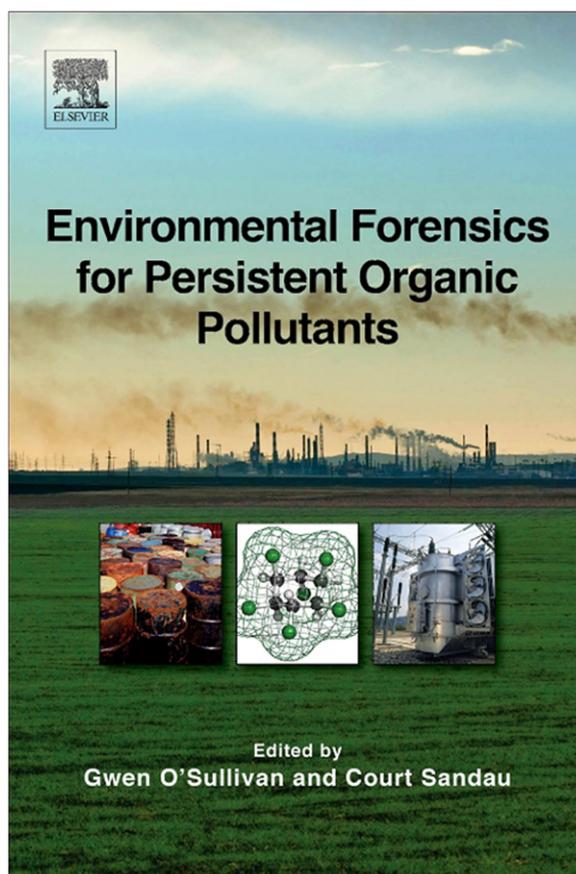


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# POPs in the Terrestrial Environment

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## 7.1 INTRODUCTION

Terrestrial refers to land-based areas and the biota that live there. It includes man-made and natural surfaces, subsurface features, and the interfaces with the atmosphere and the oceans. Persistent organic pollutants (POPs) have entered the terrestrial environment from both use and disposal; this includes intentional discharges and unintentional spillages and leaks. Since POPs do not readily degrade and are relatively immobile, after releases to the environment they can remain in soils and sediments in localized areas at high concentrations. Gradual advection from these localized sources has resulted in many POPs being globally distributed contaminants.

A variety of post release processes may alter source signatures of POPs, including volatilization and dispersion, biodegradation, uptake in biota, and biotransformation and elimination. When undertaking a forensic investigation it is important to understand and account for these processes. They will have different importance when assessing POPs in different media and in different parts of the world. To clarify processes and describe the potential changes that may occur to the pattern of POPs in different media examples are given using polychlorinated biphenyls (PCBs). Further information relating to the history of PCB production may be found in [Box 7.1](#). It is the job of the forensic practitioner to identify the important processes affecting their contaminant(s) of interest. The following sections outline the source, fate, and behavior of POPs in a variety of terrestrial media.

### Box 7.1 Polychlorinated Biphenyls

PCBs are a group of 209 “man-made” chlorinated organic compounds that were widely used in the twentieth century for a variety of industrial uses. PCBs were first produced in 1929 and were manufactured until the 1970s and 80s when their use was phased out due to environmental and human health risks [1,2]. PCBs are very stable compounds that do not readily degrade, they are POPs and are listed under the Stockholm convention as part of the “dirty dozen.” Even though the use of PCBs has been phased out they are still routinely detected in soils and animal tissue today. Their lipophilic nature means that they have the ability to bioaccumulate in adipose tissue and have been found in relatively high concentrations in top predators, such as polar bears and humans [3–5].

PCBs are not produced naturally as single congeners, instead they were artificially synthesized as blends, containing a mixture of different PCBs which were sold under trade names based on their chlorine content. The market leader for PCB production was Monsanto a US-based company who manufactured PCB mixtures called Aroclors. Estimates of Monsanto's production were between 499,000 and 635,000 tonnes, which accounted for more than half of the global total of roughly 1.2 million tonnes [6]. Other major producers of PCBs were Bayer AG (Germany) producing Clophens, Kanegafuchi Chemical Company (Japan) producing Kanechlor, Prodolec (France) producing Phenoclor and Pyralene, and Delor which was produced in former Czechoslovakia. Monsanto produced nine main Aroclor blends, each were identified with a four digit code. For example Aroclor 1254 contained 12 carbon atoms and had a mixture of PCBs that makes the end product 54% chlorine by weight. Similar naming systems and production methods were used by the other brands which meant that the proportions of congeners in Aroclor 1260, Clophen A60, and Kanechlor 600 are almost identical [2].

The most commonly produced Aroclor was Aroclor 1242, which contributed over 50% of Monsanto's total sales between 1957 and 1974. In 1971, a new Aroclor was produced (Aroclor 1016), which directly affected sales of the heavier Aroclors and especially Aroclor 1242. Research in the 1970s has indicated a greater environmental persistence of tetra- and higher chlorinated PCBs, therefore Aroclor 1016 was produced to replace Aroclor 1242 as a more “environmentally friendly” alternative [7]. Aroclor 1016 was produced in the same way as Aroclor 1242 by chlorinating a biphenyl up to approximately 42%. However, the product was then fractionated to yield a product with fewer tetra and higher chlorinated congeners and fewer mono- and non-ortho congeners whilst maintaining 41.5% chlorine by weight [8]. The resulting by-product of the production of Aroclor 1016 was a mixture that was about 49% chlorine by weight, which was further chlorinated and sold as Aroclor 1254. This resulted in two different variants of Aroclor 1254 that each contains a slightly different mixture of PCB congeners [2].

## 7.2 SOILS AND SEDIMENTS

### 7.2.1 Pathways for Introduction

POPs can enter the soil through intentional discharges, unintentional spillages and leaks, and aerial deposition. Once POPs have been released to the environment they can undergo further cycling which transports them all over the globe. Atmospheric transport of POPs can occur through the vapor pathway and also through windblown dust and particulate matter which has been contaminated with POPs. Global distillation and cold condensation describe the process whereby semivolatile chemicals like POPs would volatilize from warm source areas, undergo long-range atmospheric transport (LRAT), and subsequently condense onto surfaces, such as soil, vegetation, or snow, at low temperatures, effectively accumulating in the polar regions [9]. It was postulated that a “global fractionation” effect would occur whereby a POP mixture would become fractionated during LRAT based on the ambient temperature and the physical/chemical properties of the individual compounds [9]. This would result in the more volatile compounds being preferentially transported and deposited in higher latitudes, whereas less volatile compounds would remain closer to source regions. Supporting evidence for this theory was provided by McLachlan and Horstmann [10], including a significant ( $P < 0.05$ ) trend between increasing tri- and tetra-PCB proportions, and decreasing hepta- and octa-PCB concentrations with increasing latitude. However, there was a large amount of scatter in the data which was attributed to environmental and soil-related processes, such as organic matter content and degradation, indicating that these processes are also highly important.

In 2008, 10 years later, the same study was repeated by Schuster et al. [11] to see how the distribution of PCBs and polybrominated diphenyl ethers (PBDEs) had changed in European background soils. Their results showed an overall decline of both PBDEs and PCBs. POP concentrations were again correlated to distance and strength of possible sources, although the relationship was weaker than it was in the 1998 data. Also, the significant trend of fractionation observed in the 1998 study was not observed in the 2008 data. This was believed to be due to weathering of the signature in the soil samples, indicating that primary sources of POPs have declined.

Soils and sediments have been proven to be sinks for POPs, however, in some instances they can also be sources of POPs. For example, agricultural soils act as a primary source of agrochemical POPs to the atmosphere [12]. Soils in remote regions, away from industrial, urban, and agricultural areas can act as sinks and contain background concentrations of POPs. The organic matter content of a soil plays a vital role in determining if a soil is a source or sink. POPs bind to organic matter and therefore soils with high organic matter contents like forest soils have a greater capacity to be sinks [13].

It has been determined that in Germany 70% of soil-borne POPs are present in the soils of forests which account for 30% of the land area [10].

## 7.2.2 Post Deposition Change

POPs are well known for their resistance to degradation; however, once they have entered soils and sediments they can undergo subtle transformations. For example not all congeners from a family of compounds will be degraded at the same rate. This can alter the original signature of a POP and complicate source identification. However, if the processes altering the signature are understood they may be accounted for and in some instances used to help age date a release. The changes that may occur to POPs in soils and sediments from a variety of different processes are outlined below.

### 7.2.2.1 Losses to Ambient Air

As discussed in Section 7.2.1, POPs can enter the atmosphere through vapor transport or through the particulate phase. Removal of POPs through vapor transport will preferentially remove the more volatile compounds. This can lead to an enrichment of less volatile POPs in the soil. Within a class of POPs like PCBs, it is the less chlorinated POPs that are more volatile. Therefore, over time, the PCB signature in a soil or sediment will become depleted in less chlorinated congeners due to loss from vapors. Removal of POPs from soils to the atmosphere may be significant. In studies undertaken by Chiarenzelli et al. [14], as much as 75% of the original PCB mass in small samples (0.25–1.0 g) of contaminated sediment was lost by volatilization in a 7-day period. However, this is an extreme case performed in controlled laboratory conditions. It is very unlikely that volatile losses of this magnitude would be observed in natural environments where mass transfer considerations in thicker sediment and water layers would control the availability of PCBs [15].

### 7.2.2.2 Losses to Groundwater and Surface Water

POPs are generally highly lipophilic thus not very soluble in water. Therefore, the rate of transfer of POPs to water is considered to be relatively low. Percolation of rainwater through the soil profile is unlikely to remove large quantities of POPs from the surface soils. A more important process could be the transport of POPs in surface soils into adjacent surface water features, such as lakes and rivers. Again rates of transfer are low due to the low solubility of POPs, however, intense periods of heavy rain can transport large quantities of soil containing POPs into local freshwater systems and out towards the sea [16]. This highlights another negative impact of deforestation as organic rich soils with high POP concentrations are washed into the aquatic system. When considering the leaching of POPs from soils it is the more soluble POPs that will undergo the greatest degree of leaching. As was

the case for volatilization, for a class of POPs like PCBs it is the less chlorinated POPs that are more soluble, this will lead to a relative enrichment of the more chlorinated congeners in the soil over time. In cases where POPs are dissolved in a groundwater plume, it is the more soluble POPs with the least affinity for organic matter which may travel the farthest.

When considering the leaching of POPs from soil one important factor is the possibility of cosolvation. The mobility of POPs in soil may be enhanced by the presence of another solvent. Solvents, such as chloroform and chlorobenzene, facilitate the movement of agrochemical POPs, such as Dichlorodiphenyltrichloroethane (DDT), toxaphene, and dieldrin. In an example presented by Morrison [16], a spill of xylene mobilized DDT which resulted in the distribution of DDT to the lower soil profile contaminating the underlying groundwater.

### 7.2.2.3 Losses due to Biodegradation

POPs in herbage and animals are covered in detail in Sections 7.3 and 7.4, respectively, and therefore will not be dealt with extensively in this section. Instead the focus will be on the smaller organisms in the soil that cause biodegradation potentially breaking down POPs and causing changes to the congener profiles. Rates of degradation may be affected by physical soil conditions, such as moisture content, pH, oxygen content, and nutrient content. The type of bacterial communities present may also affect the rate and extent of degradation as the mechanisms and pathways of breakdown will vary from population to population. The most complete degradation occurs when several processes are present and working in a concerted fashion [17]. Eight different degradation pathways have been observed for PCBs in soils and sediments, each one targeting specific chlorine atoms on the biphenyl producing characteristic degradation products.

Recent analytical developments have allowed for the analysis of chiral signatures in POPs. Changes to the chiral signature can be used to identify if biodegradation has occurred [18,19]. If enantiomer mixtures are racemic, then this is evidence of fresh inputs and/or lack of biodegradation (or equal rates of biodegradation for both enantiomers, which is unlikely), while the dominance of the + or - enantiomer provides evidence that (selective) biodegradation has occurred [11].

The biodegradation of POPs can lead to the formation of different degradation products. Some products may be just as toxic as the parent compounds and some may be more mobile in the environment. In the case of agrochemical POPs, such as DDT and lindane, it is important to not only determine the presence of parent compound but also the presence of potential degradation products. Under certain conditions, DDT and lindane may be broken down quickly with half-lives in the order of several days to weeks [20]. By only analyzing for the parent compounds, it is possible to reach a false conclusion

that no previous contamination had occurred. Walker et al. [21] analyzed DDT, lindane, and their degradation products in sediments from Greens Bayou, Houston, TX. Using the chemical data in conjunction with an understanding of the degradation pathways, they were able to trace the timing of the release of POPs in contaminated sediments in the region.

### 7.2.3 Background Concentrations

The distribution of POPs in background surface soils is complex, concentrations are a function of proximity to source regions, the LRAT potential of the POP in question, soil properties (especially soil organic matter), climatic conditions, land use/cover, and processes of air-surface exchange) [11]. The highest concentrations of POPs in soils are generally found in areas where localized spillages or discharges have occurred. In these instances, the soil will have a different signature to that of background soils which will have been predominantly influenced by aerial deposition. One of the largest studies of the global distributions of POPs was undertaken by Meijer et al. [22], who recorded PCB and hexachlorobenzene (HCB) concentrations in 191 global background surface soils (0–5 cm). The highest recorded concentrations for PCBs were found in mainland Europe (97,000 pg/g dw), the lowest concentrations were recorded in Greenland (26 pg/g dw). Background soil PCB concentrations were strongly influenced by proximity to source region and soil organic matter content. The results showed that over 80% of the estimated soil PCB burden remains in the “global source region” of the Northern Hemisphere within 30–60°N, and in the organic matter rich soils just to north of it. Similar distributions were also reported for HCB with the reported concentration range of 10–5210 pg/g dw. However, this type of distribution is not displayed for all POPs. In a study undertaken by Kurt-Karakus et al. [12], total concentrations of DDT and its metabolites ( $\Sigma$ DDTs) ranged from <10 to 426,000 pg/g dw but correlated poorly with both soil organic matter content and latitude.

On a local scale, the profile of background POP concentrations may be strongly influenced by the diversity of local point sources. Concentrations of PCBs, polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) were studied in rural and urban parts of the United Kingdom as part of the United Kingdom Soil and Herbage Survey (UK SHS). The findings of the survey were reported by Creaser et al. [23,24] and a discussion of the results of the study is presented in Section 7.3.3.

## 7.3 HERBAGE

### 7.3.1 Pathways for Introduction

In theory, POPs can enter vegetation through two main media, air and soil; however, the exact pathways are not fully understood or quantified.

There are many variations, such as wind speed, temperature, the reactive surface of the leaf, and the permeability of cuticle wax, which can all affect the intake of POPs through air [23]. For most vegetation, the uptake from the soil is considered negligible [25]. A summary of potential pathways for POPs to enter vegetation includes:

- contamination of shoots and cuticles from aerial deposition of wet and dry particulates [26,27],
- uptake through roots and xylem transport to other parts of the plant [26],
- uptake of airborne vapors through stomata [26],
- adsorption and absorption onto roots and tubers in the ground and parts of the plant in close proximity to the ground [26].

POPs are generally highly lipophilic, have a low volatility and low solubility. Therefore, the transfer of POPs from the soil to vegetation would be expected to be relatively low, however, the uptake of POPs in herbage does occur. Members of the Cucurbitaceae family have been shown to accumulate PCDDs/PCDFs and PCBs [28] and elevated concentrations of PBDEs were reported in spinach in Japan [29]. Interestingly, not only were higher total concentrations of PBDEs recorded in the spinach but also the congener composition was different to root vegetables, such as potato and carrot, analyzed in the same study. The spinach was found to contain a larger fraction of the relatively volatile BDE-28 and BDE-47 and a smaller fraction of the less volatile BDE-153. The results indicate that the two types of crop were contaminated by different pathways and that the dominant transport pathway for PBDE contamination of the spinach was through aerial deposition. For the majority of herbage, the main contamination pathway for POPs appears to be through aerial deposition [26]. Fruit and herbage studies often show a better correlation between air signatures than soil signatures [27] along with significantly higher concentrations of POPs on the skin and peel of fruit than the flesh or core [27,30].

The uptake of PCDDs/PCDFs and PCBs into roots and their subsequent translocation to other parts of the plant is generally considered to be low [26], however, it does occur to some degree. Rates of uptake are highly dependent on soil conditions, moist soils with low organic matter contents were found to produce the greatest rates of uptake [31]. Results from a study by Kacalkova and Tlustos [32] showed that maize and sunflower roots accumulated PCBs from soil. The authors reported varying rates of uptake for the different congeners with hexa- and heptachlorobiphenyl congeners being taken up more than the tri-, tetra-, and pentachlorobiphenyl congeners.

Investigations into the uptake of PCDDs/PCDFs and PCBs using growth chambers and greenhouses have demonstrated that volatilization from the soil and uptake of vapors was the main source of fruit and vegetable contamination. However, under outdoor conditions this pathway has been shown to be of minor importance [26].

For root and tuber vegetables, adsorption and absorption can be an important pathway. Results from carrots and potatoes showed that concentrations were high in the peels of the vegetables but relatively lower in the core [31].

### 7.3.2 Post Intake Change

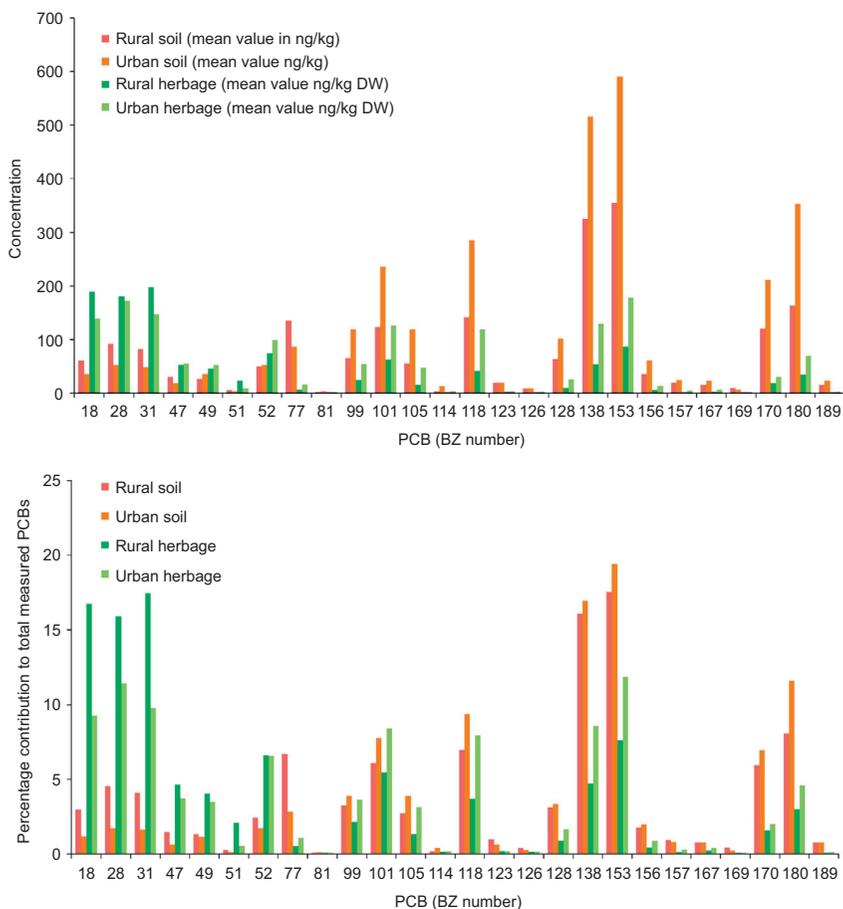
Post intake changes in the congener profile of plants are not well understood. Subtle changes may occur to the signature of POPs in vegetation. Most recent studies into the uptake of POPs from plants have focused on using the technique for phytoremediation or rhizoremediation. The majority of degradation from these techniques is believed to occur due to the microbial community that is stimulated by release of phytochemicals upon fine root death from plant species, such as *Salix alaxensis* (felt-leaf willow) [33]. However, evidence of partial metabolism of PCBs has been recorded in some plant species [34].

If volatilization and uptake of vapors is an important pathway then the signature in the vegetation would be expected to contain higher proportions of more volatile compounds than the source material. Likewise if uptake of POPs from the soil through the roots and transfer in the xylem is an important pathway then the signature in the herbage should theoretically contain higher proportions of more soluble compounds than the source material.

On the whole, plants can act as sinks for POPs and will retain a similar signature to the air they were grown in. One of the most important things to understand is that the overall signature in herbage at a contaminated site is unlikely to form a direct match with the source material and will more likely reflect the atmospheric conditions.

### 7.3.3 Background Concentration and Signatures in Soils and Herbage

Processes, including global distillation and cold condensation, have transported POPs all over the globe leading to different concentrations of POPs in soil and vegetation at different latitudes [9,35]. On a more local scale, POPs in vegetation in different land uses were compared in the United Kingdom by Creaser et al. [23,24]. Figure 7.1 shows the total concentrations and the signatures of PCBs in urban and rural soils and herbage across the United Kingdom. The charts present the results from 366 rural soils and herbage samples, 87 urban soils and herbage samples, for 26 PCBs taken from Creaser et al. [23]. Overall concentrations of PCBs, PCDDs/PCDF were found to be greater in urban soils and herbage than in rural soils and herbage. However, proportions and concentrations of the less chlorinated



**FIGURE 7.1** PCB signature of 26 PCBs analyzed from 366 rural soil and herbage samples and 87 urban soil and herbage samples taken across the United Kingdom. Figure plotted using data taken from Creaser et al. 2007 [23].

biphenyls along with penta- and hexa-dioxins and furans were found to be greater in rural herbage than urban herbage.

In long-lived plants and trees, dendrochemistry has been used to understand past local atmospheric concentrations of POPs [36]. Historically, dendrochemistry has focused primarily in identifying metal and volatile organic compound (VOC) concentrations and has been used in conjunction with dendrochronology. These applications have been developed and helped to form a new branch of environmental forensics called phytoforensics. Although research on the fundamentals of phytoforensic methods had been initiated over half a century ago, developments in this field have expanded greatly over recent years to better utilize plant sampling in novel bio-sensing

applications assessing contaminant distribution and historic release events. Recent uses of dendrochemistry include:

- The use of tree bark samples to monitor brominated and chlorinated flame retardants [37], PCBs, PCDDs/PCDFs [38], lindane, and DDT [39].
- The use of archived herbage samples to calculate past PBDE concentrations from samples taken in the United Kingdom from 1930 to 2004 [40].
- The use of pine needles as passive biosamplers to determine atmospheric concentrations of PBDEs [41].

