The distribution of octachlorostyrene (OCS) in environmental samples from Europe

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Although octachlorostyrene (OCS) was never used as a commercial product, it may be produced during incineration and combustion processes involving chlorinated compounds. Its environmental spreading was evaluated through the analysis of several representative samples. OCS could not be measured in soil samples collected from urban and rural areas or sediments, but was present (up to 5.41 ng/g dry weight) in industrial soil collected near chemically polluted areas. For aquatic biota samples, the OCS concentrations in freshwater mussels ranged from <0.01 ng/g wet weight (ww) to 0.18 ng/g ww (mean 0.06 ng/g ww) and similar levels could be measured in 11 freshwater fish species from Belgium and Romania. A higher OCS contamination level was found in shrimps (mean 0.08 ng/g ww) compared to marine fish (mean 0.02 ng/g ww for bib and 0.01 ng/g ww for sole and whiting, respectively). OCS could also be measured in 19 harbour porpoise (*Phocoena phocoena*) liver samples with a mean value of 1.90 ng/g ww. According to these data, it could be computed that the biomagnification factor for OCS was one order of magnitude lower than that of HCB in the fish–porpoise food chain. The mean OCS concentrations in blue tits (*Parus caeruleus*) eggs and great tits (*Parus major*) adipose tissue were 1.24 ng/g ww and 3.24 ng/g ww, respectively. OCS could be measured in different tissues of hedgehog (*Erinaceus europaeus*), with the highest concentrations found in adipose tissue (mean 0.34 ng/g ww) and liver (mean 0.39 ng/g ww). In contrast, only low concentrations of OCS could be measured in human adipose tissue (up to 0.38 ng/g ww) and liver (up to 0.05 ng/g ww), while it could not be detected in human brain or lung. The relationship between the concentrations of OCS and HCB was also discussed for each species.

Introduction

While the global environmental distribution of chlorinated aromatic compounds, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides, has been well-documented,[1–3] much less is known about the extent of global contamination with octachlorostyrene (OCS). Firstly found in samples of dead cormorants,[4] OCS was occasionally measured in environmental samples such as sediments,[5,6] fish,[7–12] marine mammals[13,14] and human blood.[15–16]

Although OCS exhibited no mutagenicity in a bacterial bioassay and it was not considered acutely toxic,[17] the long-lasting environmental impact of chlorinated styrenes is still unclear. It was reported that workers exposed to OCS had a statistically significant increase in urinary total porphyrins, which remained detectable even years after exposure ceased.[16,18] There is also a lack of eco-toxicological information for this pollutant. The half-life time of OCS in artificially raised rainbow trout liver[17,19] was nearly twice as long as for hexachlorobenzene (HCB), while under natural conditions, the elimination half-life time of OCS in yellow eel was in the same order of magnitude as for tetra- and penta-CB congeners.[20]

The presence of OCS in the environment has been particularly puzzling since this compound has never been a commercial product, but instead used only for experimental synthetic purposes. Little is known about global emissions of OCS and its geographical distribution. Magnesium production, chlorinated solvents manufacturing and aluminium degassing with hexachloroethane used to be the most important historical source of OCS,[21] while its chemical formation as a by-product from waste material burning at temperatures between 600–800 °C is considered as the main present pollution source.[22] The production of OCS was linked to the production of HCB and polychlorinated dibenzodioxins (PCDDs); in general, it appears that whenever HCB and/or PCDDs are formed and emitted from a chemical reaction (combustion, incineration, fusion of chloride salts at carbon electrodes, *etc.*), OCS is also potentially formed.[21]

OCS was only occasionally detected in some environmental investigations that had other pollutants (PCBs and organochlorine pesticides, such as HCB) as targeted analytes. However, OCS was consistently found in fish and sediment samples collected near incineration areas[10] or near potential point sources due to industrial discharges.[21] Systematic studies of environmental distribution of OCS residues are scarce in literature, while the relationship between OCS and other persistent organic pollutants is often not investigated.

The aim of the present study is to obtain comparative data and background information on OCS residues in species from European aquatic and terrestrial ecosystems and to explore possible relationships between OCS and other pollutants, especially HCB.

