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Polycyclic Aromatic Hydrocarbon Distributions in Sediments from the Mar Piccolo, Ionian Sea, Italy

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The basin of Mar Piccolo with an area of $2,176 \cdot 10^4$ m^2 and with a water volume of about $152 \cdot 10^6$ m^3, lies at the north of Taranto. It is divided by two strips of land into the first and the second inlet and it is connected with the Mar Grande basin (Ionian Sea) through two narrow passages, Canal of Porta Napoli and Canal Navigabile. Some superficial rivers drain into the basin: Galeso, with a more significant flow, in the upper part of the first inlet; Marrese Canal and Cervaro river in the upper part of the second inlet. More, eight urban discharges drain directly into the basin, and the most significant is Canale D'Aiedda (south, second inlet). Mar Piccolo, because of its characteristic of semi-enclosed basin with marked problems of water exchange due mainly to moderate sea-tides, represents a marine ecosystem where biological balances have been modified, in relation to the anthropic development and, in particular, the large industrial settlement.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and occur primarily as a result of anthropogenic inputs, while a little contribution comes from events as forest fires (Compaan et al.,1992). Transport to the marine environment occurs both via surface waters and the atmosphere; because of their low aqueous solubilities, PAHs tend to adsorb to particulate material and to be deposited to the underlying sediments (Law & Biscaya, 1994), where they can accumulate to high concentrations. Due to their wide environmental distribution, mutagenic and carcinogenic properties, PAHs merit concerted environmental monitoring.

The objective of this study was to determine the concentrations, distribution and sources of PAHs in surface sediments from the Mar Piccolo (Ionian Sea), adjacent area of Taranto harbour one of the mains in Italy.

MATERIALS AND METHODS

Samples were collected in June 1999 from ten stations in Mar Piccolo (Fig 1). From each station, sediment samples to a depth of 2 cm, were collected with Van Veen type apparatus. After collection, all samples were placed in ice-filled coolers and transferred to storage at -20° C until analysis. Frozen aliquots of sediment samples were air dried for three to four days. Dried aliquots were ground using a

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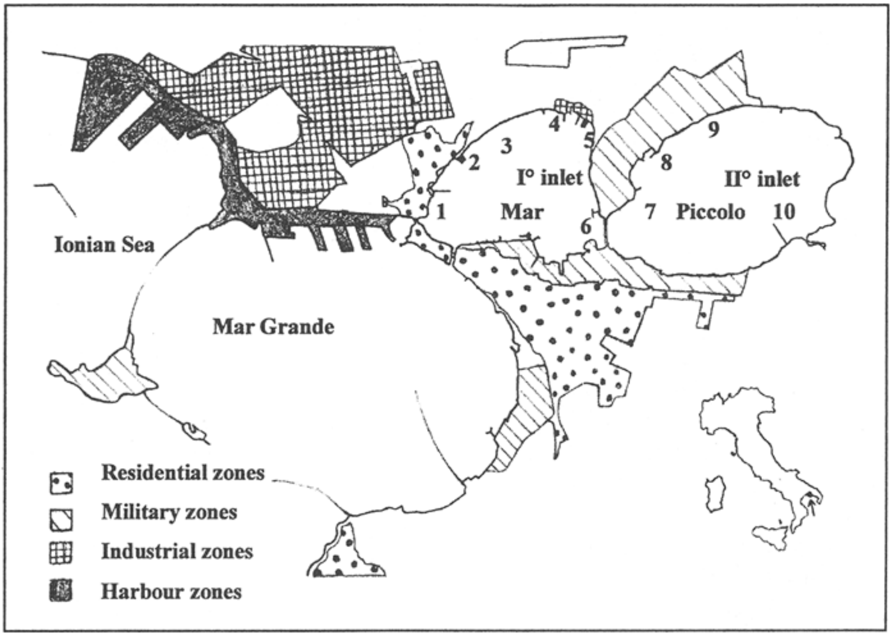

Figure 1. Map showing sampling sites in Mar Piccolo-Taranto (Italy).