Research is currently being undertaken as part of the international Pollution Investigation by Trees program (PIT), which is looking at further applications of phytoforensics, including phytoscreening and dendrochemistry of POPs. In recent years, it appears that analysis of trees and plants has become a powerful tool to monitor past and present atmospheric concentrations of POPs.

## 7.4 WILDLIFE

In comparison to herbage and soil, animals are generally mobile and therefore sources of POPs may be more variable. Furthermore, POPs that are present in animal tissue may have undergone specific metabolic breakdown or elimination processes, thus changing the initial POP signature. The main advantage of measuring concentrations of POPs in animals is that it provides a direct assessment of the (internal) exposure to POPs and thus allows for a better exposure/risk assessment to be completed. Therefore this method is more biologically relevant than measuring concentrations in environmental media, such as water, air, and soil.

### 7.4.1 Pathways for POPs to Enter Wildlife

POPs enter animals mainly through ingestion of contaminated food. PCBs and other POPs present in fish strongly influence the profile in fish eating birds, whereas the profile in insect eating birds has a markedly different profile with a higher ratio of PCB101/118 than other homeotherms [42]. In addition, different concentrations and profiles have been found in terrestrial predatory birds feeding on small mammals in comparison to predatory birds feeding on small passerine birds [43].

For example, Voorspoels et al. [44] investigated the biomagnifications (BMFs) of PBDEs in three small terrestrial food chains: great tit<sup>1</sup>—sparrow hawk,<sup>2</sup> small rodents—buzzard,<sup>3</sup> and small rodents—fox.<sup>4</sup> PBDEs were clearly biomagnified in both predatory bird species (BMFs ranged from 2 to 34),

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1. *Parus major*.

2. *Accipiter nisus*.

3. *Buteo buteo*.

4. *Vulpes vulpes*.

while this was not the case for the fox. Levels in sparrow hawk (mean sum PBDEs in liver: 9500 ng/g lipid weight (lw)) were approximately 1 order of magnitude higher than those in buzzard (mean sum PBDEs in liver: 720 ng/g lw). Differences in diet composition have been shown to partly explain the high concentrations of PBDEs in sparrow hawks. Sparrow hawks feed primarily on locally available small birds like passerines, while buzzards prefer small mammals, such as mice and voles. On the other hand, the low levels found in the fox (mean sum PBDEs in liver: 8.9 ng/g lw) are probably related to its high metabolic capacity (see Section 7.4.2).

Food chain accumulation studies in terrestrial mammals are scarce. One recent study [45] investigated the accumulation of POPs in the soil–earthworm–hedgehog food chain. The soil contamination was heterogeneously distributed within the study sites. Despite mostly background concentrations in soil (ranging from 1.3 to 9.3 ng/g for DDTs, 2.3 to 6.5 ng/g for PCBs, and 0.08 to 0.20 ng/g for PBDEs), biota-soil accumulation factors (BSAFs) indicated that earthworms accumulated POPs (0.48–1.70 for DDTs, 1.09–2.76 for PCBs, and 1.99–5.67 for PBDEs) and that animals feeding on earthworms (e.g., hedgehogs) are potentially exposed to higher concentrations of pollutants. Therefore, the BMF of POPs through the food chain is an important factor which determines the exposure to POPs through the diet.

Dietary changes over time might also influence the exposure to POPs. Fernie et al. [46] investigated the temporal and spatial patterns of POPs in watersnakes<sup>5</sup> from Lake Erie before and after an invasion with round goby.<sup>6</sup> The watersnakes changed from a diet in 1990 of 75% fish and 25% amphibians, which avoid zebra mussels,<sup>7</sup> to a diet of 95% round gobies, which extensively feed on zebra mussels. However, the authors found no evidence of differences in POPs exposure related to the dietary switch. Probably the temporal stability of PCBs and dichlorodiphenyldichloroethylene (DDE) (the two contaminants with the greatest burdens) in sediment from Lake Erie is responsible. The concentrations of some pesticides, particularly dieldrin and the chlordane metabolites, heptachlor epoxide and oxychlordane declined between 1990 and 2003. These declines are likely reflecting the temporal changes in historical land use from vineyards to tourism, and suggest that these pesticides have not yet reached equilibrium in the biotic environment of western Lake Erie. Therefore, the temporal changes in POPs exposure found in the study of Fernie et al. [46] were due to differences in land use and not to dietary changes in the watersnakes over time. Therefore, caution should be paid when interpreting POPs results from temporal and spatial studies, as diet is not the only potential confounding factor.

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5. *Nerodia sipedon*.

6. *Apollonia melanostomus*.

7. *Dreissena polymorpha*.

### 7.4.2 Post Intake Changes

Once taken up, metabolism and elimination of POPs are strongly species-dependent. For example, foxes, dogs, and grizzly bears have been shown to have a high potential to break down POPs [47–49], while this high metabolic capacity has not been found in predatory birds. The observation that metabolism can have a high influence on the concentrations in certain top predators means that not all top predators present a suitable reflection of their habitat, which is an important condition for environmental monitoring purposes.

Metabolites of PCBs may be formed in different organisms, including humans and birds of prey. Hydroxylated polychlorinated biphenyls (HO-PCBs) are metabolites of PCBs that show structural similarities with the hormone thyroxin (T4), produced by the thyroid gland. In addition, some HO-PCBs may also display estrogenic activity. HO-PCBs are generated through cytochrome P450 (CYP) enzyme-mediated phase I metabolism of PCBs. Within an animal group, differences in metabolic capacity may be of importance, resulting in different exposure patterns among species. For example, Jaspers et al. [50] compared the levels and profiles of hydroxylated metabolites of PCBs (HO-PCBs) in four predatory bird species (buzzard, sparrow hawk, long eared owl,<sup>8</sup> and grey heron<sup>9</sup>). Levels of HO-PCBs were found lowest in the sparrow hawk, which is remarkable as levels of PCBs were high in this species (median sum PCBs 1500 ng/g ww). Maximum concentrations were found in the buzzard up to 13,700 pg/g ww for sum HO-PCBs. The ratio of the main HO-PCBs (sum of 4-HO-PCB187, 4-HO-PCB146, 3'-HO-PCB138) to the corresponding precursor PCBs (sum of PCB 187, 183, 146, 153, and 138) was 0.1% for the heron, 0.3% for the owls, 0.3% for the buzzard, and 0.04% for the sparrow hawk. In comparison, Hasegawa et al. [51] also reported that ratios of sum HO-PCBs to sum PCBs were apparently lower in the black kite,<sup>10</sup> which belongs to the same Accipitridae family<sup>11</sup> as the sparrow hawk, than in grey herons and great cormorants.<sup>12</sup> Therefore, it may be possible that birds from the Accipitridae family could have lower metabolic capacities for PCBs compared to other predatory birds. Concerning the HO-PCBs profile, the grey heron differed in the HO-PCBs profile from the other species with 3'-HO-PCB138 and 4-HO-PCB163 contributing more to the sum HO-PCBs. This indicates that aquatic and terrestrial predatory bird species may show differences in their HO-PCBs profiles. In conclusion, both variations in diet and species-specific accumulation as well as metabolism of PCBs may be important factors to

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8. *Asio otus*.

9. *Ardea cinerea*.

10. *Milvus migrans*.

11. The Accipitridae family is one of the largest avian families, including many diurnal bird of prey, such as hawks, eagles, and kites.

12. *Phalacrocorax carbo*.

explain the HO-PCBs levels and profiles that were observed in different predatory bird species [50].

Another important consequence of post intake changes in wildlife is that concentrations in the environment are not predictable for concentrations and potential effects in biota. For example, Vermeulen et al. [45] investigated the bioaccumulation of POPs in the soil–earthworm–hedgehog food chain. Low relationships were found between levels in soil and earthworms and no relationship was found between POPs levels in earthworms and hedgehog hair. The authors concluded that samples should be taken from a sufficient number of individual hedgehogs per population to measure POPs, and that one should not rely on indirect estimates from levels in soil or prey. Instead it was suggested that samples should be taken from a sufficient number of individuals per population of the species of interest itself (e.g., hedgehogs [45]). Therefore, although sampling soil, water, air, herbage, or even prey species may be more practical, the relevance for exposure (and risk) assessment in animals higher up the food chain (including humans) is rather low. In order to address this problem, several nondestructive methods have been developed, which will be discussed in [Section 7.4.3.2](#).

### 7.4.3 Background Concentrations and Signatures

To investigate the local and geographical distribution of POPs in animals, different biological tools have to be used. In contrast to environmental samples, biological tools present a picture of the bioavailable fraction of the commercial mixtures. Biomonitoring is the direct measurement of concentrations in biota to reveal if and to what extent the organisms have been exposed. Because of ethical, scientific, and practical drawbacks to take samples from wildlife specimens, nondestructive methods have been developed, such as the use of eggs, feathers, hair, and plasma (although the last one is more invasive). The development and application of such tools also follow the recommendations for alternative methods promoted by REACH (ECHA).<sup>13</sup>

#### 7.4.3.1 *The Use of Bird Samples as Tools to Study Terrestrial POPs Contamination*

POPs encompass a large variety of organic substances with different sources in terms of time and space. For example, PCBs were mainly produced and used by industry, mostly located close to cities, while organochlorine pesticides (OCPs) are mainly used for agricultural purposes and higher levels can be expected in rural areas. To assess the emission patterns and the spatial distribution of POPs, studies looking at a local scale as well as covering

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13. Regulation of the European Union (EU), adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry.

large geographical areas are important. Birds have often been used in different studies to investigate regional and geographical patterns of contamination with POPs [52–54]. Passerine birds have been used in many studies [55–57], as they are easy to capture and handle. Many of these species are widespread and are therefore useful to study contamination over large geographical areas. Residential passerine species are expected to reflect local contamination because of their small home ranges, territories, and foraging areas [58,59]. Nondestructive samples, such as eggs and feathers, are relatively easily obtained.

#### 7.4.3.1.1 Eggs

Several studies have used eggs of passerine species to investigate the local and large-scale contamination of the terrestrial environment with POPs. One local study on passerine birds [52] investigated variation in POPs contamination among urban, industrialized, and rural areas in Flanders (Belgium) using eggs of great tits. The authors reported a larger variation among areas for PCBs and DDTs than for PBDEs. PCBs and PBDEs were found at higher concentrations in industrialized areas (up to 6050 and 79 ng/g lw, respectively), such as the harbor of Antwerp (Belgium). Other studies have reported high levels of PCBs in marine species and sediments close to harbors [60–62], including the harbor of Antwerp [63]. Previous studies with great tit eggs from sampling locations near Antwerp showed similar concentrations [59,64]. While no clear differences were found for the PCB profile among areas, lower brominated PBDE congeners were more prominent in great tit eggs from rural areas compared to more industrialized areas [55].

On a larger scale, great tit eggs were collected from 14 European countries, in urban, rural, and remote areas [56]. Sum PCB levels were found significantly higher at the urban and rural sampling locations compared to the remote locations. PBDEs were significantly higher in the urban locations, while significantly higher levels of OCPs were detected in the rural sampling locations. A significant positive correlation between PCBs and PBDEs suggested similar spatial exposure and/or accumulation pathways. Yet, the highest mean PCB levels were found in a rural areas of the Czech Republic (3600 ng/g lw) and in a sampling location near the city of Barcelona (Spain;  $\pm 3000$  ng/g lw). Local contamination sources may be responsible for the unexpected relatively high PCB levels. The highest PCB levels in the rural sampling location of the Czech Republic may be explained by metal and chemical industries in the neighborhood (17–30 km). Similarly, heavy industrial activities were reported in the sampling location near Barcelona (Spain). Further, the higher concentrations found in countries from Eastern Europe could reflect the fact that PCB production and use stopped somewhat later in this region compared to the rest of Europe. Contamination profiles of PCBs, PBDEs, and OCPs were also different among sampling locations, probably



**FIGURE 7.2** Common starling (*S. vulgaris*) eggs. Source: Picture courtesy of Pierre Selim, Wikimedia Commons, [http://en.wikipedia.org/wiki/File:Toulouse\\_-\\_Sturnus\\_vulgaris\\_-\\_2012-02-26\\_-\\_3.jpg](http://en.wikipedia.org/wiki/File:Toulouse_-_Sturnus_vulgaris_-_2012-02-26_-_3.jpg).

related to local usage and contamination sources. The higher variance among sampling locations for PCBs and OCPs suggested that local contamination sources are more important for PCBs and OCPs than for PBDEs.

In Canada [65], starling<sup>14</sup> eggs (Figure 7.2) were used to determine the contamination with flame retardants in the surroundings of five major cities. Starlings are relatively high on the food chain, feeding mainly on soil invertebrates, and therefore have the potential to accumulate high concentrations of POPs. Chen et al. [65] demonstrated that there were orders of magnitude, higher levels of PBDEs (up to 800 ng/g ww), and other flame retardants in starling eggs from populations nesting in landfill sites relative to those from urban, industrial, and rural environments. Further,  $\Sigma$ PBDE levels in eggs from landfills were significantly correlated with the human population density of the metropolitan region using the landfill. The results of Chen et al. [65] indicated that landfills are an important source of flame retardants to starlings nesting nearby, which suggests that other terrestrial organisms may also be exposed.

Starling eggs were even used to investigate POPs contamination on a global scale [57]. Starlings are ubiquitous and make use of nest boxes for breeding, which makes it relatively easy to sample eggs for large-scale studies. Eens et al. [57] found significant different POPs concentrations in eggs among sampling locations, except for hexachlorocyclohexanes (HCHs). The country-specific results for PCBs are presented in Box 7.2.

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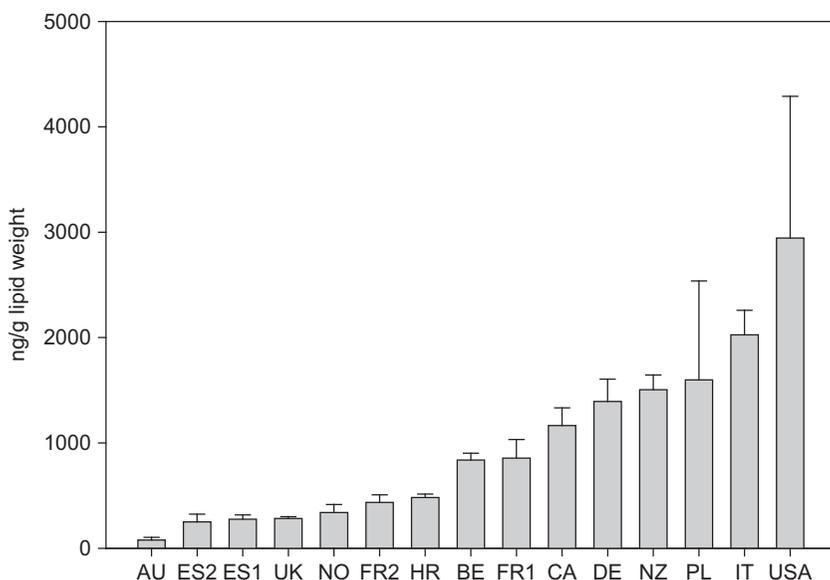
14. *Sturnus vulgaris*.

**Box 7.2 Global PCB Patterns in Starling Eggs**

In the study of Eens et al. [57], starling eggs were collected on a global scale to investigate geographical differences in contamination patterns. PCB concentrations differed significantly among the sampling locations (Figure 7.3). The lowest concentrations of sum PCBs were found in Australia, while the highest concentrations were found in the United States. The high concentrations in the United States are probably due to the fact that large amounts of PCB commercial mixtures were produced and used in the United States [66]. PCB concentrations in eggs from European countries in the study of Eens et al. [57] were comparable with the concentrations in European great tit and blue tit eggs [56]. In Europe, the highest PCB concentrations were found in the urban locations in Italy and Poland. PCB concentrations at the urban site from Italy were significantly higher compared to the rural locations from Norway, Croatia, Spain (ES1 and ES2), France (FR2), and the United Kingdom. However, results from the urban sampling location in Poland did not show significantly higher PCB concentrations compared to the other locations. This might be due to the high variation in PCB concentrations within this location, which may be related to eggs being collected from two nest box colonies, 3 km apart. Therefore, individual variation and local contamination sources (one colony was near a landfill rehabilitation area) may be of concern. Moreover, PCB concentrations at the urban site from Italy were higher than concentrations previously found in great tit and blue tit eggs collected from the same site [56]. This may be related to dietary differences among tits and starlings and possibly to different physiological sensitivities to bioaccumulation of PCBs. The geographical patterns of PCBs found in starling eggs reflected the expected emission patterns and were in accordance with data from human and environmental samples [57].

Mean concentrations of sum PCBs in eggs ranged from  $78 \pm 26$  ng/g lw in Australia to  $2900 \pm 1300$  ng/g lw in the United States. The PCB profile was dominated by PCB 153 and PCB 138 in all locations, except for New Zealand. The highest mean sum PBDE concentrations were found in Canada ( $4400 \pm 830$  ng/g lw), while the lowest were measured in Spain ( $3.7 \pm 0.1$  ng/g lw). The PBDE profile in starling eggs was dominated by PBDE-47 and PBDE-99 in all countries, but in Belgium the higher brominated PBDEs had a higher contribution compared to other countries. The OCP profile in all countries was largely dominated by p,p'-DDE. Chlordanes were remarkably high in eggs from the United States ( $2500 \pm 1300$  ng/g lw). In general, the worldwide trends observed in starling eggs were in accordance with the literature on human and environmental POPs data, which indicates the potential for using starling eggs as a biomonitoring tool on a large geographical scale.

Besides passerine species, predatory bird eggs have also been used. One recent study by Guerra et al. [67] looked at brominated flame retardants



**FIGURE 7.3** Mean concentrations  $\pm$  standard error of sum PCBs in starling eggs collected worldwide. Sampling sites were located in Australia (AU), Belgium (BE), Canada (CA), Germany (DE), Spain (ES1 and ES2), France (FR1 and FR2), Croatia (HR), Italy (IT), Norway (NO), New Zealand (NZ), Poland (PL), United Kingdom (UK), and United States of America (USA). Concentrations are expressed per gram lipid weight. Reproduced with permission from Environment International, Eens et al. 2013 [57].

(BFRs) in eggs from a predatory bird species, the peregrine falcon.<sup>15</sup> The authors measured the levels and profiles of emerging and historical BFRs in peregrine falcon eggs from Canada and Spain and compared the results to previous reports on BFRs in peregrine falcon eggs from Sweden [68–70], Greenland [71], and the United States [53,72–75]. The *in ovo* concentrations of BFRs in the peregrines were significantly greater in the Canadian than in the Spanish birds. Furthermore, Guerra et al. [67] found an overall pattern of higher contaminant concentrations in peregrine falcon eggs from Canada/North America than Spain/Europe. Peregrines breeding in North America had higher concentrations of BFRs than those in Greenland, followed by Sweden and then Spain. This pattern is likely reflecting the greater usage of these BFRs in North America than in Europe [76,77].

#### 7.4.3.1.2 Feathers

In addition to eggs, feathers have also been used to monitor POPs contamination in several studies, mostly with aquatic and predatory birds [54,78–82]. These studies showed high correlations between levels of most

15. *Falco peregrines*.

POPs in feathers and internal tissues [78,81–82]. Predatory birds are, however, highly mobile and therefore not particularly useful to investigate POPs contamination on a local scale.

Therefore, Jaspers et al. [83] used magpie<sup>16</sup> feathers to investigate POPs contamination on a local scale. Feathers were used as a nondestructive biomonitor to investigate the local contamination with PCBs and other POPs in an urbanized area around Antwerp (Belgium) and from two local areas in Flanders (Belgium). The results showed that PCBs were significantly more available in the urban environment (Antwerp) compared to the rural areas (sum PCBs—rural: 2.9–22 ng/g feather, urban: 41–240 ng/g feather). Furthermore, differences in the PCB profile were found with lower halogenated congeners being more prominent in the urban area. Although external contamination on the feathers could potentially occur [84,85], atmospheric transport of lower PCB congeners was probably not an important factor in explaining these differences, as then their contribution would be expected to be higher in rural areas. It is possible that the higher concentrations of PCBs and other contaminants (e.g., PCDDs) in birds from the urban area lead to the induction of metabolic processes and the subsequent formation of lower chlorinated less persistent PCB congeners in these birds, which were accumulated into growing feathers via the blood. Overall, the study of Jaspers et al. [83] provided clear indications that feathers seem to reflect regional variations in contamination, which strengthens their usefulness as a nondestructive biomonitor for POPs.

Feathers could be very useful for large-scale monitoring studies, seeing their nondestructive sampling, their easy storage and transport and the fact that large feather collections are available in museums or private collections, which can potentially be used to study time trends [86]. Their ease of storage and shipping also provides opportunities to perform large-scale geographical studies, to investigate geographical contamination patterns and sources, as was done previously using bird eggs [56,57]. Additionally the nondestructive sampling of feathers allows the follow-up of population characteristics, such as mortality and reproduction. Finally, they seem to be a promising matrix for a wide variety of elements, including hormones [87]. Therefore, feathers are very promising alternative tools that are expected to be employed in routine monitoring schemes in the future.

### 7.4.3.2 Nondestructive Monitoring of POPs in Terrestrial Mammals

#### 7.4.3.2.1 Hedgehog Hair

Similar to feathers, hair is a keratinous tissue that is able to accumulate pollutants during growth. However, in contrast to feathers, hair is continuously

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16. *Pica pica*.

growing and the length of the hair is proportional to the period of growth. Older parts of the hair are disconnected from the bloodstream, while the hair portion near the root is connected to the blood and thus represents recent accumulation of pollutants. Hair has been used in many analyses on drugs and other toxic substances [88,89]. Recently, polar bear hair has also been investigated as a potential biomonitoring tool for POPs [90]. For monitoring pollutants in a terrestrial environment, hedgehog<sup>17</sup> hair has been used in several studies [45,91–93].

The first study that demonstrated the suitability of hedgehog hair looked at concentrations of PBDEs and brominated biphenyl 153 in tissues and hair of the European hedgehog in Belgium [91]. Positive relationships were found between BFR levels in hair and internal tissues for sum PBDEs and BDE-47 ( $0.37 < r < 0.78$ ). Therefore, this study indicated hair as a suitable indicator of PBDE exposure in terrestrial mammals and its suitability for nondestructive monitoring schemes.

