figs. 3.11 and 3.12), most designed to exert a particular biological activity. Some of them are also transformed into products that are of environmental concern. One example is the phototransformation of triclosan to 2,8-dichlorodibenzodioxin (Kliegman et al., 2013; see Chapter 24).

## 3.9 Fighting Pests: Herbicides, Insecticides, and Fungicides

We complete our look into the world of anthropogenic organic chemicals by introducing pesticides, a group of biologically active compounds with an even larger structural diversity than pharmaceuticals. The annual global consumption of active pesticide ingredients is estimated at about 2.5 million metric tons, of which about 40% are used as herbicides followed by insecticides and fungicides (Grube et al., 2011). The major use of pesticides is in commercial agriculture, but they are also used in our homes and public spaces for pest control measures such as weed prevention, insect control, and plant pathogen treatment.



**Figure 3.12** Some ingredients of personal care products of environmental concern, particularly with respect to water pollution.

In contrast to many other industrial chemicals, pesticides are purposely introduced into the environment. Therefore, particularly rigorous environmental assessments must be completed before regulatory agencies allow an active pesticide to be used. In principle, the assessment needs to demonstrate that the pesticide does not persist in the environment much longer than its intended use period and that its impact on non-target organisms is minimal. However, as pesticides are directly applied to the environment, they can be immediately transported to places where degradation occurs more slowly than at the site of application. For example, depending on its physicochemical properties, a pesticide applied to an agricultural field may reach the atmosphere by volatilization, be transported by run-off into surface waters, or leach through the soil into groundwater (see Reichenberger et al., 2007; Kurt-Karakus et al., 2011). Therefore, not surprisingly, pesticides are ubiquitously found in the environment, although they are designed to persist for only a short time. In fact, several pesticides have been detected rather unexpectedly in regions far from their use, and surveys of groundwater and raw drinking water reveal the presence of certain pesticides that have long been phased out of use (Fenner et al., 2013).

Obviously, pesticides are a group of compounds that highlight the conflict of interest between the usefulness of a chemical in human society and concern about its potential to contaminate the environment. This potent conflict is illustrated by the continual use in some parts of the world of polychlorinated pesticides that cause well-known environmental problems. Today, such pesticides are classified as POPs (see Section 3.2). These compounds are still favored because they are comparatively cheap and effective. For example, DDT is still the dominant insecticide used for malaria control (van den Berg et al., 2012).

The structures of some representative members of important pesticide groups illustrate the chemical diversity involved (Fig. 3.13). The simplest pesticides are fumigants,

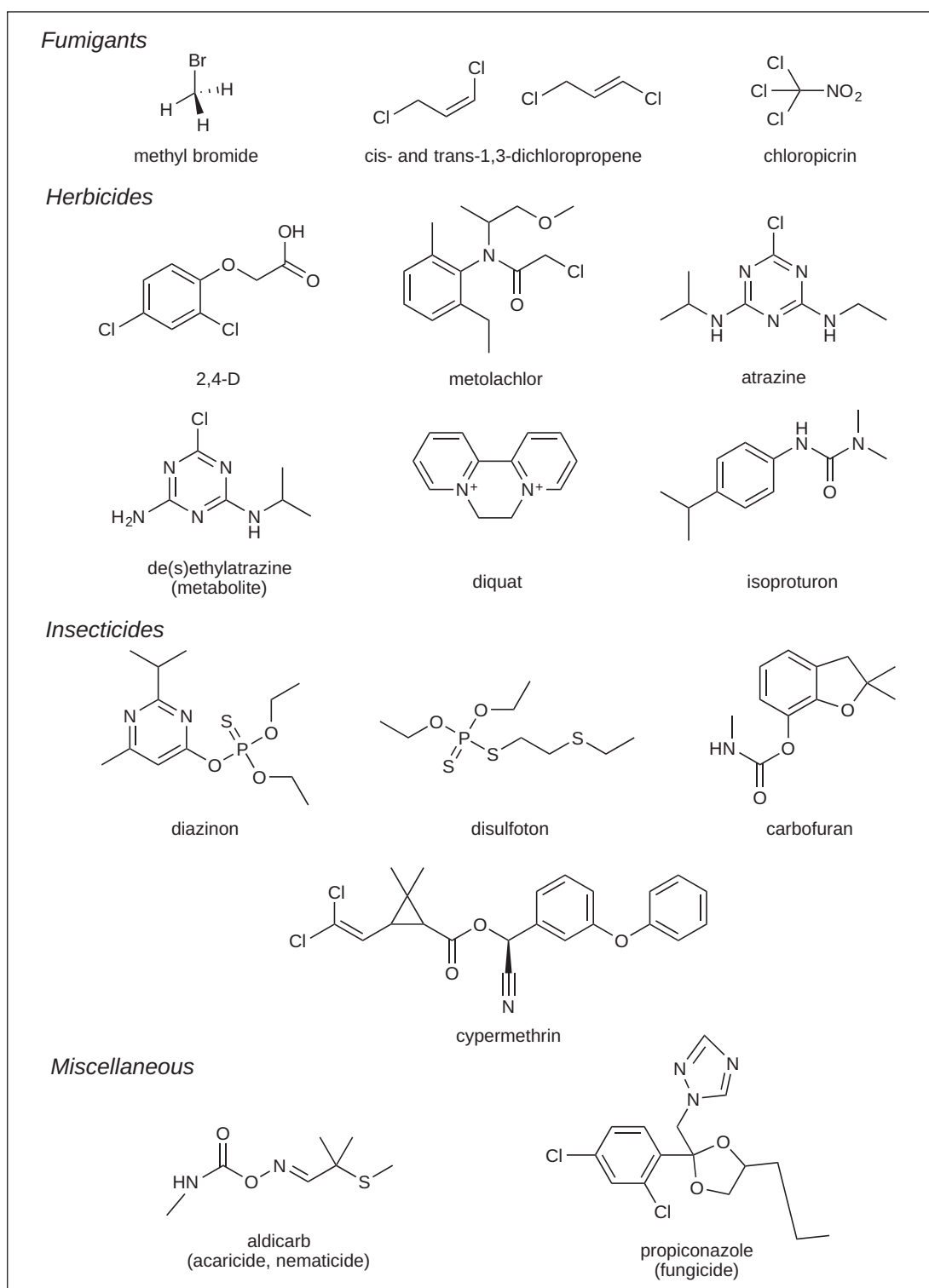


Figure 3.13 Examples of frequently used pesticides: herbicides, insecticides, and fungicides.

