Levels of PCB in Cod Liver from Danish Waters 1988-2004

Fromberg, Arvid; Granby, Kit; Højgård, A.

Published in:
Organohalogen Compounds

Publication date:
2005

Document Version
Publisher's PDF, also known as Version of record

Levels of PCB in Cod Liver from Danish Waters 1988 - 2004

Arvid Fromberg[1], Kit Granby[1], Arne Højgård[2]

[1]Danish Institute For Food And Veterinary Research
[2]Regional Veterinary and Food Control Authority Århus

Introduction

The Danish monitoring programme for contaminants in food include investigations of persistent organochlorine contaminants such as PCB (polychlorinated biphenyls) and compounds that have earlier been widely used as pesticides (for example DDT).[1] Because of their stability and tendency to accumulate in fatty tissues they can enter the food chain and therefore be found in marine species. Relatively high levels occur in cod liver, which has high lipid content and for that reason is suitable for monitoring purposes.

Figure 1. Waters around Denmark.

Cod liver was used for monitoring the pollution levels of the different Danish waters from the Baltic Sea in the East to the North Sea and Skagerrak in the West. The inner Danish waters comprise of the Sound, the Belts (between the main islands and the large peninsula) and the Kattegat (Figure 1). Results from 1988 to 2004 are presented looking at differences between the waters and the decline in the contaminants levels during the period.

Methods and Materials

Samples: 274 samples of cod from Danish waters were collected from 1988 to 2004. The cod livers were used for chemical analyses.

Compounds: All the samples were analysed for their content of the following organochlorine pesticides: α-HCH (hexachlorocyclohexane), B-HCH, γ-HCH (lindane), HCB (hexachlorobenzene), heptachlorepoxide, aldrin, dieldrin, *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT. Furthermore samples were either analysed for total-PCB using Aroclor 1260 as references (1988-1996) or for the following PCB congeners (1994-2004): PCB-28, PCB-52, PCB-101, PCB-105, PCB-118, PCB-138, PCB-153, PCB-156, PCB-170 and PCB-180.

Sample clean-up: The homogenized cod liver was mixed with sodium sulfate and Soxhlet extracted using pentane after which the solvent was evaporated. About 0.6 – 0.8 g of fat was added to a Florisil column deactivated by water and eluted with dichloromethane:pentane (1:4). The eluate was carefully evaporated and the sample dissolved in isooctane.

Fractionation (1988-1996): The samples were further fractionalized using a silica gel column elution fraction A using pentane (PCB, HCB, aldrin and DDE) and Fraction B using diethyl ether:pentane (1:9) (other organochlorine pesticides).

The final sample was analysed by gas chromatography using two different columns and electron capture detectors.

GC-ECD parameters (1988-1996): Chrompack gas chromatograph. Column: 0.8% DC200/3.2% QF_1 on Chrom W.-AW DMCS 80-100 mesh and 1% OV17 on Chrom W.-AW DMCS 80-100 mesh. Carrier gas: Helium, 20 ml/min.

5 µl injected. Injector held at 225°C. Oven temperature: 170°C. Detector temperature 320°C. PCB was quantified by comparing response to Aroclor 1260 and organochlorine pesticides were quantified by comparing responses with those of standard mixtures. Limits of detection for organochlorine pesticides and Total-PCB were 1 to 5 µg/kg.

GC-ECD parameters (1994-2004): Perkin Elmer autosystem gas chromatograph. Column: 50 m CP-Sil-5CB (Chrompack) and 60 m DB-17 (J&W), 0.25 mm i.d., 0.25µm film thickness. Carrier gas: Helium, 15 psi (CP-Sil-5CB) or 37 psi (DB-17). 2 µl injected splitless, splitless time 2.5 min. Injector held at 220°C. Temperature programme: 90°C for 1 min., 30°C/min. to 180°C in 10 min., 2°C/min. to 240°C, 10°C/min. to 280°C in 20 min. (CP-Sil-5CB) or 30 min. (DB-17). Detector temperature 320°C. PCB congeners and organochlorine pesticides were quantified by comparing responses with those of standard mixtures. Limits of detection for organochlorine pesticides and PCB congeners were 0.5 to 4 µg/kg.

Results and Discussion

Contents of organochlorine environmental contaminants in fish have significantly decreased during the 1970s and the beginning of the 1980s.[2] However developments in recent years do not show a clear trend, but rather a more or less steady state condition. The contents of contaminants in fish depend on a number of factors, not accounted for in the monitoring, *e.g.* the food basis of the fish, their age, weight and sex, and the time of year. For instance, the concentration over time may decline if the fish caught today are younger, and thus, other things being equal, have not had the same time to accumulate the contaminants. Such an effect will hardly be distinguishable from the effect of lower concentrations in the marine environment over time.

Cod liver was selected to study the development over time, since almost all the cod liver results are above the limit of detection. Statistical analyses of data from cod liver showed that the distribution of concentrations is best described by a logarithmic normal distribution, and that the development over time can be described by a linear regression based on logarithmized data. As the cod liver data set contain observations below the limit of detection, a special programme was used to estimate regression lines for the organochlorine compounds. The programme describes results by means of a logarithmic normal distribution estimating values below the limit of detection on the basis of values above the limit of detection. By means of an analysis of variance, the programme did at the same time assess whether the regression lines for different waters could be pooled. Waters that have been pooled because their regression lines do not differ significantly, and because the waters are at the same time physically joined, are indicated by the same symbol in Figure 2.

