

# Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea

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“**Capsule**”: *The combustion sources of PAHs were identified.*

## Abstract

Distribution of the sixteen polycyclic aromatic hydrocarbons (PAHs) indicated from USEPA as priority pollutants was studied in surface sediments of two coastal areas of the Adriatic Sea. PAHs were recovered from the sediments by solvent extraction and then analyzed by means of gas chromatography–mass spectrometry. Total concentrations of the analytes in the range 24.1–501.1 ng/g were detected. The observed distribution has been discussed taking into account different aspects, such as the fluvial inputs and the grain size of the sediments. By using a molecular marker approach and characteristic compositional patterns it was possible to ascribe to combustion processes the main source of PAHs. Furthermore a good correlation between benzo[*a*]pyrene and the total concentration of PAHs ( $r = 0.953$ ) has been pointed out. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polycyclic aromatic hydrocarbons; Marine sediments; GC/MS; Sediment grain size

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment. These hydrocarbons can become dangerous especially if they come into the alimentary chain, since some of the higher PAHs, and their metabolites, can form DNA adducts which can induce mutations (Henner et al., 1997; Singh et al. 1998).

Because of their carcinogenic and mutagenic properties the USEPA classified 16 of them as priority pollutants (Gremm and Frimmel, 1994).

These compounds have been studied for a long time as markers of anthropogenic input into the sea, since their finding in the environment is due mainly to the combustion and pyrolysis of fossil fuels or wood, and to the release of petroleum products (Canton and Grimalt, 1992; Kowalewska and Konat, 1997). Nevertheless, a number of PAHs have natural sources, and derive from biogenic precursors which are common constituents of terrestrial higher plants, through diagenetic processes (Boulobassi and Saliot, 1993). Some authors suggested that PAHs can be synthesized by unicellular algae, higher plants or bacteria but at the same time others concluded that organisms accumulate PAHs rather than

synthesize them. It is commonly accepted that predators accumulate non-metabolized pollutants and thus have higher level than their food supply (Cripps, 1992).

Once PAHs are released in the environment they can undergo microbiological degradation and photochemical oxidation. However, PAHs ubiquity in the sediments indicates that accumulation phenomena dominate degradation processes in sedimentary matrices (Soclo et al., 2000). PAHs form a widespread class of environmental pollutants. Anthropogenic activity is generally the major source of these compounds and association with fast sinking particles is considered the major mechanism of hydrocarbon transport from the surface to the deep-water column and accumulation in sediment (Gogou et al., 2000).

Sources from which the pollutants are derived will determine the species of existing compound, for example PAHs derived from oil would be expected to behave differently from PAHs occluded in combustion particulate, with regard to possible degradation (Readman et al., 1984). The distribution of PAHs found in sediments gives information about the precursor sources (Budzinski et al., 1997). Molecular indices based on PAHs physical–chemical behaviour covariability were developed to assess the origin of these pollutants; making use of these parameters it is possible to suppose which process generated such hydrocarbons in the studied

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matrices (Soclo et al., 2000). For example, phenanthrene/anthracene and fluoranthene/pyrene ratio has been commonly used to determine the dominant origin of PAHs (Sicre et al., 1987; Budzinski et al., 1997). Phenanthrene is a thermodynamically more stable isomer than anthracene and so petroleum usually contains higher phenanthrene quantities. Hence, PAHs of petrogenic input are generally characterized by high phenanthrene/anthracene ratio (Gui-Peng, 2000). On the contrary, high levels of five-ring and four-ring hydrocarbons are characteristic of PAHs mixtures formed during combustion of fossil fuels (Gogou et al., 2000).

The present work has been performed inside the research project for the safeguard of Adriatic Sea "PRISMA 2", developed to study the physical and biogeochemical mechanisms involved in the transport and diffusion of the substances introduced in the marine environment by the freshwater of the Po river. Two coastal areas of the Adriatic Sea, Chioggia and Ancona, were chosen for their geographical location. In fact, the Po estuary is quite close to Chioggia, so this area is influenced by fluvial inputs and by a high anthropic activity. Once joining the Adriatic, freshwaters follow the coast until Ancona and change direction toward the open sea. For this reason also, this area was investigated.

