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RESEARCH ARTICLE

Polycyclic aromatic hydrocarbons pollution in sediments: distribution and sources in a lagoon system (Orbetello, Central Italy)

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Abstract

1 - The presence, distribution and origin of 16 US EPA polycyclic aromatic hydrocarbons (PAHs) in the surface sediments of Orbetello lagoon (Tuscany, Italy) were investigated by high pressure liquid chromatography (HPLC).

2 - PAH concentrations in the sediments (Σ16PAHs) ranged from 0.92 to 279.38 ng/g of dry matrix, indicating low PAHs pollution. A prevalence of high molecular weight PAHs was observed (>90% of Σ16PAHs) with a considerable predominance of 4-rings PAHs; fluoranthene was the dominant compound.

3 - A comparison with other studies of total PAHs suggests that the levels are within the concentration ranges already reported by the other authors. Total PAH concentrations measured in the studied area indicate a relatively clean environment when compared to values reported by the literature for Mediterranean lagoons.

4 - Molecular ratios were calculated in order to estimate PAH origin and transport from sources. As indicated by the Phen/Ant and Flu/Pyr molar ratio, the main source of PAHs is pyrolityc.

Keywords: Coastal lagoon; Sediment; Polycyclic aromatic hydrocarbons; Petrogenic; Pyrolytic; Tuscany; Orbetello Lagoon

Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a widespread class of environmental chemical pollutants and are ubiquitous contaminants in marine environments, particularly in highly stressed areas such as harbours, estuaries and other shallow coastal zones exposed to anthropogenic inputs. As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated to the particulate matter (Knap and Williams, 1982; Chiou *et al.*, 1998). Sediments therefore represent the most important reservoir of PAHs in the marine environment. For that reason, sediments are economically attractive in environmental assessment of aquatic ecosystems and can represent an useful tool for monitoring inputs of PAH in coastal areas. PAHs accumulation in coastal sediments is both due to anthropogenic and natural emissions. Among anthropogenic factors, petrogenic and pyrolytic sources are the most important. Whereas pyrolytic sources include combustion processes (e.g., fossil fuel combustion, forest fires, shrub and grass fires), the petrogenic input is closely related to petroleum products (e.g., oil spills, road construction materials) and the pyrolytic inputs (anthropogenic combustions) are largely prevalent in aquatic environments. Furthermore, PAHs from pyrolytic and petrogenic sources exhibit different chemical behaviours and distribution in marine sediments. In particular, PAHs from pyrolytic processes are more strongly associated to sediments and much more resistant to microbial degradation than PAHs of petrogenic origin. The use of ratios of PAHs of the same molecular mass represents a well-established method for interpreting PAHs composition and evaluating its sources. The interest in these indices is based on the fact that PAHs distribution is governed by thermodynamics in low-temperature processes such as the formation of petroleum. In contrast, kinetic factors are predominant in high-temperature processes (e.g., the pyrolysis of organic matter). Different criteria were adopted in order to substantiate the origin of PAHs in marine sediments. In particular, the ratios of phenanthrene/anthracene and fluoranthene/pyrene (Sicre *et al.*, 1987; Budzinski *et al.*, 1997) were applied to evaluate the nature of processes responsible for PAHs levels in abiotic matrices. In particular, PAHs levels dominated by petrogenic inputs are generally characterized by a high phenanthrene/anthracene ratio (Gui-Peng, 2000), whereas high levels of five- and four-ring hydrocarbons are distinctive of PAHs mixtures formed by the combustion of fossil fuels (Gogou *et al.*, 2000).

This preliminary work studied the presence, the distribution and the origin of 16 US-EPA PAHs in the superficial sediments of the Orbetello lagoon (Tuscany, Italy). This ecosystem represents a wetland of particularly ecological relevance due to the peculiar multiplicity of aquatic habitats and the presence of species that typically breed in Mediterranean areas, nevertheless it is characterised by considerable inputs of different contaminants originated from the urbanized area and from the former industrial site. This ecosystem during the years, due to its closeness to the town and to the richness of human activities (e.g. industrial, aquaculture, urban activities), have accumulated in sediments both high PAHs and organic matter levels (Specchiulli *et al.*, 2010).

Methods

Study site

Orbetello lagoon (Figure 1) is located in the Southern Tuscany (Italian West Coast), between 42° 25’ and 42° 29’ lat. north and between 11° 10’ and 11° 17’ long. East, and covers a total surface of 25.25 km^2 (Table1). This lagoon is divided by an artificial dam in two communicating basins known as Western (Ponente) and Eastern (Levante) with a surface of 15.25 and 10.00 km^2 respectively (Travaglia and Lorenzini, 1985). Only three communicating canals (Nassa, Fibbia, and Ansedonia) ensure lagoon–seawater exchanges. The average depth is about 1 m (0.30–1.70 m ranged) with maximum reported for the lagoon centre in both basins. The geomorphology of the Orbetello lagoon and the presence of the dam reduce water circulation. To face the occurrence of anoxia phenomena, during the summertime, seawater are pumped throughout the Nassa and Fibbia communicating canals into the Ponente basin and are forced to flow through the Levante basin and to flux towards the sea throughout the Ansedonia canal. This ecosystem represents one of the largest lagoons in the western Mediterranean, nevertheless the presence of shallow waters and low sea-water exchanges limits the water turnover reducing the dilution potential of organic additions, nutrients (from urban effluent, aquaculture plants and agricultural waste water) and anthropogenic contaminants (Specchiulli *et al.*, 2008).

Samplings

Seven-eight superficial sediment samples were collected during the spring of 2003.

