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SPATIAL AND TIME TRENDS OF DIOXINS AND PCBS IN COD LIVERS FROM THE NORTH SEA

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Introduction

Persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) accumulate in cod fish (Gadus Morhoa). Levels in the lean muscle tissue (i.e. the fillet) are low, while in the high-lipid liver POPs accumulate to high levels as has been shown in several studies [1,2]. In the mid 1970s, a monitoring program was installed in the Netherlands on the monitoring of POPs in the marine environment in the North Sea. Cod was chosen as the target species as it was widely distributed in the North Sea. In addition, from an analytical point of view, the high lipid content in the liver and high POP levels facilitated the detection of the contaminants, initially using techniques such as gas chromatography (GC) with electron capture detection (ECD). The cod liver program covered the Northern, Central and Southern North Sea and the contaminants studied were PCBs and organochlorine pesticides (OCPs). In 2003, the cod liver monitoring program was redesigned for including a wider range of contaminants such as heavy metals, organotin compounds, toxaphene, PCDD/Fs and dioxin-like PCBs (dl-PCBs) and perfluorinated alkyl substances (PFASs). Here we present spatial and time trends of PCDD/Fs and PCBs in cod liver.

Figure 1

Materials and methods

The cod liver samples were collected annually on trips by the research vessel Tridens and from commercial fishing vessels on the North Sea. From every location, the livers of 25 individual fish were pooled resulting in 1 composite (pooled) sample. The fish sampled were in the size range of 30-40 cm, although exceptions occurred if limited numbers were available. Samples were taken from the Northern, Central and Southern parts of the North Sea. In addition, hake liver composite samples were taken from the Irish Sea (South-West of Ireland, SWI), which was regarded the reference location because of the lower contamination levels. The contaminant levels were determined for the following analytes: PCDD/Fs and dl-PCBs (2010-2014 only), ndl-PCBs, OCPs, heavy metals and OTCs. Here we report on the results for PCDD/Fs and PCBs. Samples were extracted with the Smedes approach [3]. Sample purification was performed by an automated system (Power Prep™, FMS Inc., Waltham, MA, USA) equipped with an acid silica column, a neutral silica column, a basic alumina column and an activated carbon/celite column. After clean-up, every sample resulted in fraction A containing the mono-ortho and ndl-PCBs in 500 µl iso-octane and fraction B non-ortho PCBs and dioxins in 500 µl toluene. These fractions were analysed with gas chromatography coupled to high resolution mass spectrometry (GC-HRMS), as described by Tuinstra et al. [4].
The determined levels were evaluated against maximum levels from a food safety point of view (EU regulation 1881/2006). Additionally, the levels were evaluated against the Good Environmental Status (GES) limits as defined by the Marine Strategy Framework Directive (MSFD).

Results and discussion

In this study, time trends could be established for the ndl-PCBs from 2003 to 2014. Figure 2 shows the levels of the six ndl-PCBs on a ww (top) and PCB 153 on a lw basis (bottom) respectively. Expression on a lw basis allows a better comparison across several years and locations as lipid content as a co-factor has been ruled out. The results clearly show that the sum ndl-PCB levels exceed the EU ML of 200 ng/g (Figure 2, top), particularly in the Southern North Sea (SNS). The Central North Sea (CNS) samples originally exceeded this limit, but levels have dropped to approx. 100 ng/g in recent years.

Figure 2

De Boer [1] reported earlier on trends in cod livers from the early days of this monitoring program. Between 1980-1987, levels of PCB-153 ranged (on ng/g lw basis) as follows: 1500-2500 (SNS), 500-1000 (CNS) and 200-250 (Northern North Sea, NNS) which is much higher than the currently reported levels (Figure 2, bottom). This suggests that the marine environment has improved. However, it should be taken also into account that at those early days, the caught cod was larger. Julshamn et al. [5] showed that cod livers of Arctic cods of >80 cm may be 1.5 to 2.5 fold more contaminated than in cod livers of cods <70 cm. The average cod size in this study decreased 20-38% compared to those reported by de Boer [1]. Therefore, some caution is needed when drawing conclusions on time trends in North Sea cod livers. It should also be taken into account that POPs accumulation and growth dynamics may be different for Arctic cods compared to North Sea cods.