mortar and pestle and sieved through a 0.5 mm screen. The analytical procedures for extration and purification of PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracene, benzo(*a*)pyrene, dibenzo(*ah*)anthracene, benzo(*ghi*)perylene) were carried out by the methods proposed by Dunn & Armour 1980. In brief, 50 g of sediment samples were added with 150 ml ethanol and 7 g of KOH and then the PAHs extracted three times with 200 ml of isooctane. The isooctane was rotary evaporated and the extracts were re-dissolved in toluene. The samples were applied to a column (florisil 60-100 mesh, deactivated with 5% water and prewashed with 100 ml of toluene, which was discarded) eluted with toluene, and 5 ml of dimethyl-suphoxide (Me_2SO) was added to the eluate, and the mixture was rotary evaporated to remove the toluene, leaving the samples in Me_2SO. The quantification of the PAHs content in the samples was performed with HPLC apparatus (Beckman System Gold) equipped with a ultrasphere ODS-C-18 column (Beckman, i.d.:4.6 mm, length: 25 cm; particle size:5 µm). The eluting solution was acetonitrile:water (45:55, v:v) with a flow rate of 1.5 ml/min. Separation was obtained with a gradient in which the acetonitrile concentration increased from 45% to 100% in 40 min. A fluorimetric detector (Luminescence spectrometer Perkin Elmer LS-5) (excitation wavelength 290 nm; emission wavelength 430 nm) and PS2/80 IBM computer integrator were used for the determination of the peak areas. The PAHs were identified on the basis of retention time and quantified by comparison with the fluorescence response of the appropriate standard (Supelco Park, Bellefonte, PA 16823-0048 USA). Confirmation of the identities of individual PAH was made using stop-flow conditions to obtain the complete emission spectrum corresponding to each peak in the chromatogram. Recoveries, determined by making standard additions to samples, were in the range 70-98%, and all results reported have been corrected for recovery. Precision was estimated from the results of three replicate analyses of the samples. Organic carbon (OC) content was determined using the back-titration method (Walkley and Black, 1934).

RESULTS AND DISCUSSIONS

Total PAHs (Table 1) in sediments from all stations (1-10) ranged from 355- 5193 ng g^{-1} dry wt with a mean value of 2014 ng g^{-1}. PAHs were found in all the stations examined except benz(*a*)anthracene which was absent in the stations 5 and 6, benzo(*a*)pyrene in the stations 6, 8 and 9 and benzo(*ghi*) perylene in the stations 5, 6, 8 and 9. In the first inlet (stations 1-6) the concentrations ranged from 355 to 5193 ng g^{-1} dry wt with a mean value of 2163.6 ng g^{-1}. The stations showing the highest total concentrations of PAHs were stations 1 and 6 with values of 5193 ng g^{-1} dry wt and 4143 ng g^{-1} dry wt respectively. The station 1 is near to one of the two narrow passages, Canal of Porta Napoli, that opens on Mar Grande in vicinity of the Taranto harbour, where an intense activity is carried out: 48% of the movement of goods is represented by metallic minerals destined to metallurgic industry, 27% oil and its derivatives, 24% solid combustible (carbon) and 1% bitumen. The station 6, which also showed PAHs high values is near to a naval base of Italian Military Marine. High concentrations of 1479 ng g^{-1} dry wt were also observed in station 4, located near the mouth of the Galeso river. In the second inlet (stations 7-10) the levels ranged from 622-3891ng g^{-1} dry wt with a mean value of 1789.7 ng g^{-1}. The highest concentration of 3891 ng g^{-1} dry wt was found at station 10 located in vicinity of Canale d'Aiedda discharge.

The acquirement of the ratio phenanthrene/anthracene and fluoranthene/pyrene allows us to appreciate the source of contamination (Raoux, 1991). A ratio phenanthrene/anthracene < 10 and fluoranthene/pyrene >1 indicates that the contamination by PAHs was due to combustion processes (Colombo et al. 1989; Garrigues et al. 1991). The data found relative at the two ratios above mentioned (Table 2, Fig. 2) indicates that PAHs in the sediments seemed to be of pyrolityc origin, except for station 10, where the contamination source could arise from petrogenic contamination. Close to this latter station is located, besides to a discharge of Canale d'Aiedda, also a refuelling station wharf. Accidental spilling of fuel into the sea during the loading operations might be the cause of petrogenic contamination. No significant correlation was observed between the concentration of PAHs and sedimentary organic carbon ($r=0.18$). It is suggested, therefore, that the observed distribution of PAHs in sediments was not governed by sedimentary characteristics, but, it might be due to the localised sources of inputs.

The comparison with published data from other aquatic systems (Table 3) showed that sediment PAH concentrations in Mar Piccolo were lower than those detected in some areas of urbanised estuaries in USA, but were also about an order of

Table 1. Concentration (ng g^{-1} dry wt) of individual PAHs in Mar Piccolo (Ionian Sea) sediments by sampling area and percentage of organic carbon.

