PRESENCE OF Q1, A NEW $C_9H_3Cl_7N_2$ ORGANOCHLORINE CONTAMINANT IN ENVIRONMENTAL SAMPLES

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Introduction

Q1, a heptachloro compound of unknown structure, was recently identified as a major contaminant in samples from Africa and the Antarctic [1][2][3]. In a parallel study we established that Q1 has the elemental composition $C_9H_3Cl_7N_2$ [4]. The Q1 levels in seal blubber from Namibia and the Antarctic seals were estimated on the basis of the ECD response factor of trans-nonachlor. The seal species accumulated up to 350 µg/kg [2]. In skua eggs from the Antarctic, we measured up to 126 µg/kg wet weight which corresponded to 3 mg/kg lipid weight [3]. Only low Q1 levels were found in samples from the North Sea and the Baltic Sea. Therefore, Q1 represents the unique case of an organochlorine compound which is more abundant in the remote area of the Antarctic than in the otherwise highly polluted waters of Middle and Northern Europe. These results were interpreted by Q1 being a contaminant mainly occuring in the southern hemisphere [1]. New data is added to the knowledge on Q1.

Material and methods

GC/MS investigations. GC/MS studies were performed on an HP 5989B mass spectrometer operated in the electron capture negative ion mode. In the full scan mode, m/z 50-550 were monitored and in the selected ion monitoring mode m/z 384, m/z 386, and m/z 388 for Q1 as well as m/z 442 and m/z 444 for trans-nonachlor and m/z 302. A chiral stationary phase consisting of 25% ß-BSCD in PS086 was used. The oven program started at 80°C (4 min), which then was raised at 20°C/min, respectively, to 180°C (15 min), 200°C/min (25 min), and 230°C (15 min). All other parameters were recently described in detail.
GC/ECD investigations. Separations were carried out on an HP 5890 series II gas chromatograph (Hewlett-Packard) equipped with two capillary columns and two electron capture detectors (ECDs). Helium, maintained at a constant flow of 1.3 mL/min, was used as the carrier gas and nitrogen as the make-up gas. The injector and detector temperatures were 250°C and 300°C, respectively. The 50 m length x 0.25 mm internal diameter fused silica capillary columns coated with 0.25 µm CP-Sil 2 and CP-Sil 8/C18 20%, respectively (both Chrompack, Middelburg, The Netherlands). The GC oven program was as follows: 60°C (1.5 min), 40°C/min to 180°C (5 min), 2°C/min to 230°C (0 min), and 5°C/min to 270°C (15 min).
Sample clean-up. Environmental samples were prepared using the methods presented earlier in detail [5][6]. One is mainly based on liquid/liquid partitioning and acid treatment, the second includes microwave-assisted extraction and gel-permeation chromatography.

Results and Discussion

Due to similar behavior on silica and similar GC retention times on different stationary phases, we estimated Q1 levels in samples by using the ECD response factor of trans-nonachlor. Table 1 lists levels of trans-nonachlor, ΣDDT (p,p´-DDT + p,p´-DDE + p,p´-DDD), ΣPCB (PCB 101 + PCB 118 + PCB 138 + PCB 149 + PCB 153 + PCB 163 + PCB 170 + PCB 180), and Q1 in the blubber of South African fur seals (*Arctocephalus pusillus pusillus*).

Table 1: Levels of organochlorines (µg/kg) in the blubber of South African fur seals (*Arctocephalus pusillus pusillus)* [1][2]

sample:	**# 176**	**# 174**	**# 183**	**# 184**	**# 177**	**# 175**	**# 182**	**# 178**	**# 180**	**# 181**	**# 179**
Compound	**f, 2 ***	**f, 3**	**f, 4**	**f, 5**	**f, 5-6**	**m, 2**	**m, 3**	**m, 4**	**m, 5**	**m, 5**	**m, 6**
Σ PCBs	55	24	101	35	4	35	65	22	83	697	25
Σ DDT	266	53	361	148	11	173	216	112	424	1115	155
tr-nonachlor	40	8	54	24	2	23	28	15	33	148	17
Q1	314	73	318	136	28	164	351	120	273	172	11

* sex (f = female, m = male), age in years

The most of the samples exhibited Q1 concentrations on the same level or higher than PCBs and DDT (see Table 1). This clearly confirms the environmental relevance of Q1. Q1 level did not correlate with DDT, PCB, chlordane, toxaphene, and dieldrin [1]. Tissue of blubber, liver, kidney, and lung were available for one sample of South African fur seals (see Table 2).

Table 2: Q1 levels (µg/kg wet weight) and Q1/p,p´-DDE ratios in different tissues of a South African fur seal (*Arctocephalus pusillus pusillus)* [7]

	Q1	***p,p´-DDE***	***ratio Q1/p,p´-DDE***
blubber	288 µg/kg	280 µg/kg	1.0
kidney	55 µg/kg	45 µg/kg	1.2
liver	7 µg/kg	5 µg/kg	1.4
lung	1.4 µg/kg	1.2 µg/kg	1.1

In the four tissue samples p,p´-DDE and Q1 clearly dominated in the ECD chromatograms. The data confirm that Q1 has a potential to bioaccumulate which is comparable with p,p´-DDE [7]. Figure 1 shows the GC/ECNI-MS full scan chromatogram of a sample of in the brain of a brown skua from the Antarctic. Q1 was the dominating organochlorine compounds in the brain sample. Both the GC/ECNI and the GC/EI mass spectrum of Q1 showed an abundant heptachloro pattern starting at m/z 384, which is most likely the molecular ion [1][2]. Three significant ions, i. e. m/z 384, m/z 386, and m/z 388, were extracted from the full scan mass spectrum of Q1 in order to establish a suitable GC/MS method in the selected ion monitoring mode. In addition, m/z 442 and m/z 444 were monitored since we have suggested to use trans-nonachlor as an internal standard for quantification of Q1 in biological samples by GC/ECD [1][2].

