ChEmiTecs

Internal exposure of chemicals in high trophic wildlife

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ChEmiTecs
ChEmiTecs is a research program funded by the Swedish EPA. The program's goal is to improve the understanding of emissions of organic substances from articles and to clarify and determine the magnitude of this problem. The program aims to support development of Swedish and EU management programs to minimise risks from harmful substances. The program started in December 2007 and will proceed until November 2012. Participating organisations and organisation representatives are:

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Contents

Summary

The aim of this deliverable was to synthesize available data on chemicals of anthropogenic origin that bioaccumulate in wildlife vertebrates; fish, birds, and mammals. The report is based on published scientific literature for species at high trophic level (predators or pray animals). It is a review and not a complete meta analysis of data. These data are representing bioavailable and bioaccumulating contaminants that may cause toxic effects. This undertaking is limited by the extensive data set available and accordingly boarders were drawn for the data retrieval. The limitations include selection of case species for the study. Unfortunately the survey is suffering from the fact that there are basically NO data on anything but the legacy POPs and a limited number of chemicals with POP characteristics (BFRs and PFCs).

We can conclude that biomonitoring data are non-existing on the vast majority of chemicals present in articles, goods and materials. In case any data are reported it may be coming from sediment or sewage sludge but the present review is not including these matrices.

1. Background

The scientific literature contains a very large number of studies on concentrations/levels of organic environmental pollutants in high trophic animals. The analytes are preferentially those known as persistent organic pollutants (POPs), c.f. below. Studied species span from predatory fishes and birds of prey, up to big mammals such as polar bears, seals and even tigers and lions. The number of species studied is very large.

Spatial and temporal trend studies including different species could be very difficult to interpret. For high quality spatial and/or temporal trend studies we need specific species, preferentially circumpolar species or at least with wide geographical distribution. In case different species are to be compared/used for trend studies we need species that are closely related to each other with similar migration and feeding habits.

According to Law et al (2003), the most reliable data in wildlife relates to seabirds (their eggs). This is also the view of Bignert et al (1993). Examples of high quality time trend studies are those from late 60's up to the late 90's/early 00's, based on guillemot egg from Sweden and the Northeast Atlantic (Bignert et al 1995, Sellström et al 2003, Jörundsdóttir et al 2006, Holmström et al 2005, Helgason 2008). It is important to point out that species differences among birds may be very large (Jörundsdottir et al 2010), indicating birds being very different depending on species.

Marine mammals have been used in efforts to monitor pollutants, particularly in Canada and Norway, but also from e.g. Sweden (Law et al 2003 and 2008). They have applied beluga whales, ringed seals and polar bears for this purpose. The variation in concentrations is much wider than in bird (eggs) and accordingly it is more difficult to establish trends (Frostne 2008, Vorkamp et al 2008). Still, monitoring mammals may be relevant for screening "new" POPs.

Fish is sampled as part of the Swedish monitoring program, but unfortunately the same species are not analysed elsewhere making it complicated, and even impossible, to pursue comprehensive comparisons. However, perch and herring sampled in Sweden are assessed for the POPs and time trend studies are available from the Swedish Museum of Natural History:
www.nrm.se/sv/meny/forskningochsamlingar/enheter/miljogiftsforskning/overvakning.932.html
A comparative study on POPs in several salmon species around the world was published by Carlsson and Hites (2005). In a project on Greenland shark it has been possible to trace a large number of environmental contaminants; including some endogenous compounds as well (Strid et al 2006 and 2007). Apart from these reports there are numerous disparate fish assessment studies.

2. Chemicals in high trophic wildlife

Most studies on chemicals in wildlife animals, report persistent organic chemicals such as polychlorinated biphenyls (PCBs), chlorinated pesticides or brominated flame retardants (BFRs). During the late 10 years studies of polyfluorinated compounds (PFCs) in high trophic wildlife has increased. The major classes of chemicals assessed are addressed in short below. Structures of the most chemicals mentioned in this report are shown in Appendix 1.

PCBs

Polychlorinated biphenyls can theoretically form 209 congeners. All these congeners are not present in technical PCB mixtures and are therefore not distributed to the environment and accordingly not found in biota. The congeners have different lipofilicity depending on the number of chlorine atoms. Higher halogenation increases lipofilicity and with that bioaccumulation. The most common congeners in biota have six or more chlorines. Some of the PCB congeners are biomagnified in the environment, e.g. CB-138, -138, -170, -180. Seven CB-congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180) are listed as mandatory contaminants that should be analysed and reported within both the OSPARCOM and the HELCOM conventions. In the proposed revised guidelines for OSPARCOM (1996) the congeners CB-105 and CB-156 are added to this list. (Bignert et al 2010). The number of chlorines and their position matters greatly for their absorption, distribution, metabolism and excretion (ADME) characteristics

BFRs

Among the BFRs it is polybrominated diphenyl ethers (BPDEs) together with hexabromocyclododecan (HBCDD) that are of the most frequently reviewed compounds in studies of wildlife exposure. These compounds have been widely distributed all over the world. However, all three commercial PBDE products are either banned or under a phase out in most parts of the world, limiting future interest in this group of BFRs. HBCDD has been proposed as a new POP by POPRC (UNEP). Since not yet regulated it is reasonable to keep this compound among those being monitored for.

Most important is however to check for the emerging BFRs. The compounds have been listed in e.g. a recent report by the Harju et al (2009). It is also clear, based on communication from the most recent International BFR Symposium (Kyoto, 2010), that several of the non-PBDE BFRs are now identified in different environmental matrices.

BFRs are used as flame retardants in materials such as: building materials, plastics, furniture, electronics, electric devices, textiles and polymers. There are both additive chemicals (which mean that they can migrate in the material) and reactive chemicals that does react with for example polymers in the material. BFRs came slowly into use during the 1960's.

PFCs

Polyfluorinated compounds (PFCs) is mainly used for their grease and water repelling properties. They have been produced for over 40 years and can be found in paper, textiles and leather as surfactants, as well as in fire extinguishing foams and household utensils. PFOA is also used in the production of PTFE poly(tetrafluoroethylene (Teflon ®)). It was not until the early 2000's that PFCs were discovered as environmentally persistent pollutants accumulating in biota. It is scientifically confirmed that the PFCs are circum-navigating the globe.

