coastal environment of Leghorn—(Tyrrhenian Sea)

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Abstract

The levels of dissolved and particle-associated *n*-alkanes, alkylbenzenes, phthalates, PAHs, anionic surfactants and surfactant fluorescent organic matter (SFOM) were measured in sea-surface microlayer (SML) and sub-surface water (SSL) samples collected in the Leghorn marine environment in September and October 1999.

Nine stations, located in the Leghorn harbour and at increasing distances from the Port, were sampled three times on the same day. At all the stations, SML concentrations of the selected organic compounds were significantly higher than SSL values and the enrichment factors (EF = SML concentration/SSL concentration) were greater in the particulate phase than in the dissolved phase.

SML concentrations varied greatly among the sampling sites, the highest levels (*n*-alkanes 3674 μg/l, phthalates 177 μg/l, total PAHs 226 μg/l) being found in the particulate phase in the Leghorn harbour.

To improve the knowledge on pollutant exchanges between sea-surface waters and atmosphere, the validity of spray drop adsorption model (SDAM) was verified for SFOM, surface-active agents, such as phthalates, and compounds which can interact with SFOM, such as *n*-alkanes and PAHs. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last decades many investigations have been conducted on the physical properties and chemical composition of the sea-surface microlayer (SML) as well as on exchange processes at the air/sea interface (GESAMP, 1995; Liss and Duce, 1997; CIESM Workshop, 1999). These studies have highlighted that a wide variety of natural and anthropogenic contaminants concentrate in the SML because of their surfactant nature, hydrophobic properties, possible association with floatable particles, vertical diffusion mechanisms or bubbles scavenging. The transfer of such materials from the sea-surface to the atmosphere may take place through the volatilisation due to their high vapour tension, the

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Abbreviations: EF, enrichment factor; Er, enrichment ratio; FA, fulvic acids; HS, humic substances; MBAS, methylene-blue active substances; SDAM, spray drop adsorption model; SFOM, surfactant fluorescent organic matter; SML, sea-surface microlayer; SOM, surfactant organic matter; SSL, subsurface water.

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stripping by the bubbles and the formation of wind-generated aqueous aerosols (Wallace and Duce, 1978; Hardy, 1982; Buat-Ménard, 1983; Blanchard, 1989; Cini et al., 1994a; Lepri et al., 1995; Gustafson and Dickhut, 1997). In fact, when air bubbles burst at the sea-surface they generate an aerosol which is contaminated and enriched with material scavenged from the sea-surface microlayer and the water column (Blanchard, 1975; Tseng et al., 1992). Several studies (Blanchard, 1983; Liss and Duce, 1997) have shown that bacteria and viruses in aerosol particles have concentrations significantly higher than those obtained in the bulk-water from which they were generated. Analogous results were found for lipids (Gagosian, 1986; Simò et al., 1991) and surfactants (Blanchard, 1964; Garrett, 1967) transported via marine aerosol to the coastal regions where hazardous effects on animals and vegetation (Giovannelli et al., 1989; Bussotti et al., 1995), together with toxic effects on human health (WHO, 1998), have been observed. In addition, high concentrations of toxic metals (Hoffmann et al., 1974; Hunter, 1980; Hardy et al., 1985) and organic pollutants (Williams et al., 1986; Hardy et al., 1987; Cross et al., 1987; Sauer et al., 1989; Hardy et al., 1990) have been found in the SML compared to the sub-surface water (SSL) throughout various coastal environments. However, a few investigations have been carried out on the characterisation of organic pollutants in the SML of Mediterranean waters (CIESM Workshop, 1999).

To this end, aliphatic and aromatic hydrocarbons and phthalates have been determined in SML, SSL and aerosol samples collected in the Tyrrhenian Sea near Leghorn. Size fractionated aerosol samples were collected to provide more information on air–sea processes, as well as verify the validity of Spray Drop Adsorption Model (SDAM) (Oppo et al., 1999). Moreover, the compounds measured were particularly useful for evaluating the degree of marine pollution because alkylbenzenes, phthalates and PAHs enter the marine environment only by anthropogenic sources, while *n*-alkanes may have biogenic and/or anthropogenic origin.

2. Experimental method

2.1. Sample collection

2.1.1. SML and SSL

SML and SSL samples were collected between September and October 1999 at nine different sites in the Tyrrhenian Sea, near Leghorn and Gorgona island. Table 1 gives some information about the sampling sites including location, water depth, distance from the coast, temperature and pH.

Our sampling strategy included stations in areas believed to receive different amounts of pollutants in

Table 1
Description of SML and SSL sampling sites and some characteristics of sea-water samples

Station	Sample number	Location	Collection date (1999)	Latitude	Longitude	Sea depth (m)	Distance from the Leghorn coast (km)	T^a (°C)	pH[a]
1	1SML, 1SSL	Gorgona Island	Sept. 9	43°25,030N	009°54,020E	35	33.3[b]	20.4	7.4
2	2SML, 2SSL	Castel Sonnino #1	Sept. 10	43°27,550N	010°21,400E	36	0.2	22.5	7.6
3	3SML, 3SSL	Quercianella	Sept. 27	43°27,070N	010°21,030E	43	0.4	21.6	7.9
4	4SML,4SSL	"Pancaldi"	Sept. 28	43°31,875N	010°18,139E	5	0.2	24.0	8.2
5	5SML, 5SSL	"Pejani"	Oct. 6	43°31,070N	010°18,139E	9.5	0.1	23.6	8.0
6	6SML, 6SSL	Fishing boats quay	Oct. 7	43°33,000N	010°18,231E	4	–	21.7	7.3
7	7SML, 7SSL	Castel Sonnino #2	Oct. 8	43°27,550N	010°21,825E	5	0.1	22.3	7.7
8	8SML, 8SSL	Meloria's Tower	Oct. 12	43°32,892N	010°13,079E	4	5.9	21.5	8.5
9	9SML, 9SSL	"Medicean" quay	Oct. 13	43°32,885N	010°18,112E	6	–	23.8	7.6

