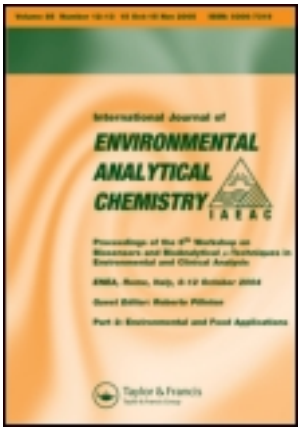

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Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of some Italian lagoons exploited for aquaculture and fishing activities

Antonietta Specchiulli[a]*, Monia Renzi[b], Guido Perra[b], Lucrezia Cilenti[a], Tommaso Scirocco[a], Marisa Florio[a], Silvia Focardi[c], Paolo Breber[a] and Silvano Focardi[b]

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The concentrations of 16 PAHs in surface sediments collected from four Italian lagoons, exploited for aquaculture and fishing activities, during the period 2004–2007, were analysed. Some molecular ratios and Pearson correlations were used in order to estimate the origin of the pollution and similar transport of PAH sources. Principal Component Analysis (PCA) and Cluster Analysis were used in order to highlight dissimilarities among sampling sites. Concentrations of total 16 PAHs varied significantly among the lagoons as well as within the same basin. Sediments of Orbetello lagoon showed the highest level of contamination (mean of 98.78 ng g^{-1}), followed by that in Santa Giusta (48.15 ng g^{-1}), Lesina (31.06 ng g^{-1}) and Varano (25.19 ng g^{-1}). These results were linked to the greater industrialisation and urbanisation of the catchment area of both Orbetello and Santa Giusta compared with Lesina and Varano. A considerable predominance of 4-rings PAHs was observed for Lesina (52%,), Varano (77%), Orbetello (50%) and Santa Giusta (57%) and Pyrene was the dominant compound. On the other hand, phenanthrene is the dominant compound of low molecular weight contaminants for all the studied lagoons. A meaningful pyrolytic contribution to pollution was found in the sediments of Lesina lagoon, dominated by benzo[a]pyrene (7.27 ng g^{-1}) and benz[a]anthracene (4.14 ng g^{-1}), due to intensive traffic. For Varano, an evident petrogenic contamination was observed along the western area, due probably to accidental oil spillage. All 16 PAHs were found to be correlated in Orbetello and Santa Giusta lagoons and the compounds present in Santa Giusta sediments, near the urban centre, were shown to be mainly of pyrolytic origin. A much more complex situation was observed in Orbetello, where a mixed pattern of pyrolytic and petrogenic inputs was observed.

Keywords: coastal lagoon; Italian coast; multivariate analysis; polycyclic aromatic hydrocarbons; sediment; sources

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a widespread class of environmental chemical pollutants and are ubiquitous contaminants in the marine environment, particularly in stressed area like harbours, estuaries and other shallow coastal zones exposed to anthropogenic inputs [1–4]. Due to their carcinogenic and/or mutagenic effects on human and ecosystem health [5,6], the distribution of these contaminants has been widely studied in the various compartments of the environment [2,7–12]. Most of these studies were focused on sediments, as these organic compounds tend to rapidly adsorb to sediment particles through chemical and physical complex mechanisms of adsorption. Therefore sediments can be considered as a pollution reservoir and source from which toxic substances may once again be released into the environment [13]. Accordingly, sediments are economically attractive in environmental assessment of aquatic systems [14] and can represent a useful tool for monitoring inputs of PAH in coastal areas. Polycyclic aromatic compounds can naturally occur (during early diagenesis process), but human activity (e.g. anthropogenic activity, wastes from industrialised and urbanised areas) is considered the major input of these compounds in the environment. These pollutants can be introduced in the environment by two main processes: pyrolytic (fast and incomplete combustion processes at higher temperatures of recent and fossil organic matter) and petrogenic (slow maturation of organic matter under the geochemical gradient conditions). Each source generates a characteristic PAHs distribution pattern with different chemical behaviour [12] and, by studing PAHs distributions in an area, it is possible to identify the probable source of these compounds. A number of molecular indices based on individual compound concentration ratios were used to distinguish between the two sources [7,15–18].

The interest of this work is to identify and quantify polycyclic aromatic hydrocarbons PAHs cited by the US Environmental Protection Agency (US-EPA) as priority pollutants to be monitored in the framework of environmental quality control. Four socio-economically important Italian lagoons were selected to achieve this goal. Both the origin and distribution of PAHs were analysed in surface sediment samples collected in Lesina and Varano lagoons (southern Adriatic coast), in Orbetello (northern Tyrrhenean coast) and in Santa Giusta (western Sardinia). Previous pollution monitoring activities in these areas have taken into account mostly trace metals and organic pollutants (PCBs) and no attempt has been made to quantify levels of the PAHs. The present study represents the first detailed investigation of the distribution and sources of PAHs in sediment samples collected from these Italian lagoons and it could provide a baseline data of PAHs accumulation for future monitoring studies.

2. Experimental

2.1 *Study locations*

As has been mentioned, four Italian coastal lagoons were chosen in this study (Figure 1), according to their similar catchment land use and economic activities. Their main physical and environmental characteristics are summarised in Table 1. Lesina and Varano lagoons communicate with the Adriatic Sea by means of two artificial channels, located in the western and the eastern side of the two basins. Both lagoons receive freshwater inputs from urban wastewaters, agricultural run-off and zoo-technique activities [19] and suffer from episodic anoxic events in the summer months. Their economic relevance is mostly related

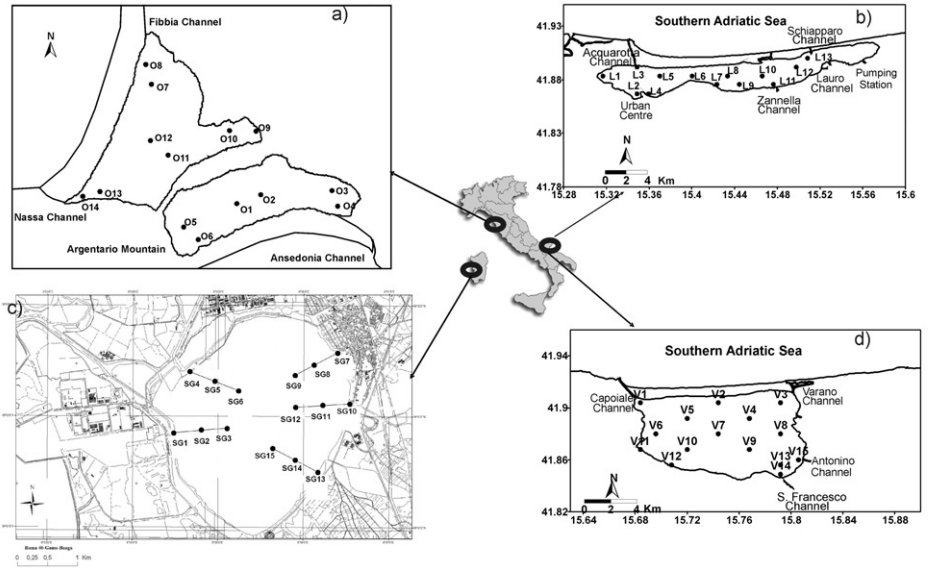

Figure 1. The studied areas and sampling sites location in (a) Orbetello, (b) Lesina, (c) Santa Giusta and (d) Varano lagoons.