Our research group studied trace metals distribution in surface coastal sediments of both areas by means of a sequential extraction technique obtaining information about their chemical speciation and bioavailability (Ianni et al., 2000). In order to obtain more information about the pollution levels of the studied sediments, also polycyclic aromatic hydrocarbons were considered.

The goal of this work was to study the distribution of the sixteen PAHs indicated from USEPA as priority pollutants by means of gas chromatography–mass spectrometry.

## 2. Materials and methods

### 2.1. Sampling

The studied sediments were collected in September 1996 during an oceanographic cruise of the PRISMA research project. The sampling was carried out by means of a stainless steel grab, along transects perpendicular to the coast. Eleven sediment samples were collected beside the industrial zone of Chioggia and twelve were collected close to the coast of the city of Ancona.

The external layer was suddenly discarded and the resulting sediment samples were stored at  $-20\text{ }^{\circ}\text{C}$  until analysis.

### 2.2. Chemicals

Reagents and chemicals were of analytical or chromatographic grade. Methylene chloride was purchased

from Riedel-de Haën, n-hexane and isooctane from Merck, while methanol and acetonitrile from Carlo Erba.

A standard solution of the analytes (100  $\mu\text{g/ml}$  each in methylene chloride) was obtained from Hewlett Packard. This standard contains the following sixteen PAHs: naphthalene (Nap), acenaphthylene (Acl), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BA), chrysene (Chr), benzo[*b*]fluoranthene and benzo[*k*]fluoranthene (BF), benzo[*a*]pyrene (BP), indeno[1,2,3-*c,d*]pyrene (IP), dibenzo[*a,h*]anthracene (dBA), benzo[*g,h,i*]perylene (BPer). Working standards were prepared by dilution with isooctane. Quantitative determinations were performed by means of five perdeuterated PAHs standards (1000  $\mu\text{g/ml}$  each in methylene chloride, purchased from Dr. Ehrenstorfer GmbH):  $\text{d}_8$ -naphthalene,  $\text{d}_{10}$ -acenaphthene,  $\text{d}_{10}$ -phenanthrene,  $\text{d}_{12}$ -chrysene and  $\text{d}_{12}$ -perylene. A certified reference material (HS-3 Marine sediment) was purchased from National Research Council of Canada and used to test the validity of the entire method.

### 2.3. Preparation of the samples

The PAHs were extracted from 10 g of dry sediment by a continuous extractor with 60 ml of methylene chloride for 8 h; before extraction the mixture of five perdeuterated PAHs was added to the dry sediment as internal standard. Methylene chloride was then removed by a rotary evaporator, at low temperature (less than  $35\text{ }^{\circ}\text{C}$ ).

The extract was recovered with three portions of n-hexane (1 ml each) and purified by solid phase extraction. A glass column was filled up with 8 g of  $\text{Al}_2\text{O}_3$ ; after the sample was added onto the column, 40 ml of n-hexane were used to remove hydrocarbons and other non-polar impurities. PAHs were then eluted by means of methylene chloride (40 ml); the resulting solution was dried and redissolved in 1 ml of isooctane.

### 2.4. Analysis by GC/MS

The purified extracts were analyzed by GC/MS, using a Hewlett Packard 5890 series II gas chromatograph equipped with a Phenomenex ZB5 (30  $\text{m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ ) column coated with 5% phenylpolysiloxane. The oven temperature was programmed as follows:  $55\text{ }^{\circ}\text{C}$  for 1 min, from  $55\text{ }^{\circ}\text{C}$  to  $133\text{ }^{\circ}\text{C}$  at  $30\text{ }^{\circ}\text{C/min}$ , from  $133\text{ }^{\circ}\text{C}$  to  $285\text{ }^{\circ}\text{C}$  at  $12\text{ }^{\circ}\text{C/min}$  and then held at  $285\text{ }^{\circ}\text{C}$  for 10 min. Helium was used as carrier gas, at a flow rate of 1.4 ml/min. Samples were injected by auto-sampler, using an on-column injector equipped with electronic pressure control, that allows to maintain a constant flow rate during the entire separation. The injector temperature program was the same of the oven.