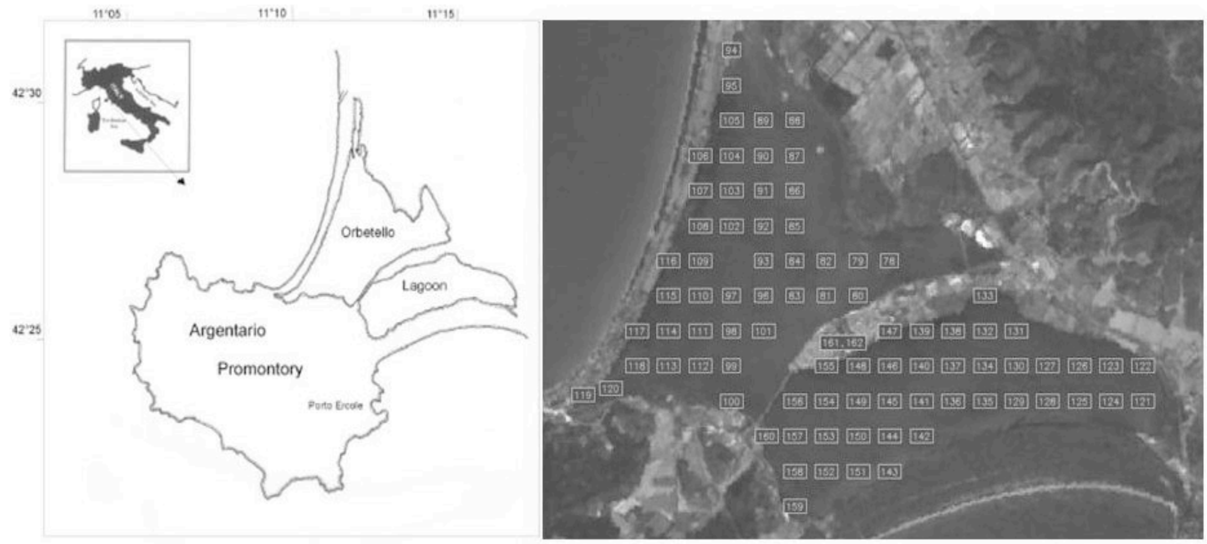


Figure 1. Study area and location of sampling sites.

Figure 1 shows the location of the sampling sites, equally and randomly distributed in Ponente and Levante basins. A total of 500 g of surface sediment was manually collected from each site using an HDPE core tube and placed in Teflon bottles. Samples were thoroughly homogenized and immediately refrigerated (4 °C) on site, stored avoiding exposure to the sunlight, and then rapidly transported to the laboratory where they were frozen prior to analyses.

Table 1 - Main geomorphological and trophic characteristics of Orbetello lagoon.

Location	Surface area (km^2)	Mean depth (m)	Activities present in the catchment area	Activities on the lagoon	Trophic state	Sediment Characteristics	References
NW Italy 42.30°N 11.10°E	27	1.2	Urban, Agricultural	Intensive Fish farming Tourism Industrial	Eutrophic	2-7% TOC	Lenzi *et al*., 2005; Specchiulli *et al*., 2008

Chemicals

All materials were previously washed with ultrapure water, acetone and dichloromethane. Chemicals, if not otherwise indicated, were trace analysis (TA), chromatographic (HPLC) or ACS grade. Glassware was washed prior to use with *n*-hexane (ACS, Fluka) and dried at 105 °C.

Sample treatment

PAH isolation was performed following SW846 USEPA methods (US EPA, 1996). About 10 g (exactly weighted, accuracy: ± 0.0001 g) of the homogenised sediment (air dried) were Soxhlet extracted with 250 mL of dichloromethane (16 h). The extracts were reduced to about 2 mL under a gentle stream of nitrogen and then cleaned up on a micro-column of silica gel and anhydrous sodium sulphate (Na_2SO_4) activated at 120 °C for 24 h. The column was previously conditioned and washed with n-hexane. PAHs were eluted from the silica gel column using 15 mL of hexane:dichloromethane solution 1:1 (v/v). The solvent of this fraction was removed and the residue was analysed by HPLC.

Quantification and validation of analytical data

The aromatic molecules analyzed in this study are abbreviated as follows: naphthalene (N, 2-rings), acenaphthene (Ace, 3-rings), acenaphthylene (Acy, 3-rings), fluorene (Fl, 3-rings), phenanthrene (Phe, 3-rings), anthracene (Ant, 3-rings), fluoranthene (Flu, 4 rings), pyrene (Pyr, 4-rings), chrysene (Chry, 4-rings), benz[a]anthracene (BaA, 4-rings), benzo[b]fluoranthene (BbF, 5-rings), benzo[k]fluoranthene (BkF, 5-rings), benzo[a]pyrene (BaP, 5-rings), dibenzo[a,h]anthracene (DBA, 5-rings), benzo[ghi]perylene (BghiP, 6-rings), and indeno[1,2,3-cd]pyrene (IP, 6-rings). Total PAHs is the sum of the previous cited 16 compounds, given in ng/g dry weight (d.w.).

