Seasonal and Species Specific Differences of PCB Burden and Pattern in Animals of the Marine Food Web investigated by Congener Specific Determination of all PCB Congeners

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The congener specific determination of PCB mixtures in routine environmental analysis has been possible only partly. Investigations on different numbers of congeners were carried out e.g. on birds[1,2] or mammals[3]. Just the determination of all congeners gives new understanding of changes in PCB burden of animals and shows pattern differences between species.

In this paper PCB burden and pattern of two fish species, sand eel (Ammodytes tobianus) and cod (Gadus morhua) caught in the North Sea near the island Helgoland, are presented. Furthermore Kittiwakes (Rissa tridactyla), breeding on Helgoland and feeding to a more or less part on these fish were investigated. The change of PCB burden and pattern through month and the differences between the species are, among other, the most important results of this investigation.

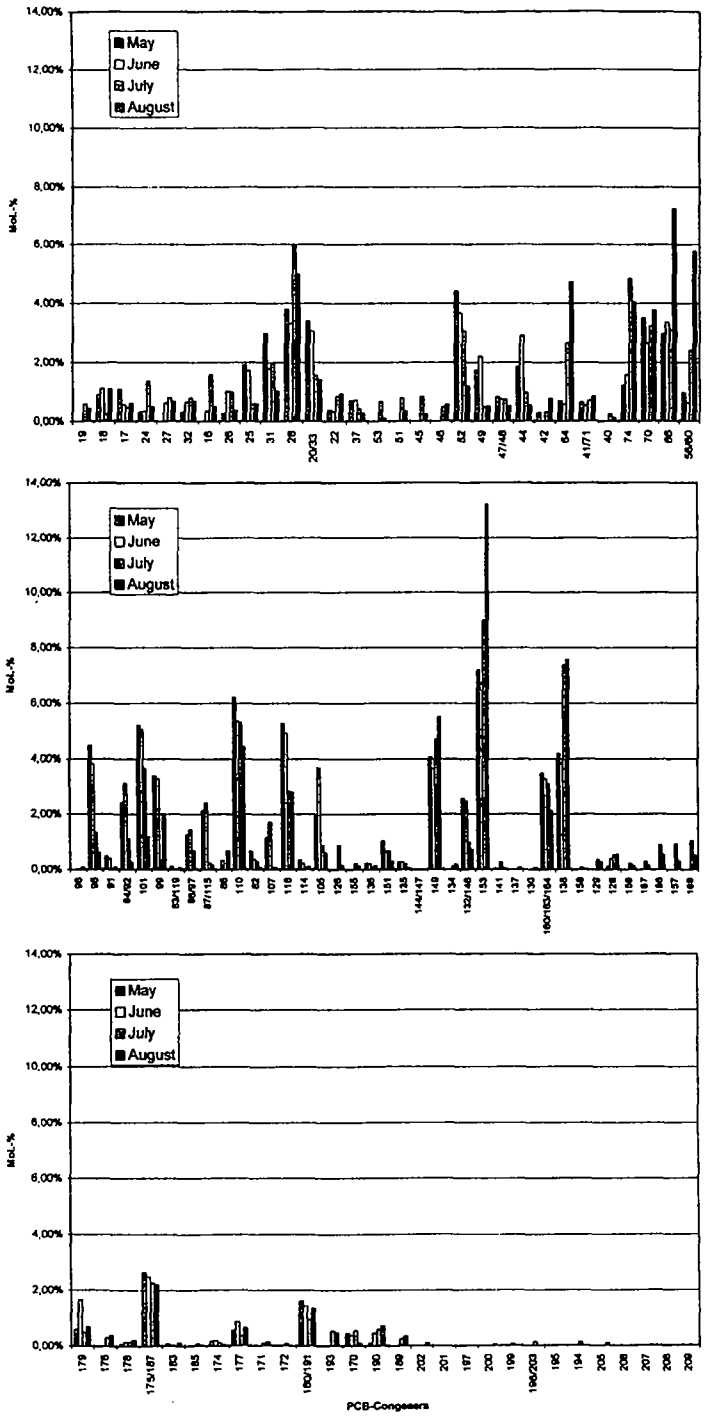
Materials and Methods

The fish were caught between May and August 1993. The length of the sand eels varieed between 11 and 18 cm, the weight between 4 and 20 g. 68 single sand eels were pooled to 13 samples in May, 9 in June, 12 in July and 10 in August. Six cod were caught per month, their length varieed between 27 and 34 cm, their weight between 207 and 440 g. Unfortunately no cod from August were available. All cods belong to the immature two years age group, so that the occurence of sex-dependent differences in PCB content was excluded.
Chicks of the kittiwake were collected in the breeding season between May and July. Only chicks which were fallen down the cliff were available, totally 29 chicks from 1 to 37 days age were collected. Their weight was between 23 and 347 g.