Stations	1*	2*	3*	4*	5*	6*	7*	8*	ΣPAH	% OC
1	3050	1190	351	220	161	163	12	46	5193	0.93
2	180	50	83	55	502	42	13	39	964	0.45
3	250	80	187	120	129	14	24	64	868	1.89
4	350	150	396	254	141	150	13	25	1479	1.56
5	120	40	89	31	ND	45	10	ND	335	1.65
6	3170	579	200	136	ND	ND	58	ND	4143	1.72
7	220	70	118	68	52	42	13	39	622	1.60
8	599	200	409	210	134	ND	33	ND	1585	1.85
9	400	126	72	ND	402	ND	61	ND	1061	2.12
10	2820	365	86	517	56	20	10	17	3891	1.74
means	1115.9	285	199.1	179	197.1	68	24.7	38.3.	2014.1	---

PAH number 1*: phenanthrene, 2*: anthracene, 3*: fluoranthene, 4*: pyrene, 5*: benz(*a*)anthracene, 6*: benzo(*a*)pyrene, 7*: dibenzo(*ah*)anthracene, 8*: benzo(*ghi*)perylene. ND: Not Detected.

Table 2. Ratio phenanthrene/anthracene and fluoranthene/pyrene

Stations	Phenanthrene/Anthracene	Fluoranthene/Pyrene
1	2,5	1.6
2	3.6	1.5
3	3.1	1.6
4	2.3	1.6
5	3.0	2.8
6	5.5	1.6
7	3.1	1.7
8	2.8	1.9
9	3.1	2.2
10	7.7	0.16

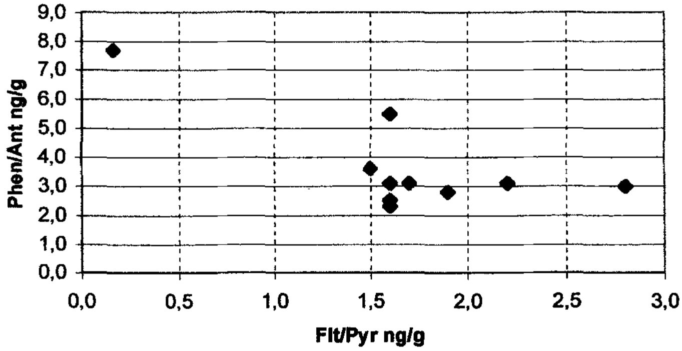

Figure 2 Relationship between isomer compounds.

Table 3. Comparison of sediment PAH concentrations (ng g^{-1} dry wt) measured in this study with those in other countries.

Sites	n	Average	Range	Reference
Taranto Gulf, Italy	8	2014	335-5193	This study
Adriatic Sea	12	200	18-580	Caricchia et al. (1993)
Adriatic Sea	9	130	27-530	Guzzella & De Paolis (1994)
Western Mediteranean Sea	31	1300	180-3200	Lipiatou Saliot (1991)
San Diego Bay, USA	36	3000	80-20000	Anderson et al. (1996)
Casco Bay, USA	23	2900	16-21000	Kennicutt et al. (1994)
Penobscot Bay, USA	12	2600	290-8800	Jonhson et al. (1985)
Washington coast, USA	13	200	29-460	Prahl & Carpenter (1983)
Passaic River, USA	19	150	0.22-8000	Huntley et al. (1995)
Chesapeake Bay, USA	15	52	0.56-180	Foster & Wright (1988)
Manukau Harbour, New Zealand	10	820	16-5300	Holland et al. (1993)
Baltic Sea	15	1200	720-1900	Witt (1995)
Chetumal Bay, Mexico		2340	340-8910	Norena -Barroso et al.(1998)

n: number of PAH compounds analysed in each study magnitude greater than those reported for the western Mediterranean and Baltic Sea, and markedly higher than the values encountered in the Adriatic Sea. The data found here for the Mar Piccolo basin were, hence, indicative of a polluted environment. It is believed that the sources of this pollution are of anthropogenic origin due to an high urbanization of the Ionian seashore, and a large industrial activity of the eastern coast of Taranto. In this area stand a great metallurgic center, and an oil-refinery, which are the most significant industrial settlements of the Ionian area. The presence of these industries yields a huge amount of particulate matter, which is directly let in the atmosphere as smokes, as well as a great mass of waste. This mass, together with the waste waters coming from the various processes and treatment installations, are disposed in a sea area adjacent to Mar Grande. The problems of environmental impact that occur are very complicated because, besides the suspended material, the waste waters contain also toxic pollutants (ammonia, phenols, mineral oils, metals etc,). The metallurgic industry averages 1.700.000 t /year of waste, a fraction of which are toxic and harmful; most of these waste are utilized again, while other are discharged. This stockage is a source of problems because of the possibility of a dismissal of toxic compounds in lower strata.

On this basis can be presumed that pollution in Mar Piccolo originates mainly from urban effluents, discharges from the local industries, spillages from vessels, harbour operations and presumably also atmospheric transport. The level of contamination detected, even if not comparable with that found in areas strongly industrialised (e.g. San Diego and Casco Bay USA), is relatively high and suggests the need for an increasing effort in controlling sources of pollution in this area.

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