The capillary column was directly connected, by means of a transfer line maintained at 280 °C, to the ion source of a quadrupole mass spectrometer HP mod. 5989A operating in EI mode.

The EI ion source conditions were: electron energy 70 eV, temperature 250 °C. The analyzer temperature was set at 100 °C. The analytes were identified by acquiring their spectra in scan mode from 45 to 300 a.m.u. The analyses of real samples were performed by single ion monitoring (SIM), measuring the molecular ion of each compound.

Quantitative determination was made by isotopic dilution analysis. A fixed quantity (1 µg) of the five perdeuterated PAHs was mixed with variable quantities of the analytes standard solution. The resulting mixtures were then analyzed and a calibration curve was obtained by plotting the ratios of the measured areas against the ratios between concentrations. Since the perdeuterated compounds are subjected to the same matrix interferences as the analytes, the isotopic dilution method enables recovery problem to be overcome. The whole methodology was verified on a Certified Reference Material, obtaining results in good agreement with the certified values.

### 3. Results and discussion

#### 3.1. Concentration and distribution of PAHs

In order to study the PAHs distribution in the considered area, 23 sampling stations were chosen, 11 nearby Chioggia and 12 close to Ancona. The geographical location of the sampling sites is reported in Fig. 1.

Contents of PAHs determined in sediments from Chioggia and from Ancona are reported in Table 1 and 2, respectively. With regard to PAHs concentration in the sediment, detection limits (estimated as three times background noise) were in the range 2–4 ng/g for all the analytes with the exception of BP (6 ng/g) and IP, dBA, BPer (8 ng/g).

As expected of its geographical position, the values of Chioggia are slightly higher: the total concentration of the 16 PAHs detected in the sediment ( $\Sigma$ PAH) varies from 24.1 to 501.1 ng/g, with a mean value of 333.9 ng/g, against 33.8–306.7 ng/g, with a mean value of 184.6, for those of Ancona. The obtained data are in good agreement with those reported in the literature for the Adriatic Sea (Dujmov et al., 1994; Guzzella and De

Table 1  
Concentration (ng/g) measured in the dry sediment of the area of Chioggia<sup>a</sup>

Station No.	Nap	Acl	Ace	Flu	Phe + Ant	Flt	Pyr	BA + Chr	BF	BP	IP	dBA	BPer	$\Sigma$ PAH
105	28.1	3.5	d.l.	4.7	33.9	69.9	62.3	30.1	36.6	117.8	27.1	d.l.	41.5	455.5
49	39.8	d.l.	d.l.	6.4	24.8	76.2	73.7	33.9	47.3	125.8	30.2	d.l.	43.0	507.1
26	17.7	d.l.	d.l.	5.1	12.4	49.3	42.6	19.6	42.2	98.1	36.7	9.2	53.1	386.0
45	9.3	7.9	d.l.	d.l.	14.4	34.5	24.7	8.2	38.1	73.6	31.3	d.l.	53.5	295.5
103	19.6	d.l.	d.l.	d.l.	15.3	35.5	28.3	18.2	25.1	109.9	30.7	d.l.	30.3	312.9
905	d.l.	d.l.	d.l.	4.6	16.4	47.2	39.2	20.7	33.7	119.8	38.9	d.l.	46.3	366.8
73	10.9	d.l.	d.l.	4.9	13.5	49.9	41.3	24.8	52.2	131.8	47.9	d.l.	64.1	441.3
71	12.3	d.l.	d.l.	4.9	12.8	51.7	40.9	17.5	49.7	115.9	38.5	12	67.9	424.1
69	d.l.	6.2	6.8	d.l.	17.3	35.4	29.5	11.3	27.6	80.4	29.3	d.l.	39.6	283.4
66	d.l.	d.l.	d.l.	d.l.	d.l.	13.6	6.8	7.1	24.3	55.6	40.6	d.l.	35.4	183.4
64	d.l.	d.l.	d.l.	d.l.	4.6	4.5	3.3	d.l.	d.l.	d.l.	11.7	d.l.	d.l.	24.1

<sup>a</sup> The symbol “d.l.” indicates that the measured signal was lower than detection limit, estimated as 3 $\sigma$  (three times background noise).

