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Determination of toxaphene congeners in fish samples from Danish waters

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Introduction

Toxaphene is a persistent chlorinated pesticide which is distributed globally in the environment mainly due to aerial transport[1]. The technical toxaphene mixture consist primarily of polychlorinated bornanes, as well as small amounts of polychlorinated bornenes and bornadienes[2]. Like other persistent organochlorine compounds, such as DDT and PCB, high concentrations are found in biological fatty tissues. Human exposure to toxaphene residues is mainly through food consumption and especially from intake of fish with high fat content[3]. There are considerable gabs in the effect database, as well as major deficiencies in the exposure information on toxaphene, both due to limitations in availability of data and difficulties in analytical determination of toxaphene. Toxaphene has shown to be mutagenic in the Ames *Salmonella* test, but there are insufficient data to evaluate the carcinogenic of toxaphene in humans[4]. Regulatory guidelines for toxaphene have been made by several countries, with the German maximum residue limit (MRL) as one of the lowest: 0.1 mg/kg in commercial fish (the sum of three congeners)[5].

In this paper preliminary results are presented concerning determinations of three toxaphene congeners in fish samples from Danish waters.

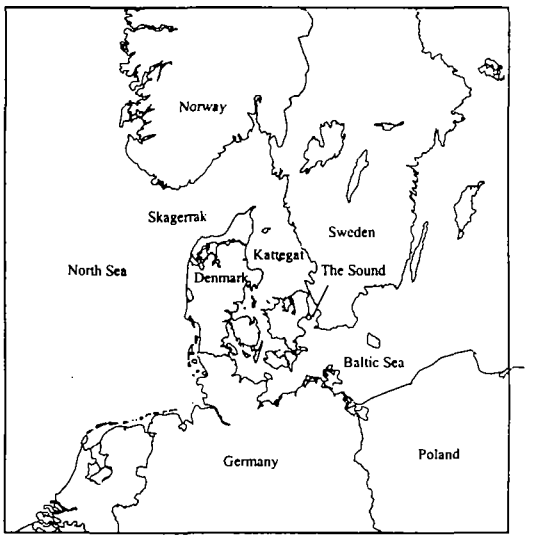

Figure 1. Waters around Denmark.

Samples: The samples are selected fish from the Danish monitoring program for 1996, where single fish has been analysed for PCB congeners and organochlorine pesticides (OCP). Fish of herring, salmon, eel, mackerel and cod liver from the Western Baltic Sea, the Sound, Kattegat, Skagerrak and the North Sea (see Figure 1) were filleted, comminuted and homogenised.

Experimental method

Determination of toxaphene: About 10-12 g of the homogenised fish sample (7 g eel and 3 g cod liver) was mixed with 50 g sodium sulphate (40 g and 15 g, respectively) and 150 ml petroleum ether. The sample was blended with an Ultra-Turrax blender as described previously[6]. Cleanup was preformed on a multi-layer column. A quantitative mixture of three toxaphene congeners (Parlar #26, #50 and #62) was obtained from Promochem, Germany[6]. The toxaphene congeners were measured by high resolution capillary gas chromatography interfaced to a Micromass AutoSpec Ultima high resolution mass spectrometer.
GC parameters: Column: 30 m DB-5 (J&W), 0.25 mm I.D., 0.25 μm film thickness. Carrier gas helium at 12 psi head pressure. 1 μl injected splitless, splitless time 1 min. Injector held at 240°C. Temperature program: 100°C for 2 min., 20°C/min. to 180°C, 3°C/min. to 265°C, 20°C to 290°C, isothermal for 30 min.
MS parameters: Ionisation by electron impact, resolution 10,000, ion energy 37 eV, trap 650 μA. Source temperature 260°C, transfer lines at 270°C and 280°C. Selected ion monitoring of mass fragments at m/z 340.8806 and 342.8776 (toxaphene #26), m/z 338.8649 and 340.8620 (toxaphene #50 and #62) & m/z 335.9236 and 337.9206 (^{13}C-PCB 105). PFK was used as lock mass.

Determination of PCBs and OCPs: Fish or liver was treated with sand and water free sodium sulphate. The sample was Soxhlet extracted with *n*-pentane for three hours. Fat were dissolved in *n*-pentane and added to a standardised Florisil column eluted with dichloromethane: *n*-pentane (1:4). The PCB congeners and OCPs were measured by high resolution capillary gas chromatography with electron capture detection. Single PCB congeners were used as standards as well as standards for organochlorine pesticides.
GC-ECD parameters: Perkin Elmer autosystem gas chromatograph. Column: 50 m CP-Sil-5CB, 0.25 mm I.D., 0.25 μm film thickness. Carrier gas helium, 15 psi (CP-Sil-5CB) 37 psi (DB-17). 2 μl injected splitless, splitless time 2.5 min. Injector held at 220°C. Temperature program: 90°C for 1 min., 30°C/min. to 180°C in 10 min., 2°C/min. to 240°C, 10°C to 260°C in 20 min. (CP-Sil-5CB) 30 min. (DB-17). Detector temperature 320°C.

Results and discussion

Toxaphene quantification was performed by determination of relative response factors towards the internal standard ^{13}C-PCB 105. Quality assurance criteria for peak detection included retention time window and correct isotope ratio for the two mass fragments monitored for each chlorine homologue series. PCB congeners and organochlorine pesticides were quantified by comparing to individual standard mixtures.

The content in 18 fish samples from the Danish monitoring program is displayed in Figure 2, showing the levels of PCB-153 and the sum of DDT (*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT). The highest content of PCB-153 is found in the Sound and is expected to be caused by local sources. The level for the sum of DDT is found to be highest in the western Baltic and the Sound and might also be the result of prior local use of DDT. Low levels of PCB-153 and the sum of DDT were found in Skagerrak and the North Sea.