Experimental procedures

Sample collection

A large number of samples, which included soil, sediment, mussels, shrimps, fish, cod liver oil, harbour porpoise liver, birds (adipose tissue and eggs), hedgehogs (liver, adipose tissue, muscle and kidney), human serum and tissues (liver, lung, adipose tissue and brain) were collected during the period of other investigation projects from different locations in Belgium, Romania and the United Kingdom between 1997–2002. Sample details and the scientific names of the investigated species are given in Table 1. The shrimp and fish samples from

the Belgian North Sea and Scheldt estuary were pooled according to the sampling locations. All samples were kept at −20 °C until analysis.

Materials

Standard solutions of OCS, HCB, PCB 46 and 143 were purchased from Dr. Ehrenstorfer (Augsburg, Germany). All solvents (hexane, acetone, iso-octane and dichloromethane) were of pesticide grade purity (Merck, Darmstadt, Germany). Anhydrous sodium sulfate (Merck) was heated at 600 °C for 6 h in a muffle furnace. The acidified silica (45%, w/w) was prepared by dropwise addition of concentrated sulfuric acid (95–97%) to activated silica gel under continuous stirring.

Sample extraction and clean up

Accurate sample amounts (2–5 g soil, sediment or tissue and 0.2–0.5 g adipose tissue) were ground with anhydrous sodium sulfate until a free-flowing powder was obtained. Samples were spiked with 10 ng internal standards PCB 46 and PCB 143 (PCB numbering based on Ballschmiter and Zell[23]) and then were extracted with a B-811 Büchi extraction system (Büchi, Zwitzerland) in hot extraction mode for 4 h with 100 ml hexane–acetone (3 : 1, v/v). After concentration, the extract was cleaned-up on an 8 g acidified silica column and the analytes were eluted with 30 ml hexane. The eluate was concentrated with a rotary evaporator and the solvent was then evaporated to near dryness under a gentle nitrogen stream. The analytes were re-dissolved in 100 μl iso-octane.

The analysis of OCS in serum samples was based on a previously described procedure for the analysis of organochlorine compounds, including PCBs and HCB.[24] Briefly, serum samples were mixed with formic acid, followed by solid-phase extraction, elution with hexane and clean-up by acidified silica.

Determination

The determination of OCS and HCB in soil, sediment, mussels, shrimp, harbour porpoise and cormorant samples was performed on an Agilent 6890 gas chromatograph (GC) coupled with a 5973 mass selective detector (MSD) operated in selected ion monitoring (SIM) mode. The separation was carried out on a 20 m × 0.18 mm × 0.20 μm AT-5 column (Alltech, Lokeren, Belgium). Helium was used as carrier gas at a constant flow of 0.5 ml min^{-1}. The oven temperature was programmed as follows: 90 °C, held for 2 min, then at 20 °C min^{-1} to 200 °C, at 3 °C min^{-1} to 250 °C and then at 15 °C min^{-1} to 290 °C, finally held for 20 min. The injector and interface temperatures were 280 and 300 °C, respectively. One μl extract was injected in splitless mode. The quadrupole mass spectrometer was used with an electron impact (EI) source at 70 eV electron energy. Three characteristic ions m/z = 376, 378 and 380 and m/z = 284, 286 and 288 were monitored for OCS and HCB, respectively.

The human serum and tissues, hedgehog, great tit, and fish samples were analyzed by GC/MS with electron capture negative ionization (ECNI) source. One μl extract was injected in splitless mode into a 25 m × 0.22 mm × 0.25 μm HT-8 (SGE, Zulte, Belgium) capillary column. Helium was used as carrier gas at a constant flow of 1.0 ml min^{-1}. The oven temperature was programmed as follows: 90 °C, held for 1.5 min, then at 15 °C min^{-1} to 200 °C, held for 2 min, then at 5 °C min^{-1} to 270 °C, held for 1 min and then at 25 °C min^{-1} to 290 °C, finally held for 10 min. The injector and interface temperatures were 280 °C and 300 °C, respectively. Because of the poor sensitivity of PCB 46 in ECNI, PCB 143 was used as internal standard. The monitored ions were m/z = 306, 308, 310 and m/z = 284, 286 and 288 for OCS and HCB, respectively.