D'Havé et al. [92] then evaluated the use of hedgehog hair as a nondestructive biological monitoring tool for organochlorine contamination in terrestrial ecosystems by investigating the relationships between levels in hair and internal tissues. Significant positive relationships were found between levels in hair and levels in tissues for PCBs, DDTs, HCB, HCHs, and chlordane related compounds (CHLs) ( $0.49 < r < 0.91$ ). These results further confirm the usefulness of hedgehog hair as a biomonitoring tool for POPs. In addition, the authors calculated regression models to predict organochlorine compound concentrations in internal tissues and the associated toxicological risks, based on the levels found in hedgehog hair.

Another study from the same authors [93] indicated that hair is a better indicator than soil for exposure and risk assessment of PCBs and OCPs in hedgehogs. PCBs, DDTs, HCHs, and HCB were investigated in soils and hedgehog hair from seven study sites around the urban area of Antwerp (Belgium). No relationships were observed between levels in soil and hair and also the relative profiles of PCBs, DDTs, and HCHs were different between soil and hair samples. When comparing the levels in soil to background levels, information on the degree of pollution could be obtained. However, to address the risks to the organisms living there, concentrations in biological samples (i.e., hedgehog hair) needed to be obtained. Using concentrations in hair, the authors calculated the expected liver concentrations based on the regression equations obtained in the previous study [92]. The predicted internal tissue concentrations suggested a minimal risk for the hedgehogs to be adversely affected by the organochlorine contamination. In summary, the results of D'Havé et al. [93] indicated that concentrations of organochlorine compounds in soils alone are not predictive of the risk of

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17. *Erinaceus europaeus*.

these pollutants to hedgehogs and that tissue or hair analyses are preferred to soil analyses in exposure and risk assessment studies.

#### 7.4.3.2.2 Milk and Butter

POPs concentrate in lipid rich substances like dairy fats. This means that important food items, such as butter and milk, could be highly contaminated with POPs and may therefore be useful tools to monitor the environmental levels and human exposure to POPs. Many studies have been conducted on PCDD/Fs and dioxin like PCBs in cow's milk from farms in various European countries [94–99].

A recent study on cow's milk was performed in Italy. Esposito et al. [100] investigated the levels and profiles of PCBs, PCDDs/PCDFs on a local scale in cow's milk from Campania, Italy. The authors divided the milk samples into two groups based on the maximum permitted limit set by regulations EC 1881/2006<sup>18</sup> of WHO-TEQ = 3.0 pg/g fat. Mostly low contamination in milk samples was found with some critical levels in restricted areas only. All samples with a toxic equivalent (TEQ) above 3 ng/g fat were located in the same areas (Napoli and Caserta districts), where also buffalo herds contaminated with PCDD/Fs were found in 2007 (unpublished data, EU monitoring plan). Significant differences in the profile were found for PCDDs/PCDFs, but not for dioxin like PCBs between the two groups of samples. In samples with PCDD/PCDF TEQ values above 3 pg/g fat, PCDFs were more prevalent (PCDD/PCDF ratio was 0.7), while in samples with levels below the 3 pg/g fat this ratio was higher (0.9) and in 19 milk samples PCDDs were found to prevail (ratio 1.4). These last samples were collected in farms located in rural areas with background contamination levels. Because the detection in milk is a reflection of PCDDs/PCDFs presence in the cow's diet [101], the source of the contamination could probably be identified in the feed and may be attributed to illegal waste burning, with a possible contamination of grasslands and other local feed given to cows, such as hay and maize silage. The study of contaminants in the milk of grazing cows seems thus a good approach to assess the presence and levels of pollutants in the environment. Furthermore, the congener-specific approach is very useful to characterize the sources of PCDDs/PCDFs and to plan effective measures to reduce the contamination.

Kalantzi et al. [102] investigated the use of butter as a tool to reflect local and global distribution of PCBs and OCPs in air. Indeed, cattle are mostly feeding on pasture and silage, which may be exposed to contaminants via atmospheric deposition. Kalantzi et al. [102] found that  $\Sigma$ PCB concentrations in butter varied between 230 (New Zealand) and 14,100 (Czech Republic) pg/g lipid (a factor of about 60) in samples from 23 countries. PCB

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18. European regulation setting maximum levels for certain contaminants in foodstuffs.

concentrations were highest in (Eastern) European butter, followed by North American butter and lowest in southern hemisphere (Australian, New Zealand) samples, consistent with known patterns of historical global usage and estimated emissions. Elevated concentrations in Eastern Europe could reflect the fact that PCB production and use stopped somewhat later in this region than the rest of Europe. Furthermore, concentrations in butter reflected differences in the propensity of PCB congeners to undergo LRAT from global source regions to remote areas and the relatively even distribution of HCB in the global atmosphere. Concentrations of DDT (80–25,000 pg/g), DDE (380–180,000 pg/g), and HCH isomers (60–98,000 pg/g for  $\alpha$ -HCH, 20–110,000 pg/g for  $\beta$ -HCH, and 88–18 000 pg/g for  $\gamma$ -HCH) varied over many orders of magnitude in the butter samples, with highest levels in areas of current use (e.g., India and south/central America for DDT; India, China, and Spain for HCH). In conclusion, butter seems to be sensitive to local, regional, and global scale spatial and temporal atmospheric trends of several POPs and may therefore provide a useful sampling medium for monitoring purposes (Box 7.3).

## 7.5 HUMANS

### 7.5.1 Pathways for POPs to Enter Humans

POPs can enter humans through three main pathways: ingestion, inhalation, and dermal contact (through the skin). The vast majority of people will only be exposed to background concentrations of POPs, which will occur throughout their lifetime. The majority of this exposure will occur through ingestion of contaminated foods [107]. For the UK population, it was calculated that food consumption was responsible for 97% of the total exposure to PCBs [108]. Therefore, for the majority of people their diet will have the largest impact on their exposure to POPs. However, other important exposure pathways such as inhalation of indoor dust have been identified for PBDEs in humans and especially toddlers [109,110].

POPs are lipophilic and so high concentrations are often found in fatty tissues of high trophic level animals. A review of human exposure to PBDEs undertaken by Frederiksen et al. [111] identified that average PBDE concentrations in fish were more than an order of magnitude higher than the other food groups. As well as affecting the total intake of POPs, a person's diet will influence their specific congener profile, as the proportions of congeners are different in each food group [42]. With respect to PCBs, vegetables contain higher proportions of the lighter congeners like PCB 28, whilst fatty foods contained higher proportions of the more chlorinated congeners [108]. The main dietary source of POPs varies between countries due to different diets. The major source of PCBs in India was cereals and vegetables [112], in Finland it was fish [113], and meat in Canada [114]. Similar

**Box 7.3 POPs in Terrestrial Wildlife around the Great Lakes (Canada)**

Most studies in the Great Lakes area have been performed on fish and gulls. However, some recent studies have been performed on snapping turtles, mink, and peregrine falcons living around the Great Lakes.

In the study of de Solla and Fernie [103], eggs and plasma of snapping turtles (*Chelydra serpentina*) were used to study the contamination with PCBs, OCPs, and PCDD/Fs at three areas of concern (AOC) on Lake Erie and two inland reference sites. The authors found that contaminant levels were sufficiently high in turtle eggs to be of concern in the Canadian AOCs, particularly near the Wheatley Harbour and Detroit River AOCs. The organochlorine profile of the eggs from near the Wheatley Harbour AOC was also found different from the profile of the other sites. In comparison, Kelly et al. [104] have shown that the Detroit River is the largest source for the majority of POPs, including PCBs and organochlorine pesticides. However, on a smaller scale, contaminant inputs into the Wheatley Harbour AOC are from local sources, largely through the processing of fish. Therefore the POP levels and profiles found in turtle eggs reflected the known sources of contaminant inputs into Lake Erie.

The same contamination pattern was found by Martin et al. [105], who investigated temporal and spatial trends of organochlorines (OCs) in carcasses from trapped mink from Lake Erie and St. Clair. Mink from shoreline marshes and tributaries of the western basin of Lake Erie tended to be more highly contaminated while those from inland sites contained the lowest concentrations of contaminants. Animals from eastern Lake Erie, Lake St. Clair, and Walpole Island in the St. Clair River AOC, had intermediate concentrations of most contaminants. Thus again the highest concentrations were found in western Lake Erie. Furthermore, PCB concentrations remained at least as high if not higher than those from the 1970s and indicated that almost 40% of individuals could be subject to reductions in reproductive success through impacts on kit growth and survival.

Fernie and Letcher [106] studied concentrations and spatial patterns of POPs, flame retardants, and hydroxylated (HO-) PBDEs and PCBs in plasma from nestling peregrine falcons across the Canadian Great Lakes Basin. Their results indicated important regional differences in the PCB and PBDE concentrations and congener profiles. However, these spatial differences were likely a partial reflection of dietary differences among chicks, with some nestlings consuming a broader diet incorporating aquatic avian species (more BDE-47) and others having a largely terrestrial diet comprised mainly of Columbidae species. Some differences may also reflect differential exposure to local sources of flame retardants, in particular hexabromocyclododecane (HBCD) was only detected in plasma of urban peregrine nestlings. Metabolic processes in the peregrines, for example, debromination and oxidation of accumulated PCB and/or PBDE congeners, were indicated as source contributors of lower brominated PBDE congeners, OH-PBDEs, and OH-PCBs. The study of Fernie and Letcher [106] illustrates the importance to account for confounding factors, such as dietary habits and metabolic capacity, in wildlife monitoring studies.

results have been reported for PBDEs by Frederiksen et al. [111], where in Finland the main source was from fish (55% of the total intake) and in America the main source was from meat (60–70% of the total intake).

Although POPs are not particularly volatile, in some instances inhalation may prove an important exposure pathway. In a school in Boston, USA, inhalation of PCBs leaching from caulking materials and sealants was determined as the main route of exposure for teachers [115]. This exposure resulted in teachers having total PCB concentrations five times higher than the control group. DeCaprio et al. [116] also noted that inhalation of PCBs may be an underappreciated transport pathway. DeCaprio et al. [116] studied the PCB signature in sera of Mohawks at Akwesasne who had historically been exposed to PCBs. The study identified that some of Mohawks appeared to have been recently exposed to volatilized Aroclor 1248. As well as inhalation of vapors, inhalation of dust can form a significant pathway by which humans are exposed to POPs. PBDE concentrations have been monitored outdoors, at home, at work and even in the car; the results of these studies were collated and summarized by Frederiksen et al. [111]. Concentrations of outdoor air were generally 1 or 2 orders of magnitude lower than indoor air. The signature of indoor air was dominated by the presence of BDE-209 which contributed 32–97% of total PBDEs. PBDE concentrations varied across the globe with the highest concentrations being reported in the United States and the United Kingdom, BDE-209 was consistently the dominant congener but slightly different PBDE signatures were reported between the United States and parts of Europe [111].

Due to the high lipophilic nature of POPs, the skin is unlikely to form an effective barrier against dermal uptake. Studies by Staskal et al. [117] showed that 62% of the dermally applied dose of BDE-47 was absorbed through the skin in mice. Humans may be exposed to POPs like PBDE by direct contact with items, such as furniture, textiles, and electronic equipment, or through contact with house dust. Webster et al. [118] estimated that dermal contact accounted for 10% of adults and 35% of children exposure to PBDE. Not all congeners are taken up to the same extent, less chlorinated PCBs have been shown to be taken up more readily than more chlorinated congeners [119].

### 7.5.2 Post Intake Changes

The previous section has focused on the intake of POPs (POPs entering the body) and how the signature can be altered by a variety of external processes. The following section will focus on the processes that determine POP uptake, biotransformation, and elimination. These are all processes that occur once the POPs have entered the body. These alterations mean that the levels of POPs in an individual are not controlled exclusively by exposure. There are several physiological characteristics, such as body fat, serum albumin,

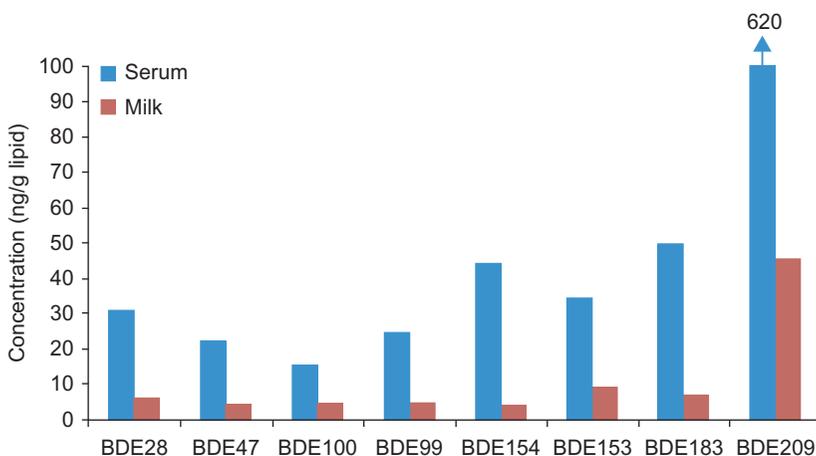
age, and smoking, that can all influence the uptake and retention of POPs [120–123]. These various factors make the forensic analysis in humans a complex task.

In general, POPs appear to be readily absorbed by humans, especially in the gastrointestinal tract after oral exposure. Price et al. [124] recorded that 88% of PCBs ingested by preadolescent girls were not excreted and therefore presumed to remain in the body. This is believed to be primarily due to the lipophilic nature of POPs and the high octanol water coefficients ( $\log K_{ow}$ ). When POPs enter humans not all congeners have the same rates of uptake, biotransformation, and elimination. Therefore, the signature from the source of contamination may be significantly different to the signature recorded in an individual who has been exposed.

There are several POPs, such as PCBs, dioxins, furans, and PBDEs, that contain a large number of individual congeners. All congeners do not behave in the same way and there can be a significant difference in the retention of different congeners in humans. Several studies have calculated PCB residence times [125] and identified steady state (those that are persistent in the body) and episodic (identified in humans transiently) PCBs [126]. Generally coplanar PCBs and those with a high degree of chlorination are most persistent in the body [42,115,127,128]. This is believed to be because these congeners are more resistant to the first metabolic breakdown step, which is hydroxylation involving the cytochrome P450 system [128].

There are a large number of factors that should be considered when undertaking a forensic investigation into human exposure to POPs. Within the body different POPs have the potential to accumulate in different proportions in different places, the highest concentrations are often found in fatty tissue and organs like the liver. Different concentrations of POPs will be found in a sample of breast milk compared to a sample of serum from the same individual. For PCBs there are various rough correction factors that can be performed on the data to compare total concentrations from different human samples [129]. As well as effecting the total concentration, the signature also changes slightly in different parts of humans. Shifts in congener composition of PBDEs have been recorded from maternal blood to umbilical cord blood with higher proportions of BDE-47 present in the cord blood [111]. A study undertaken by Jin et al. [130] measured PBDE concentrations in serum and breast milk samples from the resident population of a PBDE production area in China. Figure 7.4 presents the results from Jin et al. [130] showing changes in total concentration and relative proportions for the mean concentrations of eight PBDE congeners in serum and breast milk.

For PCBs, rates of biotransformation and elimination of both total PCBs and individual congeners have been shown to vary greatly between different subgroups [121,131,132]. Elevated concentrations of PCBs have been found in non-Hispanic black subgroups who consumed a lot of catfish [123]. There is also a positive correlation between PCB concentration and age due to the



**FIGURE 7.4** Concentration of eight PBDEs in serum and milk samples taken from the resident population of a PBDE production area in Laizhou Bay, Shandong Province, China. Figure plotted using data taken from Jin et al. 2009 [130].

bioaccumulation of persistent congeners. This results in a different total PCB concentration and also a distinct PCB signature for different age groups [133,134]. Results from Jain and Wang [122] showed that smoking and drinking coffee can actually reduce a person's total PCB concentrations. This is believed to be due to the presence of other contaminants like PAHs which activate the same metabolic pathways that break down PCBs. However, a healthier alternative to reducing PCB concentrations would be to eat cruciferous vegetables, as these have also been shown to activate PCB metabolizing pathways [127].

### 7.5.3 Background Concentrations and Signatures

There have been a large number of studies which have recorded concentrations of POPs in humans due to background exposure. Samples have been obtained from a variety of media, including serum, breast milk, whole blood, adipose tissue, and placenta. The results of many of the studies undertaken on PCBs were collated and summarized by Longnecker [129], who converted values into microgram per liter of serum to allow for a more direct comparison to be made between the different datasets. Total PCB concentrations in human samples generally ranged from around 1  $\mu\text{g/L}$  to a maximum of 14.2  $\mu\text{g/L}$  in the Faroe Islands. The high value in the Faroe Islands was attributed to the fact that whale blubber contributed an important part of their diet [135]. It is apparent that PCB concentrations generally increased with age [136] and populations with large intake of seafood appear to have higher than average concentrations [137,138].

**TABLE 7.1** Range in Concentrations of BDE-47 in Blood Samples in Different Parts of the World

Location	BDE-47 Concentrations (ng/g lw)
North America	0.63–46
Europe	0.24–2.4
Asia	1.5–28
Oceania	2.7–20

A review on the levels of human exposure to PBDEs was undertaken by Frederiksen et al. [111]. The review covers a huge number of studies and provides an excellent source of background data for different sample types taken from various parts of the world. The studies of blood (plasma and serum) and breast milk indicate that PBDE levels are 1 order of magnitude higher in North America than in Europe (Table 7.1).

PCBs are one of the most studied POPs in humans. Because of their persistence and toxicity, PCB concentrations in the US population are routinely monitored within The United States National Health and Nutrition Examination Survey (NHANES) [139–141]. NHANES is a continuous survey that was designed to monitor the health of the US population through interviews, physical examination, and laboratory analysis of human samples, including PCB analysis of serum. This data is freely available and provides excellent information on background concentrations of PCBs in the US population.

The NHANES data has been used to study the total concentrations of PCBs and how these levels have decreased in recent years [142]. However, it can also be used to improve our understanding of the persistence of PCBs in humans. Most PCB metabolism studies have been conducted by undertaking tests on animals or in the unfortunate events where humans have been exposed to high concentrations of PCBs. The NHANES data has been used by Megson et al. [134] to provide a useful insight to the persistence of PCBs in humans. The PCB signature recorded in humans exposed to background contamination is dominated by PCBs that are more resistant to biotransformation and elimination. These include PCBs with a higher degree of chlorination and coplanar PCBs with no ortho chlorines [42,115,127,128]. However, the exact position of chlorine atoms on the biphenyl is also important in determining the retention of PCBs in humans. Congeners with chlorine atoms in the 2,5- and 2,3,6- positions appear to be more susceptible to biotransformation whereas congeners with chlorine bonds in the 2,3,4-, 2,4,5-,3,4,5-, and 2,3,4,5- positions appear to be more persistent [134]. When undertaking environmental forensics investigations of POPs in

humans, it is important to consider how the congener profile may be altered by differences in exposure pathways, e.g., oral, inhalation, or dermal and through post uptake processes, such as biotransformation and elimination.

## 7.6 CASE STUDY 1: PERFLUORINATED CHEMICALS IN THE URBAN TERRESTRIAL ENVIRONMENT NEAR ANTWERP (BELGIUM)

### 7.6.1 Introduction

The city of Antwerp is located in the Northern part of Belgium, on the right bank of the river Scheldt. The total population of Antwerp is about half a million inhabitants [143]. Crucial for the economy is the harbor of Antwerp, which houses a great number of chemical plants and other industrial activities. One of the largest perfluorochemical plants, from the 3M group, is located near Antwerp (on the left bank of the river Scheldt; Figure 7.5). The importance of this plant as a potential source for perfluoroalkyl substances (PFASs)<sup>19</sup> was investigated in a number of studies starting from 2003. This case study is a compilation of the studies that were performed investigating PFASs near the city of Antwerp, with a special emphasis on the studies performed in the terrestrial environment.

PFASs, and in particular perfluorooctane sulfonate (PFOS), have been used for over 50 years in a variety of industrial and consumer products thanks to their surface-active properties. Examples of their use include fire-fighting foams used to extinguish chemical, oil, and aviation fires, critical components in military and civilian aircraft, and industrial fluids used to make computer components and other electronic devices (*source*: www.3m.com). PFOS-related product uses included stain resistant treatments for carpets, fabrics, and paper products. PFOS is the terminal degradation product of many of the commercially used PFASs (referred to as PFOS-related substances, 96 in total), highly persistent, and the main compound found in the environment and in biota (Figure 7.6). Furthermore, PFOS and related substances have been distributed on a worldwide scale with higher local contamination near densely populated and industrialized areas [144]. In the body, PFOS strongly binds to proteins like albumin and accumulates mainly in the liver and gall bladder [145]. The global production of PFOS-based chemicals was 4481 tons in 2000 [146]. In the same year, 3M decided to phase out the production of PFOS [147].

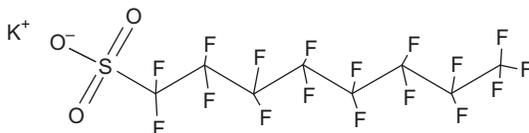
One of the first studies that investigated environmental concentrations of PFASs near Antwerp [148] showed widespread distribution of PFOS in the

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19. PFASs were formerly referred to as PFCs (perfluorinated chemicals). Since PFCs were too general, Buck et al. *Integr. Environ. Assess Manag.* 7 (2011) 513–541, proposed to use perfluoroalkyl and polyfluoroalkyl substances (PFASs) instead.



**FIGURE 7.5** Study area for PFAS studies near Antwerp. The asterisk is the approximate location of the fluorochemical plant near Antwerp. *Source:* Map adapted from <http://www.portofantwerp.com>.



**FIGURE 7.6** Structural formula of PFOS shown as its potassium salt.

Belgian and Dutch marine and estuarine environment at rather high concentrations (levels on a wet-weight basis in soft tissues of shrimp, crab, and starfish ranged from 19 to 520 ng/g, from 24 to 877 ng/g, and from 9 to 176 ng/g, respectively). Furthermore, a PFOS gradient in the Western Scheldt Estuary was found, with the highest concentrations near Antwerp. The authors suggested that the elevated levels of PFOS in aquatic invertebrates near Antwerp could be related to the presence of the PFASs plant. The results were in accordance with a previous study that also found a PFOS pollution gradient for fish in the Western Scheldt [149].