to fishing activity and extensive aquaculture farming. Orbetello lagoon is a coastal pond divided by a dam in two communicating basins known as Western and Eastern. Due to its geomorphology and the presence of the dam, the water circulation is reduced and the lagoon is subjected to recurrent eutrophication and severe dystrophic crises, enhanced by the economic development and tourism of the area and by the increment of urban, agricultural and fish-farm wastewaters [20]. Santa Giusta lagoon is one of the most important lagoons of Sardinia with high naturalistic and economic value. A coastal sandbar divides the lagoon from the sea. Originally, it communicated with the sea through the outlet of the River Tirso (via the Pesaria Channel) in the north-western side of the lagoon. This channel permitted the only freshwater inflows in the wet period and the only seawater inflows in the dry period. Subsequently, man-made interventions allowed the direct connection with the sea, through the separation of the Pesaria Channel from the Tirso river along with a fish catch system halfway down the channel. A further communicating channel with the sea was built during the construction of an industrial harbour on the western side of the basin. Also, man-made interventions included a diversion channel for urban wastes (in the north-western side of the basin) thought to reduce the nutrient flow into the lagoon, but, given the high trophic level of the basin, there was no evidence of such diversion system.

2.2 *Experimental design*

The studied sediments were collected in each site in different periods inside specific monitoring programmes, in 2004 (Santa Giusta), 2005 (Orbetello) and 2007 (Lesina and Varano). In order to quantify PAHs levels, 13 stations were selected in Lesina lagoon, 15 in Varano, 14 in Orbetello and 15 in Santa Giusta (Figure 1). The distribution of sites

Table 1. Main geomorphological and trophic characteristics of Lesina, Varano, Orbetello and Santa Giusta lagoons.

	Location	Surface area (km^2)	Mean depth (m)	Activities present in the catchment area	Activities on the lagoon	Trophic state	Sediment characteristics	Reference
Lesina	SE Italy 41.88°N 15.43°E	51	0.8	National Park, Urban Agricultural Zoo-technical	Fish farming Fishing harbour Tourism	Eutrophic	3.31% TOC	[39]
Varano	SE Italy 41.88°N 15.74°E	65	4	National Park, Urban Agricultural Zoo-technical	Mussels farming Fishing-harbour Tourism	Mesotrophic	2.52% TOC	[40]
Orbetello	NW Italy 42.30°N 11.10°E	27	1.2	Urban, Agricultural	Intensive fish farming Tourism Industrial	Eutrophic	2–7% TOC	[40,41]
Santa Giusta	West Sardinia 39.87°N 8.60°E	8,4	1.5	Urban, Agricultural Industrial	Extensive fish farming Tourism Industrial harbour	Hypertrophic	0.48–3.9% TOC	[42]

was intended to provide representation of the whole lagoon surface, its morphology and sediment granulometry as well as to ensure some correspondence in the position of sites along pollution gradients due to external influences. Superficial sediment samples (0–10 cm) were collected in triplicate using a box-corer ($15 \times 15 \times 15$ cm). The sediment samples were transported back to the laboratory on ice, air dried, in the dark, in shallow aluminium pans, sieved through a 1 mm stainless steel screen into clean glass vials and stored at –20°C before analyses.

2.3 *Sample preparation for chemical analyses*

PAH isolation was performed following SW846 USEPA methods [21]. About 10 g (exactly weighted, accuracy: ±0.0001 g) of the homogenised sediment (air dried) was 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.

2.3.1 *Quantification and validation of analytical data*

The aromatic molecules analysed 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 (Py, 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^{-1} dry weight.

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 eluation time was 50 min. The wavelength (excitation/emission) programme is shown in Table 2. 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 ranged from 0.01 to 0.5 ng g^{-1} 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

Table 2. The wavelength (excitation/emission) program during PAH analysis.

	Wavelengths	
Time (min)	Excitation (nm)	Emission (nm)
0	220	330
14	270	323
3	248	374
4	237	460
2	270	400
5	290	418
9.50	270	490
10	270	490

relative standard deviation, ranged between 4.3% (DBA) and 18.5% (N) and, in most cases, was below 10%.

2.4 *Data analysis*

In order to estimate the origin of the pollution in the studied lagoons, some characteristics molecular indices reported in the literature [7,15,17,22] were used in this study. A first step to discriminate between petrogenic and pyrolytic contamination consisted of comparing low-molecular-weight (LPAHs) and high-molecular-weight (HPAHs) congener abundances through the calculation of ratio LPAHs/HPAHs. Based on the grouping of PAHs into different classes depending on the number of aromatic rings present in their structure, LPAHs was obtained by the sum of congeners N + Ace + Acy + Fl + Phe + Ant, while HPAHs was obtained by the sum of congeners Flu + Py + Chy + BaA + B[b + k] F + BaP + DBA + BghiPer + IP [12]. Further investigation was based on calculating the ratios Phe/Ant and Flu/Py. Correlation factors (Pearson's correlation) between PAHs concentrations and some molecular ratios were calculated in each lagoon in order to know whether all contaminant originate from the same source. Multivariate analysis (PCA and cluster analysis) was run on transformed and normalised [23] levels of 16 PAHs in order to investigate the relationship between chemical variables and the number of components needed in explaining variance in observed data. For simplicity, concentrations less than the detection limit were substituted by the detection limit value. Statistical analyses were performed using the Primer-E Software package v6.0 (Plymouth Marine Laboratory, UK).

3. Results and discussion

3.1 *Sediment pollution levels and PAHs profile*

In Tables 3–6, concentration of PAHs (ng g^{-1}; d.w.), ΣPAHs groups according to number of rings and selected molecular ratios are reported for sediment samples collected in each lagoon. Total PAH (ΣPAHs) concentrations in the studied sediments varied significantly among lagoons as well as within the same basin. As expected, the lowest contamination levels occurred in Varano (25.19 ng g^{-1} d.w.), while the highest occurred in Orbetello

Table 3. Concentration of PAHs (ng g^{-1}; d.w.), ΣPAHs groups according to number of rings and selected molecular ratios fro sediment samples collected in Lesina lagoon.

