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# Perfluorinated Organic Compounds and Polybrominated Diphenyl Ethers Compounds – Levels and Toxicity in Aquatic Environments: A Review

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Additional information is available at the end of the chapter

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## 1. Introduction

Organochlorine pesticides are well known by the scientific literature to be persistent in the environment, toxic for wildlife and potential dangerous for humans since the publication of the famous volume "Silent Spring" by Rachel Carson in 1962 [1]. Due to their massive industrial production and commercialization for various human purposes, these chemicals have reached concentrations in worldwide environments that are able to significantly affect terrestrial and marine wild species [2], remote world habitats [3] including the remote deep-sea [4], and protected species listed in the IUCN Red List of Threatened Species [5]. Actual concentrations are able to severely affect trophic webs [6] and top-predators [7; 8]. As animal, humans are not excluded by the effects of pollution and concerning these compounds, feeding represents the principal and worldwide diffuse exposure mechanism for human populations rather than inhalation and dermal contact [9; 10; 11; 12]. In spite of that, only in USA, chemical industry produces about 70,000 new products and organic chemicals accounted for the greatest share of production (364.2 million tons) in 1997 [13].

The continuous research of new substances able to cover the great request from engineering, chemistry, pharmaceuticals, medical, commercial and social activities led to the direct and indirect release in environment and the consequent exposure of living organisms to new compounds. Once released in the environment, new chemicals interact with the abiotic and biotic matrices producing mixture composed by pure chemicals which auto-interact, their metabolites and/or reaction and degradation by-products. These mixture are characterized by a progressive increase of complexity and by a clear geographical footprint with percentages of chemical composition that are dependent both by physico-chemical properties of

compounds making the mixture and latitude/altitude of the geographical area considered [14]. Unluckily the effects induced by pure compounds on non-target species are frequently unknown at the time of their commercialization as well as possible by-products which are produced by the interaction with the environment. Usually, undesirable consequences of new synthesized chemicals are discovered many years later their distribution in commerce, often dramatically. This is the well-known case of the pesticide dichloro-diphenyl-trichloro-ethane (DDT) largely used to control malaria diffusion and publicized before 1970' as "the best friend of housewives in controlling pests".

Persistent organic pollutants (POPs) are characterized by molecular stability, high persistence due to the resistance to natural degradation processes derived by physical (i.e. temperature or photo-degradation), chemical (i.e. redox and acid-basic reactions, chemical interactions), and biological (i.e. metabolic or microbial deteriorations) aggressions. As reported by the European Community [15], to be classified as "persistent", chemicals must evidence a half-life in water superior than two months and in sediments/soils superior than six months.

POPs concentrate in environment for a very long time and, due to their vapor pressure  $<1000$  Pa and a half-life  $>2$  days in atmosphere, evidence long range transport reaching, also, remote areas [16]. These chemicals usually are low water soluble but evidence a great affinity towards lipids and tend to accumulate in sedimentary organic matter and biological tissues affecting the trophic web along which tend to biomagnificate [17]. Chemicals characterized by  $\log K_{ow} >5$  and by a bio-concentration factor (BEF)  $>5,000$  are considered "bioaccumulable" [15]. POPs are not biologically inert, on the contrary, they actively interact with physiological biochemistry of species inducing toxicity on wildlife species and humans.

Among POPs, perfluorinated organic compounds (PFCs) and polybrominated diphenyl ethers (PBDEs) are known as "emergent pollutants". PFCs and PBDEs are recently commercialized chemicals of particular ecotoxicological concern which are relatively little described by the literature [18]. PFCs and PBDEs increased levels during the latest decades both in environments and wildlife. Several studies have assessed them in a wide range of organisms [19], including humans [20; 21], from low latitude regions to remote areas, suggesting atmospheric transport of volatile precursor compounds and/or transport in ocean currents [22; 23; 24].

This chapter will focuses:

- general physico-chemical properties,
- sources, distribution dynamics, and environmental levels (in air, soil, water, sediment) with a particular attention on aquatic ecosystem;
- levels in wildlife tissues focusing evidences of bioaccumulation throughout the trophic web. Studies reporting levels both in red-list included species and foods at the basis of the human diet will be considered and included;
- phenomena of contamination in humans;
- evidences on toxicity based on results of ecotoxicological tests;
- international normative and guidelines developed to control considered chemicals

The following paragraphs aims to summarized actual knowledge on PFCs and PBDEs principal characteristics including environmental levels and toxicity on biota.

## 2. Physico-chemical properties of considered molecules

PFCs and PBDEs include molecules characterized by a similar chemical formula but also by very different physico-chemical properties. As consequence of the structural dissimilarities, differences concerning environmental distribution dynamics, and levels in abiotic and biological matrices are observed among PFCs and PBDEs congeners. Furthermore, the ecotoxicological risk associated to the diffusion of these persistent organic pollutants could be notably dissimilar. In fact, physico-chemical properties of molecules influence possible adverse effects on non-target biological communities. In addition, observed toxicity is notably affected by the interaction among considered chemicals and environmental matrices caused by the photo-chemical deterioration and the production of metabolites during microbial biodegradation phenomena.

### 2.1. Perfluorinated organic compounds (PFCs)

Concerning chemicals of ecotoxicological interest, perfluorinated organic compounds (PFCs) are of particular emerging interest due their documented presence both in wildlife's tissues and human blood PFCs [25].

PFCs are anionic, and fluorine-containing surfactants (both soluble in water and oil) and are applied for a large industrial and commercial employment to produce surfactants, lubricants, paints, polishes, food packaging, and fire-fighting, foams propellants, agrochemicals, adhesives, refrigerants, fire retardants, and medicines [26; 27].

Their structure consisting of a fluorine atom with which all hydrogen atoms from the linear-alkyl chain, which is a hydrophobic group, are replaced. Physico-chemical properties of PFCs favour the occurrence of long-range transport dynamics, as they are more volatile than chlorine or bromine analogues.

Among PFCs, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) represents the principal compounds of environmental concern.

Salts of perfluorooctanoic acid (PFOA,  $C_8HF_{15}O_2$ ) have been used as surfactants and processing aids in the production of fluoropolymers, and these salts are considered critical to the production of certain fluoropolymers and fluoroelastomers [28]. The functional chemical structure is  $C_7F_{15}COOH$  and for this reason tends to behavior like an acid dissociating as follows:  $C_7F_{15}COO^- + H^+$ .