which are broad-spectrum pesticides targeting various organisms applied as gaseous compounds into enclosed areas and then released into the atmosphere. Agricultural use is the largest source of fumigants to the atmosphere. The most prominent fumigant is methyl bromide. However, because of its high potential to deplete stratospheric ozone, methyl bromide is being phased out of agricultural use (Ristaino, 1997; U.S. EPA, 2015b). Other prominent fumigants include *cis*- and *trans*-1,3-dichloropropene, chloropicrin, and methyl iodide ( $\text{CH}_3\text{I}$ ).

The next group of pesticides, the herbicides, are comprised of chemicals with quite different structural characteristics. Widely used classes of herbicides include phenoxy alkanolic acids (e.g., 2,4-D and its esters and salts), chloroacetanilides (e.g., metolachlor), triazines (e.g., atrazine), bipyridyls (e.g., diquat), and urea derivatives (e.g., isoproturon). Except for the positively charged bipyridyls, which sorb strongly to soil particles (Chapters 13 and 14), many of these herbicides have been frequently detected in surface and groundwater (Reichenberger et al., 2007; Kurt-Karakus et al., 2011). Also, compounds like desethylatrazine (Fig. 3.13), a persistent and toxic metabolite of atrazine, are often found in natural waters at similar concentrations as the parent compound (Squillance et al., 2002; Loos et al., 2010). This example of desethylatrazine's high frequency of detection in groundwater illustrates that stable transformation products of a given chemical should be included in assessments of the parent compound. Such widened assessments are of particular importance for biologically active chemicals, as their transformation products likely retain at least some of the bioactivity (Fenner et al., 2013).

Many herbicides, as well as other biologically active chemicals, are chiral, meaning they exist as enantiomers or optical isomers (see Chapter 2), which usually exhibit different biological activities. An interesting example is metolachlor. This compound has an asymmetric carbon center (indicated in Fig. 3.13) much like the herbicide mecoprop, discussed earlier (Fig. 2.4). In both cases, only one of the two enantiomers has a significant herbicidal activity; the *S*-form in the case of metolachlor and the *R*-form in the case of mecoprop. Actually, a total of four metolachlor isomers exist because two geometric *cis/trans* isomers are also possible. Both the *cis-S*-form and the *trans-S*-form are active herbicides, whereas the corresponding *R*-forms are not.

Prominent classes of insecticides include organophosphates (e.g., diazinon, disulfoton), carbamates (e.g., carbofuran), and pyrethroids (e.g., cypermethrin). Some organophosphates are also used as flame retardants (see Fig. 3.8's example). However, they contain three identical alkyl or phenyl ester groups, which render them rather non-toxic. In contrast, the organophosphates used as insecticides contain one ester group with a more complex structure, making them more toxic. Furthermore, these insecticides are thionate ( $\text{P}=\text{S}$ ) esters rather than oxonate ( $\text{P}=\text{O}$ ) esters. The main reason for including thionate esters is to lower the mammalian toxicity. However, in most cases, these esters are converted to the more active oxonates in target organisms (Eto, 1979; Hassal, 1990). We conclude this section by adding the fungicide propiconazole and the acaricide/nematicide aldicarb, two more examples that illustrate the vast structural variety present in pesticides (Fig. 3.13).



### 3.10 Our Companion Compounds: Representative Model Chemicals

To illustrate how one may think about and evaluate various organic chemicals that occur in the environment, we chose a subset of the diverse array of synthetic compounds to serve as our “companions” or model compounds throughout the book (Table 3.1). This does not mean we will not encounter numerous other chemicals. This group of companions includes compounds of different sizes, polarities, and reactivities meant to reflect the large structural variety one comes across when assessing environmental organic chemicals. In addition to the compounds that we have already encountered in this chapter, a few new chemicals have been added as companions because they are interesting in terms of persistence and transport.