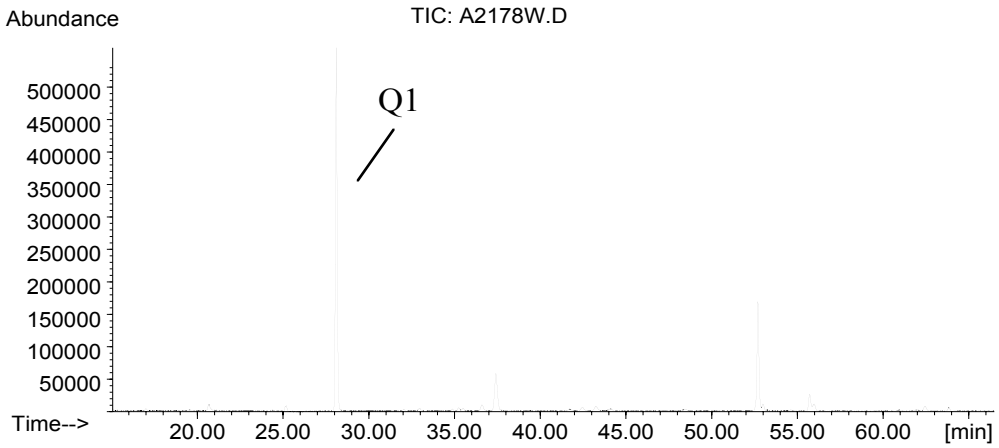

Figure 1: GC/ECNI-MS full scan chromatogram (m/z 50-550) of skua brain (Antarctic)

Table 3 lists samples which have been analyzed for Q1. Most of the identification was performed with GC/ECNI-MS only on a qualitative basis while with GC/ECD, Q1 was quantified on the basis of the response of an external trans-nonachlor standard. Work is ongoing to establish the ratio of Q1/trans-nonachlor in ECNI-MS and to include an appropriate internal standard for MS quantitation.

Table 3: Samples and matrices with Q1 levels

Sample	origin	year	n	Ref.	level* or presence
African fur seal blubber	Namibia	1996/97	11	[2]	11 - 351 µg/kg
seal blubber	Antarctic	1985-94	20		major contaminant
ringed seal	Spitsbergen	1988	11	[1]	not detected
skua liver,blubber,brain,kidney	Antarctic	1994	8		major contaminant
penguin tissue	Antarctic	1994	3		clearly detected
penguin eggs	Antarctic	1994	10	[3]	20-
skua eggs	Antarctic	1994	9	[3]	0.2 - 1.3 µg/kg
human milk	Faeroe Islands	1994	4	[8]	12 - 230 µg/kg
ringed seals	Canada	1998	2	[7]	not detected
beluga whale	Canada	1988	2	[7]	low levels
harbor porpoise	Iceland	1994	4	[7]	low levels
harbor seal	North Sea	1990	1	[7]	traces
grey seal	Baltic Sea	1994	1	[7]	traces
monk seal	Madagascar	1997			high levels
fish (deep sea)	Mediterranean Sea	1994	1		medium levels
whale blubber	(can)	1994	1	[8]	high levels

* all levels were determined using the ECD response factor of trans-nonachlor.
Other comments (present, low levels, major abundant) refer to MS detection, and quantitative levels have not been established yet

Note that Q1 quantitation should be performed before any separation of PCBs and alicyclic compounds such as toxaphene and chlordane since Q1 is distributed in both fractions. The samples in Table 3 can be summarized in the following way. Highest levels were found in marine mammal and bird samples from the Antarctic as well as fur seal blubber from the Southwest of Africa (Namibia). High levels were also found monk seals from Madagascar but they were lower than those of the Namibian samples.
High Q1 levels were also determined in a whale sample from a Supermarket on the Faeroe islands as well as in human milk from Faeroean women who regularly consumpted whale blubber [8]. Q1 is most likely not be a local problem of the Faeroe Islands since the whales may have been hunted somewhere else.
In samples unequivocally originated from the northern hemisphere, Q1 levels were much lower than in samples from the southern hemisphere. We found only low levels in beluga whales from Canada and harbor porpoises from Iceland. No Q1 levels were found in ringed seal blubber samples from the Arctic (Spitsbergen) and Canada. More data is necessary for species on a lower trophic level. So far, only one fish sample from the Mediterranean Sea was investigated.
The high level in the brain of the brown skua (see Figure 1) demonstrates that Q1 has a strong ability for transfer into the brain, which was less pronounced for contaminants such as toxaphene. This emphasizes the environmental and toxicological relevance of Q1.

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