

Monitoring of brominated flame retardants, dioxins, PCBs and other organohalogen compounds in fish from The Netherlands

Stefan Van Leeuwen¹, Wim Traag², Jacob de Boer¹

¹Netherlands Institute for Fisheries Research

²State Institute for Quality Control of Agricultural Products

Introduction

A new monitoring program on organic contaminants in fish from the Netherlands has begun in 2003. The aim of this program is to determine the levels and temporal trends of contamination for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenylethers (PBDEs), hexabromocyclododecane (HBCD) tris(4-chlorophenyl)methane (TCPM_e) and –methanol (TCPM) and polychlorinated dibenzodioxins and –furans (PCDD/Fs) in fish that is regularly consumed by the Dutch population. Earlier studies indicated that these contaminants are present in fish but no comprehensive dataset was available for evaluation of possible risks for consumers¹. The results of the first year are shown in this paper.

Methods and Materials

Sampling

Various fish samples have been collected between May 2003 and December 2003. Table 1 shows the fish species sorted by origin of the sample. The samples have been obtained from the local auction (farmed salmon, eel), caught during stock assessment cruises of the research vessel Isis, from local fishermen or by electro fishery (eel).

Table 1. Overview of the samples analysed

Location	Species and number of samples analysed
North Sea	Cod (1), herring (4), shrimp (1), mackerel (2), sole (2), plaice (1), coalfish (2), haddock (1)
Wadden Sea/ delta area	Mussels (3), shrimps (1)
Freshwater	Eel (10), pike perch (2)
Farmed	Eel (2), salmon* (2)

* Norwegian and Scottish salmon

After transportation of to RIVO, the lengths and weights of each individual fish were recorded. The laboratory sample was prepared by pooling 25 g of filet of each of 25 individual fishes.

Analytical methods

The complete WHO set of dioxins and furans (17 congeners) and dioxin-like PCBs (12 congeners) were analysed in the 4 herring and 3 mackerel samples (1 additional sample south-west of Ireland) according to an earlier described method¹. The same was true for the indicator PCBs and OCPs². TCPM(e) was extracted according to the before mentioned PCB/OCP extraction. The lipids were removed using gel permeation chromatography (GPC) on a PL-GEL column (600*25 mm, 10 µm, 50 Å particles). The extract was eluted two times over the GPC column. Further clean-up was carried out by silica chromatography and the final extract was analysed on a Perkin-Elmer GC-MS. TCPMe was analysed on a DB-5 capillary column (15m, 0.25 mm i.d., 0.25 µm film thickness), whereas TCPM was analysed on a CP-Sil-8 (50m, 0.15 mm i.d., 0.30 µm film thickness). The ionisation mode was negative chemical ionisation (NCI) for TCPM and electron impact (EI) for TCPMe as different ionisation provided highest sensitivity³. ¹³C-TCPM and -TCPMe (Wellington Laboratories, Guelph, Ontario, Canada) were used as internal standards.

The PBDEs, dimethyl-TBBP-A and total HBCD have been analysed by Soxhlet extraction, clean-up by GPC and silica and chemical analysis by GC-NCI-MS, according to the method described in the literature⁴. The diastereoisomers HBCD (α -, β - and γ HBCD) and TBBP-A were (also) analysed by LC-MS⁵.

