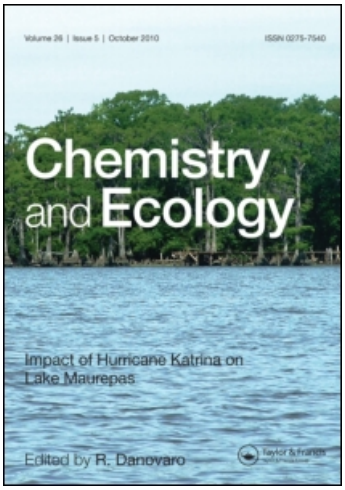

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CHLORINATED HYDROCARBONS IN SURFACE SEDIMENTS FROM THE OPEN ADRIATIC

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This paper presents the results of the examination of concentrations of chlorinated hydrocarbons in surface sediments from the middle of the Adriatic. The sampling area was chosen as part of the protection programme of the Adriatic Sea and is located at two transverse transects, each consisting of four stations. The sediments were collected during the summer cruise of 1990. Quantification of individual components was performed by Capillary Gas Chromatography (CGC) using reference standards. Areal distribution of the concentrations of HCB, lindane, DDT and its metabolites, dieldrin, endrin and PCBs are presented. The values obtained varied within a wide range of concentration from 20 pg/g dry weight for lindane to 700 pg/g dry weight for Σ DDT and the sum of PCBs as Aroclor 1254 from 0.3 to 6.6 ng/g.

The main source of these compounds is thought to be from suspended matter entering the Adriatic sea via the River Po and transported by currents to its middle part.

KEY WORDS: chlorinated hydrocarbons, sediments, Adriatic Sea

INTRODUCTION

In the broad field of water management, surveillance of various pollutants, one of the important activities is to provide information on present levels. This information alerts pollution control authorities to assess the degree of hazard and to take appropriate action. An important component in an environmental study is pesticide residues. Because of their hydrophobic nature, sorption on soils and sediments is the main process that determines the fate of these compounds. It is generally accepted that sediments act as a sink for the more hydrophobic compounds and they reflect long continued contaminant loading. The transport mechanisms of water and particulates are different, but particles with low size/density characteristics may be transported like dissolved species. Transport of larger particles in estuaries and coastal regions is affected strongly by local hydrodynamic and geomorphological characteristics (Duinker, 1986).

Chlorinated hydrocarbons are semi-volatile, lipophylic and hydrophobic synthetic compounds which have environmental significance because of their stability, toxicity and wide distribution. They are used in industry (PCBs), in agriculture (HCH, lindane, DDT) and for civil purposes (DDT). Elder and Fowler (1977) suggested that residues are deposited to sediments by sinking faecal pellets, which they have shown to have about ten times more PCBs than the surrounding water, and about ten times more than the food organisms which form the faeces. For many persistent organic chemicals, as well as for chlorinated hydrocarbons, it has been shown that they can accumulate to high concentrations in aquatic organisms (Sastry and Miller, 1981; Schrap and Opperhuizen, 1990; Villeneuve *et al.*, 1987).

The Adriatic Sea is an important and interesting area for pollution study, because its northern part is a heavily industrialized, urbanized and agriculturally productive area. The contaminants enter the sea *via* the River Po and many other rivers and are

then transported by the currents to other parts (Pigorini, 1968). Due to the large water discharge and the industrial and agricultural character of the drainage basin, the River Po is the major source of pollutants (Helmer, 1977). The aim of the present paper is therefore to investigate the distribution patterns of individual organochlorines in the sediments from the middle Adriatic. This work is a part of continuing studies of the protection of the Adriatic Sea.

MATERIALS AND METHODS

The surface sediments were sampled in the middle part of the Adriatic Sea at two fixed transects between east and west coasts at eight stations (Figure 1). Sediments were collected with a gravity corer (Meischner and Rumohr, 1974). The top 5 cm of the sample was frozen at −20° C, freeze-dried, homogenized and analysed. The samples were extracted with hexane in a Soxhlet apparatus. An internal standard of (25 pg) of TCB (trichlorobiphenyl) was also added. The extracts were reduced to 15 ml by vacuum rotary pump evaporation and to 1 ml in a gentle stream of nitrogen. Sulphur was removed by shaking vigorously with mercury, then centrifuged and transferred to fluorosil column separation. Three fractions were eluted. Standard solutions of each compound were prepared (UNEP, 1988).