Table 2  
Concentration (ng/g) measured in the dry sediment of the area of Ancona<sup>a</sup>

Station No.	Nap	Acl	Ace	Flu	Phe + Ant	Flt	Pyr	BA + Chr	BF	BP	IP	dBA	BPer	$\Sigma$ PAH
1	d.l.	d.l.	d.l.	d.l.	5.0	4.3	d.l.	d.l.	3.4	8.9	12.2	d.l.	d.l.	33.8
6	15.7	d.l.	4.3	d.l.	6.1	12.1	11.3	7.0	15.3	64.2	20.3	d.l.	24.3	180.6
10	11.8	d.l.	5.0	4.9	7.1	6.2	d.l.	6.1	26.5	94.9	28.4	d.l.	33.0	223.9
13	47.9	d.l.	d.l.	d.l.	7.1	6.8	5.0	d.l.	20.0	19.2	26.5	d.l.	30.9	163.4
40	d.l.	d.l.	4.3	6.1	12.7	6.2	4.8	d.l.	d.l.	7.1	d.l.	d.l.	d.l.	41.2
37	6.3	d.l.	3.5	d.l.	13.0	29.8	21.5	13.8	42.4	56.7	31.1	d.l.	38.4	256.5
35	d.l.	d.l.	11.4	4.7	8.3	25.8	16.9	6.9	29.6	46.5	29.4	d.l.	24.0	203.5
33	19.5	d.l.	6.6	d.l.	10.9	d.l.	d.l.	6.5	13.9	50.1	22.8	d.l.	17.9	148.2
76	7.5	d.l.	d.l.	d.l.	7.4	5.9	3.5	d.l.	5.4	49.1	18.1	d.l.	11.5	108.4
80	d.l.	6.9	31.3	d.l.	5.2	35.1	31.9	10.9	3.1	59.3	29.3	d.l.	34.0	247.0
83	13.0	d.l.	3.9	d.l.	17.2	50.5	35.6	10.3	39.0	55.9	34.6	d.l.	42.4	302.4
85	5.9	d.l.	4.9	5.2	16.4	26.5	12.2	d.l.	54.4	99.3	38.3	d.l.	43.6	306.7

<sup>a</sup> The symbol “d.l.” indicates that the measured signal was lower than detection limit, estimated as 3 $\sigma$  (three times background noise).

Paolis, 1994) and for other areas of the Mediterranean (Mangani et al., 1991; Gogou et al., 2000).

For a better understanding, obtained results have been plotted on the graphs in Fig. 2 (a, b). In the area nearby Chioggia it is possible to appreciate a general decrease of the PAHs concentration from the coastline to the open sea, although the highest content was measured in the sampling station 49. As previously mentioned, Chioggia is located by the Po estuary, therefore the observed concentration gradient can be ascribed to the freshwater inputs. This is supported by results obtained from other groups of the PRISMA project, showing similar distributions for organic matter and heavy metals (Ianni et al., 2000). Yet, the relatively low PAHs concentration in samples 103 and 905, which are the closest to the coast, is not consistent with this interpretation. It is even more difficult to outline a clear trend for the sediments from Ancona: while the first and the second transect in this area show a trend with a maximum in the middle of the sampling zone, the PAHs concentration increases with the distance from the coast along the third transect.

In order to find a possible explanation we have considered an important sedimentological characteristic of the studied samples, the grain size distribution, whose data were provided by another research group participating to the project (Colantoni, 1998).

By means of the classical physical method of sieving and by the use of a sedigraph instrument, six classes of sediment granulometry have been obtained; their spatial

distribution for both sites is plotted in Fig. 3 (a, b). For our aim it was convenient to consider only two fractions, silt and clay, where silt includes all the sediment classes with a grain size lower than 63  $\mu\text{m}$ .