The identification of OCS and HCB were based on comparison of retention times and the ratio of ion abundances with those of authentic standards. Quantitation was done using five-level calibration curves. Blanks and spiked samples were also analyzed. The limit of determination (LOD) was defined as three times the standard deviation of measured values (n = 7) by spiking the amount of analytes in uncontaminated pork liver and soil samples with the concentration which produced a signal approximately equal with three times of the noise response in a blank sample. LODs for OCS and HCB were 0.01 and 0.03 ng/g wet weight (ww) in biota samples, and 0.02 and 0.04 ng/g dry weight (dw) in soil samples. The recoveries of OCS ranged from 65 to 75% at the spiking level of 0.05 ng/g OCS in pork liver (n = 7), and from 93 to 101% at a spiking level of 0.05 ng/g OCS in soil samples (n = 7). The recoveries of internal standards of PCB46 or PCB143 in the samples ranged from 60 to 97%.

Statistical analysis

Pearson's correlation coefficients and regression parameters were computed with STATISTICA for Windows, version 5.1, from StatSoft. Inc. (Tulsa, USA). For concentrations below LOD, zero was used for further calculations.

Results and discussion

Due to the wide variety of species collected from different locations, it was possible to differentiate and classify them according to their aquatic or terrestrial nature. Possible differences in uptake, distribution, occurrence and fate of OCS for these species are discussed. An overview of results obtained for OCS and HCB from the animal species and humans are given in Table 1. Typical ion chromatograms (m/z = 308 and 310) for a procedural blank (A), fish muscle at a concentration of 0.05 ng/g ww (B) and blue tits egg at a concentration of 0.94 ng/g ww (C) are presented in Fig. 1.

Marine and freshwater ecosystems

Sediment. Nine sediment samples were taken from the Danube Delta, Romania. None of the samples contained measurable concentrations of OCS (<0.02 ng/g dry weight), while the concentrations of HCB ranged from 0.04 to 0.15 ng/g dw. It was reported that the distribution of OCS in sediment greatly depended on the geography of the sampling locations. Kaminsky and Hites[5] have reported OCS concentrations as high as 360 ng/g dw in sediments from Calcasieu Lake (Louisiana, USA), while only trace concentrations of OCS (0.2 ng/g dw) were found in sediments collected from Lake Huron, Erie or Michigan in the same period.[21] High OCS concentrations (between 5,600 and 56,000 ng/g dw) were found in bottom and suspended sediments collected near an industrial outfall of Bayou d'Inde (Louisiana, USA).[21] Theoretically, OCS belongs to persistent and bioaccumulative hydrophobic compounds, and therefore sediment should be one of its main final sinks.

Mussels and shrimp. Between August and October 2002, 84 composite samples of freshwater zebra mussels (*Dreissena polymorpha*) were collected from 20 locations in Belgium. OCS could be measured in 70% of the samples. The OCS concentrations in soft tissue ranged from ND to 0.18 ng/g ww (mean 0.06 ng/g ww), while the concentration of HCB in the sample ranged from ND to 0.60 ng/g ww (mean 0.24 ng/g). No relationship was found between the concentrations of OCS and PCBs or p,p′-DDE, while a significant correlation could be computed between OCS and HCB (r = 0.6640, p < 0.001) (Table 2). Although all mussel samples were collected from Belgian inland waters, the measured OCS concentrations

Table 1 Sample details, concentration range and mean for OCS and HCB concentrations in the investigated species.

