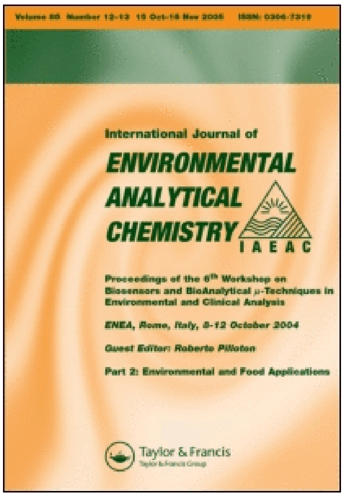

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Characteristic Levels of Chlorinated Hydrocarbons and Trace Metals in Fish from Coastal Waters of North and Baltic Sea†

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During investigations on the occurrence and distribution of contaminants in coastal waters of the North Sea and the Baltic organochlorine compounds such as hexachlorobenzene (HCB), octachlorostyrene (OCS), hexachlorocyclohexane isomers (HCH), dichlorodiphenyltrichloroethane (p,p'-DDT) and its metabolites and polychlorinated biphenyls (PCBs) and heavy metals such as mercury, cadmium and lead were determined in a selected flatfish species (flounder, *Platichthys flesus* L.).

The sampling network covered the outer estuaries of the rivers Weser and Elbe, the German Bight, the Danish North Sea coast and coastal regions of the south-western Baltic. Organochlorine compounds were determined by high-resolution glass capillary gas chromatography with electron capture detector after sample pretreatment and clean up. For the determination of heavy metals a multi-stage analytical procedure

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was used, in which graphite furnace (for Cd and Pb) resp. cold vapour (for Hg) atomic absorption spectrometry was combined with pre-instrumental separation and enrichment techniques. Evaluation of the data from the programme made obvious significant geographical differences in the levels and the pattern with regard to the substances involved. For HCB, OCS and Hg a crucial point of contamination within the German Bight was recognized that was apparently influenced to a large extent by the inflow of waters from the Elbe.

KEY WORDS: Organochlorines, heavy metals, flatfish, coastal waters, North Sea, Baltic.

INTRODUCTION

Contamination of coastal zones, estuaries and adjacent semi-closed marginal seas with potentially harmful inorganic and organic substances is generally most severe in densely populated and highly industrialized regions. It was the intention of the present study to provide baseline data of persistent, bioaccumulative organic substances (PCBs, DDT and its metabolites, HCH, HCB and OCS) and of trace metals (Cd, Pb, Hg) in fish from coastal waters of North and Baltic Sea which suffer under environmental stress through man's activities. Interests centered upon spatial changes in the contaminant concentration levels, as they might give an indication of the distribution behaviour of the investigated substances.

In order to understand the extent to which aquatic biotops have been influenced by man's activities, it becomes crucial to determine contaminant levels in different aquatic compartments with appropriate analytical certainty. Perusal of the literature over the last decade indicates that insufficient attention has been paid to the quality of data obtained in many cases. Recent intercomparison exercises for trace metals and organochlorine compounds in biological material[1,2] have demonstrated very clearly that the level of agreement between laboratories is still unsatisfying and that many of the analytical methods used to generate data are of doubtful validity. Trace analyses are subject to numerous difficulties including interferences, inappropriate instrumental settings, and uncontrolled gain or loss factors, which can complicate measurements and evaluation and introduce uncertainties in the final results. Accuracy is very difficult to achieve in environmental analyses; yet it is extremely important. The methodological approaches applied during the present study may therefore be also regarded as a contribution to harmonize analytical results with the actual contaminant levels in the material samples.

EXPERIMENTAL

Materials and methods

The sampling network covered the estuaries of the rivers Weser and Elbe close to the front between estuarine and marine water and areas within the limited range of the 10 m low water lines along the German and Danish North Sea and Baltic coasts. Figure 1 provides an overview on the areas investigated. The flounder (*Platichthys flesus* L.), a catadromus and euryhaline species, which is widely spread in coastal and estuarine regions, was selected for the present study. For chemical analysis the age group III (total length 18–

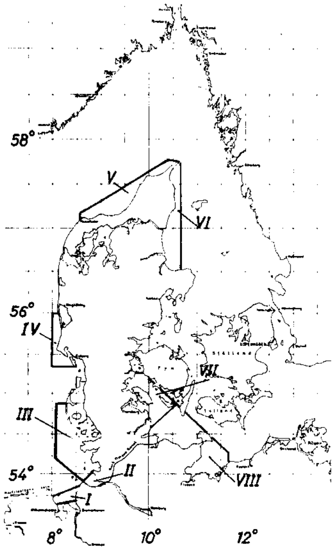

Figure 1 Overview on sampling areas.