PAHs were identified and measured by High Performance Liquid Chromatography (HPLC). Acy was determined with a Waters PDA 996 photodiode series detector, while, for all the other compounds, a Waters 474 scanning fluorescence detector was used. The chromatographic separation was performed on a Supelcosil™ LC-PAH HPLC chromatographic column (250×4.6 mm i.d., particle size 5 µm, Supelco) and the mobile phase was carried out in the following conditions: acetonitrile:water gradient of 60:40 for 40 min using a linear gradient and finally acetonitrile:water 100:0 for 10 min, with a flow rate of 1.5 mL min-1. The maximum elution time was 50 min. The quantitative analysis was performed using a three-point linear calibration of a PAHs solution obtained by dilution of the TLC PAH mix 16 certified standard mixture (Polynuclear Aromatic Hydrocarbon Mix by Supelco). A quite satisfactory linearity was obtained, with values of the R correlation coefficient above 0.99. The method detection limits, estimated as 3σ (IUPAC criterion), for each PAH compound was 0.5 ng/g d.w. sediment. A certified reference material, HS-6 harbour sediments, purchased from NRC, Canada, procedural blanks and replicate samples were used for the quality control procedures, and their reproducibility and recovery were high (70-80%). The precision, evaluated in terms of repeatability of the experimental results (n=10) for the analysis of a real sample and expressed in terms of relative standard deviation, ranged between 4.3% (DBA) and 18.5% (N) and, in most cases, was below 10%.

Results and discussions

The analytical data concerning PAHs determination in the 78 selected stations are reported in Table 2a and Table 2b. According to the measured levels, the Orbetello lagoon shows a low to moderate level of contamination by PAHs. The Σ16PAHs concentration ranges from 0.92 to 279.38 ng/g d.w., with a mean value of 38.41 ng/g d.w. Sampling sites located in Ponente basin exhibit the lowest concentration of PAHs, whereas Σ16PAHs levels increased in sediments from sampling stations located in the Levante basin where the maximum Σ16PAH concentration was measured.

Total percentages (n = 78) of the 16 US-EPA PAHs are shown in Figure 2. Fluoranthene (Flu, 19%), pyrene (Pyr, 12%), benzo[b] fluoranthene (BbF, 11%), benzo[a]pyrene (BaP, 10%), benzo[ghi]perilene and indeno[1,2,3-cd]pyrene (9%) represented about the 70% of total PAHs. A clear dominance of high molecular weight PAHs in respect to low molecular weight was observed.

To provide a comprehensive view of the contamination level by PAHs measured in the Orbetello lagoon, a comparison to other lagoons located not only along Italian coasts was made and reported in Table 3. Data were compared on the basis of the average

Table 2a - Concentration of PAHs (ng/g d.w.) and Σ16PAHs in sediment samples collected in Orbetello lagoon.

Sampling sites	N	Ace	Acy	Fl	Phe	Ant	Flu	Py	BaA	Chry	BbF	BkF	BaP	DBA	BghiP	IP	Σ16PAHs
78	<0.5	<0.5	<0.5	<0.5	5.658	<0.5	3.634	<0.5	<0.5	2.313	<0.5	<0.5	<0.5	<0.5	7.352	<0.5	18.957
79	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.765	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.765
80	<0.5	<0.5	<0.5	<0.5	8.767	<0.5	20.809	12.776	<0.5	3.120	8.012	<0.5	6.442	<0.5	<0.5	<0.5	59.926
81	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
82	<0.5	<0.5	<0.5	<0.5	6.875	1.497	19.793	14.209	7.147	7.697	14.133	<0.5	9.718	<0.5	14.224	<0.5	95.293
83	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
84	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
85	<0.5	<0.5	<0.5	<0.5	3.210	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3.210
86	<0.5	<0.5	<0.5	<0.5	7.043	0.800	20.132	8.523	4.739	6.461	11.343	4.241	7.918	<0.5	8.845	8.834	88.080
87	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.952	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.952
88	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	8.577	<0.5	1.746	<0.5	<0.5	<0.5	<0.5	8.099	5.540	23.962
89	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
90	<0.5	<0.5	<0.5	<0.5	5.763	<0.5	12.939	9.160	<0.5	2.906	6.975	3.354	<0.5	<0.5	10.024	6.379	57.500
91	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
92	<0.5	<0.5	<0.5	<0.5	12.154	<0.5	45.630	27.096	9.666	<0.5	18.682	7.208	11.785	<0.5	<0.5	8.752	140.973
93	<0.5	<0.5	<0.5	<0.5	5.466	1.251	34.939	24.543	5.681	<0.5	24.695	8.728	11.602	<0.5	15.257	18.608	150.770
94	<0.5	<0.5	<0.5	<0.5	4.555	0.768	19.171	6.068	3.674	7.472	11.627	4.652	8.195	<0.5	10.748	9.825	85.988
95	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
96	<0.5	<0.5	<0.5	<0.5	8.062	1.559	26.932	10.679	<0.5	7.124	<0.5	5.362	9.488	<0.5	9.418	13.726	92.350
97	<0.5	<0.5	<0.5	<0.5	6.022	0.744	<0.5	3.781	<0.5	5.676	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	15.480
98	<0.5	<0.5	<0.5	<0.5	3.967	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3.967
99	<0.5	<0.5	<0.5	<0.5	4.796	0.955	14.174	4.610	3.609	5.458	<0.5	4.295	3.730	<0.5	<0.5	7.421	48.094
100	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
101	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3.757	2.472	<0.5	1.035	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	7.264
102	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.978	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.978
103	<0.5	<0.5	<0.5	<0.5	4.770	<0.5	13.798	8.984	2.819	4.274	5.952	<0.5	<0.5	<0.5	<0.5	6.177	46.774
104	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
105	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	5.423	3.523	2.250	2.640	2.511	1.184	<0.5	<0.5	2.938	2.205	22.674
106	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.917	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.917
107	<0.5	<0.5	<0.5	<0.5	4.191	0.858	11.335	6.823	1.959	4.985	5.839	2.334	4.637	<0.5	6.387	<0.5	48.491
108	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.922	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.922
109	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	6.244	4.425	<0.5	3.828	7.500	3.460	<0.5	<0.5	11.024	8.477	44.958
110	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
111	<0.5	<0.5	<0.5	<0.5	3.271	<0.5	7.372	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	10.643
112	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.557	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
113	<0.5	<0.5	<0.5	<0.5	11.196	2.812	31.563	15.088	7.117	11.861	15.486	7.545	11.221	<0.5	<0.5	13.535	127.424
114	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-
115	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	-

Table 2b - Concentration of PAHs (ng/g d.w.) and Σ16PAHs in sediment samples collected in Orbetello lagoon.