Sample type/Species		Sampling location	Tissue	*n*	OCS/ng g^{-1}		HCB/ng g^{-1}	
					Range	Mean	Range	Mean
Marine and freshwater ecosystem								
Sediment	Surface sediment	Danube Delta–Romania		9	ND	ND	0.04–0.15	0.09[a]
Invertebrates	Mussels (*Dreissena polymorpha*)	Belgium	soft tissue	84	ND–0.18	0.06[b]	ND–0.60	0.24[b]
	Shrimp (*Crangon crangon*)	North Sea	soft tissue	17	0.02–0.19	0.08[b]	0.39–1.75	0.88[b]
Fish	Bib (*Trisopterus luscus*)	North Sea	muscle	6	ND–0.03	0.02[b]	0.19–0.72	0.38[b]
	Sole (*Solea solea*)	North Sea	muscle	19	ND–0.01	0.01[b]	0.05–0.29	0.15[b]
	Whiting (*Merlangius merlangus*)	North Sea	muscle	2	0.01; 0.01	0.01[b]	0.16; 0.17	0.16[b]
	Carp (*Cyprinus carpio*)	Belgium	muscle	25	0.01–0.43	0.06[b]	0.03–0.77	0.15[b]
	Gibel carp (*Carasius auratus gibelio*)	Belgium	muscle	17	0.01–0.21	0.06[b]	0.03–0.36	0.17[b]
	Tench (*Tinca tinca*), bream (*Abramis brama*), roach (*Rutilus rutilus*), perch (*Perca fluviatilis*), wels (*Silurus glanis*), pike (*Esox lucius*), pikeperch (*Stizostedion lucioperca*), white bream (*Blicca bjoerkna*), rudd (*Scardinius erythrophthalmus*), carp, gibel carp	Danube Delta Romania	muscle	36	ND–0.65	0.05[b]	0.03–0.57	0.09[b]
	Cod (*Gadus morhua*)	United Kingdom	liver oil	8	ND–1.42	0.40[b]	0.16–8.85	4.64[b]
Mammals	Harbour porpoise (*Phocoena phocoena*)	Belgium	liver	19	0.26–6.11	1.88[b]	12.46–140.84	45.97[b]
Terrestrial ecosystem								
Soil	rural	Southern Romania		5	ND	ND	0.06–0.29	0.12[a]
	urban	Southern Romania		4	ND	ND	0.10–0.20	0.13[a]
	industrial	Southern Romania		13	ND–5.41	1.82[a]	0.09–46.85	9.68[a]
Birds	Cormorant (*Phalacrocorax carbo*)	Romania	liver	4	0.59–3.45	1.38[b]	0.61–2.86	1.38[b]
	Great tit (*Parus major*)	Belgium	adipose tissue	27	1.20–8.24	3.24[b]	4.42–30.22	14.65[b]
	Blue tit (*Parus caeruleus*)	Belgium	egg	6	0.90–1.65	1.24[b]	2.36–4.62	3.30[b]
Mammals	European hedgehog (*Erinaceus europaeus*)	Belgium	adipose tissue	5	0.08–0.49	0.34[b]	1.61–82.54	20.08[c]
		Belgium	liver	10	0.14–1.10	0.39[b]	0.11–4.49	1.27[b]
		Belgium	muscle	11	0.01–0.29	0.08[b]	0.09–5.03	0.97[b]
		Belgium	kidney	11	0.01–0.32	0.12[b]	0.09–4.65	0.96[b]
Humans		Belgium	liver	11	ND–0.05	ND	0.23–11.38	2.25[b]
		Belgium	brain	11	ND	ND	0.29–1.57	0.60[b]
		Belgium	adipose tissue	29	ND–0.38	0.07[b]	ND–79.7	21.1[b]
		Belgium	lung	11	ND–0.02	ND	0.10–2.51	0.50[b]
		Belgium	serum	13	0.13–0.45	0.29[c]	58.7–238.1	99.4[c]

ND - not detected.[a]ng/g dry weight. [b]ng/g wet weight. [c]ng/g lipid weight.

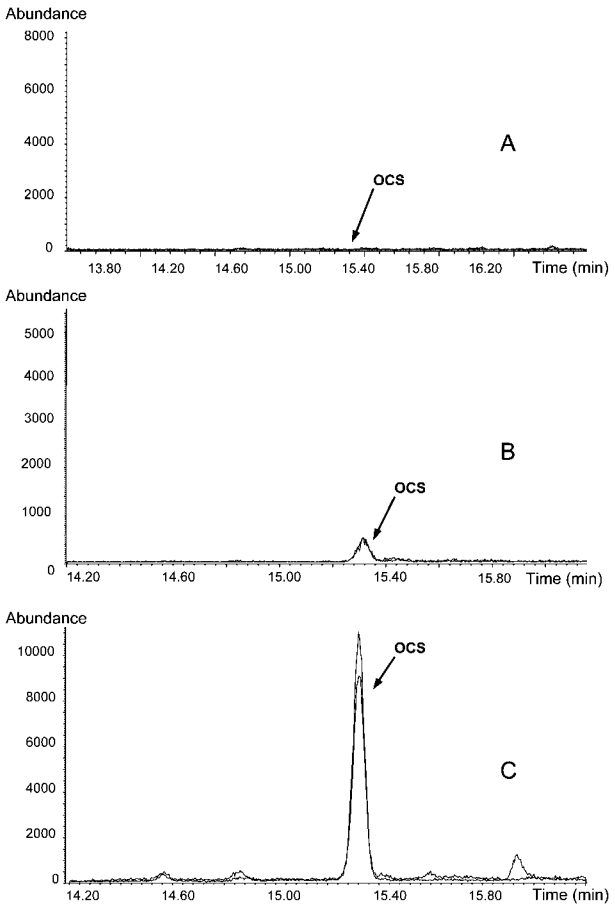

Fig. 1 Ion chromatograms (m/z = 308 and 310) for a procedural blank (chromatogram A), fish muscle at concentration of 0.05 ng/g wet weight (chromatogram B) and blue tits egg at concentration of 0.94 ng/g wet weight (chromatogram C).