Those first studies highlighted the importance of a potential source for PFASs near Antwerp. Several studies were therefore undertaken to further investigate the extent and importance (i.e., potential toxic effects) of the PFASs contamination close to Antwerp. In the following sections, PFASs studies undertaken in small mammals, passerine birds, and predatory birds will be discussed. Small mammals and passerine birds are particularly useful to monitor local contamination [64,150–152]. Therefore studies on small mammals and passerines were performed in the close vicinity of the

fluorochemical plant (mostly in a nature reserve called Blokkersdijk). Predatory birds are potentially preying on highly contaminated prey around the region of Antwerp. Therefore, the study on predatory birds aimed to provide a general integration of the PFASs contamination in the Province of Antwerp. In the last section, the measures taken by 3M and the need for further monitoring of the concentrations near Antwerp will be discussed.

### 7.6.2 FASs in Small Mammals from Blokkersdijk (Antwerp)

In 2002, wood mice<sup>20</sup> were captured at a nature reserve (Blokkersdijk) close to the fluorochemical plant of Antwerp and at a site (Galgenweel) 3 km away from the plant (Figure 7.7; [153]). Liver concentrations of PFOS and other PFASs were determined in liver tissue. In addition, several biological and biochemical effect endpoints were studied in liver and blood serum of these mice under field conditions.

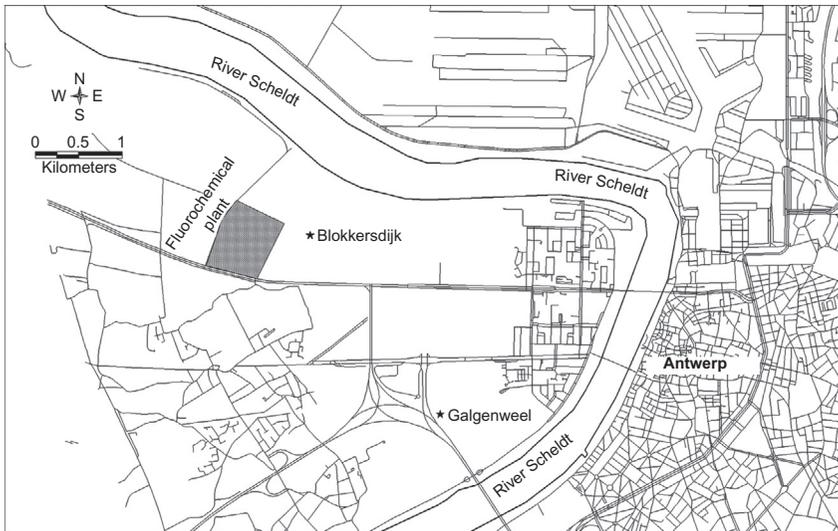
Extremely high liver PFOS concentrations were found in the mice from Blokkersdijk (0.47–180 µg/g ww), while the mice from Galgenweel showed significantly lower concentrations (0.14–1.11 µg/g ww). Other PFASs (PFNA, PFDA, PFUA, and PFDOA<sup>21</sup>) were sporadically detected in the mice from Blokkersdijk, but not in the mice from Galgenweel. Perfluorooctanoic acid (PFOA) could not be detected in the study of Hoff et al. [153]. Increased PFOS levels were found in older mice, suggesting bioaccumulation with age, and evidence was found for maternal transfer of PFOS to young (20 days old). No gender influences were found on the PFOS levels in liver.

Regarding the effect endpoints, several liver endpoints were significantly elevated at Blokkersdijk, including liver weight, peroxisomal β-oxidation, peroxisomal lipid peroxidation, and mitochondrial fraction protein content. There was an interaction between sex and location for peroxisomal lipid peroxidation and mitochondrial fraction protein content, with higher levels in the females than the males. However, none of the endpoints was affected by age. Positive correlations were found between PFOS levels and liver weight, relative liver weight and liver microsomal lipid peroxidation (indicating oxidative stress). No site or sex differences were found for the serum endpoints. However, triglyceride concentrations were significantly positively related to liver PFOS levels, while a significant negative correlation was found between alanine aminotransferase (ALT) activity and PFOS levels. The positive relation between serum triglycerides and PFOS is probably an artifact as both liver PFOS and serum triglycerides increase with age.

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20. *Apodemus sylvaticus*.

21. PFNA, perfluorononanoic acid; PFDE, perfluorodecanoic acid; PFUA, perfluoroundecanoic acid; PFDOA, perfluorododecanoic acid.



**FIGURE 7.7** Study area and sampling sites for wood mice around Antwerp. *Source: Reproduced with permission from Environmental Health Perspectives [153].*

In summary, the high PFOS concentrations and the presence of some perfluorocarboxylates, in the mice from Blokkersdijk compared to Galgenweel indicated a clear point source for PFASs contamination originating from the fluorochemical plant near Antwerp. Among the endpoints reported, the relative liver weight, the microsomal lipid peroxidation level and the serum ALT were most apparently related to the liver PFOS concentrations. It should be kept in mind though that the effects reported in the study of Hoff et al. [153] may not only be the result of PFOS exposure but also that other (nonperfluorinated) compounds may have been contributing as well, since Blokkersdijk is at the border of the heavily industrialized harbor of Antwerp. The effect of PFOS in combination with other organohalogenated compounds (OHCs) was further investigated in a study using passerine birds (see Section 7.6.3.1).

### 7.6.3 PFASs in Songbirds around the Fluorochemical Plant from Antwerp

Small songbirds (passerine species) often live in and around urban areas and have been used in many studies investigating local contamination [64,150–152,154]. Two studies were performed on passerine bird species, breeding in nest boxes, to further investigate the PFOS contamination of the terrestrial ecosystem around Antwerp. The first study focused on the

biochemical effects of PFOS in combination with organohalogenated contaminants in nestlings from two passerine species [154]. The second study looked at PFOS levels in blood and liver from adult great tits near the fluorochemical plant in Antwerp [152].

### 7.6.3.1 Biochemical Effects of PFOS and OHCs in Nestling Songbirds

In the study of Hoff et al. [154], nestlings from great tits and blue tits (*Cyanistes caeruleus*<sup>22</sup>) were sampled at Blokkersdijk and at a reference site (Fort IV) 10 km away from the fluorochemical plant. Seeing the high PFOS contamination of wood mice from Blokkersdijk [153] and the area being protected by the European Council directive 79/409/EEC on the conservation of wild birds, a study of PFOS in nestling birds from Blokkersdijk was deemed necessary [154]. Nestling birds were chosen as they are not mobile and because their food is derived from local sources (mainly butterflies and moths captured by the parents within their territory). In addition to PFOS, 11 OCPs, 20 PCBs, and 7 PBDEs were measured in liver tissue from the nestlings to investigate their potential effect on endpoints, such as relative liver weight, serum cholesterol, triglyceride levels, and ALT activity.

The liver PFOS concentrations at Blokkersdijk in great tit (86–2800 ng/g ww) and blue tit (317–3300 ng/g ww) were among the highest ever reported and were significantly higher than in the control area (17–206 and 69–514 ng/g ww for great and blue tit in Fort IV, respectively; [154]). Hoff et al. [154] therefore suggested that the fluorochemical plant might be the source of PFOS release and/or PFOS precursor release. The decrease of PFOS contamination with the distance was also observed on a local scale, as nestlings from the western side of Blokkersdijk (close to 3M) had higher concentrations than nestlings from the eastern side, although this difference was not significant. At both Blokkersdijk and Fort IV, PFOS was measured at higher concentrations than the other OHCs included in the study of Hoff et al. [154]. The PFOS concentrations found in passerine birds from Blokkersdijk are even comparable to the highest concentrations measured worldwide in top predators, such as the bald eagle,<sup>23</sup> mink,<sup>24</sup> bottlenose dolphin,<sup>25</sup> or polar bear<sup>26</sup> (discussed by Hoff et al. [154]). No significant difference in liver PFOS concentrations was found between both tit species, reflecting their similar dietary habits.

The PFOS concentration in liver correlated positively with the serum ALT and negatively with the serum cholesterol and triglyceride levels in

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22. The blue tit was formerly included in the *Parus* genus and referred to as *Parus caeruleus*.

23. *Haliaeetus leucocephalus*.

24. *Neovison vison*.

25. *Tursiops truncatus*.

26. *Ursus maritimus*.

both species. No correlation was found with condition or serum protein concentration. In the great tit, a positive correlation was found between PFOS levels and relative liver weight, while in the blue tit PFOS correlated positively with hematocrit values. Partial least square (PLS) analysis did not result in any robust models between the pollutants and the biological endpoints. Except for PFOS, none of the OHCs showed significant relations with the studied effect points. Therefore, the effects on the liver and lipid metabolism are probably largely determined by the high PFOS contamination near the point source.

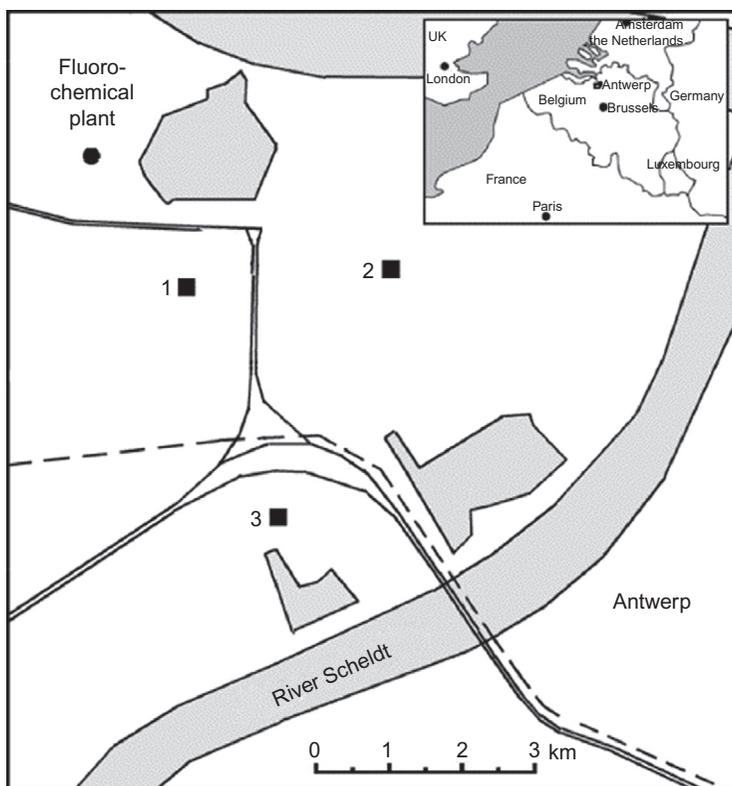
### 7.6.3.2 PFOS Levels in Adult Great Tits Close to the Fluorochemical Plant

Dauwe et al. [152] investigated the accumulation of PFOS in the liver and blood of adult great tits near the fluorochemical plant in Antwerp. Three study sites were selected within 5.5 km from the fluorochemical plant (Figure 7.8) and the great tits were caught in February 2005 while roosting in their nest boxes.

PFOS levels ranged from 550 to 11,000 ng/g ww in liver and from 24 to 1600 ng/mL in blood, which are among the highest reported for free-living animals in the literature [152]. Even in top predators, concentrations are in most cases lower. The PFOS levels in adult great tits from Antwerp exceeded in almost all birds the hepatic benchmark concentrations for the protection of avian species (600 ng/g ww; [155]). PFOS concentrations in liver and blood were higher in young birds (<1 year) than in older birds (>1 year), which could not be explained by the authors, but could be due to competition for food provided by birdfeeders in winter (that is deemed to be uncontaminated; [152]). No significant sex differences were found in PFOS levels of the adult great tits.

Compared to the liver PFOS concentrations in nestling great tits sampled within the same study area, levels in the adults were approximately four times higher (Section 7.6.3.1; [154]). However, nestlings were sampled during the breeding season, while adult birds were caught in winter, implicating that seasonal variation in diet could have an influence on the PFOS levels. Further, maximum PFOS levels in wood mice from this area (Section 7.6.3.1; [153]) were found 10 times higher than in adult great tits, but median concentrations were in the same range.

Concentrations were significantly higher at the site closest to the fluorochemical plant both in liver and blood. However, great tits caught approximately 5.5 km from the fluorochemical plant still accumulated very high levels in liver and blood (630–1800 ng/g ww in liver, 24–93 ng/mL in blood). This is contrast with the steep decline with distance reported for wood mice [153] and nestling great tits [154]. This is probably due to the increased mobility and extended home range of adult great tits and



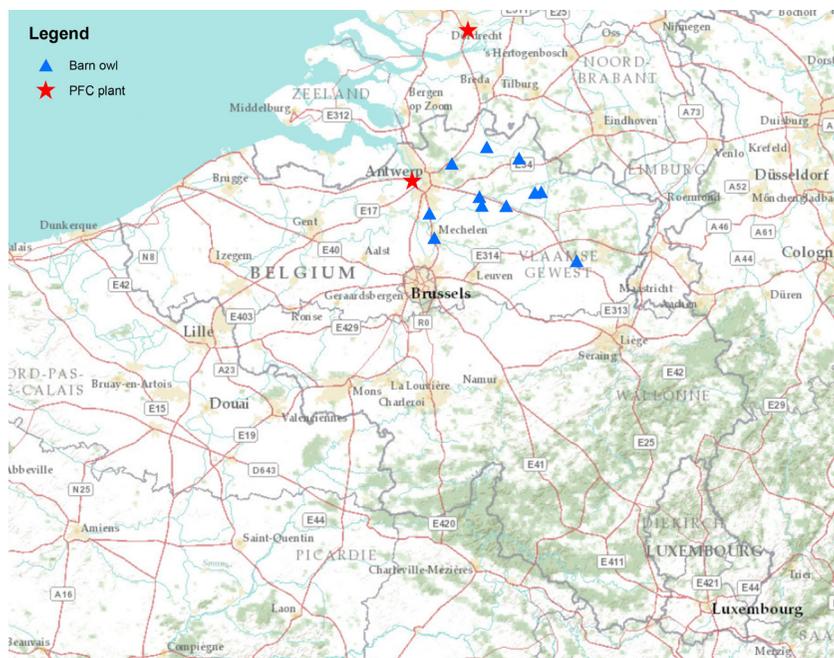
**FIGURE 7.8** Location of the three sampling sites for great tits near Antwerp. Reproduced with permission from Environment International. 33 (3) (2007) [152].

implicates that great tits from a larger area surrounding the fluorochemical plant may experience negative effects from local PFOS contamination. As discussed in Section 7.6.3.1, lower PFOS levels in nestling great tits led to altered serum levels of ALT, cholesterol, and triglycerides. The high PFOS contamination around 3M in Antwerp may thus also affect the health of adult great tits, or other wildlife and even humans.

#### 7.6.4 PFASs in Predatory Birds from the Province of Antwerp

Jaspers et al. [54] investigated PFASs in tail feathers and soft tissues of barn owls<sup>27</sup> collected in the province of Antwerp in 2008–2009 (Figure 7.9). The barn owl is resident year round and is mostly feeding on voles and mice. In

27. *Tyto alba*.

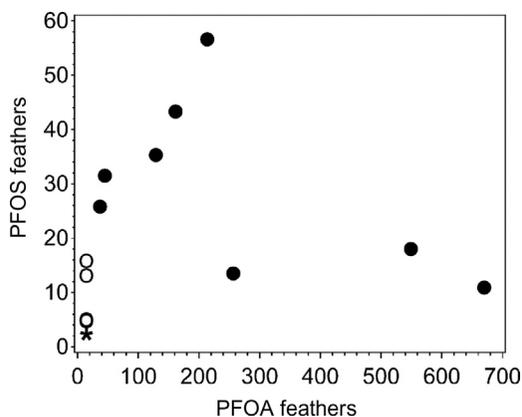


**FIGURE 7.9** Sampling sites for barn owls in Flanders, Belgium (blue triangles) and PFC chemical plant in the vicinity of the sampling area (red star). Reproduced with permission from the supporting information of Jaspers et al. [54].

contrast to songbirds and small mammals, barn owls are mobile over larger ranges and provide a more general contamination background for the whole region of Antwerp. In addition, predatory birds are protected species and collection of tissue samples is depending on available carcasses. For this reason, Jaspers et al. [54] also investigated the potential of using feathers as a nondestructive sampling method for PFASs.

Road kill victims were collected along the roads in the Province of Antwerp by the barn owl study group (kerkuilwerkgroep vzw). The carcasses were dissected for liver, muscle, preen gland, and adipose tissue (when available). Preen oil was obtained by pressing the preen gland. Tail feathers were pulled and were also analyzed for PFASs using a modified analytical protocol (for details, see Jaspers et al. [54]).

PFOS was detected in all tissues (range: 11 ng/g ww in muscle–1200 ng/g ww in preen oil) and in tail feathers (<2.2–57 ng/g ww). PFOA was measured at high levels in feathers (<14–670 ng/g ww), but not in tissues (more than 50% < LOD), suggesting that PFOA may be present on the external surface of the feathers. Perfluorohexane sulfonate (PFHxS) could only be



**FIGURE 7.10** Scatterplot of concentrations in feathers for PFOS versus PFOA. Black dots represent exact values. Open circles represent values below the limit of detection (LOD) in PFOA, plotted at the LODs. The asterisk represents values below the LOD in both PFOS and PFOA, plotted at the LODs. Reproduced with permission from Environment International, Jaspers et al. 2013 [54].

quantified in liver and preen oil, while other PFASs were sporadically detected in liver.

PFOS levels in feathers and liver were significantly correlated, in contrast to PFOA. Combined with high PFOA levels in feathers this suggests that PFOA may be present on the external surface of feathers. Still, PFOS and PFOA were significantly correlated within feathers, which seem in contradiction with different exposure pathways for PFOS and PFOA (internal vs. external contamination). Looking at Figure 7.10, it can be observed that two to three individuals showed very high levels of PFOA, likely due to point sources. Removal of those owls resulted in a higher and more significant correlation between PFOS and PFOA, suggesting similar exposure pathways in the absence of local point sources. High PFOA levels in feathers from the removed owls indicate likely different sources for PFOA, due to external contamination. Since concentrations of PFOA in preen oil were very low, external contamination with PFOA is probably originating from the air (wet or dry depositions). Therefore, Jaspers et al. [54] suggested investigating the possibility of using feathers as a passive air sampler for high PFOA levels in future studies.

The PFOS levels found in the liver (median: 300 ng/g ww, range: 42–992 ng/g ww) of the barn owls from the province of Antwerp are mostly comparable to PFOS levels in livers from other predatory birds, i.e., herring gull (*Larus argentatus*) and sparrow hawk (*Accipiter nisus*), from the Western part of Flanders (Belgium; [156]). In comparison to PFOS levels reported in adult great tits from around the fluorochemical plant near Antwerp (Section 7.6.3.2; [152]), levels in the barn owl are lower, even though the barn owl is higher on the food chain. However, no barn owls

were obtained in the vicinity of 3M and therefore the concentrations provide merely on integration on the background levels in the whole province of Antwerp. Compared to levels found in mice 3 km away from the pollution source (Galgenweel) in 2002 (Section 7.2.2; [153]), levels in the barn owl were still found lower. A more recent study on mice from Galgenweel [157] indicated lower concentrations in mice liver than reported in 2002. The recent levels in mice from Galgenweel compared to levels in barn owl liver resulted in a BMF factor of 1.99 for PFOS from mice to barn owl. However, this value should be employed with caution as the mice and barn owls were obtained in different years and at different sampling sites [54].

In light of the toxic reference value (TRV) that was estimated for avian top predators for PFOS in liver (600 ng/g ww; [158]), two barn owls showed liver concentrations greater than the TRV. This means that 15% of the birds that were included in this study may have been at risk from PFOS exposure alone. The predicted no effect concentration was estimated at 350 ng/g ww for liver tissue [158], which was exceeded by 6 birds out of 13. Therefore, current levels of PFOS in the barn owl from the Antwerp region may present a health risk, especially in combination with other pollutants.

### 7.6.5 Concluding Remarks and Reduction Measures Taken

The studies described above clearly illustrate the PFASs contamination of biota in the immediate vicinity of the fluorochemical plant near Antwerp. 3M was first suggested to act as a point source by the PFOS gradient found in the Western Scheldt and this was later confirmed by the studies on small mammals and passerine birds where a decrease in concentrations was found with the distance to the fluorochemical plant. In response to these and similar reports in biota from the United States of America, 3M decided to phase out the production of these compounds starting in 2000 [147].

3M began manufacturing and using PFASs in the 1950s for various products, including some sold under the Scotchgard™ brand. 3M was a principal manufacturer of PFOA and PFOS-related products until it decided to phase out the production of these compounds. The phase-out was concluded for PFOS in 2002, while the use of PFOA was eliminated in 2008 (source: 3M website). In the meantime, 3M has developed new technologies that enable the company to reformulate many of the products affected by the phase-out. One by-product of this technology is perfluorobutane sulfonate (PFBS). Although PFBS can persist in the environment, it was indicated to have minimal toxicity even when given in large doses to laboratory animals. PFBS is cleared from the body within several days in animals and within several weeks in humans (source: 3M website; [159]).

Since the voluntary phase-out of PFOS production in 2003 by the major global producer, 3M, the global production and use has been reduced dramatically. Quantitative data on production is only available for this company,

but it is considered that the combined capacity of the other producers was very much less than that of 3M [160]. The remaining uses in developed countries are in firefighting foams, photographic industry, photolithography and semiconductors, hydraulic fluids and in metal plating industry [161]. PFOS was banned in Europe under the Marketing and Use Directive from June 27, 2008 (Directive 2006/122/EC) in all applications except for the above-listed exempted applications. On June 2009, the Marketing and Use Directive (76/769/EEC) became Annex XVII of the REACH Regulations. Strict regulations in the United States, Canada, and Japan have been implemented as well [161]. On the contrary, the PFOS production in developing countries like China has been reported to have increased since then [162].

PFOA is still produced and is also a surfactant that is used to provide water and stain resistance to fabrics and other materials. It is widely used as a processing aid for “Teflon<sup>®</sup>.” The US Environmental Protection Agency (EPA) is planning to eliminate its use in products by 2015. The EU is currently assessing this material and although there are no restrictions in EU at present, a ban could be imposed in the future if safer alternatives are economically feasible and available.

In response to the reports on harmful PFASs in the environment, questions have been raised about levels in food for human consumption. A European project, called PERFOOD (<http://www.perfood.eu>), focuses on the development of robust and reliable analytical tools, including reference materials, for the determination of PFASs in food items. The project aims to qualify and quantify PFASs in the human diet, understand how PFASs are transferred from the environment into dietary items, and quantify the possible contribution of food/beverage contact materials and food and water processing to the overall PFAS levels in the diet. The University of Antwerp (Prof. Bervoets and Wendy D'Hollander) is also a partner in this project and samples were also analyzed from Antwerp in particular and Belgium in general. Zwijndrecht, the town near Antwerp where 3M Company is located, was pointed out as a hotspot location in Europe (PERFOOD EU; [163]). Meat, vegetables, and hen eggs from this town showed elevated levels for some of the 15 analyzed PFASs. Furthermore, PFOS levels in home produced chicken eggs from Zwijndrecht were extremely high compared to the levels found elsewhere in Flanders, Belgium [164].