By comparing Fig. 3 with Fig. 2 it is possible to appreciate a general correspondence between the most contaminated samples and the sediments with a high silt content, suggesting a better affinity of PAHs for the silt fraction of the sediment. This bearing could appear obvious because it indicates that PAHs are prevalently adsorbed on small particles, which have a better adsorbance capability, due to the greater surface. Nevertheless, in literature, this aspect is often neglected and various authors dealing with it obtained sometimes opposite results (Rao et al., 1990; Brown and Maher, 1992). In the previously cited work on the speciation of trace metals in sediments of the Adriatic (Ianni et al., 2000) we pointed out that while some metals strongly correlate with the silt fraction, others do not show this affinity. The relationship between analytes and sediment grain size then appears rather complex: some authors (Letellier and Budzinsky, 1999) suggested that the association of PAHs with sediments is also dependent on different sedimentation processes which affect each specific location.

We can conclude that the correlation between the studied analytes and the silt fraction should be carefully considered and, when verified, could be useful to interpret the obtained data, as in the present work, and also to improve the method sensitivity.

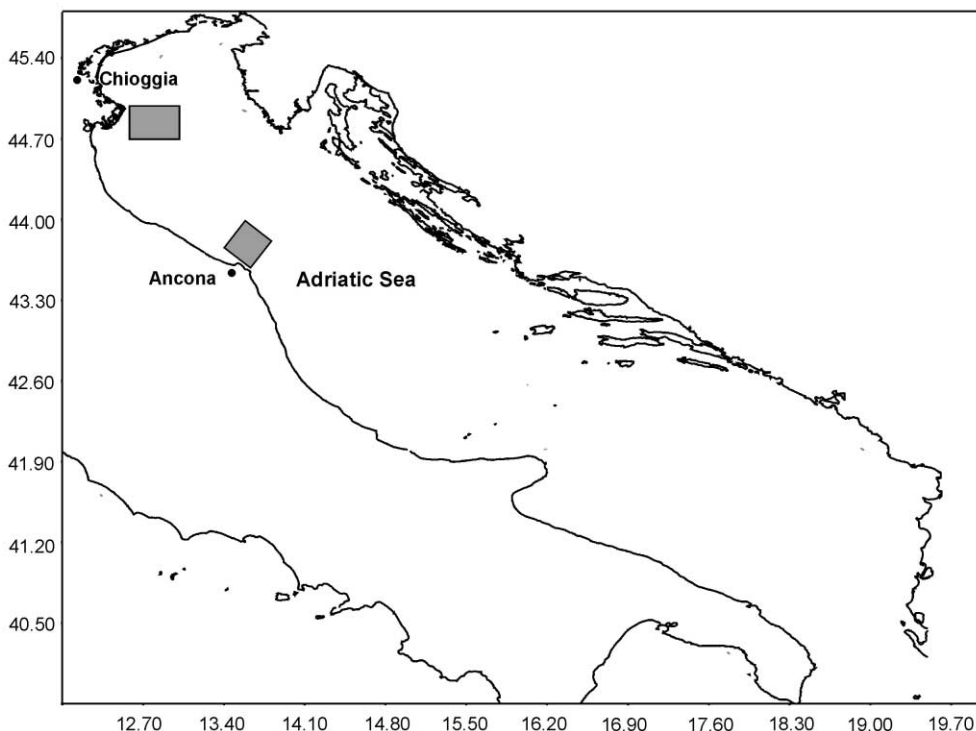


Fig. 1. Map of the studied area of the Adriatic Sea. The grey panels show the sampling zones.

### 3.2. Ratios and correlations between different PAHs

In order to individuate the main sources of the PAHs measured in the studied samples we have considered

some of the characteristic molecular markers conventionally reported in the literature to this aim (Soclo et al., 1986; Budzinsky et al., 1997; Baumard et al., 1998). Mixtures of PAHs formed during high temperature