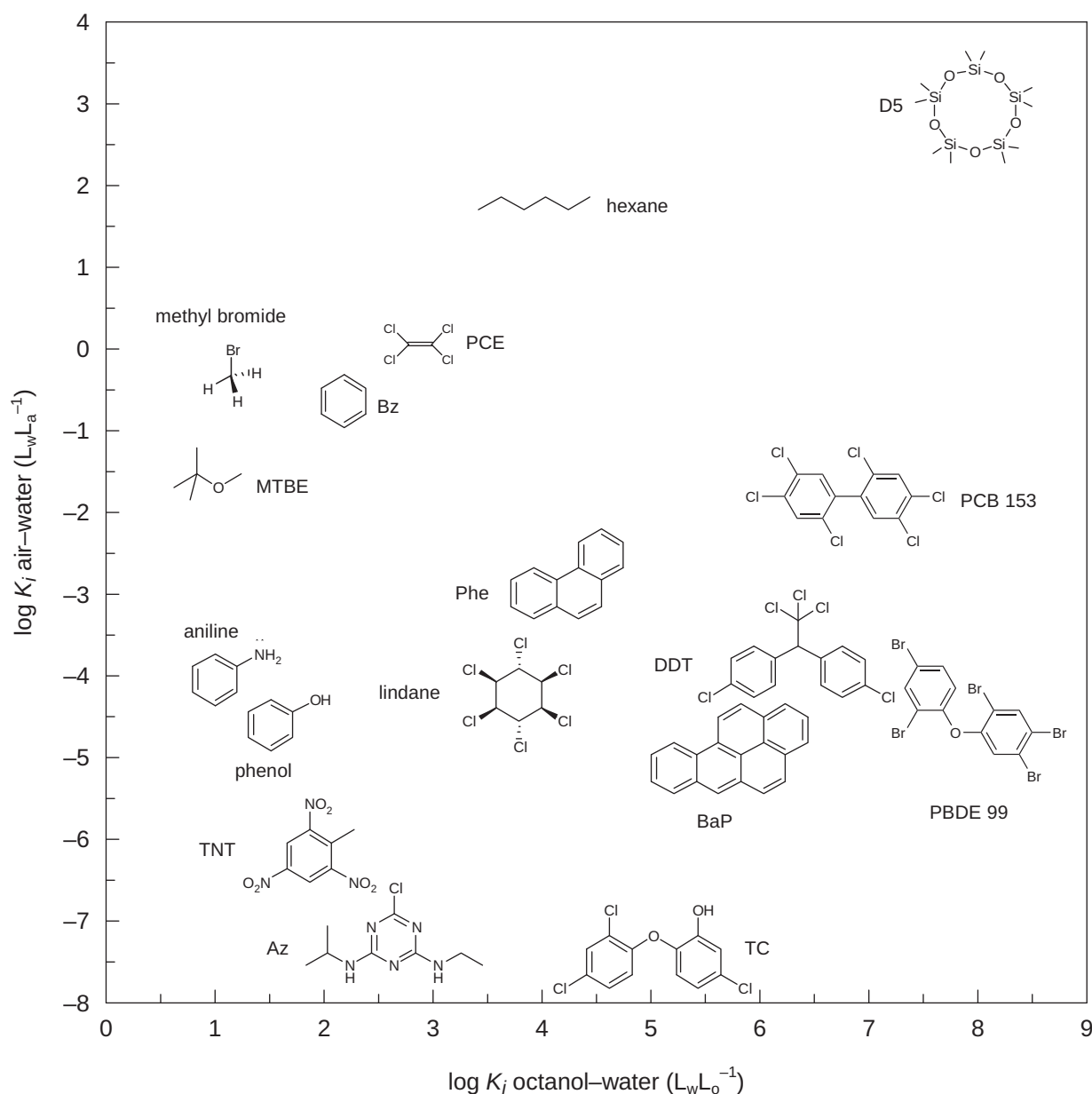
**Table 3.1** Our Companion Compounds

Chemical Name	Abbreviation/ Common Name	Molecular Formula	Structure	Uses
Bromomethane CAS: 74-83-9	methyl bromide	CH <sub>3</sub> Br		fumigant
Tetrachloroethene CAS: 127-18-4	PCE	C <sub>2</sub> Cl <sub>4</sub>		solvent
Methyl-t-butyl-ether CAS: 1634-04-4	MTBE	C <sub>5</sub> H <sub>12</sub> O		gasoline additive
Benzene CAS: 71-43-2	Bz	C <sub>6</sub> H <sub>6</sub>		solvent, gasoline component
Phenol CAS 108-95-2	Ph	C <sub>6</sub> H <sub>6</sub> O		precursor for industrial products
γ-hexachlorocyclohexane (γ-HCH) CAS: 58-89-9	lindane	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>		insecticide
Aniline CAS 62-53-3		C <sub>6</sub> H <sub>7</sub> N		precursor for industrial products
n-Hexane CAS: 110-54-3	hexane	C <sub>6</sub> H <sub>14</sub>		solvent
2-Methyl-1,3,5-trinitrobenzene CAS: 118-96-7	TNT	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>		explosive

(continued)

Table 3.1 (Continued)

Chemical Name	Abbreviation/ Common Name	Molecular Formula	Structure	Uses
Atrazine CAS: 1912-24-9	Az	$C_8H_{14}ClN_5$		herbicide
Decamethylcyclopentasiloxane CAS: 541-02-6	D5	$C_{10}H_{30}O_5Si_5$		solvent
2,2',4,4',5,5'- Hexachlorobiphenyl CAS: 35065-27-1	PCB 153	$C_{12}H_4Cl_6$		industrial fluid
2,2',4,4',5- Pentabromodiphenyl ether CAS: 60348-60-9	PBDE 99	$C_{12}H_5Br_5O$		flame retardant
Triclosan CAS: 3380-34-5	TC	$C_{12}H_7Cl_3O_2$		biocide
<i>p,p'</i> -DDT CAS: 50-29-3	DDT	$C_{14}H_9Cl_5$		insecticide
Phenanthrene CAS: 85-01-8	Phe	$C_{14}H_{10}$		combustion product
Benzo(a)pyrene CAS: 50-32-8	BaP	$C_{20}H_{12}$		combustion product



**Figure 3.14** The air–water and octanol–water equilibrium partition constants for our companion compounds (data from Appendix C) illustrating the wide range of physical–chemical properties encountered when assessing organic pollutants in the environment.

As an illustration of the varying partitioning behavior of our chemical companions in the environment, Fig. 3.14 shows the wide range (i.e., many orders of magnitude) of air–water and octanol–water equilibrium partition constants encountered for these compounds. A key goal throughout the book is to utilize quantitative approaches that can systematically evaluate the entire array of compounds of interest. As already stated in Chapter 1, it is our goal to show that the fate of organic chemicals in the environment can be largely understood by using knowledge regarding specific environmental processes that transport and transform chemical substances as a function of the attributes that derive from their structures.

### 3.11 Questions

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

#### Q 3.1

What characteristics render an organic compound to be qualified as a POP? What are so-called "legacy POPs?" Give some examples of these compounds. What other compounds exhibit typical POP characteristics?

#### Q 3.2

What is the composition of petroleum and what are its major components? What happens to petroleum after a spill?

