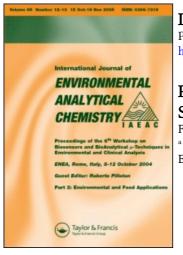
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PAHs, PCBs AND CHLORINATED PESTICIDES IN MEDITERRANEAL COASTAL SEDIMENTS

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Polynuclear aromatic hydrocarbons, chlorinated pesticides and polychlorobiphenyls have been identified and determined in coastal sediments by capillary gas chromatography-mass spectrometry after Soxhlet extraction with a petroleum ether-acetone mixture. Samples collected in three different areas along the Italian coast were analyzed and consistently different concentrations were found for the three locations. Possible sources of pollution have been investigated and identified.

KEY WORDS: Mediterranean sediments, PAHs, PCBs, pesticides.

INTRODUCTION

It is well known that marine sediments may selectively collect organic substances and strongly retain hydrophobic compounds of environmental interest. They have therefore been used for the determination of polynuclear aromatic hydrocarbons (PAHs), chlorinated pesticides and polychlorobiphenyls (PCBs)¹⁻³. Sediments can be a good tool for monitoring marine pollution as well as for identifying possible sources of pollutants in the surrounding environment. PAHs are ubiquitous contaminants and, because of their potential carcinogenic effects, attention has also been paid to their transport through the environment² and methods have been developed to identify their origin in marine sediments³. Significant sources of PAHs are oil spills and emissions from combustion of organic compounds^{3,4}, although they can also be produced by natural processes^{5,6}.

Chlorinated pesticides and PCBs are solely anthropogenic compounds; they are rapidly incorporated into the food chain and their chronic sub-lethal effects have been demonstrated⁷. In many countries, the production and use of these compounds have been forbidden and/or strongly reduced in an attempt to minimize the hazard to man and the environment. However, owing to their resistance to chemical and

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biological degradation, they still can be found in marine sediments as well as in other environmental matrices.

In this paper, the distribution of PAHs, PCBs and chlorinated pesticides in sediments collected in the Mediterranean Sea near the Italian coast is reported. Soxhlet extraction and capillary gas chromatography-mass spectrometry (GC-MS) have been used for the extraction and determination of these compounds.

EXPERIMENTAL SECTION

Samples Sediment samples were collected in three areas along the Italian coast (Figure 1). The first area was in the central Adriatic Sea between the towns of San Benedetto del Tronto and Termoli, the second one was in the central Tyrrhenian Sea, along the coast of Tuscany, between the harbours of Livorno and Piombino, while the third one was located in the northern Tyrrhenian Sea in front of Vado Ligure. All sampling sites were about 1 km from the coast; 25, 29, 22 samples were obtained at each location, respectively, and the 0-20 cm layer of sediment was sampled in all cases by using a shipeck grab. Samples were placed in glass containers, 5 ml of sodium azide (0.05 M) being added to avoid bacterial growth and stored in frozen conditions.

Sample treatment 25 g of sediments were centrifuged at room temperature at 3500 rpm, and the supernatant water was eliminated. The samples were then freeze-dried at -20° C and 0.01 bar to remove the water completely. 10–15 g of the sediment were placed in extraction cups and Soxhlet extracted for 12 h with 150 ml of a petroleum ether (40°C-60°C)-acetone (1:1) mixture, which has been found to be the best extracting mixture for these compounds⁸. Similar results have been achieved by other researchers using mixtures of *n*-hexane-acetone (41:59)⁹ or methylene chloride-methanol (2:1)¹⁰.

It has been shown by some of us^8 that the use of an internal standard when analysing sediments or soil is not proper. In fact, in real-life sediment or soil samples polluted with organic anthropogenic material, the compounds penetrate deeply within the solid structure and this makes extraction more difficult than with the freshly added internal standard. This may lead to an erroneous evaluation of the extraction time. However, the extraction time used in this work appears to be sufficient for the extraction of the organic material, according to previous experience^{8,9}.