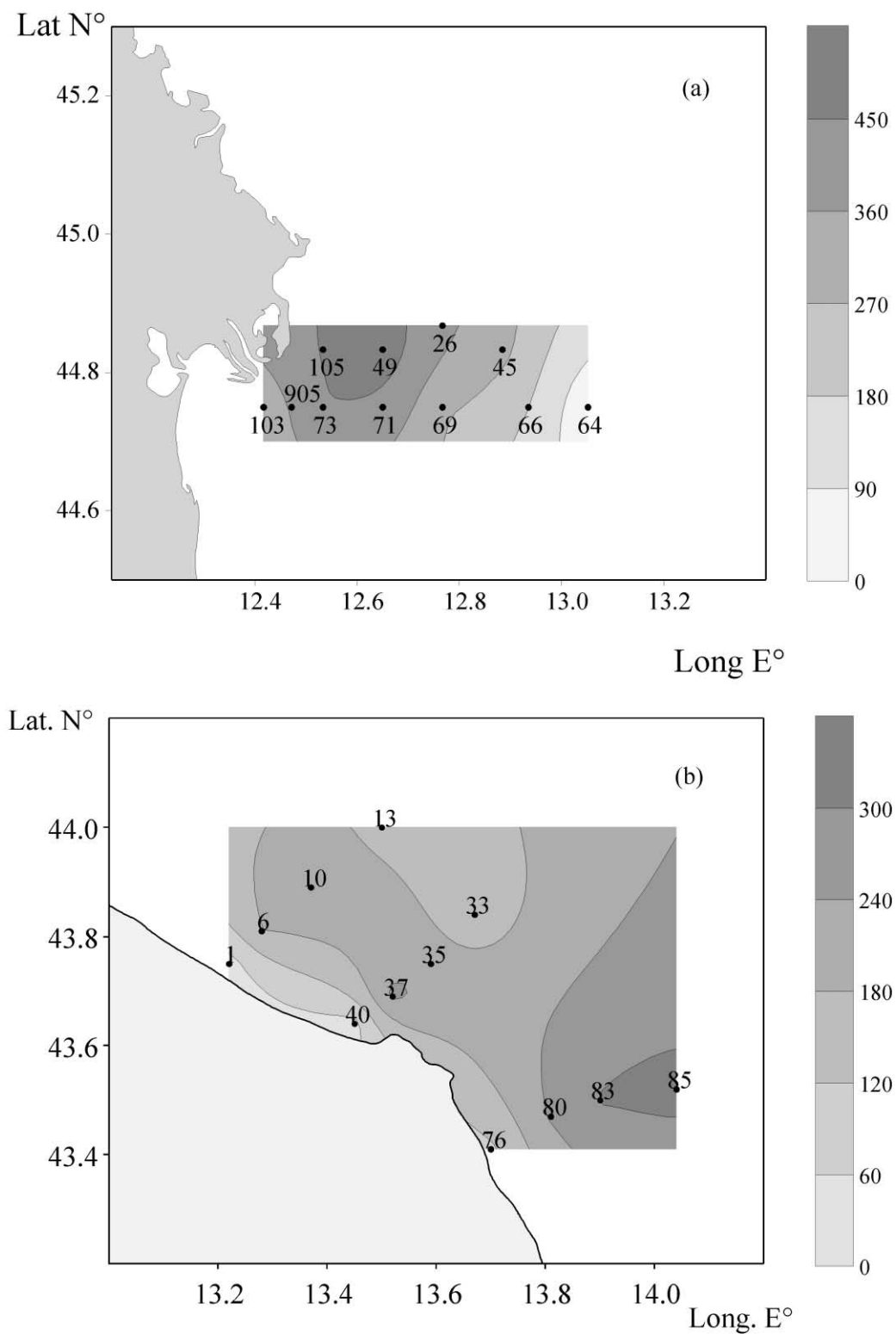


Fig. 2. Spatial distribution of PAHs concentration (ng/g) in the area of Chioggia (a) and in the area of Ancona (b). The numbers inside pictures represent the sampling stations.

combustion of fossil fuels are usually characterized by the dominance of PAHs with high molecular weight. A numeric index related to such consideration (Soclo et al., 2000) is the ratio between LMW and HMW PAHs (Phe + Ant + Flt + Pyr/BA + Chr + BF + BP + IP + dBA + BPer). Regarding the samples of Chioggia we obtained a LMW/HMW range of 0.12–0.66 and a range of 0.07–

0.57 for Ancona. As these values are decidedly < 1 they suggest a pollution of pyrolytic origin. This kind of source is confirmed by two other parameters, Flt/Flt + Pyr and IP/IP + BPer, already used by Gogou et al. (1998) studying different marine matrices of the Mediterranean. In fact we obtained the following ranges: Flt/Flt + Pyr 0.51–0.67, IP/IP + BPer 0.36–0.50 for