Results and Discussion

PCDD/Fs and DL-PCBs

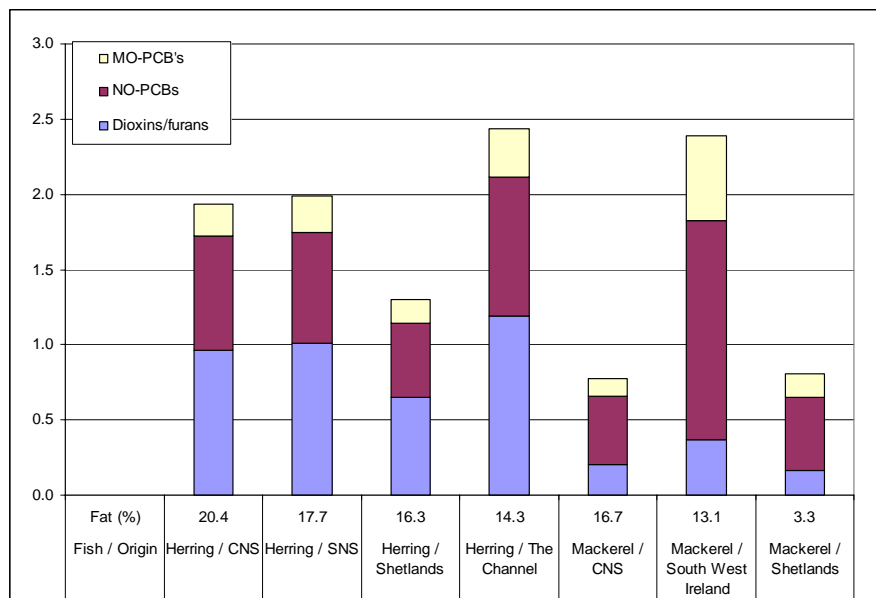


Figure 1. Concentrations of PCDD/Fs, non-ortho-PCBs (NO-PCBs) and mono-ortho-PCBs (MO-PCBs) in herring and mackerel from different locations (CNS = Central North Sea, SNS = Southern North Sea).

The levels of PCDD/Fs in the fish samples do not exceed the current European MRL of 4 pg TEQ/g ww (Figure 1). Concentrations in herring and mackerel landed in Scottish harbours in 1995/1996 showed levels up to 3.8 pg PCDD/F TEQ/g ww and 10.4 pg PCB-TEQ/g ww. The relative contributions of PCDD/Fs in that study was 25-53% of the total TEQ for herring, whereas in the current study the contribution is very constant at 49-50%. The contribution of PCDD/Fs in the 1995/1996 study for mackerel was 14-30%, whereas in the current study PCDD/Fs contribute 15-26% to the total-TEQ. The higher contribution of PCBs to the total-TEQ shows different contamination sources which might be associated to feeding at other locations (compared with herring) during the first and second year of the mackerel life time.

PCBs

Figure 2 shows a very wide range of concentrations of PCBs from 2 to 1,750 $\mu\text{g}/\text{kg}$ ww in freshwater fish (eel). The high concentrations are found downstream the highly industrialised and urbanised river Rhine and Meuse, and have been observed before at these locations⁶. The median concentrations of fish from the other locations range from 4.1 to 11.7 $\mu\text{g}/\text{kg}$ ww. PCB 153 was

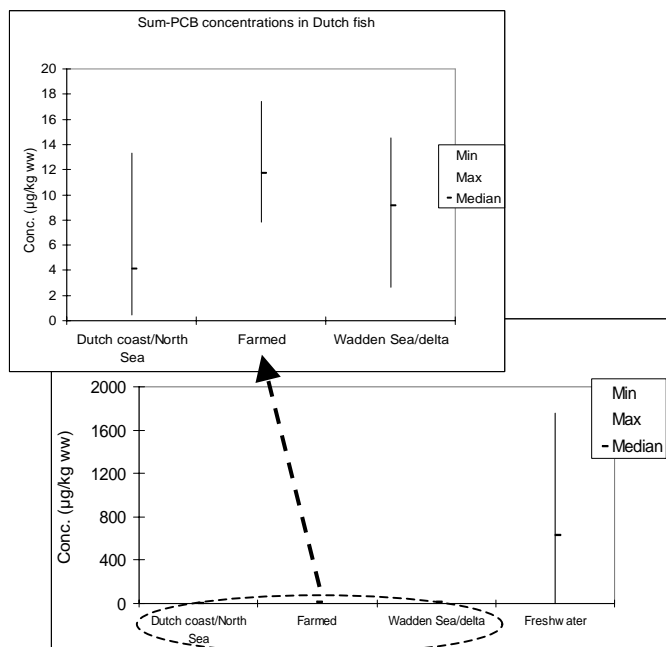


Figure 2. Concentrations of the sum of PCB 28, 52, 110, 118, 138, 153 and 180 ($\mu\text{g}/\text{kg}$ ww).

the predominant congener in all samples. Eel sampled at three downstream locations (Nieuwe Merwede, Meuse at Keizersveer and Haringvliet-Oost) exceeded the Dutch CB-153 maximum residue limit (MRL) of 500 $\mu\text{g}/\text{kg}$ ww.

OCPs

The highest OCP concentrations are also found at freshwater locations. Table 2 shows the percentage of samples in a concentration range of 1-10 and 10-100 µg/kg ww. The OCP concentrations in most samples were <1 µg/kg ww or lower than the limit of quantification. Median

Table 2. Relative amount (% of samples) in concentration ranges per origin.

