

Potential Use of Chlorinated Biphenyls (CBs) as Indicators of Biological Activity and Ecotoxicological Stress in the Marine Environment

N.Kannan, D.E.Schulz-Bull, G.Petrick and J.C.Duinker

Institute for Marine Research, Düsternbrooker Weg 20, 24105 Kiel, Germany

Abstract: *Separate analysis of solution and suspended particulate matter (SPM) in Baltic Sea water for chlorinated biphenyls (CBs) revealed yet another use of these persistent compounds as indicators of biological activity. The relationship between the biologically altered composition of CB mixtures as seen in X/153 ratios in SPM and organisms in spring against that of winter indicate that SPM reflects the situation in aquatic organisms. It is proposed that simultaneous measurement of CBs in solution and SPM may help to assess the health of the marine ecosystem.*

Introduction : Chlorinated biphenyls (CBs) as environmental contaminants are identified also in the marine environment. They are bioaccumulative and several are persistent and potentially harmful. These properties are considered in developing CBs as model substances, a). to trace the migratory paths of marine animals ¹, b). to understand the metabolic potency of various aquatic organisms ²⁻⁴, c). to understand the interaction between toxic CB congeners and biota ^{5, 6}. We found during our recent experimentation in the Baltic Sea that the affinity of these substances for organic material can be used to study biological events occurring in marine environment. The application of large-volume water sampling ^{7, 8} techniques and measurement of CBs with multidimensional gas chromatography - electron capture detector (MDGC-ECD) ⁹ appeared to be extremely useful.

Materials and Methods: Water samples were taken during cruise 165 (Oct.-Nov. 1989) of R.V.Poseidon and cruise 17 (Mar.-Apr.1991) of R.V.Aikor. The sampling tracks and other

details of these cruises are given elsewhere ¹⁰. Water was taken from about 1 m under the ship's hull while steaming ⁷. Sea water was filtered through GF/C filters (142 mm ϕ) at a rate of 30 dm³h⁻¹ and the filtrate was extracted by a 120 cm³ XAD-2 column (4 bedvolumes per minute). The procedure has been described in detail before ¹¹. In two investigations in the south-west Baltic (at 54°22'N, 10°00'E and 54°49'N, 9°46'E) *in-situ* high-volume water pumps were used ⁸. Details of CB analyses in biological samples are given elsewhere ¹².

Results and Discussion: The distribution of individual chlorinated biphenyls in solution (41 tracks) and suspension (20 tracks) in the Baltic mainly and some positions in the North Sea has been described recently ¹⁰. Attempts were made to correlate concentrations and salinity and temperature to establish sources. It was pointed out that CBs are scavenged from solution during a plankton bloom. Toxic CBs were measured and their TEFs were calculated. In addition we shall use the data of four tracks in the present communication to show the utility of CBs as biological indicators. These four tracks represent measurements of CBs in solution and SPM in two seasons, namely in winter and in spring. It was shown using the recently introduced concept of metabolic slopes ⁴ that even the lower aquatic organisms in the Baltic are capable of metabolising CBs to some extent. Lenz ¹³ has shown that particulate organic carbon (POM) in the Baltic consisted essentially of autotrophic phytoplankton, herbivorous and carnivorous zooplankton, heterotrophic microorganisms (bacteria, flagellates and fungi) and organic detritus (remains and faeces of pelagic organisms). It is logical that the suspended particulate matter (SPM) which we have analysed should reflect the composition of CBs after biological alteration. The biological activity in the Baltic is lowest in winter and reaching its maximum in summer months^{14, 15}. The ratio of X/153 is a good indicator of biological alteration of CBs ^{3, 4}. Analyses of these ratios in solution and suspension during biologically inactive months should resemble each other more closely than during biologically active months. Principal component analysis of X/153 ratios in solution and suspension in four tracks during winter and spring supports this view (Fig. 1). The distribution of winter points (solution vs suspension) falls within a narrow bracket (see the box) whereas the spring points are wide apart from each other. This indicates the

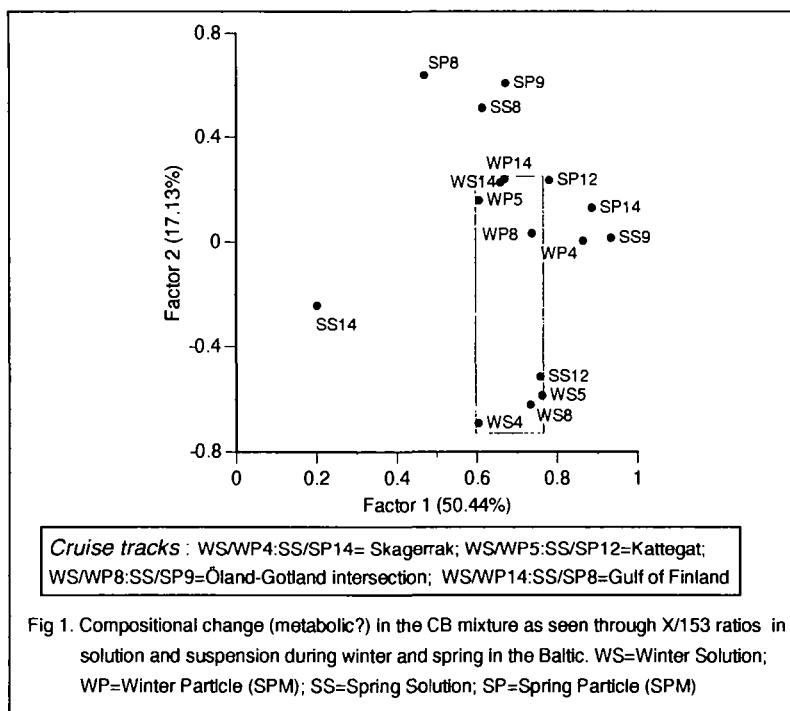


Fig 1. Compositional change (metabolic?) in the CB mixture as seen through X/153 ratios in solution and suspension during winter and spring in the Baltic. WS=Winter Solution; WP=Winter Particle (SPM); SS=Spring Solution; SP=Spring Particle (SPM)

non-equilibrium condition due to biological activity.

