Composition, Distribution, and Sources of Polycyclic Aromatic Hydrocarbons in Sediments of the Gulf of Milazzo (Mediterranean Sea, Italy)

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This article describes the characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of Milazzo Gulf (Italy) located in front of an oil refinery and a power plant. The investigated area is characterized by urban and industrial activities. The sixteen PAHs identified by the USEPA, as requiring priority monitoring, and other non USEPA listed PAHs, namely perylene and some methyl derivatives, were investigated The total PAHs concentrations, expressed as $\sum$ 19 PAH ranges from 5.6–7402 μg/Kg d.w., with a mean value of 492 μg/Kg d.w. The concentrations of PAHs found in 64 out of 67 samples were lower than the effect range low (ERL = 2460 μg/Kg) concentration, while the remaining samples were in the range between ERL and effect range middle (ERM) concentrations. The mean values of all samples of the same stations were lower than the ERL. These findings indicated that the sediments from the entire sampling area should have no potential biological impact.

Key Words: Milazzo, PAHs, power plant, refinery, sediment

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), include aromatic molecules containing fused aromatic rings, are of special concern because of their widespread distribution in the environmental matrices and their toxic and carcinogenic properties (1–5). As a consequence of their hydrophobic nature, PAHs in aquatic environments rapidly tend to become associated with particulates. Sediments are composite materials consisting of inorganic components, mineral particulates and organic matter in various stages of decomposition (6). Sediments represent the most important reservoir of PAHs in the marine environment. Sedimentary PAHs are a source of exposure of hazardous compounds (7) directly to benthic organisms and indirectly (i.e., via resuspension) to pelagic organisms (8). Some PAHs are persistent, toxic and bioaccumulates in aquatic organisms. Fishes and higher organisms in the food chain tend to metabolise and excrete PAHs relatively rapidly. However, PAHs can influence the development of liver tumors in several fish species and may adversely affect the reproductive process in fish and other aquatic species. Several studies have found the correlation between cancer development in marine animals and distance from oil spills (8,9).

Therefore, many studies have examined PAHs levels in coastal and oceanic sediments (10,11). The PAHs distribution in waters and sediments of the Mediterranean Sea has been the subject of several studies (12–19). However, no comprehensive surveys of PAHs in coastal environments have been performed in Southern Italy. Thus, in this article, the distribution of sedimentary PAHs around the Sicilian coast, especially the Gulf and the harbor of Milazzo, has been studied.

Sicily benefits from the coast through extensive economic and industrial activities, including shipping, oil refining, fishery, coastal aquaculture, and tourism. Wastes associated with such anthropogenic activities could increase the inputs of contaminants, including PAHs.

The identification of PAHs sources is essential to the regulation of their inputs to marine environments because there are various potential sources. In general, the two main sources of PAHs in the environment are fossil fuels and the incomplete combustion of organic materials such as wood, coal and oil. Moreover, PAHs can enter the sea by both atmospheric and aquatic routes. In addition to the domestic and industrial combustion processes in use today, the other main inputs of PAHs include coal-tar containing coating systems, offshore activities, oil spills and shipping exhausts (20). Under anaerobic conditions, some PAHs can be derived from biogenic precursors such as pigments and steroids (21–24). PAHs formed by natural processes (such as forest fires and volcanic eruptions) include perylene, retene, and phenanthrene homologs. Background levels of PAHs in the marine environment are a result of biosynthesis and natural oil seeps. Anthropogenic activities are generally recognized

to be the most important source of PAH release into the environment. Background values for PAHs in sediments appear to be within the large range of concentrations. The highest levels of PAHs in sediments typically occur in river mouths, estuaries, and bays, as well as in areas of regular shipping, oil production, and transportation.

Many studies have been carried out to explain the possible origins of PAHs in marine sediments. They indicated that sedimentary PAHs are derived mainly from pyrogenic sources (10,15,23,24) although some reports indicate accumulation of petrogenic PAHs in coastal sediments (25,26).

The evaluation of PAHs in sediments from circumscribed sites (harbors, lagoons, and closed bays) is a quite complex task due to the potential complexity and variability of anthropogenic contributions coupled with reduced water circulation. These sites could receive effluents from water streams, industrial and urban sewage systems, agricultural runoff, etc. The limited water exchange with the open sea is often responsible for localised pollution. In addition, the intense traffic of motorboats and oil tankers could contribute to the pollution load of the area.

The goal of this study was to determine the distribution of PAHs in the superficial sediments of the Milazzo Gulf (Italy), to establish whether the compounds are of biogenic or anthropogenic derivation. The 16 PAHs identified by the USEPA, as requiring priority monitoring, and other non USEPA (27), were investigated in this study. Moreover, considering that perylene in sediments is usually considered a marker of the terrestrial origin of organic matter (10,11,28), other non USEPA-listed PAHs, namely perylene and some methyl derivatives, were also investigated in order to obtain further information's on their origins. Together with PAHs, we analyzed water and organic contents because it has been demonstrated that the concentrations of PAHs in sediments were affected by these parameters (29). Generally, sediments with high water content (40% = muddy) were characterized by high values of PAHs, while sandy (about 20% water) sediments with low PAHs content (30). Sediments with high organic content were characterised by high values of PAHs (31). Relationships between PAH concentration and distribution, which are useful for evaluating possible sources of contamination, were defined by comparing the profiles of 19 PAH compounds recovered from sediments.

STUDY SITE

The investigated area (Figure 1) is one of the most important harbor in Sicily in terms of passenger and goods (mainly hydrocarbons and petrochemical products) traffic. An oil refinery and a power plant are located nearby (a few hundred meters from the shoreline). In the 1960s, the oil refinery was the most important petrochemical plant in the Mediterranean basin and nowadays

Figure 1: Locations of 19 sampling sites in the area of Milazzo (Mediterranean Sea).

processes the oil coming from the Mediterranean area and the Middle East and export the refined product.

SAMPLE COLLECTION AND PREPARATION

Sediments were collected at, during four monitoring phases in the period spring 2004–autumn 2005 from 19 stations selected in the Milazzo harbor and Gulf (Figure 1). A global positioning system (GPS) was employed to identify the exact location of each site (Table 1). Figure 1 shows the location of the sampling sites. Sediments were collected through a steel gravity grab (dredge) ($0.50{\times}0.50$ m). A total of 1 Kg surface sediment was sub-sampled from triplicate grab samples from each site and mixed thoroughly after removing any pebbles and twigs. The samples were immediately refrigerated ($4°C$) on site, stored avoiding exposure to light, and then rapidly transported to the laboratory where they were frozen at $-20°C$ prior to analysis. Sub-samples of ca. 10 g sediments were used to analyze total organic matter and water content. Each sample was identified by two numbers (for example, 10-1) the first one indicates the geographical position and the second the sampling period (1 = November 2004; 2 = April 2005; 3 = July 2005; and 4 = November 2005)

Table 1: Characteristics and coordinates of sampling sites

Station n°	Dept m	Characteristics	Coordinates	
			N	W
1	*9.1*	*Gray-green* (Harbor activities)	**38°12′.875″**	**15°14′.983″**
2	*9.6*	*Gray-green* (Harbor activities)	**38°12′.989″**	**15°14′.861″**
3	*9.0*	*Brown* (Harbor activities)	**38°13′.061″**	**15°14′.694″**
4	*9.1*	*Brown* (Harbor activities)	**38°13′.096″**	**15°14′.588″**
5	*9.0*	*Gray* (Harbor activities)	**38°13′.057″**	**15°14′.554″**
6	*8.3*	*Brown – Anossic* (Harbor activities)	**38°13′.001″**	**15°14′.613″**
7	*9.3*	*Brown* (Harbor activities)	**38°13′.019″**	**15°14′.712″**
8	*6.9*	*Brown* (Harbor activities)	**38°12′.915″**	**15°14′.772″**
9	*32.3*	*Brown* (Fishing activities)	**38°12′.757″**	**15°15′.340″**
10	*8.0*	*Brown (Oil refinery area)*	**38°12′.602″**	**15°15′.607″**
11	*27.3*	*Brown (Oil refinery area)*	**38°12′.753″**	**15°15′.630″**
12	*30.0*	*Gray (Oil refinery area)*	**38°12′.745″**	**15°15′.813″**
13	*46.3*	*Gray-green (Berthing docks of oil tankers)*	**38°12′.780″**	**15°15′.743″**
14	*25.0*	*Grigio* (Berthing docks of oil tankers)	**38°12′.699″**	**15°16′.125″**
15	*7.18*	*Grigio (Power plant area)*	**38°12′.529″**	**15°17′.084″**
16	*31.8*	*Brown (Power plant area)*	**38°12′.678″**	**15°17′.200″**
17	*53.8*	*Brown (Power plant area)*	**38°12′.852″**	**15°17′.347″**
18	*55.0*	*Gray-green (Fishing activities)*	**38°13′.584″**	**15°14′.719″**
19	*33.0*	*Gray (Fishing activities)*	**38°14′.395″**	**15°15′.074″**

CHEMICALS

All chemicals used were of analytical grade with high purity. In particular, n-pentane and dichloromethane, from Fluka, were 99.8% pure. Acetone (Envisolv for analysis of dioxins, furans and PCB) from Fluka was 99.8% pure. HCl suprapur for trace analysis from Fluka, Standard PAH mixtures (EPA 610 PAH mix, lot LA-96245) and perdeuterated internal standards (fortification solution B Lot N8 LA-92479) were from Supelco.

