TRENDS OF POPS IN BIOTA OF THE ATLANTIC OCEAN – SAMPLES OF 1981/82 REANALYZED AND CHARACTERIZED WITH GC/ECD, GC/EI-MSD AND GC/NCI-MSD

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Introduction

The pollution of the North Atlantic with persistent anthropogenic organohalogens (POPs) and their accumalation in biota is a field of research for now over twenty years[1,2,3]. The development of new analytical techniques and the availability of a greater variety of quantitative standards give access to more detailed data than decades ago. Further on, groups of organohalogens have become of interest that were not target of analysis twenty years ago. We have reanalyzed samples which were collected in the 1980s for a second time. Deep sea fish from the Bermuda region caught in 1981 and ´82[4] were analyzed in the same way as more recent objects with respect to clean-up and fractionation by NP-HPLC. They were characterized by HRGC/ECD, HRGC/EI-MSD and HRGC/NCI-MSD. A decline of pollution levels in samples from the years 1981 to 1998 is not given for all the groups of contaminants that were compared. Chlordane levels –perhaps in account of a regional input – have even increased in relative amounts as well as the PCB in surface living species. Organobromine POPs, that were found in the more recent samples are hardly detectable in the 1980's samples.

Origin and biological properties of the fish samples [5,6]

Samples of the early ´80

Sixgill shark (*Hexanchus griseus*) benthopelagic species, the habitat ranges from the surface to a depth of 2000 meters. **Oilfish** (*Ruvettus pretiosus*): this species can be found at continental shelfs but also in oceanic waters. A preferred depth range is 100 to 800 meters. The diet consists of fish, crustaceans and squid. These two samples were caught in 1981 in the north-east of the Bermuda Islands; **Black grouper** (*Mycteroperca bonaci*): demersal species, adults feed on fish, juveniles mainly on crustaceans. This fish was also caught in the Bermuda region (1982) in a depth of about 400 m. **Samples of the late ´90: Menhaden** (*Brevoortia tyrannus*): pelagic species, feeds by filtration of phyto- and zooplancton in surface water. Analyzed sample was crude fish oil (1997) that originated from the east coast of the USA. **Blacktip shark** (*Carcharhinus limbatus*): pelagic species, lives in upper water layers down to 50 m; caught in the Gulf of Mexico 1995. **Black halibut** (*Reinhardtius hippoglossoides*): Arctic predatory species, found at 200 – 2000 m; Iceland Basin, 1994 (Halibut 1) and 1998 (Halibut 2). **Grenadier** (*Coryphaenoides armatus*): deep-sea species, feeds on invertebrates and fish; Iceland basin, 1992 (2900 meters).

Sample preparation

Extraction and clean-up of samples was done as described by Froescheis and Looser[7,8,9]. Here only the conditions of chromatographic separation are summarized. HRGC/ECD: Varian GC 3800, CP Sil19 (60 m, 0,25 mm i.d., 0,25 µm film thickness); carrier gas H_2; HRGC/EI-MSD: HP GC 6980, HP MSD

5973, CP Sil 19 as above; carrier gas He; HRGC/ NCI-MSD: system and column as above; reactand gas CH_4, source temperature 150 °C

Table 1. Levels [µg/kg extracted lipid] of organochlorine POPs in two temporal groups of fish samples from the North Atlantic, 1981-1997 (n.d.: not detected, n.q.: not quantified)

	Deep sea fish, Bermudas, 1982		
Sample	Sixgill Shark	Oilfish	Black Grouper
Year	1981	1981	1982
Σ Chlordanes	660	370	230
Σ 3 Toxaphenes	870	475	160
Σ DDX	31990	5440	3010
Σ 3 HCH	n.d.	n.d.	3
Σ 28 PCB	11870	3910	2320
Total PCB	28940	8840	5490
S 3 PBDE	n.q.	n.q.	n.q.

	Deep sea fish Eastern North Atlantic, 1992-98				
Sample	Grenadier 1	Grenadier 2	Grenadier 3	Halibut 1	Halibut 2
Year	1992	1992	1992	1994	1998
Σ Chlordanes	140	165	170	350	140
Σ 3 Toxaphenes	235	345	450	280	215
Σ DDX	760	1180	1335	680	220
Σ 3 HCH	15	8	21	9	13
Σ 28 PCB	680	940	960	740	200
Total PCB	1610	2280	2320	1530	480
Σ 3 PBDE	28	62	n.q.	25	7

	Surface, Gulf of Mexico,1995			Surface, Gulf Stream, 97	
Sample	Blacktip Shark 1	Blacktip Shark 2	Blacktip Shark 3	Menhaden 1	Menhaden 2
Year	1995	1995	1995	1997	1997
Σ Chlordanes	970	1260	545	66	100
Σ 3 Toxaphenes	n.d.	n.d.	n.d.	25	12
Σ DDX	1910	2745	1230	250	205
Σ 3 HCH	n.d.	n.d.	n.d.	8	24
Σ 28 PCB	15950	7010	3980	390	645
Total PCB	37600	17060	9500	690	1150
Σ 3 PBDE	200	260	210	42	50

Targets of quantitative analysis

PCB: 28 single PCB congeners were quantified using NIST standard reference materials SRM 2262 and SRM 2274; „Total PCB“ is the multiplication of the sum of the seven indicator congeners (PCBs 28, 52, 101, 118, 138, 153, 180) with a factor of four. Toxaphenes: Congeners T 26, T 50 and T 62 – that represent up to 50 % of the total Toxaphene level in fish samples- were quantified with single congener standards[10]. The sum of chlordane compounds includes cis-heptachloroepoxide, oxy-chlordane, cis- and trans-chlordane, cis- and trans-nonachlor. S (3 HCH) sums up the content of α, ß and γ-HCH. The DDX group sums up 4,4'- DDT, 4,4'-DDD, 4,4'- DDE and the respective 2,4' isomer of each compound. S PBDE sums up the brominated diphenyl ethers PBDE 47, 99 and 100.