Area 1: Weser estuary; Area II: Elbe estuary; Area III: Helgol. Bight (Germ. Bight); Area IV: Fanö-Bight; Area V: Skagerrak region; Area VI: Kattegat region; Area VII: Little Belt region; Area VII: Kiel and Mecklenb. Bight.

24 cm) was selected. Samples were taken in spring with a dragnet (mesh width 10 mm, 3 m wide). At least 50 specimens were collected in each area and analysed individually.

The *organochlorine compounds* were determined in *muscle tissue* by high-resolution silica-fused glass capillary gas chromatography with electron capture detector in combination with an earlier approved sample pretreatment. The latter consisted of liquid–liquid extraction, solvent partition and sulphuric acid clean up.[3]

For the determination of *cadmium and lead in liver* tissue of the individuals a multi-stage analytical procedure was used, in which graphite furnace atomic absorption spectrometry was combined with pre-instrumental separation and enrichment technique.[4, 5] *Mercury* was determined in *muscle tissue* by cold vapour atomic absorption spectrometry after pressure decomposition of the organic material with nitric acid.[6]

RESULTS

In Tables I–IV the analytical data obtained are summarized. The presentation of mean values and concentration ranges has been chosen because of the biologically induced variability of data undoubtedly present in all samples. Figure 2 shows chromatograms typical for the respective areas indicated. The necessity of quantitative investigations of PCB residues on the basis of individual congeners was stated previously.[7, 8] Those congeners prevailing in the residues of fish are obviously the persistent ones. Two hexachlorobiphenyls (IUPAC no. 138 and 153) were found to be the main constituents in those residues (Table I). Generally, it became clear that the PCBs as a group were the most occurring organochlorine contaminants in the fishes analysed during the present study. The chromatograms obtained suggested that at present there seems to be a rather uniform pattern with respect to these substances (compare Figure 2). The Elbe revealed to be rather significantly contaminated by PCBs. Samples from areas IV and V exhibited the lowest PCB contents measured during the present study.

Due to the ban placed on the use of DDT this pesticide poses today a minor problem to the marine environment. This was confirmed by the relatively low DDT residues found in the organ-

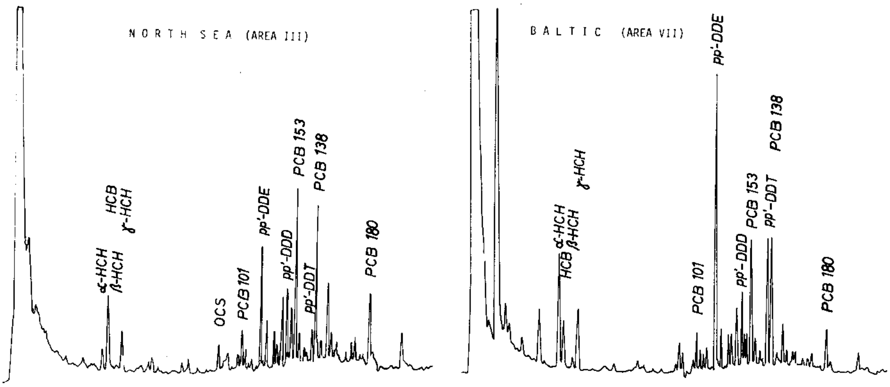

Figure 2 Characteristic chromatograms on a SE54 column of organochlorine residues in flounder (*Platichthys flesus* L.) from the North Sea (area III) and the Baltic (area VII). GLC conditions: Injector 250°C (split 1:40), detector 300°C (ECD), carrier gas 2 ml/min (argon/methane); temp.-programme: 170–190°C 4°C/min, 190°C 8 min, 190–250°C 4°C/min, 250°C 16 min.

Table I Values of organochlorine compounds (PCBs) in flounder from selected sampling areas. Data (range, mean) in μg/kg muscle tissue (wet weight).