In conclusion, reports on high concentrations of PFASs in the environment and in biota have led to the phase-out of PFOS and PFOA by 3M, the main producer in Antwerp (Belgium) and worldwide. However, as these compounds are persistent, PFOS and PFOA may still be around for a very long time. In addition, releases from older products may further increase the concentrations in the environment, as well as continued production in developing countries. Release of other PFASs may also be of concern and should be followed up closely. Therefore, continued monitoring of the concentrations in the environment and biota is warranted.

## 7.7 CASE STUDY 2: PCDD/F CONTAMINATION OF ALLOTMENTS IN THE UNITED KINGDOM

### 7.7.1 Introduction

Many allotments (community gardens) in use in the United Kingdom today are situated on urban brownfield areas (former industrial and commercial land); this creates the potential for human health risks from soil-borne contamination. Under Part IIA legislation (the UK version of Superfund), local authorities are required to identify sites that have the potential to be contaminated and undertake an investigation to establish the risks to human health and ground/surface waters. If they can prove that the site is contaminated and can pose a significant possibility of significant harm (SPOSH), the local authority can apply for funds from government to remediate the site. Bay Street Allotments was identified as a potentially contaminated site due to the presence of an adjacent landfill and former waste incinerator. The site was subject to intrusive investigation works and a human health risk assessment in 2009–10.

This case study presents the story of the Part IIA contaminated land investigation undertaken at Bay Street Allotments site, which includes:

- forensic interpretation of data to establish the source of the dioxin and furan contamination,
- an assessment of the potential risks to human health,
- an overview of the remediation works undertaken on the site.

### 7.7.2 Contaminant Background

PCDDs and PCDFs are a group of environmentally persistent contaminants, which together form a group of 210 theoretical compounds or congeners. There are 75 possible PCDDs and 135 possible PCDFs. There are some natural background sources of PCDDs/PCDFs like forest fires, however, these are not a significant source of PCDD/F in the United Kingdom [165]. The main sources in the United Kingdom tend to be anthropogenically produced through the production and use of organochlorine chemicals contaminated with PCDDs/PCDFs and the combustion of materials that contain trace amounts of chlorine, such as wood, plant matter, fossil fuels, and municipal and industrial waste [166]. These can either be transferred through aerial deposition or through the spreading of combustion residues like ash. In 2000, in the United States localized burning of “yard waste and household trash” was considered to be the number one source of PCDD/F accounting for approximately 32% of emissions [167]. However, the Environment Agency (2007) [166] calculated that in the United Kingdom in 1999, domestic burning only accounted for 3% of the total PCDD emissions.

In most contaminated land investigations only the 17 PCDDs/PCDFs non-ortho and mono-ortho congeners with 2,3,7,8 chlorine substitution are

reported. It is these congeners that are used to identify risks to human health. When used correctly, basic forensic information can be obtained from these 17 PCDDs/PCDFs; however, further analysis may be required to distinguish potential sources with similar congener profiles [168].

### 7.7.3 Site Background

The parcel of land now known as Bay Street Allotments once formed the northeast tip of a much larger site (Figure 7.11). This larger site contained a refuse destructor (waste incinerator) and a brick field which later became a landfill accepting residues from the incinerator along with industrial and domestic wastes. Both facilities were closed in the 1970s and the majority of the area was landscaped.

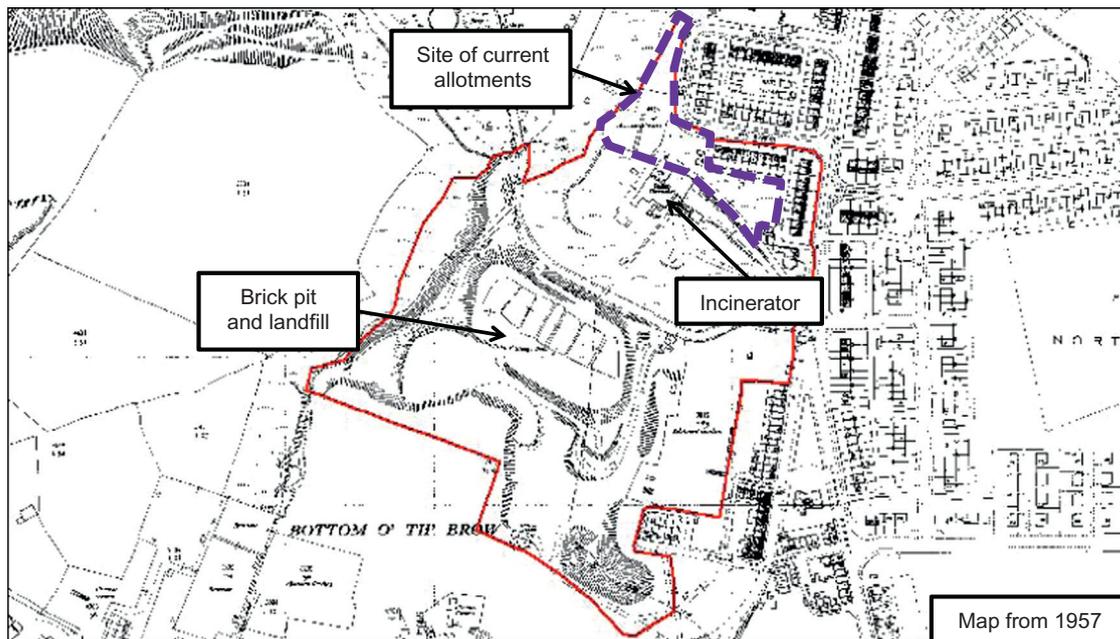
In early 2009, the area outlined in red in Figure 7.12 was investigated by Rochdale Metropolitan Borough Council (MBC) to assess the levels of contamination and to establish the risks of ground gas migration from the landfill to the surrounding properties. The investigation of the former landfill revealed there were no significant risks from ground gas migration. However, the investigation did raise some concerns as the upper 0.4 m of ground towards the northeast corner of the site contained an ashy fill material. Due to the potential human health risks to allotment users, a site investigation was undertaken on Bay Street Allotments.

Bay Street Allotments is approximately 0.41 ha and is located off Bay Street, Rochdale. The allotment plots vary in size from approximately 250 to 1250 m<sup>2</sup> with the larger plots appearing to have formed by the amalgamation of smaller plots over time. Although the site is listed as allotments, the majority of plots tend to be used as gardens with children's play equipment and small vegetable beds, or for the keeping of chickens and ducks rather than growing produce at a usual allotment scale (Figure 7.13).

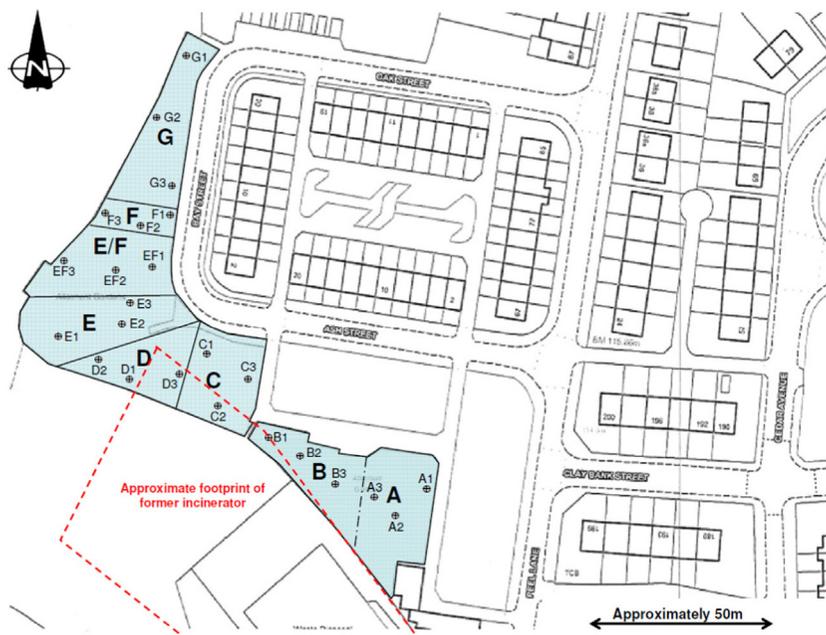
### 7.7.4 Details of Site Investigation

The intrusive investigation works were undertaken by Mouchel and Discovery Drilling Ltd. This comprised the excavation of 19 hand dug pits to a maximum depth of 0.4 m and 5 window samples to a maximum depth of 3.0 m. The site was divided into eight allotment areas (A, B, C, D, E, F, E/F, and G) to represent the different plots and land uses at the site. The locations of the exploratory holes are presented in Figure 7.12.

Three soil samples were obtained from each of the eight allotment areas to allow spatial analysis of a wide range of contaminants. The samples were stored in airtight containers which were appropriately labeled and transported with frozen ice packs in cool boxes under completed chain of custody documentation to ALcontrol Laboratories to prevent any loss of volatiles and degradation of contaminants. Due to cost restrictions, a total of eight samples



**FIGURE 7.11** Historical map of the wider site area produced in 1957. Based map used for image was provided by Michael Moore of Rochdale MBC.



**FIGURE 7.12** Site investigation plan showing sample locations and the footprint of the former incinerator. Reproduced with permission from Megson and Dack 2011 [168].



**FIGURE 7.13** Photographs of allotment site showing play areas and chicken/duck enclosures.

were analyzed for the 17 2,3,7,8-substituted PCDDs and PCDFs (from locations A1, A2, B1, B2, C1, E1, F2, G1). These samples were selected from an ashy material that formed part of the upper soil profile. Concentrations of individual PCDDs/PCDFs were all above the analytical limits of detection of 2 ng/kg, except TCDD in sample F2 and the majority of congeners in C1. Concentrations of each congener analyzed in the batch reference material were recorded within the defined acceptable range (70–130%).

### 7.7.5 Comparison of Results with Background Concentrations of PCDD/F

In 2007, the Environment Agency published the results of the United Kingdom Soil and Herbage Survey (UK SHS). In total 10 reports were published which documented the concentrations of heavy metals, PCBs, PAHs, and PCDDs/PCDFs in samples of soil and herbage taken from urban, rural, and industrial areas across the United Kingdom. Report 10 is dedicated to PCDDs/PCDFs; the 17 non-ortho and mono-ortho (2,3,7,8-substituted) congeners were analyzed in soil and herbage samples from 366 rural sites, 87 urban sites, and 216 industrial sites. As well as presenting the data for the whole United Kingdom, the data was presented separately for England, Wales, Scotland, and Northern Ireland. Results showed slight differences across the individual regions with England showing the highest concentrations. The congener profiles from urban, rural, and industrial areas were broadly similar, however, slightly elevated proportions of the less chlorinated congeners were recorded in rural soil and herbage [166] mainly as a result of diffuse aerial deposition. The UK SHS can be used to represent “background” concentrations of PCDDs/PCDFs in UK soil and herbage.

The mean background concentrations of the 17 PCDDs/PCDFs in English urban soils were estimated at 534 ng/kg. The mean concentration of the 17 PCDDs/PCDFs in samples taken from Bay Street Allotments was 4284 ng/kg indicating that there was an additional source of contamination at the site. Table 7.2 presents the results from the UK SHS and the results from the soil samples obtained from Bay Street Allotments.

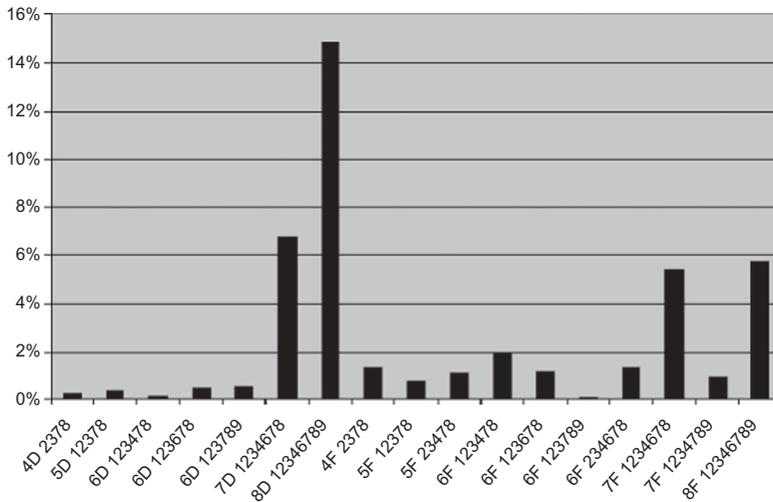
In many environmental studies, results of PCDDs/PCDFs analysis are presented as a TEQ. The TEQ is calculated by multiplying the concentration of a congener by its TEF (toxic equivalency factor). The TEF is a substance's relative toxicity compared to the most toxic dioxin 2,3,7,8-TCDD, where a value of 1 means that the substance is as toxic as 2,3,7,8-TCDD. The results for the 17 PCDD/F are then summed to give a TEQ for the PCDD/F mixture. The reader is encouraged to note that the TEF of PCDDs, PCDFs, and PCBs was updated in 2006 by Van den Berg et al. [169]. When comparing datasets the assessor should always check that all values have been derived using the same TEF. Previous TEF schemes include I-TEQ [170], TEQ-WHO94 [171], and TEQ-WHO98 [172].

TEFs and TEQs are used for undertaking human health risk assessments and assessing the toxicity of a PCDDs/PCDFs mixture. These values are of limited use in forensic investigations, as more information can often be gained by comparing the individual proportions of each congener than comparisons of the overall toxicity.

The average concentration of PCDDs/PCDFs at Bay Street Allotments was approximately eight times greater than the UK urban background. The

**TABLE 7.2** Comparison of PCDD/F Concentrations at Bay Street Allotments with Background Levels

Compound	TEF 2006	TEF 1998	Mean Concentration in English Urban Soils (ng/kg)	Maximum Concentration in English Urban Soils (ng/kg)	% Contribution to $\sum$ PCDD/F in English Urban Soils	Mean Concentration at Allotment site (ng/kg)	Maximum Concentration at Allotment site (ng/kg)	% Contribution to $\sum$ PCDD/F at Allotment site
<i>Dioxins</i>								
2,3,7,8-TCDD	1	1	0.692	2.14	0.130	2.9	5.0	0.07
1,2,3,7,8-PeCDD	1	0.5	3.10	9.20	0.581	7.6	13	0.18
1,2,3,4,7,8-HxCDD	0.1	0.1	3.36	10.3	0.630	7.0	12	0.16
1,2,3,6,7,8-HxCDD	0.1	0.1	6.08	19.9	1.14	15	29	0.35
1,2,3,7,8,9-HxCDD	0.1	0.1	6.10	21.6	1.14	8.9	14	0.21
1,2,3,4,6,7,8-HpCDD	0.01	0.01	52.7	350	9.88	210	650	4.9
OCDD	0.0003	0.001	282	4050	52.8	2303	9400	53.8
<i>Furans</i>								
2,3,7,8-TCDF	0.1	0.1	5.61	18.0	1.05	23	78	0.54
1,2,3,7,8-PeCDF	0.03	0.05	5.83	18.1	1.09	31	96	0.72
2,3,4,7,8-PeCDF	0.3	0.5	8.82	26.5	1.65	28	50	0.65
1,2,3,4,7,8-HxCDF	0.1	0.1	8.41	25.6	1.58	76	340	1.77
1,2,3,6,7,8-HxCDF	0.1	0.1	7.02	25.2	1.32	66	80	1.54
1,2,3,7,8,9-HxCDF	0.1	0.1	2.73	11.8	0.512	14	280	0.33
2,3,4,6,7,8-HxCDF	0.1	0.1	9.48	42.3	1.78	40	130	0.93
1,2,3,4,6,7,8-HpCDF	0.01	0.01	66.0	515	12.4	347	1800	8.1
1,2,3,4,7,8,9-HpCDF	0.01	0.01	3.68	12.8	0.690	108	480	2.52
OCDF	0.0003	0.001	61.6	312	11.54	997	6300	23.3
<i>Total (<math>\sum</math>PCDD/F)</i>			534	5471	100	4284	19,757	100
<i>TEQ (2006 TEFs)</i>			12.8	47.5		52.5	166.2	
<i>TEQ (1998 TEFs)</i>			13.4	51.7		57.2	182.6	



**FIGURE 7.14** PCDD/F profile of municipal waste incinerator from US EPA [173].

additional source of PCDDs/PCDFs was suspected to be due to the presence of ash from the former waste incinerator which had been spread on the allotments. Chemical fingerprinting was used to compare the signature of PCDDs/PCDFs at the site to the typical signatures of different sources produced by the US EPA [173] (Figure 7.14).

Since concentrations of PCDDs/PCDFs in environmental media can vary by many orders of magnitude, standardization of the results is necessary to compare the congener profiles from different samples and media [167]. This was performed on each sample by dividing each individual congener by the sum of all 17 2,3,7,8-substituted congeners. The results from Bay Street Allotments (Figure 7.15) were plotted and compared with the profile taken from US EPA [173] (Figure 7.14).

The results show that octachlorodibenzodioxin (OCDD) was the dominant congener, indicating that ash from the waste incinerator is the probable source. The two profiles are not an exact match as the proportions of OCDD and octachlorodibenzofuran (OCDF) are much greater in the samples from Bay Street Allotments. The US EPA profile (Figure 7.14) represents the signature from stack emissions, which will comprise a large proportion of fly ash. Evidence from the site investigation suggests that significant quantities of bottom ash were spread on the allotments. The difference in profiles could be explained as bottom ash and slag have been shown to have higher proportions of the OCDD and OCDF than the fly ash produced from the same incinerator [174]. Weathering and biodegradation may have also altered the

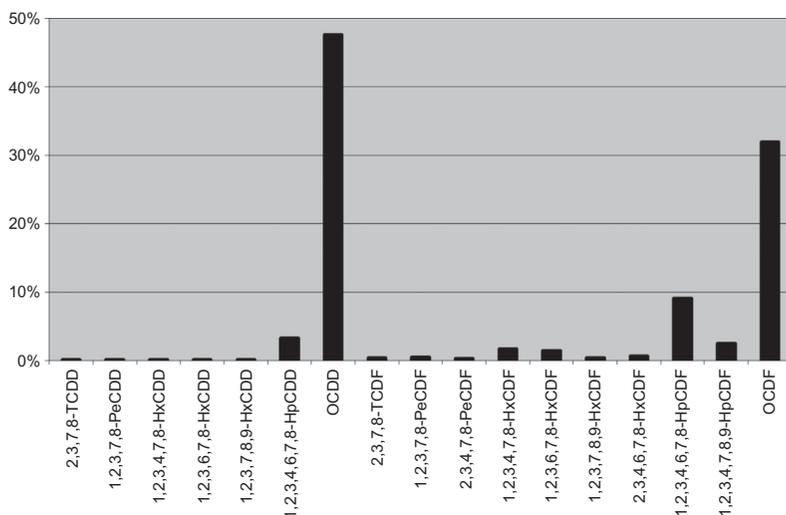


FIGURE 7.15 Averaged PCDD/F profile in soil samples taken from Bay Street Allotments.

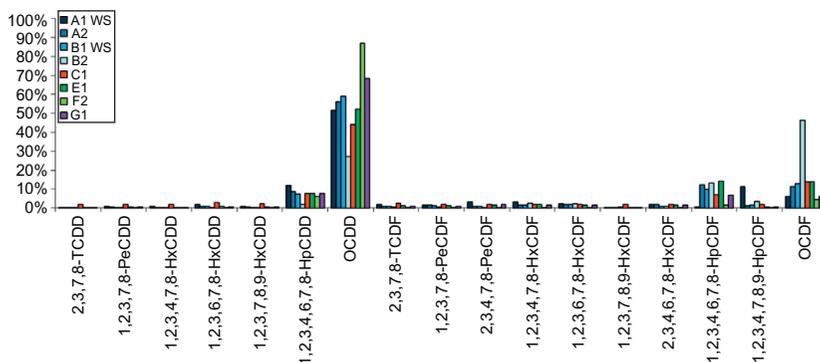


FIGURE 7.16 PCDD/F profile in each soil sample obtained at the site.

signature by preferentially removing the less chlorinated congeners. Although PCDD/F are considered persistent a small degree of weathering would be expected as the incinerator was removed in the 1970s.

The eight soil samples analyzed for PCDDs/PCDFs at Bay Street Allotments showed a broadly similar congener profile except the sample taken from B2 (Figure 7.16). This sample displayed a profile that was more similar to medical/hospital waste or hazardous waste incineration.

The emission profiles of PCDD/F for a large number of potential sources have been widely reported and are covered in great detail by US EPA [173]. The congener profiles produced in the US EPA report provide an excellent tool for identifying the source of PCDDs/PCDFs in an unknown sample. However, care should be taken as these profiles have been generated based on emission data directly from the source. Post depositional processes including mixing with other sources, uptake by biota and weathering can all alter the original signature. The extent of these changes tends to vary depending on the degree of chlorination, although these changes seem to be less pronounced between congeners of the same homolog class [167,175].

Forensic investigations are most effective when they rely on multiple lines of evidence. The congener profile of soils at Bay Street Allotments matched the profile of weathered bottom ash from waste incinerator. However, there should be a plausible explanation describing the pathway between the potential source (waste incinerator) and the receptor (in this case the soil). A review of historical maps had already identified the close proximity to the former incinerator. Anecdotal information was also collected which suggested that bottom ash from the incinerator had been spread on the site. It was concluded that ash from the former incinerator was the most likely source of PCDD/F at Bay Street Allotments.

### 7.7.6 Overview of Human Health Risk Assessment

In the United Kingdom, quantitative assessments on the risks to human health are undertaken using CLEA v1.06, a free-ware program developed by the Environment Agency on Microsoft Excel for commercial/public use. In addition to the CLEA v1.06 program, the Environment Agency has also published associated guidance and specific generic screening value (SGV) and toxicity (TOX) reports for a selection of contaminants, including PCDDs/PCDFs and dioxin like PCBs [170,173]. Details of the human health risk assessment undertaken on the site are provided by Megson et al. [176]; only the results are summarized in the following section.