The extracts were then concentrated to a volume of $200 \ \mu$ l by using a rotary evaporator at 30°C. Blank extraction of the whole apparatus was carried out each time before use, employing the same solvent mixture under the same conditions. The solvent was then concentrated to $200 \ \mu$ l and analyzed by GC-MS.

Instrumental analysis Identification and determination of PCBs, PAHs and chlorinated pesticides were carried out by computerized capillary GC-MS. A Hewlett-Packard 5970 quadrupole GC-MS system (Hewlett-Packard, Palo Alto, CA, USA)

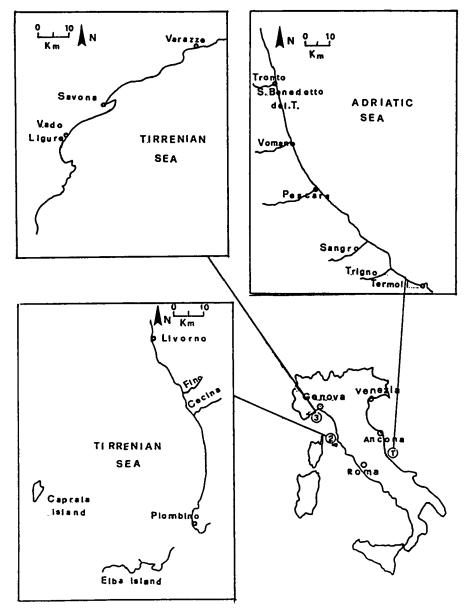


Figure 1 Sediments sampling location.

equipped with a split-splitless injector was used. The gas chromatograph was supplied with an SPB-5 chemically bonded fused silica capillary column (30 m \times 0.25 mm i.d.) (Supelco, Bellefonte, PA, USA). The column temperature was set at 50°C for 1 min and then programmed to increase to 300°C at 10°C/min. 2-µl samples were injected; helium was used as carrier gas (20 cm/sec at 200°C) and *n*-C₃₀ was used as internal standard for the GC-MS calibration.

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The mass spectrometer was used in the SIM mode. Mass spectrometer conditions were as follows: electron energy, 70 eV; source temperature, 220°C; electron multiplier voltage, 2200 V. The SIM programmes used for the analysis of PAHs, PCBs and chlorinated pesticides were selected to enable the simultaneous determination of more than fifty compounds. The following ions were monitored for different classes of compounds: m/z 152, 186, 188, 220, 222, 254, 256, 258, 290, 292, 324, 326, 360, 394, 396, for PCBs; m/z 181, 219, for α -BHC, β -BHC, γ -BHC and δ -BHC; m/z 272, 274 for heptachlor and endosufan sulfate; m/z 263 for aldrin; m/z 263, 279 for dieldrin; m/z 263, 317 for endrin; m/z 263, 353 for heptaclor epoxide; m/z 235, 237, 318 for *p*,*p*'-DDT and metabolites; m/z 152, 154 for acenaphtylene and acenaphthene; m/z 165, 166 for fluorene; m/z 178 for phenanthrene and anthracene; m/z 200, 202 for fluoranthene and pyrene; m/z 228 for benzo(a)anthracene and chrysene; m/z 252 for benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene; m/z 276 for benzo(g,h,i)perylene and indeno(c,d)pyrene; m/z 278 for D(a,h)anthracene.

Compounds with the same characteristic ions show in general different retention times, while only endosulfan sulfate and p,p'-DDT are co-eluted. In the latter case different ions were monitored for each compound. Figure 2 shows the selected ion chromatogram for an actual sediment sample, collected at location 2, where only PAHs have been found. All compounds were separated and identified using the temperature programme described above.

The limit of detection is slightly different for the single compounds but generally lies in the ng/g range. The relative standard deviation ranges between 7 and 10%.