SAMPLE TREATMENT

After 10 min centrifugation (4000 rpm), overlying water was pipetted off and 5 g, exactly weighted, of sediment were treated with precleaned (Soxhlet extracted with dichloromethane for 24 h) anhydrous Na_2SO_4 (Fluka) to removal residual moisture. Activated copper (200 mg) was added to the sample to remove elemental sulphur. The copper (Aldrich 40 mesh, 99.5% purity) was activated with HCl 1M and then washed with water, acetone and CH_2Cl_2.

EXTRACTION OF PAHS

The PAH extraction was carried out as reported in literature (14,16,17). In particular all samples were extracted in a Soxhlet extractor for 24 h using a dichloromethane-pentane 1:1 solvent mixture (Carlo Erba, Milano, Italy). The extracts were filtered through a pre-cleaned Pasteur pipette filled with solvent-rinsed glass wool and pre-cleaned anhydrous Na_2SO_4, previously rinsed with dichloromethane and concentrated in a rotary evaporator with thermostatic bath at T $= 35 \pm 0.5°$C. The final volume was around 2 mL. The last stage in the procedure involved drying the solution containing PAHs under a weak nitrogen flow at room temperature. The dry residue was dissolved in 1 ml solution containing the following perdeuterated internal standards in cyclohexane (0.2 mg/L each): acenaphthene d_{10}; phenanthrene d_{10}, chrysene d_{12}, and perylene d_{12}.

PAH recoveries were in good agreement with literature data (32).

PAH ANALYSIS

Analysis of marine sediment extracts was made using a gas chromatograph (Shimadzu mod.GC-17A) coupled with a mass spectrometer (Shimadzu, quadrupole detector mod. GCMS-QP5000) equipped with an acquisition data system (Shimadzu, CLASS 5000). The GC was equipped with a Equity-5 (30 m $\times$ 0.25 0.25 mm film thickness) fused-silica capillary column from Supelco (Milano, Italy). The injector mode was splitless (0.61 min) and a total flow of 20.6 mL/min was used. The injection of both extracts from samples and standard solutions was performed by hand.

The injector temperature was maintained at 280°C. The GC temperature program was from: 40°C (2 min) to 100°C at 40 °C/min; 200°C at 10°C/min; and 325°C (8 min) at 30 °C/min. The carrier gas was helium (flow rate 2.6 mL/min) and the interface temperature was 325°C.

A multiple selected ion monitoring (MS/SIM) method was capable of monitoring up to 12 ions (primary and confirming ions) in each of three retention time windows including selected ions of the internal standards (Table 2). Response factors and retention times were determined in relation with four deuterated internal standards (acenaphtene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10}, and perylene-d_{12}) and a standard PAHs test mixture.

Identification of the components of the standard mixture was carried out by comparing retention times for each component in the mixture with those of pure components analyzed under the same experimental conditions. Identification was confirmed by comparing the spectra of the single components with those stored in the acquisition system library. The identification of PAHs in the solutions extracted from sediment was carried out on the basis of previously determined retention times and confirmed using mass spectra.

Table 2: List of groups of PAHs formed for analysis, the deuterated standards employed (underlined), the quantification ion, and confirmation ion for SIM GC-MS mode

Group	Chemical	Quantification ion	Confirmation ions
1	Acenaphthylene	152	76, 151
	Acenaphthene	154	152, 76
	Fluorene	166	164, 165
	Acenaphthene d$_{10}$	164	
	Phenanthrene	178	188, 89
	Anthracene	178	188, 89
	2 methyl anthracene	192	96, 82
2	9 methyl anthracene	192	96, 82
	Fluoranthene	202	101, 200
	Pyrene	202	101, 200
	1 methyl pyrene	216	108, 94
	Benzo(*a*)anthracene	228	114, 226
	Phenanthrene d$_{10}$	188	
	Chrysene	228	114, 226
	Benzo(b)fluoranthene	252	126, 250
	Benzo(k)fluoranthene	252	126, 250
3	Benzo(a)pyrene	252	126, 250
	Chrysene d$_{12}$	240	
	Perylene	252	126, 250
4	Indeno(*1,2,3-cd*)pyrene	276	277, 138
	Dibenzo(*a,h*)anthracene	278	279, 139
	Benzo (*g,h,i*)perylene	276	138, 124
	Perylene d$_{12}$	264	

The PAHs content in the sample was quantified with respect to the perdeuterated PAHs added to the dry residue. The response factors for different compounds were measured by injecting a mixture containing standard compounds and having the same concentration of perdeuterated PAHs as that used for spiking the sample. The most abundant ion was used for quantification and two other ions were additionally used for confirmation. The list of PAHs grouped together for concentration analysis, the deuterated standards employed, the quantification ion, and the confirmation ion for each PAH are shown in Table 2.

Method detection limits (MDL) were statistically estimated. MDL values for PAHs compounds varied between 0.06 and 3.5 μg/Kg d.w. The standard deviations calculated from the results of four analysis on the same sample varied from 4.7% for fluorene to 20% for dibenzo(*a,h*)anthracene (Table 3).

WATER CONTENT ANALYSIS

About 2 g of sediment, previously centrifuged at 4000 rpm for 10 min, was dried at T = 105°C for one night. The water content was determined by weight loss and was utilized to correlate all the results with dry weight.

Table 3: Results of analysis of individual total PAHs (μg/Kg d.w), water (%), and organic matter (%) content