The PFC chemicals are produced through electrochemical fluorination or through telomerisation. PFOA is released to the environment by emissions during production of PTFE and during application of materials and goods, as well as through leakage from the final products, biotransformation and atmospheric transformation of fluorotelomers and so forth. The total number of PFC type compounds is not known but we guess that there are at least 50 classes of PFCs (S. Mabury, personal communication).

PFCs are accumulated in blood and are persistent due to the very strong carbon-fluorine bond. They have intermediate high molecular weights and are if present in ionic form, non-volatile. The neutral polyfluorotelomers are far more volatile. PFOS is the stable end product of the degradation of various sulfonated fluorochemicals.

Pesticides

The pesticides may be divided into the historical organochlorine pesticides (OCPs) and modern pesticides. OCPs are still reported in wildlife studies and include for example 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (4,4´-DDT), often measured as the metabolite 1,1´-dichloro-2,2 bis(4-chlorophenyl)ethene (4,4´-DDE), hexachlorbenzene (HCB), hexachlorocyclohexane (HCH), chlordanes heptachlor, dieldrin, aldrin and mirex. However, several of these OCPs, independent of their status as legacy POPs, are still used by numerous countries. Accordingly it is relevant to monitor the OCPs. Their contribution from articles and materials is unlikely.

Examples of halogenated chemicals used as biomonitors for measurements of environmental exposure to high trophic wildlife species in northern Europe are shown in table 2.1. The table illustrates the differences in levels between different species. In table 2.2 PCB concentrations in various low and high trophic marine organisms from the Great Lakes in Canada are listed, illustrating increasing concentrations with increasing trophic level.

Table 2.1. Examples of halogenated chemicals found in some high trophic wildlife species (different tissues) from North West Europe and the European Arctic. Concentrations in ng/g lipid weight (lw) (from Jörundsdóttir, 2009)

POPs	4,4'-DDE	CB-153	HCB	BDE-47	HBCDD
Region/Species:					
Greenland:					
Common eider (liver)			71		
Glaucous gull (liver)	14000	7300	1400		
Black guillemot (egg)	Σ^1 1310		390	52	
Brünnich guillemot (liver)	140		110	6.7	
Ringed seal (liver)			12		
Ringed seal (muscle)			13		
Ringed seal (blubber)	Σ^1 1130		19		
Polar bear (blubber)		1700		380	
Polar bear (liver)		8500		150	
Iceland:					
Common eider (muscle)	Σ^1 450		29		
Black guillemot (muscle)	Σ^1 900		260		
Grey seal (blubber)	890	420	17		
The Faroe Islands:					
Fulmar (egg)	2800	2500	330	4.3	
Pilot whale (blubber)[2]	8000	2900	290		
Norway					
Brünnich guillemot (yolk sac)	2300	580	712	60	35
Common eider (yolk sac)	78	77	50	0.74	6.2
Common guillemot (egg)					
Grey seal (blubber)	Σ^1 2000		43		
Svalbard					
Ringed seal (blubber)				17	
Polar bear (blubber)[2]				37	
The Baltic Sea:					
Common guillemot (egg)	10 000	2200			
Common guillemot (egg)				89	140
Common guillemot (egg)	10 000	2300	620	60	170
Grey seal (blubber)	15 000	21 000			

1 Sum of 4,4'-DDT, 4,4'-DDE, 3,3'-DDD and 2,4'-DDT
2 Mean of male and female

Table 2.2. Mean concentration in µg/kg wet weight (ww) of the sum of 10 PBDEs in marine organisms (different tissues), from low to high trophic levels in the Lawrence Estuary, Canada, 1999-2000 (from Law et al, 2003)

Species	Tissue	n	Lipid (%)	Σ_{10}PBDE
Shrimp	muscle	3	0.9	0.24
Zooplankton	whole	5	16	1.5
Rainbow smelt	liver	4	5.4	34
Atlantic herring	liver	3	3.4	13
Atlantic tomcod	liver	6	21	274
American eel	muscle	3	24	101
American plaice	liver	3	7.7	17
Smooth flounder	liver	3	5.5	41
Greenland halibut	muscle	3	7.3	13
Greenland halibut	liver	2	19	12
Harbour seal (M)	blubber	4	92	709
Beluga whale (F)	blubber	8	88	471

3. Chemicals in fish

As mentioned before, there are many studies on fish but due to the disparate species investigated it is difficult to do comparisons. Within one of the Swedish contaminant monitoring programmes; The National Swedish Contaminant Monitoring Programme in Marine Biota, Bignert et al (2010) have recently presented a summary report of the monitoring activities in Sweden between the years 1986 and 2010. One example from this report is the decreasing trend in the ΣPCB concentration in herring (muscle) sampled at three different sites in the Baltic Sea during the time period 1978 to2008.

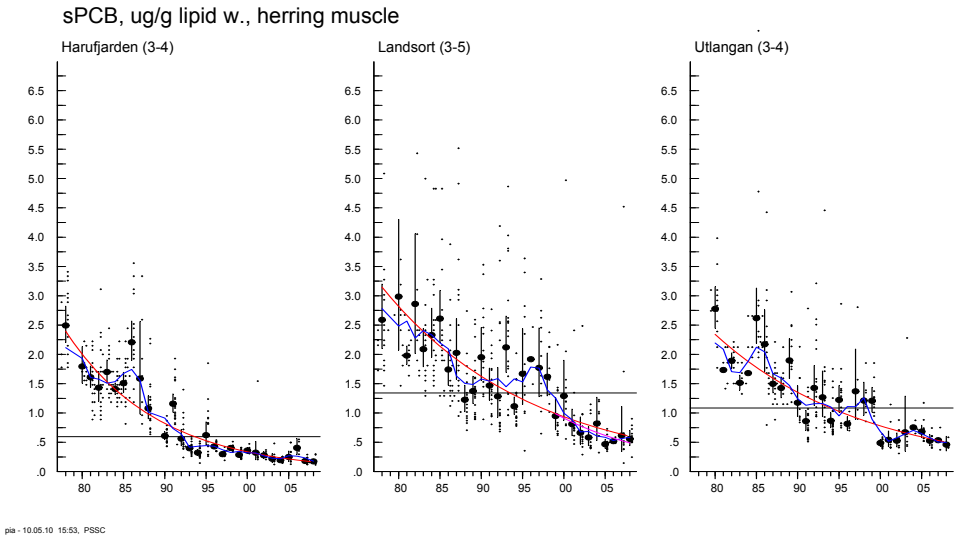


Figure 3.1. A part of the results from a temporal trend study on muscle in herring, captured at three different sites in the Baltic Sea between the years 1978 and 2008. Concentrations in µg/g lw. (Figure from A. Bignert, The Swedish Museum of Natural History).