Origin	1-10 µg/kg ww (% samples)	10-100 µg/kg ww (% samples)
Dutch coast/North Sea (n=14)	HCB (21), ppDDD (7), ppDDE (43)	-
Farmed (n=4)	α-HCH (25), HCB (100), ppDDD (75), ppDDE (50), ppDDT (50)	ppDDE (50)
Wadden Sea/delta (n=4)	ppDDE (50)	-
Freshwater (n=13)	β-HCH (46), γ-HCH (69), QCB (46), HCB (46), HCB (38), ppDDD (46), ppDDE (15), ppDDT (38)	γ-HCH (8), HCB (38), HCB (8), ppDDD (38), ppDDE (77), ppDDT (23)

concentrations of ppDDE are 0.75, 12, 0.7 and 29 µg/kg ww for Dutch coast/North Sea, farmed, Wadden Sea/delta and freshwater fish respectively.

TCPM(e)

The TCPM levels are generally higher than those of TCPMe. Similar to the PCBs, the highest value is this case also detected in eel from the Nieuwe Merwede location (330 µg/kg ww). Although relatively high levels of TCPM have been detected earlier in some eel samples from the Netherlands³ this sample is an exception in this dataset. This is also clear from the median values, which vary only from 0.2 to 3.2 µg/kg ww.

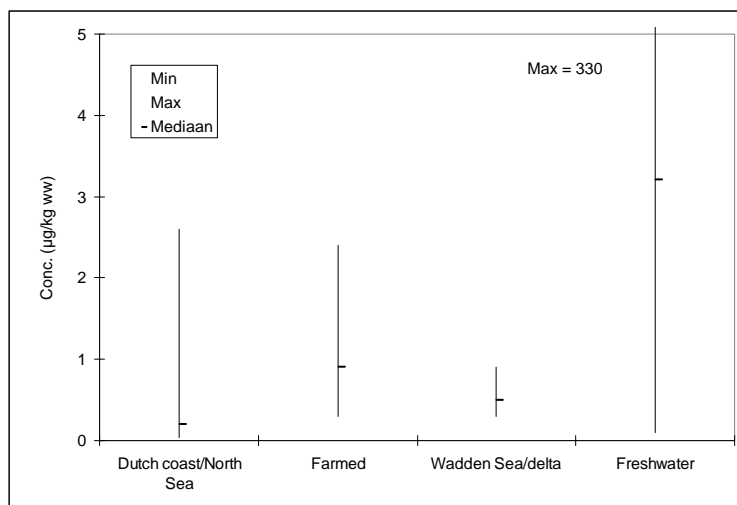


Figure 3. Concentrations of TCPM (µg/kg ww).

PBDEs HBCD and (Me-)TBBP-A

The data in Figure 4 show the distribution of the predominant congeners in fish samples from different origin. All median concentrations are (far) below 2.5 $\mu\text{g}/\text{kg}$ ww, except for BDE 47 and BDE 100 in eel. The high levels in eel are explained by the high fat content of the eel, but also by the high degree of industrialisation and urbanisation along the river Rhine and Meuse and the use of BDEs in German mining activities⁷. Total BDE concentrations based on the sum of BDE 28, 47, 49, 99, 138 and 154 are similar to the levels reported by Voorspoels *et al.*, although he reported the sum of a different suite of congeners (BDE 28, 47, 99, 100, 153 and 154)⁸. Rice *et al.* reported levels of fish collected from two USA rivers (Detroit river and Des Plaines River)⁹, which are in the same range as the BDE concentrations in eel reported here, but when expressed on a fat weight basis, ca. 10-fold higher than the median concentrations found in this study, indicating a higher Penta-mix related BDE contamination in the US.. For nearly all samples, the levels of TBBP-A, BDE 71, 75, 79, 85, 119, 183, 190 and 209 were below the limit of detection (data not shown).