Perfluorooctane sulfonate (PFOS;  $C_8HF_{17}O_3S$  even in this case it dissociates as follows:  $C_7F_{17}SO_3^- + H^+$ ) evidences an excellent chemical and thermal stability and is a chemical precursor for the synthesis of other molecules [26] such as fluorinated surfactants and pesticides (Abe and Nagase., 1982 in [29]). Perfluoroalkanesulfonate salts and

perfluorocarboxylates are reported to be present in fire-fighting foam formulations, including aqueous film forming foams which are fire-fighting materials largely used by military bases and airports to face hydrocarbon fuel fires or to prevent the potential risk of fire [30; 31]. Moody and colleagues [32] reported for the 2001, an estimated PFOS annual production quantity in United States of America of 2,943,769 kg.

Principal PFOA and PFOS chemical properties are summarized in Table 1.

	PFOA	PFOS
Extended name	Perfluorooctanoic acid	Perfluorooctanesulfonic acid
Other names	Perfluorooctanoate Perfluorocaprylic acid FC-143 F- <i>n</i> -octanoic acid	1-Perfluorooctanesulfonic acid Heptadecafluoro-1-octanesulfonic acid Perfluoro- <i>n</i> -octanesulfonic acid
<b>SUBSTANCE IDENTIFICATION</b>		
CAS numb	335-67-1	1763-23-1
Pubchem	9554	74483
EC number	206-397-9	217-179-8
<b>MOLECULAR PROPERTIES</b>		
Molecular formula	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	C <sub>8</sub> HF <sub>17</sub> O <sub>3</sub> S
Molecular mass	414.07 g mol <sup>-1</sup>	500.13 g mol <sup>-1</sup>
Boiling point	189–192 °C	133 °C (6 torr)
Appearance (25 C, 100 kPa)	colorless liquid	white powder
Vapor pressure	4.2 Pa (25 °C)	3.31 × 10 <sup>-4</sup> Pa (20 °C)
Melting point	40–50 °C	>400 °C
Solubility in water	3,400 mg L <sup>-1</sup>	519 mg L <sup>-1</sup> (20 ± 0.5 °C) 680 mg L <sup>-1</sup> (24 - 25 °C)
Solubility in other solvents	polar organic solvents	56 mg L <sup>-1</sup> (octanol)
Acidity (pKa)	2-3 <sup>[23]</sup>	calculated value of -3.27 <sup>[33]</sup>
<b>RELATED RISKS</b>		
<i>S</i> -phrases	S36, S37, S39	S61
<i>R</i> -phrases	R22, R34, R52/53	R61, R20/21, R40, R48/25, R64, R51/53

**Table 1.** Substance identification (extended names and international classification numbers), principal molecular properties, and related risks of PFOA (perfluorooctanoic acid) and PFOS (perfluorooctanesulfonic acid) are summarized in table. Specific references: record of PFOA were extracted from the GESTIS Substance Database from the IFA (last access on 5<sup>th</sup> November, 2008).

## 2.2. Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are a class of organohalogen compounds used worldwide over the past three decades as chemical additives to reduce the flammability of common use products [34]. These chemicals were first introduced to the market in the 1960s and their global demand has increased rapidly since the end of the 1970s, due to the growing popularity of personal computers and other electronic equipment, to which they were added to improve fire safety [35].

Since '70 PBDEs were used as flame retardants in a wide range of common use such as cloths, foam cushions, polyurethane sponges, carpet pads, chairs, couches, electronic instruments including computer castings, and insulating materials [36].

In 2000, the industrial production of these chemicals has been esteemed to be around the 64,000 cubic tons per year. The 50% of this annual production was commercialized in America, while in Europe only 12% [37].

Because of toxicity and persistence of PBDEs, these chemicals are included in the persistent organic pollutants (POPs) Reviewing Committee ([www.pops.int](http://www.pops.int)) and their industrial production is to be eliminated under the Stockholm Convention.

Polybrominated diphenyl ethers are, apart from the oxygen atom between the phenyl rings, structurally similar to PCBs, consisting of two halogenated aromatic rings linked by an ether group. PBDEs chemical synthesis is performed by the diphenyl-ethers bromination in presence of dibromomethane as solvent. Diphenyl-ethers have 10 hydrogen atoms and each of them can be replaced by an atom of bromine. This reaction could produce 209 possible congeners, numbered from 1 to 209 in relation to the number of bromine atoms substituting hydrogen ones and their relative position within the molecule [38].

The general chemical formula for PBDE family is  $C_{12}H_{(10-x)}Br_xO$  (where  $x = 1, \dots, 10$ ).

In the United States, PBDEs are marketed with trade names: DE-60F, DE-61, DE-62, and DE-71 applied to penta-BDE mixtures; DE-79 applied to octa-BDE mixtures; DE 83R and Saytex 102E applied to deca-BDE mixtures.

The available commercial PBDE products are not single compounds or even single congeners but rather a mixture of congeners. Nevertheless, commercial mixtures are constituted by a little part of the 209 possible congeners due to the instability of a large part of them [39] which tend to quickly debrominate.

Three technical mixtures are available and commercialized and differ related to the bromination levels:

- Mixture penta-BDE (24-38% tetra-BDE, 50-60% penta-BDE, 4-8% esa-BDE). In these mixtures, most abundant congeners are constituted by tetra-BDE 2,2',4,4' (IUPAC n. 47), penta-BDE 2,2',4,4',5 (IUPAC n. 99) and penta-BDE 2,2',4,4',6 (IUPAC n. 100), esa-BDE 2,2',4,4',5,5' (IUPAC n. 153) and esa-BDE 2,2',4,4',5,6' (IUPAC n. 154). These mixtures are viscose liquids principally used in industrial fabrication of clothes, foams, resins, polyurethane foam products such as furniture and upholstery in domestic furnishing, and in the automotive and aviation industries. The European Union banned the use of this mixture in August 2004.



- Mixture octa-BDE (10-12% esa-BDE, 44% epta-BDE, 31-35% octa-BDE, 10-11% nona-BDE, <1% deca-BDE). In these mixtures, most abundant congeners are epta-BDE 2,2',4,4',5',6 (IUPAC n. 183), and esa-BDE 2,2',4,4',5,5' (IUPAC n. 153). These mixtures are white dusts and are commonly used in little objects for house and office purposes made by plastic products, such as housings for computers, automobile trims, telephone handsets and kitchen appliance casings.
- Mixture deca-BDE (<3% nona-BDE, >97% deca-BDE (IUPAC n. 209). These mixtures are white dusts. In 2003 they represent above the 80% of the annual production of PBDE and they are, currently, the only PBDE product in production. Deca-BDE are commonly used in the following applications: thermoplastic, elastomeric, and thermo set polymer systems, including high impact polystyrene (HIPS), polybutylene terephthalate (PBT), nylon, polypropylene, low-density polyethylene (LDPE), ethylene-propylene-diene rubber and ethylene-propylene terpolymer (EPDM), unsaturated polyester, epoxy. Are used for wire and cable insulation, coatings and adhesive systems, including back-coatings for fabrics, and electronic instruments [36; 38].

