

## Distribution of chlorobiphenyls in solution and suspension in the Baltic.

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### Introduction:

Chlorinated biphenyls are ubiquitous contaminants. Their presence in the marine environment has important aspects. Firstly, several congeners are persistent and accumulate in lipid tissues of marine organisms. Some have toxicities and modes of action in marine organisms resembling those of the most toxic synthetic compound known, i.e., 2,3,7,8-TCDD (Safe1991). The levels of apolar compounds such as PCBs in tissues of lower marine organisms are determined primarily by their levels in the surrounding sea water. Information on the concentrations in sea water may thus assist to understand the levels in marine organisms and to evaluate the associated risks. Existing literature on concentrations and distributions of organic contaminants in Baltic waters and suspended particles is very limited.

The present paper is concerned with the concentrations of CBs in water and suspended particles. In order to obtain sufficient material for reliable analyses well above the detection limits, large volumes of sea water were extracted, as the concentrations of CBs in sea water are extremely low (typically in the low pgdm-3 range or even below 0.1 pg/dm-3 in the North Sea and in the open ocean (Schulz et al., 1988; Schulz-Bull et al., 1991; Iwata et al., 1993). Also, contamination was reduced to an acceptable level or even eliminated. In order to investigate possible seasonal differences, data were collected during cruises in late autumn 1988 and 1989 as well as in a spring period (1991). Most samples were obtained in the Baltic, with some data in the adjacent North Sea for comparison with the Baltic sea as well as earlier data reported for the North Sea (Schulz-Bull et al., 1991).

### MATERIALS AND METHODS

#### Sampling

Samples were taken during cruises 152 (November 1988) and 165 (November 1989) of RV Poseidon and cruise 17 (March/April 1991) of RV Alkor. The Baltic sea represents an hydrographically complex system. Hydrochemical properties and biological production show large variations in the Baltic, both in place and time. We used a sampling system in which water was taken from about 1m under the ship's hull while steaming. The concentrations of CBs in water within a defined and limited range of hydrochemical characteristics were integrated in this way. Salinity, temperature, dissolved nutrients, pH and oxygen were measured continuously to assist in the selection of beginning and end of each transect as well as in the later interpretation of the CB data. The integrated samples reflect what migrating organisms may experience effectively. This approach is also useful to investigate possible regional differences, similar to our earlier approach in the North Sea (Schulz-Bull et al., 1991). Sea water was filtered through GF/C filters (142 mm Ø) at a rate of 30 dm<sup>3</sup>/h and the filtrate was extracted by a 120 cm<sup>3</sup> XAD-2 column (4 bedvolumes/minute). The procedure has been described in detail before (IOC, 1993). The volume of water extracted was between 65 and 1143 dm<sup>3</sup>. Samples did not come in contact with other materials than teflon tubes, glassware and stainless steel connections.

Organics including CBs were eluted from XAD-2 resin columns in a modified Soxhlet apparatus for 6 hours with 150 ml of acetonitrile containing 15% water. The extract was concentrated to about 50 ml in a flash vacuum evaporator and shaken three times with 10 ml portions of *n*-hexane. The extracts were combined and dried with anhydrous sodium sulphate, removed with a Pasteur pipette, concentrated to 250 µl in a rotary evaporator under a N<sub>2</sub> blanket and cleaned-up by high performance liquid chromatography (HPLC). The second HPLC fraction, containing the CBs quantitatively, was concentrated down to 20-50 µl with a gentle stream of N<sub>2</sub> at room temperature and analysed by GC-ECD and MDGC-ECD. The filters were extracted with 50 cm<sup>3</sup> acetonitrile in a Soxhlet extractor for three hours. The filter extracts were treated like those of water. Filter weights could not be determined as we had no method available to determine the mass as well as the contents of CBs or any other organics in the same filter without causing contamination. The entire procedure, including the establishment of blanks, has been described in detail (IOC, 1993).