Chlorinated hydrocarbons were determined using a Varian 3400 gas chromatograph with Ni-63 ECD detector and with a fused silica capillary column (J. & W. Sci.), 30 m × 0.30 mm, 1 μm film.

Response was measured by peak areas. All compound peaks were quantified against the standard peak areas and recovery was calculated against the peak area of the internal standard. For all samples blank measurements were also made, and detection limits of the method used were specified.

RESULTS AND DISCUSSION

The concentrations of chlorinated hydrocarbons in sediments from the open Adriatic sea are presented in Table 1. In the same table the results of the analyses obtained in coastal area in Kastela Bay sediments are also given for comparison.

Table 1 Contents of chlorinated hydrocarbons in sediments from the middle Adriatic sampled in August 1990, expressed as pg/g dry weight.

Compound	*Transect 6*				*Transect 7*				*Mean value*	*Kastela Bay*
Stations	*601*	*603*	*605*	*607*	*701*	*703*	*705*	*707*		
HCB	95	67	129	<10	180	57	30	21	74	723
Lindane	<20	<20	62	74	54	76	103	60	60	813
pp'DDE	160	78	136	110	108	106	34	220	119	<20
pp'DDD	230	142	<30	<30	260	106	338	93	154	540
pp'DDT	310	213	154	330	50	151	160	96	183	900
Total DDTs	700	433	320	470	418	363	422	409	446	1460
DDT (%)	44	49	48	70	12	41	38	23	41	62
Dieldrin	47	<30	<30	70	<30	<30	<30	48	40	–
Endrin	<30	42	<30	<30	<30	39	<30	120	43	–
Aroclor 1254 (ng/g)	2.1	4.2	4.3	0.3	6.6	3.7	2.2	0.8	3.0	37
Wet weight / Dry weight	2.1	2.0	2.3	2.5	2.1	1.5	1.9	2.1	–	2.3