	PCB congener			
Area	No. 101	No. 153	No. 138	No. 180
I	4–17 9	14–52 28	12–50 24	3–15 7
II	21–181 59	34–260 100	29–251 90	4–104 33
III	2–16 5	7–40 18	6–38 16	2–12 4
IV	1–5 2	2–19 7	1–16 6	1–3 1
V	1–2 1	5–13 9	4–10 6	1–2 2
VI	2–12 5	6–38 16	5–35 15	1–7 3
VII	1–25 8	5–180 24	4–169 23	1–52 6
VIII	4.69 9	5.84 29	4.68 27	1.27 7

Table II Values of organochlorine compounds (DDT-group) in flounder from selected sampling areas. Data (range, mean) in $\mu g/kg$ muscle tissue (wet weight).

Area	*pp'*-DDE	*pp'*-DDD	*pp'*-DDT
I	4–12 8	3–10 6	1–3 2
II	36–324 100	75–583 194	8–186 49
III	4–25 9	2–31 7	1–10 4
IV	2–11 4	1–6 2	1–6 3
V	4–22 9	1–10 3	1–9 3
VI	6–49 20	4–28 11	4–35 10
VII	2–52 19	1–42 10	2–49 15
VIII	2–48 19	3–42 11	2–32 16

isms in the present study. Generally, it can be inferred from the data obtained that the degree of total DDT contamination of fish sampled in the Baltic was on an average twice as high as that of individuals collected in the North Sea (Table II).

Unmetabolized *p,p'*-DDT and its degradation products *p,p'*-DDE and *p,p'*-DDD could be clearly identified and quantified in all samples. It was found, that the concentrations of *p,p'*-DDE were usually higher than those of *p,p'*-DDT, which in turn were either slightly higher than or nearly equivalent to those of *p,p'*-DDD. A remarkable exception was the Elbe estuary, were extraordinary high concentrations of total DDT were simultaneously accompanied by a predominance of the metabolite *p,p'*-DDD.

In case of HCH-isomers higher concentrations were recognized in the Baltic samples than in those of the North Sea. There were also area-specific differences in the relation between the α- and γ-isomers.

Generally, the ratio between α- and γ-HCH varied from about 1:0.5 to 1:0.8 in the Baltic sampling stations. The ratio was approximately 1:1 to 1:2 when traversing the coastal zones in the North Sea from the German Bight to the Skagerrak area (Table III).

Although the β-isomer is a minor constituent of technical HCH it deserves still some attention. β-HCH was clearly discernable in all chromatograms of Baltic fish samples, while it was below the detection limit of the analytical procedure used in samples of the German and Danish North Sea coasts. Significantly enhanced β-HCH concentrations occurred only in the material collected from the Elbe estuary (area II). The adjacent area (area III) in northerly direction revealed no β-HCH contamination.

HCB is no longer introduced into the environment in larger amounts, because its use as fungicide is banned. However, it still appears as by-product of many chlorination processes and the HCB-contamination of rivers and the sea might be derived from such activities. Earlier investigations[9] showed that fish samples from the Elbe on its lower course between the city of Hamburg and its mouth near Cuxhaven were significantly contaminated with respect to this substance. Data gained during the present study confirmed that the Elbe obviously contributes to a large extent to the HCB-contamination of adjacent marine waters (Table III). The HCB concentrations appeared to be rather uniform with minor statistical variations in the Baltic.

The Elbe can be also regarded as main source for octachlorostyrene (OCS) similarly as this was observed for HCB. The distribution showed a clear decrease of concentrations in going north from the German Bight and along the Danish coast. In the locations north of the 56° latitude no gradient could be established, because the concentration values observed were only slightly above the limit of detection of the method applied (Table III).

Table IV shows cadmium and lead concentrations predominantly below 100 μg/kg in the most areas listed. Significant, element-specific differences between areas along the North Sea and the Baltic coasts studied could not be identified. Both of the rivers Elbe and Weser revealed in their estuaries elevated cadmium and lead concentration levels. Especially in the Elbe estuary the mean concentrations measured were clearly higher than those of the marine sampling stations.

Table III Values of organochlorine compounds (HCH-isomers, HCB, OCS) in flounder from selected sampling areas. Data (range, mean) in μg/kg muscle tissue (wet weight).