Figure 3

As for the dioxins and dl-PCBs, the results for total-TEQ are shown in Figure 3 top (wet weight) and Figure 3 bottom (lipid weight). The maximum level (ML) for dioxins and dl-PCBs is 20 pg TEQ /g (sum-TEQ). Clearly, all samples from the North Sea are exceeding the ML and should therefore not be brought on the market. The Dutch population generally doesn't consume cod liver, so although the levels are high, there is no health risk associated with these findings. The levels in the samples from the reference location (SWI) are well below the ML. The levels from the reference location are very stable around approx. 10 pg TEQ/g ww (20 pg TEQ/g lw), whereas the levels of the SNS and CNS show more variance. Because of the relatively short timeframe and limited number of samples no conclusion can be drawn on temporal trends. The levels we report are slightly lower than those by Karl et al. [2], who reported 44-123 pg TEQ/g for the sum-TEQ. The North Sea samples from that study are from the same area as CNS in our study. This is partly caused by the use of different TEF systems. Using the 1998 TEFs for our samples would result in a 16-27% higher sum-TEQ levels.
Apart from the food safety perspective, the cod liver monitoring can attribute to assessing the Good Environmental Status (GES) for the Marine Strategy Framework Directive (MSFD). Though fish liver is not a designated matrix for MSFD monitoring, the levels of POPs in cod liver, especially over such a long period, can indicate the trend in the marine ecosystem. The environmental quality standards (EQS), both for secondary poisoning as well as human health, is 6.5 pg sum TEQ/g. The lipid content of the filet (around 1%), which is the primary human consumption, is more than 10 times lower than that of the liver (30-50%). Therefore, the sum-TEQ levels in filets of cod, also from relatively highly polluted cod, will be much lower than this threshold level of 6.5 pg sum-TEQ/g.

Figure 4

The dl-PCBs make up 78-90% of the sum-TEQ in our samples. There was no clear distinction among the different sampling locations. The congener profile for the dioxins (Figure 4 bottom) is dominated by the furans, particularly 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF. This is slightly different from the study by Roszko et al. [6] on livers from Baltic cods, where 1,2,3,7,8-PeCDF dominated (30%), followed by 2,3,7,8-TCDF (15%) and 2,3,4,7,8-PeCDF (11%). On a dioxin-TEQ basis, in our study 2,3,7,8-TCDF dominates (~30%), followed by 2,3,7,8-TCDD (15-20%) and 1,2,3,7,8-PeCDD (10-15%) (data not shown). There were nearly no differences between the locations, although 2,3,7,8-TCDF was slightly higher in the SNS samples (Figure 4). For the PCBs, on a concentration basis, PCB 153 dominated the profile, followed by PCB 138 and PCBs 101, 118 and 180. On a TEQ basis, PCB 126 dominated and contributed 67-76% to the sum-TEQ.

Acknowledgements
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Figure 1

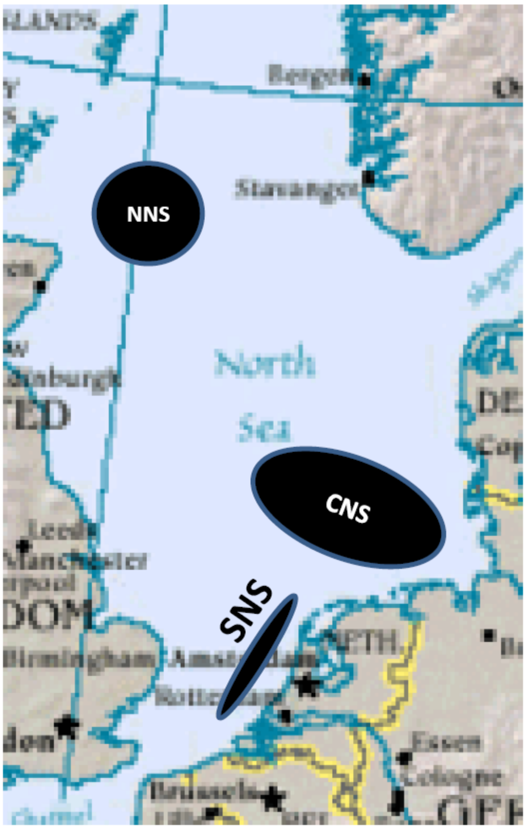

Figure 1. Overview of the North Sea and sampling areas. Please not that the location South-West of Ireland is not indicated on the map. NNS = Northern North Sea, CNS = Southern North Sea, SNS = Southern North Sea