	1-1	1-2	1-3	1-4	2-1	2-2	3-1	3-2	3-3	3-4	4-1	4-2	4-3	4-4	5-1	5-2	5-3	5-4	6-1	6-2	6-3a	6-3b	6-3c	6-4
Acenaphthylene	0.05	0.05	1.0	0.69	0.05	0.05	0.54	1.3	1.2	8.4	0.71	0.04	1.0	0.59	0.05	0.05	0.36	3.59	1.1	0.05	1.6	1.9	2.4	0.56
Acenaphthene	0.99	0.10	1.0	1.0	1.1	0.21	0.82	3.7	1.5	21	0.53	0.16	0.48	1.3	0.31	0.10	0.52	10	66	2.5	0.70	0.75	11	3.4
Fluorene	0.80	1.9	4.6	1.0	2.9	0.30	1.0	5.1	2.3	12	0.58	0.35	1.4	1.1	1.0	14	0.72	6.8	69	8.5	2.2	1.3	10	2.6
Phenanthrene	4.3	9.3	8.2	2.83	21	2.8	4.8	38	39	81	3.1	3.5	4.4	5.8	8.3	3.43	2.8	33	1160	29	23	14	66	16
Anthracene	1.0	0.90	0.91	0.44	0.67	0.30	1.6	10	7.5	18	0.81	0.43	0.60	0.92	0.58	1.07	0.18	5.9	254	2.6	2.4	2.5	16	4.5
2 methyl anthracene	0.09	0.65	0.47	0.18	4.3	0.08	1.6	1.9	2.1	4.0	0.19	0.08	0.80	0.36	0.09	0.20	0.09	1.5	29	0.09	1.7	1.5	7.4	1.7
9 methyl anthracene	0.05	1.0	0.49	0.08	0.05	0.05	0.05	0.05	0.05	0.85	0.05	0.05	0.55	0.18	0.05	0.92	0.05	0.27	4.1	0.05	0.05	0.05	0.05	0.18
Fluoranthene	11.9	5.6	8.5	3.0	9.3	3.69	15	67	115	165	5.5	2.5	7.1	8.9	13	1.1	4.5	66	1561	57	37	57	137	21
Pyrene	11	5.8	9.5	2.7	10	4.8	18	67	123	144	5.8	2.9	10	8.8	12	1.1	6.3	58	1360	64	44	70	136	19
1 methyl pyrene	0.25	0.66	0.69	0.18	4.9	0.50	1.6	5.4	3.0	3.2	0.39	0.31	1.3	0.48	0.85	1.31	0.27	2.3	35	5.4	4.2	3.7	9.6	0.83
Benz(a)anthracene	10	4.7	4.4	2.4	4.0	5.2	17	43	67	61	4.2	21	6.0	3.1	5.0	7.24	4.3	31	470	24	26	60	94	7.1
Chrysene	7.3	2.9	3.1	2.9	8.73	2.8	13	62	34	82	6.3	20	5.0	5.0	13	0.08	2.1	43	822	46	23	34	68	13
Benzo(b)fluoranthene	3.6	0.08	3.6	4.4	0.08	4.7	13	60	37	76	15.4	2.0	5.5	5.5	5.6	0.05	4.9	44	319	29	30	38	52	8.2
Benzo(k)fluoranthene	2.8	0.05	2.1	3.5	0.05	5.80	16	47	36	71	4.93	1.8	4.1	3.9	0.05	0.05	2.2	33	309	17	19	38	55	8.4
Benzo(a)pyrene	4.3	0.10	3.0	4.10	0.10	8.30	20	70	41	77	14	3.0	4.7	4.1	0.10	0.10	1.1	33	303	14	15	36	59	8.0
Perylene	0.10	0.10	0.39	0.15	14	1.01	0.89	2.9	1.3	2.3	0.31	1.3	0.28	0.23	5.0	0.10	0.30	0.98	14	1.5	2.3	1.4	1.5	0.49
Ind(1.2.3-cd)pyrene	1.10	0.94	3.1	3.1	0.12	0.83	9.3	26	17	43	1.4	2.0	2.90	2.7	5.0	0.08	0.66	1.3	188	14	5.9	14	20	5.2
Dibenz(a.h)anthracene	0.82	0.90	0.81	1.2	0.08	0.83	9.3	26	7.1	17	1.00	1.7	0.90	1.7	0.08	0.08	0.34	13	153	16	2.75	7.7	8.7	2.01
Benzo(g.h.i)perylene	0.08	0.08	1.5	4.9	0.38	2.6	13	25	24	61	0.08	4.3	3.7	4.7	0.08	0.08	1.1	37	285	9.8	14	22	31	7.7
Water	25	22	23	22	26	27	28	32	31	33	16	17	16	17	4.6	2.9	3.0	12	32	33	32	31	30	27
Organic matter	1.0	1.4	1.5	1.8	1.6	2.0	3.0	3.5	3.0	3.6	1.4	1.5	1.2	1.4	0.68	0.70	0.80	1.2	4.6	4.0	3.3	3.5	3.0	2.6

	7-1	7-2	8-1	8-2	8-3	8-4	9-1	9-2	9-3	9-4	10-1	10-2	10-3	10-4	11-1	11-2	11-3	11-4	12-2	12-3	12-4
Acenaphthylene	0.05	0.05	0.66	0.28	0.49	0.40	0.05	0.05	0.87	0.48	0.05	0.05	0.51	0.29	0.45	0.05	2.9	1.2	1.6	0.05	25
Acenaphthene	0.10	8.3	8.80	1.1	0.95	2.3	2.78	0.10	4.5	5.0	0.77	1.3	0.10	0.30	2.4	2.4	5.4	3.5	6.9	2.0	6.7
Fluorene	18	15	12	1.82	0.74	0.67	2.2	0.82	2.8	5.0	0.83	3.0	2.0	0.35	4.0	2.7	3.1	2.1	4.4	3.3	5.9
Phenanthrene	34	214	111	11	6.6	3.5	20	13	18	22	5.3	6.1	3.4	0.87	33	17	19	16	21	25	67
Anthracene	19	64	71	11	6.6	3.5	5.6	3.2	2.0	4.5	4.6	6.1	3.4	0.87	33	17	19	16	21	21	21
2 methyl anthracene	0.09	0.09	12	0.50	0.58	0.32	0.71	0.09	0.55	1.2	0.79	0.76	0.32	0.11	4.6	3.6	2.5	2.9	2.0	5.0	3.1
9 methyl anthracene	0.05	0.05	1.9	0.36	0.43	0.32	0.37	0.05	0.05	0.14	0.09	0.09	0.24	0.06	1.2	0.09	0.82	0.99	0.86	0.09	0.39
Fluoranthene	61	591	245	11	20	7.0	47	75	43	36	7.4	16	8.6	0.63	39	54	71	37	65	62	143
Pyrene	57	482	181	12	23	6.6	41	61	45	30	6.1	17	9.4	0.76	37	48	70	33	66	51	140
1 methyl pyrene	5.0	0.05	6.1	0.71	0.70	0.38	1.4	0.05	2.7	0.74	0.29	0.93	0.55	0.05	1.7	1.5	2.3	1.3	3.6	0.38	3.3
Benz(a)anthracene	41	273	137	6.6	13	2.4	27	64	27	19	7.6	16	16	0.41	24	70	68	21	73	19	48
Chrysene	42	194	132	13	11	5.8	40	20	27	22	7.1	11	4.9	0.76	33	30	30	32	23	38	40
Benzo(b)fluoranthene	29	117	64	9.7	11	4.4	24	0.08	26	13	0.08	0.51	8.3	0.67	20	53	36	30	36	43	21
Benzo(k)fluoranthene	22	114	71	10	14	4.1	21	0.08	19	11	0.05	0.40	9.3	0.62	18	48	46	27	37	18	21
Benzo(a)pyrene	0.10	145	72	12	6.6	4.5	19	0.10	18	12	0.10	0.10	8.2	0.52	16	65	36	27	33	13	27
Perylene	51	4.2	1.6	3.0	1.1	0.38	0.98	0.10	1.3	0.43	0.10	0.34	0.29	0.08	1.3	1.9	1.3	0.92	1.2	6.0	1.8
Ind(1.2.3-cd)pyrene	180	44	44	6.6	3.8	2.5	8.8	0.08	8.5	8.3	0.40	0.10	4.5	0.40	13	3.2	22	16	21	4.7	26
Dibenz(a.h)anthracene	256	0.08	19	8.8	0.98	1.6	4.2	0.08	5.0	4.1	0.33	0.08	2.4	0.09	10	1.1	11	8.8	11	9.8	12
Benzo(g.h.i)perylene	171	54	44	21	5.9	4.4	4.2	0.08	13	13	0.08	0.08	5.0	0.73	23	3.9	31	22	27	5.7	40
Water	32	29	40	31	28	32	25	23	27	25	24	16	19	20	33	31	34	33	34	30	35
Organic matter	2.5	3.2	5.0	3.5	1.8	2.6	3.5	1.7	1.9	1.5	1.2	1.1	1.0	1.1	1.3	3.0	3.2	3.1	3.5	2.9	3.6

Table 3: Results of analysis of individual total PAHs (μg/Kg d.w), water (%), and organic matter (%) content *(Continued)*