Lesina	Sampling sites												
	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13
N	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Ace	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acy	<0.5	<0.5	<0.5	<0.5	<0.5	3.35	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fl	<0.05	<0.05	<0.05	<0.05	<0.05	1.62	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phe	4.95	<0.02	2.33	<0.02	<0.02	4.33	2.36	3.03	4.95	<0.02	<0.02	5.08	2.37
Ant	<0.01	<0.01	1.15	<0.01	<0.01	<0.01	1.16	1.48	<0.01	<0.01	<0.01	<0.01	1.17
Flu	6.11	<0.02	2.94	<0.02	5.84	4.12	3.01	3.87	6.14	<0.02	<0.02	11.08	2.92
Py	<0.05	<0.05	<0.05	<0.05	<0.05	4.20	0.05	7.35	<0.05	<0.05	<0.05	24.42	<0.05
Chry	6.20	8.51	2.96	<0.03	7.91	1.64	2.98	3.81	6.21	<0.03	<0.03	6.67	2.96
BaA	<0.03	<0.03	2.95	<0.03	<0.03	1.73	2.93	3.73	6.20	<0.03	<0.03	8.47	2.95
BbF	2.53	<0.01	<0.01	<0.01	<0.01	6.99	1.23	1.58	2.54	<0.01	<0.01	5.00	<0.01
BkF	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.18	1.51	2.49	<0.01	<0.01	1.45	1.19
BaP	10.59	<0.03	5.01	<0.03	<0.03	<0.03	5.00	6.37	10.61	<0.03	<0.03	8.26	5.03
DBA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	14.83	<0.1	<0.1	<0.1	<0.1	<0.1
BghiPer	<0.04	<0.04	<0.04	<0.04	<0.04	6.49	4.65	5.92	<0.04	<0.04	<0.04	<0.04	<0.04
IP	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Σ16PAHs	30.38	8.51	17.35		13.75	34.48	24.56	53.48	39.14			70.41	18.59
ΣPAHs (2–3-rings)	4.95		3.48			9.30	3.52	4.51	4.95			5.08	3.54
ΣPAHs (4-rings)	12.31	8.51	8.86		13.75	11.70	8.98	18.76	18.55			50.63	8.83
ΣPAHs (5-rings)	13.12		5.01			13.47	12.07	30.21	15.64			14.71	6.22
ΣPAHs (6-rings)													
ΣLPAHs	4.95		3.48			9.30	3.52	4.51	4.95			5.08	3.54
ΣHPAHs	25.43	8.51	13.87		13.75	25.17	21.04	48.97	34.19			65.34	15.05
LPAHs/HPAHs	0.19		0.25			0.37	0.17	0.09	0.14			0.08	0.24
Phe/Ant	495.30		2.02			432.85	2.03	2.06	495.30			507.53	2.02
Flu/Py	122.12		58.88		116.77	0.98	60.28	0.53	122.76			0.45	58.31

Table 4. Concentration of PAHs (ng g^{-1}; d.w.), ΣPAHs groups according to number of rings and selected molecular ratios fro sediment samples collected in Varano lagoon.

	Sampling sites														
Varano	V1	V2	V3	V4	V5	V6	V7	V8	V9	V10	V11	V12	V13	V14	V15
N	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Ace	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acy	<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
Fl	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phe	4.65	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	2.32	<0.02
Ant	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flu	8.16	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	5.45	<0.02	<0.02	<0.02	2.44
Py	20.70	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	28.37	<0.05	<0.05	<0.05	<0.05
Chry	5.66	<0.03	<0.03	<0.03	3.65	<0.03	<0.03	<0.03	<0.03	<0.03	5.48	<0.03	<0.03	<0.03	<0.03
BaA	7.42	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	5.71	<0.03	<0.03	2.88	4.18
BbF	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
BkF	1.34	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
BaP	7.12	<0.03	<0.03	<0.03	5.49	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	4.92	<0.03
DBA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BghiPer	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
IP	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Σ16PAHs	55.06				9.13						45.01			10.12	6.61
ΣPAHs (2–3-rings)	4.65													2.32	
ΣPAHs (4-rings)	41.95				3.65						45.01			2.88	6.61
ΣPAHs (5-rings)	8				5									5	
ΣPAHs (6-rings)															
ΣLPAHs	4.65													2.32	
ΣHPAHs	50.41				9.13						45.01			7.80	6.61
LPAHs/HPAHs	0.09													0.30	
Phe/Ant	465.07													231.83	
Flu/Py	0.39										0.19				48.74

Table 5. Concentration of PAHs (ng g^{-1}; d.w.), ΣPAHs groups according to number of rings and selected molecular ratios fro sediment samples collected in Orbetello lagoon.

	Sampling sites													
Orbetello	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14
N	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Ace	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acy	<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
Fl	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phe	18.60	24.30	4.49	5.36	4.01	1.65	4.72	14.17	6.63	7.93	10.38	21.80	16.96	12.12
Ant	4.97	5.55	0.98	1.31	<0.01	<0.01	0.74	1.86	1.48	2.06	1.67	3.76	4.51	2.80
Flu	33.34	30.64	6.84	21.03	8.50	<0.02	<0.02	20.72	17.14	18.43	12.09	33.96	42.00	3.29
Py	25.60	32.36	<0.05	10.11	8.95	2.17	7.27	11.78	20.96	19.12	5.77	22.09	40.92	<0.05
Chry	21.45	26.02	5.13	<0.03	3.58	<0.03	1.88	11.11	6.53	8.88	5.26	12.78	20.28	11.21
BaA	14.15	24.03	4.99	5.18	3.57	<0.03	<0.03	9.04	6.40	9.43	4.63	13.09	6.07	5.47
BbF	17.08	36.91	<0.01	5.89	6.64	<0.01	<0.01	5.68	6.47	11.26	7.38	24.73	22.98	17.42
BkF	15.77	15.59	2.27	2.58	2.35	<0.01	<0.01	4.90	2.88	5.08	2.30	7.94	9.95	7.52
BaP	25.78	23.93	6.14	6.37	4.69	<0.03	<0.03	9.31	5.32	8.99	<0.03	11.38	20.38	13.53
DBA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
BghiPer	<0.04	15.36	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	15.21	15.46	14.70
IP	17.04	16.18	<0.03	<0.03	<0.03	<0.03	<0.03	5.40	<0.03	<0.03	<0.03	12.99	<0.03	13.10
Σ16PAHs	193.78	250.86	30.85	57.82	42.31	3.82	14.62	93.98	73.81	91.19	49.48	179.72	199.52	101.16
ΣPAHs (2–3-rings)	23.57	29.85	5.47	6.67	4.01	1.65	5.46	16.03	8.12	9.99	12.05	25.56	21.47	14.92
ΣPAHs (4-rings)	94.54	113.05	16.97	36.31	24.61	2.17	9.15	52.65	51.03	55.86	27.76	81.91	109.27	19.97
ΣPAHs (5-rings)	58.63	91.78	8.41	14.84	13.68			19.89	14.66	25.34	9.68	59.26	68.78	53.18
ΣPAHs (6-rings)	17.04	16.18	<0.03	<0.03	<0.03	<0.03	<0.03	5.40	<0.03	<0.03	<0.03	12.99	<0.03	13.10
ΣLPAHs	23.57	29.85	5.47	6.67	4.01	1.65	5.46	16.03	8.12	9.99	12.05	25.56	21.47	14.92
ΣHPAHs	170.21	221.01	25.38	51.15	38.29	2.17	9.15	77.95	65.70	81.20	37.43	154.16	178.05	86.25
LPAHs/HPAHs	0.14	0.14	0.22	0.13	0.10		0.60	0.21	0.12	0.12	0.32	0.17	0.12	0.17
Phe/Ant	3.74	4.38	4.58	4.08	401.46	165.46	6.35	7.62	4.47	3.85	6.22	5.79	3.76	4.33
Flu/Py	1.30	0.95	136.77	2.08	0.95	0.01		1.76	0.82	0.96	2.10	1.54	1.03	65.74