Site-specific human health screening values were derived for Bay Street Allotments based on the congener profile of the PCDDs/PCDFs at the site for a variety of receptors under different site-specific scenarios. Modeling showed that the most sensitive receptor using the site was children who lived adjacent to the allotments and played regularly on the plots. It was recognized that they did not actually eat/grow many vegetables. Using CLEA v1.06 human health screening values, called site-specific assessment criteria (SSAC), were generated and are presented in Table 7.3. An SSAC is a site-specific screening value created by using modeling parameters from the subject site, instead of using the default parameters specified by the Environment Agency to generate an SGV. If the mean concentration of the 17 2,3,7,8-substituted PCDDs/PCDFs was above this screening value (at a

**TABLE 7.3** Comparison of PCDDs/PCDFs Concentrations Against SSAC

Receptor	SSAC ( $\mu\text{g}/\text{kg}$ )	Bay Street Soils Mean Value ( $\mu\text{g}/\text{kg}$ )	Bay Street Soils 95% LCL value ( $\mu\text{g}/\text{kg}$ )
Child	15.9	4.2	0.8

95% confidence level) then the site may be classified as contaminated land under Part IIA legislation.

The results are presented as  $\sum 17$  PCDDs/PCDFs not as a TEQ as the site-specific toxicity of the mixture and WHO06 TEFs are used to derive the screening value. The results show that the concentration of PCDDs/PCDFs at the site did not pose a significant risk to human health. However, this assessment was based on the generic pathways within the CLEA model (soil and vegetable ingestion, dust inhalation, dermal contact). This did not include the consumption of eggs from poultry reared on the site.

### 7.7.7 Summary of Soil Analysis

Concentrations of PCDDs/PCDFs in the soil at the Bay Street Allotments were approximately eight times higher than the background concentration in English Urban soils. The main source of PCDD/F contamination at the allotments site was identified as ash from the former waste incinerator. However, the initial human health risk assessment indicated that there was no significant risk from PCDDs/PCDFs in the soil, based on standard UK exposure pathways.

As mentioned earlier, although the site is listed as allotments, several plots were used exclusively for keeping of chickens and ducks rather than growing produce at a usual allotment scale. PCDDs and PCDFs are almost insoluble in water; however, they can be fairly soluble in organic solvents and fats. Due to this increased solubility in lipids, PCDDs and PCDFs have been found in elevated concentrations in eggs [177,178]. Further work was undertaken to identify if there were any risks to human health through the consumption of eggs produced by chickens and ducks reared on the site.

### 7.7.8 Results of Egg Analysis

Eggs were collected from the plots in May 2010 and tested for PCDD/F by The Food and Environment Research Agency (FERA). The following samples were collected for analysis: two duck eggs from Plots A and B, six chicken eggs from Plot C, six chicken eggs from Plots E and F, and six chicken eggs from Plot G. Concentrations of PCDDs/PCDFs in the eggs

**TABLE 7.4** Comparison of Estimated PCDD/F Exposure Through CLEA Pathways and Egg Consumption Against the Tolerable Daily Intake

	Adult Scenario	Child Scenario
TDI (tolerable daily intake) (pg WHO-TEQ kg <sup>-1</sup> BW day <sup>-1</sup> )	2	2
Reasonable worst case exposure (pg WHO-TEQ kg <sup>-1</sup> BW day <sup>-1</sup> )	3.6	19
Average estimated exposure (pg WHO-TEQ kg <sup>-1</sup> BW day <sup>-1</sup> )	1.1	5.9

ranged from 0.49 to 3.93 ng WHO06-TEQ kg<sup>-1</sup>. The concentrations of PCDDs/PCDFs in the eggs were used along with concentrations of PCDDs/PCDFs in the soil and receptor data collected from surveys of allotment users, to calculate an average estimated exposure and a reasonable worst case exposure to PCDDs/PCDFs. Details for the calculations of these values are presented by Megson et al. [176] and the results are summarized in Table 7.4.

The results of the exposure modeling showed that children living adjacent to the site who were eating eggs and playing on the southern plots could be exposed to concentrations of PCDD/F approximately 10 times greater than the TDI. Approximately 95% of this exposure originated from the consumption of eggs from poultry reared on the site. The task in the forensic investigation was to establish if there was a viable pathway between the PCDD/F in the eggs and the PCDD/F in the soil which originated from the former incinerator.

### 7.7.9 Forensic Investigation into the Source of PCDDs/PCDFs in Chickens

Congener profiles were produced from the egg data (Figures 7.17 and 7.18) to allow a comparison with the congener profile of PCDDs/PCDFs in the soil (Figures 7.15 and 7.16).

The congener profile in the eggs was different to the congener profile of the soil. In both profiles, the dominant congener was OCDD; however, it contributed 44–87% of the total PCDDs/PCDFs in soil samples but only 20–43% in the egg samples. Principal component analysis (PCA) was undertaken on the data which showed how the profiles in the soil and egg were distinctly different, the scores and loadings plot from the PCA are presented as Figures 7.19 and 7.20, respectively.

PCA is a statistical technique that is often used to simplify complex datasets. PCA reduces the dimensionality of the data by transforming it to a set

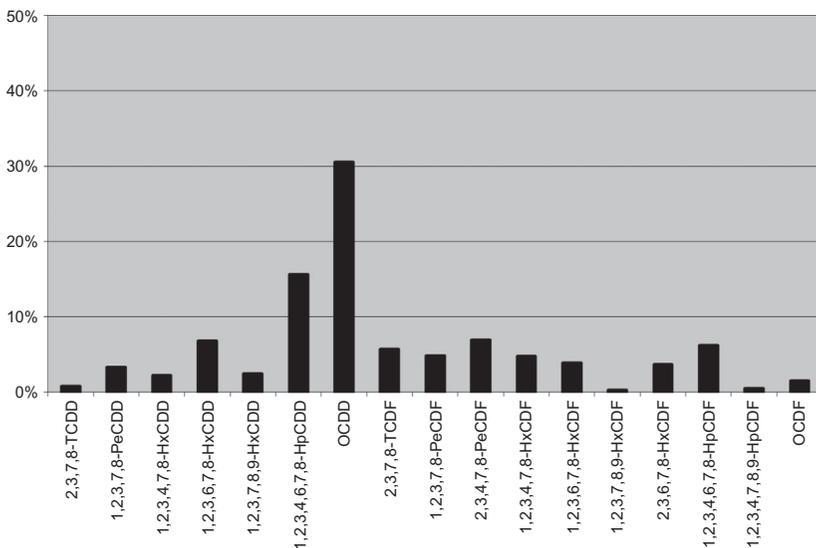


FIGURE 7.17 Averaged PCDD/F profile in egg samples.

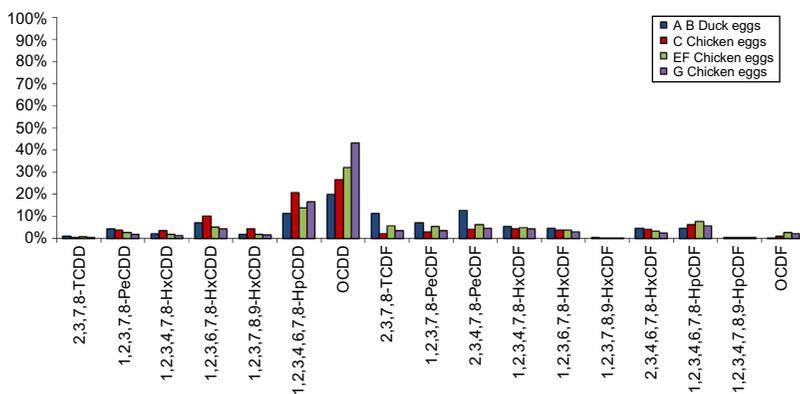
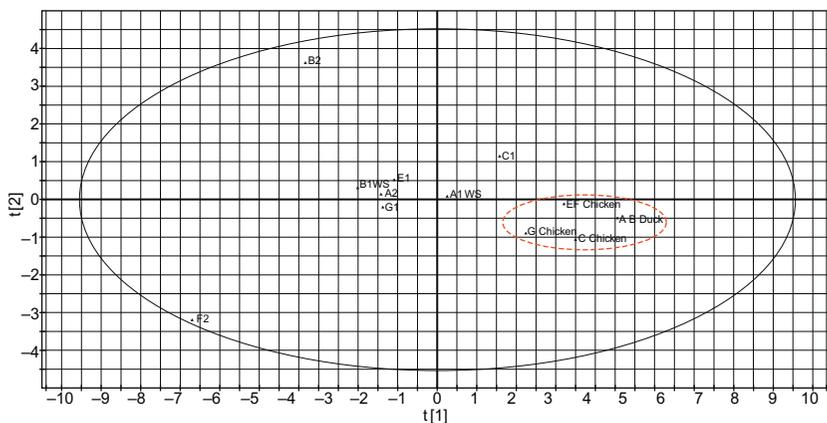
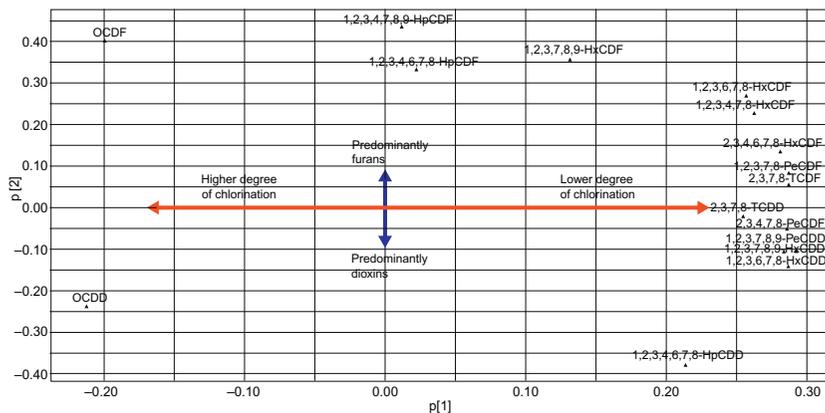


FIGURE 7.18 PCDD/F profile in each egg sample.

of new uncorrelated reference variables called principal components [179]. Prior to undertaking PCA, the data was transformed by dividing each individual congener by the sum of all 17 congeners analyzed. This proportioned data was normalized in two steps: firstly by performing a log transformation ( $10 \log(x + 0.001)$ ) and secondly by subtracting the mean and dividing by the standard deviation. These types of transformations are commonly performed prior to undertaking PCA on environmental contamination datasets



**FIGURE 7.19** Scores plot of PC1 and PC2 showing a separation between the egg samples (circled in red) and the soil samples.



**FIGURE 7.20** Loadings plot showing a separation based on the degree of chlorination along PC1 and separation of dioxins and furans along PC2.

to reduce concentration and dilution effects [180]. The results of PCA are commonly displayed as a scores and loadings plot for the two principal components that explain the greatest degree of variation in the original dataset. A grouping of samples in the scores plot indicates that these samples have a similar chemical signature. A grouping of compounds in the loadings plot indicates that those compounds co-vary in the samples. The two plots can be compared and used to establish which compounds are influencing the signature of each sample. For a more in-depth discussion on the use of PCA in environmental forensics, the reader is directed to Johnson et al. [179].

The scores plot (Figure 7.19) clearly separates the egg data from the soil data with the loadings plot (Figure 7.20) identifying that the signature from the eggs was enriched in the less chlorinated congeners compared to the soil samples.

On first glance, it could be concluded that the source of PCDDs/PCDFs in the eggs was different to that from the soil. However, these results do not take into account post depositional changes to the congener profile that occur after uptake of PCDDs/PCDFs by an organism.

Chickens scratch up the soil, feed in it, and dust bathe, therefore large quantities of soil can be consumed by the chicken. This happens by directly eating seed with soil attached, by the preening of dusty feathers, or by eating insects. These habits mean that up to 10% of a chicken's diet may be soil based [181]. Once PCDDs/PCDFs have been ingested by the chicken, they pass through the gastrointestinal tract and into the bloodstream. Whilst in the organism there is a fractionation process which appears to be driven primarily by  $\log K_{ow}$ . This results in higher proportions of the less chlorinated congeners (with a lower  $\log K_{ow}$ ) accumulating in eggs and higher proportions of the more chlorinated congeners (with a higher  $\log K_{ow}$ ) accumulating in the liver [168,182].

There can be large differences in the degree of weathering and bioaccumulation between 2,3,7,8-substituted congeners, however, differences are likely to be less pronounced for congeners in the same homologous class. Therefore, instead of comparing the entire congener profile of the soil and egg samples, the proportions of congeners within each homolog class were compared. This technique is often referred to as the relative homolog technique and was first proposed by Hagenmaier et al. [175] to neutralize the effects of differential weathering and bioaccumulation resulting from degree of chlorination [167]. The relative proportions of the HxCDD/F in the soil and egg samples are presented as radial plots in Figure 7.21.

The plots created using the relative homolog standardization technique showed a much better correlation between the soil and the egg data. This is visually presented in the radial plots (Figure 7.21) and also quantitatively by using PLS regression. The PCDDs/PCDFs and HxCDD/F (hexa-chlorinated) results from the soil samples from each plot were used to create a specific signature for that plot. The amount of variance in the egg data that could be explained from the soil results was determined by PLS.

The results presented in Table 7.5 show that using the signature from the HxCDD/F produced higher Q2 (cross validated fraction of explained variance) values, indicating a better match than the signature generated from all 17 2,3,7,8-substituted PCDD/Fs. However, the reduction in the number of variables in the HxCDD/F fraction could also have improved the Q2 value to some degree.

Although the profiles in the eggs and soil were not an exact match, the differences between the signature in the soil and the eggs could be explained

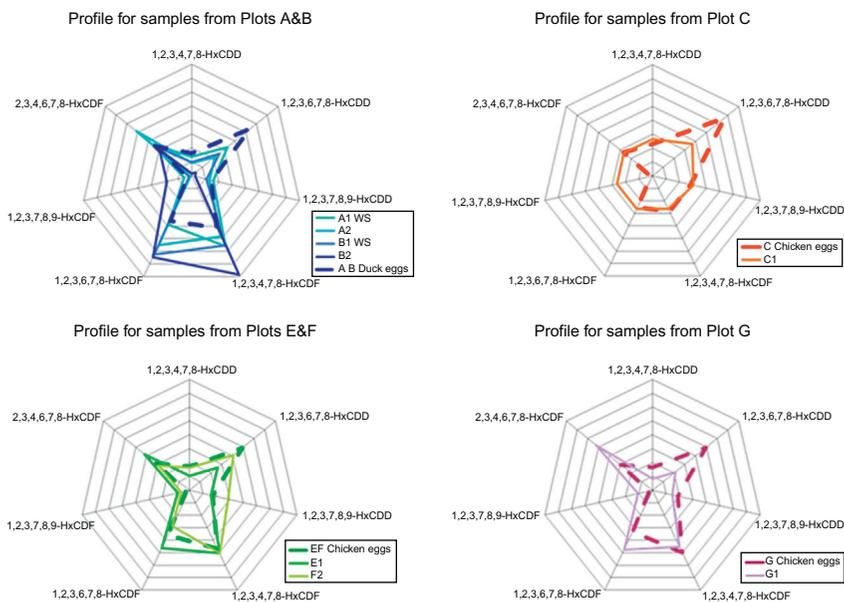


FIGURE 7.21 Radial plots of HxCDD/F profiles in soil and egg samples.

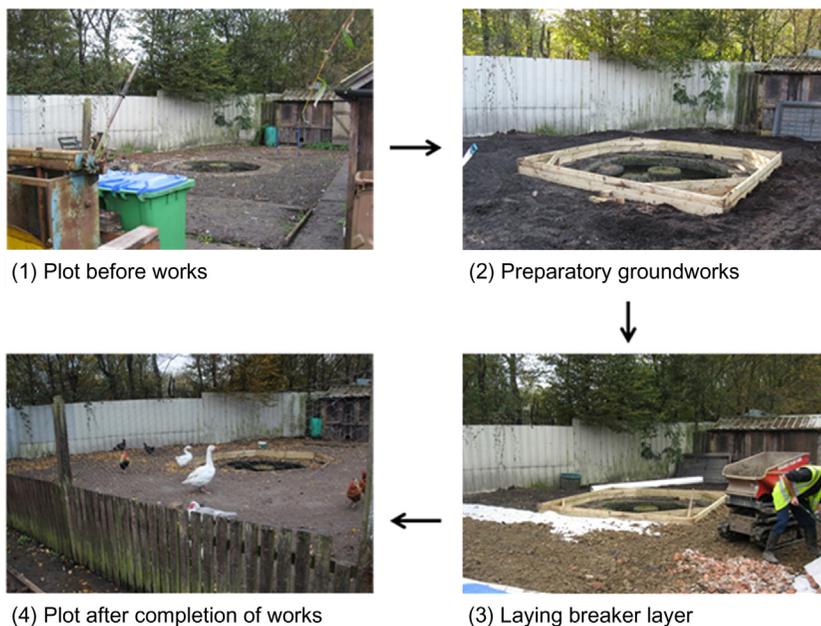
**TABLE 7.5** Amount of Variance Explained (Q2) in the Egg Data Using the Source Soil as the Signature from All 17 PCDD/F Compared with the 7 HxCDD/F

	AB Duck	C Chicken	EF Chicken	G Chicken
Q2 for 17 2,3,7,8 PCDD/F	0.217	0.523	0.568	0.679
Q2 for HxCDD/F	0.839	0.673	0.832	0.850

by preferential transport of less chlorinated congeners into the eggs. Each plot was managed individually with poultry consuming a wide range of different food sources which meant that contaminated feed was an unlikely source of the PCDDs/PCDFs. The HxCDD/F profile in the soil and eggs showed a good correlation and therefore it was deemed that the most likely source of PCDDs/PCDFs in the eggs was from the contaminated soil.

### 7.7.10 Legislative Aspect and Site Remediation

The investigation was commissioned to determine if the site could be classified as contaminated land under Part IIA of the Environmental Protection Act.



**FIGURE 7.22** Stages of the remediation works at one plot. *Source: Photographs supplied by Michael Moore of Rochdale MBC.*

The human health risk assessment identified that exposure to the soil alone did not provide enough evidence to indicate a SPOSH to human health. However, when the exposure from the soil was combined with exposure from consumption of site laid eggs, the potential risks from PCDDs/PCDFs did constitute SPOSH. The allotments site was consequently determined as statutory contaminated land on November 22, 2010. The forensic analysis showed that the elevated concentrations of PCDDs/PCDFs in the eggs could be linked to accumulation of PCDDs/PCDFs from the soil. Rochdale MBC submitted an application to the Environment Agency for funds to undertake the remedial works which was accepted and the remediation works were completed in December 2011. The remediation works involved installing a capping system over the contaminated soils with a barrier and clean soils to prevent contact with the contaminants. This form of remediation involved breaking the contaminant pathway and was more cost-effective and sustainable than the removal and thermal treatment or landfilling of large volumes of soil. [Figure 7.22](#) details the stages of the remediation works, photographs were kindly provided by Michael Moore, the Environmental Health Officer of Rochdale MBC.

## 7.8 CONCLUDING REMARKS

In comparison to data on POPs in the marine and freshwater ecosystems, information about the contamination in the terrestrial ecosystem has always been behind. The information in this chapter, however, indicates that recently (even large-scale) studies in the terrestrial environment are becoming more frequent. Still, information is limited about the current contamination of the terrestrial ecosystems in the (sub)Arctic [183], although some recent studies have been undertaken in predatory birds [184–186], mammals [187,188], and even a terrestrial food chain bioaccumulation model has been proposed [104]. Hopefully an increased effort to perform terrestrial studies is on its way in the (sub)Arctic as well, as this region has become an important sink for POPs [189], which emphasizes the importance of completing environmental monitoring and forensics studies.

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## REFERENCES

- [1] M.D. Erickson, Introduction: PCB properties, uses, occurrences and regulatory history, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, University of Kentucky Press, Kentucky, USA, 2001.
- [2] G.W. Johnson, J.F. Quensen III, J.R. Chiarenzelli, M. Coreen Hamilton, Polychlorinated biphenyls, in: R.D. Morrison, B.L. Murphy (Eds.), *Environmental Forensics. Contaminant Specific Guide*, Academic Press, London, UK, 2006, pp. 187–226.
- [3] M.A. McKinney, R.J. Letcher, J. Aars, E.W. Born, M. Branigan, R. Dietz, Flame retardants and legacy contaminants in polar bears from Alaska, Canada, East Greenland and Svalbard, 2005–2008, *Environ. Int.* 37 (2011) 365–374.
- [4] C.D. Sandau, A. Sjödin, M.D. Davis, J.R. Barr, V.L. Maggio, A.L. Waterman, et al., Comprehensive solid-phase extraction method for persistent organic pollutants. Validation and application to the analysis of persistent chlorinated pesticides, *Anal. Chem.* 75 (2003) 71–77.