4. Chemicals in common guillemot

Temporal trend studies

The common guillemot are circumpolar and hence found in North Europe (Iceland, Scandinavia, Great Britain and along the Atlantic coast), Asia (Russia, North Korea, Japan) and North America (Alaska, Canada, USA, and on Greenland). It is possibly the best studied bird species with a particularly extensive data set from the Baltic Sea guillemots. There are several published studies on environmental contaminants in guillemots from Stora Karlsö in the Baltic Sea. The guillemot is resident in the Baltic throughout the year and is therefore useful for time-trend studies of persistent chemicals.

One of the first time trend analyses of contaminants in guillemots from Stora Karlsö was performed by Olsson and Reutergård (1986) and with a more recent follow up by Bignert et al (1995). They studied a time related influence on the DDT and PCB concentrations in Guillemot egg and egg shell parameters. The eggs were sampled between 1969 and 1989 and the analyses showed decreasing levels for both ΣDDT and ΣPCBs during this time period. Concentrations during the years: from ca 600 to 50 mg/kg lw for ΣDDT and from ca 400 to 80 mg/kg lw for ΣPCB.

Sellström et al (2003) analyzed PBDEs (BDE-47, BDE-99, BDE-100) and HBCDD in common guillemot eggs (from Stora Karlsö, Sweden), sampled between 1969 and 2001. During this time period the PBDE concentrations at first increased and peaked around the mid to the late 1980´s, then decreased during the years thereafter. The major BDE finally decreased to below 100 ng/g l.p. (less than 10% of its peak value). The HBCDD concentrations did not show any decreasing trend over the period. In contrast; it ended up to a higher concentration (ca 130 ng/g lw) compared to the concentration at the beginning of the period.

A temporal trend of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) concentrations in common guillemot egg was performed by Holmström et al (2005). Samples were collected from Stora Karlsö (Sweden) between 1968 and 2003. PFOS concentrations increased 30-fold from 25 ng/g w.w. to 614 ng/g ww, a significant trend, with 7-11% per year. PFOA was not detected in any of the samples.

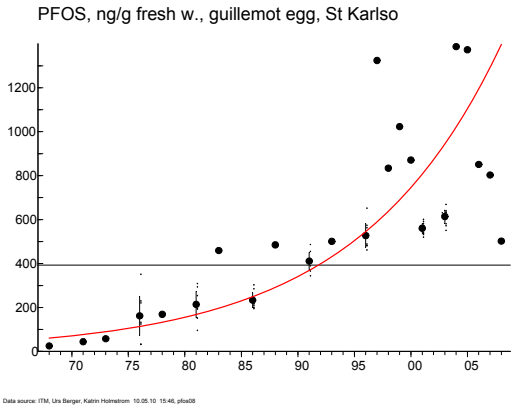


Figure 4.1. Temporal trend study of PFOS in common guillemot egg from 1968-2003. Concentrations in µg/g ww.
(Figure from A. Bignert, The Swedish Museum of Natural History)

Jörundsdóttir et al. (2006) did a temporal trend study of five chlorinated chemicals in guillemot eggs collected at Stora Karlsö in the Baltic proper (Sweden). All chemicals showed a decreasing trend, but the "new" contaminants BCPS and tris(4-chlorophenyl) methane (TCPMe) had a less slope factor compared with PCB and DDE (see Table 4.1)

Table 4.1. Temporal trends (1971-2001) of some chlorinated POPs in eggs from common guillemot collected at Stora Karlsö. Geometric mean concentrations (µg/g lw) (from Jörundsdóttir et al. 2006)

Sampling year	n	BCPS	CB-101	CB-153	DDE	TCPMe
1971	5	1.4	0.58	75	950	12
1976	5	1.5	0.46	68	560	6
1981	5	1.2	0.29	30	87	3
1986	5	1.1	0.037	7.8	79	2
1991	5	0.9	0.039	7.0	36	2
1996	5	0.89	0.091	2.4	14	1
2001	5	1.0	0.017	2.2	10	1
Slope (%)		-1.6	-11	-13	-16	-8.2

All the previous reported decreasing trends for the concentrations of, at least, the "old" POP compounds in common guillemot eggs are confirmed in The National Swedish Contaminant Monitoring Programme in Marine Biota (Bignert et al 2010), here illustrated first by the temporal trend curve for ΣPCB concentrations in common Guillemot egg collected at Stora Karlsö from mid-60`s to 2008 (Figure 4.2), showing a decreasing trend at least from the mid-80´s.

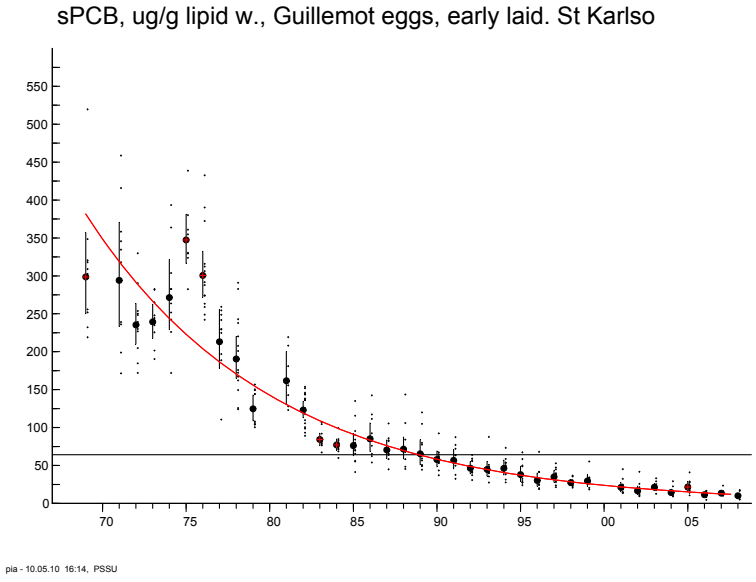


Figure 4.2. Temporal trend curve for ΣPCB in common Guillemot egg from St Karlsö, Sweden, from mid-60´s to 2008. Concentrations in µg/g lw.
(Figure from A. Bignert, the Swedish Museum of Natural History).