[a] Mean value based on three samples.
[b] 50 m from Gorgona Island coast.

order to have a representative picture of sea surface contamination in the investigated zone (Fig. 1). SML and SSL samples were taken in the harbour of Leghorn (stations 6 and 9), which is highly contaminated from a variety of pollutant sources including industrial discharges, petroleum spills and marine
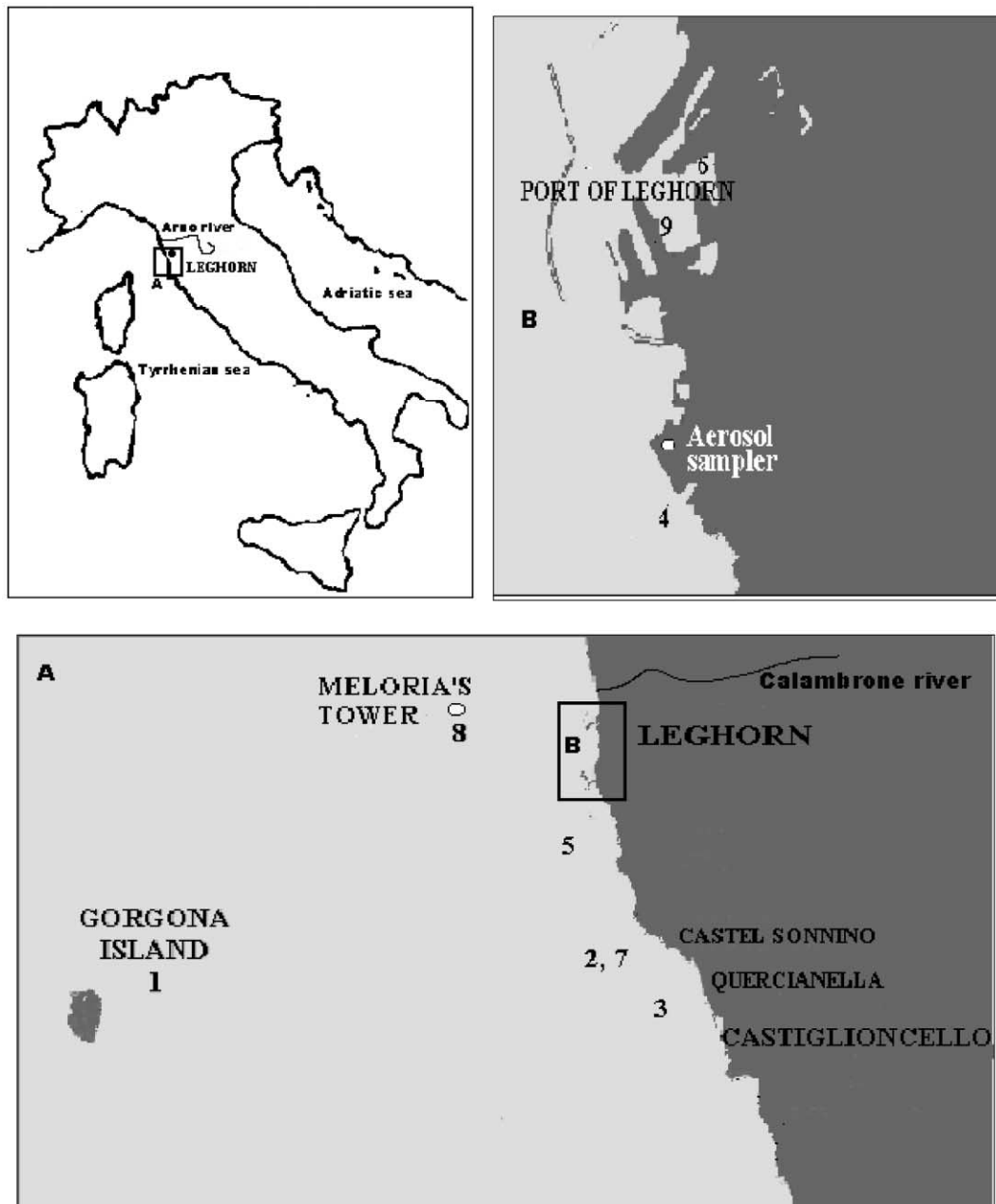
Fig. 1. Map showing locations of sampling stations.

transportation. The station 6 is situated in an inner zone of the harbour with respect to the station 9 and is characterised by visible surface slicks and limited water mass circulation. SML and SSL samples were also taken along the coast at increasing distances from the urban and industrialised area of Leghorn.

Stations 4 and 5, were chosen in the proximity of the harbour area: they are characterised by a low water depth and are influenced by the near "Pancaldi" and "Pejani" bathing facilities.

Stations 2 and 3 were located at Castel Sonnino and Quercianella, coastal sites characterised by water depths of 36 and 43 m, respectively, and receiving low contaminant inputs. A further sample was taken in the coastal area of Castel Sonnino (station 7) at a different water depth, time and distance from the shore with respect to station 2.

Station 1, located in a hold of the Gorgona Island at about 33.3 km from the Leghorn coast, is influenced by minimal local sources because only a little penitentiary is present and the traffic of ships is prohibited in the proximity of the island.

Finally, station 8 was chosen near Meloria's Tower, an offshore zone with shallow water, with a distance of about 5.9 km from the coast: this station is affected by the small Calambrone river and probably also reflects the influence of the Arno river discharge.