PBDEs are semi volatile compounds characterized by a low vapor pressure and a scarce water solubility. These properties tends to decrease with the level of substitutions by bromine atoms in the molecular structure whereas hydrophobic properties increase. Octanol/water distribution coefficients ( $K_{ow}$ ) are variable with substitutions and are included within: 5.9-6.2 for tetra-BDE, 6.5-7.0 for penta-BDE, 8.4-8.9 for octa-BDE, and 10.0 for deca-BDE. PBDEs half-life in air are estimated to be about two days, while in water longer times are modeled (two months) whereas in soils and sediments average half-lives are six months [40].

PBDEs	Isomer	Molecular formula	Molecular mass	% bromine	Vapor pressure	Octanol/water distribution coefficient	Solubility in water
	-	-	<i>g/mol</i>	<i>m/m</i>	<i>25°C, Pa</i>	<i>log Pow</i>	<i>21 °C, µg/L</i>
mono-PBDE	3	C <sub>12</sub> H <sub>9</sub> BrO	249.0	32.09		3.6	4000
di-PBDEs	12	C <sub>12</sub> H <sub>8</sub> Br <sub>2</sub> O	327.9	48.74	2.0	5.1	500
tri-PBDE	24	C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	406.8	58.93	2.0 10 <sup>-2</sup>	5.9	90
tetra-PBDE	42	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	485.7	65.81	4.0 10 <sup>-4</sup>	6.3	20
penta-PBDE	46	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	564.6	70.77	3.0 10 <sup>-5</sup>	6.8	5
hexa-PBDE	42	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	643.5	74.51	9.0 10 <sup>-6</sup>	7.3	2
hepta-PBDE	24	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	722.4	77.43	5.0 10 <sup>-6</sup>	7.9	0.7
octa-PBDE	12	C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	801.3	79.78	4.0 10 <sup>-6</sup>	8.5	0.3
nona-PBDE	3	C <sub>12</sub> HBr <sub>9</sub> O	880.1	81.71	3.0 10 <sup>-6</sup>	9.0	0.16
deca-PBDE	1	C <sub>12</sub> Br <sub>10</sub> O	959.0	83.32	2.6 10 <sup>-6</sup>	9.5	0.10

**Table 2.** Substance identification and principal molecular properties of PBDEs (polybrominated diphenyl ethers) are summarized. The number of isomers, the molecular formula, molecular mass, % of bromine, vapor pressure, octanol/water distribution coefficients, and solubility in water are reported. Data collected by the European Food Safety Authority [41].

### 3. Sources, distribution dynamics, and environmental levels

Concerning PFCs, principal environmental sources are represented by the direct diffusion of surfactants, lubricants, paints, polishes, foams propellants, agrochemicals, adhesives, refrigerants, fire retardants, and medicines containing these chemicals. Indirect releases could occur from food packaging and painted manufacturing when discharged and exposed to rain and bad weather conditions. Nevertheless, the large use of fire-fighting materials containing PFCs both when a critical fire occurs and to prevent accidents in high risk procedure (i.e. military or firemen exercitations, routine activities, airports activities), represents the principal direct diffusion of these chemicals on the ground able to affect wide geographical surfaces, superficial and groundwater [31].

As regard as PBDEs, environmental releases could occur during manufacturing lifetimes. Releasing mechanism are not completely cleared, however, it is believed that PBDEs are released to the air when objects are manufactured and during object's life span. Their disposal and waste could produce releases too [42]. In the last years recycling of end products containing PBDE is becoming the principal source of release of these chemicals in the environment [43]. Burning of plastics, waste electronic goods, and oil shale may provide an additional PBDEs loads both in atmosphere and soil. Also, productive processes represents an important source, high levels are measured in environmental matrices closed to the flame-retardants factories [40].

Monitoring PFCs and PBDEs in environmental matrices evidenced first of all the need to develop accurate sampling strategies to collect representative samples from heterogeneous and quickly variable matrices such as air and water are. On the contrary, soils and sediments even if much more stable present structural heterogeneity (i.e. organic matter content and composition, grain-size structure, redox conditions) which could interfere with quantifications and data interpretation. Concerning biota the matter (if it is possible!) is quite more complex. Measured levels could be affected by a lot of different factors as well as age, sex, phase of animal life-stage, lipid content, water content in tissues, part of the animal excised for the analyses and much more other factors. Another point is represented by the sampling treatments and the detecting method adopted to perform laboratory analyses. Different methods are associated to different detection limits, precision and accuracy. Low polluted matrices such as air and water required methods able to detect levels of chemicals at concentrations measured in pg/L, whereas biological tissues allowed the adoption of quite less sensible methods as well as concentrations are usually measured in mg/kg or ng/g.

Hereby levels reported by the literature in different environmental matrices are reported organizing them per matrix. When possible information about the sampling strategies adopted are reported (i.e. depth of sampling for water and soils or sediments, geographical areas, type of tissues), nevertheless a complete data selection related to the sampling strategies, sampling treatments, and detecting methods has not been possible due to the wide heterogeneity in data acquisition procedures.



Extremely summarizing, perfluorooctanoic acid (PFOA) is dominant in environmental matrices whereas perfluorooctane sulfonates (PFOS) represents the predominant compound found in biota [44].

### 3.1. Air

Low data are available on air levels, probably due to the great difficulty associated to the sampling of this matrix and samples treatment strategies in laboratory. Laboratory (i.e. air, laboratory rooms, instruments, vials, etc.) and cross-over contaminations are extremely simple to occur treating air samples. Furthermore, adopted methods have to be extremely sensitive.

In the period from 1994 to 1995, measured levels of total PBDEs (congeners not specified) reached maximum values of 28 pg/m<sup>3</sup> in samples collected in Alert, Canadian Arctic [36]. The rural area of southern Ontario showed in the Early spring of 2000, notably higher levels of total PBDEs (as sum of 21 congeners detailed in the paper) ranging within 10-1,300 pg/m<sup>3</sup> [45].

Samples collected in Great Lakes from 1997-1999 evidenced total PBDEs ranging within 5.5-52 pg/m<sup>3</sup> [46], comparable levels (3.4-46 pg/m<sup>3</sup>) were measured in Ontario (2000) by Harner and colleagues [47].

### 3.2. Terrestrial environments and soils

Soil pollution could be derived by direct local sources but also by dry-air depositions or run-offs. Humus represents the soil fraction able to accumulate chemicals due to the presence of both hydrophobic and hydrophilic molecules. From here chemicals could be re-volatilized in air, transferred throughout the soil trophic web or be leached throughout rains affecting groundwater ecosystems with possible important consequences for humans. The net dominance of one of these phenomena is a factor dependent to the geographical position of the area (affecting air/soil temperature, sun irradiance, quantities of rains, etc.) and to the soil physico-chemical characteristics.