Sampling sites	N	Ace	Acy	Fl	Phe	Ant	Flu	Py	BaA	Chry	BbF	BkF	BaP	DBA	BghiP	IP	Σ16PAHs
116	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
117	< 0.5	< 0.5	< 0.5	< 0.5	2.256	< 0.5	14.644	12.866	4.063	8.563	7.44	4.813	8.524	< 0.5	8.851	< 0.5	64.580
118	< 0.5	< 0.5	< 0.5	< 0.5	8.590	1.315	29.028	17.859	7.547	9.408	< 0.5	5.928	11.596	< 0.5	13.890	13.503	118.664
119	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.749	< 0.5	< 0.5	1.028	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	2.777
120	< 0.5	< 0.5	< 0.5	< 0.5	1.578	< 0.5	10.882	10.135	4.812	7.433	6.34	3.241	5.975	< 0.5	4.829	5.586	54.471
121	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
122	< 0.5	< 0.5	< 0.5	< 0.5	3.162	< 0.5	10.962	4.251	5.431	3.992	< 0.5	1.650	5.051	< 0.5	3.336	< 0.5	37.835
123	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
124	< 0.5	< 0.5	< 0.5	< 0.5	6.736	1.661	18.321	12.561	4.093	< 0.5	7.04	3.621	7.507	< 0.5	7.671	5.586	67.757
125	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
126	< 0.5	< 0.5	< 0.5	< 0.5	4.358	< 0.5	31.681	22.588	11.324	17.299	18.24	8.618	17.485	< 0.5	14.471	14.574	142.399
127	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
128	< 0.5	< 0.5	< 0.5	< 0.5	10.384	2.402	37.148	18.57	17.050	12.374	21.90	0.000	14.384	< 0.5	11.489	< 0.5	105.233
129	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
130	< 0.5	< 0.5	< 0.5	< 0.5	4.695	< 0.5	16.787	11.458	7.098	8.597	9.57	4.663	10.939	< 0.5	9.654	7.189	81.080
131	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
132	< 0.5	< 0.5	< 0.5	< 0.5	31.073	< 0.5	49.187	49.69	13.519	16.277	12.06	6.622	11.682	< 0.5	7.172	10.269	145.802
133	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
134	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
135	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.094	< 0.5	< 0.5	0.602	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.094
136	< 0.5	< 0.5	< 0.5	< 0.5	8.465	< 0.5	24.551	11.136	4.250	9.452	7.46	4.681	10.359	< 0.5	< 0.5	8.873	81.767
137	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
138	< 0.5	< 0.5	< 0.5	< 0.5	7.319	1.1275	< 0.5	2.574	< 0.5	3.314	7.387	2.897	< 0.5	< 0.5	9.877	< 0.5	44.643
139	5.888	< 0.5	< 0.5	< 0.5	1.906	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.906
140	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
141	< 0.5	< 0.5	< 0.5	< 0.5	1.391	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.391
142	< 0.5	< 0.5	< 0.5	< 0.5	5.126	< 0.5	13.687	14.677	4.094	3.834	< 0.5	3.423	10.751	< 0.5	9.367	8.100	73.059
143	7.616	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
144	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	4.970	2.612	2.264	3.129	< 0.5	1.551	< 0.5	< 0.5	< 0.5	< 0.5	14.526
145	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
146	< 0.5	< 0.5	< 0.5	< 0.5	18.835	< 0.5	65.165	46.129	24.480	25.847	24.125	10.806	25.577	< 0.5	20.524	17.895	279.383
147	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
148	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	11.883	4.469	5.039	6.338	7.095	2.817	9.383	< 0.5	6.748	6.718	60.490
149	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
150	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
151	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.454	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.454
152	< 0.5	< 0.5	< 0.5	< 0.5	9.112	1.550	27.884	14.585	7.992	11.522	17.03	7.862	13.735	< 0.5	13.175	16.386	123.804
153	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-
154	< 0.5	< 0.5	< 0.5	< 0.5	4.951	1.383	16.877	19.153	6.546	4.631	13.84	< 0.5	14.210	< 0.5	13.210	14.100	95.062
155	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	-