	13-1	13-3	14-3	14-4	15-1	15-2	15-3	15-4	16-1	16-2	16-3	16-4	17-1	17-3	17-4	18-1	18-3	18-4	19-1	19-2	19-3	19-4
Acenaphthylene	1.26	3.1	0.59	0.92	0.05	0.05	0.05	0.35	0.05	1.2	0.05	0.65	0.05	0.05	0.69	1.18	2.96	2.5	0.63	0.19	0.71	0.06
Acenaphthene	15	13	2.5	1.5	0.51	2.6	0.10	0.30	1.74	1.8	0.10	0.69	1.1	2.6	2.4	3.30	2.67	18	51	2.8	1.3	0.29
Fluorene	8.5	10	2.0	0.77	0.82	1.9	2.7	0.25	5.3	2.0	7.6	0.61	2.4	4.52	1.3	4.11	3.03	10.5	68	4.0	1.1	0.34
Phenanthrene	168	50	5.2	4.5	2.2	13	4.0	0.86	34	16	7.5	4.0	21	6.6	11	61	41	109	56	31	9.	1.7
Anthracene	66	8.2	0.32	0.68	0.29	0.86	0.77	0.19	5.3	2.8	1.0	0.74	1.9	1.2	2.6	8.3	5.1	22	209	2.5	0.98	0.36
2 methyl anthracene	8.2	4.2	0.33	0.23	0.09	0.09	0.78	0.06	0.67	0.09	0.43	0.26	0.92	0.51	0.76	1.8	7.5	7.2	24	0.85	0.26	0.13
9 methyl anthracene	1.6	2.1	0.05	0.05	0.05	0.05	1.2	0.05	0.08	0.08	1.2	0.13	0.08	0.92	0.19	0.83	0.08	0.93	3.5	0.19	0.08	0.08
Fluoranthene	443	103	11	9.4	1.4	26	9.0	0.66	21	36	15	6.5	24	17	20	181	152	241	712	34	27	1.3
Pyrene	405	115	12	8.53	1.4	21	9.0	0.62	23	34	17	5.6	22	18	17	157	164	203	552	28	32	1.1
1 methyl pyrene	8.7	6.3	0.63	0.38	0.21	0.30	0.99	0.05	2.0	1.7	1.5	0.33	1.2	1.0	0.52	2.6	8.0	5.70	11	0.72	2.4	0.06
Benz(a)anthracene	485	106	21	3.6	1.5	21	7.0	0.15	9.7	60	16	2.7	13	19	7.53	43	121	107	265	14	25	0.38
Chrysene	214	41	6.5	8.2	0.94	8.0	8.6	0.37	18	19	7.3	6.1	16	9.7	15	134	66	167	365	265	18	0.68
Benzo(b)fluoranthene	285	52	12	5.4	1.3	11	5.2	0.27	9.2	40	11	3.1	13	9.7	8.8	64	66	107	166	14	19	0.57
Benzo(k)fluoranthene	229	57	15	4.7	0.63	15	5.2	0.20	6.2	28	11	3.0	11	14	7.9	42	71	97	188	15	18	0.60
Benzo(a)pyrene	308	10	10	5.2	0.10	4.4	0.10	0.20	4.1	32	2.8	2.8	13	9.3	7.6	43	76	96	163	14	14	0.44
Perylene	4.8	1.7	0.82	0.24	0.08	0.44	1.42	0.08	11	1.1	8.6	0.29	3.3	0.55	0.35	4.0	1.70	3.32	5.77	4.48	0.66	0.08
Ind(1.2.3-cd)pyrene	56	26	6.1	3.6	0.10	0.10	3.02	0.10	0.10	3.4	0.75	2.5	22	5.3	5.5	20	35	62	54	17	5.1	0.48
Dibenz(a.h)anthracene	46	15	3.32	3.5	0.08	0.08	5.7	0.09	0.08	0.08	5.73	1.5	21	1.7	2.1	8.0	16	33	34	14	3.3	0.16
Benzo(ghi)perylene	45	36	9.6	4.4	0.08	0.08	2.0	0.53	0.08	3.3	6.7	4.6	26	6.5	7.0	24	56	82	54	28	10	0.67
Water	31	33	29	26	19	18	19	20	34	31	33	27	33	34	32	33	35	36	33	37	35	24
Organic matter	4.4	3.7	1.8	2.0	0.71	1.2	0.80	0.82	3.5	3.0	3.4	1.8	5.7	4.5	4.2	4.8	4.8	6.4	5.1	5.1	4.5	2.0

*The accuracy (yield on the certificate material) for the different PAHs ranged from 82 to 106%.Reproducibility of analyses was tested by four replicate analyses of sediments; it ranged from 4.7% to 19% of relative standard deviation.

ORGANIC MATTER

Since the following procedure is known to overestimate organic matter content owing to the simultaneous elimination of carbonates, we applied it only after carbonates have been removed. Sediment samples were treated, homogenized at room temperature and then dried at T = 60°C overnight. An aliquot (2–3 g) was weighed and placed in a platinum crucible. To remove inorganic carbon 6 M hydrochloric acid was added to the sample, which was then heated gradually to about 120°C on a hot plate for 15 min. The crucible was removed, cooled and the sample treated again with HCl and dried at T = 120°C for 90 min. Total organic matter (including water soluble organic carbon fraction) in the sediment was measured by determining the weight loss after combustion at T = 550°C for 4 h.

RESULTS

Water and Organic Matter

The results of the different analyses described above are shown in Table 3. For PAHs, water and organic matter content the average of three independent measurements is reported. From data analysis is possible to make the following observations:

in analyzed samples water content ranged from 2.9–40%. On the basis of literature data (13,14), two types of sediments can be characterized by water content: about 20% for sand and more than 40% for mud. Muddy sediments are known to accumulate hydrophobic compounds to a greater extent than sandy sediments.

The organic matter content varies in the percentage range 0.68–6.4. A good linear correlation between water and organic matter content was found with r = 0.80 (Figure 2).

Literature data demonstrated that water/matrix ratios could have significant effects on the results of organic matter partitioning (33). For contaminated sediments, partitioning involves various processes that result in the distribution of hydrophobic organic compounds, such as PAHs, between aqueous and non polar phases. Sorption, therefore, can be considered as one type of partitioning process because it involves the distribution of organic pollutants between pore water and sediments components (34). The availability of PAHs in sediments depends on the sorbent characteristics, environmental conditions and the properties of the pollutants. In particular, the content of water and organic matter in sediments influences the sorption of PAHs (35–37).

As a consequence of the different mechanisms of interaction between PAHs and sediments, PAHs remain for a longer time in the labile fraction of muddy
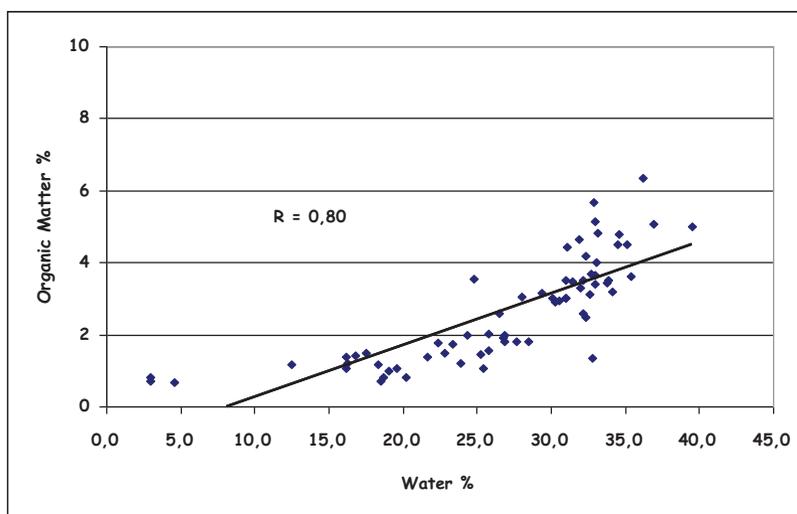
Figure 2: Correlation between water and organic matter content.

sediments. Hence, organic contaminants are available to the aquatic system for a longer time in muddy sediments than in sandy ones.

PAHs

Considering the results of all the analyses (generally 2–4 samplings during the considered period), the $\sum 19$ PAH concentration ranged from 5.6–7402 μg/Kg d.w. (Table 3) (Figure 3) with a mean value of 492 μg/Kg d.w. Results for the PAH analyses are shown in Figure 4.

In most of the sampling sites the same distribution of 19 polycyclic aromatic compounds (expressed as weight percentage) was observed (Figure 5). Four-ring aromatic hydrocarbons, such as fluoranthene, pyrene, benzo(a)anthracene, and chrysene, were predominant among the 19 PAHs analyzed. The 4-ring PAHs accounted for over 50% of the total PAH concentrations in Milazzo sediments.