Table 6. Concentration of PAHs (ng g^{-1}; d.w.), ΣPAHs groups according to number of rings and selected molecular ratios fro sediment samples collected in Santa Giusta lagoon.

	Sampling sites														
Santa Giusta	SG1	SG2	SG3	SG4	SG5	SG6	SG7	SG8	SG9	SG10	SG11	SG12	SG13	SG14	SG15
N	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Ace	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acy	<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
Fl	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.05	<0.05	<0.05	<0.05	<0.05
Phe	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	3.09	30.64	0.65	<0.02	2.45	<0.02	<0.02	<0.02	<0.02
Ant	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	5.27	68.02	0.85	1.43	4.83	0.79	<0.02	1.35	<0.02
Py	<0.05	0.62	<0.05	<0.05	<0.05	<0.05	4.54	66.97	1.04	1.24	4.68	<0.05	<0.05	1.60	<0.05
Chry	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	2.26	41.31	0.47	1.39	3.30	<0.03	<0.03	1.04	<0.03
BaA	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	1.78	27.03	0.35	<0.03	2.18	0.25	<0.03	0.65	<0.03
BbF	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	2.54	42.47	0.50	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
BkF	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.75	13.51	<0.01	<0.01	1.09	<0.01	0.28	0.35	<0.01
BaP	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	2.48	35.16	0.48	0.75	2.69	<0.03	<0.03	0.48	<0.03
DBA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
BghiPer	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	1.095	10.51	<0.04	0.84	1.37	<0.04	<0.04	0.71	<0.04
IP	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	1.375	20.96	<0.03	0.63	1.94	<0.03	<0.03	0.67	<0.03
Σ16PAHs		0.62					25.19	364.28	4.33	6.28	24.52	1.04	0.28	6.84	
ΣPAHs (2–3-rings)							3.09	38.35	0.65		2.45				
ΣPAHs (4-rings)		0.62					13.86	203.33	2.71	4.06	14.98	1.04		4.63	
ΣPAHs (5-rings)							6.87	101.65	0.97	1.59	5.14		0.28	1.54	
ΣPAHs (6-rings)							1.38	20.96		0.63	1.94			0.67	
ΣLPAHs						3.09	38.35	0.65		2.45					0.65
ΣHPAHs		1					22.10	325.93	3.68	6.28	22.07	1.04	0.28	6.84	
LPAHs/HPAHs							1.74			0.39					
Phe/Ant							308.62	3.97	64.67		244.92				
Flu/Py		0.03					1.16	1.02	0.82	1.15	1.03	15.71		0.84	

(98.78 ng g^{-1} d.w.), due to greater industrialisation and urbanisation of the catchment area. It has been demonstrated that the nature of the sediment (organic matter and grain-size) influences the distribution and concentration of PAHs. Di Leonardo *et al.* [24] found sediments containing higher concentrations of TOC to be well correlated with PAHs, due to the strong affiliation of most organic contaminants to organic matter. On this basis, sediments of Orbetello, which contain higher percentages of TOC than those of Varano (Table 1), should have a higher accumulation potential. The results show that in Varano lagoon the highest concentrations were observed only at sites V1 (close to the main channel), V11 (near ex Military base) and V14 and V15 (close to the urban and agricultural wastewater discharges). PAH inputs in these sites are most likely related to intensive traffic of boats (V1), accidental oil spillage (V11) and agricultural inputs and sewage outfall of the urban centre (V14 and V15). In Lesina, the sites showing a greater PAHs pollution were L6, L8 and L9, situated in the central part of the basin, affected by a very localisated source and L12, near the channel, where pollution is mainly affected by traffic of boats and agricultural drainage watercourses. It is significant to note that PAH pollution in L6 sediments was different from that in the other sediments of Lesina lagoon. In fact, L6 was the only site with a significant presence of 2–3-rings PAHs (Acy, Fl and Phe). In Orbetello, all sites were contaminated and only the site O6 (Eastern basin) showed a lower pollution compared to the other sites. The Western basin (sites O7–O14) is much more crossed by small and bigger boats just for fishing, tourism and seaweed collection than the Eastern basin and an accidental oil spillage occurred one year before the sampling in the Western basin, as result of the breakdown of a private petrol station located along the northern coastline. In Santa Giusta, the most of contaminated sites (SG7–SG12) are located near the town, where there are wastewater discharged coming from the urban centre. Generally, for all the lagoons studied, the results showed that PAHs with 4-rings were dominant in all the studied lagoons (means of 54% Lesina, 76% Varano, 50% Orbetello and 58% Santa Giusta), suggesting a prevalent pyrolytic and/or biogenic origin for the PAHs (Figure 2). In details, as it can be observed in Tables 3–6 and Figure 2, different sites of the lagoons were also dominated by different compounds, varying from LPAHs (Phe and Ant) to 5-rings PAHs. In particular, BaP and BaA, indicated as markers of intensive traffic [25,26], were frequently detected in sediment samples of the lagoons,