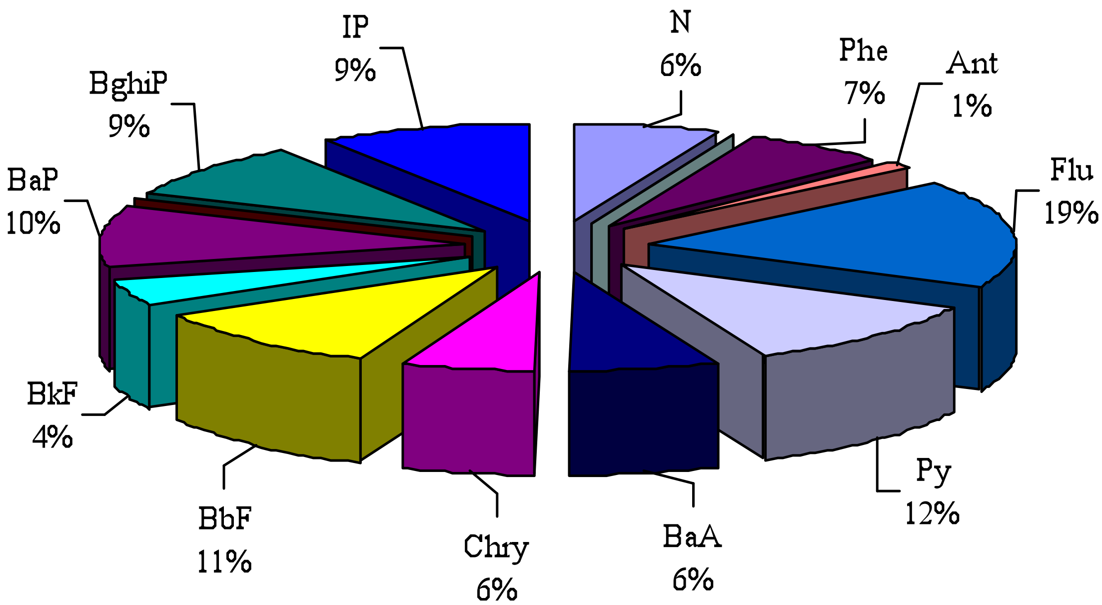


Figure 2. The average distribution of 16 EPA PAHs in sediments of Orbetello lagoon.

Table 3 - Level of PAHs measured in surficial sediments from several lagoon sites (ng/g d.w.).

Location	Number of PAH found	Number of sampling station	Concentration range	References
Laguna dello Stagnone, (Marsala, Italy)	22	8	72-18381	Culotta *et al.*, 2006
Laguna Oliveri-Tindari (Messina, Italy)	16	3	< LOD	Ruta *et al.*, 2009
Pialassa Baiona (Ravenna, Italy)	16	4	2500-120000	Fabbri *et al.*, 2006
Lago di Faro e Ganzirri (Messina, Italy)	21	16	74-5755	Giacalone *et al.*, 2004
Laguna di Venezia (Venezia, Italy)	15	3	315-810	Frignani *et al.*, 2003
Lesina lagoon (Foggia, Italy)	16	13	8.51-70.41	Specchiulli *et al.*, 2010
Varano lagoon (Foggia, Italy)	16	15	6.61-55.06	Specchiulli *et al.*, 2010
Santa Giusta lagoon (Oristano, Italy)	16	14	3.82-250.86	Specchiulli *et al.*, 2010
Orbetello lagoon (Grosseto, Italy)	16	15	0.62-203.33	Specchiulli *et al.*, 2010
Bizerte lagoon (Tunis)	16	10	83.3-447.08	Trabelsi and Driss, 2005
Cotonou lagoon (Benin)	14	6	25-1450	Soclo *et al.*, 2000
Vietnamese lagoons	18	9	112-628	Giuliani *et al.*, 2008

superficial values calculated with respect to sediment dry weights.
The evaluation of PAHs in sediments from circumscribed sites (harbours, lagoons and closed bays) represents a quite complex task due to the potential complexity and variability of anthropogenic contributions coupled to reduced water circulation. These sites could receive effluents from water streams, industrial and urban sewage systems, and agricultural runoff. The limited water exchanges with the open sea are often responsible for localised pollution. In addition, the potentially traffic of motorboats often greatly contributes to the pollution load of the area. What makes it difficult to accurately identify the PAH origins is the presence of a large number of possible sources and processes which could affect PAHs prior to their deposition in sediments. The molecular patterns generated by each source, however, are like finger prints, which make it possible to hypothesize processes which generate PAHs throughout the study of their distribution in sediments.
Pyrolytic sources are characterized by the presence of PAHs over a wide range of molecular weights, while petroleum sources are dominated by the lowest molecular weight PAHs. Grouping polycyclic aromatic compounds into different classes depending on the number of aromatic rings present in their structure (Figure 3), it can be observed that the PAHs with 4, 5 and 6-rings found in sediments at the sites under investigation constitute the 90% of the total. This evidence suggests that PAH contamination in the Orbetello lagoon might be originated mainly from the atmospheric pollution causes by the burning of fossil fuels. In fact, pyrogenic polycyclic aromatic hydrocarbons are generally characterized by the dominance of high molecular mass (4-6 rings) PAHs over those with low (2-3 rings) molecular mass (Witt and Trost, 1999).
The distribution of low and high molecular weight PAHs (LPAHs and HPAHs, respectively) is functional for discerning the