Fish muscle and the liver of the kittiwakes were investigated. The preparation of the fish samples including fat extraction was described[4], a slightly modified method was used[5]. Results are given in ppb/Lipid Weight (LW). The preparation of the liver samples was also published[6], results are given in ppb/Fresh Weight (FW). The samples were measured by GC-MS, the determination method was already published[7]. The detection limit was matrix-dependent about 1.1 ng/CB. The numbering of the single congeners was published[8].

Results and Discussion

The sum PCB values of the sand eels vary between 1094 and 3377 ppb/LW (Mean: 2028) in May, in June between 1538 and 4988 ppb/LW (3269), in July between 1018 and 4611 ppb/LW (2057) and in August between 1201 and 2872 ppb/LW (1791). The total number of congeners in the PCB mixtures of the different month shows interesting differences. For May and June this number is 58



Figures 1,2,3: Sand eels, Mol-% distribution of the single CBs from May to August, Fig. 1: Tri- and Tetra-CBs, Fig. 2: Penta- and Hexa-CBs, Fig. 3: Hepta- to Deca-CBs

and 57, for July and August 86 and 87. This is in contrast to the mean of congeners of the samples for the single month, which is 34.2 for May, 38.8 for June, 33.8 for July and 38.6 for August, and indicates the appearance of a lot of additional congeners in the sand eels of the midsummer months which is visible in the Fig. 1-3.

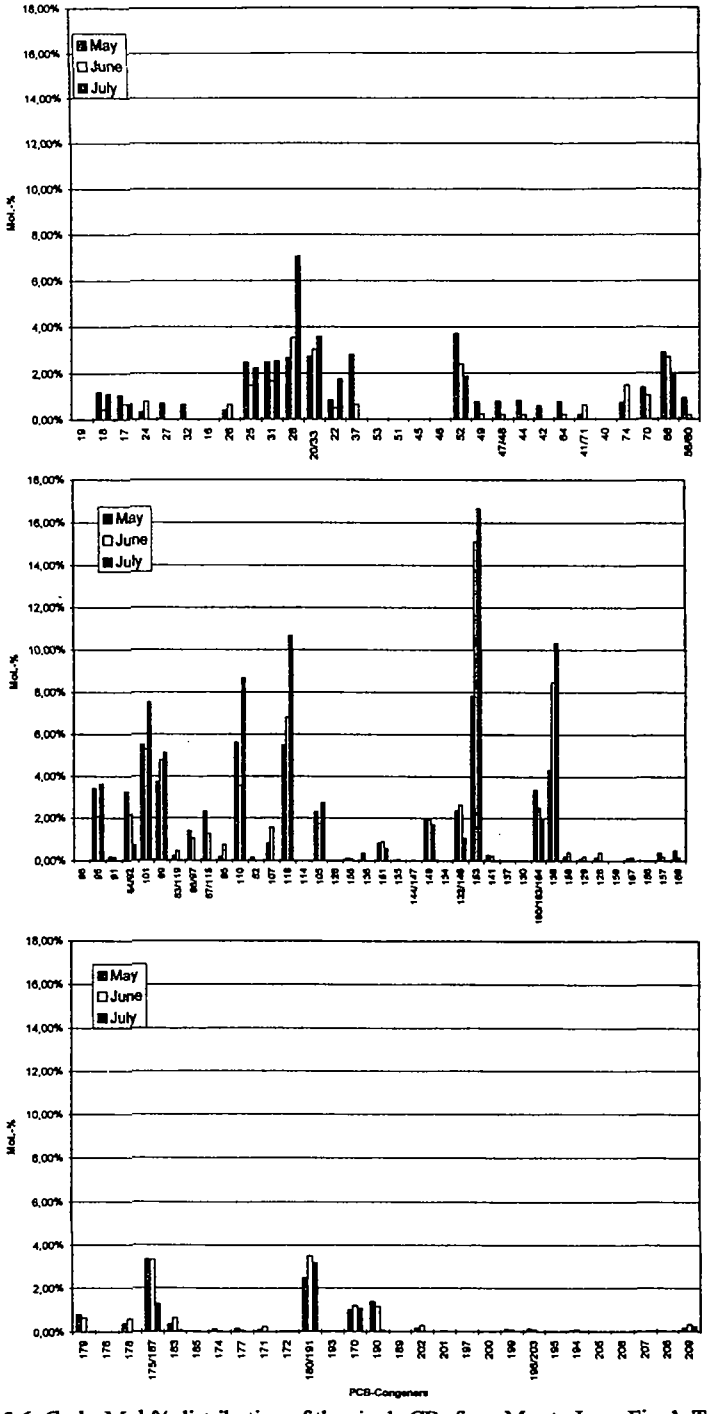
The sum PCB values for the cods vary between 2900 and 13151 ppb/LW (Mean: 5154) in May, between 1286 and 14046 in June (6587) and between 1181 and 2913 in July (2018). The cods caught in July show distinctly the lowest values of all. The total number of congeners in the cods declines from 69 in May over 67 in June to only 28 in July. This correlates with the mean number of congeners which is in May 39.3, in June 37.8 and in July 16.5. The big decline of sum PCB and the number of congeners (Fig. 4-6) in July shows a very fast loss of congeners within four weeks to one third of the level of May and June, which is surely a consequence of equilibrium partitioning with the surrounding water. Fast uptake and elimination processes were e.g. also reported for roach in a swedish lake[9].