In figure 4.3 below, the temporal trend curves from three PBDE congeners in guillemot egg are showing an increase from the mid-70´s to the mid.80´s, and then probably a decrease to 2008.

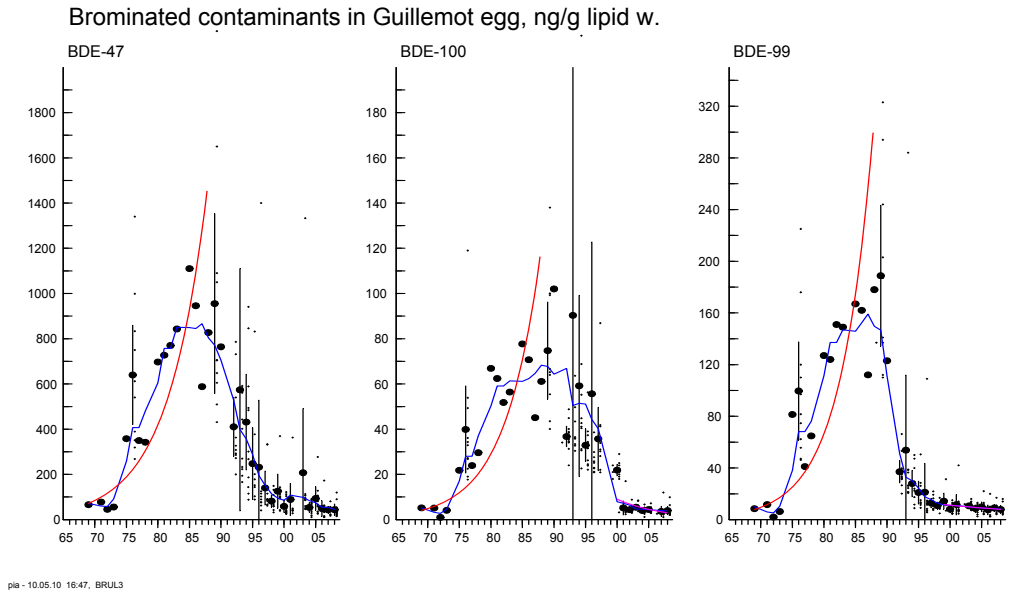
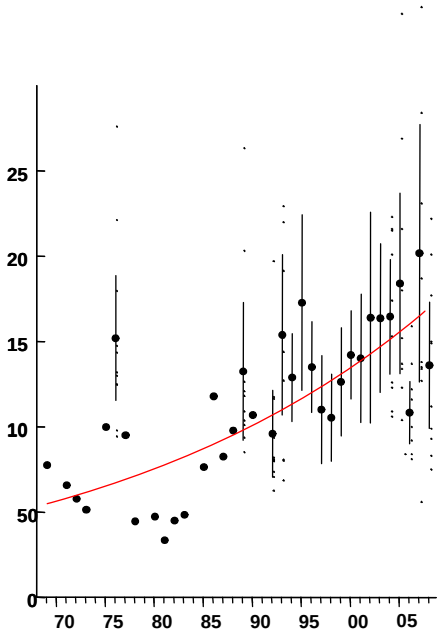


Figure 4.3. Temporal trend curve for three PBDE congeners in common guillemot's egg from St Karlsö, Sweden, from mid-70´s to 2008. Concentrations in µg/g lw.
(Figure from A. Bignert, The Swedish Museum of Natural History).

The temporal trend for the concentration of HBCDD (a so called emerging BFR) in Guillemot egg is not showing any decrease in the Baltic Sea. Instead, the results (Figure 4.4) indicate an ongoing increase for the concentrations of HBCDD in common guillemot egg, collected at St Karlsö between 1969-2008.



Figur 4.4. Temporal trend curve for HBCDD concentration in Guillemots egg collected between 1969 and 2008. Concentrations in µg/g lw. (Figure from A. Bignert, the Swedish Museum of Natural History).

Spatial trend studies

Jörundsdóttir et al.(2010) and Löfstrand et al (2008) performed spatial trend studies of some chlorinated (Figure 4.5), brominated (Figure 4.6) and fluorinated (Figure 4.7) compounds in Guillemot egg, collected at 5-6 different sites in Northern Europe; Iceland, Faeroe Islands, Norway and Sweden (Baltic Sea). The result showed that the most contaminated sampling site was Stora Karlsö in the Baltic Sea.

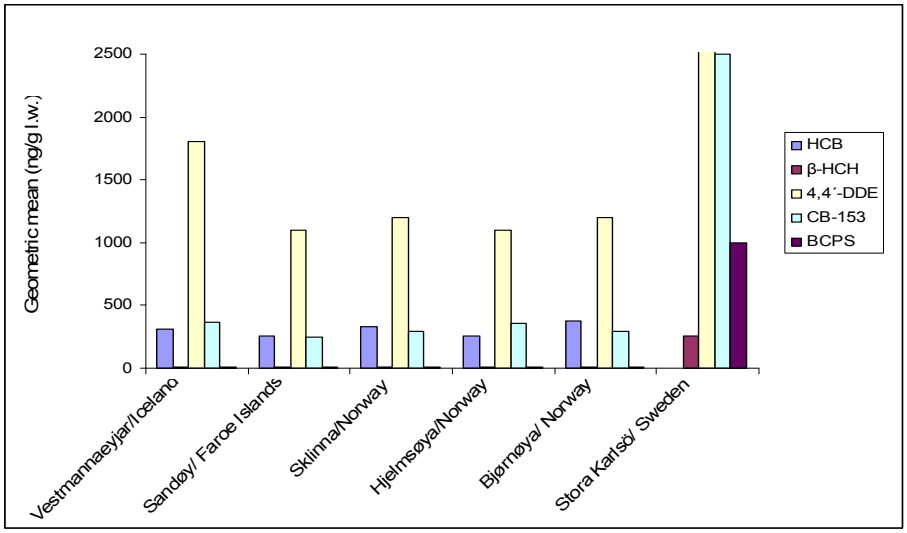


Figure 4.5. Spatial trend study of the concentration levels of five chlorinated compounds, HCB, β_HCH, 4,4´-DDE, CB-153 and BCPS in guillemot egg colleted at six different places in the Northern Europe. Concentrations in ng/g lw. (from Jörundsdóttir et al 2010)