- [5] J.U. Skaare, A. Bernhoft, A. Derocher, G.W. Gabrielsen, A. Goksoyr, E. Henriksen, et al., Organochlorines in top predators at Svalbard—occurrence, levels and effects, *Toxicol. Lett.* 112 (2000) 103–109.
- [6] I. Holoubek, Polychlorinated biphenyl (PCB) contaminated sites worldwide, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, University of Kentucky Press, Kentucky, USA, 2001, pp. 17–26.
- [7] V.W. Burse, R.D. Kimborough, E.C. Villanueva, R.W. Jennings, R.E. Linder, G.W. Sovovool, Polychlorinated biphenyls: storage, distribution, excretion and recovery: liver morphology after prolonged dietary ingestion, *Arch. Environ. Health* 1974 (1974) 301–307.
- [8] G.M. Frame, Improved procedure for single DB-XLB column GC–MS–SIM quantitation of PCB congener distributions and characterization of two different preparations sold as "Aroclor 1254", *J. High Resolut. Chromatogr.* 22 (1999) 533–540.
- [9] F. Wania, D. Mackay, Tracking the distribution of persistent organic pollutants, *Environ. Sci. Technol.* 30 (1996) 390A–396A.
- [10] M.S. McLachlan, M. Horstmann, Forests as filters of airborne organic pollutants: a model, *Environ. Sci. Technol.* 32 (1998) 413–420.
- [11] J.K. Schuster, R. Gioia, C. Moeckel, T. Agarwal, T.D. Bucheli, K. Breivik, et al., Has the burden and distribution of PCBs and PBDEs changed in European background soils between 1998 and 2008? Implications for sources and processes, *Environ. Sci. Technol.* 45 (2011) 7291–7297.
- [12] P.B. Kurt-Karakus, T.F. Bidleman, K.C. Jones, S.N. Meijer, R.M. Staebler, Persistent organic pollutants (POPs) and air–soil exchange: case studies for DDTs, in: E. Mehmeli, B. Koumanova (Eds.), *Fate of Persistent Organic Pollutants in the Environment*, Springer, Dordrecht, 2008, pp. 315–331.
- [13] Z. Wang, X.D. Ma, G.S. Na, Z.S. Lin, Q. Ding, Z.W. Yao, Correlations between physico-chemical properties of PAHs and their distribution in soil, moss and reindeer dung at Ny-Alesund of the arctic, *Environ. Pollut.* 157 (11) (2009) 3132–3136.
- [14] J. Chiarenzelli, R. Serudato, G. Arnold, M. Wunderlich, D. Rafferty, Volatilization of polychlorinated biphenyls from sediment during drying at ambient conditions, *Chemosphere* 33 (1996) 899–911.
- [15] B. Bhattacharya, S.K. Sarkar, N. Mukherjee, Organochlorine pesticide residues in sediments of a tropical mangrove estuary, India: implications for monitoring, *Environ. Int.* 29 (2003) 587–592.
- [16] R.D. Morrison, Forensic techniques for establishing the origin and timing of a contaminant release, *Environ. Claims J.* 9 (2) (1997) 105–122.
- [17] D.L. Bedard, Microbial dechlorination of PCBs in aquatic sediments, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, The University Press of Kentucky, Kentucky, USA, 2001.
- [18] J. Borja, D.M. Taleon, J. Auresenia, S. Gallardo, Polychlorinated biphenyls and their biodegradation, *Process Biochem.* 40 (6) (2005) 1999–2013.
- [19] M. Koblickova, L. Ducek, J. Jarkovsky, J. Hofman, T.D. Bucheli, J. Klanova, Can physicochemical and microbial soil properties explain enantiomeric shifts of chiral organochlorines? *Environ. Sci. Technol.* 42 (16) (2008) 5978–5984.
- [20] R.D. Horsak, P.B. Bedient, M.C. Hamilton, F.B. Thomas, Pesticides, in: R.D. Morrison, B.L. Murphy (Eds.), *Environmental Forensics. Contaminant Specific Guide*, Academic Press, London, UK, 2006.
- [21] W.J. Walker, C.G. Schreier, L.E. Pucik, Use of degradation rates of DDT and lindane isomers for determining the timing of release to sediments of Greens Bayou: Houston ship channel, Texas, *Environ. Forensics* 5 (2004) 45–57.

- [22] S.N. Meijer, W.A. Ockenden, A. Sweetman, K. Breivik, J.O. Grimalt, K.C. Jones, Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes, *Environ. Sci. Technol.* 37 (2003) 667–672.
- [23] C.S. Creaser, M.D. Wood, R. Alcock, D. Copplestone, P.J. Crook, UK Soil and Heritage Pollutant Survey Report No. 8, Environmental Concentrations of Polychlorinated Biphenyls (PCBs) in UK Soil and Heritage. Environment Agency, UK, 2007.
- [24] C.S. Creaser, M.D. Wood, R. Alcock, D. Copplestone, P.J. Crook, UK Soil and Heritage Pollutant Survey Report No. 8, Environmental Concentrations of Polychlorinated Dibenzop-Dioxins and Polychlorinated Dibenzofurans in UK Soil and Heritage. Environment Agency, UK, 2007.
- [25] J.L. Barber, G.O. Thomas, G. Kersteins, K.C. Jones, Current issues and uncertainties in the measurement and modeling of air-vegetation exchange and within plant processing of POPs, *Environ. Pollut.* 128 (2004) 99–138.
- [26] A.A. Lovett, C.D. Foxall, C.S. Creaser, D. Chewe, PCB and PCDD/F congeners in locally grown fruit and vegetable samples in Wales and England, *Chemosphere* 34 (1997) 1421–1436.
- [27] J.F. Muller, A. Hulster, O. Papke, M. Ball, H. Marschner, Transfer pathways of PCDD/PCDF to fruits, *Chemosphere* 27 (1993) 195–201.
- [28] A. Hulster, J.F. Muller, H. Marschner, Soil-plant transfer of polychlorinated dibenzo-*p*-dioxins and dibenzofurans to vegetables of the cucumber family (cucurbitaceae), *Environ. Sci. Technol.* 28 (1994) 1110–1115.
- [29] S. Ohta, D. Ishizuka, H. Nishimura, T. Nakao, O. Aozasa, Y. Shimidzu, et al., Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan, *Chemosphere* 46 (2002) 689–696.
- [30] H.K. Wipf, E. Homberger, N. Neimer, U.B. Randaler, W. Vetter, J.P. Vuilleumeir, TCDD levels in soil and plant samples from the Seveso area, in: O. Hutzinger (Ed.), *Chlorinated Dioxins and Related Compounds: Impact on the Environment*, Pergamon, New York, 1982.
- [31] A. Zohair, A.B. Salim, A.A. Soyibo, A.J. Beek, Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically farmed vegetables, *Chemosphere* 63 (2006) 541–553.
- [32] L. Kacalkova, P. Tlustos, The uptake of persistent organic pollutants by plants, *Central Eur. J. Biol.* 6 (2011) 223–235.
- [33] H. Slater, T. Gouin, M.B. Leigh, Assessing the potential for rhizoremediation of PCB contaminated soils in northern regions using native tree species, *Chemosphere* 84 (2011) 199–206.
- [34] M. Mackova, P. Prouzova, P. Stursa, E. Ryslava, O. Uhlik, K. Beranova, et al., Phyto/rhizoremediation studies using long-term PCB-contaminated soil, *Environ. Sci. Pollut. Res.* 16 (2009) 817–829.
- [35] D. Calamari, E. Bacci, S. Focardi, C. Gaggi, M. Morosini, M. Vighi, Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons, *Environ. Sci. Technol.* 25 (1991) 1489–1495.
- [36] J.G. Burken, D.A. Vroblesky, J.C. Balouet, Phytoforensics, dendrochemistry, and phytoscreening: new green tools for delineating contaminants from past and present, *Environ. Sci. Technol.* 45 (15) (2011) 6218–6226.
- [37] A. Salamova, R.A. Hites, Brominated and chlorinated flame retardants in tree bark from around the globe, *Environ. Sci. Technol.* 47 (2012) 349–354.

- [38] F. Gueguen, P. Stille, M. Millet, Air quality assessment by tree bark biomonitoring in urban, industrial and rural environments of the Rhine Valley: PCDD/Fs, PCBs and trace metal evidence, *Chemosphere* 85 (2011) 195–202.
- [39] H. Schulz, P. Popp, G. Huhn, H.J. Stark, G. Schuurmann, Biomonitoring of airborne inorganic and organic pollutants by means of pine tree barks. I. Temporal and spatial variations, *Sci. Total Environ.* 232 (1999) 49–58.
- [40] A. Hassanin, A.E. Johnston, G.O. Thomas, K.C. Jones, Time trends of atmospheric PBDEs inferred from archived UK herbage, *Environ. Sci. Technol.* 39 (2005) 2436–2441.
- [41] N. Ratola, A. Alves, L. Santos, S. Lacorte, Pine needles as passive bio-samplers to determine polybrominated diphenyl ethers, *Chemosphere* 85 (2011) 247–252.
- [42] L.G. Hansen, *The Ortho Side of PCBs*, Kluwer Academic Publishers, London, UK, 1999.
- [43] V.L.B. Jaspers, A. Covaci, S. Voorspoels, T. Dauwe, M. Eens, P. Schepens, Brominated flame retardants and organochlorine pollutants in aquatic and terrestrial predatory birds of Belgium: levels, patterns, tissue distribution and condition factors, *Environ. Pollut.* 139 (2006) 340–352.
- [44] S. Voorspoels, A. Covaci, V.L.B. Jaspers, H. Neels, P. Schepens, Biomagnification of PBDEs in three small terrestrial food chains, *Environ. Sci. Technol.* 41 (2) (2007) 411–416.
- [45] F. Vermeulen, A. Covaci, H. D'Have, N.W. Van den Brink, R. Blust, W. De Coen, et al., Accumulation of background levels of persistent organochlorine and organobromine pollutants through the soil–earthworm–hedgehog food chain, *Environ. Int.* 36 (7) (2010) 721–727.
- [46] K.J. Fernie, R.B. King, K.G. Drouillard, K.M. Stanford, Temporal and spatial patterns of contaminants in Lake Erie watersnakes (*Nerodia sipedon insularum*) before and after the round goby (*Apollonia melanostomus*) invasion, *Sci. Total Environ.* 406 (1–2) (2008) 344–351.
- [47] I.G. Sipes, M.L. Socumb, D.F. Perry, D.E. Carter, 2,4,5,2',4',5'-hexachlorobiphenyl: distribution, metabolism, and excretion in the dog and the monkey, *Toxicol. Appl. Pharmacol.* 65 (1982) 264–272.
- [48] J.R. Christensen, M. Macduffee, R.W. Macdonald, M. Whitar, P.S. Ross, Persistent organic pollutants in British Columbia grizzly bears: consequence of divergent diets, *Environ. Sci. Technol.* 39 (18) (2005) 6952–6960.
- [49] S. Voorspoels, A. Covaci, P. Lepom, S. Escutenaire, P. Schepens, Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (*Vulpes vulpes*), *Environ. Sci. Technol.* 40 (9) (2006) 2937–2943.
- [50] V.L.B. Jaspers, A.C. Dirtu, M. Eens, H. Neels, A. Covaci, Predatory bird species show different patterns of hydroxylated polychlorinated biphenyls (HO-PCBs) and polychlorinated biphenyls (PCBs), *Environ. Sci. Technol.* 42 (9) (2008) 3465–3471.
- [51] J. Hasegawa, M.H. Matsuda, T. Enomoto, M. Kawano, T. Wakimoto, PCBs and hydroxylated PCBs in the tissues of wild birds and fish prey from Japan, *Organohalogen Compd.* 69 (2007) 1495–1498.
- [52] R.J. Norstrom, M. Simon, J. Moisey, B. Wakeford, D.V.C. Weseloh, Geographical distribution (2000) and temporal trends (1981–2000) of brominated diphenyl ethers in Great Lakes herring gull eggs, *Environ. Sci. Technol.* 36 (2002) 4783–4789.
- [53] D. Chen, R.C. Hale, B.D. Watts, M.J. La Guardia, E. Harvey, E.K. Mojica, Species-specific accumulation of polybrominated diphenyl ether flame retardants in birds of prey from the Chesapeake Bay region, USA, *Environ. Pollut.* 158 (2010) 1883–1889.

- [54] V.L.B. Jaspers, D. Herzke, I. Eulaers, B.W. Gillespie, M. Eens, Perfluoroalkyl substances in soft tissues and tail feathers of Belgian barn owls (*Tyto alba*) using statistical methods for left-censored data to handle non-detects, *Environ. Int.* 52 (2013) 9–16.
- [55] E. Van den Steen, V.L.B. Jaspers, A. Covaci, T. Dauwe, R. Pinxten, H. Neels, et al., Variation, levels and profiles of organochlorines and brominated flame retardants in great tit (*Parus major*) eggs from different types of sampling locations in Flanders (Belgium), *Environ. Int.* 34 (2008) 155–161.
- [56] E. Van den Steen, R. Pinxten, V.L.B. Jaspers, A. Covaci, E. Barba, C. Carere, et al., Brominated flame retardants and organochlorines in the European environment using great tit eggs as a biomonitoring tool, *Environ. Int.* (35) (2009) 310–317.
- [57] M. Eens, V.L.B. Jaspers, E. Van den Steen, M. Bateson, C. Carere, P. Clergeau, et al., Can starling eggs be useful as a biomonitoring tool to study organohalogenated contaminants on a worldwide scale? *Environ. Int.* 51 (2013) 141–149.
- [58] N.W.A. Moore, A pesticide monitoring system with special reference to the selection of indicator species, *J. Appl. Ecol.* 3 (1966) 261–269.
- [59] T. Dauwe, V.L.B. Jaspers, A. Covaci, M. Eens, Accumulation of organochlorine and brominated flame retardants in the eggs and nestlings of great tits (*Parus major*), *Environ. Sci. Technol.* (40) (2006) 5297–5303.
- [60] J. de Boer, T.E. van der Zande, H. Pieters, F. Ariese, C.A. Schipper, T. van Brummelen, et al., Organic contaminants and trace metals in flounder liver and sediment from the Amsterdam and Rotterdam harbours and off the Dutch coast, *J. Environ. Monit.* 3 (2001) 386–393.
- [61] A.O. Barakat, K. Moonkoo, K. Yoarong, T.L. Wade, Organochlorine pesticides and PCB residues in sediments of Alexandria Harbour, Egypt, *Mar. Pollut. Bull.* 44 (2002) 1426–1434.
- [62] M. Sprovieri, M.L. Feo, L. Prevedello, D.S. Manta, S. Sammartino, S. Tamburrino, et al., Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy), *Chemosphere* 67 (2007) 998–1009.
- [63] S. Voorspoels, A. Covaci, J. Maervoet, P. Schepens, PBDEs in marine and freshwater sediments from Belgium: levels, profiles and relations with biota, *J. Environ. Monit.* 6 (2004) 914–918.
- [64] E. Van den Steen, T. Dauwe, A. Covaci, V.B. Jaspers, R. Pinxten, M. Eens, Within- and among-clutch variation of organohalogenated contaminants in eggs of great tits (*Parus major*), *Environ. Pollut.* 144 (2006) 355–359.
- [65] D. Chen, P. Martin, N.M. Burgess, L. Champoux, J.E. Elliott, J.F. Douglas, A. Idrissi, R. J. Letcher, European starlings (*Sturnus vulgaris*) indicate that landfills are an important source of bioaccumulative flame retardants to Canadian terrestrial ecosystems, *Environ. Sci. Technol.* (under review).
- [66] K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, Towards a global historical emission inventory for selected PCB congener—a mass balance approach. 1. Global production and consumption, *Sci. Total Environ.* 290 (2002) 181–198.
- [67] P. Guerra, M. Alae, B. Jimenez, G. Pacepavicius, C. Marvin, G. MacInnis, et al., Emerging and historical brominated flame retardants in peregrine falcon (*Falco peregrinus*) eggs from Canada and Spain, *Environ. Int.* 40 (2012) 179–186.
- [68] P. Lindberg, U. Sellstrom, L. Haggberg, C.A. De Wit, Higher brominated diphenyl ethers and hexabromocyclododecane found in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden, *Environ. Sci. Technol.* 38 (2004) 93–96.

- [69] A.K. Johansson, U. Sellstrom, P. Lindberg, A. Bignert, C.A. De Wit, Polybrominated diphenyl ether congener patterns, hexabromocyclododecane, and brominated biphenyl 153 in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden, *Environ. Toxicol. Chem.* 28 (2009) 9–17.
- [70] A.K. Johansson, U. Sellstrom, P. Lindberg, A. Bignert, C.A. De Wit, Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in Swedish Peregrine Falcon (*Falco peregrinus peregrinus*) eggs, *Environ. Int.* 37 (2011) 678–686.
- [71] K. Vorkamp, M. Thomsen, K. Falk, H. Leslie, S. Moller, P.B. Sorensen, Temporal development of brominated flame retardants in peregrine falcon (*Falco peregrinus*) eggs from South Greenland (1986–2003), *Environ. Sci. Technol.* 39 (2005) 8199–8206.
- [72] D. Chen, M.J. La Guardia, E. Harvey, M. Amaral, K. Wohlfort, R.C. Hale, Polybrominated diphenyl ethers in peregrine falcon (*Falco peregrinus*) eggs from the northeastern US, *Environ. Sci. Technol.* 42 (2008) 7594–7600.
- [73] J.S. Park, A. Holden, V. Chu, M. Kim, A. Rhee, P. Patel, et al., Time-trends and congener profiles of PBDEs and PCBs in California peregrine falcons (*Falco peregrinus*), *Environ. Sci. Technol.* 43 (2009) 8744–8751.
- [74] J.S. Park, A. Fong, V. Chu, A. Holden, J. Linthicum, K. Hooper, Prey species as possible sources of PBDE exposures for peregrine falcons (*Falco peregrinus*) nesting in major California cities, *Arch. Environ. Contam. Toxicol.* 60 (3) (2011) 518–523.
- [75] K.E. Potter, B.D. Watts, M.J. La Guardia, E.P. Harvey, R.C. Hale, Polybrominated diphenyl ether flame retardants in Chesapeake Bay region, USA, peregrine falcon (*Falco peregrinus*) eggs: urban/rural trends, *Environ. Toxicol. Chem.* 28 (2009) 973–981.
- [76] M. Alaee, P. Arias, A. Sjödin, Å. Bergman, An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release, *Environ. Int.* 29 (2003) 683–689.
- [77] C.A. de Wit, A. Kierkegaard, N. Ricklund, U. Sellström, Emerging brominated flame retardants in the environment, in: E. Eljarrat, D. Barceló (Eds.), *Brominated Flame Retardants*. 16. *The Handbook of Environmental Chemistry*, 2011, pp. 241–286.
- [78] V.L.B. Jaspers, S. Voorspoels, A. Covaci, M. Eens, Can predatory bird feathers be used as a non-destructive biomonitoring tool of organic pollutants?, *Biol. Lett.* 2 (2006) 283–285.
- [79] R.D. Behrooz, A. Esmaili-Sari, S.M. Ghasempouri, N. Bahramifar, A. Covaci, Organochlorine pesticide and polychlorinated biphenyl residues in feather of birds from different trophic levels of South-West Iran, *Environ. Int.* 35 (2009) 285–290.
- [80] S. Espin, E. Martinez-Lopez, P. Maria-Mojica, A.J. Garcia-Fernandez, Razorbill (*Alca torda*) feathers as an alternative tool for evaluating exposure to organochlorine pesticides, *Ecotoxicology* 21 (1) (2012) 183–190.
- [81] I. Eulaers, A. Covaci, D. Herzke, J.O. Bustnes, M. Eens, D.J. Halley, et al., A first evaluation of the usefulness of feathers of nestling predatory birds for non-destructive biomonitoring of persistent organic pollutants, *Environ. Int.* (37) (2011) 622–630.
- [82] I. Eulaers, A. Covaci, J. Hofman, T. Nygård, D.J. Halley, R. Pinxten, et al., A comparison of non-destructive sampling strategies to assess the exposure of white tailed eagles (*Haliaeetus albicilla*) to persistent organic pollutants, *Sci. Total Environ.* (410) (2011) 258–265.
- [83] V.L.B. Jaspers, A. Covaci, P. Deleu, M. Eens, Concentrations in bird feathers reflect regional contamination with organic pollutants, *Sci. Total Environ.* 407 (4) (2009) 1447–1451.

- [84] V.L.B. Jaspers, S. Voorspoels, A. Covaci, G. Lepoint, M. Eens, Evaluation of the usefulness of bird feathers as a non-destructive biomonitoring tool for organic pollutants: a comparative and meta-analytical approach, *Environ. Int.* 33 (3) (2007) 328–337.
- [85] V.L.B. Jaspers, Covaci, E. Van den Steen, M. Eens, Is external contamination with organic pollutants important for the concentrations measured in bird feathers, *Environ. Int.* 33 (2007) 766–772.
- [86] D.A. Rocque, Use of bird collections in contaminant and stable-isotope studies, *The Auk* 122 (3) (2005) 990–994.
- [87] G.R. Bortolotti, Flaws and pitfalls in the chemical analysis of feathers: bad news—good news for avian chemoecology and toxicology, *Ecol. Appl.* 20 (6) (2010) 1766–1774.
- [88] A. Covaci, P. Schepens, Chromatographic aspects of the analysis of selected persistent organochlorine pollutants in human hair, *Chromatographia* 53 (2001) 366–371.
- [89] V.A. Boumba, K.S. Zivrou, T. Vougiouklakis, Hair as a biological indicator of drug use, drug abuse or chronic exposure to environmental toxicants, *Int. J. Toxicol.* 25 (2006) 143–163.
- [90] V.L.B. Jaspers, R. Dietz, C. Sonne, R.J. Letcher, M. Eens, H. Neels, et al., A screening of persistent organohalogenated contaminants in hair of East Greenland polar bears, *Sci. Total Environ.* 408 (2010) 5613–5618.
- [91] H. D'Havé, A. Covaci, J. Scheirs, P. Schepens, W.D. Coen, Hair as an indicator of endogenous tissue levels of brominated flame retardants in mammals, *Environ. Sci. Technol.* 39 (2005) 6016–6020.
- [92] H. D'Havé, J. Scheirs, A. Covaci, P. Schepens, R. Verhagen, W.D. Coen, Non-destructive pollution exposure assessment in the European Hedgehog (*Erinaceus europaeus*). III. Hair as an indicator of endogenous organochlorine compound concentrations, *Environ. Toxicol. Chem.* 25 (1) (2006) 158–167.
- [93] H. D'Have, J. Scheirs, A. Covaci, N.W. van den Brink, R. Verhagen, W. De Coen, Non-destructive pollution exposure assessment in the European hedgehog (*Erinaceus europaeus*). IV. Hair versus soil analysis in exposure and risk assessment of organochlorine compounds, *Environ. Pollut.* 145 (2007) 861–868.
- [94] C. Rappe, M. Nygren, G. Lindstrom, H.R. Buser, O. Blaser, C. Weuthrich, Polychlorinated dibenzofurans and dibenzo-*p*-dioxins and other chlorinated contaminants in cow milk from various locations in Switzerland, *Environ. Sci. Technol.* 21 (1987) 964–970.
- [95] P. Schmid, C.h. Schlatter, Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in cow's milk from Switzerland, *Chemosphere* 24 (1992) 1013–1030.
- [96] L. Ramos, E. Eljarrat, L.M. Hernahdez, L. Alonzo, J. Rivera, M.J. Gamilez, Levels of PCDDs and PCDFs in farm cow's milk located near potential contaminant sources in Asturias (Spain). Comparison with levels found in control, rural farms and commercial pasteurized cow's milks, *Chemosphere* 35 (1997) 2167–2179.
- [97] J.F. Focant, C. Pirard, A.C. Massard, E. de Pauw, Survey of commercial pasteurised cows' milk in Wallonia (Belgium) for the occurrence of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and coplanar polychlorinated biphenyls, *Chemosphere* 52 (2003) 725–733.
- [98] P. Schmid, E. Gujer, M. Zennegg, C. Studer, Temporal and local trends of PCDD/F levels in cow's milk in Switzerland, *Chemosphere* 53 (2003) 129–136.
- [99] M. Rappolder, N. Bruders, C. Schroter-Kermani, Comparison of congener patterns and TEQs in environmental and human samples, *Organohalogen Compd.* 67 (2005) 2086–2089.