The reason for the changes in PCB sum and pattern are the blooms of phytoplankton, which cause adsorption of big parts of formerly free PCB from the water. The living, not sinking phytoplankton enables as a consequence of equilibrium partitioning the release from sediment bound PCB into the water. Additionally the bottom-living cod profits from the plankton bloom and eliminates big parts of its PCB load. Contrary to that, the sand eel, in summer a surface fish, feeding on plankton, is in the upper water layers in direct contact to the adsorbed PCB. The result is the apppearance of 30 further, often higher chlorinated congeners in the sand eels in July and August, this effect is promoted by the uptake via food. These results show the importance of equilibrium partition processes in the water and the complex relationships between all, biotic and abiotic parts of ecosystems.

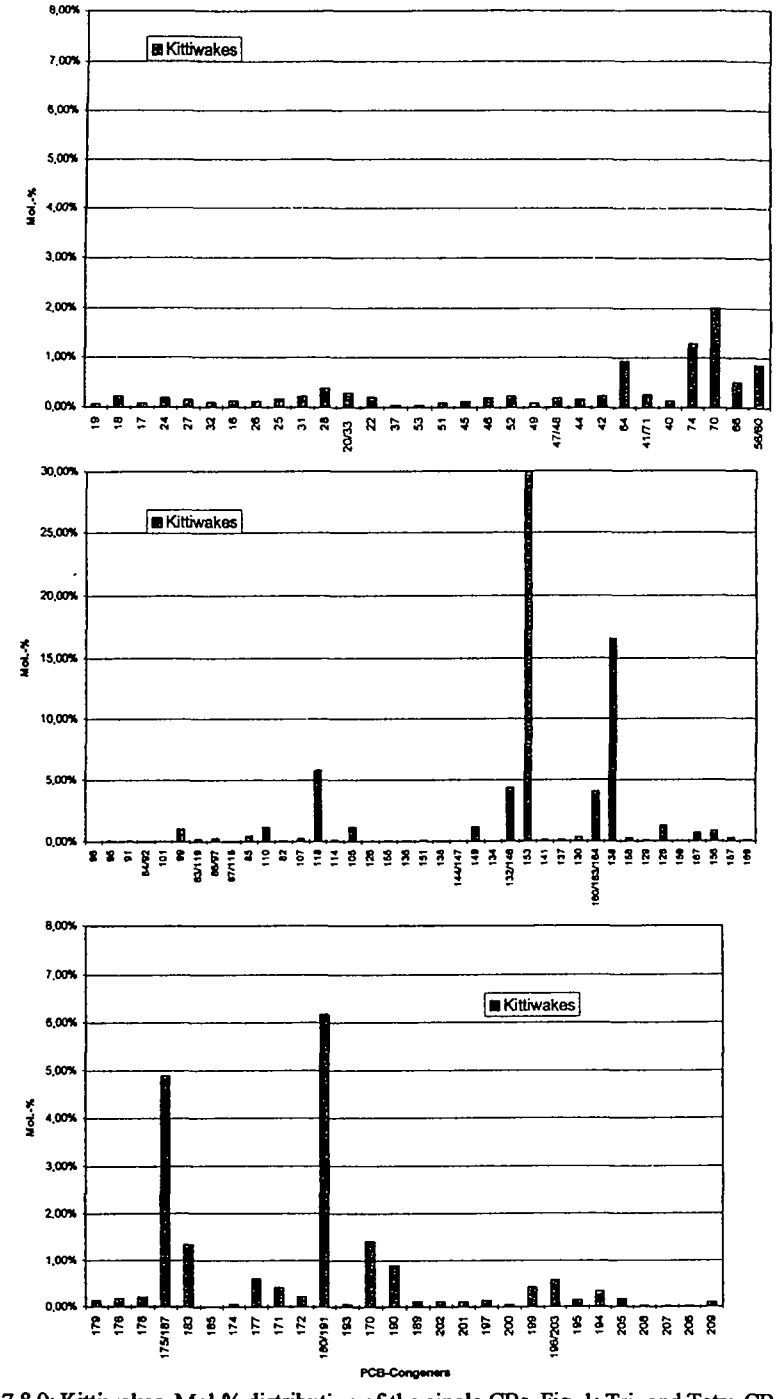
The highest number of congeners with all 97 investigated congeners/pairs of congeners was found in the kittiwakes. The mean of congeners in the single samples was 55.3. The sum PCB deviates very much between single chicks, which is no wonder, because nothing is known about age, origin and winter quarters of their parents and the dependent burden with xenobiotics. So, the lowest value is 133 ppb/FW, the highest 22885 ppb/FW (Mean: 3211). In spite of this big variation in PCB burden, the PCB pattern is surprisingly identical between low and high contaminated or younger and older chicks. Merely the Tri- Tetra- and Octa-CBs seem to get slightly higher molar percent parts during the growth of the chicks, but this change is not statistically significant, so that one common PCB pattern was established for the kittiwake (Fig. 7-9).