We don't have noticed particular trend in the period between the first and the last sampling. Considering the total PAHs mean value (for a single station) obtained in the different samplings, site n° 1, located in front of the harbor entrance, showed the lowest concentration of PAHs (47 μg/Kg d.w) while sites n°6, n°7, and n°13 had the highest concentrations (1553, 1653, and 1749 μg/Kg d.w, respectively). High concentrations of PAHs in inner harbor sediments suggest localized inputs of PAHs from the inland area or directly from shipping activities in Milazzo Harbour. Site n°13 is located near the berthing docks of oil tankers.
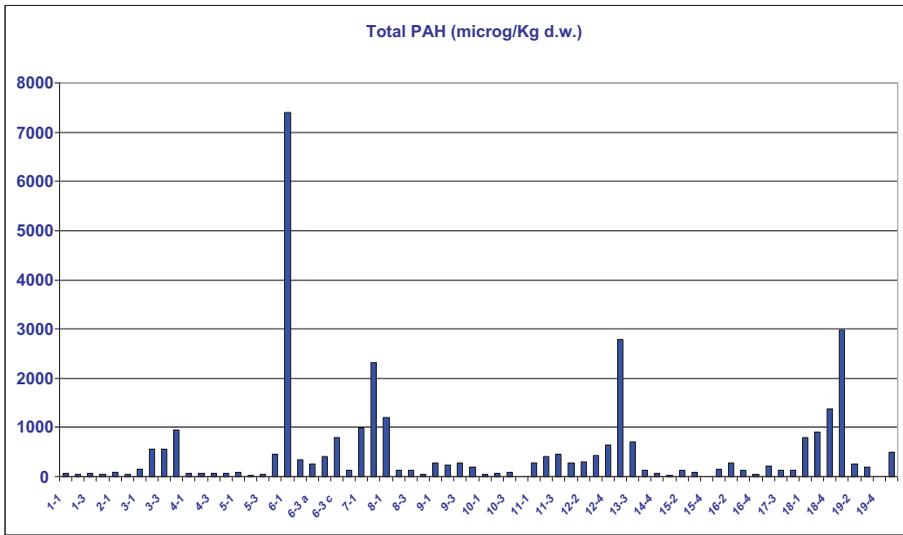
Figure 3: Total PAHs (μg/Kg d.w.) in all analysed samples.

As can be seen, the range of PAHs concentration found in the sediments is very large and the area shows heterogeneous levels of contamination. This can be explained by considering both the different geochemical constitution of the sediments, which determines a different capacity of absorption and the different content of organic matter.
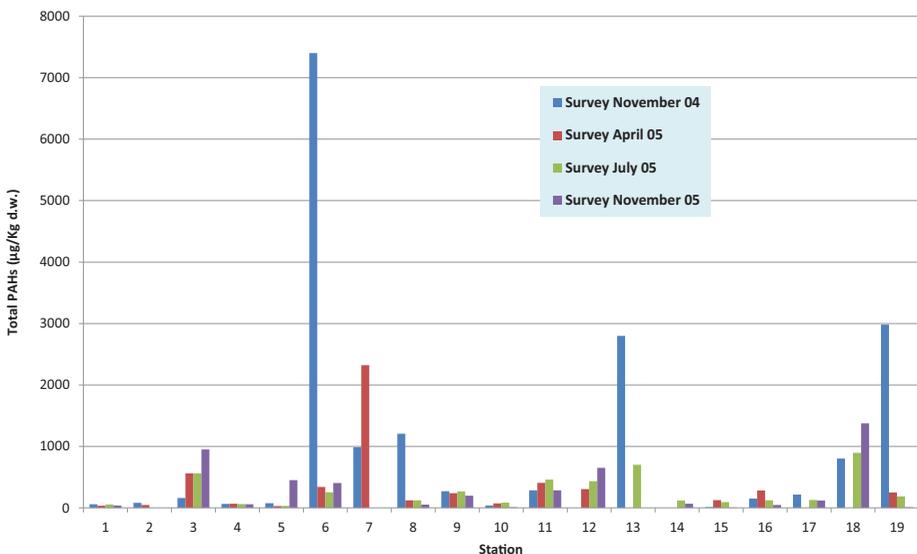
Figure 4: Results of analysis of total PAHs (μg/Kg d.w) in the different surveys.
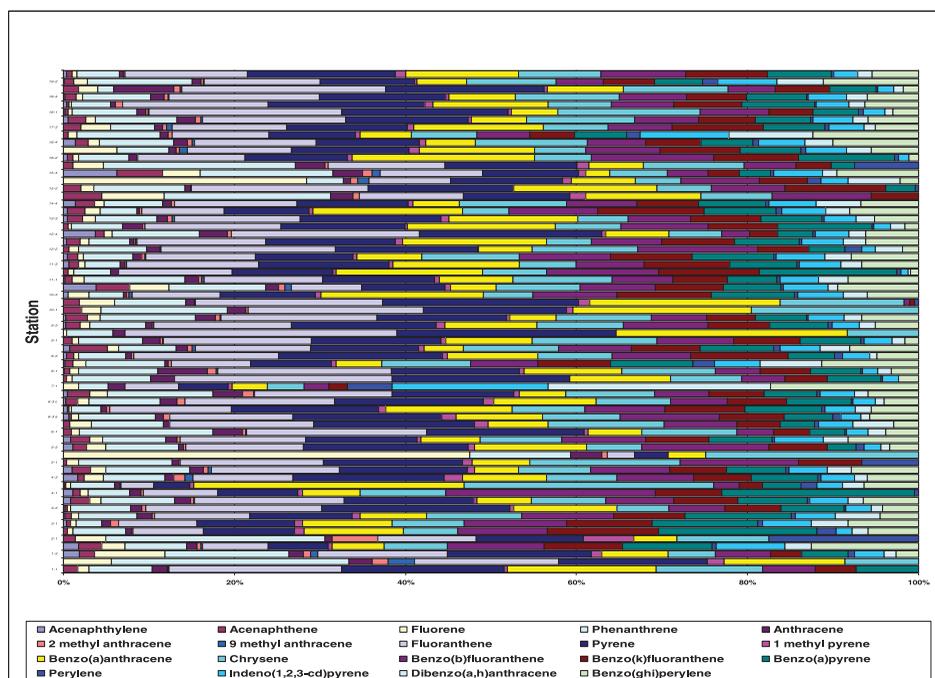
Figure 5: Percentage distribution of PAHs in sediments.

Analysis of the organic matter in sediments shows that concentrations of polycyclic aromatic compounds generally increase with increasing organic matter content. This trend has already been observed by some authors (38–40). With the aim of identifying a relationship between the water and organic matter content and PAH concentrations determined in the sediments investigated, we carried out a linear regression analysis. Linear correlations between total PAHs concentration and water and total PAHs concentration and organic matter content were found with r values, respectively, of 0.62 and 0.55 (Figures 6 and 7). Five points out of 67, exhibit a strong deviation from the curve in both correlations and were not taken into account in the fits. The linear correlations suggest that most of the PAHs identified in the samples originate from the same organic matter and that PAHs accumulate mostly on muddy sediments. For some samples was not observed the above correlation, the points do not fall on a straight. In these few cases we can suppose that the origin of PAHs may be different from those of organic matter or are characterized by closely localized sources (as the sample 6-1) or occasional.

ECO-TOXICOLOGICAL RISK AND COMPARISON WITH OTHER STUDIES

To evaluate the potential eco-toxicological risk of contaminants, obtained concentrations can be compared with Sediment Quality Guidelines (SQG) often
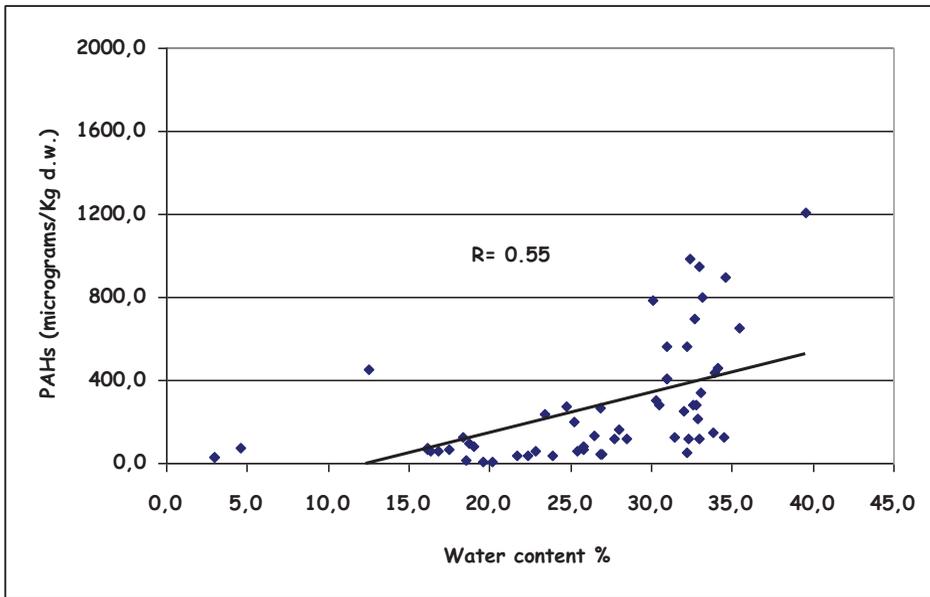
Figure 6: Correlation between water and total PAHs content.