#### Q 3.3

What are the main sources of polycyclic aromatic hydrocarbons (PAHs) in the environment? Why are PAHs a problem?

#### Q 3.4

What are the main sources of BTEX compounds in the environment? Which is the most problematic among these compounds and why?

#### Q 3.5

When considering organic solvents as groundwater pollutants, what are the main differences between the polychlorinated  $C_1$ - and  $C_2$ -compounds and other solvents, including BTEX and dialkyl ethers such as MTBE?

#### Q 3.6

Which characteristics make volatile methylsiloxanes (VMS) special as compared to other organic solvents? For what purposes are VMS primarily used?

#### Q 3.7

Explain how organic flame retardants work. Why are polybrominated aromatic compounds well suited as flame retardants? Why are many of these compounds considered to be of particular environmental concern?

#### Q 3.8

Phthalates are ubiquitous pollutants in the environment. What are they primarily used for and why do they, like many of the flame retardants, escape in large quantities into the environment?

#### Q 3.9

In which materials that you are exposed to every day would you expect the presence of low molecular weight polyfluorinated compounds (PFCs)?

**Q 3.10**

Give some examples of organic chemicals present in detergents that are used in households. Explain their function and comment on why some of them are of environmental concern. How do these chemicals get into the environment?

**Q 3.11**

What are the main routes by which pharmaceuticals are introduced into the environment? Which pharmaceuticals are of particular concern and why?

**Q 3.12**

Why is the environmental assessment of pesticides of particular importance? What makes them different from other groups of anthropogenic compounds?

**3.12 Bibliography**

- Aeppli, C.; Carmichael, C. A.; Nelson, R. K.; Lemkau, K. L.; Graham, W. M.; Redmond, M. C.; Valentine, D. L.; Reddy, C. M., Oil weathering after the Deepwater Horizon disaster led to the formation of oxygenated residues. *Environ. Sci. Technol.* **2012**, 46(16), 8799–8807.
- Ahel, M.; Giger, W.; Koch, M., Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment: I. Occurrence and transformation in sewage treatment. *Water Res.* **1994**, 28(5), 1131–1142.
- Ahrens, L., Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* **2011**, 13(1), 20–31.
- Alder, A. C.; Siegrist, H.; Gujer, W.; Giger, W., Behavior of NTA and EDTA in biological wastewater treatment. *Water Res.* **1990**, 24(6), 733–742.
- Bansal, V.; Kim, K. H., Review of PAH contamination in food products and their health hazards. *Environ. Int.* **2015**, 84, 26–38.
- Barber, L. B.; Keefe, S. H.; Brown, G. K.; Furlong, E. T.; Gray, J. L.; Kolpin, D. W.; Meyer, M. T.; Sandstrom, M. W.; Zaugg, S. D., Persistence and potential effects of complex organic contaminant mixtures in wastewater-impacted streams. *Environ. Sci. Technol.* **2013**, 47(5), 2177–2188.
- Barro, R.; Regueiro, J.; Llompert, M.; Garcia-Jares, C., Analysis of industrial contaminants in indoor air: Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *J. Chromatogr. A* **2009**, 1216(3), 540–566.
- Beard, A., *Flame Retardants: Frequently Asked Questions*; European Flame Retardants Association (EFRA), 2007; p 37. [www.flameretardants.eu](http://www.flameretardants.eu).
- Beesoon, S.; Webster, G. M.; Shoeib, M.; Harner, T.; Benskin, J. P.; Martin, J. W., Isomer profiles of perfluorochemicals in matched maternal, cord, and house dust samples: Manufacturing sources and transplacental transfer. *Environ. Health Perspect.* **2011**, 119(11), 1659–1664.
- Benotti, M. J.; Trenholm, R. A.; Vanderford, B. J.; Holady, J. C.; Stanford, B. D.; Snyder, S. A., Pharmaceuticals and endocrine disrupting compounds in US drinking water. *Environ. Sci. Technol.* **2009**, 43(3), 597–603.
- Benskin, J. P.; Ahrens, L.; Muir, D. C. G.; Scott, B. F.; Spencer, C.; Rosenberg, B.; Tomy, G.; Kylin, H.; Lohmann, R.; Martin, J. W., Manufacturing origin of perfluorooctanoate (PFOA) in Atlantic and Canadian Arctic seawater. *Environ. Sci. Technol.* **2012a**, 46(2), 677–685.
- Benskin, J. P.; Muir, D. C. G.; Scott, B. F.; Spencer, C.; De Silva, A. O.; Kylin, H.; Martin, J. W.; Morris, A.; Lohmann, R.; Tomy, G.; Rosenberg, B.; Taniyasu, S.; Yamashita, N., Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. *Environ. Sci. Technol.* **2012b**, 46(11), 5815–5823.