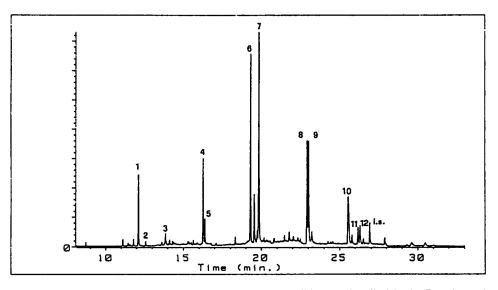


Figure 2 Total Ion Chromatogram of an actual sample. Conditions as described in the Experimental section. Compounds: 1) Acenaphtylene, 2) Acenaphthene, 3) Fluorene, 4) Phenanthrene, 5) Anthracene, 6) Fluoranthene, 7) Pyrene, 8) Benzo(a)anthracene, 9) Chrysene, 10) Benzo(b)fluoranthene, 11) Benzo(e)pyrene, 12) Benzo(a)pyrene.

RESULTS AND DISCUSSION

Polynuclear aromatic hydrocarbons

In Table 1 the PAHs concentrations (in ng/g) at the three locations are reported. Dashes indicate values below 0.1 ng/g. From a general point of view, sediments from location 1 (Table 1A) show a much lower PAH content than the other two locations. Most of the compounds are present at all stations at individual concentrations well below 20 ng/g and all together not exceeding 50 ng/g. Concentrations near these limits are found at some of the stations (2, 5, 11, 17, 23, 24, 25). The iso-concentration curves drawn for some PAHs and based on the actual sampling point, did not show any concentration gradient going toward the off-shore stations. All these facts seem to indicate that there is no contribution from stationary pollution sources (e.g. oil spills). The presence of PAHs can be explained by (i) transport due to the water circulation pattern proper of the Adriatic Sea¹¹, (ii) direct input from the atmosphere, (iii) input from rivers.

If the data reported from the literature on the Mediterranean Sea are considered¹²⁻¹⁷, a comparison can be made with the data reported by Mille *et al*¹² on the French coast, by Grimalt *et al*¹³ on the Spanish coast and those of Marcomini *et al*¹⁴ and Pavoni *et al*¹⁵ on the lagoon of Venice. Comparison with other data^{16,17} may be difficult because data on total non-volatile hydrocarbons or total PAHs determined by UV fluorescence spectroscopy are reported. With these limitations our data at location 1 are similar to the lower values obtained on the French and Spanish coasts for unpolluted areas.

The situation is slightly different at location 2 (Table 1B) where values above the limits mentioned are found for some stations, e.g., 7, 10, 11, 19 and 20. Such stations are near the ports of Piombino (station 7 and 19) and Livorno (11, 12, 20), so that the higher values may be due to the input from the harbour activities taking place in these areas. Values at other stations are still lower than those reported for Venice and similar to those reported for the unpolluted areas of the Western Mediterranean.

In the case of location 3 (Table 1C), consistently higher concentrations than with the other two locations were obtained. In many cases, PAH concentrations reach values around and above $0.5-1 \,\mu g/g$ and, on the average, are higher than those reported for the lagoon of Venice and for the areas close to Marseille and Barcelona possibly polluted by a nearby refinery¹² or denser traffic of vessels¹³. Iso-concentration curves have been drawn for benzo(a)pyrene (Figure 3) which immediately visualize a concentration gradient from inner to outer stations and a well-defined emission point.

Further, the total ion chromatograms (not shown) reveal the absence of n-alkanes and the presence of an unresolved complex mixture (UMC) of hydrocarbons, while the selected ion chromatograms at m/z 191.0 and m/z 217.0 reveal the presence of steranes and hopanes. It is well known that these compounds are present only in oil and related derivatives, being considered as oil 'biomarkers'^{13.18}, while *n*-alkanes are selectively metabolized by bacteria¹⁹⁻²¹.