SML and SSL samples at all these stations were collected simultaneously under calm sea conditions, using a Multiple Use Microlayer Sampler (MUMS) constructed on the idea of rotating drum samplers by Harvey (1966), Carlson et al. (1988) and Hardy et al. (1988). Briefly, the operation principle of the MUMS is based on the collection of SML by capillary, through a rotating Pyrex glass drum collector ($\varnothing$ 315–500 mm length). Electrical components, batteries and collector system are enclosed inside boxes in the floating structure. The movement of the whole sampler is given by an electrical motor (Evinrude 12 V). The material adsorbed on the drum surface is removed by a Mylar scraper. The collected liquid is carried to a cleaned aluminium bottle by a Teflon membrane pump (12 V). The rotating drum (speed 6 rpm), as well as the collector pipe line, was washed with seawater for 10 min before sampling. The flux of collected liquid was switched in the bottle or in the sea by a Teflon solenoid three-way valve. For

collection of subsurface water (-0.50 m), a probe connected with the on-board MUMS collector system was used.

Three 4-l replicates were collected at each site in order to obtain a measure of the average concentrations of pollutants. The SML sample represents an integration of the surface microlayer over an area of about 40 m^2. Particular care was taken to avoid contamination from the boat and, therefore, all the parts of the equipment were thoroughly cleaned before use.

The thickness of the SML was calculated from the sample volume divided by the surface area swept by the drum and was estimated to be about 100 μm.

The ratio between the concentration of any substance in the SML and SSL samples collected at the same time gave the enrichment factor (EF).

The pH was measured just after sampling using a pH-meter, model HI 8417 (Hanna Instrument, Italy) (see Table 1).

2.1.2. Aerosol

Aerosol sampling was performed using a five-stage cascade impactor (SA 235, Sierra, USA) located at the top of a high volume sampler (G 1200 PM10 Graseby Andersen, USA), which separated atmospheric particles into six different size fractions. Equivalent aerodynamic cut-offs for 1 g/m^3 density particles at a flow rate of 68 m^3/h where as follows: stage 1, $d > 7.2$ μm; stage 2, $7.2 > d > 3.0$ μm; stage 3, $3.0 > d > 1.5$ μm; stage 4, $1.5 > d > 0.96$ μm; stage 5, $0.96 > d > 0.49$ μm. Particles with a radius < 0.49 μm were collected on the final quartz fiber filter QM-A (Whatman, USA) with an efficiency of 98% (Butcher and Charlson, 1972).

Aerosol sampling was performed by a computerised meteorological system (Schiavuta et al., 1992) which activated the sampler device only under well-defined weather conditions: absence of rain, winds from the sea in a sector between 185° and 225° and wind speed > 10 m/s. Sampling started when all these conditions were constant for at least 30 min.

The instrument was situated on the balcony of the Inter University Center of Marine Biology (Leghorn) at approximately 100 m from the sea and about 9 m above sea level (see Fig. 1). Two aerosol samples (7002 and 8439 m^3) were collected in the period September–October 1999.

2.2. Reagents and materials

Ultrapure water (> 18 MΩ), obtained from a Millipore Milli-Q system, was used to extract aerosol filters. Anhydrous sodium sulphate was heated for 12 h at 450 °C to remove any organic matter and kept at 20 °C until use. Glass fiber filters GF/F (Whatman, USA) were pre-treated at 450 °C for 12 h. Solvents were all for organic trace analysis (Baker); they were triple distilled in our laboratory before use. Standard organic compounds were commercially available from Supelco (Bellefonte, PA, USA) and Altech (Deerfield, USA). All glassware was cleaned before use by repeatedly washing with chromic and concentrated sulphuric acid mixture, ultrapure water and acetone and keeping at 130 °C for 30 min.

2.3. Extraction of organic compounds

2.3.1. Sea-water samples

Sea-water samples were separated into particulate and dissolved components by filtering through glass-fibre filters (porosity $\cong 0.45$ μm), within 12 h from the sampling, using an all-glass vacuum holder (Sartorius apparatus, Italy). Sea salts were removed from the filters by rinsing with about 20 ml ultrapure water.

The extraction of dissolved organic compounds was performed by adding 3 ml n-hexane to 3 l of sea-water and then stirring the resulting mixture for 15 min in a special glass apparatus (Desideri et al., 1992). After leaving the mixture to stand for 10 min, the n-hexane was collected into a microburette. A second extraction of the same sample was performed with 2 ml n-hexane and the resulting extract was added to the first.

The organic extract was dried over anhydrous sodium sulphate, evaporated to 100 μl under nitrogen flow (0.2 l/min) and then fractionated into four fractions of increasing polarity on a column (0.6 × 10 cm) containing Silica gel 60 HR (Merck), previously activated to 120 °C for 3 h. This procedure, described elsewhere (Desideri et al., 1995), allows organic compounds to be eluted according to their increasing polarity. Each fraction was cold evaporated to 100 μl under nitrogen flow. The PAH fraction was again concentrated and solvent-ex-changed to acetonitrile under a stream of nitrogen for HPLC analysis.

The extraction efficiency for the different chemical classes was calculated using a standard mixture containing aliphatic and aromatic hydrocarbons and phthalates at concentration levels of 10 ng/l (Desideri et al., 1998).

Particulate organic matter was extracted using the same method described below for the extraction of aerosol samples.

2.3.2. Aerosol samples

Quartz fibre filters were purified over night at 500 °C. After collection, filters were wrapped in pre-rinsed aluminium foil and stored at -20 °C until analysis.

Before extraction, the filters were spiked with internal standards (400 ng tetradecene and 200 ng di-heptylphthalate) for recovery determination. Filters were treated with a mixture of 3 ml ultrapure water and 1 ml methanol in an ultrasonic bath (Bransonic 3200, USA) for 15 min. The organic compounds were then extracted with 3 ml n-hexane-methylene chloride (1:1 v/v) by magnetic stirring for 15 min. The hydrophobic phase was obtained by centrifugation (5 min at 2500 rpm) and the extraction procedure was repeated three times. The second and third extracts were added to the first and the resulting solution was passed through an anhydrous sodium sulphate microcolumn and evaporated to 100 μl (Desideri et al., 1987).