- Borga, K.; Fjeld, E.; Kierkegaard, A.; McLachlan, M. S., Food web accumulation of cyclic siloxanes in Lake Mjosa, Norway. *Environ. Sci. Technol.* **2012**, 46(11), 6347–6354.
- Brausch, J. M.; Rand, G. M., A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. *Chemosphere* **2011**, 82(11), 1518–1532.
- Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C., Towards a global historical emission inventory for selected PCB congeners - A mass balance approach-3. An update. *Sci. Total Environ.* **2007**, 377(2-3), 296–307.
- Buser, A. M.; Kierkegaard, A.; Bogdal, C.; MacLeod, M.; Scheringer, M.; Hungerbühler, K., Concentrations in ambient air and emissions of cyclic volatile methylsiloxanes in Zurich, Switzerland. *Environ. Sci. Technol.* **2013**, 47(13), 7045–7051.
- Corcoran, J.; Winter, M. J.; Tyler, C. R., Pharmaceuticals in the aquatic environment: A critical review of the evidence for health effects in fish. *Crit. Rev. Toxicol.* **2010**, 40(4), 287–304.
- Doherty, R. E., A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 1 - Historical background; Carbon tetrachloride and tetrachloroethylene. *Environ. Forensics* **2000**, 1(2), 69–81.
- EFRA: European Flame Retardant Association, *Flame Retardants for a Changing Society*; **2010**; p 42. <http://www.cefic-efra.com/index.php/en/brochures>.
- Egeback, A. L.; Sellstrom, U.; McLachlan, M. S., Decabromodiphenyl ethane and decabromodiphenyl ether in Swedish background air. *Chemosphere* **2012**, 86(3), 264–269.
- Eguchi, A.; Isobe, T.; Ramu, K.; Tue, N. M.; Sudaryanto, A.; Devanathan, G.; Viet, P. H.; Tana, R. S.; Takahashi, S.; Subramanian, A.; Tanabe, S., Soil contamination by brominated flame retardants in open waste dumping sites in Asian developing countries. *Chemosphere* **2013**, 90(9), 2365–2371.
- Eto, M., *Organophosphorous Pesticides: Organic and Biological Chemistry*. CRC Press: Boca Raton, 1979.
- European Commission, *Study on Enhancing the Endocrine Disrupter Priority List with a Focus on Low Production Volume Chemicals*; 2007; p 249. [http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances\\_en.htm](http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm).
- Farhadian, M.; Vachelard, C.; Duchez, D.; Larroche, C., In situ bioremediation of monoaromatic pollutants in groundwater: A review. *Bioresour. Technol.* **2008**, 99(13), 5296–5308.
- Fenner, K.; Canonica, S.; Wackett, L. P.; Elsner, M., Evaluating pesticide degradation in the environment: Blind spots and emerging opportunities. *Science* **2013**, 341(6147), 752–758.
- Flint, S.; Markle, T.; Thompson, S.; Wallace, E., Bisphenol A exposure, effects, and policy: A wildlife perspective. *J. Environ. Manage.* **2012**, 104, 19–34.
- Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E., Human internal and external exposure to PBDEs - A review of levels and sources. *Int. J. Hyg. Environ. Health* **2009**, 212(2), 109–134.
- Friden, U. E.; McLachlan, M. S.; Berger, U., Chlorinated paraffins in indoor air and dust: Concentrations, congener patterns, and human exposure. *Environ. Int.* **2011**, 37(7), 1169–1174.
- Genualdi, S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansen, K. M.; van Egmond, R.; Shoeib, M.; Lee, S. C., Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environ. Sci. Technol.* **2011**, 45(8), 3349–3354.
- Giesy, J. P.; Kannan, K., Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, 35(7), 1339–1342.
- Glennie, E. B.; Littlejohn, C.; Gendebien, A.; Hayes, A.; Palfrey, R.; Sivil, D.; Wright, K., *Phosphates and Alternative Detergent Builders-Final Report*; EU Environment Directorate, 2002; p 172. <http://ec.europa.eu/environment/water/pollution/phosphates/>.
- Goss, K. U.; Bronner, G., What is so special about the sorption behavior of highly fluorinated compounds? *J. Phys. Chem. A* **2006**, 110(30), 9518–9522.
- Greaves, A. K.; Letcher, R. J., Linear and branched perfluorooctane sulfonate (PFOS) isomer patterns differ among several tissues and blood of polar bears. *Chemosphere* **2013**, 93(3), 574–580.

- Grube, A.; Donaldson, D.; Kiely, T.; Wu, L., *Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates*; EPA 733-R-11-001. U.S. EPA, Office of Chemical Safety and Pollution Prevention: 2011, p 33. [www.epa.gov/pesticides](http://www.epa.gov/pesticides).
- Hassall, K. A., *The Biochemistry and Uses of Pesticides*. 2nd ed.; VCH: Weinheim, **1990**.
- Hites, R. A., Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*(4), 945–956.
- Horii, Y.; Kannan, K., Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Arch. Environ. Contam. Toxicol.* **2008**, *55*(4), 701–710.
- Houde, M.; De Silva, A. O.; Muir, D. C. G.; Letcher, R. J., Monitoring of perfluorinated compounds in aquatic biota: An updated review. *Environ. Sci. Technol.* **2011**, *45*(19), 7962–7973.
- Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G., Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.* **2006**, *40*(11), 3463–3473.
- Houde, M.; Muir, D. C. G.; Tomy, G. T.; Whittle, D. M.; Teixeira, C.; Moore, S., Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environ. Sci. Technol.* **2008**, *42*(10), 3893–3899.
- Howard, P. H.; Muir, D. C. G., Identifying new persistent and bioaccumulative organics among chemicals in commerce. *Environ. Sci. Technol.* **2010**, *44*(7), 2277–2285.
- Howard, P. H.; Muir, D. C. G., Identifying new persistent and bioaccumulative organics among chemicals in commerce II: Pharmaceuticals. *Environ. Sci. Technol.* **2011**, *45*(16), 6938–6946.
- Hughes, S. R.; Kay, P.; Brown, L. E., Global synthesis and critical evaluation of pharmaceutical data sets collected from river systems. *Environ. Sci. Technol.* **2013**, *47*(2), 661–677.
- Janna, H.; Scrimshaw, M. D.; Williams, R. J.; Churchley, J.; Sumpter, J. P., From dishwasher to tap? Xenobiotic substances benzotriazole and tolyltriazole in the environment. *Environ. Sci. Technol.* **2011**, *45*(9), 3858–3864.
- Jenkin, M. E.; Clemitshaw, K. C., Ozone and other secondary photochemical pollutants: Chemical processes governing their formation in the planetary boundary layer. *Atmos. Environ.* **2000**, *34*(16), 2499–2527.
- Kaplan, S., Review: Pharmacological pollution in water. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*(10), 1074–1116.
- Kierkegaard, A.; van Egmond, R.; McLachlan, M. S., Cyclic volatile methylsiloxane bioaccumulation in flounder and ragworm in the Humber Estuary. *Environ. Sci. Technol.* **2011**, *45*(14), 5936–5942.
- Kim, K. H.; Jahan, S. A.; Kabir, E.; Brown, R. J. C., A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environ. Int.* **2013**, *60*, 71–80.
- Kliegman, S.; Eustis, S. N.; Arnold, W. A.; McNeill, K., Experimental and theoretical insights into the involvement of radicals in triclosan phototransformation. *Environ. Sci. Technol.* **2013**, *47*(13), 6756–6763.
- Knapp, C. W.; Dolfing, J.; Ehlert, P. A. I.; Graham, D. W., Evidence of increasing antibiotic resistance gene abundances in archived soils since 1940. *Environ. Sci. Technol.* **2010**, *44*(2), 580–587.
- Krafft, M. P.; Riess, J. G., Per- and polyfluorinated substances (PFASs): Environmental challenges. *Curr. Opin. Colloid Interface Sci.* **2015**, *20*(3), 192–212.
- Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M., Occurrence and seasonality of cyclic volatile methyl siloxanes in arctic air. *Environ. Sci. Technol.* **2013**, *47*(1), 502–509.
- Kujawinski, E. B.; Soule, M. C. K.; Valentine, D. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C., Fate of dispersants associated with the Deepwater Horizon oil spill. *Environ. Sci. Technol.* **2011**, *45*(4), 1298–1306.