compare well with concentrations found in 194 blue mussel (*Mytilus edulis*) samples (mean 0.03 ng/g ww, range: ND–0.05 ng/g ww) collected between 1990 and 2000 along the Norwegian Atlantic coast.[25]

Shrimp (*Crangon crangon*) samples were collected from the Belgian North Sea and Scheldt estuary and thirty individuals per location were pooled, resulting in 17 pooled samples. The concentration of OCS ranged from 0.02 to 0.19 ng/g ww (mean 0.08 ng/g), while the concentration of HCB ranged from 0.39 to 1.75 ng/g ww (mean 0.88 ng/g). As for mussels, a significant correlation between OCS and HCB concentrations was observed in the shrimp samples (r = 0.8938, p < 0.001) (Table 2).

Fish and fish oil. More than 100 marine fish samples including bib (*Trisopterus luscus*), sole (*Solea solea*) and whiting (*Merlangius merlangus*) were collected from the Belgian North Sea and the Scheldt estuary and pooled according to the sampling location, resulting in 27 pooled samples. For most of the fish samples, OCS concentrations in muscle were below LOD and, within the same location, the levels were several times lower than in shrimp samples (Table 1). The mean HCB concentrations in bib, sole and whiting were 0.38, 0.15, and 0.16 ng/g ww, respectively. No correlation between OCS and HCB concentrations was found for the three fish species (Table 2). Additionally, one sediment and one plaice (*Pleuronectus platessa*) sample collected at the same location (Western Scheldt) were also analyzed for OCS. The OCS concentrations in sediment and fish were 0.03 ng/g dw and 0.07 ng/g ww, respectively. The values found for OCS from fish collected from the Belgian North Sea and Scheldt estuary compare well with reported OCS concentrations in muscle of dab, plaice, lemon sole (range ND–0.10 ng/g ww) collected between 1990 and 2000 along the Norwegian Atlantic coast.[25]

Mattig *et al.*[26] have reported that OCS residues were detected in only 40% of benthic invertebrates and fish samples collected in 1992 from the back barrier of Spiekeroog in the East Frisian Wadden Sea (North Sea). The highest concentrations, up to 50 ng/g lipid weight (lw) were found in the sandmason worm (*Lanice conchilega*), while OCS did not appear in samples of plankton, common cockle (*Cerastoderma edule*) and blow lug (*Arenicola marina*). Dethlefsen *et al.*[10] have reported elevated OCS concentrations in dab liver samples (mean 30, 7, and 7 ng/g lw for samples collected in 1988, 1989 and 1990, respectively) from an off-shore incineration area (North-West of the Dutch coast). In these samples, OCS and HCB concentrations were highly correlated and were associated with incomplete combustion of chlorine containing products. In contrast, OCS levels from a reference area (20–30 km North-East of the incineration area) were 2, 2, and 1 ng/g lw for samples collected in 1988, 1989 and 1990, respectively.[10] If our data are expressed on a lipid weight basis, the concentrations in the fish muscle (Table 1) are in the same range as those from the reference area. Recently, residues of chlorostyrenes (one penta-, three hexa-, six heptachlorostyrenes and OCS) have been reported for marine fish (herring, mackerel, halibut) from different regions of the Northern Atlantic.[12] In all but one fish sample, (*E*)-β,2,3,4,5,6-hexachlorostyrene was the dominant isomer, while OCS levels ranged between 0.08 and 2.03 ng/g ww[12] and were in the same range as our samples from the

Table 2 Pearson's correlation coefficients (r) and linear regression parameters between the concentrations of OCS and HCB ($C_{HCB} = AC_{OCS} + B$) in several investigated species. Complete sample details are given in Table 1