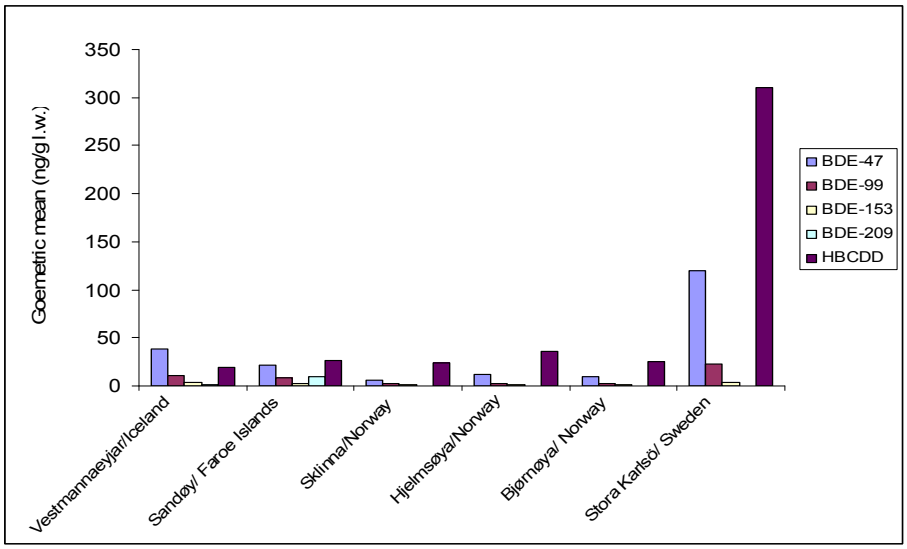


Figure 4.6. Spatial trend study of the concentration levels of five brominated compounds, five PBDE congeners (PBDE-47, -99, -153 and -209) and HBCDD, in guillemot egg colleted at six different places in the Northern Europe. Geometric mean concentrations in ng/g lw. (from Jörundsdóttir et al 2010)

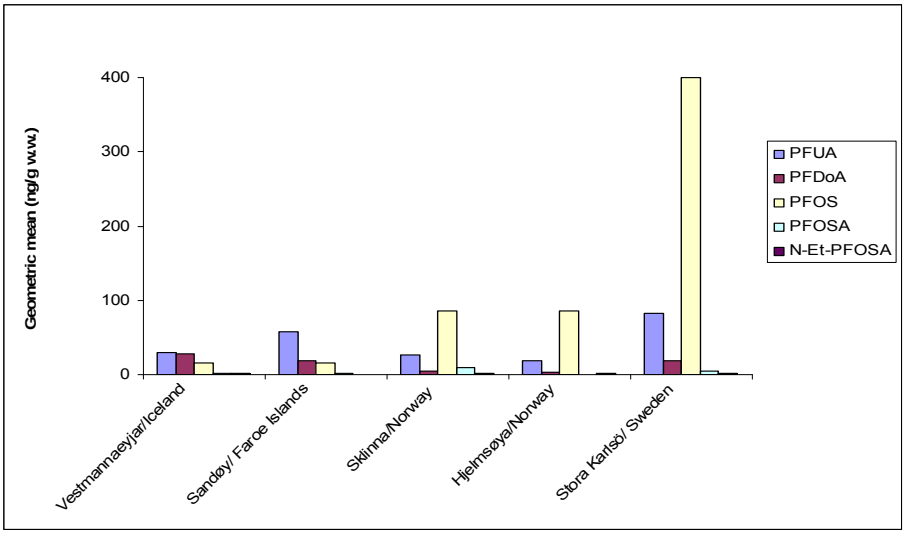


Figure 4.7. Spatial trend study of the concentration levels of five brominated compounds, PFUA, PFDoA, PFOS, PFOSA ans N-ET-PFOSA, in guillemot egg colleted at six different places in the Northern Europe. Geometric mean concentrations in ng/g ww. (From Löfstrand et al 2008)

Other studies

Norström et al (2004) performed a screening study on bis(4-chlorphenyl)sulfone (BCPS), in Swedish marine and fresh water wildlife. Four fish species from the Baltic Sea, the west coast and the inland were studied, together with fish-eating grey seal (blubber) and common guillemot (muscle) from the Baltic Sea. Beside BCPS, 2,2´-4,4´-5,5´-hexachlorobiphenyl (CB-153) and 4,4´-DDE were analyzed. BCPS was detected in all of the examined marine species but only in one of the fresh water fish samples. The highest BCPS concentrations, 1600 and 1900 ng/g lw, were found in guillemot muscle. The concentrations in grey seal were between 50-500 ng/g lw and the levels found in fish from the Baltic Sea ranged between 15-37 ng/g lw (in freshwater fish up to 1.8 ng/g lw). The author's conclusion was that BCPS was found at low concentrations in all investigated species. However the common guillemot levels indicate biomagnification to occur in this species.

Holmström and Berger (2008) determined perfluorinated surfactants in tissues and organs of the common guillemot from the Baltic Sea. Perfluorinated sulfonamide (PFOS) was predominant, followed by perfluorotridecanoate (PFTriDA) and perfluoroundecanoate (PFUnDA) in common guillemot egg, liver, kidney, liver and muscle. The concentration of PFOS was highest in eggs (325 ng/g ww) followed by chick lever (309 ng/g ww), chick kidney (127 ng/g ww), adult liver (121 ng/g ww), and adult muscle (14 ng/g ww).

Jörundsdóttir et al. (2010) analysed organochlorine compounds in eggs from seven Icelandic seabird species sampled between 2002 and 2004 The results showed very large variations in concentrations level in the different species (see Table 4.2). Congener patterns of PCB differed also between the studied bird species.

Table 4.2. Geometric mean concentrations (ng/g lw) of chlorinated compounds in eggs from different Icelandic bird species (2002-2004). Concentration levels in ng/g lw. (from Jörundsdóttir et al. 2010).