- Kurt-Karakus, P. B.; Teixeira, C.; Small, J.; Muir, D.; Bidleman, T. F., Current-use pesticides in inland lake waters, precipitation, and air from Ontario, Canada. *Environ. Toxicol. Chem.* **2011**, 30(7), 1539–1548.
- Li, Q. Q.; Loganath, A.; Chong, Y. S.; Tan, J.; Obbard, J. P., Persistent organic pollutants and adverse health effects in humans. *J. Toxicol. Env. Health Part A* **2006**, 69(21), 1987–2005.
- Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L., Polyfluorinated compounds: Past, present, and future. *Environ. Sci. Technol.* **2011**, 45(19), 7954–7961.
- Liu, J. L.; Wong, M. H., Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China. *Environ. Int.* **2013**, 59, 208–224.
- Logan, D. T., Perspective on ecotoxicology of PAHs to fish. *Hum. Ecol. Risk Assess.* **2007**, 13(2), 302–316.
- Lohmann, R.; Breivik, K.; Dachs, J.; Muir, D., Global fate of POPs: Current and future research directions. *Environ. Pollut.* **2007**, 150(1), 150–165.
- Lohmann, R.; Gioia, R.; Jones, K. C.; Nizzetto, L.; Temme, C.; Xie, Z.; Schulz-Bull, D.; Hand, I.; Morgan, E.; Jantunen, L., Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. *Environ. Sci. Technol.* **2009**, 43(15), 5633–5639.
- Loos, R.; Locoro, G.; Comero, S.; Contini, S.; Schwesig, D.; Werres, F.; Balsaa, P.; Gans, O.; Weiss, S.; Blaha, L.; Bolchi, M.; Gawlik, B. M., Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res.* **2010**, 44(14), 4115–4126.
- Ma, Y. N.; Venier, M.; Hites, R. A., 2-Ethylhexyl tetrabromobenzoate and bis(2-ethylhexyl) tetrabromophthalate flame retardants in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2012a**, 46(1), 204–208.
- Ma, Y. N.; Venier, M.; Hites, R. A., Tribromophenoxy flame retardants in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2012b**, 46(24), 13112–13117.
- Martin, J. W.; Asher, B. J.; Beesoon, S.; Benskin, J. P.; Ross, M. S., PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* **2010**, 12(11), 1979–2004.
- McKenna, A. M.; Nelson, R. K.; Reddy, C. M.; Savory, J. J.; Kaiser, N. K.; Fitzsimmons, J. E.; Marshall, A. G.; Rodgers, R. P., Expansion of the analytical window for oil spill characterization by ultrahigh resolution mass spectrometry: Beyond gas chromatography. *Environ. Sci. Technol.* **2013**, 47(13), 7530–7539.
- McLachlan, M. S.; Kierkegaard, A.; Hansen, K. M.; van Egmond, R.; Christensen, J. H.; Skjoth, C. A., Concentrations and fate of decamethylcyclopentasiloxane (D-5) in the atmosphere. *Environ. Sci. Technol.* **2010**, 44(14), 5365–5370.
- Metcalf, C. D.; Alder, A. C.; Halling-Sorensen, B.; Krogh, K.; Fenner, K.; Larsbo, M.; Straub, J. O.; Ternes, T. A.; Topp, E.; Lapen, D. R.; Boxall, A. B. A., Exposure assessment methods for veterinary and human-use medicines in the environment: PEC vs. MEC comparisons. In *Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks*, 3rd ed.; Springer-Verlag: Berlin, 2008; pp 147–171.
- Moran, M. J.; Zogorski, J. S.; Squillace, P. J., Chlorinated solvents in groundwater of the United States. *Environ. Sci. Technol.* **2006**, 41(1), 74–81.
- Moskowitz, S., Synthetic organic chemicals, Economic evaluation. In *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc.: **2010**.
- Muir, D. C. G.; Howard, P. H., Are there other persistent organic pollutants? A challenge for environmental chemists. *Environ. Sci. Technol.* **2006**, 40(23), 7157–7166.
- Net, S.; Sempere, R.; Delmont, A.; Paluselli, A.; Ouddane, B., Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environ. Sci. Technol.* **2015**, 49(7), 4019–4035.
- Nizzetto, L.; Macleod, M.; Borga, K.; Cabrerizo, A.; Dachs, J.; Di Guardo, A.; Ghirardello, D.; Hansen, K. M.; Jarvis, A.; Lindroth, A.; Ludwig, B.; Monteith, D.; Perlinger, J. A.; Scheringer,