Species	Correlation coefficient (r)	p	N	A	B
Mussels	0.6640	<0.001	84	1.4746	0.1628
Shrimps	0.8938	<0.001	17	6.5981	0.3295
Sole	0.2081	n.s.	19	4.9922	0.1199
Carp	0.4559	<0.05	25	0.9752	0.0949
Gibel carp	0.2588	n.s.	17	0.5357	0.1332
Cod liver oil	0.3241	n.s.	8	1.7877	3.9267
Fish (Danube Delta)	0.9647	<0.001	36	0.7925	0.0470
Porpoise (liver)	0.7801	<0.001	19	13.624	20.311
Soil (industrial)	0.8512	<0.001	13	4.8728	0.8034
Great tits (adipose tissue)	0.6190	<0.001	27	2.0943	7.8761
Blue tits (egg)	0.8514	<0.05	6	2.1289	0.6729
Hedgehogs (liver)	0.3148	n.s.	10	1.6882	0.6138
Human adipose tissue	0.6472	<0.001	29	100.66	14.04
Human serum	0.1074	n.s.	13	50.57	84.68

n.s. – not significant (p > 0.05).

North Sea (Table 1). Flounder (*Platichthys flesus*) liver samples from the Rotterdam and Amsterdam harbour[27] were reported to contain OCS concentrations ranging between 3 and 100 ng/g lw, while cod liver collected along the Norwegian coast[25] had OCS concentrations between 1 and 70 ng/g ww (mean 3 ng/g ww). Much higher OCS concentrations (up to 431 000 ng/g) were reported in cod, eel and whiting samples collected in 1975 from the area surrounding a magnesium-producing factory (Frierfjord, Norway).[8]

In the present study, cod liver oil samples ($n = 8$) marketed in 2001 in the United Kingdom as dietary supplements were also analysed (Table 1). The OCS concentrations ranged from ND to 1.42 ng/g ww (mean 0.53 ng/g ww), while the HCB concentration ranged from 0.16 to 8.85 ng/g ww (mean 4.67 ng/g ww). The levels of OCS in these samples compare favourably with similar fish oils marketed in 1998–1999 in Germany, England, USA and Iceland as dietary supplements,[12] where they ranged between 0.49 and 4.80 ng/g ww. These concentrations are much lower than the OCS concentration (31.5 ng/g ww) measured in cod liver oil used as certified reference material (CRM 349, BCR, Brussels). This sample was collected in 1985 off shore of the Dutch coast of the North Sea and only limited pre-treatment has been applied. Presumably, during the manufacturing process, fish oils used as dietary supplements are steam-distilled and thus the levels of volatile organochlorine pollutants (including OCS) are greatly reduced.

Separately, 42 freshwater fish samples, including 25 carp (*Cyprinus carpio*) and 17 gibel carp (*Carasius auratus gibelio*) were collected in 2002 from several Belgium inland waters (Table 1). There were no significant differences found in mean concentrations of OCS between the 2 species. A weak, but significant correlation ($r = 0.4559$, $p < 0.05$) could be computed between the OCS and HCB concentrations only in the carp samples (Table 2). Obviously, the contamination level of OCS in the freshwater fish species was higher than in marine fish species from the North Sea (Table 1), though the contamination level of HCB was in the same range for both aquatic systems.

Additionally, OCS levels above LOD (0.01 ng/g ww) could be measured only in 37% of 36 fish samples from 11 species collected from the Danube Delta, Romania. The highest OCS levels were found in one bream (*Abramis brama*) and two carp (*Cyprinus carpio*) samples with concentrations of 0.42, 0.13 and 0.65 ng/g ww, respectively (Table 1). In contrast, HCB could be measured in all analyzed samples and ranged between 0.03 and 0.57 ng/g ww (Table 1). Due to the small sample size for each fish species, no correlation between the OCS and HCB levels for each fish species could be computed. Therefore, the relationship between the 2 pollutants was investigated only for all samples taken together (Table 2). A very good correlation ($r = 0.9647$, $p < 0.001$) was observed, though there were 11 different species.

The OCS levels measured in the freshwater fish samples from Belgian inland waters and the Danube Delta are lower than levels reported in other investigations. OCS concentrations up to 280 and 400 ng/g ww were reported in pike and carp from Lake Ontario[28] and Ashtabula River[29] (USA), respectively. Recently, chlorostyrenes (including hexachlorostyrenes, heptachlorostyrenes and OCS) were identified and quantified in bream (*Abramis brama*) liver samples from the river Elbe.[11] OCS concentrations ranged between 10 and 45 ng/g ww and were related to point sources situated near the river and not to atmospheric transport (diffuse sources).