2.4. Fluorescence spectra

A Perkin Elmer LS50B Luminescence Spectrometer was used to scan emission fluorescence spectra, (excitation wavelength 308 nm, emission wavelength interval 320–550 nm, em. slit 8 nm, exc. slit 8 nm, scan speed 360 nm/min). From the emission spectra, we calculated the maximum normalised fluorescence intensity (I_n) defined by:

$$I_n = I_{max}/I_{Raman} \times 100$$

where I_{max} is the maximum fluorescence intensity of fulvic acid (FA) band (440–460 nm) and I_{Raman} is the maximum intensity of the Raman peak of water (Degli Innocenti, 1993). I_n is a quantity defined in

arbitrary units, requires a calibration procedure (Cini et al., 1994b) and it is used here as an index of surfactant fluorescent organic matter.

2.5. Sodium ion analysis

The sodium ion concentration in the aerosol fractions was determined using portions of the hydroalcoholic solution obtained by sonication. An ion chromatography apparatus (Dionex 4500i) equipped with a gradient pump, a conductivity detector (CDM-1) and an eluent gas module (EDM-2) was used for the determination of the inorganic ions. A Dionex CS10 column (eluent = 1.0 ml/min of 20 mM HCl + 0.5 mM diaminopropionic acid) followed by a CMMS-2 micromembrane suppressor were employed for cation separation (Udisti et al., 1994). Chromatographic data acquisition and elaboration were performed by a Dionex AI-450 integration software.

2.6. HRGC and GC-MS analysis

The organic fractions were analysed by a Varian 3400 (Palo Alto, USA) gas chromatograph (GC) equipped with a FID detector. Samples were injected into the GC using a septum programmable injector (SPI, Varian) according to the following temperature program: injection at 40 °C, followed by a rapid increase to 300 °C and isotherm for 1 min. The GC column temperature program was: 40 °C for 1 minute, followed by a ramp of 4 °C/min to 300 °C where it was held for 15 min. A Supelco capillary column PTE-5 (30 m, 0.25 mm i.d., 0.25 μm thickness) was used with high purity grade helium carrier gas at a flow of 1 ml/min. The chromatographic peaks were analysed with a Varian 3400 integrator.

Confirmatory GC/MS analyses of the organic compounds were performed using a Varian 4290 gas chromatograph coupled with a Finnigan ion trap mass detector. Electron impact mass spectra were obtained at 70 eV of ionization energy.

All peaks were identified by using gas chromatographic indices with eight *n*-alkanes as standards (C_8, C_{12}, C_{16}, C_{20}, C_{24}, C_{28}, C_{32}, C_{34}) and a reference calibration table.

The quantities of organic compounds were determined by comparing their peak areas with the nearest *n*-alkanes peaks as standards.

2.7. HPLC analysis

HPLC analysis was carried out by a double-pump liquid chromatograph (LC-10AD VP, Shimadzu) equipped with a diode array detector SDP M10AVP and a fluorescence detector RF-551. A CLASS VP 4.2 chromatographic data system (Shimadzu) was used for chromatogram acquisition and handling. The separation of PAHs was carried out using a reversed phase Supelcosil™ LC-PAH column (5 μm particle size, 4.6 mm ID × 25 cm). The PAHs were eluted by an acetonitrile gradient in water (flow 1.5 ml/min) according to the following sequence: after 5 min, the initial 40% concentration of acetonitrile in water was increased linearly to 100% in 25 min and held under these conditions for 15 min. PAHs concentrations were obtained by comparing the peak areas with those of known amounts of standards run under the same analytical conditions.

2.8. Methylene blue active substances (MBAS)

Anionic surfactants were estimated by MBAS method according to IRSA-CNR method (1983).

2.9. Blanks and detection limit

Precautions were taken to avoid contamination in the laboratory. Blank filters yielded only traces of interferents for the organic matter.

Sea-water detection limits were 2 ng/l for *n*-alkanes and 1 ng/l for alkylbenzenes and phthalates. The sea-water detection limits for PAHs ranged from 0.008 ng/l for individual compounds with more than three rings to 0.4 ng/l for naphthalene.

For aerosol samples, the detection limit for *n*-alkanes and phthalates was 0.1 ng/m^3 while for PAHs it ranged from 0.001 ng/m^3 for individual compounds with more than three rings to 0.1 ng/m^3 for naphthalene.

3. Results

3.1. SML and SSL samples

Table 2 reports the mean concentrations, expressed in μg/l, of individual *n*-alkanes, phthalates,

Table 2

Mean concentration (μg/l) of selected organic compounds in three samples taken in Quercianella (Station 3). The amount of suspended material (mg dry wt./l) in the SSL was 3.9 and in the SML was 5.2