All these data lead to the conclusion that 'chronic' pollution by oil and/or oil

ioi (°,	Bable 1A PAH concentrations in marine sediments (n) Acc = Accnaphthene, Fl-Fluorene, Ph = Phenanthren Acc = Accnaphthene, Fl-Sluorene, Phenanthren S(e)Pyr = Benzo(e)pyrene, I(c,d)Pyr = Indeno(1,2,3cd)p acc Fi on the second seco
ions in marine sediments (ng/g of dry weight) at location 1 (A), location 2 (B) and location 3 (C). Compounds: $Acy = Acenaphtylene$, luorene, Ph = Phenanthrene, An = Anthracene, F = Fluoranthene, B(b)F = Benzo(b)fluoranthene, B(a)An = Benzo(a)anthracene, l(c,d)Pyr = Indeno(1,2,3cd)pyrene,B(g,h,i)P = Benzo(g,h,i)Perylene, Cry = Chrysene, B(a)Pyr = Benzo(a)pyrene, Pyr = Pyrene. Aci Ace Fl Ph An F $B(b)F$ $B(a)An$ $B(e)Pyr$ $I(cd)Pyr$ $B(ghi)P$ Cry $B(a)Pyr$ Pyr	ioi (°,
ioi (°,	ioi (°,
	PAH concentrat laphthene, Fl-Fl kenzo(e)pyrene, I Lon.E St.

B(c)Pyr =	B(e)Pyr = Benzo(e)pyrene, I(c,d	ene, I(c,d)Pyr	= Indeno()	eno(1,2,	3cd)pyr	ene,B(g	,h,i)P =	Benzo(g,h,i)	perylene, Cry	n I	Chrysene, B(a)Pyr =	⊧ Benzo(a)pyrene,	yrene, P	Pyr = Pyrene	
Lat.N	Lon.E	St.	Aci	Ace	FI	Чd	An	F	B(b)F	B(a)An	B(e)Pyr	I(cd)Pyr	B(ghi)P	Cry	B(a)Pyr	Pyr
43°01'00"	14°01'00"	-	2.6	0.4	2.6	6.2	1.1	/	29	5.5	6.4	/	/	7.5	8.0	-
43°02'30"	14°04'00"	2	3.4	/	2.6	8.5	2.1	31	4	8.8	14	37	25	13	20	19
43°09′30″	14°23'45"	m	/	. ~	/	1.4	/	1.4	2.1	/	0.8	/	/	0.7	_	0.8
42°54'00"	14°03'30"	4	1.5	_	1.5	/	3.8	0.8	13	33	=	7.8	_	/	5.7	/
42°55'00"	14°06'45"	Ś	2.8	. ~	2.0	7.2	1.5	27	35	7.5	13	/	_	11	20	16
43°01'30"	14°21'00"	9	/	-	0.7	1.8	/	2.5	12	1.1	2.4	7.7	3.5	2.2	2.3	1.7
43°00'45"	14°29'45"	2	-	-	/	2.7	-	3.4	4.5	1.1	1.5	/	/	1.6	2.1	1.7
42°10′30″	14°51'30"	œ	~	. ~	. ~	1.7		1.6	1.4	/	/	. ~		/	/	/
42°52'00"	14°22'30"	6	-	. ~	_	4.0	-	5.6	19	1.9	3.2	9.7	3.5	3.8	2.6	3.7
42°31′00″	14°11'45"	0	-	-	_	2.3	-	1.7	1.5	/	/	/	/	0.8	/	1.0
42°40′00″	14°24'30"	Ξ	0.9	_	1.3	5.7	0.5	8.6	35	3.0	6.9	19	_	5.9	_	5.9
42°54'00"	14°44'00"	12	-	/	/	1.4	/	1.8	5.1	0.6	0.0	-	_	1.1	/	1.1
42°30′00″	14°13'15"	13	-	-	_	1.2	-	0.8	0.0	/	/	_	_	0.4	_	0.5
42°32′00″	14°15'30"	14	0.8	-	~	6.5	0.6	9.2	16	3.2	3.6	_	~	4.2	6.1	6.1
42°33′30″	14°17'15"	15	1.7	-	2.9	10	2.4	/	23	5.1	6.9	20	_	13	7.0	7.0
42°51'45"	14°50'00"	16	/	_	/	7.2	_	6.5	14	1.4	2.6	T.T	_	2.7	2.4	3.0
42°26′30″	14°37'45"	17	2.6	0.5	2.1	8.7	1.5	17	36	7.7	12	/	_	12	11	13
42°44′15″	14°57'30"	18	0.4	/	0.6	1.5	0.2	1.8	3.2	0.7	1.0	1.4	_	1.3	/	0.8
42°18'00"	14°33'00"	61	/	-	/	1.4	-	/	5.9	1.3	1.3	/	_	1.7	_	3.4
42°20'00"	14°35′30″	20	1.0	0.2	1.8	5.3	2.3	-	20	5.4	5.4	_	_	6.1	7.0	-
42°14′15″	14°34'45"	21	0.6	-	0.9	5.9	1.2	9.6	2.4	2.7	0.8	/	/	2.4	1.6	6.0
42°16′00″	14°39'00"	2	3.7	-	5.1	16	6.8	/	7	7.2	4.7	-	-	9.7	6.2	27
42°21'30"	14°46′30″	33	4.5	2.0	10	18	2.7	2	30	9.6	9.3	14	_	15	8.0	26
42°17'45"	14°56′15″	24	3.7	/	7.4	18	3.1	36	51	9.6	9.7	23	_	17	8.0	5 9
42°12'00"	15°02′00″	52	2.0	0.5	1.4	6.0	1.0	13	30	5.8	11	/	-	8.6	10	9.9