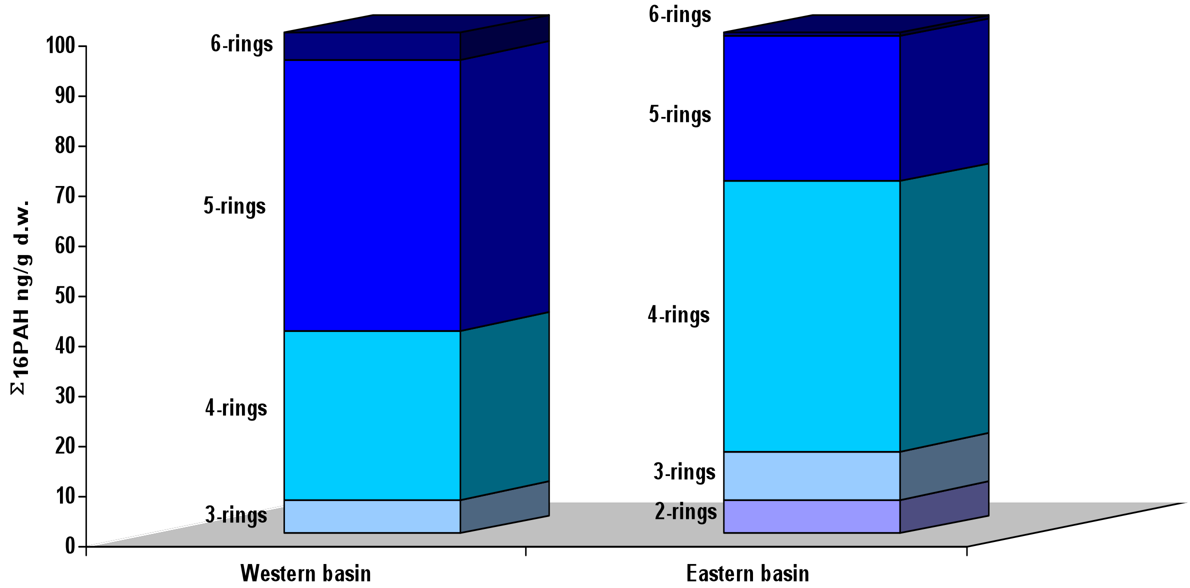


Figure 3. Group profiles of LPAHs (two or three-fused rings) and of HPAHs (four or five-fused rings) in the sediments from Orbetello lagoon.

petrogenic or pyrolytic origin of PAHs; in fact, the higher the LPAHs/HPAHs ratio, the higher the prevalence of petrogenesis (Wise *et al*., 1988). For thirteen sediment samples from Ponente basin and seventeen samples from Levante basin of the Orbetello lagoon, the LPAHs/HPAHs ratio were calculated and the resulting mean value was 0.2 in Ponente basin and 0.09 in Levante basin (Figure 4). This substantiates pyrolytic pollution in the whole lagoon (Soclo *et al*., 2000; Magi *et al*., 2002).

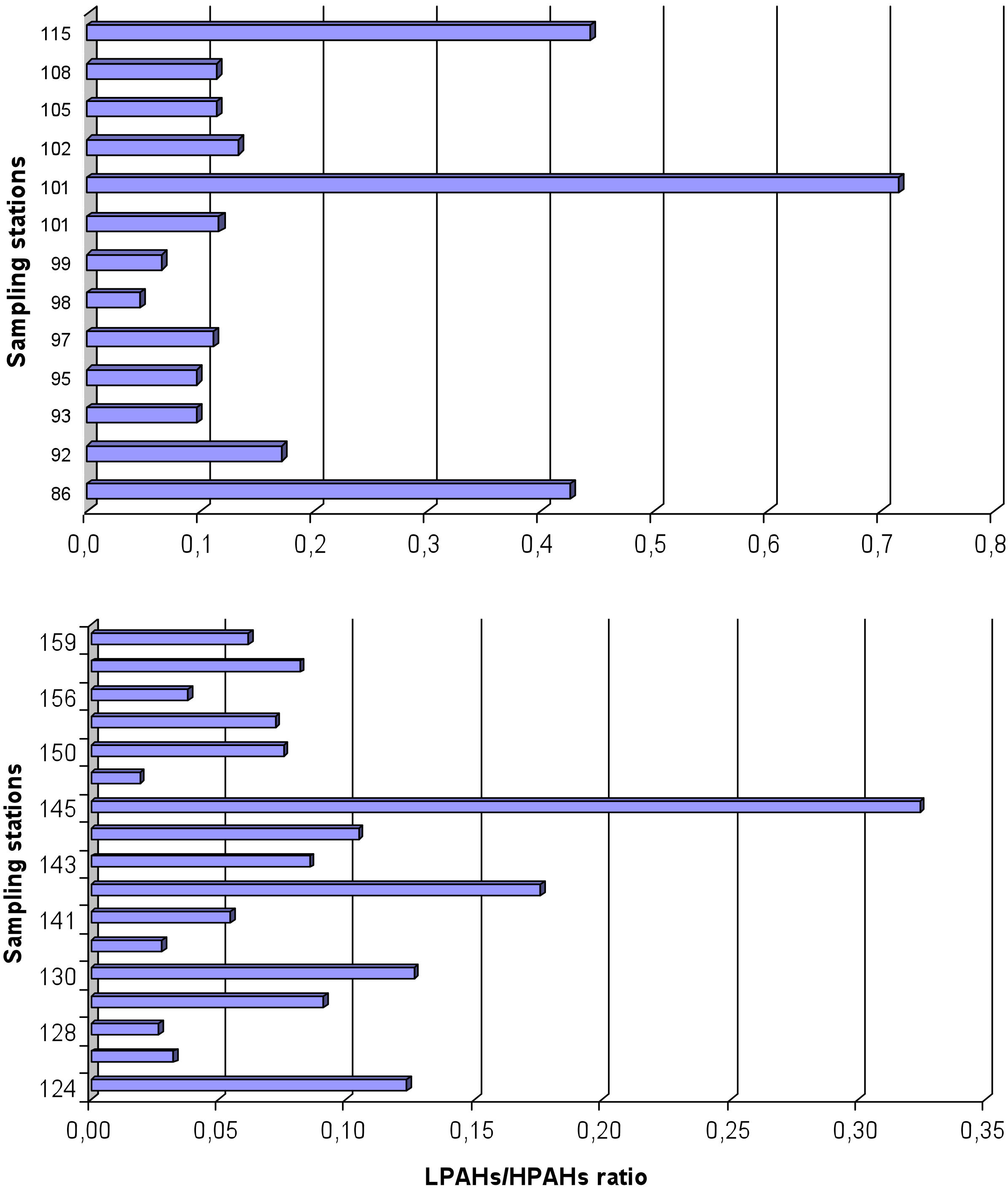
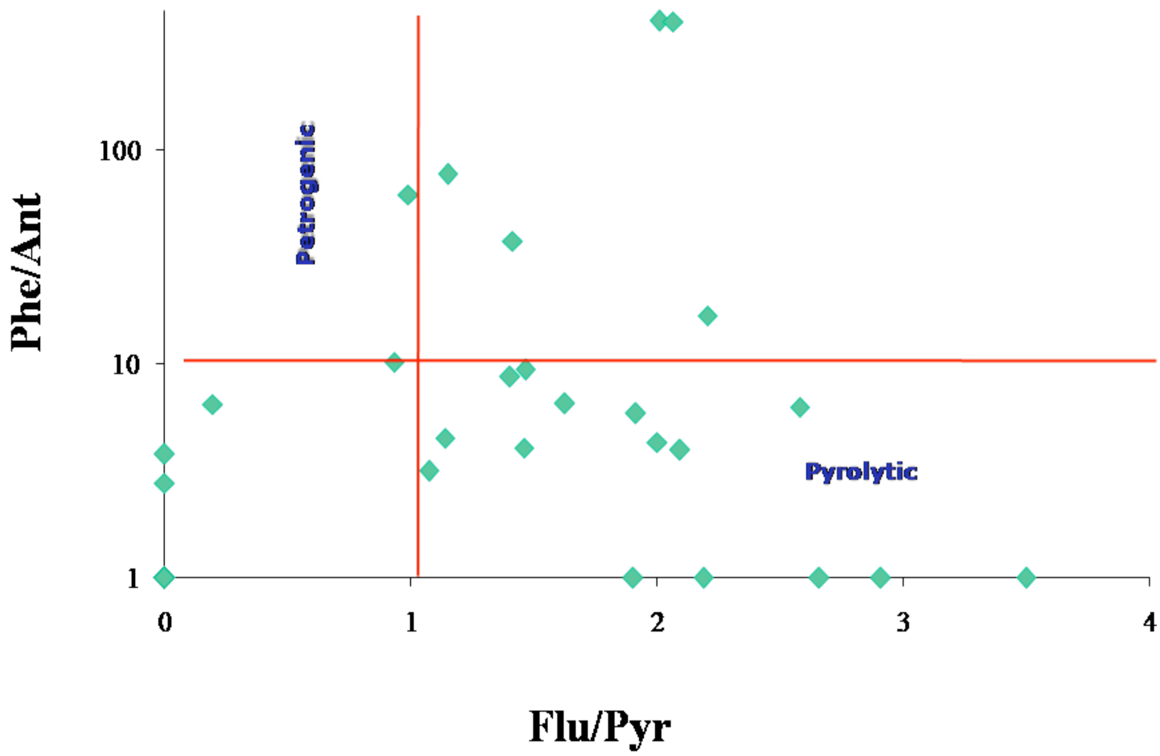