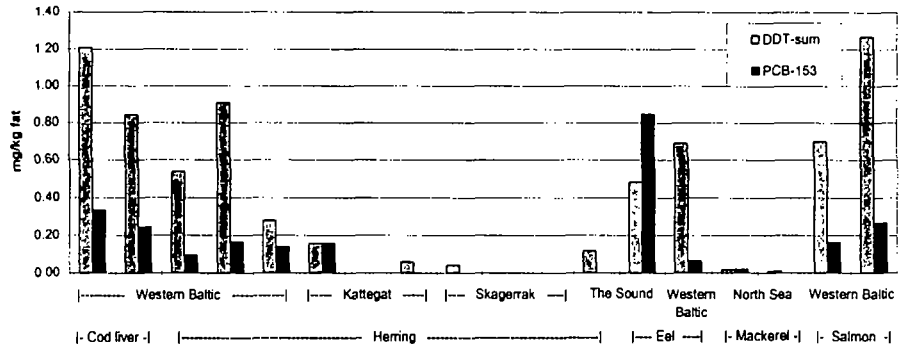

Figure 2. Distribution of contaminants. The DDT-sum and PCB-153.

The same pattern as mentioned above is not observed when picturing the graph in Figure 3 for the toxaphene congener level. The samples have almost the same levels for the toxaphene congeners, indicating the main source of toxaphene is not local, but a result of a global distribution and accumulation which is in agreement with previously observations[3,7,8]. The exceptions are the two samples of eel with low content and one herring with an high content of toxaphene, but with a very low fat content (1.3 %).

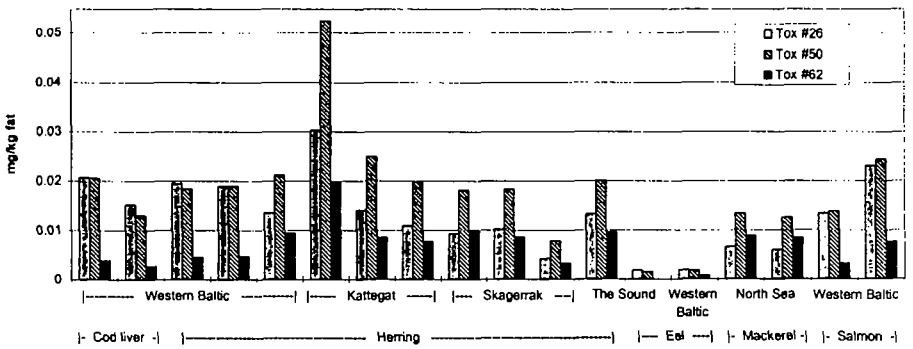

Figure 3. Toxaphene congeners #26, #50 and #62.

The congener specific distribution in Figure 3 shows similar patterns for Kattegat, Skagerrak, the Sound and the North Sea, whereas the pattern is different in samples from the Western Baltic. The different patterns indicates, despite that the sum of the three congeners are almost the same, that the pollution might be influenced either by wind or water movements around Denmark or by local sources. The local sources could arise from different composition of toxaphene formulations[9] nearby the Baltic Sea, with a higher content of congeners with a low boiling point.

Our results are in agreement with previously reported results for mackerel, eel, salmon and herring from Skagerrak, whereas our results are 3-8 times lower than previously reported results for herring from the Baltic Sea[3]. However, fish, especially herring are not stationary and results might be influenced by migration. One known stock is to be found in the North Sea and in Skagerrak, whereas another stock is in Skagerrak during the summer and then migrates into Kattegat, through the Sound and spawn in the western Baltic Sea.

Literature cited

1. Muir, D.C.G. & de Boer, J. (1995). Recent developments in the analysis and environmental chemistry of toxaphene with emphasis on the marine environment. *Trends in Analytical Chemistry* **14** (2) 56-66.
2. Saleh, M.A. (1991) Toxaphene: Chemistry, Biochemistry, Toxicity and Environmental Fate. *Rev. Environ. Contam. Toxicol.*, **118** (1) 1-85.
3. Alder, L.; Beck, H.; Khandker, S.; Karl, H. & Lehmann, I. (1995) Levels of toxaphene indicator compounds in fish. *Chemosphere* **34** 1389-1400.
4. Nordic risk assessment of toxaphene expursure (1997) TemaNord 1997:549, Nordic Council of Ministers, Copenhangen 1997. 70p.
5. Bundesgesetzblatt (1997) Bonn (1) **66** 2370.
6. Cederberg, T.; Fromberg, A. & Sørensen, M.K. (1997) Determination of toxaphene in fish samples - a congener specific approach using high resolution mass spectrometry. *Organohalogen Compounds* **31** 64-68.
7. Andersson, Ö.; Linder, C.E.; Olsson, M.; Reuthergårdh, L.; Uvemo, U.B. & Wideqvist, U. (1988) Spatial differences and temporal trends of organochlorine compounds in biota from the northwestern hemisphere. *Arch. Environ. Contam. Toxicol.* **17** 755-765.
8. Jansson, B.; Vaz, R.; Blomkvist, G.; Jensen, S. & Olsson, M. (1979) Chlorinated terpenes and chlordane compounds found in fish, guillemot and seal from Swedish waters. *Chemosphere* **4** 181-190.
9. Saleh, M.A. & Casida, J.E. (1977) Consistency of toxaphene composition analyzed by open tubular column gas-liquid chromatography. *J. Agric. Food Chem.*, **25** (1) 63-68.