Pyr B(a) PyrCry B(ghi)P334 / 1226 23 23 23 23 [98 _ 48 33 3 2 B(e)Pyr I(cd)Pyr 541 247 86 223 118 / 11 B(a)An $\begin{smallmatrix} 1.2 \\ 1.2 \\ 0.5 \\ 0.$ B(b)F $\begin{smallmatrix} & 10 \\ & 10 \\ & 2.5 \\ & 2.5 \\ & 2.5 \\ & 2.5 \\ & 2.5 \\ & 2.5 \\ & 2.6 \\ & 2.$ ĹĽ, An $\begin{smallmatrix} & 1.2 \\ & 2.5 \\ &$ Чd $\begin{array}{c} 1.2\\ 2.22\\$ F Ace Aci St. 10° 18′84″ 10° 21′52°90″ 10° 21′52° 10° 31′52″ 10° 31′58″ 10° 31′58″ 10° 31′58″ 10° 25′33″ 10° 25′35″ 10° 25′35″ 10° 22′35″ 10° 22′35″ 10° 22′35″ 10° 22′35″ 10° 22′37″ Lon.E 43°16′18″ 43°11′88″ 43°08′60″ 43°05′10″ 43°00'13" 43°00'00" 42°52'65" 43°29'08" 43°26′20″ 43°24′30″ 43°11'28" 43°07'90" 43°04'75" 42°51'07" 42°58'18" 43°25'53" 43°23'42" 43°10'77" 43°10'77" 43°01'05" 43°2500" 43°2500" 43°01'28" 43°24'75" 43°17'66" 43°20'95" t3°30'02" t3°27'87" 13°15'08" Lat.N