used in sediment quality evaluation, for example, identifying as Effect Range low (ERL) and Effect Range Medium (ERM). These quality guidelines are sediment toxicity thresholds which define, for each pollutant, values that are rarely (<ERL), frequently (>ERM), or occasionally (>ERL, <ERM) linked with
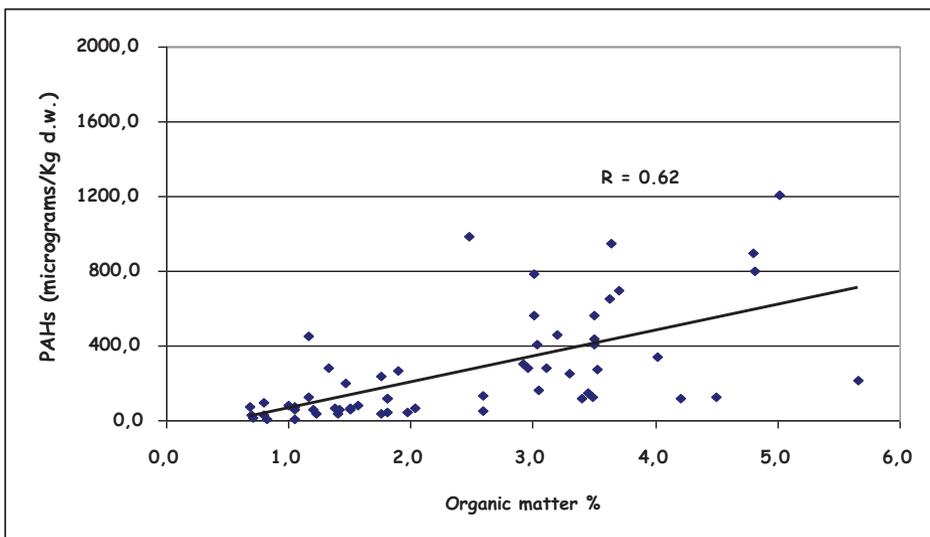
Figure 7: Correlation between organic matter and total PAHs content.

Table 4: Standard pollution criteria of PAHs for sediments (μg/Kg)

Compound	ERL	ERM	MPC	This study Average	This study Maximum
Acenaphthylene					
Acenaphthene					
Fluorene	19	540		6.2	69
Phenanthrene	240	1500	510	44	1160
Anthracene	85.5	1100	120	13	254
2 methyl anthracene					
9 methyl anthracene					
Fluoranthene	600	5100	2600	93	1561
Pyrene	665	2600		83	1360
1 methyl pyrene					
Benzo(a)anthracene	261	1600	360	50	485
Chrysene			10700	49	822
Benzo(b)fluoranthene	NA[a]	NA[a]		34	319
Benzo(k)fluoranthene	NA[a]	NA[a]	2400	31	309
Benzo(a)pyrene	430	1600	2700	32	308
Perylene					
Indeno(1,2,3-cd)pyrene	NA[a]	NA[a]	5900	17	188
Dibenzo(a,h)anthracene					
Benzo(ghi)perylene			7500	22	285
Total	2460	16140		474	7120

NA[a] = not avalaible.

unfavorable biological effects. The ERL and ERM are the 10th and 50th percentiles, respectively, on an ordered list of concentrations in sediment found in the literature that co-occur with any biological effect.

As shown in Table 4, the sediment quality guidelines (41,42) were applied to evaluate the possible eco-toxicological risks of PAHs in the study area. The mean value of our samples (474 μg/Kg) is lower than the effect range low (ERL = 2460 μg/Kg d.w.) concentrations indicated by some authors (35,36)

Results on single compounds showed that the fluorene concentrations were higher than the ERL value at station 15-3, phenanthrene and anthracene at station 6-1, fluoranthene at stations 6-1 and 19-1, pyrene at station 6-1, and benzo[a]anthracene at stations 6-1 and 13-1. All the investigated compounds are significantly lower than the ERM values.

The concentrations of PAHs found in 64 out of 67 samples were lower than the effect range low, while the remaining samples are in the range between the ERL and the ERM concentrations. The mean values of all samples of the same station were lower than the ERL. These findings indicated that the sediments from the entire sampling sites should have no potential biological impact.

Total PAHs concentrations found in Milazzo sediments were within the range of concentrations found in other coastal areas (14,16). In other Italian areas (Baia and harbor of Naples) (43), PAHs concentrations are between ERL–ERM values, so a biological effect will occur occasionally. In the area of

the Sarno River, PAHs levels are well below guideline values regarding the ERL, so biological effects may be rare. The same so verified for the areas of Portici, Punta Campanella, Punta Licosa and Punta Tresino (43). Considering the Gulf of Lions, located in the NW Mediterranean, all stations show PAHs concentrations (113–1529 μg/Kg) below the ERL value (44). The concentrations (72–18381μg/Kg) of PAHs found in 7 out of 8 stations from Stagnone coastal lagoon, Marsala (Italy) (16) were lower than ERL. In only one station was the ERM exceeded. This station is located in a sheltered area of the lagoon where weaker currents result in a depositional environment.

The Maximum Permissible Concentrations (MPCs) represent the potential effect of the substance in question to ecosystems. The aim of environmental quality standards is that the MPC is set at a level that protects all species in ecosystems. PAHs have different types of toxicity, such as narcosis, photo-induced toxicity, mutagenicity, and carcinogenicity. Some compounds, such as anthracene and benzo(k)fluoranthene, have a different toxic response compared with other PAHs. Therefore, it is advised to avoid one single MPC for all investigated compounds. MPCs are thus preferably derived from experimental data for each single PAH and are not presented as sum values.

A reference limit value of each PAH in sediments is the value proposed in references (45,46) (Table 4). In our case the limits were exceeded only four times for anthracene (samples 6-1 and 19-1) and for benzo[*a*]anthracene (samples 6-1 and 13-1).

PAHS SOURCES

In the environment, generally, some processes can generate PAHs. What makes it difficult to accurately identify PAH origins.

Pyrogenic (fossil fuel combustion, vegetation fires, etc.) and petrogenic (oil spill, petroleum products inputs) are the most important sources of PAHs found in environmental matrices (47-49) and in particular in coastal marine sediments (13,14,16,17).

In sediments of Milazzo Gulf, the predominance of fluoranthene, pyrene, benzo[*a*]anthracene and chrysene indicates that PAHs most likely did not originated from the spill oil, because, according to some authors (50), in crude, oil, low molecular weight PAHs (2–3 rings) are the dominant homologs, accounting for 86% of total PAHs. These results are similar to those obtained from Wang (51); in this case, PAHs in sediment were due to a long accumulation mainly originated from combustion or industrial activities.

Sources of the PAH pollution in aquatic ecosystems under investigation have been estimated by using distribution indexes relative to concentration ratios of some polycyclic aromatic compounds (52,53).