Compounds	Dissolved			Particulate			Compounds	Dissolved			Particulate		
	3SML	3SSL	EF	3SML	3SSL	EF		3SML	3SSL	EF	3SML	3SSL	EF
nC_{14}	0.011	0.002[a]	5.5	0.057	0.004	14.7	Naphthalene	0.051	0.047	1.1	0.578	0.158	3.7
nC_{15}	0.007	0.002[a]	3.5	0.395	0.016	25.3	Acenaphthylene	0.353	0.254	1.4	13.3	1.17	11.4
nC_{16}	0.014	0.009	1.6	0.624	0.051	12.3	Acenaphtene	0.020	0.012	1.7	0.169	0.861	0.2
nC_{17}	0.008	0.008	1.0	0.718	0.066	10.8	Fluorene	0.008	0.018	0.4	0.041	0.016	2.6
nC_{18}	0.008	0.009	0.9	0.577	0.066	8.7	Phenanthrene	0.020	0.002	10.0	0.210	0.007	30.0
nC_{19}	0.007	0.002[a]	3.5	0.213	0.043	5.0	Anthracene	0.002	0.015	0.1	0.124	0.088	1.4
nC_{20}	0.007	0.002[a]	3.5	0.120	0.043	2.8	Fluoranthene	0.012	0.007	1.7	0.449	0.046	9.8
nC_{21}	0.007	0.002[a]	3.5	0.073	0.031	2.3	Pyrene	0.033	0.010	3.3	0.178	0.028	6.4
nC_{22}	0.009	0.004	2.3	0.057	0.023	2.4	Benzo(a)anthracene	0.001	0.001	1.0	0.052	0.014	3.7
nC_{23}	0.009	0.004	2.3	0.042	0.031	1.3	Chrysene	0.001	0.001	1.0	0.038	0.014	2.7
nC_{24}	0.037	0.032	1.2	0.707	0.144	4.9	Benzo(b)fluoranthene	0.022	0.019	1.2	0.061	0.007	8.7
nC_{25}	0.020	0.015	1.3	0.031	0.027	1.1	Benzo(k)fluoranthene	0.011	0.008	1.4	0.026	0.003	8.7
nC_{26}	0.013	0.008	1.6	0.031	0.043	0.7	Benzo(a)pyrene	0.003	0.002	1.4	0.005	0.006	0.8
nC_{27}	0.012	0.007	1.7	0.057	0.086	0.7	Dibenzo(a,h)anthracene	0.003	0.001	3.0	0.027	0.004	6.7
nC_{28}	0.023	0.018	1.3	0.770	0.140	5.5	Benzo(g,h,i)perylene	0.001	0.001	1.0	0.031	0.008	3.9
nC_{29}	0.013	0.008	1.6	0.104	0.156	0.7							
nC_{30}	0.011	0.006	1.8	0.073	0.031	2.3	Total PAHs	0.539	0.398	1.4	15.3	2.42	6.3
nC_{31}	0.010	0.009	1.1	0.068	0.078	0.9							
nC_{32}	0.025	0.019	1.3	0.796	0.055	14.6	Ethylbenzene	0.009	0.006	1.6			
nC_{33}	0.007	0.006	1.2	0.014	0.016	0.9	m/p-Xylene	0.033	0.023	1.4			
nC_{34}	0.026	0.011	2.4	0.322	0.078	4.1	o-Xylene	0.002	0.011	0.2			
							n-Propylbenzene	0.012	0.007	1.7			
Total n-alkanes	0.284	0.183	1.6	5.85	1.23	4.8	1-Methyl-3-ethylbenzene	0.005	0.003	1.7			
							Mesytilene	0.008	0.006	1.3			
Di-n-propylphthalate	b.d.l.	b.d.l.		0.140	0.020	7.2	1,2,4- Trimethylbenzene	0.015	0.007	2.1			
Di-isobutylphthalate	0.188	0.092	2.0	0.057	0.015	3.8							
Di-n-butylphthalate	0.223	0.065	3.4	0.213	0.057	3.7	Total alkylbenzenes	0.084	0.063	1.3			
Bis-(2-ethylhexyl)phthalate	0.154	0.097	1.6	1.58	0.498	3.2							
Di-n-nonylphthalate	0.003	0.002	1.5	0.335	0.252	1.3	MBAS	45	39	1.2			
Total phthalates	0.568	0.256	2.2	2.33	0.842	2.8	I_n (arbitrary units)	66.8	36.1	1.8			

b.d.l. = below detection limit.

[a] Detection limit.

PAHs and alkylbenzenes found in the SML samples and in their related underlying water collected at Quercianella (station 3). Such compounds represent almost all the organic substances extractable with *n*-hexane or *n*-hexane-methylene chloride (1:1 v/v).

Dissolved *n*-alkanes in SML exhibit a different distribution with respect to the particulate hydrocarbons, which reflects the probable loss of low molecu-lar weight compounds from the surface film by evaporation.

Aliphatic hydrocarbons appear to be accumulated in the surface microlayer with reference to the under-lying water, according to the enrichment factors (EF) shown in Table 2. At the station 3, the particulate alkane enrichment factor (4.8) is greater than the dissolved alkane enrichment factor (1.6). This could

Table 3
Total concentration (μg/l) of organic compounds extractable with *n*-hexane in dissolved fractions of SML and SSL samples. Mean values based on three samples collected in the same site

	n-Alkanes (C_{14}–C_{34})	Alkylbenzenes	Phthalates	PAHs	MBAS	I_n
Station 1						
SML	0.483	0.024	0.658	0.214	40	31.9
SSL	0.173	0.028	0.458	0.063	37	24.3
EF	2.8	0.9	1.4	3.4	1.1	1.3
Station 2						
SML	0.826	0.074	1.70	5.31	45	23.4
SSL	0.530	0.046	0.641	0.418	38	24.0
EF	1.6	1.6	2.7	12.7	1.2	1.0
Station 3						
SML	0.284	0.084	0.568	0.539	45	66.8
SSL	0.182	0.063	0.256	0.398	39	36.1
EF	1.6	1.3	2.2	1.4	1.2	1.8
Station 4						
SML	0.213	0.077	0.760	0.661	43	29.3
SSL	0.140	0.079	0.497	0.194	40	33.3
EF	1.5	1.0	1.5	3.4	1.1	0.9
Station 5						
SML	0.254	0.132	0.191	0.322	44	39.7
SSL	0.187	0.103	0.095	0.095	41	26.9
EF	1.4	1.3	2.0	3.4	1.1	1.5
Station 7						
SML	1.40	0.072	0.273	12.0	63	125
SSL	0.824	0.052	0.241	0.297	44	35.0
EF	1.7	1.4	1.1	40.3	1.4	3.6
Station 8						
SML	1.81	0.113	0.852	15.2	49	110
SSL	0.628	0.163	0.588	3.05	42	22.7
EF	2.9	0.7	1.4	5.0	1.2	4.8
Station 9						
SML	0.675	0.519	12.6	3.33	68	190
SSL	0.287	0.247	0.396	1.06	45	102
EF	2.4	2.1	31.9	3.1	1.5	1.9

be partially explained by the higher concentration of particulate matter in the SML sample (5.2 mg/l) compared to the SSL sample (3.9 mg/l).

