This article was downloaded by: On: 18 January 2011 Access details: Access Details: Free Access Publisher Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37- 41 Mortimer Street, London W1T 3JH, UK

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information: <http://www.informaworld.com/smpp/title~content=t713640455>

PAHs, PCBs and Chlorinated Pesticides in Mediterraneal Coastal Sediments

F. Manganiª; G. Crescentiniª; E. Sistiª; F. Brunerª; S. Cannarsab

ª Istituto di Scienze Chimiche, Università di Urbino, Urbino, Italy ^ь Centro Ricerche Energia Ambiente, Enea, La Spezia, Italy

To cite this Article Mangani, F. , Crescentini, G. , Sisti, E. , Bruner, F. and Cannarsa, S.(1991) 'PAHs, PCBs and Chlorinated Pesticides in Mediterraneal Coastal Sediments', International Journal of Environmental Analytical Chemistry, 45: 2, 89 — 100

To link to this Article: DOI: 10.1080/03067319108026979 URL: <http://dx.doi.org/10.1080/03067319108026979>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use:<http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PAHs, PCBs AND CHLORINATED PESTICIDES IN MEDITERRANEAL COASTAL SEDIMENTS

F. MANGANI, G. CRESCENTINI*, E. SISTI, F. BRUNER

Istituto di Scienze Chimiche, Universita di Urbino, Piazza Rinascimento, 6-61029 Urbino, Italy

and

S. CANNARSA

Centro Ricerche Energia Ambiente, S. Teresa, Enea, La Spezia, Italy.

(Received 10 August 1990; in final form 4 January 1991)

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 demonstrated'. 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

^{*} **To whom correspondence should be addressed**

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 $(40^{\circ}C - 60^{\circ}C)$ -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 $us⁸$ 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 exper i ence 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- μ l samples were injected; helium was used as carrier gas (20 cm/sec at 200°C) and $n-C_{30}$ was used as internal standard for the GC-MS calibration.

92 **F. MANGANI** *er al.*

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 a-BHC, B-BHC, y-BHC and 8-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)fluoran thene, benzo(a)pyrene, benzo(e)p yrene; 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 ;is described in the Experimental section. Compounds: I) 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)pyr**ene,** 12) **Benzo(a)pyrene.**

RESULTS AND DISCUSSION

Polynuclear aromatic hydrocarbons

In Table 1 the PAHs concentrations (in $\pi g/g$) 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 $al¹³$ 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 lC), 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

 \bar{z} \approx $\frac{1}{2}$ \approx \approx $\frac{1}{2}$ \approx \approx \approx \approx \approx Pyr $B(a)$ Pyr $\frac{1}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ a staa warxas dernyy 4 2 4 2 3 3 4 3 8 2 9 8 2 9 7 7 2 3 9 9 9 8 1 9 9 1 \tilde{C} $B(ghi)P$ ີ ສ ສ <u>ສ</u> ສ ສິສ ି <u>`</u> ଛୁ ್ದ $\boldsymbol{3}$ \mathbf{z} 48 $B(e)Pyr$ $I(cd)Pyr$ $\begin{bmatrix} 2 & 1 \\ 2 & 3 \end{bmatrix}$ a compared that $\frac{1}{54}$ 86 $B(a)/An$ 7133525 $\frac{1}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $B(b)F$ $\frac{1}{2} \times \frac{1}{2} \times \frac{1$ Ŀ. $\frac{1}{2}$ $\ddot{\bm{z}}$ $\frac{1}{3}$ a g $\frac{1}{2}$ g $\frac{3}{2}$ a g $\frac{3}{2}$ a g $\frac{3}{2}$ a g $\frac{3}{2}$ a $\frac{1}{2}$ $\frac{4}{3}$ g $\frac{3}{2}$ a g $\frac{3}{2}$ Ě $15332 - 5 - 5$ m $-$ m $\frac{1}{3}$ m $\frac{1}{2}$ m $\frac{1}{2$ \overline{R} Ace 4ci S. $\begin{smallmatrix} \textbf{1}_{11} & \textbf{1}_{22} & \textbf{1}_{33} & \textbf{1}_{34} & \textbf{1}_{35} & \textbf{1}_{36} & \textbf{1}_{37} & \textbf{1}_{38} & \textbf{1}_{39} & \textbf{1}_{30} & \textbf{$ $Lon. E$ $\begin{array}{l} 43^{\circ}16'18''\\ 43^{\circ}11'88''\\ 43^{\circ}08'60''\\ 43^{\circ}05'10'' \end{array}$ $43°00'13"$
 $43°00'00"$
 $42°52'65"$
 $43°29'08"$ 43°26'20"
43°24'30" 43°11'28"
43°07'90" 43°04'75"
42°51'07" $\begin{array}{l} 42^{\circ}58'18^{\circ}\\ 43^{\circ}25'33^{\circ}\\ 43^{\circ}25'42^{\circ}\\ 44^{\circ}31'3'42^{\circ}\\ 45^{\circ}10'77^{\circ}\\ 44^{\circ}94'9'43'\\ 45^{\circ}31'30'\\ 43^{\circ}08'56'\\ 43^{\circ}08'36'\\ 43^{\circ}01'28'\\ \end{array}$ 43°24'75" 43°17'66"
43°20'95" $13^{\circ}30'02''$ $13°27'87'$ $13^{\circ}15^{\prime}08^{\circ}$ Lat.N