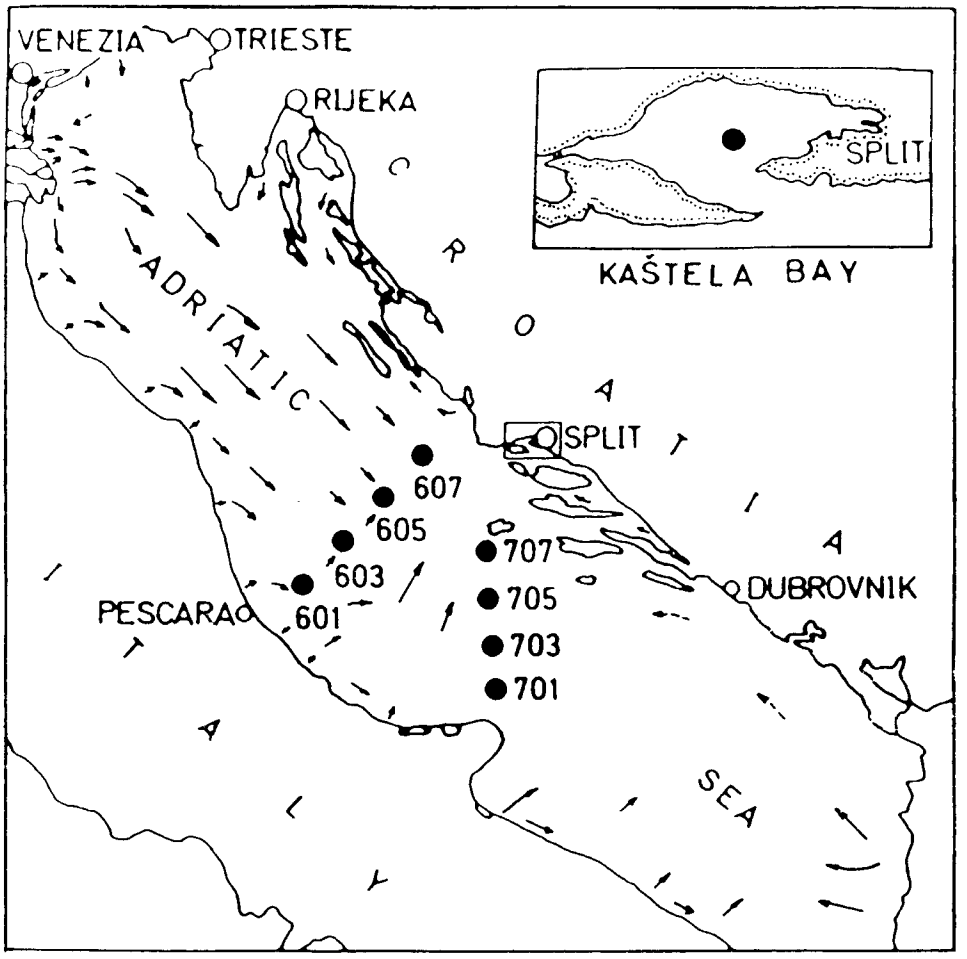

Figure 1 Sampling locations (•) in the investigated area with vector maps of the general patterns of sedimentary distribution (Pigorini, 1968).

If we look at the concentrations of each compound it can be seen that, except for PCB, the largest concentrations were found for DDD and DDT compounds and smallest for dieldrin.

Concentrations of HCB in marine sediments from the middle open Adriatic ranged from below the detection limit (10 pg/g) to 180 pg/g. Use of this compound has been controlled in agriculture in Italy over the last few years, so the values determined could have originated from HCB impurities in pesticides, or by its formation as a by-product during the synthesis of various organic substances. HCB is highly resistant to chemical, biological and physical degradation and is known to accumulate in organisms (Zell and Ballschmiter, 1980).

Lindane is a synthetic compound containing at least 99% of the γ – isomer and is available in many countries. In the middle Adriatic it was found at relatively low concentrations of 20 pg/g to 103 pg/g dry weight sediment. The water solubility of this compound is two to three orders of magnitude higher than the solubility of, for

example, DDT compounds (Table 2), so that on entering the sea, lindane has the possibility to remain dissolved, and the sediments do not reflect the proportional loading quantity (Burns and Villeneuve, 1983).

Concentrations of DDT and its metabolites DDD and DDE in sediments ranged from 320 to 700 pg/g. On the basis of the contribution of each compound in this mixture, DDT degradation is evident; it ranges from 30% at station 607 to 88% at station 701 (Table 1). The quantitative data for these organochlorines in sediments show that, in spite of the restricted use of chlorinated pesticides and ban on DDT use since 1978 by Italian regulation (Fossato *et al.*, 1987), DDT is probably still being used in the region in agricultural management.

Dieldrin and endrin as insecticides are used significantly in the treatment of soil for growing fruits, grains, nuts and vegetables. They could be transferred to marine environment *via* land-based runoff and river drainage. The concentrations of dieldrin and endrin in surface sediments obtained in this investigation are low and at most sites are less than detection limits. Water solubility is one factor which has again to be considered, since for dieldrin and endrin it is an order of magnitude higher than for PCB compounds (Table 2).

Compared to other literature data, it can be seen that these compounds are more detectable in marine organisms than in sediments (Wade *et al.*, 1988; Hargrave *et al.*, 1989).

Table 2 Solubility of the major organochlorine pesticides and PCBs (Callahan *et al.*, 1979).