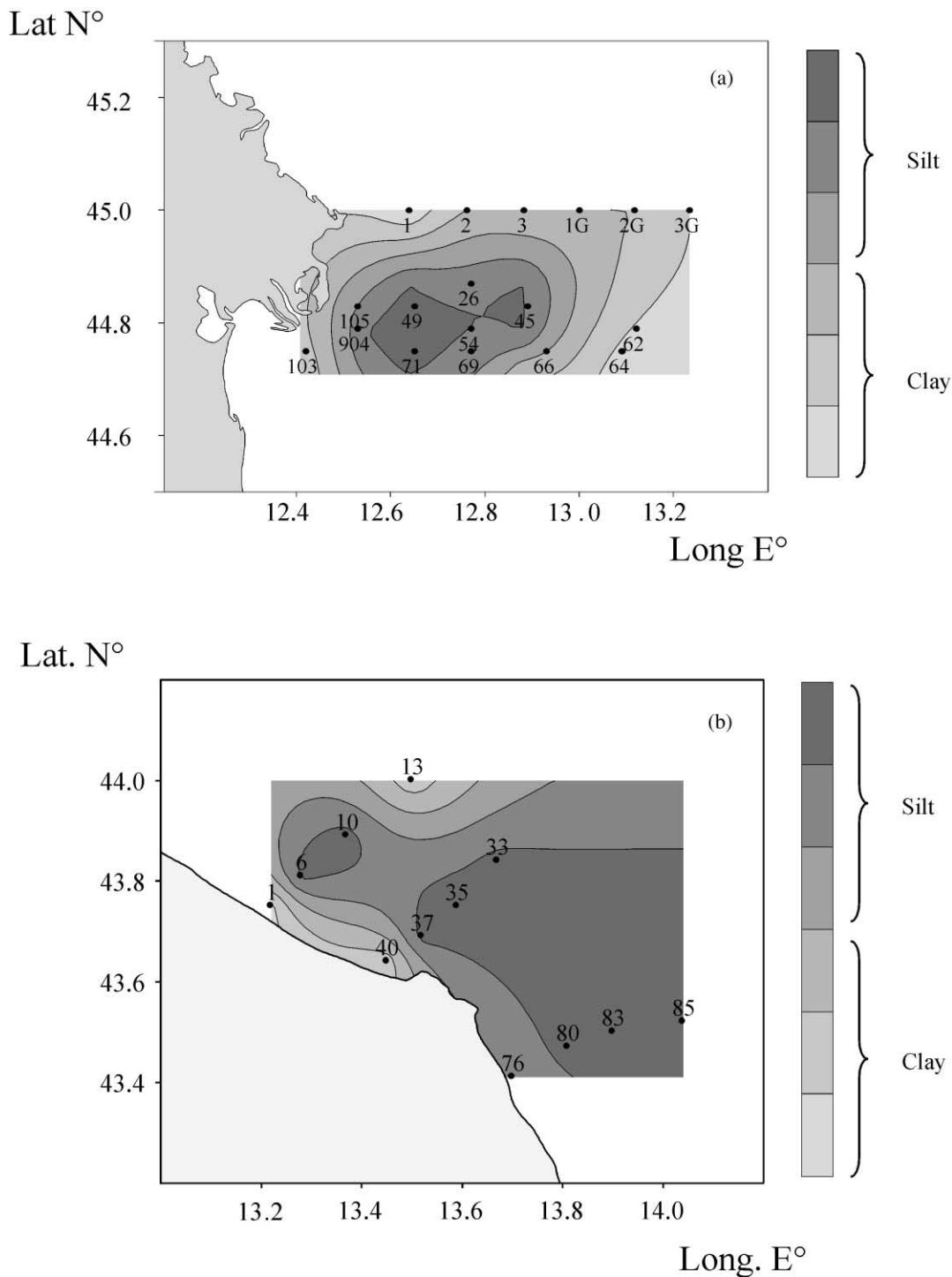


Fig. 3. Grain size distribution in the area of Chioggia (a) and in the area of Ancona (b). The area of Chioggia reports some stations whose samples were not available for PAHs determination.

