Brominated Flame Retardants in Dutch North Sea Surface Sediments

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Abstract

Brominated flame retardant (BFR) concentrations were determined in the fine fraction (<63µm) of 10 surface sediments located in the southern part of the Dutch section of the North Sea Continental Shelf. Concentrations generally decreased with increasing distance from the Dutch shore. Highest levels were found off the Western Scheldt, which is in accordance with findings reported by other authors.

Introduction

Early 2000, the managing authorities of the Dutch North Sea, the North Sea Directorate, requested a report on the distribution of 'new', potentially harmful compounds in surface sediments and sediment cores in the southern part of the North Sea. Compounds selected for this project were Irgarol 1051 (an antifouling agent), phthaltes (o.a., plastizisers), and brominated flame retardants (BFR), i.e. Polybrominated Biphenyls (PBBs), Polybrominated Diphenylethers (PBDEs) and hexabromocyclododecane (HBCD).

In this paper, the results will be presented of BFR analyses in ten surface sediments off the Dutch coast, locations chosen to cover both remote off-shore areas as well as near-shore coastal sediments.

Methodology

Surface sediments were sampled using a box-core; at each location, the top 5 cm of six individual cores were pooled and further treated as one sample. Each sample was sieved through a 63µm nylon mesh, freeze-dried and homogenized. BFR were determined after hexane:acetone Soxhlet extraction, clean-up over two PL gel columns and further purification by elution over a silica column and sulphuric acid treatment. The final analyses were carried out on GC/MS, using EC/NCI with methane as reagent gas. Peak identification was based on retention time and the recognition of the Br^--ion (m/z 79/81). The following compounds were

determined: PBB congeners 15, 49, 52, 101, 153 and 209; PBDE congeners 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 190 and 209, and hexabromocyclododecane (HBCD; PBB and PBDE nomenclature being similar to that of the PCBs; Ballschmiter *et al.*, 1992).

Results and Discussion

Decabromobiphenyl (PBB 209) levels were below 0.54-0.70 µg/kg dry weight (d.w.: average 0.63 ± 0.06), with no apparent relationship between location and PBB 209 level. PBDE 209 levels, however, showed a clear trend with remote locations having lower and near-shore levels having higher levels: Figure 1.

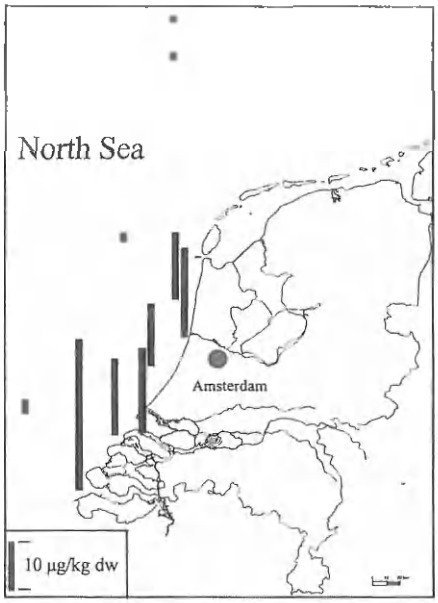

Figure 1: PBDE 209 levels in North Sea surface sediments (fraction <63µm).

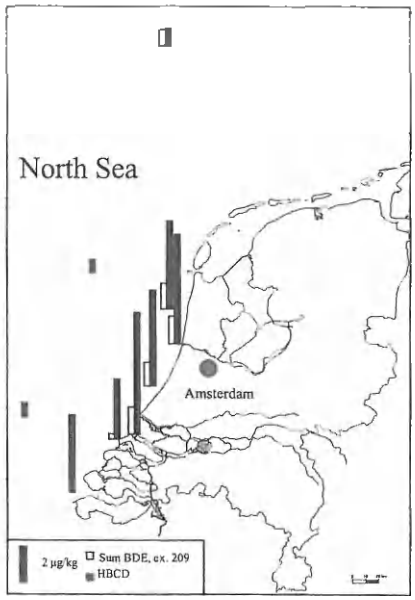

Figure 2: Levels of PBDE and HBCD in North Sea surface sediments (fraction <63µm).

With 32 µg/kg d.w., PBDE 209 levels off the Western Scheldt were higher than those reported by de Boer *et al.* (2000), who found a decreasing trend in the Western Scheldt from 510 µg/kg at the upper estuary to less than 4 µg/kg near Vlissingen at the mouth. As the PBDE levels in suspended matter in the Western Scheldt were variable and depended on sampling period (de Boer *et al.*, 2000), the results of the present study are probably within the normal concentration range of these compounds.

Figure 2 shows levels of the sum of the determined PBDE congeners minus PBDE 209, as well as the levels of HBCD. Locations with high PBDE 209 levels (Figure 1) were generally

high in these other BFRs as well.

With the exception of PBB 169, all PBB levels were below 0.10 µg/kg d.w.; PBB 169 levels were between 0.05 and 1.10 µg/kg, without apparent relationship between location and contaminant level.

HBCD and PBDE 209 levels showed a positive correlation between locations; contrary, PBDE 209 and PBB 169 levels were *inversely* correlated. This may suggest a different source (either in time or space) of the brominated biphenyls with respect to the other BFR compounds.

From Figures 1 and 2 it becomes evident that the hightest BFR contamination is found in near-coastal sediments. This corresponds with the fresh water plumes of the rivers Scheldt and Rhine, being pushed towards the Dutch coast through the counter-clockwise orientated residual currents of the North Sea.

On the sideline of this study, additional parameters (e.g., sediment toxicity) were determined that could be used as indications of sampling site contamination. The genotoxicity of sediment extracts was determined using the Mutatox bacterial genotoxicity test (Klamer *et al.*, 1997). In this assay, incubation of a dark strain of otherwise light-emitting bacteria in the prescence of genotoxic compounds (i.e. an extract), may result in a restoration of bioluminescence. The lowest concentration that induces significant light emission was recorded. BFR levels generally correlated positively with genotoxicity; as, however, BFR compounds themselves are not genotoxic in this assay (de Boer *et al.*, 1998), the positive correlation is probably indicative for the prescence of unknown genotoxic compounds.

References

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The Second International Workshop on Brominated Flame Retardants

May 14-16
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