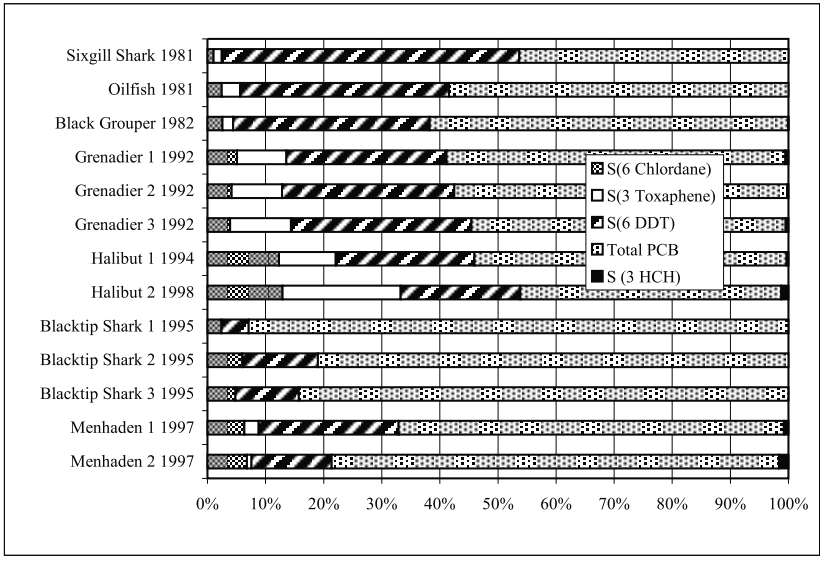

Figure 1. Relative amounts of organochlorine POPs in samples from the Gulf of Mexico to Iceland in the North Atlantic, 1981-1998

Results

a) *Organochlorine POPs*

The highest levels of chlordane compounds are measured in the livers of blacktip shark (#1, #2, 1995) caught in the Gulf of Mexico with 970 ng/g and 1260 ng/g. They exceed even the level in the highly contaminated liver of the 1981 sixgill shark (660 ng/g). Also the relative amounts of chlordanes have increased since 1981/82 (Figure 1). The 1995 sharks show also high levels of PCB, which point to a regional direct input from industrial sources.

The assumption that the blacktip sharks caught in the Gulf of Mexico show a rather regional pattern of contamination is supported by the absence of toxaphene compounds that are present in all other samples, especially in deep-sea species. This can be interpreted as a consequence of the restricted use of toxaphene in the USA since 1982 and the total ban of this pesticide in 1990, whereas chlordane was produced until 1997. Restricted environmental input of a persistent compound should be observable in coastal regions and surface water at first, whereas in deeper layers these POPs are still present and accumulated. The relative contribution of toxaphene to the total level of organochlorines in menhaden fish is definitely lower than in the deep-sea species Grenadier and Halibut.

The DDX levels have been clearly decreasing since the beginning 1980's, in total as well as in relative amounts. In all surface-living samples, the relative amount of DDX has sunk below 25 %. This trend is not so obvious when the samples from 1981/82 are compared to the deep-sea species of the ´90ies. Here, similar to the toxaphenes, the deep-sea biota apparantly act as a depot that responds slowly to a varied input – in absolute as well as in relative scales.

Due to the low trophic level of this species, the results from menhaden oil give a good approximation of the actual contamination of their surface water habitat. The measured levels suggest that in oceanic water off the East Coast of the USA (and thus also in the Gulf Stream) the PCB represent the most abundant group of organochlorines. The HCHs, if detectable at all, show low levels. For this group, a trend can hardly be stated.

A yet not fully identified heptachlorinated dipyrrol compound (labeled „U3" or „Q1") of possible biogenic origin was also detected by full-scan NCI-MSD in the deep sea fish samples from the Bermudas collected 1981/82 [11,12,13].

b) *Organobromine POPs*

Components of the technical product Bromkal 70-5 DE, which mainly consists of tetra- and pentabrominated diphenyl ethers, could be detected and quantified in the more recent samples (except Grenadier #3). The samples from 1981/82 were also analyzed with NCI-MSD which is, especially in the SIM-mode (m/z = 79 and 81), a highly efficient method for the selective detection of organobromines. In these samples several brominated compounds could be detected and the mass spectra of two of them were interpreted as methoxylated tetra-BDE. As to the components of 70-5 DE, only signals at the retention time of tetra-BDE 47 could be detected in the SIM-mode. The main compound of the technical product Bromcal 73-5 PE, a pentabrominated phenyl-propyl ether, was also detected in the 1982 Black Grouper [14,15].

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