Area	HCB	OCS	α-HCH	β-HCH	γ-HCH
I	1–4 2	n.d.	1–4 2	n.d.	4–14 8
II	115–472 269	61–415 151	7–46 22	8–60 30	8–64 27
III	2–17 5	3–18 6	1–4 3	n.d.	1–6 3
IV	1–5 2	n.d.	1–7 3	n.d.	1–7 3
V	1–2 1	n.d.	1–4 2	n.d.	1–3 2
VI	1–6 3	n.d.	2–17 7	1–2 1	1–9 4
VII	1–10 4	n.d.	3–43 14	1–8 2	2–29 8
VIII	1.7 3	n.d.	3.40 13	1.3 2	2.5 8

Table IV Values of heavy metals in flounder from selected sampling areas. Data (range, mean) in μg/kg muscle tissue (wet weight) for Hg and μg/kg liver (wet weight) for Cd and Pb.

Area	Hg	Cd	Pb
I	120–280 196	103–360 182	42–122 78
II	144–1190 322	140–560 286	50–160 122
III	110–190 132	40–121 77	29–91 52
IV	30–90 57	40–112 66	32–82 45
V	14–38 21	32–98 48	15–64 39
VI	23–47 31	28–103 54	11–58 32
VII	9–65 30	17–144 52	10–106 34
VIII	15–60 33	25–113 56	13–103 38

With regard to mercury a more detailed picture could be drawn. The concentrations within the Elbe estuary were exceptionally high, most of them exceeding the "upper level" ($>300\,\mu g/kg$) as defined by the "Joint Monitoring Group" guidelines.[10] A concentration range between 100 and $200\,\mu g/kg$ prevailed in the German Bight. Data clearly below $100\,\mu g/kg$ were measured in the remaining two North Sea stations. Such a geographical gradient was also found by Jensen.[11] By means of blue mussels as indicator organism the aforementioned author measured for a variety of elements, especially also for mercury, a concentration decrease in going north from the German Bight along the Danish North Sea coast. Concentrations were generally below $100\,\mu g/kg$ in all sampling locations of the Baltic. The data were within the "lower level" as defined by the JMG guidelines.

DISCUSSION

Data generated during the present study supported the impression that compound-specific differences in the concentration levels existed between the North Sea and the Baltic. This was most obvious for the DDT-group, the HCH-isomers and for mercury. The first two showed higher levels in the Baltic, the latter was found in higher concentrations in the North Sea. It is most probable that diffuse inputs of the various substances and the prevailing hydrographic conditions in the Baltic might lead to the rather uniform contamination situation within its coastal areas studied.

In contrast, the data of the North Sea indicated considerable differences in the contamination levels along the coastal areas between the Elbe estuary and the Skagerrak. It seemed that the observed structured distribution of substances was to a large extent influenced by the inflow of waters from the river Elbe and the prevailing residual currents in the German Bight.[12,13] Apart from the significance of hydrographic conditions an explanation for the spatial changes of the contaminant pattern may be found in specific differences in the mobility of each single compound in the aquatic environment. Regarding organochlorine compounds, one may assume that depending on certain physico-chemical properties, in particular vapour pressure and water solubility, a compound-specific equilibrium will tend to be established between detectable concentrations in fish and amounts distributed between the different compartments of the aquatic medium. On this basis one would expect the more volatile and more water soluble substances (typical examples are α-HCH and *p,p'*-DDE) to reach the more distant waters. Other substances with lower volatility and water solubility (i.e. β-HCH and *p,p'*-DDD) will show a minor tendency to be transported over longer distances. Results obtained during the present study confirm these assumptions. β-HCH and *p,p'*-DDD concentrations were significantly elevated in specimens collected within the Elbe estuary. But the concentration levels were below the detection limit β-HCH) or extremely low respectively (*p,p'*-DDD) in the adjacent coastal areas of the German Bight. In the case of trace metals, interactions with soluble and insoluble water components influence their transport and their impact on the biota in natural waters. The combination of high reactivity with suspended particulate material and physico-chemical conditions in estuarine and near-shore waters conducive to high rates of sedimentation provides a mechanism for trapping large quantities of metals in those areas. The pronounced steep decrease of concentration levels (especially of mercury) at the transect Elbe/Weser–open sea reflected a situation typical for zones were intermixing of estuarine and marine waters occur. Changes of physico-chemical conditions in the mixing zone might be responsible for adsorption and precipitation processes in consequence of which the bio-available proportions of the investigated metals were considerably reduced.

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