In soils sampled close to a polyurethane foam manufacturing facility in the United States, concentrations of total PBDEs (tetra- and penta-BDE) of 76 µg/kg dry weight are reported. Average values measured in soil downwind from the facility were significantly lower 13.6 µg/kg dry weight [48; 49].

In a study performed throughout the Estonian State, PBDEs levels are defined in soils for the first time. Total values observed ranging within <0.01-3.2 ng/g (d.w.) as reported by Kumar and colleagues [50]. Even if measured values are not excessive, authors predict a possible increase in the near future due to the particular waste policy of the Estonia.

In Australia, superficial samples collected in 39 remote, agricultural, urban and industrial locations from all states and territories evidenced highest (but not indicated) values from "*urban and industrial areas, particularly downstream from sewage treatment plants*" (Australian Government, on-line available at: <http://www.environment.gov.au/settlements/publications/>)

chemicals/bfr/pubs/factsheet.pdf.). In the same report, levels are indicated to be comparable to values measured in other European and Asian Countries.

### 3.3. Aquatic environments

Aquatic ecosystems represent the final reservoir for PFCs and PBDEs due to their great affinity towards sedimentary and living organic matter. In these systems, measured levels of POPs could increase along the trophic web affecting humans feeding aquatic species.

A recent study performed by Nakata and colleagues [51] evidenced significant differences among tidal and coastal levels of PFOA and PFOS in all considered environmental matrices supporting the existence of different dynamics affecting PFCs distribution and ingress in trophic webs that are zone dependant in marine ecosystems.

Even if some researchers, as reported below, have been performed to evaluate PFCs and PBDEs levels in environmental matrices and biota from river and marine ecosystems, no data are available on environmental levels, bioaccumulation and biomagnification dynamics occurring in coastal lagoons and transitional areas which are completely non explored. This lacking in scientific data could affect risk evaluations linked to human exposure to these chemicals in transitional areas. In fact lagoons and estuaries are the most populated, polluted and productive areas in the world. Feeding exploitation of these not explored ecosystems could represent a notable and not considered risk for humans.

#### 3.3.1. Water

A report produced by IFA [52] documented PFOAs levels in drinking and surface fresh water ( $n=440$ ) ranging within 0.05-456 ng/L. In Europe ( $n=119$ ) levels recorded are included within 0.33-57.0 ng/L. On the contrary, in the same dataset, measured PFOS levels in drinking and surface fresh water range within 7.1-135 ng/L, while, in Europe values are included within 21.8-56.0 ng/L reporting minimum values notably higher than PFOA levels.

Data acquired on PFOS levels from Six U.S. Urban Centres [53] evidenced ranges within <0.01-0.063 (ppb) in drinking water and values included within 0.041-5.29 (ppb) in Municipal wastewater treatment plant effluents (MWTP). Surface water are included within <0.01-0.138 (ppb) while "quiet" water values are similar to those observed in MWTP (<0.01-2.93 ppb). These data evidenced that treatment plant effluents could contribute significantly to superficial watercourse pollution.

In 2004, Boulanger and colleagues [54] explored for the first time perfluorooctane surfactants concentrations in sixteen Great Lakes water also determining PFOA and PFOS precursors samples from Great Lakes. Levels measured in water ranged within 27-50 ng/L (PFOA) and 21-70 ng/L (PFOS). The presence of PFOS precursors was recorded in all samples above the LOQ.

Hansenk and colleagues [55] performed a monitoring of the superficial Tennessee River water to evaluate possible contribution to water levels due to the activity of a fluorochemical manufacturing site (settled in Decatur, AL). PFOA levels reported are always below the de-

tection limit (25 ng/L) with the exception of samplings collected closed to the fluorochemical plant where PFOA values ranged within 140-598 ng/L. PFOS are recorded at low but often measurable levels (<25-52 ng/L) in river sampling stations evidencing a significant increase closed to the fluorochemical manufacturing facility (74.8-144.0 ng/L). This research suggests a strong contribution of plant's outflows to river PFOA and PFOS levels.

In 2005, Yamashita and colleagues [56] developed a reliable and highly sensitive analytical method to monitor PFCs in oceanic water. Between 2002-2004, levels measured in Pacific Ocean ( $n=19$ ), South China Sea and Sulu Seas ( $n=5$ ), north and mid Atlantic Ocean ( $n=12$ ), and the Japan Sea ( $n=20$ ) were respectively of: 15-142 pg/L, 76-510 pg/L, 100-439 pg/L, 137-1,070 pg/L for PFOA and 1.1-78 pg/L, <17-113 pg/L, 8.6-73 pg/L, and 40-75 pg/L for PFOS. Concerning PFOA, samples collected along coastal seawater from several Asian countries (Japan, China, Korea) evidenced levels included within: 1,800-19,200 pg/L (Tokyo Bay), 673-5,450 pg/L (Hong-Kong), 243-15,300 pg/L (China), and 239-11,350 pg/L (Korea). On the contrary, concerning PFOS values in the same sampling sites were: 338-57,700 pg/L (Tokyo Bay), 70-2,600 pg/L (Hong-Kong), 23-9,680 pg/L (China), and 39-2,530 pg/L (Korea).

A research performed in 2007 by Senthilkumar and colleagues [44] evidenced in Japan water PFOA concentrations of 7.9–110 ng/L and PFOS values ranging within <5.2–10 ng/L.

In 1999, PBDEs levels (mono- to hepta-BDE congeners) concentrations of approximately 6 pg/L were measured in Lake Ontario surface waters [57]. In this study, more than 60% of the total was composed of BDE47 (tetra-BDE) and BDE99 (penta-BDE), with BDE100 (penta-BDE) and BDEs 153 and 154 (hepta-BDE congeners) each contributing approximately 5% to 8% of the total.

Stapleton and Baker [58] analyzed water samples from Lake Michigan in 1997, 1998 and 1999 founding total PBDEs concentrations (BDEs 47, 99, 100, 153, 154 and 183) ranging within 31-158 pg/L.

### 3.3.2. Sediment

In Japan aquatic environments, Senthilkumar and colleagues [44] observed PFOA measurable levels only in sediments sampled from the Kyoto river ranging within 1.3–3.9 ng/g dry weight (dw) and not measurable PFOS levels.

Becker and colleagues [59] evidenced that once released in water, PFCs accumulate into sediments with a PFOA/PFOS ratio of about 10. In particular, PFOA were 10-fold less than PFOS but enrichment observed on sediment was not correlated to the total organic carbon contents.

In 1998, Lake Michigan evidenced average values of total PBDE of 4.2  $\mu\text{g}/\text{kg}$  dw [58].