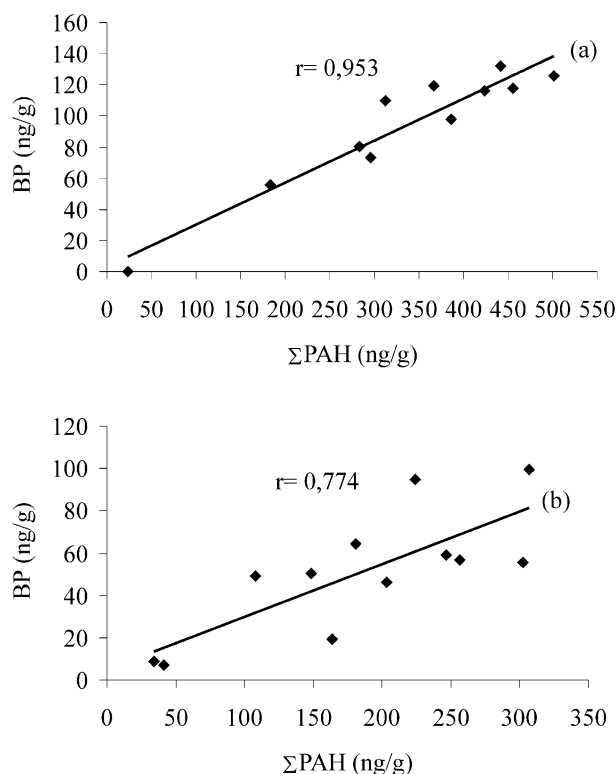


Fig. 4. Correlation between benzo[a]pyrene and total concentration of the 16 PAHs detected in the area of Chioggia (a) and in the area of Ancona (b).

Chioggia; Flt/Flt+Pyr 0.52–0.68, IP/IP+Bper 0.45–0.61 for Ancona. These values are very close to those reported by the cited authors for marine sediments (Flt/Flt+Pyr 0.51–0.82, IP/IP+BPer 0.52–0.65) and ascribed to pyrolytic sources.

Finally we have considered the ratio Flt/Pyr, a widely used marker together with the ratio Phe/Ant (Gschwend and Hites, 1981; Sicre et al., 1987; Colombo et al., 1989). It is generally accepted that Flt/Pyr values greater than 1 are related to pyrolytic origins: as we found ranges of 1.03–2.00 for Chioggia and 1.07–2.17 for Ancona, we have once more the evidence that pyrolysis is the major source of PAHs measured in our samples.

Observing the data of Tables 1 and 2 it is easy to note that benzo[a]pyrene presents the higher concentration in about each sample. Some authors (Kowalewska and Konat, 1997) indicate BP as a potential marker in the study of PAH pollutants. Particularly, BP can be used as an indicator of some combustion-derived PAHs since its concentration in petroleum is usually negligible.

In Fig. 4 (a, b) we have reported the measured concentration of BP against the total PAHs content. The linear regression between BP and ΣPAH shows a significant correlation coefficient, at the 99% confidence level, for both Chioggia ( $r = 0.953$ ) and Ancona

( $r = 0.774$ ). It is interesting to note that the correlation coefficient is particularly high for Chioggia, where the sediments were mostly contaminated. The observed correlation needs to be confirmed by further studies; anyway, as BP is known to be probably the most carcinogenic PAH and because it is frequently formed during pyrolysis processes, this compound could be chosen as an indicator of the total PAH concentration and to assess the contamination level of a sediment.

#### 4. Conclusions

Results obtained with the present study provided useful information in order to evaluate PAH contamination in sediments of the Adriatic Sea. In fact, the geographical distribution of the 16 PAHs classified by EPA as priority pollutants has been discussed taking into account different aspects as the fluvial inputs and the grain size of the sediments.

The values measured close to Ancona indicate that this area is not heavily polluted, while the considerable concentrations of PAHs in some sediments sampled in the area of Chioggia highlight not negligible anthropic inputs.

Considering some concentration ratios between the different PAHs it was possible to indicate pyrolysis processes as the most probable source of contamination.

Finally an interesting correlation between benzo[a]pyrene and the total concentration of PAHs has been pointed out, suggesting the possibility of using the measurement of BP as a useful indicator of the PAHs contamination in marine sediments.

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