Further evidence for this conclusion comes from another study in which CB composition in solution, SPM and blue mussels have been investigated. Slopes of regression lines of X/153 in solution, SPM and mussel in winter and in spring are plotted and shown in Fig.2. The slope of the SPM in low biological activity season i.e.winter, resembles closely that of solution. On the other hand the slope shifts its position in favour of the organisms during the spring (the bottom figure). This means that the composition of CB mixture is biologically altered. This biotransformation is usually effected with induction of certain MFO enzymes in the organisms. Kannan et al. 4 have described recently how this could be interpreted as indicator of ecotoxicological stress. In this sense, SPM which contains living organisms as well as remains of organisms may reflect the health of an ecosystem. This can be further verified using bioassays in fish and other aquatic organisms. This is part of our on going research.

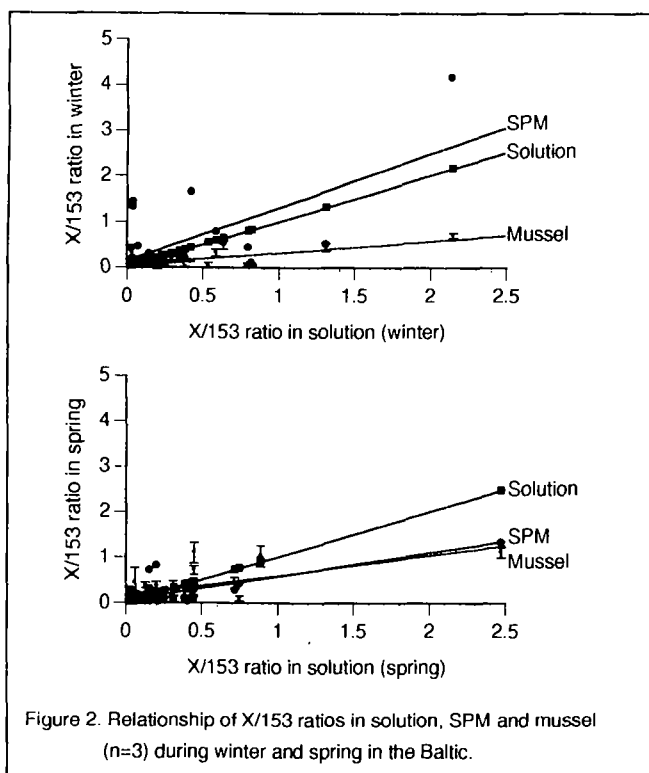


Figure 2. Relationship of X/153 ratios in solution, SPM and mussel (n=3) during winter and spring in the Baltic.

Reference :

- 1 Subramanian, A., Tanabe, S. & Tatsukawa, R. *Mar. Pollut. Bull.* 19, 284-287 (1988).
- 2 Tanabe, S., Watanabe, S., Kan, H. & Tatsukawa, R. *Marine Mammal Sci.* 4, 103-124 (1988).
- 3 Boon, J.P., Eijgenraam, F., Everaarts, J.M. & Duinker, J.C. *Mar. Environ. Res.* 27, 159-176 (1989).
- 4 Kannan, N., Reusch, T.B.H., Schulz-Bull, D.E., Petrick, G. & Duinker, J.C. *Environ. Sci. Technol.* July, 1995.
- 5 Kannan, N., Tanabe, S., Ono, M. & Tatsukawa, R. *Arch. Environ. Contam. Toxicol.* 18, 850-857 (1989).
- 6 de Voogt, P.M., Wells, D.E., Reutergårdh, L. & Brinkman, U.D.T. *Intern. J. Environ. Anal. Chem.* 40, 1-46 (1990).
- 7 Kremling, K. *Nature* 303, 225-227 (1983).
- 8 Petrick, G., Schulz-Bull, D.E., Martens, V., Scholz, K. & Duinker, J.C. (submitted to *Marine Chemistry* - 1995).
- 9 Duinker, J.C., Schulz, D.E. & Petrick, G. *Anal. Chem.* 60, 478-82 (1988).
- 10 Schulz-Bull, D.E., Petrick, G., Kannan, N. & Duinker, J.C. *Mar. Chem.* 48, 245-270 (1995).
- 11 Duinker, J.C., Schulz-Bull, D.E. & Petrick, G. *IOC Manual and Guides, UNESCO* 27, 1-39 (1993).
- 12 Petrick, G., Schulz, D.E. & Duinker, J.C. *J. Chromatogr.* 435, 241-248 (1988).
- 13 Lenz, J. *Sonderdruck aus Bd. 23*, 209-225 (1974).
- 14 Smetacek, V., et al. in *Lecture notes on coastal and estuarine studies* (eds. Bowman, M.J., Barber, R.T., Mooers, C.N.K. & Raven, J.A.) 34-56 (Springer-Verlag, Berlin, 1987).
- 15 Meyer-Reil, L. in *Lecture notes on coastal and estuarine studies* (eds. Bowman, M.J., Barber, R.T., Mooers, C.N.K. & Raven, J.A.) 93-110 (Springer-Verlag, Berlin, 1987).