Figure 4. Plot of the LPAHs/HPAHs ratio in the sediments of Orbetello lagoon basins.

A further contribution to the knowledge of PAH origin is given by analyzing the phenantrene/anthracene and fluoranthene/ pyrene ratio on sediments from Orbetello lagoon. The ratio between Phen and Ant was extensively used to infer the nature of PAH pollution in sediments (Sicre *et al.*, 1987, Budzinski *et al.*, 1997, Soclo *et al.*, 2000; Magi *et al.*, 2002). Phenanthrene and anthracene are structural isomers; phenanthrene is more thermodynamically stable than anthracene, therefore, in petrogenic PAH pollution the Phe/Ant ratio is very high, while high temperatures during the combustion process help the formation of anthracene and a lowering of the Phe/Ant ratio. Because of the differences in reactivity and solubility of these two pairs of isomers, their respective ratios are not expected to remain constant and cannot, therefore, provide a picture of the progress of PAHs from their origin through environmental transport, to deposition in marine sediments.

Fluoranthene and pyrene, both with a mass of 202, have the greatest range in stability and hence are good as indicators of thermodynamic vs. kinetic (e.g. petroleum vs. combustion) effects. Generally, Flu/Pyr ratios above 1 indicate a pyrogenic origin, whereas values below 1 are typical of petroleum hydrocarbons (Khim *et al.*, 1999). In particular, the high Flu/Pyr (>0.8-1) and low Phe/Ant ratios (<30) are characteristic of PAHs of pyrolytic origin, while low Flu/ Pyr and high Phe/Ant ratios indicate PAHs to possibly derive from petroleum (Sicre *et al.*, 1987; Budzinski *et al.*, 1997); a Phe/Ant ratio of about four is typical of urban area (Ohkouchi *et al.*, 1999).
The average Phe/Ant ratio for all the sites investigated in this work was 5.5, which is consistent with the presence of a nearby urban site. Orbetello lagoon sediments show a Flu/ Pyr ratio > 1 in western and eastern basins; six sediment from eastern basin show a Flu/ Pyr ratio very close to 1, an intermediate