Phenanthrene (Ph) and Anthracene (An) are two structural isomers. In particular, Phenanthrene is more thermodynamically stable than Anthracene;
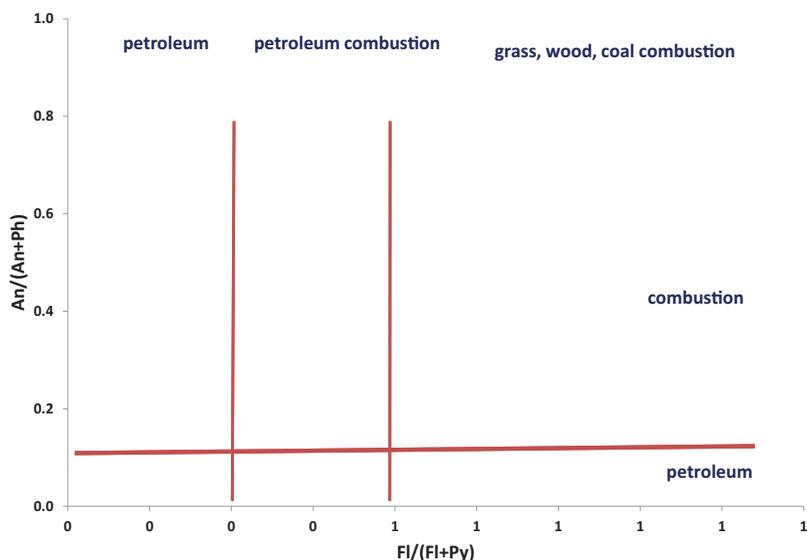
Figure 8: PAH cross plots for the ratios of Fl/(Fl+Py) vs An/(An+Ph).

therefore, in PAHs petrogenic pollution the Ph/An ratio is very high, while during combustion processes the high temperatures favor Anthracene formation with a lowering of the Ph/An ratio (54).

The values of ratio An/(An + Ph) in the sample investigated range from 0.03–0.79, while the ratios An/(An+Ph) in the different surveys, range from 0.06–0.30, excluding only a station (n°2) whose ratio is 0.10 (Figure 8). Ratio <0.10 usually is an indication of low temperature sources (petroleum) while, a ratio >0.10 indicates a dominance of combustion (14,34,55–57). In our case, An/(An+Ph) ratios suggest combustion (petroleum, grass, wood and coal) sources excluding the station n°2 probably contaminated by crude oil (55).

The Fl/(Fl + Py) ratios are in the range 0.40–0.50 (Figures 8–10) with average value of 0.50. The narrow range of Fl/(Fl+Py) ratios (relative standard deviation is 4%) found in the stations, indicates homogeneous sources in the investigated area. Generally, for environmental matrices (sediments, organism, air, etc.), the Fl/(Fl+Py) (10,58) ratio is below 0.50 for most petroleum samples and above 0.50 in grass, coal and wood combustion samples. The petroleum limit ratio appears closer to 0.40 than 0.50 for Fl/(Fl+ Py) and ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel combustion whereas ratios >0.50 are characteristic of grass, wood or coal combustion.

In accordance with ratios Fl/(Fl + Py) reported in literature (55), PAHs in the investigated area can be considered from pyrolytic origin.
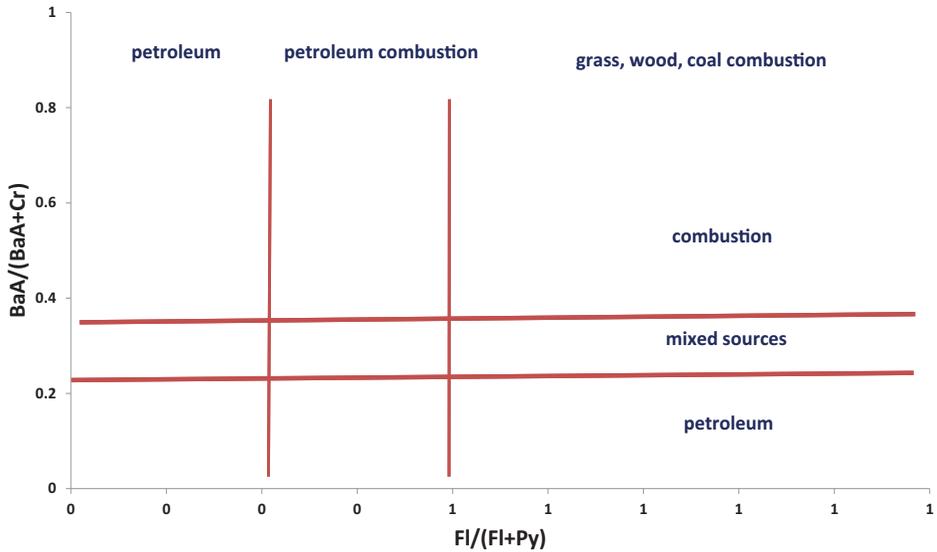
Figure 9: PAH cross plots for the ratios of Fl/(Fl+Py) vs BaA/(BaA+Cr).

In our case, ratios BaA/(BaA + Chr) (Figure 9) are in the range 0.15–0.77 (mean value = 0.50) and indicate that PAHs found in Milazzo coastal area principally are of pyrolytic origin in good agreement to the literature data (59,60): BaA/(BaA+Chr) ratios <0.20 involve low temperature sources (petroleum),
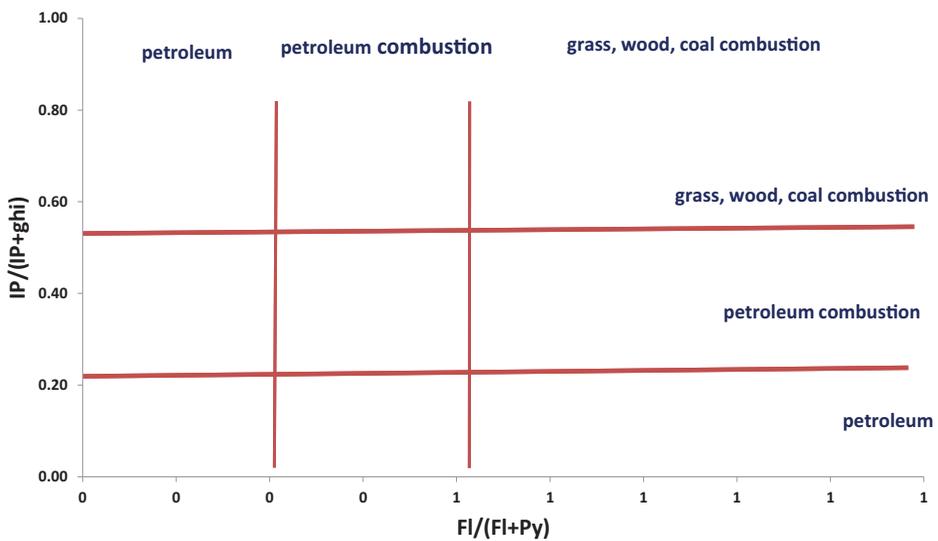
Figure 10: PAH cross plots for the ratios of Fl/(Fl+Py) vs IP/(IP+ghi).

from 0.20–0.35 indicate either petroleum or combustion and >0.35 indicate high temperature processes (combustion).

The high value of BaA/(BaA+Chr) ratio (0.71) for the station n°13 suggests that there have been no significant photolytic losses of benz[a]anthracene (61,62), in fact, in this sampling point, the bottom is about 46 m deep while the average depth of all the stations is 23 m.

According to literature data (59), IP/(IP+B(ghi)P) ratios of 0.20 most likely imply a petroleum origin, between 0.20 and 0.50 liquid fossil fuel combustion (vehicle and crude oil) and ratios >0.50 imply grass, wood and coal combustion. In our case, considering all the surveys, the mean ratios ranged from 0.24–0.70. The analytical data (Figure 10) indicate that PAHs found in the most of stations seem to be of pyrolytic origin. The lowest IP/IP+BghiP ratio is found in the sediments collected at station n°2 adjacent to the dock while the highest ratio (0.70) is referred to the station n°1 located at the exit of the harbor where the water circulation is greater than the points within the basin.

Considering that, in some cases, the values of four ratios are not in agreement, we calculated the total index (56) as the sum of single indexes (discussed before) respectively normalized for the limit value (low temperature sources and high temperature sources) reported in literature (55):

$$\text{Total index} = \{Fl/(Fl + Py)\}/0.4 + \{An/(An + Ph)\}/0.2 + \{B[a]A/(B[a]A + Chr)\}$$
$$/0.1 + \{IP/(IP + B[g, h, i]P)\}/0.5.$$

When the total index is >4 we consider PAHs originating prevalently from high temperature processes (combustion) while lower values indicate prevalently low temperature sources (petroleum products). For the analyzed samples, the total index ranges from 5–11 with an average value equal to 8, indicating high temperature sources.

Only two sample stations (n°2, n°14 in two different sampling surveys), located, respectively, near the docks of passenger ferry docks near the berthing docks of oil tankers (Figure 1), appear to be more contaminated by petroleum inputs than the other points. It is possible that some sites receive occasionally PAHs input from petrogenic sources originating from shipping activities and/or from the oil refinery.