- [100] M. Esposito, S. Cavallo, F.P. Serpe, R. D'Ambrosio, P. Gallo, G. Colarusso, et al., Levels and congener profiles of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls in cow's milk collected in Campania, Italy, *Chemosphere* 77 (9) (2009) 1212–1216.
- [101] G. Rychen, S. Jurjanz, H. Toussaint, C. Feidt, Dairy ruminant exposure to persistent organic pollutants and excretion to milk, *Animal* 2 (2008) 312–323.
- [102] O.I. Kalantzi, R.E. Alcock, P.A. Johnston, D. Santillo, R.L. Stringer, G.O. Thomas, et al., The global distribution of PCBs and organochlorine pesticides in butter, *Environ. Sci. Technol.* 35 (6) (2001) 1013–1018.
- [103] S.R. de Solla, K.J. Fernie, Characterization of contaminants in snapping turtles (*Chelydra serpentina*) from Canadian Lake Erie Areas of Concern: St. Clair River, Detroit River, and Wheatley Harbour, *Environ. Pollut.* 132 (1) (2004) 101–112.
- [104] B.C. Kelly, F.A.P.C. Gobas, An arctic terrestrial food-chain bioaccumulation model for persistent organic pollutants, *Environ. Sci. Technol.* 37 (13) (2003) 2966–2974.
- [105] P.A. Martin, T.V. McDaniel, B. Hunter, Temporal and spatial trends in chlorinated hydrocarbon concentrations of mink in Canadian Lakes Erie and St. Clair, *Environ. Monit. Assess.* 113 (1–3) (2006) 245–263.
- [106] K.J. Fernie, R.J. Letcher, Historical contaminants, flame retardants, and halogenated phenolic compounds in peregrine falcon (*Falco peregrinus*) nestlings in the Canadian Great Lakes Basin, *Environ. Sci. Technol.* 44 (9) (2010) 3520–3526.
- [107] D.G. Patterson, G. O'Sullivan, C.D. Sandau, The use and misuse of the National Health and Nutrition Examination Survey (NHANES) data for assessing human exposure to environmental chemicals, in: R.D. Morrison, G. O'Sullivan (Eds.), *Environmental Forensics*, RSC Publishing, Cambridge, 2009, pp. 188–201.
- [108] R. Duarte-Davidson, K.C. Jones, Polychlorinated-biphenyls (PCBs) in the UK population—estimated intake, exposure and body burden, *Sci. Total Environ.* 151 (1994) 131–152.
- [109] A. Covaci, S. Voorspoels, L. Roosens, W. Jacobs, R. Blust, H. Neels, Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in human liver and adipose tissue samples from Belgium, *Chemosphere* 73 (2008) 170–175.
- [110] S. Harrad, C. Ibarra, M. Diamond, L. Melymuk, M. Robson, J. Douwes, et al., Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States, *Environ. Int.* 34 (2008) 232–238.
- [111] M. Frederiksen, K. Vorkamp, M. Thomsen, L.E. Knudsen, Human internal and external exposure to PBDEs—a review of levels and sources, *Int. J. Hyg. Environ. Health* 212 (2009) 109–134.
- [112] A. Ramesh, S. Tanabe, K. Kannan, A.N. Subramanian, P.L. Kumaran, R. Tatsukawa, Characteristic trend of persistent organochlorine contamination in wildlife from a tropical agricultural watershed, South India, *Arch. Environ. Contam. Toxicol.* 23 (1992) 26–36.
- [113] R. Moilanen, H. Pyysalo, J. Kumpulainen, Average total dietary intakes of organochlorine compounds from the Finnish diet, *Z. Lebensm. Unters. Forsch.* 182 (1986) 484–488.
- [114] K. Davis, Human exposure pathways to selected organochlorines and PCBs in Toronto and Southern Ontario, in: J.O. Nriagu, M.S. Simmonds (Eds.), *Food Contamination from Environmental Sources*, John Wiley and Sons, New York, 1990.
- [115] R.F. Herrick, J.D. Meeker, L. Altshul, Serum PCB levels and congener profiles among teachers in PCB-containing schools: a pilot study, *Environ. Health* 10 (2011) 56.

- [116] A.P. DeCaprio, G.W. Johnson, A.M. Tarbell, D.O. Carpenter, J.R. Chiarenzelli, G.S. Morse, et al., Akwesasne task force E. Polychlorinated biphenyl (PCB) exposure assessment by multivariate statistical analysis of serum congener profiles in an adult Native American population, *Environ. Res.* 98 (2005) 284–302.
- [117] D.F. Staskal, J.J. Deliberto, M.J. De Vito, L.S. Birnbaum, Toxicokinetics of BDE 47 in female mice: effect of dose, route of exposure, and time, *Toxicol. Sci.* 83 (2005) 215–223.
- [118] T.F. Webster, V. Vieira, A. Schecter, Estimating human exposure to PBDE-47 via air, food, and dust using Monte Carlo methods, in: *Proceedings DIOXIN'05, 2005*, pp. 505–508.
- [119] M.O. James, Polychlorinated biphenyls: metabolism and metabolites, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, The University Press of Kentucky, Kentucky, USA, 2001, pp. 35–46.
- [120] J.F. Brown, R.W. Lawton, Factors controlling the distribution and levels of PCBs after occupational exposure, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, The University Press of Kentucky, Kentucky, USA, 2001.
- [121] D.A. Axelrad, S. Goodman, T.J. Woodruff, PCB body burdens in US women of child-bearing age 2001–2002: an evaluation of alternate summary metrics of NHANES data, *Environ. Res.* 109 (2009) 368–378.
- [122] R.B. Jain, R.Y. Wang, Association of caffeine consumption and smoking status with the serum concentrations of polychlorinated biphenyls, dioxins, and furans in the general U.S. population: NHANES 2003–2004, *J. Toxicol. Environ. Health A* 74 (2011) 1225–1239.
- [123] M. Weintraub, L.S. Birnbaum, Catfish consumption as a contributor to elevated PCB levels in a non-Hispanic black subpopulation, *Environ. Res.* 107 (2008) 412–417.
- [124] N.O. Price, R.W. Young, J.K. Dickinson, Pesticide residues and polychlorinated biphenyl levels in diets, urine, and fecal matter of preadolescent girls, *Proc. Soc. Exp. Biol. Med.* 139 (4) (1972) 1280–1283.
- [125] R. Ritter, M. Scheringer, M. MacLeod, C. Moeckel, K.C. Jones, K. Hungerbühler, Intrinsic human elimination half-lives of polychlorinated biphenyls derived from the temporal evolution of cross-sectional biomonitoring data from the United Kingdom, *Environ. Health Perspect.* 119 (2011) 225–231.
- [126] L.G. Hansen, Identification of steady state and episodic PCB congeners from multiple pathway exposures, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, The University Press of Kentucky, Kentucky, USA, 2001, p. 2001.
- [127] M.O. James, J.C. Sacco, L.R. Faux, Effects of food natural products on the biotransformation of PCBs, *Environ. Toxicol. Pharmacol.* 25 (2008) 211–217.
- [128] R.F. Seegal, E.F. Fitzgerald, E.A. Hills, M.S. Wolff, R.F. Haase, A.C. Todd, et al., Estimating the half-lives of PCB congeners in former capacitor workers measured over a 28-year interval, *J. Expo. Sci. Environ. Epidemiol.* 21 (2011) 234–246.
- [129] M.P. Longnecker, Endocrine and other human health effects of environmental and dietary exposure to polychlorinated biphenyls, in: L.W. Robertson, L.G. Hansen (Eds.), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, The University Press of Kentucky, Kentucky, USA, 2001, pp. 111–118.
- [130] J. Jin, Y. Wang, C.Q. Yang, J.C. Hu, W.Z. Liu, J. Cui, et al., Polybrominated diphenyl ethers in the serum and breast milk of the resident population from production area, China, *Environ. Int.* 35 (2009) 1048–1052.

- [131] R.B. Jain, R.Y. Wang, Regression models to estimate total polychlorinated biphenyls in the general US population: 2001–2002 and 2003–2004, *Chemosphere* 79 (2010) 243–252.
- [132] International Programme on Chemical Safety (IPCS), *Environmental Health Criteria 140, Polychlorinated Biphenyls and Terphenyls*, second ed. <<http://www.inchem.org/documents/ehc/ehc/ehc140.htm/>>, 1993 (accessed 28.10.11).
- [133] B.R. Nichols, K.L. Hentz, L. Aylward, S.M. Hays, J.C. Lamb, Age-specific reference ranges for polychlorinated biphenyls (PCB) based on the NHANES 2001–2002 survey, *J. Toxicol. Environ. Health A* (70) (2007) 1873–1877.
- [134] D. Megson, G. O'Sullivan, S. Comber, P. Worsfold, M.C. Lohan, M. Edwards, et al., Elucidating the structural properties that influence the persistence of PCBs in humans using the National Health and Nutrition Examination Survey (NHANES) dataset, *Sci. Total Environ.* 461–462 (2013) 99–107.
- [135] U. Steuerwald, P. Weihe, P.J. Jorgensen, K. Bjerve, J. Brock, B. Heinzow, et al., Maternal seafood diet, methylmercury exposure, and neonatal neurologic function, *J. Pediatr.* 136 (2000) 599–605.
- [136] F. Laden, L.M. Neas, D. Spiegelman, S.E. Hankinson, W.C. Willett, K. Ireland, et al., Predictors of plasma concentrations of DDE and PCBs in a group of US women, *Environ. Health Perspect.* 107 (1999) 75–81.
- [137] P. Bjerregaard, J.C. Hansen, Organochlorines and heavy metals in pregnant women from the Disko Bay area in Greenland, *Sci. Total Environ.* 245 (2000) 195–202.
- [138] B.G. Svensson, T. Hallberg, A. Nilsson, A. Schutz, L. Hagmar, Parameters of immunological competence in subjects with high consumption of fish contaminated with persistent organochlorine compounds, *Int. Arch. Occup. Environ. Health* 65 (1994) 351–358.
- [139] CDC, Centres for Disease Control and Prevention (CDC), National Health and Nutrition Examination Survey, <<http://www.cdc.gov/nchs/nhanes.htm/>>, 2011 (accessed 21.10.11).
- [140] D.G. Patterson, W.E. Turner, S.P. Caudill, L.L. Needham, Total TEQ reference range (PCDDs, PCDFs, cPCBs, mono-PCBs) for the US population 2001–2002, *Chemosphere* 73 (2008) S261–S277.
- [141] D.G. Patterson, L.Y. Wong, W.E. Turner, S.P. Caudill, E.S. Dipietro, P.C. McClure, et al., Levels in the US population of those persistent organic pollutants (2003–2004) included in the Stockholm convention or in other long-range transboundary air pollution agreements, *Environ. Sci. Technol.* 43 (2009) 1211–1218.
- [142] J.S. Lakind, S.M. Hays, L.L. Aylward, D.Q. Naiman, Perspective on serum dioxin levels in the United States: an evaluation of the NHANES data, *J. Expo Sci. Environ. Epidemiol.* 19 (2009) 435–441.
- [143] Yearly Report 2008, Burgerlijke stand en bevolking, Jaarverslag, Groot Antwerpen, Antwerp, 2008.
- [144] J.P. Giesy, K. Kannan, Global distribution of perfluorooctane sulfonate in wildlife, *Environ. Sci. Technol.* 35 (2001) 1339–1342.
- [145] R. Bossi, F.F. Riget, R. Dietz, C. Sonne, P. Fauser, M. Dam, et al., Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish, birds and marine mammals from Greenland and the Faroe Islands, *Environ. Pollut.* 136 (2) (2005) 323–329.
- [146] 3M Company, Voluntary Use and Exposure Information Profile for Perfluorooctanesulfonic acid and Various Salt Forms, 3M Company, St. Paul, MN, USA, 2000 (Submitted to the US EPA, April 27, 2000).
- [147] 3M Company, (Submitted to US EPA, July 7, 2000) Phase-out Plan for POSF-Based Products, 3M Company, St. Paul, MN, USA, 2000.

- [148] K.I.V. De Vijver, P.T. Hoff, W. Van Dongen, E.L. Esmans, R. Blust, W.M. De Coen, Exposure patterns of perfluorooctane sulfonate in aquatic invertebrates from the Western Scheldt estuary and the southern North Sea, *Environ. Toxicol. Chem.* 22 (9) (2003) 2037–2041.
- [149] P.T. Hoff, K. Van de Vijver, W. Van Dongen, E.L. Esmans, R. Blust, W.M. De Coen, Perfluorooctane sulfonic acid in bib (*Trisopterus luscus*) and plaice (*Pleuronectes platessa*) from the Western Scheldt and the Belgian North Sea: distribution and biochemical effects, *Environ. Toxicol. Chem.* 22 (3) (2003) 608–614.
- [150] T. Dauwe, L. Bevoets, E. Janssens, R. Pinxten, R. Blust, M. Eens, Great and blue tit feathers as biomonitors for heavy metal pollution, *Ecol. Ind.* 1 (2002) 227–234.
- [151] T. Dauwe, S.G. Chu, A. Covaci, P. Schepens, M. Eens, Great tit (*Parus major*) nestlings as biomonitors of organochlorine pollution, *Arch. Environ. Contam. Toxicol.* 44 (2003) 89–96.
- [152] T. Dauwe, K. Van de Vijver, W. De Coen, M. Eens, PFOS levels in the blood and liver of a small insectivorous songbird near a fluorochemical plant, *Environ. Int.* 33 (3) (2007) 357–361.
- [153] P.T. Hoff, J. Scheirs, K. Van de Vijver, W. Van Dongen, E.L. Esmans, R. Blust, et al., Biochemical effect evaluation of perfluorooctane sulfonic acid-contaminated wood mice (*Apodemus sylvaticus*), *Environ. Health Perspect.* 112 (6) (2004) 681–686.
- [154] P.T. Hoff, K. Van de Vijver, T. Dauwe, A. Covaci, J. Maervoet, M. Eens, et al., Evaluation of biochemical effects related to perfluorooctane sulfonic acid exposure in organohalogen-contaminated great tit (*Parus major*) and blue tit (*Parus caeruleus*) nestlings, *Chemosphere* 6 (11) (2005) 1558–1569.
- [155] S.A. Beach, J.L. Newsted, K. Coady, J.P. Giesy, Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS), *Rev. Environ. Contam. Toxicol.* 186 (2006) 133–174.
- [156] J. Meyer, V.L.B. Jaspers, M. Eens, W. De Coen, The relationship between perfluorinated chemical levels in the feathers and livers of birds from different trophic levels, *Sci. Total Environ.* (407) (2009) 5894–5900.
- [157] W. D'Hollander, A. Hagensnaars, L. De Bruyn, J. Meyer, P. de Voogt, L. Bervoets, Distribution of perfluorooctane sulfonate in a simple wood mouse food chain, *Environ. Pollut.* in preparation.
- [158] J.L. Newsted, P.D. Jones, K. Coady, J.P. Giesy, Avian toxicity reference values for perfluorooctane sulfonate, *Environ. Sci. Technol.* 39 (23) (2005) 9357–9362.
- [159] G.W. Olsen, S.C. Chang, P.E. Noker, G.S. Gorman, D.J. Ehresman, P.H. Lieder, et al., A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans, *Toxicology* 256 (2009) 65–74.
- [160] ChER, The Scientific Committee on Health and Environmental Risks (SCHER) opinion on “RPA’s report, Perfluorooctane Sulphonates Risk Reduction Strategy and Analysis of Advantages and Drawbacks”, European Commission, Luxembourg, 2005.
- [161] D. Carloni, Perfluorooctane Sulfonate (PFOS) Production and Use: Past and Current Evidence, United Nations Industrial Development Organisation (UNIDO), Beijing, China, 2009.
- [162] T. Wang, Y. Wang, C. Liao, Y. Cai, G. Jinag, Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm convention on persistent organic pollutants, *Environ. Sci. Technol.* 43 (2009) 5171–5175.
- [163] D. Herzke, S. Huber, L. Bervoets, W. D'Hollander, J. Hajslova, G. Brambilla, et al., Perfluorinated alkylated substances in vegetables and fruits collected in four European countries; PERFOOD, *Organohalogen Compd.* (2011).

- [164] W. D'Hollander, Accumulation of perfluorinated chemicals in Belgian home produced chicken eggs, *Organohalogen Compd.* (2011) 917–920.
- [165] Environment Agency, Contaminants in Soil: Updated Collation of Toxicological Data and Intake Values for Humans Dioxins, Furans and Dioxin-like PCBs, Science Report SC05002/TOX12, 2009.
- [166] Environment Agency, Soil Guideline Values for Dioxins, Furans and Dioxin-like PCBs in soil, Science Report SC050021/DioxinsSGV, 2009.
- [167] W. Shields, Y. Tondeur, L. Benton, M. Edwards, Dioxins and furans, in: R.D. Morrison, B.L. Murphy (Eds.), *Environmental Forensics. Contaminant Specific Guide*, 2006, Academic Press, London, UK, 2006, pp. 293–312.
- [168] D. Megson, S. Dack, Assessing changes to the congener profile of PCDD and PCDF during bioaccumulation in chicken and duck eggs, in: R.D. Morrison, G. O'Sullivan (Eds.), *Proceedings of the 2011 INEF Conference on Environmental Forensics*, 2011, RSC Publishing, Cambridge, UK, 2011, pp. 244–261.
- [169] M. Van den Berg, L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, et al., The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds, *Toxicol. Sci.* 93 (2006) 223–241.
- [170] United States Environmental Protection Agency (US EPA), Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-*p*-Dioxins and -Dibenzofurans (CDDs and CDFs) and 1989 Update. Risk Assessment Forum, US EPA, Washington, DC, 1989.
- [171] U.G. Ahlborg, G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, et al., Toxic equivalency factors for dioxin-like PCBs, *Chemosphere* 28 (1994) 1049–1067.
- [172] M. Van den Berg, L. Birnbaum, A.T.C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, et al., Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife, *Environ. Health Perspect.* 106 (1998) 775–792.
- [173] U.S. EPA (Environmental Protection Agency). (2006) An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. National Center for Environmental Assessment, Washington, DC; EPA/600/P-03/002F. Available from: National Technical Information Service, Springfield, VA, and online at <http://epa.gov/ncea>.
- [174] K.H. Kim, Y.C. Seo, H. Nam, H.T. Joung, J.C. You, D.J. Kim, et al., Characteristics of major dioxin/furan congeners in melted slag of ash from municipal solid waste incinerators, *Microchem. J.* 80 (2005) 171–181.
- [175] H. Hagenmaier, C. Lindig, J. She, Correlation of environmental occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans with possible sources, *Chemosphere* 29 (1994) 2163–2174.
- [176] D. Megson, S. Dack, M. Moore, Limitations of the CLEA model when assessing human health risks from dioxins and furans in soil at an allotments site in Rochdale, NW England, *J. Environ. Monitor.* 113 (2011) 1983–1990.
- [177] T. Pless-Mulloli, V. Air, C. Vizzard, I. Singleton, D. Rimmer, P. Hartley, The Legacy of historic land-use in allotment gardens in industrial urban settings, *Land Contam. Reclam.* 12 (2004) 239–251.
- [178] G.T. Ankley, G.J. Niemi, K.B. Lodge, H.J. Harris, D.L. Beaver, D.E. Tillitt, et al., Uptake of planar polychlorinated-biphenyls and 2,3,7,8-substituted polychlorinated

- dibenzofurans and dibenzo-*p*-dioxins by birds nesting in the lower Fox River and Green Bay, Wisconsin, USA, *Arch. Environ. Contam. Toxicol.* 24 (1993) 332–344.
- [179] G.W. Johnson, R. Ehrlich, W. Full, Principal component analysis and receptor models in environmental forensics, in: B.L. Murphy, R.D. Morrison (Eds.), *Introduction to Environmental Forensics*, Academic Press, London, UK, 2002, pp. 461–517.
- [180] M. Kent, *Vegetation Description and Data Analysis*, Wiley-Blackwell, Chichester, UK, 2012.
- [181] G.J. Cross, E.R. Taylor, *Human Exposure to Soil Contaminants through the Consumption of Home-Grown Produce*, Glenelg Press, Adelaide, AUS, 1996 (Contaminated Sites Monograph Series No. 6. 1996).
- [182] S.M. Mudge, Changes in Signature During Material Transfer of PCBs in the European Place, in: *International Network of Environmental Forensics Conference*, Cambridge, UK, 2011.
- [183] C.A. de Wit, D. Herzke, K. Vorkamp, Brominated flame retardants in the Arctic environment—trends and new candidates, *Sci. Total Environ.* 408 (15) (2010) 2885–2918.
- [184] L. Ahrens, D. Herzke, S. Huber, J.O. Bustnes, G. Bangjord, R. Ebinghaus, Temporal trends and pattern of polyfluoroalkyl compounds in Tawny Owl (*Strix aluco*) eggs from Norway, 1986–2009, *Environ. Sci. Technol.* 45 (19) (2011) 8090–8097.
- [185] J.O. Bustnes, N.G. Yoccoz, G. Bangjord, A. Polder, J.U. Skaare, Temporal trends (1986–2004) of organochlorines and brominated flame retardants in tawny owl eggs from northern Europe, *Environ. Sci. Technol.* 41 (24) (2007) 8491–8497.
- [186] I. Eulaers, A. Covaci, D. Herzke, M. Eens, C. Sonne, T. Moum, et al., A first evaluation of the usefulness of feathers of nestling predatory birds for non-destructive biomonitoring of persistent organic pollutants, *Environ. Int.* 37 (2011) 622–630.
- [187] E. Mariussen, E. Steinnes, K. Breivik, T. Nygård, M. Schlabach, J.A. Kålås, Spatial patterns of polybrominated diphenyl ethers (PBDEs) in mosses, herbivores and a carnivore from the Norwegian terrestrial biota, *Sci. Total Environ.* 404 (2008) 162–170.
- [188] Z. Wang, X.D. Ma, G.S. Na, Z.S. Lin, Q. Ding, Z.W. Yao, Correlations between physicochemical properties of PAHs and their distribution in soil, moss and reindeer dung at Ny-Alesund of the Arctic, *Environ. Pollut.* 157 (11) (2009) 3132–3136.
- [189] UNEP/AMAP, *Climate Change and POPs: Predicting the Impacts*. Report of the UNEP/AMAP Expert Group, Secretariat of the Stockholm Convention, Geneva, 2011.