L-I1

The identification of Decachlorobiphenyl as an environmental contaminant in sediments from the Po River (Italy)

M. FRIGNANI*, R.F. BOPP** and H.J. SIMPSON**

* Istituto di Geologia Marina, CNR, Via Zamboni 65, 40127 Bologna (Italy)
** Lamont-Doherty Geological Observatory, Palisades, N.Y. 10964 (U.S.A.)

Analyses of chlorinated hydrocarbons in sediments recovered in 1977 from this coastal area (Frignani and Ravaioli, 1982) had shown the presence in the chromatograms of a large peak with a relatively high retention time. This work is based on the identification of this peak as decachlorobiphenyl (DCB) and reports some considerations on its source and behavior in sediments off the Po delta.

Sediment samples were collected in 1979 at eleven locations (Fig. 1) with a Van Veen grab and carefully handled to avoid contamination. The analyses were carried out on the top 3 cm of the sediment according to Bopp (1979) and Bopp et al. (1981). The PCB content of samples was calculated peak by peak on the basis of the average Aroclor 1254 and 1260 compositions reported by Webb and McCall (1973). Cs-137 activities were also determined because they are correlated with the fine sediment fraction and can be used as an indicator of the sediment texture (Albertazzi et al., 1984). Weight loss on ignition (LOI) at 375 °C for 16 hours was chosen as an index of the organic matter concentration in sediments. The analytical results are summarized in Table 1.

Table 1. Concentration ranges and average values in bottom sediments classified according to their lithology (Shepard, 1954).

Sample n.	DCB ng/g	PCBs ng/g	Cs-137 pCi/kg	Lithology	LOI %
11	0.2	8	80 ± 19	sand	1.36
6	1.0	21	113 ± 18	sandy silt	0.78
1,7,9	11.8 1.0-21.9	84 39-110	295 258-330	silt	4.52 4.00-5.06
2,3,4, 5,8,10	6.0 2.0-8.8	64 39-85	400 203-484	clayey silt	4.55 3.04-6.35

From these data some simple considerations can be drawn: 1) peak by peak composition points out that the PCBs in sediments are mainly derived from mixtures such as Aroclor 1254 rather than Aroclor 1260; 2) DCB concentrations range from 0.2 to 19.9 ng/g (dry weight) and these values are surprisingly high (up to 19% of the amount of PCBs in sample 9); 3) a comparison with sediment samples from other areas (Tyrrhenian Sea, Raritan Bay) shows that DCB in sediments off the Po delta have a different source from ordinary PCBs. In fact DCB, the fully chlorinated biphenyl, was produced in a factory in Brescia (Italy) from 1973 to 1975. Although the period of commercialization was short, the compound was synthetized as a reaction intermediate until 1980. Therefore high DCB concentrations and DCB/PCB ratios are characteristic of the sedimentary materials carried to the sea by the Po River; 4) there is no significant correlation between these chlorinated hydrocarbons and Cs-137 activities in sediments. This means that PCBs and DCB do not show a great affinity for all fine particles, as already pointed out by Frignani and Ravaioli (1982). The correlation in fact is stronger for the silt fraction.

Fig. 1

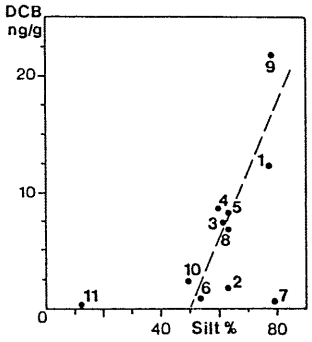

Fig. 2

The relationship between the DCB concentration and the silt content of the samples is shown in fig. 2. The correlation is significant at a high level (r = 0.85772) if samples 2, 7 and 11 are not considered. This observation points out that other factors besides the grain size composition of the sediment influence the DCB concentration. In fact the superficial sediments in the area can present very different levels of DCB because of the different accumulation rates of recent materials from the Po effluents. Therefore sample 11, which is a relict sand scarcely influenced by deposition of recent fine particles, shows the minimum concentrations of both DCB and PCBs. The silty sediment at station 7 also shows a low DCB content (and a very low DCB/PCB ratio) because it is only marginally influenced by the river flow. On the other hand the sediment at station 2 is characterized by a low concentration of DCB and a relatively low DCB/PCB ratio which may be due to its very fine grain size composition and to its distance from the delta. A decrease of the PCB content in superficial sediments off the delta with increasing distance from the coast was also reported by Frignani and Ravaioli (1982).