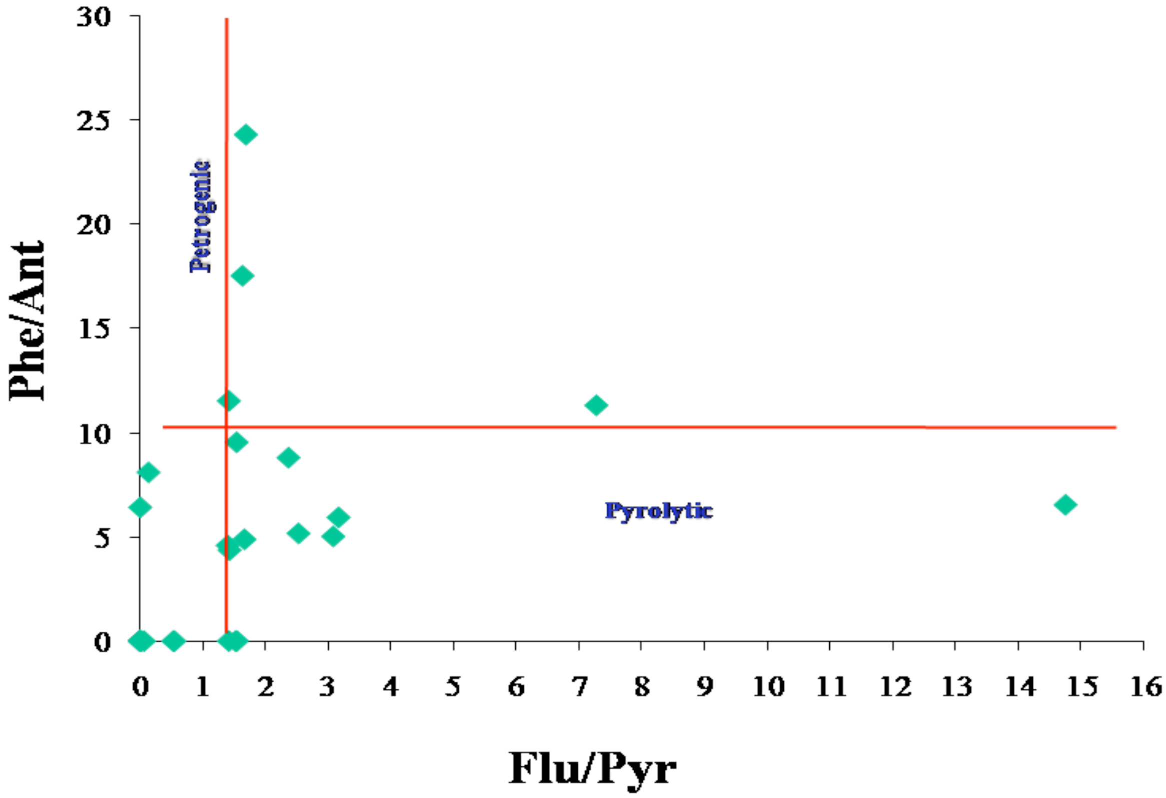


Figure 5. Cross plot of the Phen/Ant versus Flu/Pyr ratio values for sediments of Orbetello lagoon basins.

value between pyrolytic (Flu/Pyr ratio > 1) and petrogenic (Flu/Pyr <1) genesis of PAHs (Baumard *et al.*, 1998). Figure 5 shows cross plots of the Phen/Ant versus Flu/Pyr ratio values for sediments of the Orbetello lagoon. Results achieved in this study have been compared to the Sediment Quality Guidelines (SQG) proposed by US-NOAA's National Status and Trends Program and used to assess the sediments potential toxicity on organisms (Long *et al.*, 1995).

Both ERL (Effect Range Low), that represents the concentration below which it is few probable (<10%) to have toxic effects, and ERM (Effect Range Medium), that represents the concentration beyond which it is very probable (>75%) to observe toxic effects, have been considered.

The comparison to the thresholds of guidelines proposed US NOAA shows safe values, both for ERL and ERM (Table 4), for the whole complex of the Orbetello Lagoon sediments (Table 2).

Table 4 - ERL and ERM levels (ng/g d.w.) for PAHs (from Long *et al.*, 1995).

	N	Ace	Acy	Fl	Phe	Ant	Flu	Py	BaA	Chry	BaP	DBA	Σ16PAHs
ERL	160	16	44	19	240	85	600	670	261	384	430	63	4000
ERM	2100	500	640	540	1500	1100	5100	2600	1600	2800	1600	260	45000

Conclusions

A first analysis (presence, distribution and origin) of US EPA polycyclic aromatic hydrocarbons (PAHs) was performed in the sediments of Orbetello lagoon. The ∑PAH concentrations indicate a low to moderate level of PAH pollution and a heterogeneous distribution of these molecules inside the lagoon basin. The PAH group profile substantiates a predominance of high molecular weight over low molecular weight PAHs. Fluoranthene, pyrene, benzo[b] fluoranthene and benzo[a]pyrene account for ≈50% of ΣPAHs. The dominance of PAHs characterized by high molecular weights (4–6 rings) in the Orbetello lagoon sediments and the Phe/Ant and Flu/Py ratio values used as PAH distribution indexes demonstrate that most samples owe their PAHs to a predominant anthropogenic combustion or pyrolytic processes.

Total PAH concentrations of the Orbetello lagoon (Table 3) is representative of a relatively clean environment when compared to other Italian sites (e.g. Venice lagoon: 315-810 ng/g d.w. and Stagnone coastal lagoon: 72-18381 ng/g d.w., reported by Frignani *et al*., 2003 and by Culotta *et al*., 2006).

The comparison to ERL and ERM values showed that the contamination levels of superficial sediments from the Orbetello Lagoon are not so high to determine negative effects for the benthonic communities of this fragile transitional ecosystem.

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