- M.; Schwendenmann, L.; Semple, K. T.; Wick, L. Y.; Zhang, G.; Jones, K. C., Past, present, and future controls on levels of persistent organic pollutants in the global environment. *Environ. Sci. Technol.* **2010**, *44*(17), 6526–6531.
- Nowack, B., Environmental chemistry of aminopolycarboxylate chelating agents. *Environ. Sci. Technol.* **2002**, *36*(19), 4009–4016.
- Oliaei, F.; Kriens, D.; Weber, R.; Watson, A., PFOS and PFC releases and associated pollution from a PFC production plant in Minnesota (USA). *Environ. Sci. Pollut. Res.* **2013**, *20*(4), 1977–1992.
- Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froehlich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R., Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. *Environ. Health Perspect.* **2007**, *115*(9), 1298–1305.
- Orias, F.; Perrodin, Y., Characterisation of the ecotoxicity of hospital effluents: A review. *Sci. Total Environ.* **2013**, *454*, 250–276.
- Poiger, T.; Field, J. A.; Field, T. M.; Siegrist, H.; Giger, W., Behavior of fluorescent whitening agents during sewage treatment. *Water Res.* **1998**, *32*(6), 1939–1947.
- Reddy, C. M.; Arey, J. S.; Seewald, J. S.; Sylva, S. P.; Lemkau, K. L.; Nelson, R. K.; Carmichael, C. A.; McIntyre, C. P.; Fenwick, J.; Ventura, G. T.; Van Mooy, B. A. S.; Camilli, R., Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*(50), 20229–20234.
- Reemtsma, T.; Weiss, S.; Mueller, J.; Petrovic, M.; Gonzalez, S.; Barcelo, D.; Ventura, F.; Knepper, T. P., Polar pollutants entry into the water cycle by municipal wastewater: A European perspective. *Environ. Sci. Technol.* **2006**, *40*(17), 5451–5458.
- Reichenberger, S.; Bach, M.; Skitschak, A.; Frede, H. G., Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness: A review. *Sci. Total Environ.* **2007**, *384*(1–3), 1–35.
- Reznik, G. O.; Vishwanath, P.; Pynn, M. A.; Sitnik, J. M.; Todd, J. J.; Wu, J.; Jiang, Y.; Keenan, B.; Castle, A. B.; Haskell, R. F.; Smith, T. F.; Somasundaran, P.; Jarrell, K. A., Use of sustainable chemistry to produce an acyl amino acid surfactant. *App. Microbiol. Biotechnol.* **2010**, *86*(5), 1387–1397.
- Ristaino, J. B.; Thomas, W., Agriculture, methyl bromide, and the ozone hole: Can we fill the gaps? *Plant Dis.* **1997**, *81*(9), 964–977.
- Rücker, C.; Kümmerer, K., Environmental chemistry of organosiloxanes. *Chem. Rev.* **2015**, *115*(1), 466–524.
- Ruggirello, R. M.; Hermanson, M. H.; Isaksson, E.; Teixeira, C.; Forsstrom, S.; Muir, D. C. G.; Pohjola, V.; van de Wal, R.; Meijer, H. A. J., Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. *J. Geophys. Res.-Atmos.* **2010**, *115*, DOI:10.1029/2010jd014005.
- Rutishauser, B. V.; Pesonen, M.; Escher, B. I.; Ackermann, G. E.; Aerni, H. R.; Suter, M. J. F.; Eggen, R. I. L., Comparative analysis of estrogenic activity in sewage treatment plant effluents involving three in vitro assays and chemical analysis of steroids. *Environ. Toxicol. Chem.* **2004**, *23*(4), 857–864.
- Schenker, U.; Scheringer, M.; Macleod, M.; Martin, J. W.; Cousins, I. T.; Hungerbühler, K., Contribution of volatile precursor substances to the flux of perfluorooctanoate to the arctic. *Environ. Sci. Technol.* **2008**, *42*(10), 3710–3716.
- Scheringer, M., Long-range transport of organic chemicals in the environment *Environ. Toxicol. Chem.* **2009**, *28*(4), 677–690.
- Secretariat of the Stockholm Convention, Stockholm Convention. **2015** [accessed on November 2015]. <http://chm.pops.int>.
- Seeland, A.; Oetken, M.; Kiss, A.; Fries, E.; Oehlmann, J., Acute and chronic toxicity of benzotriazoles to aquatic organisms. *Environ. Sci. Pollut. Res.* **2012**, *19*(5), 1781–1790.
- Shih, T.; Rong, Y.; Harmon, T.; Suffet, M., Evaluation of the impact of fuel hydrocarbons and oxygenates on groundwater resources. *Environ. Sci. Technol.* **2004**, *38*(1), 42–48.

