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PERSISTENCE OF PCB'S IN THE ECOSPHERE: WILL SOME PCB-COMPONENTS "NEVER" DEGRADE?

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The identification of more than 80 structurally defined polychlorobiphenyls (PCB's) in marine fishes [1,2] has been achieved by high resolution glass capillary gaschromatography (Fig. 1)[3].

The fact of a nearly unchanged relative occurence of more than 10 major PCB-components compared to technical PCB-mixtures is the most striking result of the identification and the quantification of the PCB-components. Persistent PCB-components mainly present in 54 % chlorine PCB mixtures (Aroclor 1254, Monsanto, USA; Clophen A 50, Bayer, Germany) are

2,2',4,4',5-pentachloro-biphenyl (peak 51)
2,2',4,4,4'-pentachloro-biphenyl (peak 52) and the sum of
2,2',4,4,4',5-hexachloro- and
2,2',3,3',4,5'-hexachloro-biphenyl (peak 74) (Fig. 1).

PCB-compounds mainly present in 60 % chlorine PCB's (Aroclor 1260, Clophen A 60) contain the following four octachloro-biphenyls,

2,2',3,3',4,5,5',6-octachloro- (peak 101)
2,2',3,3',4',5,5',6-octachloro- (peak 102)
2,2',3,3',4,4',5,6-octachloro- (peak 104) and
2,2',3,3',4,4',5,5'-octachloro-biphenyl (peak 105) (Fig. 1).

These PCB-components are found in marine fish liver in the same ratios as measured in the technical PCB-mixtures Aroclor 1254 and Aroclor 1260.

The unchanged ratios of distinct PCB-components like mentioned above can be explained in three ways:

1. We observe a recent pollution. However, this can be excluded as shown below.

MONS 001319

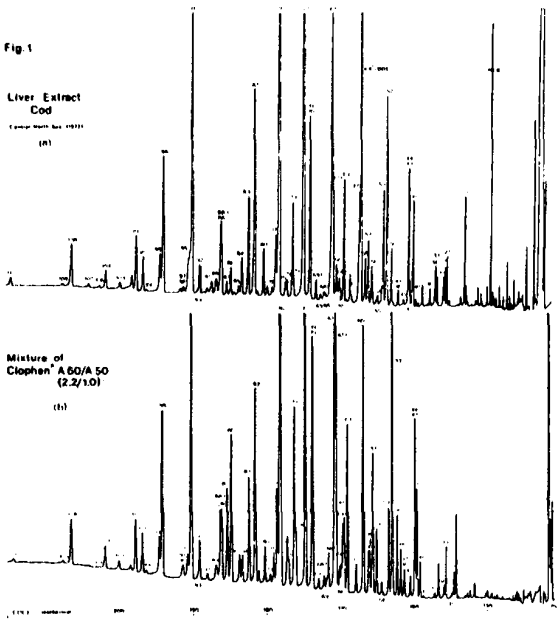

Fig. 1: (a) PCB-content of hexane extract of cod liver. Numbering of PCB peaks according to M. Zell, H. J. Neu, K. Hallschmiter, Chemosphere 6, 69-76 (1977) (b) Simulation of original environmental input of 54 % - and 60 % -chlorine PCB mixtures on the basis of unchanged internal ratios of recalcitrant PCB-components.

Conditions of gas chromatography: Glass capillary gas chromatography with electron capture detector; column length 40 m; i.d. 0.3 mm; liquid phase SE 30; separation number C_{12}/C_{13} 45; carrier gas H_2; temperatures: injection port 250° C; column (temperature programmed, 1° C/min) with cold injection; detector 270° C; gaschromatograph Carlo Erba model 2300 AC 1.

MONS 001320

2. Input of PCB's into the environment and any output due to biotic or abiotic degradation, however complex, do not result in observable changes of their relative occurence.
3. Differences in the degradation rates of the PCB-components are too small, to give an observable change of the relative occurence since their time in the ecosphere (20 - 40 years).

We consider the third explanation as the more likely one. Firstly, the chlorine substitution pattern of the stable PCB's fulfills in all cases the recalcitrance conditions [3]. Secondly, the environmental accumulation of the PCB's within the last 40 years of production has brought a PCB-content within the upper 10 - 1000 meters of the global hydrosphere of 1 - 5 ppt (ng/kg), measured at places as far as the North Atlantic [4], the German Bight [5] and the open Pacific [6]. An even distribution between the northern and southern hydrosphere seems to be given. The PCB-concentrations in marine planctons (200 ng/kg wet weight) are more or less evenly distributed in the North- and South Atlantic [7]. Assuming 1 ppt as a mean value of PCB-contamination in the upper 500 m layer of the global hydrosphere [8] (mean depth 3800 m), the PCB's content of this water layer amounts to $0,75 \cdot 10^{12}$ g. The overall world production since 1929 is guessed to be close to $2 - 10^{12}$ g PCB's [9]. Even this rough calculation backs the above findings of PCB-persistence, which is correlated to a defined molecular structure. The decline of PCB-content in the Ocean water commonly observed by several authors [4], we relate to a more critical assessment of the applied analytical techniques [5].

Using the above constant ratios of PCB-components the original PCB-input into the environment can be calculated. A simulation of the original contamination by 54 % chlorine- and 60 % chlorine PCB-mixtures is shown in Fig. 1.

Rather basic conclusions about the behaviour of PCB-components under environmental conditions can be deduced from this simulation. The decline of the relative content of 2,2',3,4,5',6-hexachloro-biphenyl (peak 67.1), a major component in 54 % chlorine PCB's and 60 % chlorine PCB's, down to about 20 % of its calculated original input excludes a recent pollution. A decline of the same extent is observed for the 2,2',3,3',4-pentachloro- (peak 61), the 2,2',3,3',4,5'-hexachloro- (peak 78), and the 2,2',3,3',4,5,6-heptachloro-biphenyl (peak 87). All these PCB's have an non-recalcitrant substitution pattern in one ring. As already stated [10,11] recalcitrant PCB-components contain no vicinal hydrogens and are substituted in the 4,4'-position. The last condition seems to be overweightingly responsible for the persistence [3].

The octachloro-biphenyl-group mentioned above, can give a "global pollution standard". This standard can easily be identified even in complex mix-

MONS 001321

tures and quantification is easily done, too. It could give a reporting basis for any other global pollutants already known or be detected in the future. Of course only a globally spread analysing program using glass capillary gas chromatography and the necessary concern about the errors possible in the determination of PCB's at the ppt-level could verify the above statements about the out-standing persistence of quite a few PCB-components. Moreover, the widespread range of water solubility and vapor pressure of PCB's could make this group of compounds extremely helpful for tracing global transport phenomena, since the analysis of single PCB-components is possible now.

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MONS 001322