PAHs show a similar behaviour. EF values were 1.4 for dissolved compounds and 6.3 for particulate ones. The stronger enrichment observed in the particulate phase for these compounds reflects their stronger tendency to be associated with particulate matter (Cripps, 1990). The major contributors to PAH concentrations are naphthalene, acenaphthylene, acenaphthene, phenantrene, fluoranthene and pyrene: acenaphthylene gives the highest contribution, being 64–65% in the dissolved SML and SSL samples and 48–87% in the particulate SML and SSL samples.

Di-n-propyl, di-n-butyl, di-isobutyl, di-2-ethylhexyl and di-n-nonylphthalate represent the whole class of phthalates; the first and the last compounds in the series give a minor contribution to total phthalates. The enrichment factors of phthalates in the dissolved and particulate phases are similar (2.2 and 2.8, respectively) and reflect a smaller affinity of phthalates for the particulate matter (presumably due to their surfactant properties) with respect to aliphatic hydrocarbons and PAHs.

The C_2 and C_3 alkylbenzenes are the only components of this class: their concentrations in the dissolved phase are very low and are under the detection limit in the particulate phase.

Table 2 also reports the MBAS concentrations and the maximum normalized fluorescence intensity (I_n), which is an index of surfactant fluorescent organic matter SFOM, particularly fulvic acids of biogenic origin. These compounds can form organic complexes with hydrophobic compounds such as aliphatic hydrocarbons and PAHs and enhance their solubility in sea-water. MBAS and I_n values were not measured in the particulate fractions.

Tables 3 and 4 summarize the mean total concentration (expressed in µg/l) of organic compounds extractable with n-hexane or n-hexane-methylene chloride (1:1 v/v) as well as their EF values for all SML and SSL samples collected, with the exception of the strongly polluted sample taken in the inner zone of the harbour of Leghorn (station 6).

The chemical composition of all the classes of organic compounds is similar to that reported in Table 2 and for this reason the concentration of every single compound is not listed.

Experimental data show variations in the levels of the different classes of compounds in the study area.

As regards the dissolved fraction (see Table 3), it can be observed that the concentrations and also the EF values at stations 1, 4 and 5 are similar to those found at station 3 (Quercianella), suggesting a similar slight pollution in these zones. Higher levels of

Table 4
Total concentration (µg/l) of organic compounds extractable with n-hexane-methylene chloride (1:1 v/v) in the particulate fractions of SML and SSL samples. Mean values based on three samples collected in the same site

	n-Alkanes (C_{14}–C_{34})	Phthalates	PAHs	Particle amount (mg/l)
Station 1				
SML	1.23	1.76	9.01	13.6
SSL	0.452	0.983	0.785	8.7
EF	2.7	1.8	11.5	1.6
Station 2				
SML	46.5	5.86	98.0	8.3
SSL	1.01	0.825	0.869	3.7
EF	46.0	7.1	112.8	2.3
Station 3				
SML	5.85	2.33	15.3	5.2
SSL	1.23	0.827	2.42	3.9
EF	4.8	2.8	6.4	1.3
Station 4				
SML	1.41	2.62	10.0	3.9
SSL	0.267	0.684	4.00	2.1
EF	5.3	3.8	2.5	1.8
Station 5				
SML	0.427	2.76	0.826	3.6
SSL	1.13	0.456	0.551	3.0
EF	0.4	6.1	1.5	1.2
Station 7				
SML	1.85	1.37	9.59	3.9
SSL	0.307	1.06	2.42	2.5
EF	6.0	1.3	4.0	1.6
Station 8				
SML	39.1	24.4	45.8	6.5
SSL	1.84	0.396	3.02	2.1
EF	21.3	61.6	15.2	3.1
Station 9				
SML	410	69.9	154	31.2
SSL	5.62	1.81	7.54	7.5
EF	73	38.7	20.4	4.2

Table 5
Mean concentration (μg/l) of selected organic compounds in three samples taken in "fishing boats quay" (Harbour of Leghorn) (station 6). The amount of particulate matter (mg dry wt./l) in the SSL was 5 and in the SML was 72.5