- Shoeib, M.; Harner, T.; Webster, G. M.; Lee, S. C., Indoor sources of poly- and perfluorinated compounds (PFCS) in Vancouver, Canada: Implications for human exposure. *Environ. Sci. Technol.* **2011**, 45(19), 7999–8005.
- Simmons, D. B. D.; Trudeau, V. L.; Marlatt, V. L.; Moon, T. W.; Sherry, J. P.; Metcalfe, C. D., Interaction of stilbene compounds with human and rainbow trout estrogen receptors. *Environ. Toxicol. Chem.* **2008**, 27(2), 442–451.
- Squillace, P. J.; Scott, J. C.; Moran, M. J.; Nolan, B. T.; Kolpin, D. W., VOCs, pesticides, nitrate, and their mixtures in groundwater used for drinking water in the United States. *Environ. Sci. Technol.* **2002**, 36(9), 1923–1930.
- Stoll, J. M. A.; Ulrich, M. M.; Giger, W., Dynamic behavior of fluorescent whitening agents in Greifensee: Field measurements combined with mathematical modeling of sedimentation and photolysis. *Environ. Sci. Technol.* **1998**, 32(13), 1875–1881.
- Stempel, S.; Scheringer, M.; Ng, C. A.; Hungerbuhler, K., Screening for PBT chemicals among the “existing” and “new” chemicals of the EU. *Environ. Sci. Technol.* **2012**, 46(11), 5680–5687.
- Sumpter, J. P.; Johnson, A. C., 10th anniversary perspective: Reflections on endocrine disruption in the aquatic environment: from known knowns to unknown unknowns (and many things in between). *J. Environ. Monit.* **2008**, 10(12), 1476–1485.
- Sverko, E.; Tomy, G. T.; Reiner, E. J.; Li, Y. F.; McCarry, B. E.; Arnot, J. A.; Law, R. J.; Hites, R. A., Dechlorane Plus and related compounds in the environment: A review. *Environ. Sci. Technol.* **2011**, 45(12), 5088–5098.
- Swackhamer, D. L.; Needham, L. L.; Powell, D. E.; Muir, D. C. G., Use of measurement data in evaluating exposure of humans and wildlife to POPs/PBTs. *Integr. Environ. Assess. Manage.* **2009**, 5(4), 638–661.
- Tue, N. M.; Takahashi, S.; Subramanian, A.; Sakai, S.; Tanabe, S., Environmental contamination and human exposure to dioxin-related compounds in e-waste recycling sites of developing countries. *Env. Sci. Process. Impacts* **2013**, 15(7), 1326–1331.
- Tyler, C. R.; Jobling, S.; Sumpter, J. P., Endocrine disruption in wildlife: A critical review of the evidence. *Crit. Rev. Toxicol.* **1998**, 28(4), 319–361.
- U.S. EPA, *UST Program Facts*; Solid Waste and Emergency Response: Washington D.C., **2013**; p 2. <http://www.epa.gov/oust/pubs/ustfacts.htm>.
- U.S. EPA, Toxic Release Inventory (TRI) Program Release Reports. 2015a [accessed on November 2015]. [http://iaspub.epa.gov/triexplorer/tri\\_release.chemical](http://iaspub.epa.gov/triexplorer/tri_release.chemical).
- U.S. EPA, The Phaseout of Methyl Bromide. 2015b [accessed on November 2015]. <http://www.epa.gov/ozone/mbr/>.
- Valsecchi, S.; Rusconi, M.; Polesello, S., Determination of perfluorinated compounds in aquatic organisms: A review. *Anal. Bioanal. Chem.* **2013**, 405(1), 143–157.
- van den Berg, H.; Zaim, M.; Yadav, R. S.; Soares, A.; Ameneshewa, B.; Mnzava, A.; Hii, J.; Dash, A. P.; Ejov, M., Global trends in the use of insecticides to control vector-borne diseases. *Environ. Health Perspect.* **2012**, 120(4), 577–582.
- van der Veen, I.; de Boer, J., Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012**, 88(10), 1119–1153.
- van Wezel, A.; Puijker, L.; Vink, C.; Versteegh, A.; de Voogt, P., Odour and flavour thresholds of gasoline additives (MTBE, ETBE and TAME) and their occurrence in Dutch drinking water collection areas. *Chemosphere* **2009**, 76(5), 672–676.
- Venier, M.; Ma, Y. N.; Hites, R. A., Bromobenzene flame retardants in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2012**, 46(16), 8653–8660.
- Vestergren, R.; Cousins, I. T.; Trudel, D.; Wormuth, M.; Scheringer, M., Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA. *Chemosphere* **2008**, 73(10), 1617–1624.

- Wallace, L. A.; Pellizzari, E. D.; Hartwell, T. D.; Whitmore, R.; Sparacino, C.; Zelon, H., Total exposure assessment methodology (team) study: Personal exposures, indoor-outdoor relationships, and breath levels of volatile organic compounds in New Jersey. *Environ. Int.* **1986**, *12*(1–4), 369–387.
- Wang, D.-G.; Norwood, W.; Alaei, M.; Byer, J. D.; Brimble, S., Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. *Chemosphere* **2013**, *93*(5), 711–725.
- Wang, R.; Moody, R. P.; Koniecki, D.; Zhu, J. P., Low molecular weight cyclic volatile methyl-siloxanes in cosmetic products sold in Canada: Implication for dermal exposure. *Environ. Int.* **2009**, *35*(6), 900–904.
- Warner, N. A.; Evenset, A.; Christensen, G.; Gabrielsen, G. W.; Borga, K.; Leknes, H., Volatile siloxanes in the European Arctic: Assessment of sources and spatial distribution. *Environ. Sci. Technol.* **2010**, *44*(19), 7705–7710.
- Weber, R.; Kuch, B., Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environ. Int.* **2003**, *29*(6), 699–710.
- Wildes, S. G., *Solvents: A Market Opportunity Study*; United Soybean Board, Midland, Michigan, 2007; p 29. <http://soynewuses.org/reports/>.
- Williams, P. R. D.; Pierce, J. S., Overview of methyl tertiary butyl ether (MTBE) detections in public drinking water supplies in the United States. *Environ. Forensics* **2009**, *10*(1), 33–50.
- Yamaji, N.; Hayakawa, K.; Takada, H., Role of photodegradation in the fate of fluorescent whitening agents (FWAs) in lacustrine environments. *Environ. Sci. Technol.* **2010**, *44*(20), 7796–7801.
- Yee, K. F.; Mohamed, A. R.; Tan, S. H., A review on the evolution of ethyl tert-butyl ether (ETBE) and its future prospects. *Renew. Sust. Energ. Rev.* **2013**, *22*, 604–620.
- Yeung, L. W. Y.; Robinson, S. J.; Koschorreck, J.; Mabury, S. A., Part II. A Temporal study of PFOS and its precursors in human plasma from two German cities in 1982–2009. *Environ. Sci. Technol.* **2013**, *47*(8), 3875–3882.
- Zareitalabad, P.; Siemens, J.; Hamer, M.; Amelung, W., Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater - A review on concentrations and distribution coefficients. *Chemosphere* **2013**, *91*(6), 725–732.