Species	n	Σ-PCB	HCB	β-HCH	4,4´-DDE	trans-Nonachlor
Eider	10	560	34	4.2	170	22
Arctic tern	6	560	57	6.4	280	8.1 (1)
Guillemot	10	1 800	310	10	1 800	7.0 (6)
Fulmar	10	5 400	270	5.1 (2)	2 800	190
Great blackbacked gull	9	7 100	330	n.d.	3 300	230
Lesser blackbacked gull	8	6 000	200	12	2 100	230
Great skua	10	62 000	710	76 (3)	23 000	1 700

In a study of levels and temporal trends of POPs (and mercury) in seabird eggs from two sites, Hornøya/Hjelmsøy in Northern Norway, Helgason et al (2008) analysed PCBs, HCB, HCH, chlordanes, nonachlors and DDT/DDEs in eggs from four different seabird species. The eggs were collected in 1983, 1993 and 2003. Generally all POP levels decreased between 1983 and 2003 in all species. The concentration levels in eggs sampled 2003 are presented in Table 4.3.

Table 4.3. Mean concentrations (ng/g lw) of chlorinated compounds in eggs from four Norwegian sea bird species, sampled at two sites in Northern Norway in 2003. (from Helgason et al 2008)

Species	Σ-PCB	HCB	β-HCH	p,p´-DDE	trans-Nonchlor
Herring gull	8 786	483	16	2 123	330
	11 596	635	31	2 687	291
Black-legged kittiwake	7 254	625	34	717	79
Guillemot	2 238	507	13	1 187	2.9
	2 333	467	13	937	3.0
Atlantic puffin	4 267	618	24	1 261	337
	4 594	665	28	1 209	243

5. Chemicals in seal

Seals are a fair choice as a species representative for studies of exposure in mammals due to its presence in so many parts of the world. However, there are many different seal species over the world and furthermore, their living areas and feeding habits are much differentiated.

In a diploma work about organic environmental pollutants in seal Frostne (2008) reviewed over 50 studies from different coastal areas as Greenland, Northern Norway, Faroe Islands, Canada Alaska,. Baltic Sea, the Bothnia Sea, Gulf of Finland, Gulf of Riga, Ladoga, White Sea. Great Britain, Denmark, West and East USA, Hawaii, Mediterranean Sea, Sahara Coast, Caspian Sea, Japan, Lake Baikal and Antarctica. The report is concentrated on data about PCB, PBDE, PCDD/PCDF. Only a few studies concerned DDT, HCH, dieldrin, chlordane, mirex and PFC. All reviewed studies were divided into sub regions, and attempts were made to perform spatial comparisons between these regions for the selected compounds. Although it was difficult to find comparable studies due to for example different choice of congeners analysed and different ways of reporting concentrations levels; wet or fresh weight (ww) or lipid weight (lw). In the following figures data from several studies from each region are summarised.

In figure 5.1 a spatial comparison of ΣPCB levels in seals, between nine regions, are shown (several studies from each regions). The result indicate higher levels in the northern Europe compared with the arctic, east North America, west USA and the middle and south Europe. However, there are large variations in published data. Figure 5.2 shows a summary of studies where the same five PBDE congeners have been analysed, in seal from five different regions. The result shows much higher PBDE-levels in seals from San Francisco Bay and the North Sea compared with the other northern regions. The levels from the other three regions are presented to the right in figure 5.2 as ΣPBDE. In figure 5.3, data from studies are shown where six congeners of PCDD/F have been analysed. Seals from the regions: San Francisco Bay and the Greenland Sea, showed lower PCDD/F-levels compared to the regions in Finland and Russia and the Gulf of Finland.

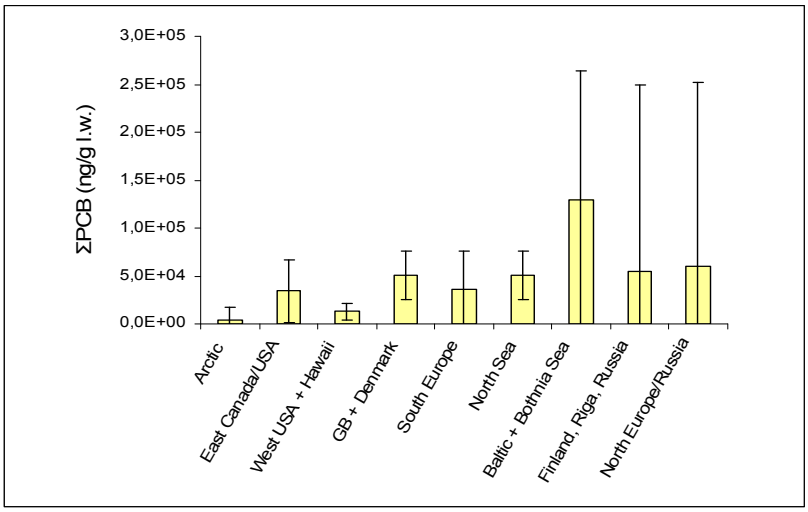


Figure 5.1. Spatial distribution of ΣPCB in blubber samples from seals collected during the years 1990-2000. Concentration levels in ng/g lw (refs in Frostne 2008).

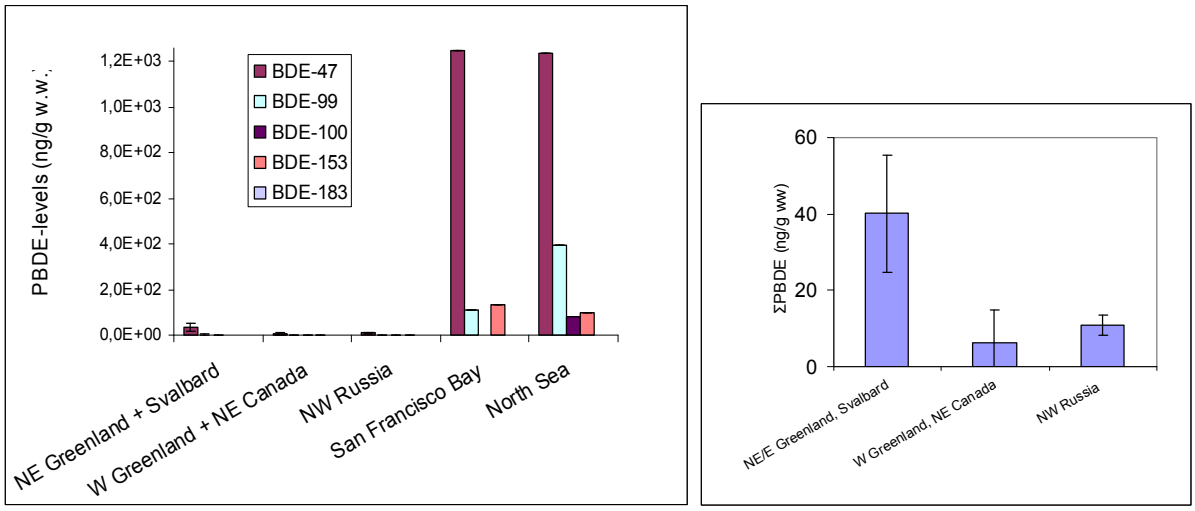


Figure 5.2 - a (left) and b (right). Spatial comparison for PBDE concentrations in seal (blubber) from different regions. a) five PBDE congeners are analysed b) calculated ΣPBDE for the three regions with too low levels to be registered in figure 5.2a. Concentration levels in ng/g ww (references in Frostne 2008).