Compounds	Dissolved			Particulate			Compounds	Dissolved			Particulate		
	SML	SSL	EF	SML	SSL	EF		SML	SSL	EF	SML	SSL	EF
nC_{14}	0.099	0.003	33.0	12.4	1.00	12.4	Naphthalene	22.0	0.274	80.2	65.5	0.150	437
nC_{15}	0.653	0.014	46.6	85.9	1.02	84.2	Acenaphthylene	33.2	0.379	87.6	77.0	0.135	570
nC_{16}	1.90	0.092	20.6	217	4.25	51.0	Acenaphtene	138	0.575	240	17.3	0.060	288
nC_{17}	3.82	0.022	173.7	432	1.49	291	Fluorene	9.29	0.095	97.8	1.10	0.020	55.0
nC_{18}	5.45	0.019	286.8	545	1.25	438	Phenanthrene	18.4	0.044	419	1.84	0.015	123
nC_{19}	5.95	0.017	349.8	741	0.335	2212	Anthracene	70.3	0.074	950	8.30	0.023	369
nC_{20}	7.21	0.037	194.9	488	0.620	787	Fluoranthene	20.1	0.144	140	6.73	0.013	539
nC_{21}	5.56	0.013	427.4	405	0.080	5066	Pyrene	11.7	0.058	202	9.19	0.015	613
nC_{22}	3.52	0.005	703.8	297	0.055	5406	Benzo(a)anthracene	3.57	0.008	446	2.83	0.020	141
nC_{23}	2.06	0.007	294.0	178	0.040	4455	Chrysene	4.87	0.014	348	8.48	0.112	75.7
nC_{24}	1.49	0.065	22.9	124	0.040	3107	Benzo (b)fluoranthene	0.143	0.005	28.6	10.2	0.120	85.0
nC_{25}	0.962	0.006	160.3	90.4	0.030	3014	Benzo(k)fluoranthene	0.068	0.002	34.0	4.48	0.060	74.6
nC_{26}	0.680	0.006	113.3	21.2	0.020	1062	Benzo(a)pyrene	0.285	0.003	95.0	2.98	0.016	186
nC_{27}	3.95	0.006	657.7	24.3	0.015	1619	Dibenzo(a,h)anthracene	0.400	0.004	100	4.14	0.010	414
nC_{28}	0.263	0.013	20.2	5.29	0.020	265	Benzo(g,h,i)perylene	0.474	0.003	158	5.86	0.027	217
nC_{29}	0.137	0.011	12.5	3.41	0.045	75.7							
nC_{30}	0.098	0.029	3.4	2.29	0.030	76.3	Total PAHs	333	1.68	198	226	0.795	284
nC_{31}	0.032	0.006	5.3	0.363	0.025	14.5							
nC_{32}	0.025	0.009	2.8	0.653	0.090	7.3	Ethylbenzene	0.173	0.017	10.2			
nC_{33}	0.004	0.002	2.0	0.218	0.020	10.9	m/p-Xylene	0.189	0.034	5.6			
nC_{34}	0.014	0.010	1.4	0.290	0.010	29.0	o-Xylene	0.172	0.029	5.9			
							Isopropylbenzene	0.132	0.010	13.2			
Total n-alkanes	43.9	0.392	112	3674	10.5	351	n-Propylbenzene	0.193	0.017	11.4			
							1-Methyl-3-ethylbenzene	0.135	0.015	9.0			
Di-ethylphthalate	0.006	0.004	1.5	6.67	0.055	121	Mesytilene	0.156	0.016	9.8			
Di-iso-propylphthalate	0.012	0.007	1.7	21.2	0.220	96.2	1,2,4-Trimethylbenzene	0.123	0.028	4.4			
Di-n-propylphthalate	0.008	0.004	20.0	7.76	0.350	22.2	sec-Butylbenzene	0.062	0.012	5.2			
Di-isobutylphthalate	0.110	0.043	2.6	29.3	0.400	73.2	p-Isopropyltoluene	0.033	0.013	2.5			
Di-n-butylphthalate	0.286	0.260	1.1	21.2	1.99	10.7							
Di-n-pentylphthalate	0.156	0.114	1.4	41.6	0.365	114	Total alkylbenzenes	1.57	0.191	8.2			
Bis-(2-ethylhexyl)phthalate	33.0	0.194	170	41.6	0.187	222							
Di-n-nonylphthalate	0.005	0.003	1.6	6.96	0.170	40.9							
Di-n-decylphthalate	b.d.l.	b.d.l.	b.d.l.	0.795	0.035	22.7	MBAS	82	46	1.8			
Total phthalates	33.6	0.629	53.4	177	3.77	46.9	I_n (arbitrary units)	539	126	4.3			

b.d.l. = below detection limit.

anthropogenic compounds have been measured at stations 2, 7, 8 and 9. The overall *n*-alkane content varied from 0.213 to 1.81 µg/l for SML and from 0.140 to 0.824 µg/l for SSL but greater variations were observed for phthalates and PAHs. The concentration of PAHs ranged from 0.214 to 15.2 µg/l for the surface films and from 0.063 to 3.05 µg/l for bulk-water, while the amounts of phthalates varied from 0.191 to 12.6 µg/l for SML and from 0.095 to 0.641 µg/l for SSL.

Concentrations of MBAS were reasonably homogeneous in the study area while I_n values were particularly high in the surface films of samples 7, 8 and 9 where elevated concentrations of dissolved PAHs were found.

Table 4 reports the mean total concentration, expressed in µg/l, of *n*-alkanes, phthalates and PAHs determined in the particulate fraction of the same samples shown in Table 3.

Also in this phase, organic compounds are preferentially enriched in the surface microlayer; particulate *n*-alkanes varied from 0.427 to 410 µg/l for SML and from 0.267 to 5.62 µg/l for SSL and phthalates from 1.37 to 69.9 µg/l for SML and from 0.396 to 1.81 µg/l for SSL, and PAHs from

0.826 to 154 µg/l in the SML and 0.551 to 7.54 µg/l in SSL.

Particulate matter was also systematically higher in the SML (range 3.6–31.2 mg/l) than in SSL (range 2.1–8.7 mg/l), partially explaining the higher concentrations of particulate organic compounds in the surface microlayer compared to sub-surface waters.

The highest concentrations of *n*-alkanes, phthalates and PAHs were found in the SML sample collected at station 9, where the amount of particulate matter (31.2 mg/l) and its EF (4.2) are also the greatest. This station, situated at the mouth of the harbour, is heavily polluted. The value of 1.07 for the odd/even ratio (C_{15}–C_{32}) suggests a high anthropogenic contribution to the particulate hydrocarbons in this station.

Station 8, situated in front of the Leghorn harbour, is also highly contaminated.