Concerning PBDEs, levels measured in sediments from taken from fourteen Lake Ontario tributary sites [60] evidenced total PBDEs (tri-, tetra, penta-, hexa-, hepta- and deca-BDEs) levels ranging within 12-430  $\mu\text{g}/\text{kg}$  dry weight, with tetra- to hexa-BDEs sum ranging within 5-49  $\mu\text{g}/\text{kg}$  dry weight. Concentrations of BDE 209 ranged from 6.9 to 400  $\mu\text{g}/\text{kg}$  dw and BDE 47, 99 and 209 were the predominant congeners measured in sediments.

From several sites sampled along the Columbia River system, in south eastern British Columbia, Rayne and colleagues [61] measured PBDE concentrations (as sum from di- to penta-BDE congeners) included within 2.7-91 µg/kg.

Sediments from two Arctic lakes in Nunavut Territory evidenced measurable concentrations from 0.075 to 0.042 µg BDE 209/kg dw. One of the two Arctic lakes sampled was located near an airport and PBDEs inputs from this source could not be excluded [62]. Authors hypothesized a particles-mediated transport to the Canadian Arctic due to its low vapour pressure and high octanol-water partition coefficient.

Sludge sampled from Municipal wastewater treatment plants evidenced total PBDEs (21 mono- to deca-BDE congeners) ranging from 1,414 to 5,545 µg/kg dw [63]. A regional sewage treatment plant discharging to the Dan River in Virginia evidenced in 2000 total PBDEs (sum of BDEs 47, 99, 100 and 209) of 3,005 µg/kg dw [48].

### 3.4. Biota

POPs could accumulate in species evidencing interspecies differences as well as sex and size-related ones [64]. Recent studies evidenced that POPs concentrations in demersal fishes varies significantly relating to the sex, maturity, and reproduction [65].

Data collected in fishes and fishery products [52] evidence PFOA levels ranging within 0.05-5.00 ng/g wet weight (w.w.) (muscle of whole body) in Europe [66], 0.13-18.70 ng/g w.w. in Asia [67; 68], and 0.70-2.40 ng/g w.w. in North America [69].

Crustaceans levels are quite similar in their edible parts and respectively of 0.80-0.90 ng/g w.w. [66], 0.13-9.50 ng/g w.w. [51], and 0.10-0.50 ng/g w.w. [70] respectively in Europe, Asia, and North America. Observed levels in edible part of molluscs ranged within 0.95-1.20 ng/g w.w. in species from Europe [66], 0.10-22.90 ng/g w.w. from Asia [67; 68]. Molluscs in North America showed levels closed to the detection limits (0.10 ng/g w.w.) as reported by Tomy and colleagues [70].

Concerning PFOS in fish muscles or whole body ranged within 0.60-230 ng/g w.w. in Europe, 0.380-37.30 ng/g in Asia [68], and 15.1-410 ng/g in North America [71]. Crustaceans evidences levels included within 8.30-319 in Europe [66], 0.15-13.9 in Asia [67], and 0.03-0.90 in North America [70], while molluscs showed PFOS levels of 0.80-79.80 in Europe [72], 0.114-47.200 in Asia [68], and 0.080-0.600 in North America.

Kannan and colleagues [73] performed a screening of PFOA and PFOS in wildlife species from different trophic levels and ecosystems. Concerning PFOS in blood samples collected in aquatic mammals and fishes, a tendency to the decrease of measured levels is reported for bottlenose dolphins>bluefish tuna>swordfish. They reported that PFOS concentrations (61 ng/g, w.w.) measured in cormorant livers collected from Sardinia Island (Italy) are lower than PFOA (95 ng/g, w.w.) but significantly correlated.

In the same research, PFOS levels measured in liver samples collected from ringed and gray seals (Bothnian Bay, Baltic Sea) range within 130-1,100 ng/g, w.w.. In this case, no relationships are observed between PFOS levels and ringed or gray seals age but levels measured in



livers are 2.7-5.5 fold higher than values in blood with a positive strong correlation between blood and liver levels. Concerning white-tailed sea eagles (Germany and Poland) indicate increasing of concentrations from 1979 to 1990s. Livers of Atlantic salmon do not evidenced measurable levels neither PFOS nor PFOA.

In 2007, Senthilkumar and colleagues [44] define levels of PFOA and PFOS in biotic compartment of aquatic ecosystems in Japan. Concerning fish tissues, only jack mackerel showed PFOA and PFOS respectively at averages of 10 and 1.6 ng/g w.w.. Wildlife livers contained PFOS levels ranging within 0.15–238 ng/g w.w. and PFOA values included within <0.07–7.3 ng/g w.w.. Cormorants showed maximum accumulation followed by eagle, raccoon dog and large-billed crow.

Kannan and colleagues [73] measured PFOA and PFOS levels in livers of birds collected from Japan and Korea ( $n= 83$ ). PFOS was found in the livers of 95% of the birds analyzed at concentrations greater than the limit of quantitation (LOQ=10 ng/g, w.w.). The greatest concentration of PFOS of 650 ng/g, w.w., was found in the liver of a common cormorant from the Sagami River in Kanagawa Prefecture.

Borghesi and colleagues [24] evidenced a PBDEs concentrations in Antarctic fish species ranging within average of 0.09 ng/g (w.w.) recorded in *G. nicholsi* to average of 0.44 ng/g (w.w.) measured in *C. gunnari*. In Mediterranean tuna PBDEs levels were two or three orders of magnitude higher (15 ng/g w.w.). Furthermore, PBDE congener profiles differ between species; low brominated congeners prevailed in Antarctic species while in tuna tetra- and penta-bromodiphenyl ethers are the most abundant groups (41% and 44%, respectively). In the same study, a strong correlation with the fish length is observed for the species *C. hamatus* but the same relation is not recorded considering the weight. Tuna evidences a gender dependency in PBDEs concentrations in fact levels are significantly high in females than in males (18 ng/g vs 13 ng/g w.w.) which authors attribute to the lower fat content in males.

#### 4. Human exposure

PBDEs levels in humans have increased over the past several decades. Schiavone and colleagues [74] measured PBDEs in human lipid tissues from Italy even if at values lower than other POPs (PCBs and DDTs). These chemicals are structurally similar to thyroid hormones (i.e. thyroxine T4) and could disrupt thyroid homeostasis as observed in laboratory experiments on animals [75] causing damages similar to thyroid hormone deficiencies [76; 77].

Effects on male reproductive system have been documented by the literature due to the weak estrogenic/antiestrogenic activity of these chemicals [78]. In rats, the exposure to a single dose of 60 µg/kg body weight (b.w.) of PeBDE-99 produces significant decreases of sperm numbers. Akutsu and colleagues [79] evidenced relationship between human serum PBDEs and sperm quality. In particular, PBDE levels in Japan men are comparable to those found in European countries and a strong inverse correlations were ob-

served between the serum concentration PeBDE-99 and sperm concentration ( $r = -0.841$ ,  $p = 0.002$ ) and testis size ( $r = -0.764$ ,  $p = 0.01$ ).