Figure 2 shows the development over time for total PCB in cod liver. Since 1988, cod liver samples show an overall tendency towards a decline in concentrations over time, but with an almost steady state since 1995. In general, when solely considering the period 1998-2003, no clear development for organochlorine pesticides and indicator PCB in fish is seen. The overall trend is that the indicator PCB concentrations in cod livers from the Baltic Sea, the Belts, and the Sound are highest, while the concentrations in cod livers from the Skagerrak and North Sea are lowest.

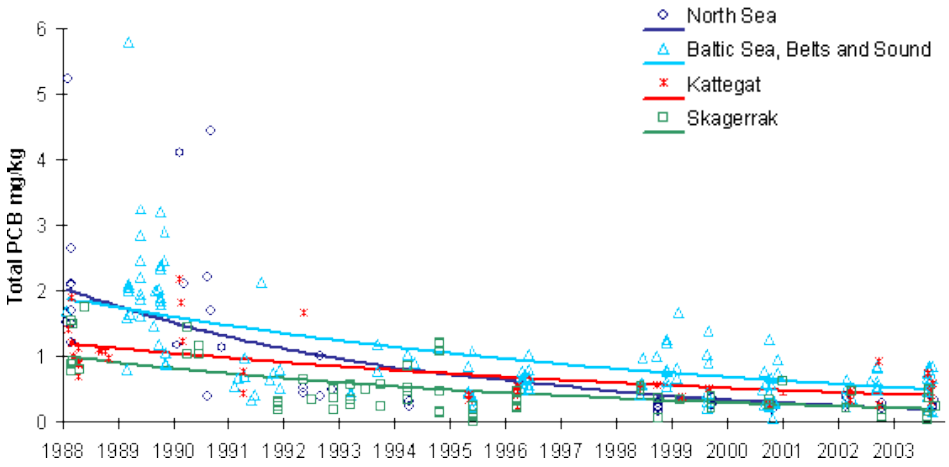

Figure 2. Total PCB in cod liver from Danish waters, 1988 - 2003. Each point represents one sample, and the lines

show the regressions based on logarithmized data. Data for the period 1998 to 2003 is estimated from the indicator PCB-sum.

Total PCB is a measure of the entire PCB content based on a previously used analytical method. The content of PCB is today estimated by summarising the content of the individual PCB compounds analysed. The two analytical methods were used in parallel in order to determine the correlation between the two methods, which provided the possibility of following the development in PCB contents over time across the change. Total PCB content for the period 1998 to 2003 is estimated using this correlation between Total PCB and indicator PCB-sum.[3]

Figure 3 shows a comparison between PCB determined by the previously used method (total PCB) and PCB determined as the sum of congeners. In view of the technical difference between the two methods, a very high degree of correlation is revealed and the development in the PCB levels over time can still be followed in spite of the change in analytical method.

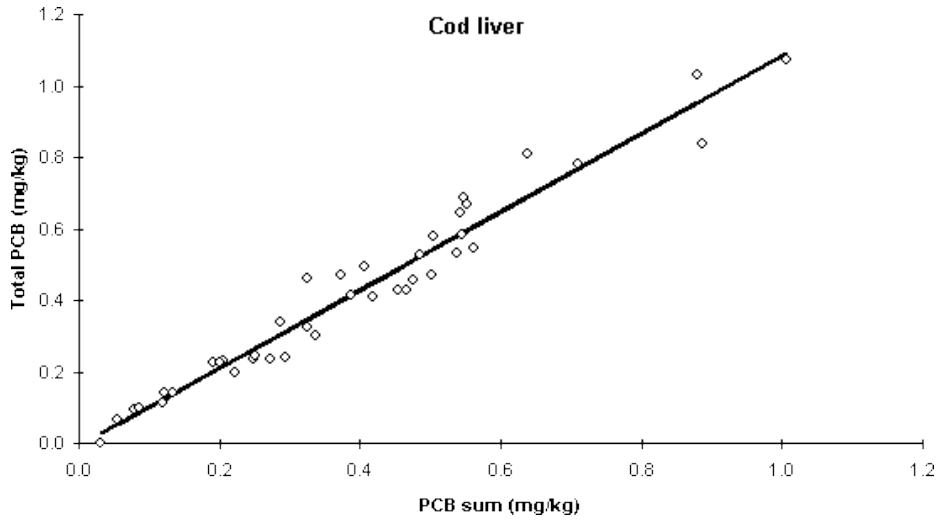

Figure 3. Comparison between measuring of PCB in cod liver, determined as PCB-sum and as total PCB, respectively. Regression line: Total PCB= -0.01+1.09×PCB-sum, R^2=0.955[3]

Conclusion

From 1988-2004 the contents of PCB in cod liver show a downward tendency in concentrations. However, for the period 1994 – 2004 no significant tendency appears and the conditions seems to be at steady state.

Acknowledgments

I would like to thank the chemists and technicians from the regional laboratories in Århus and Aalborg, Denmark for the analysis of PCB and organochlorine pesticides in the samples.

References

1. Danish Veterinary and Food Administration, Chemical Contaminants, Food Monitoring, 1998-2003, Part 1, Fødevarerapport 2005:01.

2. Hilbert, G., Lillemark, L., and Nilsson, P. (1997) PCB in cod liver - Time trend study and correlation between total PCB (Aroclor 1260) and PCB congeners, *Organohalogen Compounds* 32: 340-343.

3. Danish Veterinary and Food Administration, Chemical Contaminants, Food Monitoring, 1993-1997, Part 2, Fødevarerapport 2001:18 (October 2001).