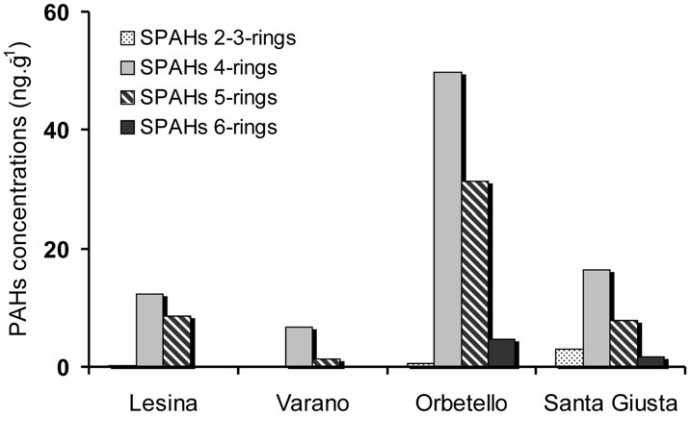

Figure 2. PAH group profiles (mean of 2–3-rings, 4-rings, 5-rings, 6-rings PAHs) from each lagoon.

characterised by intensive tourist and commercial activities (especially in summer, when the samplings were performed), suggesting a pyrolytic contamination related to the combustion particles emission of both pleasure and commercial ships. Such a wide range of PAHs at different sites indicates that there are potentially many different sources of PAHs in the same area, including combustion, followed by atmospheric fallout, oil residues, sewage outfalls and industrial wastewaters. The total contamination levels observed for the four studied systems appeared however lower than those recorded in other Italian lagoons heavily impacted by industrial activities and/or used for aquaculture and fishing exploitations, as Venice lagoon (54000–160000 ng g^{-1} d.w. [27], 20–570 ng g^{-1} d.w. [28]), Pialassa Baiona near the Ravenna harbour (300–87000 ng g^{-1} d.w. [29]), and Stagnone coastal lagoon of Marsala (72–18381 ng g^{-1} d.w. [30]). Moreover, these findings were significantly lower than those found previously from surface sediments from the French and Spanish coasts (1–8000 ng g^{-1} d.w. [2]), from Cotonou-Benin and Aquitaine Region-France (25–1205 ng g^{-1} d.w. and 3.5–853 ng g^{-1} d.w. [7]), from northern Adriatic Sea (250–6500 ng g^{-1} d.w. [9]), from northern Sardinia (70–1210 ng g^{-1} d.w. [12]; 160–770 ng g^{-1} d.w. [31]), from Ionian Sea (380–12750 ng g^{-1} d.w. [32]), from Naples (9–31774 ng g^{-1} d.w. [33]), from Gulf of Rijeka-Croatia (213–695 ng g^{-1} d.w. [34]), from Tunisia (113.2–10720 ng g^{-1} d.w. [35]), from Gulf of Fos area, France (2500–70000 ng g^{-1} d.w. [36]).

3.2 *Sources of contamination*

The use of PAH ratios provides information about PAHs anthropogenic sources, despite the variety of processes contributing to the distribution of these contaminants in the environment. LPAHs/HPAHs was the first ratio calculated in sediment samples. The higher this ratio, the higher the prevalence of petrogenesis [12,31]. All ratios calculated were much lower than 1, suggesting pyrolytic origin of PAHs, except for O6 (0.60) and SG7 (1.74) where PAHs contamination could arise from a petrogenic source (Figure 3).

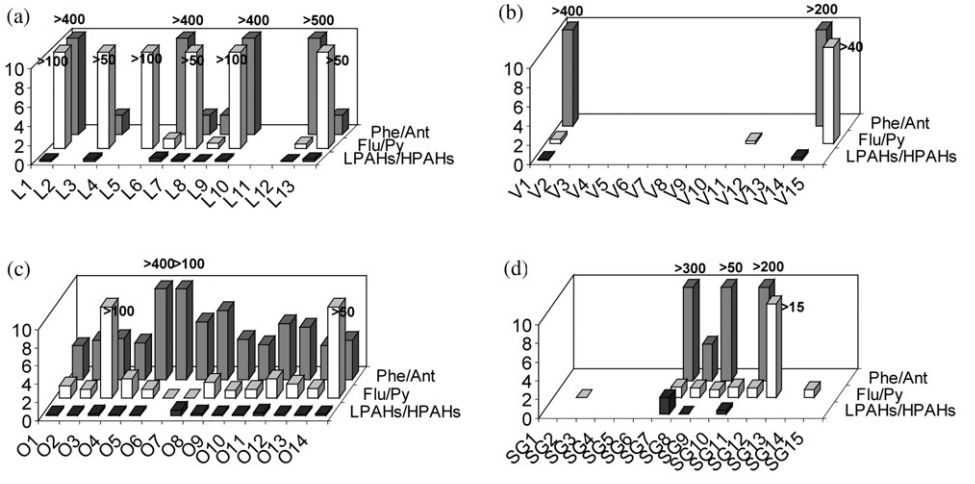

Figure 3. LPAHs/HPAHs, Phe/Ant and Flu/Py ratios for PAHs in the sediments of (a) Lesina, (b) Varano, (c) Orbetello and (d) Santa Giusta. LPAHs/HPAHs = NaP + AceP + A + Fl + Phe + Ant/Flu + Py + Chry + BaA + B[b + k]F + BaP + DBA + BghiPer + Ip.

The comparison between the mean value and each LPAHs/HPAHs performed for each lagoon suggests that more than half of the sites in Lesina (less polluted) and Orbetello (more polluted) were characterised by a clear pyrolytic origin, while the remaining areas exhibited a less clear origin of PAHs contamination. The use of other important ratios (Phe/Ant and Flu/Py) allows one to better specify the PAHs genesis in sites which do not exhibit a clear origin of contamination. Phe and Ant are both structural isomers and the first compound is more thermodynamically stable than the second one. Hence petroleum contains more Phe relative to Ant. Therefore, the PAHs of petrogenic input are generally characterised by Phe/Ant values higher than 15 [7,9,12,31,32,37]. A significant presence of Phe and concentrations of Ant often below the quantification limit (except for Orbetello) suggest a general petrogenic contribution to PAHs. In fact, values of Phe/Ant ratio much higher than 15 in sediments of sites L1, L6, L9 and L12, V1 and V14, O5 and O6, SG7, SG9 and SG11 indicate a slow maturation of petroleum at lower temperatures than pyrolysis of organic matter (Figure 3). Moreover, the absence of 6-rings PAHs (IP) in all the sites, except in SG7 and SG11, confirms a general petrogenic genesis [12,15]. Additionally, a previous study [38] reported that a small value of Phe/Ant (about 4) indicates an urban influence. Values ranged from 3 to 5 were observed in Orbetello for sites O1, O2, O9, O10, O13 and O14, which is consistent with nearby urban centre. In the same way, Flu/Py ratios <1 are generally considerated indicative of a dominance of petrogenic over pyrolytic sources [7,29,30,32]. An estimation of the Flu/Py ratio in the sediments confirm the dominant petrogenic origin of PAHs in the previous sites and contamination by PAHs due to combustion processes for the remaining sites. A good agreement between Phe/Ant and Flu/Py results was observed in Orbetello, defining a predominance of pyrolytic over petrogenic genesis for the most of sites (especially in the Western basin).