The Department of the Environment and Water Resources of Australia founded in 2004 a research aimed to evaluate PBDEs levels in indoor environments collecting and analysing samples from air, dust and surfaces from homes and offices in south-east Queensland. Concentrations of PBDEs were greater in indoor air than in outdoor once, evidencing that major risks are related to the indoor exposure. Furthermore, the lowest PBDE concentration in indoor dust was found in a house with no carpet, no air-conditioning, and which was older than five years. The highest concentration was found in an office with carpet and air-conditioning, and which had been refurbished in the last two years. A recent study developed by Meeker et al. [77] evidenced altered serum hormone levels in US men affected by infertility clinic ( $n=24$ ) as a result of indoor exposure to PBDE. BDE 47 and 99 were detected in 100% of dust samples, and BDE 100 was detected in 67% of dust samples. A significant inverse relationship between dust PBDE concentrations and free androgen index was observed. Furthermore, dust PBDE concentrations were inversely associated with luteinizing hormone (LH) and follicle stimulating hormone (FSH), and positively associated with inhibin B and sex hormone binding globulin (SHBG).

Concerning POPs levels in humans, infants show the higher feeding exposure compared to adults due to their high feed consumption per kilogram of body weight. Weijs *et al.*, [80] evidenced in not-breastfed Dutch infants a progressively increasing exposure to POPs during the first year growth from the birth due to the diet changes. Concerning PBDEs, the mean level measured in breast milk was  $3.93 \pm 1.74$  ng/g lipid and the estimated PBDE daily intake for a breastfed infant was 20.6 ng/kg b.w./day after delivery [81].

Chao and colleagues [82] evidenced that, in Taiwan, PBDEs levels in breast milk ( $n= 46$ ) are associated with demographic parameters, socioeconomic status, lifestyle factors, and occupational exposure. Average levels measured in 2010 (1.07-3.59 ng/g lipid) were 0.7-fold lower than in 2000. Furthermore higher levels of PBDEs were positively correlated to the maternal age and are not correlated with maternal pre-pregnant BMI (Body mass index), parity, and lipid contents of breast milk.

PBDEs level in breast milk is lower in more educated women after controlling for age and pre-pregnancy BMI in tested mothers, nevertheless these results are not completely in agreement with Wang and colleagues [83] which evidenced that the mean level of BDE47 in breast milk from mothers with pre-pregnant BMI  $<22.0$  kg/m<sup>2</sup> had a significantly higher magnitude compared to those with pre-pregnant BMI  $>22.0$  kg/m<sup>2</sup> (1.59 *vs* 0.995 ng/g lipid,  $p= 0.041$ ) and no relationships between PBDEs exposure levels and women's age, parity, blood pressure, annual household income, and education level.

Evidences regarding a relationship between PBDEs levels in breast milk and seafood consumptions in Taiwan has been explored by the literature [83]. Women eating more fish and meat show not significantly higher PBDE levels than others nevertheless, a significant difference in PBDE levels was demonstrated between the higher (2.15 ng/g lipid) and lower (3.98 ng/g lipid) shellfish consuming subjects ( $p = 0.002$ ) after an adjustment for the confounders.



Concerning ratios (PCB153/BDE47, PCB153/BDE153, PCB153/PBDEs) a significant correlation with frequent consumption of fish and shellfish is observed.

## 5. Ecotoxicological effects

Data collected by 3M [84; 85] on ecotoxicological effects of PFOS on aquatic species evidenced after 96h of exposure an  $E_b C_{50(\text{biomass})}$  of 71 mg/L, an  $E_g C_{50(\text{growth rate})}$  of 126 mg/L, and a  $NOEC_{(\text{biomass/growth rate})}$  of 48 mg/L on *Selenastrum capricornutum* (Algae). Acute effects on the oyster shell deposition are observed at 2.1 mg/L (96h NOEC) whereas subchronic/chronic effects were recorded on *Mysidopsis bahia* (mysid. shrimp) at 0.25 mg/L (35-day NOEC reproduction/growth). The same species evidenced respectively acute effects at 4.0 mg/L (96h  $EC_{50}$ ) and 1.2 mg/L (96h NOEC).

The species *Crassostrea virginica* evidenced acute toxicity at levels higher than 3.0 mg/L (96h  $EC_{50}$ ) and 96h NOEC at 1.9 mg/L.

Acute toxicity is observed in *Daphnia magna* exposing animals at 66 mg/L (48h  $EC_{50}$ ) whereas chronic effects are observed over 7 mg/L (28day  $NOEC_{\text{reproduction}}$ ).

*Unio compalmatus* (freshwater mussel) evidenced 96h  $LC_{50}$  of 59 mg/L and 96h NOEC of 20 mg/L.

Sanderson and colleagues [86] evidenced the ecological effects induced by the exposure to perfluorinated surfactants (PFOS and PFOA), on zooplankton species performing using classical ecotoxicological tests, 30-L indoor microcosm and 12,000-L outdoor microcosm experiments. The zooplankton community considered in this experiment was composed by the following representative species: *Cyclops diaptomus*, *C. strenuus*, *Canthocamptus staphylinus*, *D. magna*, *Keratella quadrata*, *Phyllopora sp.*, *Echninorhynchus sp.*, *Ostracoda sp.*, and total *Rotifera sp.* In addition to zooplankton and pond snails, occasional macrophytes (*Elodea canadensis* and *Myriophyllum spicatum*), and larger invertebrates (*Ephemeroptera sp.*, *Assellus aquaticus*) were present.

Results evidenced that zooplankton had lower tolerance toward PFOS than toward PFOA. Researchers observed that "with increasing concentrations the zooplankton community became simplified toward more robust rotifer species, which, as an indirect effect, increased their abundance due to a shift in competition and predation".

Concerning PFOA, classical ecotoxicological tests results on  $LOEC_{\text{community}}$  are not available, whereas 30-L indoor and 12,000-L outdoor produce similar results ( $LOEC_{\text{community}}$  30-70 mg/L).

Concerning PFOS, classical ecotoxicological tests evidenced  $LOEC_{\text{community}}$  ranges within 13-50 mg/L, while 30-L indoor and 12,000-L outdoor exposure tests produce a  $LOEC_{\text{community}}$  respectively of 1-10 mg/L and 10-30 mg/L.

Concerning fishes the species *Pimephales promelas* (fathead minnow) shows 96h LC<sub>50</sub> of 10 mg/L and 96h NOEC of 3.6 mg/L, the species *Lepomis macrochirus* (bluegill sunfish) has a 96h LC<sub>50</sub> of 7.8 mg/L and 96h NOEC of 4.5 mg/L.