Downloaded At: 15:57 18 January 2011

Table 1B

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, $\frac{Ph}{An} = 3.0$, $\frac{F}{Pyr} = 1.5$, $B(a)An/Cry = 1.0$, $B(e)Pyr/B(a)Pyr = 0.8$) 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.

Chlorinuted pesticides und 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.

In the Vado Ligure region (site 3), penta-, hexa- and heptachloro isomers were often found (1 1 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.

100 F. MANGANI *er al.*

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 an 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.

Acknowledgment

The authors thank L. Lattanzi for outstanding technical assistance.

References

- **1.** T. C. Voice and W. J. Jr Weber, *Warer Res.,* **17 (1983). 1443.**
- **2. S.** Sportsol, N. Gios, R. G. Lichthentharel, K. 0. Gustavsen, K. Urdall, F. Oreld, and J. Skel, *Enuiron. Sci. Technol.,* **17 (1983). 282.**
- **3.** A. Farran, J. Grimalt, J. Albaiges, A. V. Botello and **S.** A. Macko, *Mar. Pollur.* Bull., **18 (1987), 284.**
- **4.** "Particulate Polycyclic Organic Matter"; National Academy of Science, Washington, D.C., **1972.**
- **5.** M. Blumer, **R.** R. L. Guillard and T. Chase, *Mar. Biol.,* **8 (1971), 183.**
- **6.** Z. Aizenshtat, *Geochim. Cosmochim. Acra,* **37 (1973), 559.**
- **7. C. G.** Gustafson, *Environ. Sci. Technol.,* **4 (1970). 814.**
- **8.** F. Mangani, G. Crescentini and F. Bruner, *Anal. Chem.,* **51 (1981), 1627.**
- **9.** H. B. Lee, G. Dookharn and A. S. Chau, *Analyst,* **112 (1987). 31.**
- **10.** J. Grimalt, C. Marfil and J. Albaiges, *Inr.* J. *Enuiron. Anal. Chem.,* **18 (1984), 183.**
- **11.** M. Zore-Amanda, *Deep Sea Res.,* **16 (1969). 171.**
- **12. G.** Mille, J. **Y.** Chen and H. J. M. Dou, *Inr.* J. *Enuiron. Anal. Chem.,* **11 (1982), 305.**
- **13. J.** Grimalt, J. M. Bajona and J. Albaiges, VII Journees Etud Pollut., CIESM, **(1984) pp. 535-543.**
- **14.** A. Marcomini, A. **Sfriso** and B. Pavoni, *Mar. Chem.,* **21 (1987), 15.**
- **15. B.** Pavoni, A. **Sfriso** and A. Marcomini, *Mar. Chem.,* **21 (1987), 25.**
- **16.** J. Duimov and **P.** Sucevic, *Mar. Pollur.* Bull., **20 (1989), 405.**
- **17.** M. Marchand, J. C. Caprais and P. Pignet, *Mar. Enuiron. Res., 25* **(1988). 131.**
- **18.** D. M. Jones, S. J. Rowland and A. G. Douglas, *Mar.* Poll. *Bull.,* **17 (1986), 24.**
- **19.** D. M. Jones, A. G. Douglas, R. J. Parkes, J. Taylor, W. Giger and C. Shauffer, *Mar.* Poll. *Bull.,* **14 (1983), 103.**
- **20.** J. F. Rontani, J. Certand, F. Blanc and G. Giusti, *Mar. Chem.,* **18 (1986), I.**
- **21.** J. F. Rontani and G. Giusti, *Mar. Chem.,* **20 (1986). 197.**
- **22. B.** J. Brownawell and J. F. Farrington, *Geochim. Cosmochim. Acra, 50* **(1985). 157.**
- **23.** Kong Hay-Lomg and G. S. Sayler, *Appl. Enuiron. Microbiol.,* **46 (1983), 666.**