In order to clearly define the PAHs genesis, Phe/Ant ratio against Flu/Py ratio for each lagoon was plotted (Figure 4). Except for some sites and for the entire Varano lagoon, where the ratios cannot indicate the pollution origin for values below quantification limits, the results demonstrated that the PAHs had a dominance of petrogenic genesis in the sites L8 (Lesina). In Orbetello, the sediments of the sites O2, O9 and O10 (Orbetello) were mainly affected by petrogenic PAHs, while the pyrolytic origin was evident in sediments

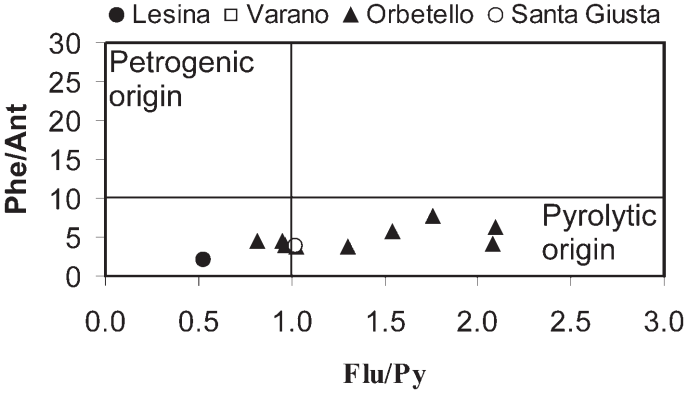

Figure 4. Plot of Phe/Ant ratios against Flu/Py ratios.

Table 7. Correlation matrix for Lesina and Varano lagoons (significant correlations at $p < 0.01$ are in bold face).

Lesina	A	Fl	Phe	An	Flu	Py	Chry	BaA	BbF	BkF	BaP	DBA	BghiP	ΣPAHs	Phe/Ant	Flu/Py
Acy		**1.00**	0.3	−0.19	0.05	0.06	−0.22	−0.06	**0.73**	−0.21	−0.28	−0.08	0.62	0.14	0.37	−0.24
Fl			0.3	−0.19	0.05	0.06	−0.22	−0.06	**0.73**	−0.21	−0.28	−0.08	0.62	0.14	0.37	−0.24
Phe				0.09	**0.77**	0.48	0.29	**0.70**	**0.77**	0.57	**0.82**	0.11	0.29	**0.84**	**0.85**	0.32
Ant					−0.07	−0.06	−0.14	0.24	−0.24	0.33	0.25	0.55	0.42	0.2	−0.44	0
Flu						**0.7**	0.57	**0.73**	0.63	0.5	0.68	0.03	0.03	**0.85**	**0.73**	0.4
Py							0.24	**0.72**	0.58	0.35	0.31	0.2	0.11	**0.79**	0.46	−0.35
Chry								0.28	0.12	0.26	0.4	0	−0.20	0.43	0.34	0.49
BaA									0.48	**0.83**	0.66	0.17	0.11	**0.83**	0.5	0.05
BbF										0.24	0.3	0.01	0.51	**0.71**	**0.82**	−0.09
BkF											**0.69**	0.32	0.16	0.66	0.34	0.23
BaP												0.18	−0.05	**0.69**	0.61	0.53
DBA													0.55	0.41	−0.9	−0.24
BghiP														0.38	0.04	−0.27
ΣPAHs															0.65	0.06
Phe/Ant																0.29
Varano																
Phe				**0.68**		0.46	0.51	**0.70**		**0.89**	**0.81**			**0.70**	**1.00**	−0.09
Flu					**0.90**	**0.84**	**0.94**			**0.80**	0.46			**0.96**	**0.68**	0.16
Py						**0.88**	**0.82**			0.55	0.30			**0.94**	0.46	−0.10
Chry							**0.74**			**0.62**	**0.60**			**0.92**	0.51	−0.13
BaA										**0.68**	0.51			**0.92**	**0.70**	0.31
BkF											**0.67**			**0.74**	**0.89**	−0.07
BaP														**0.58**	**0.81**	−0.13
ΣPAHs															**0.70**	−0.03
Phe/Ant																−0.10

Table 8. Correlation matrix for Orbetello and Santa Giusta lagoons (significant correlations at $p < 0.01$ are in bold face).

Orbetello	Phe	An	Flu	Py	Chry	BaA	BbF	BkF	BaP	BghiP	Ip	ΣPAHs	Phe/Ant	Flu/Py
Phe		**0.94**	**0.79**	**0.70**	**0.91**	**0.85**	**0.88**	**0.89**	**0.82**	**0.72**	**0.80**	**0.95**	−0.41	−0.21
Ant			**0.82**	**0.78**	**0.95**	**0.82**	**0.81**	**0.96**	**0.93**	**0.7**	**0.76**	**0.97**	−0.49	−0.15
Flu				**0.90**	**0.77**	**0.68**	**0.78**	**0.75**	**0.76**	0.49	0.42	**0.87**	−0.39	−0.35
Py					**0.78**	**0.63**	**0.65**	**0.72**	**0.73**	0.49	0.32	**0.84**	−0.24	−0.47
Chry						**0.83**	**0.79**	**0.96**	**0.94**	0.65	**0.73**	**0.96**	−0.33	−0.12
BaA							**0.83**	**0.86**	**0.78**	0.49	**0.76**	**0.86**	−0.31	−0.15
BbF								**0.9**	**0.79**	**0.74**	**0.66**	**0.94**	−0.28	−0.19
BkF									**0.97**	0.59	**0.83**	**0.95**	−0.30	−0.13
BaP										0.59	**0.75**	**0.92**	−0.29	−0.05
BghiP											0.56	**0.72**	−0.24	0.02
IP												**0.74**	−0.26	−0.02
ΣΠAHσ													−0.34	−0.23
Phe/Ant														−0.15
Santa Giusta														
Phe		**0.99**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**0l99**	**1.00**	**1.00**	0l01	−0.04
Ant			**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**0,98**	**0l99**	**1.00**	−0l11	−0.03
Flu				**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	−0l02	−0.03
Py					**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	−0.03	−0.04
Chry						**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	**1.00**	−0.03	−0.04
BaA							**1.00**	**1.00**	**1.00**	**0.99**	**1.00**	**1.00**	−0.02	−0.03
BbF								**1.00**	**1.00**	**0.99**	**1.00**	**1.00**	−0.07	−0.04
BkF									**1.00**	**0.99**	**1.00**	**1.00**	−0.03	−0.04
BaP										**1.00**	**1.00**	**1.00**	−0.02	−0.04
BghiP											**1.00**	**1.00**	0.02	−0.05
IP												**1.00**	−0.02	−0.04
ΣPAHs													−0.02	−0.04
Phe/Ant														−0.05

at the sites O1, O4, O8, O11 and O12. For the sites O13 (Orbetello) and SG8 (Santa Giusta) a slight dominance of petrogenic compared to pyrolytic origin was observed.