Chronic exposure of the fathead minnow *Pimephales promelas* reported 42-day NOEC<sub>survival</sub> of 0.33 mg/L and 47-day early life LOEC of 0.65 mg/L.

Functional studies evidenced that PFOS inhibits gap junction intercellular communication (GJIC) in rat liver epithelial cells cultured *in vitro* (personal communication reported in [29]) and that it is an uncoupler of phosphorylation in rat liver mitochondria (personal communication reported in [29]).

PBDEs can inhibit growth in colonies of plankton and algae and depress the reproduction of zooplankton.

Laboratory mice and rats have also shown liver function disturbances and damage to developing nervous systems as a result of exposure to PBDEs (<http://www.environment.gov.au/settlements/chemicals/bfrs/index.html>).

Ecotoxicological tests performed on PBDEs on different species and medium following exposed expressing results as: LC<sub>50</sub>(median lethal dose), LOAEL<sub>(Lowest-Observed-Adverse-Effect Level)</sub>, LOEC<sub>(Lowest-Observed-Effect Concentration)</sub>, NOAEL<sub>(No-Observed-Adverse-Effect Level)</sub>, and NOEC<sub>(No-Observed-Effect Concentration)</sub>. The use of the letter "a" following data means that in the study reported highest concentration (or dose) tested did not result in statistically significant results. Since the NOEC or NOAEL could be higher, the NOEC or NOAEL are described as being greater than or equal to the highest concentration (or dose) tested.

As reported by CMABFRIP [87], *Daphnia magna* (younger than 24h old at the start of the exposure) exposed to a PeBDE mixture containing 33.7% of tetra-BDE, 54.6% of penta-BDE, and 11.7% hexa-BDE following the GLP, protocol based on OECD (Organisation for Economic Co-operation and Development) 202, TSCA (*Toxic Substances Control Act*) Title 40 and ASTM E1193-87, evidences reported levels:

- 17 µg/L (96-hour EC<sub>50mortality/immobility</sub>),
- 20 µg/L (21-day LOEC<sub>mortality/immobility</sub>),
- 9.8 µg/L (21-day NOEC<sub>mortality/immobility</sub>),
- 14 µg/L (7- to 21-day EC<sub>50mortality/immobility</sub>),
- 14 µg/L (21-day EC<sub>50reproduction</sub>),
- 9.8 µg/L (21-day LOEC<sub>growth</sub>),
- 5.3 µg/L (21-day NOEC<sub>growth</sub>),
- 9.8 µg/L LOEC<sub>(overall study)</sub>,
- 5.3 µg/L NOEC<sub>(overall study)</sub>.

Exposing *Daphnia magna* to an OBDE mixture composed by 5.5% hexa-BDE, 42.3% hepta-BDE, 36.1% octa-BDE, 13.9% nona-BDE, 2.1% deca-BDE (European Communities 2003) for

21 days with the same protocol adopted for the other exposure (GLP, protocol based on OECD 202, ASTM E1193-87 and TSCA Title 40), results were the follow [13]:

- 21-day LOEC<sub>(survival, reproduction, growth)</sub> > 2.0 µg/L<sub>(nominal)</sub> or 1.7 µg/L<sub>(measured)</sub>
- 21-day NOEC<sub>(survival, reproduction, growth)</sub> >= 2.0 µg/L<sub>(nominal)</sub> or 1.7 µg/L<sub>(measured)</sub><sup>a</sup>
- 21-day EC<sub>50(survival, reproduction, growth)</sub> > 2.0 µg/L<sub>(nominal)</sub> or 1.7 µg/L<sub>(measured)</sub>

The Great Lakes Chemical Corporation [88], reported ecotoxicological results obtained on adults of the species *Lumbriculus variegatus*. The exposure mixture of PeBDE is composed by the 0.23% tri-BDE, 36.02% of tetra-BDE, 55.10% penta-BDE, 8.58% hexa-BDE and the exposure protocol is GLP, protocol based on Phipps et al. [89], ASTM E1706-95b and U.S. EPA OPPTS (Office of Prevention, Pesticides and Toxic Substances) No. 850.1735. Animals were exposed at 23 ± 2°C, pH 7.9-8.6, DO 6.0-8.2 mg/L, hardness 130 mg/L as CaCO<sub>3</sub>. On artificial sediment with the following characteristics: pH 6.6, water holding capacity 11%, mean organic matter <2%, 83% sand, 11% clay, 6% silt.

Results collected were the follows:

- 28-day LOEC<sub>(survival/reproduction)</sub> = 6.3 mg/kg dw of sediment
- 28-day NOEC<sub>(survival/reproduction)</sub> = 3.1 mg/kg dw of sediment
- 28-day EC<sub>50(survival/reproduction)</sub> > 50 mg/kg dw of sediment
- growth<sub>(dry weights)</sub> not significantly different from solvent control and not concentration-dependent.

The exposure of the same species to an OBDE (DE-79) mixture characterized by the 78.6% bromine content following the GLP, protocol based on Phipps et al. [89], ASTM E1706-95b and U.S. EPA OPPTS 850.1735, evidenced the following results [90; 91]:

- 28-day LOEC<sub>(survival/reproduction, growth)</sub> > 1,340 (2% Organic carbon, OC) or 1272 (5% OC) mg/kg dw of sediment,
- 28-day NOEC<sub>(survival/reproduction, growth)</sub> >= 1,340 (2% OC) or 1,272 (5% OC) mg/kg dw of sediment,
- 28-day EC<sub>50(survival/reproduction, growth)</sub> > 1,340 (2% OC) or 1,272 (5% OC) mg/kg dw of sediment,
- For 2% OC study: average individual dry weights for treatments statistically lower than in control; not considered treatment-related by authors, as average biomass in treatments comparable to control.

The exposure of the adult earthworm *Eisenia fetida* to an OBDE (DE-79) mixture at 78.6% bromine content following the GLP, protocol based on U.S. EPA OPPTS 850.6200, OECD 207 and proposed OECD (2000) guideline on artificial soil (sandy loam, 69% sand, 18% silt, 13% clay, 8.0% organic matter, 4.7% carbon) at 17-21°C with a photoperiod of 16:8 light:dark, pH 5.9-6.8, soil moisture 22.0-33.5%.