Table 1B

Table 1C																1
Lat.N	Lon.E	St.	Acy	Ace	FI	Чł	An	F	B(b)F	B(a)An	B(e)Pyr	I(cd)Pyr	B(ghi)P	Cry	B(a)Pyr	Pyr
44°21'18"	08°35′24″	-	14	3.8	14	127	24	317	104	74	23	51	20	67	54	203
44°19′00″	08°36'48"	7	93	Π	28	186	11	515	379	250	171	50	36	256	427	339
44°20′30″	08°33'48"	ŝ	105	8.4	19	120	75	353	408	209	182	43	31	206	481	228
44°18'54"	08°35'12"	4	2.5	/	3.7	4.3	1.5	17	14	6.6	5.7	/	/	6.7	15	10
44°19′18″	08°32′12″	Ś	223	59	108	699	273	777	481	/	215	122	_	438	593	/
44°18'00"	08°33'21"	9	54	5.1	15	58	31	190	228	/	43	9.7	. ~	122	92	135
44°19′21″	08°30'18"	7	271	19	41	266	157	766	437	344	171	80	_	350	171	491
44°18′42″	08°30'57"	×	234	35	69	429	217	_	488	403	186	103	~	413	512	/
44°17'33"	08°29′51″	6	109	15	35	193	71	477	281	191	114	72.4	_	193	267	302
44°16′18″	08°31'03″	0	76	7.4	17	6L	41	259	268	130	52	12	_	159	93	159
44°16′36″	08°29'00"	П	355	<u>9</u> 6	82	465	262	72	/	/	209	142	_	482	540	/
44°16′12″	08'27'36"	12	267	36	<i>LL</i>	292	181	59	458	/	92	34	/	/	215	46
44°16'00"	08°28'33"	13	/	/	33	19	/	/	/	10	/	/	/	15	/	/
44°15'24"	08°27'27"	14	252	96	187	1070	419	1060	4410	1890	794	/	/	1820	1530	1791
44°15'09"	08°28'36"	15	308	14	41	228	168	972	2010	780	366	_	523	683	766	6 44
44°14'33"	08°26'54"	16	100	50	89	521	153	1130	1140	518	190	/	234	501	413	653
44°14'09"	08°28'15"	17	183	36	6 6	335	171	929	1650	689	278	/	326	627	630	603
44°13′39″	08°26'03"	18	80	=	32	162	76	599	657	273	109	/	139	269	242	323
44°13'24"	08°26'18"	19	206	24	99	294	148	1060	1440	580	242	/	332	588	489	620
44°12′30″	08°25'24"	20	5.9	9.2	27	126	47	479	561	230	105	/	67	235	209	283
44°12′30″	08°26′21″	21	167	21	49	246	136	790	1270	520	213	/	282	500	473	519
44°17′06″	08°28′21″	22	890	167	337	2630	1180	4720	10600	4620	1730	/	1880	4620	4030	4900

96

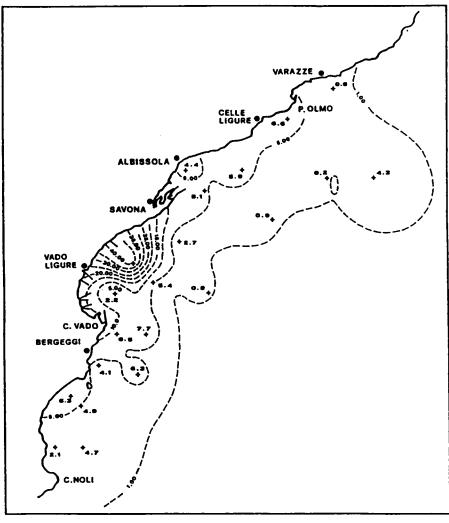


Figure 3 Iso-concentration curves for benzo(a)pyrene at location 3 (northern Tyrrhenian Sea). Values are given in $ng/g \times 10^2$ dry weight.

derivatives has occurred in the area. The calculation of some of the diagnostic¹³ PAH average ratios, (Ph/An = 3.0, F/Pyr = 1.5, B(a)An/Cry = 1.0, B(e)Pyr/B(a)Pyr = 0.8) seems to indicate oil derivatives spill as a possible pollution source. In fact, a berth buoy used in the past by ships for oil products handling, was found to be coinciding with the emission point shown in Figure 4 below.

Chlorinated pesticides and PCBs

The presence of chlorinated pesticides and PCBs has been also investigated in all sediment samples from the same three locations. Their concentrations are reported

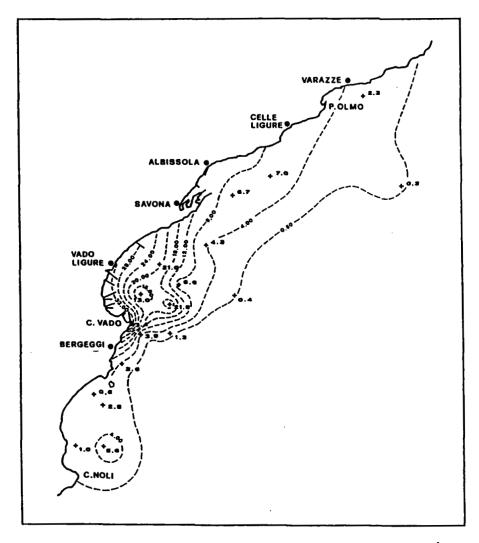


Figure 4 Iso-concentration curves of hexachlorobiphenyls at location 3. Values are given in $ng/g \times 10$ dry weight.