Compound	*Solubility, ppb (water, neutral pH, 20–25°C)*
PCBs (Arochlor 1254)	12–50
Dieldrin	186–200
Endrin	260
Hexachlorocyclohexane	
α-HCH	1200–2000
γ-HCH (lindane)	2000–12000
Hexachlorobenzene (HCB)	<20
p,p'-DDT	<1–25
p,p'-DDE	1–140

PCBs, expressed as the sum of Aroclor 1254, exhibited a relatively high concentration in sediments. This could be related to several causes: a large input, very low water solubility, short residence time in the water column and finally, high sorption affinity on particles sinking to the sediments. A great difference in concentration is evident between the stations 701 (6.6 ng/g) and 707 (0.8 ng/g); possibly indicating the presence of some local sources of industrial pollution in the west Adriatic. A significant decreasing gradient in PCB concentration eastward is also observed with some lower values found in transect 6 than in 7. A similar distribution was found for polycyclic aromatic hydrocarbons (PAH) at the same sample sites (Dujmov and Sucević, 1990), and for PCB distribution (Fossato *et al.*, 1990). The distribution pattern of PCBs and PAH components appears to be governed by the particulate matter transport established for the Adriatic Sea by Pigorini (1968) and Van Straaten (1965).

The data in Table 1 show also that the concentrations of all organochlorines, as expected, have higher values in Kastela Bay, with the expectation of DDE. Concentrations are an order of magnitude higher for HCB, lindane and PCBs, and for DDD and DDT about three times higher. The ratio between PCBs concentrations (industrial markers) and total DDTs is about 7 (mean value) for the

open Adriatic sediments while for Kastela Bay this ratio is about 24, indicating the dominance of industrial pollution in Kastela Bay. The presence of DDT compounds could be explained by their earlier use for civil purposes.

Finally, it can be concluded from the data that organochlorine concentrations in sediments from the open Adriatic Sea are in the same range of magnitude as reported for some other areas (Table 3). In spite of differences in analytical technique these results give us an integrated picture of organochlorine distribution in various world locations. The widespread occurrence of these compounds in water, sediments and organisms have been reported in recent publications (Amodio-Cocchieri and Arnese, 1988; Burns and Villeneuve, 1982; Duinker *et al.*, 1984; Fowler *et al.*, 1986; Hamilton, 1985; Hargrave *et al.*, 1989; Krause and Knickmeyer, 1992; Schulz-Bull and Duinker, 1991; Van Vleet *et al.*, 1988; Wade *et al.*, 1988).

Table 3 Organochlorine concentrations (pg/g) from the different regions.

	Adriatic Sea	*North Sea*[1]	*Gulf of Mexico*[2]
HCB	<10 to 180	1 to 261	–
Lindane	<20 to 103	1 to 16	<0.01 to 5.62
pp'DDE	34 to 220	1 to 137	–
tot.DDT	50 to 330	–	<0.01 to 454
dieldrin	<30 to 48	–	<0.01 to 4.09
ΣPCBs (ng/g)	0.3 to 6.6	0.17 to 4.4	<0.01 to 189

1. Knickmeyer and Steinhart, 1988.
2. Wade *et al.*, 1988.

CONCLUSIONS

The presence of organic pollutant residues in marine sediments in higher concentrations than expected for open sea means that a relatively high quantity of these compounds enter the sea from coastal discharges. Concentrations are of the same order of magnitude as some other seas such as the North Sea and the Gulf of Mexico. The main source is thought to be from North Italian rivers, especially the river Po, with sediment transport to the middle Adriatic where sediments are deposited. This situation is shown by PCB and PAH distribution patterns. PCB data are presented in this work while the PAH distribution was reported earlier (Dujmov and Sucevic, 1990). Both groups of compounds have a low water solubility, a high sorption activity on the particles and a corresponding high concentration in sediments. Furthermore, the highest PCB concentrations found at station 707 indicates a possible presence of some local sources of industrial pollution in the middle part of the Italian coast.

Kastela Bay could represent a small contribution to the pollution of the Adriatic Sea, although of course, not in the same proportions as the Lagoon of Venice. The concentrations of organochlorines in sediments are approximately an order of magnitude higher than those of the open sea with dominance of the industrial pollution compounds. The presence of DDT compounds in Kastela Bay sediments could be explained with their earlier use for civil purposes.

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