3.3 *Similarity within and among lagoons*

Correlation factors, obtained in each lagoon, are summarised in Tables 7 and 8. A preliminary remark was that in Lesina and Varano lagoons no correlation was observed among low-molecular-weight PAHs, while good correlations were observed between 4- and 5-rings PAHs and between high-molecular-weight hydrocarbons and ΣPAHs. Good correlations were observed between the two isomers Flu and Py for both the lagoons. On the other hand, for Orbetello and Santa Giusta basins, significant correlations were observed between low and high-molecular weight PAHs. Applying PCA analysis, two principal components (PC1 41.1% and PC2 22.1%) were obtained for Lesina lagoon, accounting for 63.2% of the total variance. In Figure 5a the loading plot is reported, showing that PC1 is mainly related to Phe and HPAHs (Flu, BaA, BbF and BaP),

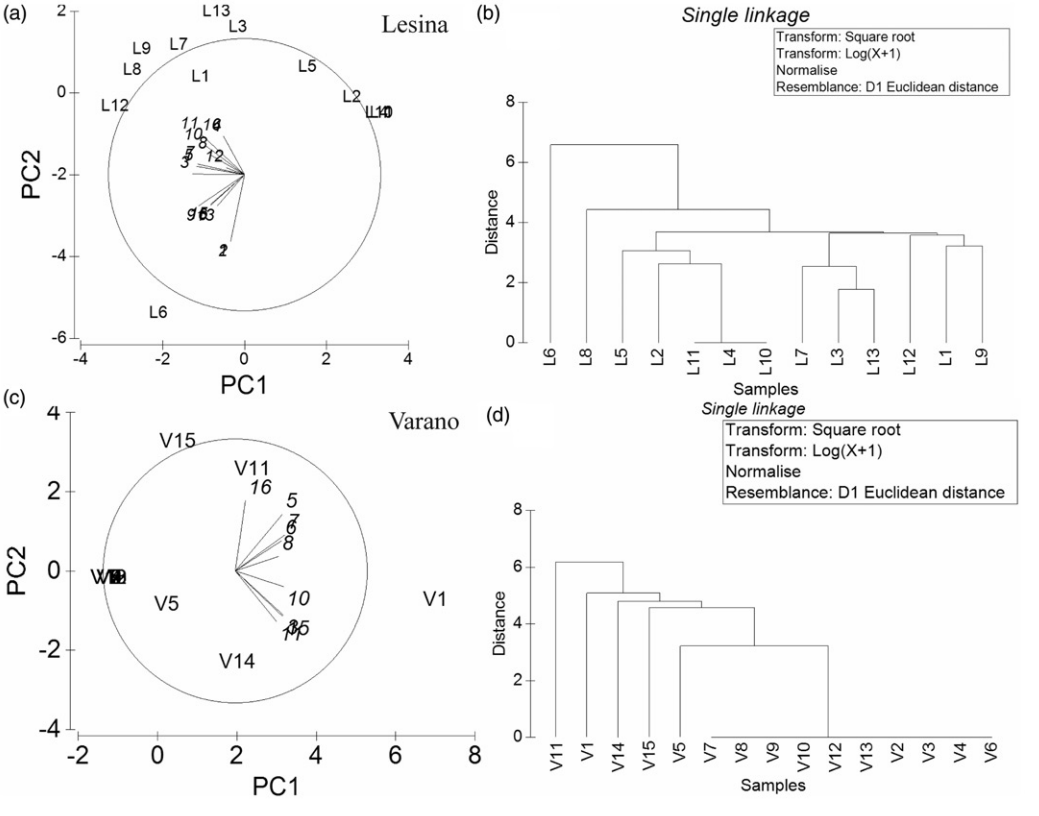

Figure 5. PCA ordination diagram of polycyclic aromatic hydrocarbons distribution in sediments of: (a) Lesina, PC1 and PC2 accounted for 63.2% of the total variance; (c) Varano, PC1 and PC2 accounted for 78% of the total variance. Similarity dendrograms for sampling sites obtained for (b) Lesina and (d) Varano systems; lower linkage distances mean higher similarities.

while PC2 is mainly related to LPAHs (Acy, Fl and Ant). These results highlight that PC1 and PC2 contains pyrolytic and petrogenic informations, respectively. The segregation of sampling sites was reported by cluster analysis (Figure 5b). The sites are grouped according to their pollution level and PAHs composition (LPAHs and HPAHs). For Varano lagoon, PC1 and PC2 accounted for 58.9% and 19.1% of the total variance. PC1 shows similar effects (good positive correlations) with both Phe and HPAHs, while PC2 shows opposite effects for Phe and some HPAHs (Flu and BaA) (Figure 5c). Sediment samples from uncontaminated sites were grouped in only one cluster (Figure 5d), while V1 and V11 were characterised by similar 4-rings PAHs composition. Regarding Orbetello lagoon, the first two components accounted for 74.6% of the total variance (PC1 60.2% and PC2 14.4%). PC1 did not discriminate between LPAHs and HPAHs, while PC2 had significant negative loadings with Py (Figure 6a). Except for O3 and O14, well differentiated by the higher scores on PC2, the remaining samples are spread along PC1. The classification of sediments in Orbetello, following PCA and cluster analysis (Figure 6b), was not clear such as that obtained by the evaluation of ratios. For Santa Giusta, PC1 accounted for 79.1% and PC2 for 9.5%. These data suggested that variables correlated with the first axe had a great significance in explaining system variability in