The analytical data indicate that polycyclic aromatic compounds found in most of all sediments seem to be of pyrolytic input and that diffuse input, such as atmospheric deposition, may be the major source of PAHs into the water bodies. In the atmosphere PAHs can be associated with particle phases. The aerosol particles are transported by the wind to distant locations and they are removed from the atmosphere by rain and dry fallout in seawater. In the course of sinking in the water column, PAHs are attacked by microbes (63) and/or can undergo photochemical breakdown (64) and a fraction should be decomposed. Photochemical behaviors of PAHs are dependent not only on their molecular

structures but also the physical–chemical properties of the substrate on which they are adsorbed (55). PAHs on the surfaces of atmospheric particulates will weather and degrade while those linked in char, soot, bitumen, tire particles, etc. will be protected from decomposition and will be preserved in sediments. On the contrary, PAHs in the sediments are more resistant to microbial degradation and therefore they accumulate (65).

Attention has been paid (10,61) to the distribution of low and high molecular weight PAHs (LPAHs = Acph+Ace+Fl+Phen+Ant and HPAHs = BaA+Cry+BbF+BkF+BaP+InP+DBA+BgP, respectively) as a reliable tool for discriminating the petrogenic/pyrolytic origin of PAHs.

Research have shown that high ΣLPAHs/ΣHPAHs ratios (>1) frequently indicate PAHs with petrogenic predominate sources while low ΣLPAHs/ΣHPAHs ratios suggest PAHs of pyrolytic origin (66). Considering the value of single sites (mean of 3–4 samplings), in the sediments of Milazzo area, the ΣLPAHs/ΣHPAHs ratios ranged from 0.10–0.54 with the average of 0.20. This value suggests that the area is mainly impacted by pyrolytic sources. In particular, the sites n° 1, 2, 5, and 15 show the higher mean values of this ratio (0.33, 0.31, 0.54, and 0.45, respectively) and always less < 1, than the other stations that suggest a major (but not predominant) contribution of petrogenic origin of PAHs. Moreover, the lower InP concentrations in the stations n°1, 2, 5, and 15 confirm the interpretation of a major petrogenic contribution of PAHs in these sites (44).

In this study, the percentage of alkylated PAHs ranged from 0.008–11.2%. The higher value was obtained in the station n°2 during the first survey. This data confirm the meaningful petrogenic origin of PAHs in this station. In general, alkylated/noalkylated ratios are low for high temperature (pyrogenic) PAHs mixtures and high in petrogenic PAHs as in the station n°2 during the first survey (alkylated/noalkylated = 6.6). However, some researchers (55,67,68), affirm that, in a few cases, alkylated/parent PAH ratios generated during biomass burning can be similar to those associated with petroleum, leading to erroneous source apportionment estimates. In the case of station n°2, is improbable that PAHs are produced by combustion of biomass because the sampling point is located within the harbor, far from the location where are active agricultural practices that involve the biomass burning.

In most of samples, the concentration of anthracene (C_0) is higher than that of methylanthracenes (C_1). The values of the ratio $C_0/(C_0+C_1)$Ant range from 0.13–1.0 with the average of 0.69 and can be attributed to combustion processes.

Considering pyrene and methylpyrene, $C_0/(C_0+C_1)$Py, ratios range from 0.68–1.0 (mean 0.95), typifying pyrolytic (>0.5) inputs. The lowest value (0.68) was determined in the station n°2 that confirms a greater intake of petroleum than other stations.

Table 5: Coefficients of correlation between total PAHs vs. single compound concentrations

	Coefficient of correlation r^2
Acenaphthylene	—
Acenaphthene	0.82
Fluorene	0.68
Phenanthrene	0.83
Anthracene	0.84
2 methyl anthracene	0.77
9 methyl anthracene	0.58
Fluoranthene	0.98
Pyrene	0.98
1 methyl pyrene	0.82
Benz(a)anthracene	0.80
Benzo(b)fluoranthene	0.87
Crysene	0.97
Benzo(k)fluoranthene	0.84
Benzo(a)pyrene	0.89
Perylene	—
Indeno(1.2.3-cd)pyrene	0.62
Dibenzo(a.h)anthracene	0.31
Benzo(ghi)perylene	0.73

A linear correlation between total PAHs concentrations and single compounds content was calculated. The values of r^2 (Table 5), for the most representative compounds, are higher to 0.8. These results suggest that most of the PAHs identified in the sediment samples originate from the same type of emissions. Therefore, considering the above correlations, we propose that, for future monitoring of PAHs on the same area, the number of compounds to analyze can be reduced resulting in a significant cost and time savings.

Regarding the origins of perylene, literature is discordant, some authors (13,54,69–71) argue that perylene can be produced from combustion of fossil fuels and biomass but the marked abundance precludes a pyrogenic origin. According to Tissier (69), a perylene contribution of more than 10% indicates a diagenic process. There is considerable evidence that it can be formed biologically under anaerobic conditions (14, 72). In a review, Wilcke (73) cites examples from literature that report these compounds in soils, flowers and termite nests. Thiele and Brummer (74) reported that biological formation of 3, 4, 5, and 6-rings PAHs was observed after incubation of fresh plant material and soil mixed with fresh plant material under reducing conditions. When only soil material was incubated, anaerobic biodegradation of three-ring was observed. Perylene quinones (pigments found in several organisms) are suspected to be degraded to perylene by anaerobic microbial metabolism (74,75). Another theory postulates production via biosynthesis, independent of special precursors (74).

A perylene index, defined as concentration of perylene divided by the total of 5 rings PAHs isomers, has been proposed to distinguish biogenic perylene from pyrogenic perylene (74). The perylene index greater than 0.1, frequently, indicates the diagenetic (biogenic) inputs, whereas when it is less than 0.1, it indicates pyrogenic as origin of the compound (76).

In the surveyed area, perylene was found at nearly all stations. Station n°7 had the highest absolute concentration (51.5 μg/Kg d.w.) and was followed in decreasing order by stations n°2 and n° 6. However, perylene relative contribution is greatest in site n°2 (17.4%). This marked abundance precludes its pyrogenic origin. Considering that the sediment was grey and anoxic, we can suppose that most of perylene in this site can be formed biologically under anaerobic conditions. The perylene index is in the range of 0.01–0.58, excluding the sample n°2-1 where the index is very high (46). In this station, the value of perylene index of the second survey results 0.051, therefore, the high value determined during the first monitoring can be attributed to an unknown source.

The amount of perylene found in the near shore sediment was believed to originate mainly from terrestrial input. Perylene has been frequently associated with inputs from rivers and estuaries (55,73).

The presence of perylene in the analyzed sediments cannot be related to vehicular traffic because this compound occurs only in small concentrations in the atmospheric urban particulate (77). In fact the perylene index, in the urban particulate, is in the range of 0.02–0.04 (average value = 0.027±0.07) (77). This conclusion is in agreement with the perylene behavior which is not present or occurs only in small amount among the products of combustion processes, probably due to its thermal instability or reactivity (10).

CONCLUSIONS

Nineteen PAHs were quantitatively analyzed in 67 samples of sediments of an area located in front of a power plant and a refinery. Our main remarks are as follows.

(a) The results reported in our work represent the first quantitative investigations of PAHs in superficial sediments of the Milazzo coastal area. Concentrations of PAHs found in this article will also serve as a baseline for the future monitoring campaigns and/or excavations or when marine works will begin in the investigated area.

(b) The greater presence of PAHs with high molecular weights in most samples, the values of isomeric ratios, the total index, the ratios ΣLPAHs/ΣHPAHs demonstrate that most sample some their PAHs a predominant single origin, i.e., anthropogenic combustion or pyrolytic processes, while a little fraction of PAHs may derive from biogenic.

(c) We haven't noticed particular trend on PAHs concentrations in the period between the first and last sampling.

(d) Total PAHs content in nearly all samples are correlated with the concentrations of many single compounds. This evidence indicates that during the process of production a characteristic mixture of PAHs is produced and consequently for routine analyses only a minor number of compounds could be analyzed.

(e) The concentrations of PAHs found in 64 out of 67 samples were lower than the effect range low (ERL), while the remaining samples are in the range between the ERL and the ERM concentrations. The mean values of all samples of the same stations were lower than the ERL. These findings indicated that the sediments from the entire sampling area should have no potential biological impact.

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