A large number of CBs appear in the sample chromatograms. We analysed most congeners with relatively high concentrations as well as toxic congeners, irrespective of their concentrations. Instrumental analysis was performed by GC-ECD. CBs reported here elute as well separated, single GC peaks. For many congeners single SE-54 column-GC was adequate to satisfy this condition. Some important congeners, including several toxic CBs, coelute from this column with one or two other CBs. In those cases, MDGC-ECD was applied (Schulz et al., 1989).

## Toxic CB congeners

The interest in the studies of chlorobiphenyls has increased strongly during recent years after information on their relative toxicities, and their mode of action have become available (Safe,1991). Moreover, the MDGC-ECD technique allows the accurate analysis of all 209 congeners (Schulz et al.,1989). The highest toxicity has been found for CBs without any chlorine atoms in the *ortho*- positions, at the same time having four Cl-atoms in the *meta*, *para* positions (CBs -77, -126 and -169, with toxicity factors 0.01 0.1 and 0.05 respectively relative to 2,3,7,8-TCDD). 10 times lower toxicities were reported for mono-*ortho*-Cl derivatives of these most toxic non-*ortho*-Cl congeners and still much lower relative toxicities (0.00002) for the di-*ortho*-Cl derivatives (Safe,1991). The concentration levels of several of these *ortho*-Cl substituted congeners are often much higher in technical mixtures and in environmental samples, however, than those of the most toxic congeners (Kannan et al.,1988,1989).

## Results and Discussion:

Concentrations of individual CBs in solution were in the sub- and low  $\text{pgdm}^{-3}$  range (detection limits being  $0.05 \text{ pgdm}^{-3}$ ), and of their sum between 2 and  $237 \text{ pgdm}^{-3}$ . These concentrations are considerably lower than previously reported data. This is attributed to the elimination of contamination and interference problems in the sampling, clean-up and GC-ECD procedures.

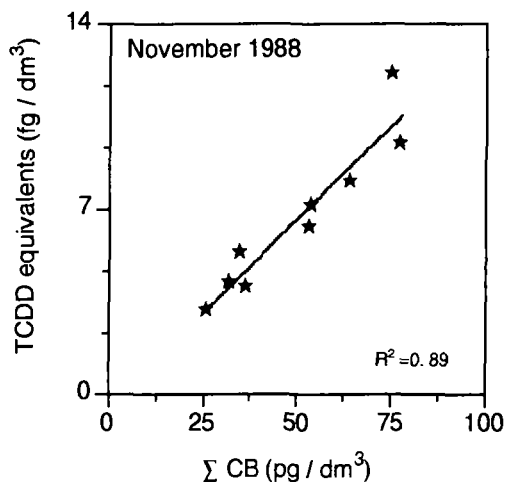
The lowest concentrations of CBs in solution were found in areas and periods of plankton production (spring 1991), with  $\sum \text{CB}$  concentrations of 2-14  $\text{pgdm}^{-3}$ . Concentrations of individual CBs in suspension were generally below  $1 \text{ pgdm}^{-3}$ , those of their sum between 4 and  $6 \text{ pgdm}^{-3}$ .

Primary production may effectively remove CBs from the water column into the sediments. The amounts of chlorobiphenyls presently stored in the sediments of the Baltic Sea exceed the amounts in the water column by several orders of magnitude. Outside the plankton production period, concentrations in solution were an order of magnitude larger, and were also linearly related to Salinity. Sources of CBs were identified in the northern Baltic and the Belt Sea.

The compositions of the CB mixtures differed considerably between solution and suspension. The relations between  $\log K_d'$  (apparent particle/water partition coefficient) and  $\log K_{ow}$  (octanol-water distribution coefficient) suggest the existence of (quasi-)

equilibrium conditions in autumn. Deviations from this behaviour arise from biological activity in spring. Regional differences were found for the compositions of the CB mixtures in solution.

The contribution of toxic congeners to the CB mixtures was dominated by the mono- and di-*ortho* -Cl substituted derivatives of the most toxic non-*ortho* -Cl CBs. The toxicity of the CB mixtures in solution was between 0.01 and 12 fgdm<sup>-3</sup> TEQs (TCDD equivalents). CBs -77, -118, -105 and -156 had the largest contributions to TEQs.



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