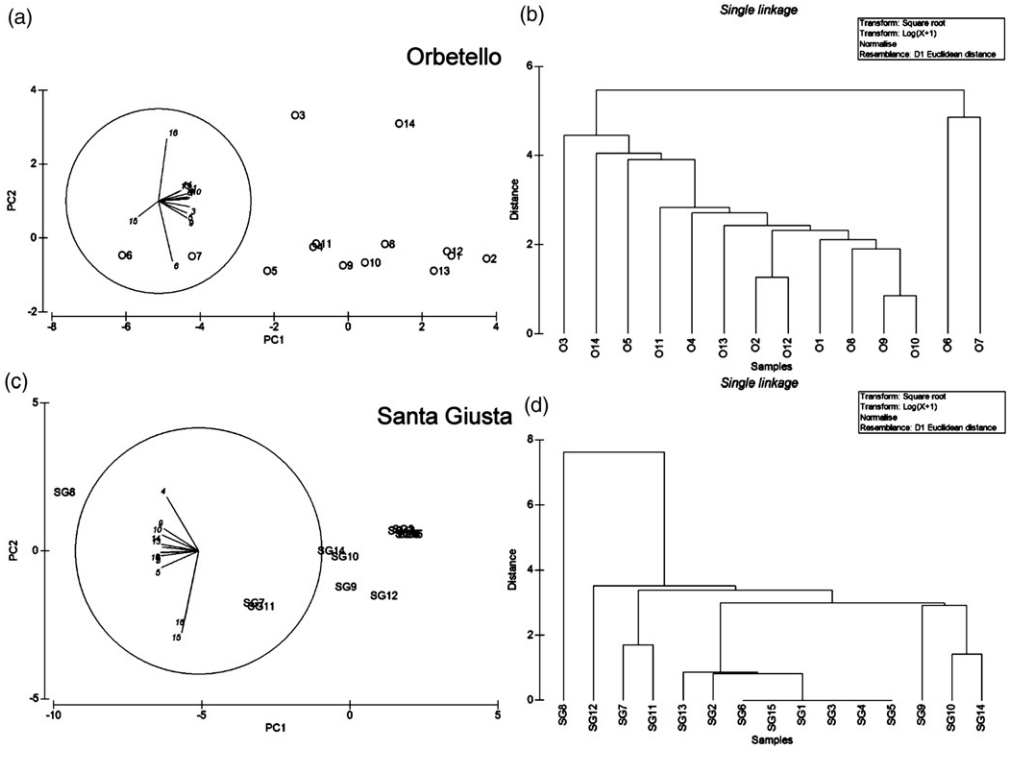

Figure 6. PCA ordination diagram of polycyclic aromatic hydrocarbons distribution in sediments: (a) Orbetello, PC1 and PC2 accounted for 74.6% of the total variance; (c) Santa Giusta, PC1 and PC2 accounted for 88.6% of the total variance. Similarity dendrograms for sampling sites obtained for (b) Orbetello and (d) Santa Giusta systems; lower linkage distances mean higher similarities.

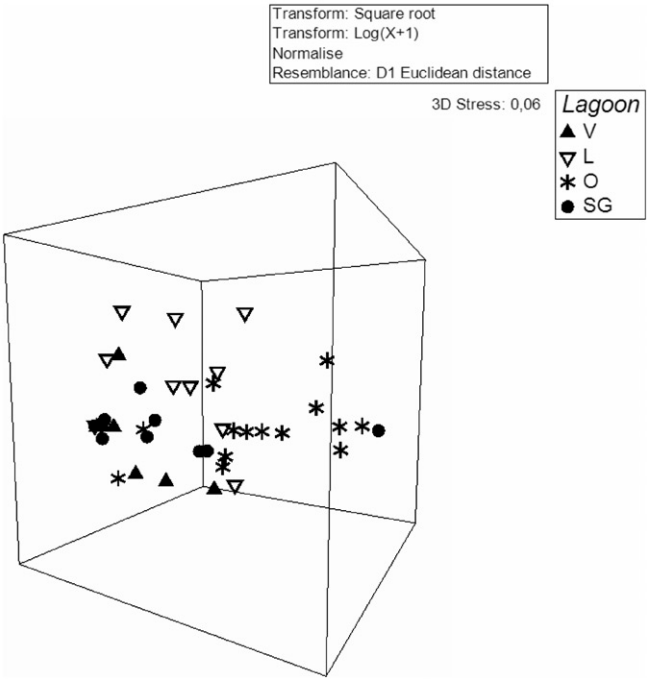

Figure 7. Non-metric Multi-Dimensional-Scaling (nmMDS) (3D projection with minimum stress of 0.06) applied to the entire transformed and normalised data set.

sediments descriptors (Figure 6c). PC1 showed similar effects for both LPAHs and HPAHs, while PC2 showed opposite effects for 2–3-rings PAHs (Ant) and Phe/Ant and Flu/Py ratios. The dendrogram obtained by cluster analysis (Figure 6d) highlighted a group of uncontaminated sites (SG6, SG15, SG1, SG3, SG4, SG5, SG2 and SG13), except SG13 which showed low values of BkF, and a cluster (SG10 and SG14) characterised by a total absence of 2–3-rings PAHs. The site SG8 was well differentiated by the other sites for its pyrolytic contamination.

In order to explore pollution-related dissimilarities among the studied lagoons, non-metric Multi-Dimensional-Scaling (*nm*MDS) was applied. The clear difference among the lagoons is shown in Figure 7. The plot showed up well the different contaminants pattern between Lesina (at the top of diagram), Orbetello (heterogeneous system on the right side), Varano and Santa Giusta (on the left side of the plot). These observed differences among the lagoons were explored and confirmed by the application of the ANOSIM test which produced a global R value of 0.309 ($P = 0.0001\%$).

4. Conclusions

There has never been a comprehensive study of PAHs contamination in sediments of Lesina, Varano, Orbetello and Santa Giusta lagoons. Different anthropogenic influence on these environments (industrial, urban and aquaculture waste, agricultural run-off, traffic of boats and other human activities) was expected. This study represents the first

detailed investigation of the distribution and sources of PAHs in sediment samples collected from these Italian lagoons. The results obtained in this study showed that concentrations of total PAHs in surface sediments varied significantly among lagoons and sampling sites, but they are shown to be substantially lower than those obtained in other urbanised and/or industrial Mediterranean areas, also exploited for aquaculture. Orbetello and Santa Giusta showed a greater pollution compared to Lesina and Varano, linked to the greater industrialisation and urbanisation of the catchment area. A greater presence of PAHs with high-molecular-weight and the ratio values used to define PAHs source demonstrated that most samples were characterised by a predominant single origin, anthropogenic combustion or pyrolytic genesis. Main sources were urban wastewaters and boats' exhausts of high-molecular-weight PAHs (4–5-rings) in all the sediment samples. Nevertheless, multiple sources were observed within each lagoon, linked to the different environmental inputs. Multivariate analysis clearly separated the sites on the basis of their different influence. It was shown that pollution coming from the traffic of boats was widely distributed over the lagoons (except for Varano), while domestic wastewaters prevailed close to the urban centres. It seemed that there was no influence due to the aquaculture farming.

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