Marine mammals. OCS could be measured at relatively high levels in all liver samples from 19 harbour porpoises (*Phocoena phocoena*) stranded on the Belgian North Sea coast. OCS levels ranged from 0.26 to 6.11 ng/g ww (mean 1.90 ng/g ww), while the HCB concentration ranged from 6.11 to 45.97 ng/g ww (mean 46.0 ng/g ww). Considering that fish (bib, sole and whiting) and porpoises were collected from the same area, it could be calculated that the biomagnification factor for OCS from fish to porpoise was one order of magnitude lower than for HCB (62 *vs.* 901, respectively). There were no significant differences in the OCS concentrations between males and females, neither between juveniles and adults. A good correlation ($r = 0.7801$, $p < 0.001$) could be computed between OCS and HCB concentrations in harbour porpoises.

The OCS levels were reported in 29 bottlenose dolphins (*Tursiops truncatus*) blubber samples from the Gulf of Mexico[13] during an unusual mortality event in 1990. The OCS concentrations ranged from ND to 84 ng/g lw with the exception of 6 immature individuals for which levels ranged from 28 to 532 ng/g lw. In contrast, much lower OCS concentrations (mean 2.3 ng/g lw) were reported in seals from the Polynya Arctic,[14] which suggests that the OCS contamination is substantially lower in the Arctic than in highly populated areas, such as North America or Europe.

Terrestrial ecosystems

Soil. In this study, the OCS contamination in 6 rural and 4 urban soil samples from Romania was analyzed. None of the samples contained detectable OCS levels (<0.02 ng/g dw), while the HCB concentrations were up to 0.20 and 0.29 ng/g dw in urban and rural soil samples, respectively. In 10 out of 13 soil samples from industrial areas, the concentrations of OCS and HCB were significantly higher than from rural and urban areas. Near a chemical factory (radius: 100–1500 m), the OCS and HCB concentrations in soil ranged from 0.44 to 0.86 ng/g dw and from 3.63 to 5.28 ng/g dw, respectively. In another set of samples collected at distances between 100 and 1500 m from a pesticide-producing factory, the OCS and HCB concentrations were between 4.29 and 5.48 ng/g dw, and between 15.42 and 46.85 ng/g dw, respectively. A good correlation could be computed between the OCS and HCB concentrations in industrial soil, suggesting that OCS and HCB may produced together as chemical by-products. The HCB contamination was more related to the distance to the factory than was the OCS contamination. However, the OCS concentrations in 3 soil samples from another two chemical facilities were low (ND to 0.07 ng/g dw), while similarly to rural and urban soil samples, the HCB concentration ranged from 0.09 to 0.31 ng/g dw.

Birds. Adipose tissue ($n = 27$) from great tits (*Parus major*) and eggs ($n = 6$) from blue tit (*Parus caeruleus*) samples were collected near Antwerp (Belgium). OCS could be measured in all samples at concentrations ranging from 0.90 to 1.65 ng/g ww (mean 1.24 ng/g ww) and from 1.20 to 8.24 ng/g ww (mean 3.24 ng/g ww) in eggs and adipose tissue, respectively (Table 1). The HCB concentrations in egg and adipose tissue samples were higher at up to 4.62 and 30.22 ng/g ww, respectively (Table 1). Good correlations between OCS and HCB concentrations could be computed for eggs and adipose tissue (Table 2). A similar phenomenon was also observed in cormorant (*Phalacrocorax carbo*) liver samples ($n = 4$) from Romania for which the OCS concentration ranged between 0.59 and 3.45 ng/g ww (Table 1).

Information on the OCS concentrations in avian species is relatively limited. Similar ranges of OCS residual levels were recently reported in fat of the Laysan albatross (*Diomedea immutabilis*) and in fat and eggs of the blackfooted albatross (*Diomedea nigripes*) from the Central North Pacific Ocean.[30] The OCS concentrations in the Laysan albatross fat ($n = 20$) ranged from 2.1 to 6.1 ng/g ww (mean 3.8 ng/g ww), while in the blackfooted albatross ($n = 6$), the OCS levels ranged between 3.7 and 6.1 ng/g ww (mean 4.8 ng/g ww) and between 0.1 and 0.5 ng/g ww (mean 0.25 ng/g ww) in fat and eggs, respectively.