in Table 2. The table is an attempt to give comprehensive view of PCBs and pesticides concentration at all three sites. The samples are numbered from 1 to 29, but it should be kept in mind that 25, 29 and 22 samples were analyzed at the three sites, respectively. Thus, the blank values (below 0.1 ng/g) refer to all three sites for samples 1-22, to sites 2 and 3 for samples 23-26 and only to site 2 for samples 27-29. Numbers in brackets indicate the site(s) where a certain compound was present. Data for PCBs with two, three or four chlorine atoms are not included since very few scattered values were obtained. These compounds were not detected in sediments from site 3 and found only in 5 samples from sites 1 and 2.

Table 2	Chlorinated pesticides and PCBs concer	itra-
tion in m	arine sediments (ng/g of dry weight) at loca	tion
	ation 2 (2) and location 3 (3).	

Samples	PCBs	γ- BH C	Σ DDT
1	33 (3)		20 (1)
2	2.4(1)		9.5(1)
	5.1(3)		
4	2.7(1)		13 (1)
5	1.6(1)	86 (3)	
	43 (3)		1.2(1)
8	37 (3)		8.3(3)
9	2.9(3)		1.7(3)
10	4.4(3)	20 (2)	1.2(1)
11			36 (2)
	36 (3)		7.8(3)
12	66 (3)		4.5(1)
13	343 (3)		
14	401 (3)		4.2(1)
15	13 (3)		
16			3.8(1)
	19 (3)		16 (3)
17			126 (1)
18	6.1(1)		12 (1)
	7.1(3)		
19	1.2(2)		
	18 (3)		5.0(3)
20	9.4(3)		18 (1)
21	2.6(2)		
	44 (3)		25 (3)
22	210 (3)		
23			5.1(2)
24			1.4(1)
			13 (2)
25			24 (1)
			1.6(2)
26			3.7(2)
27			21 (2)
28			131 (2)
29			3.6(2)

In the Vado Ligure region (site 3), penta-, hexa- and heptachloro isomers were often found (11 samples), while they were detected in only 4 samples at location 1 and in 3 samples at location 2. The wide occurrence of PCBs in the coastal environment may be due to the fact that PCBs with a higher number of chlorine atoms are more stable in the marine environment since they undergo less readily enzymatic oxidation by bacteria^{22,23}. Furthermore, because of their lower solubility in water, highly chlorinated PCBs are preferentially associated to the sediments. However, a reasonable explanation for the consistent presence of PCBs at location 1 is that in the past, these compounds have been emitted into the sea from a continental source. Again, the isoconcentration curves (Figure 4) show that this is the case and that the emission point is different from the one found for the PAHs.

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Also in this case, it has been found that a cliff was used by tank trucks for the recurring dumping of waste from a company producing chlorinated compounds.

With the exception of γ -BHC (lindane), found only at one station in sites 2 and 3, p,p'-DDT (together with p,p'-DDE and p,p'-DDD) was the only pesticide present in the sediments, as expected on the basis of the persistence of this compound in the environment. At location 1, they were found only in sediments near the estuaries, and their distribution and concentration may be explained by the agricultural activities taking place in this region.

CONCLUSIONS

The determination of individual PAHs, chlorinated pesticides and PCBs in 75 sediment samples from the Italian Mediterranean coast has allowed the recognition of different input sources for the three areas examined. In particular, two stationary sources, i.e. oil spills and waste dumping, were identified for the northern Tyrrhenian Sea and the central Adriatic Sea, respectively. PAH levels at two locations are similar to those reported for other Mediterranean areas for unpolluted or moderately polluted areas.

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