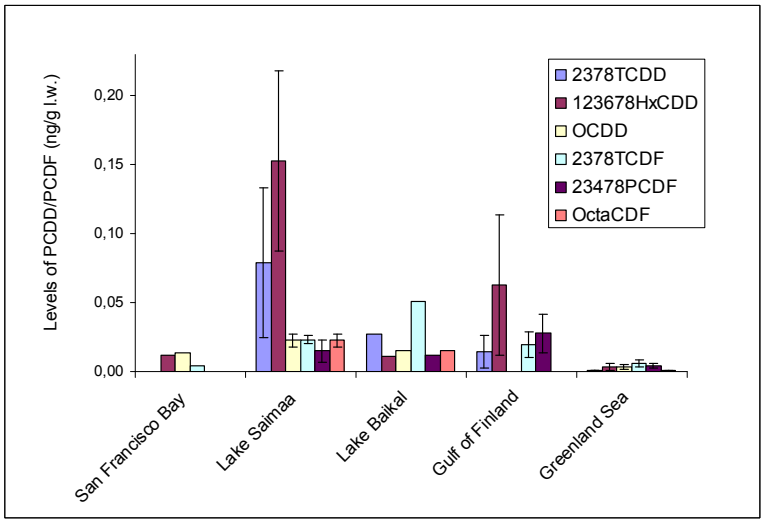


Figure 5.3. Spatial comparison of five PCDD/F congeners in seals (blubber) from seals five different regions. Concentrations in ng/g lw. (references in Frostne 2008).

A complementary literature search was performed concerning studies from more recent years. This resulted in several studies concerning studies of PFCs in seals (see below).
It also rendered a study of levels and temporal trends of organic pollutants in ringed seals. Vorkamp et al (2008) PBDEs, PCBs, DDTs, HCB, chlordane related pesticides, HCH and toxaphene were analysed in blubber of ringed seals from Central West Greenland collected between 1982 and 2006. All organochlorines showed decreasing trends. BDE-47 had a significantly annually increasing trend (5%). A clear East>West difference was found for PCBs and DDTs, but not for chlordanes, toxaphene or HCHs. Σ_{10}PCB, ΣDDT and Σchlordanes had similar annual median concentrations, typically exceeding ΣPBDE by two orders of magnitude. Statistical analyses of the compound patterns revealed significantly greater differences between seals East and West than between sampling years. Variation between locations may be due to different exposure situations but different feeding habits may also affect the contaminant composition.

In 2005 van de Vijver et al (2005) reported levels PFCs in tissues of harbor seals (Phoca vitulina) from the Dutch Wadden Sea. PFOS was the predominant compound in all samples (89-2724 ng/g ww); however with large variations between tissues. PFBS was detected (2.3±0.7 ng/g ww) in spleen tissue. The dominant perfluorinated carboxyl acids (PFCA) in all tissues was PFNA (perfluorononanoic acid), and concentrations generally decreased in tissues for all other PFCA with increasing chain length. The authors suggest large differences in tissue distribution and accumulation patterns of perfluorinated compounds in marine organisms.

Powly et al. (2008) investigated PFCs spatially and temporally, in biological samples representing an Arctic food web. Zooplankton, Arctic cod, and seal tissues from the western Canadian Arctic were analyzed for PFAS, PFCAs, and other polyfluorinated acids. PFOS was found in all samples (0.20–34 ng/g) and in the highest concentrations. PFCAs, 0-12 carbons, were quantified in most samples (0.28–6.9 ng/g). PFCAs with carbon chain lengths ≤8, 8-2 fluorotelomer acid (8-2 FTA) and 8-2 fluorotelomer unsaturated acid (8-2 FTUA), were not detected. 2H,2H,3H,3H-heptadecafluorodecanoic acid (7-3 Acid), an additional metabolite from fluorotelomer biotransformation, was detected in seal liver (0.5–2.5 ng/g). The ratios of branched to linear PFOS isomers differed between fish and seal. No branched PFCA isomers were detected. The 7-3 Acid was not correlated with either PFCAs or PFAS, which suggests a different exposure pathway.

Concentrations of PFCs in liver and serum of Baikal seals (*Pusa sibirica*) from Lake Baikal (2005) were determined by Isibashi et al. (2008). Of 10 PFC compounds measured; PFNA (3.3-72 ng/g ww) had the highest concentrations (liver), followed by PFOS (2.6-38 ng/g ww). No gender-related differences were found. Tissues from pups contained relatively higher concentrations of PFCs than tissues from adults, suggesting maternal transfer. Temporal comparisons of hepatic PFC concentrations in seal samples 1992-2005 showed that the concentrations of PFOS, PFNA and PFDA were higher in animals collected in recent years, indicating ongoing sources of PFCs. The accumulation of long-chain (C7-C12) PFCAs in particular, the predominance of PFNA, indicated that 8:2 fluorotelomer alcohol or commercially manufactured PFNA is a major local source of PFCs

Ahrens et al (2009) studied PFCs in harbour seals (*Phoca vitulina*) from the German Bight (2007). Eighteen PFCs were quantified in different tissues. PFOS was the predominant compound in all measured seal tissues (up to 1665 ng/g ww in liver). The dominant PFCAs were PFNA and PFDA, with much lower concentrations compared to PFOS.