Comparing the PCB pattern of the single species, differences between the fish species concerning the degree of chlorination occur mainly between Tetra- and Penta-CBs. An increase of the molar percent parts of the Tetra-CBs occurs at the sand eels with a simoultaneous decrease of Penta-CBs. This increase is caused by a relatively planar group of congeners with only one or two Ortho-substituted Cls (CB-60, 64, 66, 70, 74) which obviously accumulate in sand eels (Fig. 1). Contrary to that, the pattern of the cods shows a permanent decrease of Tetra-CBs and no changes in the Penta-CBs.

The PCB mixture of the kittiwake is distinctly higher chlorinated than the two fish mixtures with a mean molar percent part of 61.43 % Hexa-CBs and 16.88 % Hepta-CBs. These degrees of chlorination reach about 25-30 % for the Hexa- and 6-10 % for the Hepta-CBs in the mixtures of the fish. These relatively persistent higher chlorinated congeners accumulate in the kittiwake, where no direct equilibrium processes with the surrounding medium air are possible, contrary to the gill-breathing marine species in the water.
Concerning single CBs, CB-153 reaches highest molar parts in all three species followed by CB-138. In the sand eels the cited group of Tetra-CBs and some Penta-CBs (e.g. CB-101, 110, 118) as



Figures 4,5,6: Cods, Mol-% distribution of the single CBs from May to June, Fig. 1: Tri- and Tetra-CBs, Fig. 2: Penta- and Hexa-CBs, Fig. 3: Hepta- to Deca-CBs



Figures 7,8,9: Kittiwakes, Mol-% distribution of the single CBs, Fig. 1: Tri- and Tetra-CBs, Fig. 2: Penta- and Hexa-CBs, Fig. 3: Hepta to Deca-CBs (remember the Mol-% scale)

well as CB-28 follow with values about 4 %. In the cods also the Penta-CBs (CB-99, 101, 110, 118) and partly CB-28 follow, while in the kittiwakes only the Hepta-CB pairs CB175/187 and CB-180/191 reach noteworthy higher molar parts. The Non-ortho CB-169 was found in all three species in little amounts, CB-126 could not be detected in cods, but in the other two species. CB-77 could not be detected in all three species.

Conclusions

Distinct differences in PCB burden and pattern exist between fishspecies and even between fish of one species of the same age class even in the spring and summer month, this means that randomly collected and investigated fish samples show only the status quo of the capture date and lead to wrong interpretations concerning the ecosystem.
Fish, as gill-breathing animals dispose of a very fast possibility of elimination of xenobiotics and react very fast on changes in the surrounding water.
Complex relationships exist with respect to PCB burden and pattern in the water between biotic and abiotic parts of the ecosystem with processes of equilibrium partitioning as the most important factors. The predator kittiwake shows a higher chlorinated PCB mixture as the fish species, in this species as in other bird- and mammal-species uptake and metabolism of PCB are the dominating factors controling PCB burden and pattern.

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