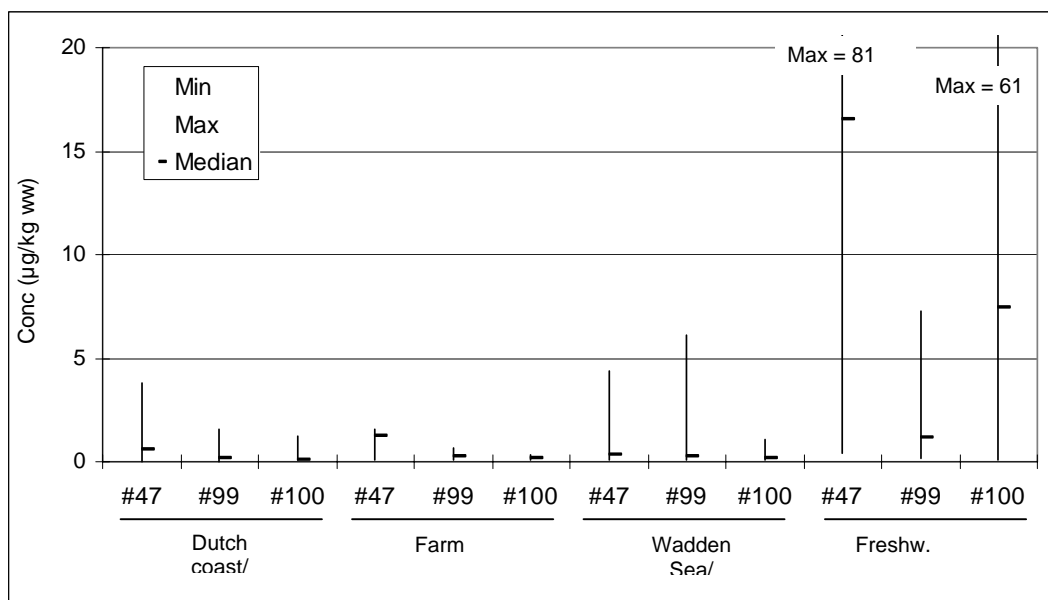


Figure 4. Concentrations of BDE congeners 47, 99 and 100 in fish from various locations.

From the individual diastereoisomers, β -HBCD was below the limit of detection in nearly all samples except in 5 freshwater eel samples (0.8-1 $\mu\text{g}/\text{kg}$ ww) from the Meuse, Roer, IJssel and Hollands-Diep. Median levels of α -, β -, and γ -HBCD in eel were 12, 0.9 and 3 $\mu\text{g}/\text{kg}$ ww respectively, whereas maximum levels were 41, 1.6 and 8.4 $\mu\text{g}/\text{kg}$ ww respectively. The ratio of α -: γ -HBCD ranges from 12:1 to 3.5:1. The levels in this study are considerably higher than the levels reported by Tomy *et al.* in lake trout from Lake Ontario (0.2-5.9 $\mu\text{g}/\text{kg}$ ww)¹⁰. Also, the ratio of α -: γ -HBCD was slightly different from 8.3:1 to 2.5:1.

Acknowledgements

The authors would like to acknowledge the Dutch Ministry of Agriculture, Nature Management and Food Safety for their financial contribution to the project.

References

1. van Leeuwen, S. P. J., W. A. Traag, L. A. P. Hoogenboom, J. de Boer (2002) *Organohalogen Compounds* 57, 217.
2. de Boer, J. (1988) *Chemosphere* 17, 1811.
3. de Boer, J., P.G. Wester, E.H.G. Evers, U.A.Th. Brinkman (1996) *Environ. Pollut.* 93, 39.
4. de Boer, J., C. Allchin, R. Law, B. Zegers, J. P. Boon (2001) *Trends Anal. Chem.* 20, 591.
5. Morris, S., C. Allchin, P. Leonards, J. de Boer (2004). The distribution and fate of HBCD and TBBP-A brominated flame retardants in North Sea estuaries and aquatic food webs. *Environ. Sci. Technol.*, in press.
6. de Boer, J., P. Hagel (1994). *Sci. Total Environ.* 141, 155.
7. de Boer, J. (1989) *Chemosphere* 18, 2131.
8. Voorspoels, S., T. De Mey, A. Covaci, P. Schepens (2003). *Organohalogen Compounds* 55, 417.
9. Rice, C. P., S. M. Chernyak, L. Begnoche, R. Quintal, J. Hickey (2002) *Chemosphere* 49, 731.
10. Tomy, G. T., W. Budakowski, T. Halldorson, M. Whittle, M. Keir, M. Alae (2003) *Organohalogen Compounds* 61: 111.