Concentrations of PFCs were determined in liver of harbor seals (n = 68) from the northwest Atlantic (2000-2007) by Shaw et al (2009*)*. PFOS concentrations were the highest (8-1388 ng/g ww), followed by perfluoroundecanoic acid (PFUn-DA) (<1–30.7 ng/g ww). This study indicates fluorotelomer alcohols (FTOHs) to be a major source of PFCAs in the northwest Atlantic. No gender-related differences were found. Concentrations of PFOS and PFDS were higher in tissues of the pups than the adults, suggesting maternal transfer. Temporal comparisons of hepatic PFC concentrations showed a marginal increase of PFOS and PFCAs in the adult seals from 2000 to 2007.

Table 5.1. Studies of PFCs in seal tissues (2004-2009)

Region	Species/tissues	Sample year(s)	Compound(s) - predominant	Conc. level (ng/g ww)	Reference
Dutch Wadden Sea	Harbour seal, several tissues		PFOS (in all samples) PFBS (in spleen)	89-2724 1.7-3.3	van der Vijver et al 2005
Canadian arctic (west)	Ringed seal and Bearded seal Liver, blubber and blood	2004	PFOS (in all samples) PFCAs, 0-12 C (in most samples)	0.20–34 0.28–6.9	Powly et al. 2008
Lake Baikal	Baikal seals/ liver, serum	2005	PFNA PFOS	3.3-72 2.6-38	Isibashi et al. 2008
German Bight	Harbour seals/ liver	2007	PFOS	up to 1665	Ahrens et al (2009)
Northwest Atlantic	Harbour seals/ liver	2000-2007	PFOS PFUn-DA	8-1388 1–30.7	Shaw et al 2009

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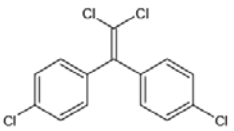
Appendix



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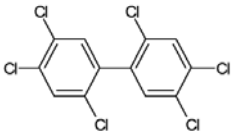

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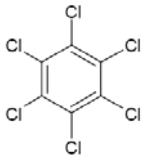

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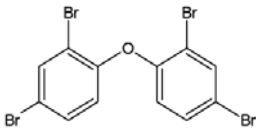

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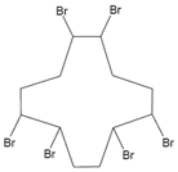

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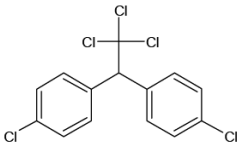

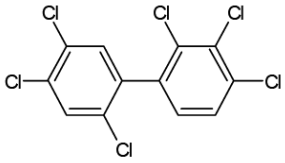

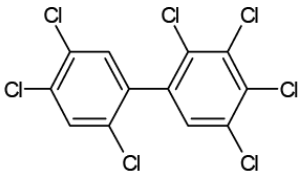

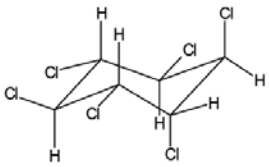

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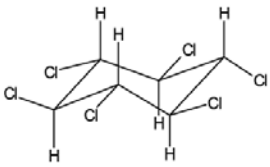

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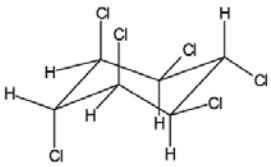

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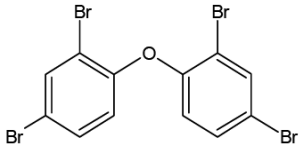

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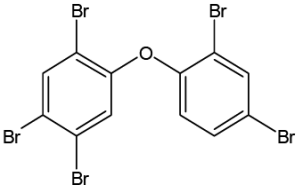

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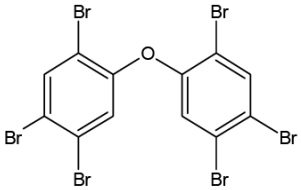

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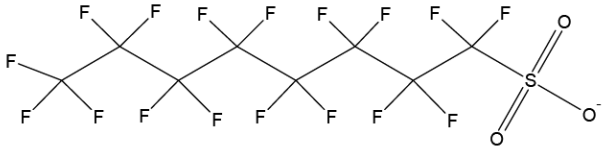

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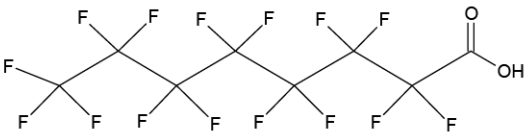

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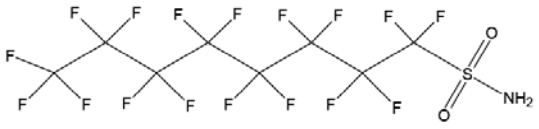

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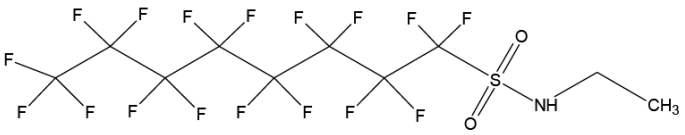

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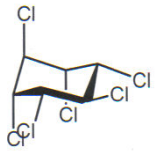
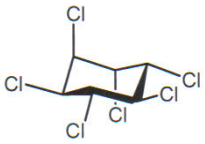


Lindan, γ–HCH



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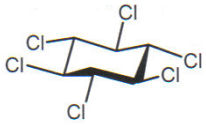
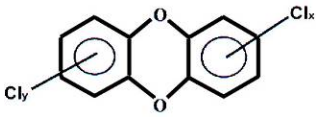
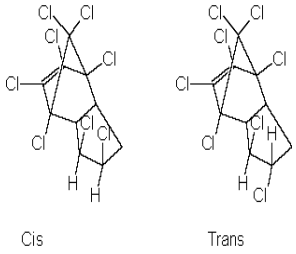


β–HCH

HCH

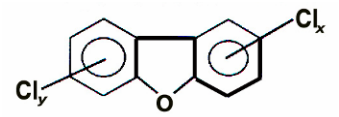


PCDD, Polychlorodibenzo-*p*-dioxins

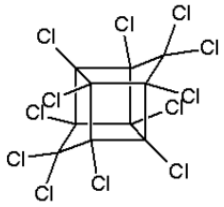


Cis Trans

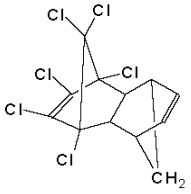
Chlordane



PCDF, Polychlorodibenzofuran



Mirex



Toxaphene