Hedgehogs. There are no reported values for OCS contamination in small mammals (mice, rats, hedgehogs, rabbits, polecats, hares, moles, *etc.*). In the present study, the OCS levels were measured in several tissues (fat, muscle, kidney and liver) of hedgehogs (*Erinaceus europaeus*) collected in 2001–2002 throughout Belgium. Interestingly, OCS concentrations in the adipose tissue (mean 0.34 ng/g ww, $n = 5$) were similar with levels in liver (mean 0.39 ng/g ww, $n = 10$) (Table 1). OCS concentrations in kidney and muscle were lower than for adipose tissue or liver (Table 1). When concentrations were expressed per lipid weight, a preferential accumulation of OCS was observed in liver with a maximum OCS concentration of 45.2 ng/g lw. No preferential distribution between different tissues could be observed for HCB, and no significant correlation could be computed between OCS and HCB levels in hedgehog tissues.

Human tissues and serum. In the present study, several human tissues (liver, brain, lung, adipose tissue) from the Belgian population were investigated for their OCS levels. OCS concentrations were below LOD in all brain ($n = 11$), in all but one lung ($n = 11$) and in all but two liver ($n = 11$) samples (Table 1). However, OCS could be measured in 38% of the adipose tissue ($n = 29$) with a maximum concentration of 0.38 ng/g ww. In contrast, HCB could be determined in all the analyzed human tissues (Table 1) and the highest concentrations were measured in adipose tissue (mean 21.1 ng/g ww). A good correlation ($r = 0.6472$, $p < 0.001$) could be computed only between OCS and HCB concentrations in human adipose tissue (Table 2). Additionally, 13 human serum samples from the general Belgian population were also analyzed. Only low OCS concentrations (expressed on lipid basis) could be measured, while there was no correlation between OCS and HCB levels in human serum.

Similarly, OCS concentrations up to 0.7 ng/g lw were reported in Swedish human serum.[16] Both data sets show that OCS is found in the human body only at low concentrations. However, high concentrations (mean 54.6 ng/g lw) were reported in serum samples ($n = 9$) from aluminium foundry workers with past use of hexachloroethane.[18] Additionally, blood samples of 135 residents living near the Elbe River estuary (Germany)[15] contained OCS concentrations up to 9.2 ng/g lw, which might correspond to high levels of OCS in Elbe fish.[11]

Relationship between OCS and HCB. Statistically significant correlations could be calculated between levels of OCS and HCB for several species, indicating an existing relationship between the two pollutants. This is probably dependent on the (bio)availability and environmental presence of each pollutant, and on the ability of each species to accumulate and/or metabolise OCS and HCB. Thus, the slope (A) of the linear regression between the levels of OCS and HCB would give an indication on the relative fate of the two pollutants. For industrial soil, $A = 4.87$ (Table 2) and corresponds to the situation where no degradation of OCS and HCB exists. Interestingly, all fish samples (except sole), birds, hedgehogs and mussels had a lower value for A than in soil, suggesting that OCS was possibly accumulating at a higher rate than HCB in these species. For sole, the value for A was similar to that in soil, indicating a relatively similar preference for the accumulation of the 2 pollutants, while for shrimp, porpoises and humans, values were above 4.87, indicating that HCB was accumulating at a higher rate than OCS. The highest slope value was found for humans, corresponding with high concentrations of HCB in human tissues correlated with low values for OCS. It seems that humans are able to metabolise OCS at a higher rate than HCB, already evidenced by Sandau *et al*,[31,32] who have found 4-HO-heptachlorostyrene (4-HO-HpCS) in relatively high concentrations in polar bear and human plasma and liver compared with other phenolic compounds (mainly HO-PCBs and pentachlorophenol). They have concluded that 4-HO-HpCS was the main metabolite of OCS and that, at least in some species at higher trophic levels, the significance of OCS as an environmental contaminant may have been underestimated.

Conclusions

From this investigation and from the comparison with other reported data, a certain degree of OCS pollution is suggested to be present in the environment. HCB and OCS seem to be closely related in some species or environmental matrices, while OCS biomagnification in marine ecosystems is lower than for HCB. The OCS residues in human tissues from non-exposed subjects were at low level.

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