Results [92] obtained are the follow:

- 28-day LOEC<sub>(mortality)</sub> > 1,470 mg/kg dry soil
- 28-day NOEC<sub>(mortality)</sub> >= 1,470 mg/kg dry soil<sup>a</sup>
- 28-day EC<sub>10</sub>, EC<sub>50(survival)</sub> > 1,470 mg/kg dry soil
- 56-day LOEC<sub>(reproduction)</sub> > 1,470 mg/kg dry soil
- 56-day NOEC<sub>(reproduction)</sub> >= 1,470 mg/kg dry soil<sup>a</sup>
- 56-day EC<sub>10</sub>, EC<sub>50(reproduction)</sub> > 1,470 mg/kg dry soil

ACCBFRIP [93] reported for the exposure of the species *Eisenia fetida* to a DBDE mixture composed by the 97.90% of deca-BDE, the following results:

- 28-day LOEC<sub>(survival)</sub> > 4,910 mg/kg dry soil<sub>(mean measured)</sub>
- 28-day NOEC<sub>(survival)</sub> >= 4,910 mg/kg dry soil<sub>(mean measured)a</sub>
- 28-day EC<sub>10</sub>, EC<sub>50(survival)</sub> > 4,910 mg/kg dry soil<sub>(mean measured)</sub>
- 56-day LOEC<sub>(reproduction)</sub> > 4,910 mg/kg dry soil<sub>(mean measured)</sub>
- 56-day NOEC<sub>(reproduction)</sub> >= 4,910 mg/kg dry soil<sub>(mean measured)a</sub>
- 56-day EC<sub>10</sub>, EC<sub>50(reproduction)</sub> > 4,910 mg/kg dry soil<sub>(mean measured)</sub>

On the contrary, the exposure of *Lumbriculus variegatus* to a DBDE mixture composed by 97.3% of deca-BDE and 2.7% of other (not specified) composite from three manufacturers), evidenced the following results [94; 95]:

- 28-day NOEC<sub>(survival/reproduction, growth)</sub> >= 4,536 (2.4% OC) or 3,841 (5.9% OC) mg/kg dw of sediment,
- 28-day LOEC<sub>(survival/reproduction, growth)</sub> > 4,536 (2.4% OC) or 3,841 (5.9% OC) mg/kg dw of sediment,
- 28-day EC<sub>50(survival/reproduction, growth)</sub> > 4,536 (2.4% OC) or 3,841 (5.9% OC) mg/kg dw of sediment.

The Great Lakes Chemical Corporation [96], reported ecotoxicological results obtained on the species *Zea mays* corn. *The exposure mixture was the same adopted on the earthworm* [97] and the exposure protocol is GLP, protocol based on U.S. EPA OPPTS Nos. 850.4100 and 850.4225 and OECD 208 (based on 1998 proposed revision). Plants were exposed on artificial soil (92% sand, 8%clay and 0% silt), with pH 7.5, organic matter content 2.9% and watering with well water using subirrigation (14:10 light:dark photoperiod, 16.0-39.9°C, relative humidity 19-85%).

Results collected were the follows:

- no apparent treatment-related effects on seedling emergence,
- 21-day LC<sub>25</sub>, LC<sub>50 (seedling emergence)</sub> > 1,000 mg/kg soil dw,

- mean shoot height significantly reduced at 250, 500 and ,1000 mg/kg soil dw relative to controls,
- 21-day  $EC_{25}$ ,  $EC_{50}$  (mean shoot height) > 1,000 mg/kg soil dw,
- mean shoot weight significantly reduced at 62.5, 125, 250, 500 and 1,000 mg/kg soil dw relative to controls,
- 21-day  $EC_{25}$  (mean shoot weight) = 154 mg/kg soil dw,
- 21-day  $EC_{50}$  (mean shoot weight) > 1,000 mg/kg soil dw,
- 21-day LOEC (mean shoot weight) = 62.5 mg/kg soil dw
- 21-day  $EC_{05}$  and (estimated) NOEC (mean shoot weight) = 16.0 mg/kg soil dw.

The Great Lakes Chemical Corporation [98], reported ecotoxicological results obtained on the Rat. The exposure mixture PeBDE (DE-71) was composed by 45-58.1% of penta-BDE, 24.6-35% tetra-BDE [99; 100]. Exposure doses of PeBDE were 0, 2, 10 and 100 mg/kg bw per day (doses adjusted weekly based on mean body weight of animals) and after 90 days observed effects were:

- decreased food consumption and body weight, increased cholesterol, increased liver and urine porphyrins at 100 mg/kg bw dose,
- increased absolute and relative liver weights at 10 and 100 mg/kg bw, with return to normal ranges after 24-week recovery period,
- compound-related microscopic changes to thyroid and liver at all dosage levels,
- microscopic thyroid changes reversible after 24 weeks,
- microscopic liver changes still evident at all dosage levels after 24-week recovery period,
- liver cell degeneration and necrosis evident in females at all dosage levels after 24-week recovery,
- LOAEL (liver cell damage) = 2 mg/kg bw,
- NOAEL could not be determined, as a significant effect was observed at the lowest dose tested.

Exposing rats to a DBDE (Dow-FR-300-BA) mixture with the relative composition of 77.4% of deca-BDE, 21.8% nona-BDE and 0.8% octa-BDE, results evidenced [101]:

- LOAEL (enlarged liver, thyroid hyperplasia) = 80 mg/kg bw per day,
- NOAEL = 8 mg/kg bw per day.

Little data have been gathered on the associations between PBDEs exposure and birth outcome and female menstruation characteristics in both epidemiological and animal studies. In rats, the *in utero* exposure to PBDEs reduces the number of ovarian follicles in rat females and causes permanent effects on rat males [81].



Breslin and colleagues [102] exposed rabbits to an OBDE (Saytex 111) mixture 0.2% penta-BDE, 8.6% hexa-BDE, 45.0% hepta-BDE, 33.5% octa-BDE, 11.2% nona-BDE, 1.4% deca-BDE evidencing the following results:

- no evidence of teratogenicity,
- $LOAEL_{(maternal, increased\ liver\ weight, decreased\ body\ weight\ gain)} = 15\ mg/kg\ bw\ per\ day,$
- $NOAEL_{(maternal)} = 5.0\ mg/kg\ bw\ per\ day,$
- $LOAEL_{(fetal, delayed\ ossification\ of\ sternebrae)} = 15\ mg/kg\ bw\ per\ day,$
- $NOAEL_{(fetal)} = 5.0\ mg/kg\ bw\ per\ day.$

## 6. Conclusions

Recent data collected on these chemicals evidence significant levels in environments, wild-life and humans. In particular, observed ecotoxicological effects on species, measured values in humans tissues and their relationships with fertility suggest that PFCs and PBDEs represent an important problem to be quickly solved. Unfortunately, collected data both on chemical distribution in abiotic and biotic matrices are fragmentary and incomplete as well as ecotoxicological studies on laboratory species and microcosms. Studies in aquatic ecosystems and, in particular, in transitional ones have to be improved to allow a correct evaluation of the exposure risk for humans to these compounds due to the dietary intakes.

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