Figure 2

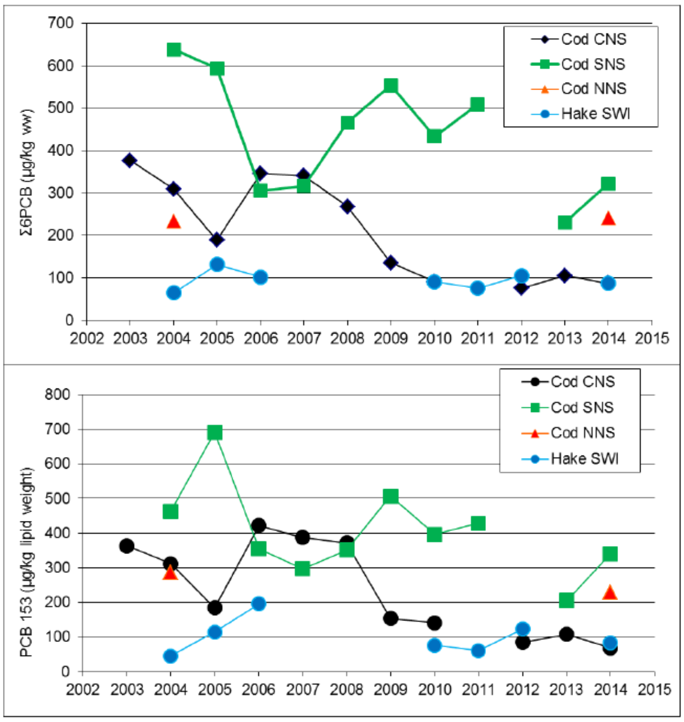

Figure 2. PCB levels in cod liver from the North Sea and hake liver from the South-west of Ireland. Sum ndl-PCB levels are expressed on ww basis (top) and PCB-153 on a lw basis (bottom). CNS = Central North Sea, SNS = Southern North Sea, NNS =Northern North Sea and SWI = South-West of Ireland

Figure 3

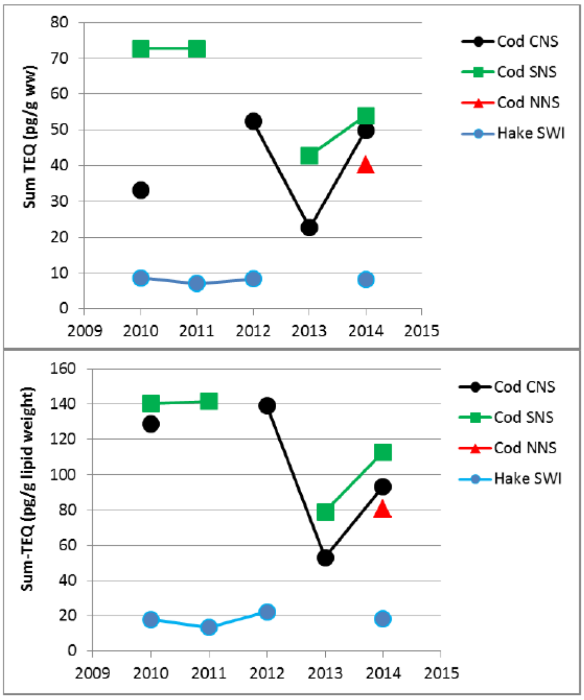

Figure 3. Sum-TEQ levels in cod liver from the North Sea and hake liver from the South west of Ireland. Levels expressed on ww (top) and lw (bottom).

Figure 4

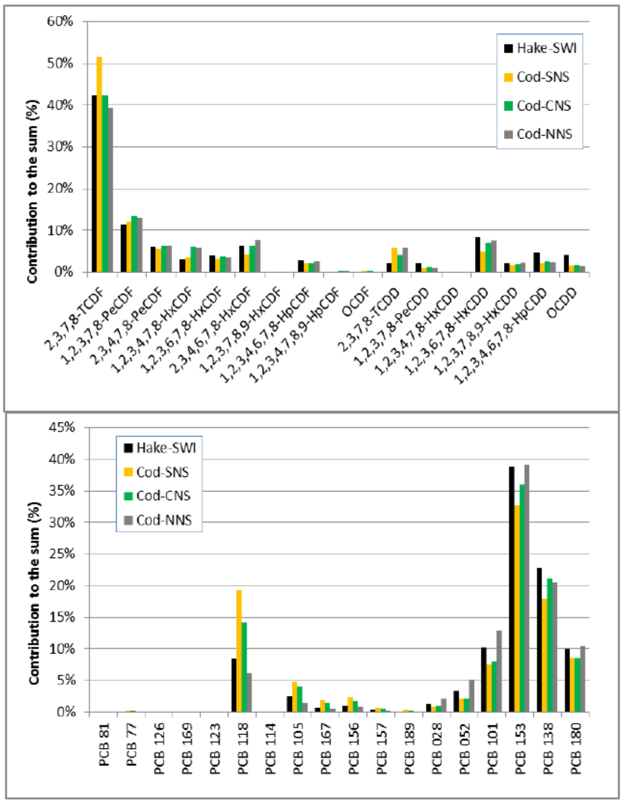

Figure 4. Relative contribution to the total concentration in cod liver from the North Sea and hake liver from the South West of Ireland for dioxins (top) and PCBs (bottom).