The Po River is the only significant source of DCB in this area. Therefore the importance of DCB as a tracer for the sediment originating from the Po is clear. If the maximum pollution occurred during the period of its commercialization, a peak value should be found in sediments deposited in the years from 1973 to 1975.

Bopp R.F. (1979) - Ph.D. Thesis, Columbia University, New York (N.Y.), pp. 191.
Bopp R.F., Simpson H.J., Olsen C.R. & Kostyk N. (1981) - Environ. Sci. Techn., 15, 210-216.
Frignani M. & Ravaioli M. (1982) - CNR, Atti Convegno Sottoprogetti "Risorse Biologiche" e "Inquinamento Marino" (Rome, 10-11 November, 1981), 815-828.
Shepard F.P. (1954) - J. Sedim. Petr., 24, 151-158.
Webb R.G. and McCall A.C. (1973) - J. Chrom. Sci., 2, 366-373.

L-I2

Trends in chlorinated hydrocarbons in organisms from the Gulf of Venice

V.U. FOSSATO and L. CRABOLEDDA

Istituto di Biologia del Mare, CNR, Venezia (Italia)

An investigation was carried out during 1986 and 1987 to establish the actual levels of chlorinated hydrocarbons (HCH, DDTs and PCBs) in two species, Mytilus galloprovincialis and Engraulis encrasicholus, for which comparison over a relatively long time can be done for the Gulf of Venice (North Adriatic Sea).

In order to assure the comparability of the results, sampling, sample preparation and analysis procedures similar to those used in a previous monitoring program (1977 - 1979) were adopted. Shortly, composite samples of soft parts of mussels and skinned fillets of anchovies were prepared. Organochlorine concentrations were determined by gas chromatography after Soxhlet extraction with n-hexane, cleanup with H_2SO_4 and Florisil, and separation of PCBs from DDTs on silica gel. The quality control of the analytical data was based on the results of two intercalibration exercises done in 1976 and 1984, respectively.

Chlorinated hydrocarbon concentrations in mussels and anchovies of the present study are reported in Table 1 and compared, using the variance analysis, with published results for the same species sampled from the same area (1; 2). Data demonstrate the overall decline of the magnitudo of Σ HCH and ΣDDT residues both in mussels ($p < 0.01$) and anchovies ($p < 0.05$). For HCH and DDT it is likely that the greatest input occurred in the past, before the ban in the use of chlorinated pesticides by Italian regulations. This is consistent with the increase of the amount of DDT degraded (DDD and DDE) versus the amount of ΣDDT between 1976/79 and 1986/87. A significant decrease ($p < 0.05$) with time of mean concentrations of PCBs was also observed in mussels, while PCB levels in anchovies appear almost unchanged. This finding may indicate that there is a trend towards a wider distribution of smaller PCB residue concentrations in the Adriatic ecosystem.

Table 1. Temporal comparison of chlorinated hydrocarbon levels in organisms collected from the Gulf of Venice. Concentrations (means ± SD) are expressed in ng g^{-1} wet tissue weight.

Mytilus galloprovincialis			
Sampling period	1976	1977/79	1986/87
Sample No.	6	15	7
Wet/Dry wt. ratio	5.5 ± 0.3	5.8 ± 1.1	5.8 ± 1.1
EOM % wet wt.	1.4 ± 0.3	1.7 ± 0.6	1.4 ± 0.2
Σ HCH	2.4 ± 1.9	1.2 ± 1.0	0.4 ± 0.1
Σ DDT	9.5 ± 6.2	13.0 ± 7.0	2.6 ± 0.7
Σ PCB (Aroclor 1254)	56 ± 26	41 ± 27	19 ± 5
Engraulis encrasicholus			
Sampling period	1976	1977/79	1986/87
Sample No.	0	10	7
Wet/Dry wt. ratio		4.2 ± 0.4	4.1 ± 0.3
EOM % wet wt.		1.8 ± 1.1	1.5 ± 0.8
Σ HCH		2.7 ± 1.7	0.9 ± 0.4
Σ DDT		53 ± 38	15.2 ± 7.6
Σ PCB (Aroclor 1260)		155 ± 75	138 ± 77
References	(1)	(2)	Present study

References

(1) Fossato V.U. and L. Craboledda. Archo Oceanogr. Limnol. 19 (1979) 169 - 178.
(2) Fossato V.U. and L. Craboledda. V^es Journées Etud. Pollutions, Cagliari, CIESM (1980) 169 - 174.