Experimental data concerning the station 6 in the inner zone of the Port of Leghorn are reported in Table 5. Phthalates and, particularly, aliphatic hydrocarbons and PAHs showed a strong increase in this zone compared to the values determined in all the other stations.

Table 6
Concentration (ng/m^3) of *n*-alkanes, phthalates and PAHs in fractionated aerosol samples

Fraction	Equivalent aerodynamic diameter (µm)	*n*-Alkanes	Phthalates	Total PAHs	PAHs with four or more rings
Sample 1 volume, 7002 m^3					
1	7.2–10	3.8	3.5	0.089	0.017
2	3.5–7.2	17.7	8.6	0.369	0.053
3	1.5–3.5	10.8	5.2	0.347	0.069
4	0.95–1.5	6.3	6.4	0.340	0.081
5	0.49–0.95	7.0	5.4	0.274	0.039
6	< 0.49	3.4	4.9	0.161	0.036
Total		49.1	33.9	1.58	0.295
Sample 2 volume, 8439 m^3					
1	7.2–10	22.7	20.5	0.265	0.005
2	3.5–7.2	14.6	11.0	0.077	0.025
3	1.5–3.5	9.1	14.9	0.265	0.055
4	0.95–1.5	21.4	11.1	0.393	0.078
5	0.49–0.95	23.1	19.1	0.391	0.076
6	< 0.49	3.5	14.3	0.229	0.052
Total		94.5	90.9	1.62	0.291

The gas-chromatograms concerning dissolved and particulate hydrocarbons present in SML samples showed a regular distribution of resolved compounds (R), mainly *n*-alkanes from C_{14} to C_{34}, over a complex mixture of unresolved substances (U). The U/R ratio was very high (> 20) for particulate hydrocarbons as in the case of chemicals from petroleum residues (Mazurek and Simoneit, 1984); the odd/even ratio (1.1) calculated for *n*-alkanes (C_{15}–C_{32}) present in surface films supports a dominance of petrogenic compounds. In bulk-water, the U/R ratios are about 3 for particulate hydrocarbons and much lower than 3 for dissolved compounds.

The large concentrations of phthalates in the site 6 underline a high deterioration of its water.

Aliphatic hydrocarbons, phthalates, PAHs and SFOM showed particularly high EF values, in agreement with the observation that slicked areas typically have higher EF for organics compared to non-slicked areas (Rumbold and Snedaker, 1999).

3.2. Aerosol samples

Table 6 shows the concentrations, expressed in ng/m^3, of *n*-alkanes, phthalates, total PAHs and PAHs with more than three rings, measured in the different fractions of the two aerosol samples collected. PAHs with more than three rings are reported separately because they are known to have mutagenic properties (Keith, 1997).

Among phthalates, di-*n*-butylphthalate, di-isobutylphthalate and bis-(2-ethylhexyl)phthalate were predominant.

Aliphatic hydrocarbons with a carbon atom number ≥ 16 were found in the Leghorn aerosol.

PAHs composition is similar to that observed in SML and SSL samples but their concentrations in the aerosol are about one or two orders of magnitude lower than *n*-alkanes in agreement to that found by Sicre et al. (1987a,b). It should be noted that PAHs, particularly those with two or three rings, are transferred slightly from water to air even in the presence of any surfactant in SML (Cini et al., 1994a)

The data of Table 6 show a homogeneous distribution of the various compounds in the two samples but different concentrations in the six size fractions.

4. Discussion

4.1. SML and SSL

Aliphatic hydrocarbons, alkylbenzenes, PAHs, phthalates, anionic surfactants and SFOM were found to be present in the surface film and the underlying water of all the samples. Hydrocarbons concentrate in the particulate phase according to their hydrophobic properties with the exception of alkylbenzenes which have been only detected in the dissolved phase at very low amounts. This behaviour seems to be general and not connected to the pollution level of the investigated sampling site, and contrasts with the results observed for *n*-alkanes by Marty and Saliot (1976) and Marty et al. (1988). These authors found higher concentrations of *n*-alkanes in the dissolved fraction with respect to the particulate fraction of sea-water samples collected in the western Mediterranean sea and northern Adriatic sea. Owing to their surfactant properties, phthalates are more homogeneously distributed between the dissolved and particulate phases.

4.1.1. n-Alkanes and PAHs

Table 7 shows the concentration ranges of *n*-alkanes found in coastal areas of Tyrrhenian sea in this study compared with those from previous studies in the Mediterranean and Adriatic sea and in the coastal waters of the English Channel.

In the samples containing a smaller anthropogenic influence (stations 1, 3, 4, 5), the amounts of dissolved and particulate *n*-alkanes in SSL and SML are similar to those reported for the Adriatic sea and open Mediterranean waters, suggesting minor contamination. These concentrations can be considered as background values for the investigated area.

Stations 2, 7, 8, 9 are exposed to an intense maritime traffic and may be influenced by local anthropogenic inputs; however, the content of dissolved hydrocarbons in subsurface water is relatively low, while greater levels of *n*-alkanes were measured in the particulate phase.

The high concentrations of *n*-alkanes in sample 6, taken in the inner zone of the harbour and characterised by a visible slick, are comparable with those

Table 7
Literature values for concentrations (μg/l) of dissolved and particulate *n*-alkanes in SSL and SML samples

Sea area	SSL		SML		References
	Dissolved	Particulate	Dissolved	Particulate	
Tyrrhenian Sea (September–October '99)					
Coastal area near Leghorn					
stations 1, 3, 4, 5	0.140–0.187	0.267–1.23	0.213–0.483	0.427–5.85	This study
stations 2, 7, 8, 9	0.287–0.824	0.307–5.62	0.675–1.81	1.85–410	This study
station 6	0.391	10.5	43.9	3674	This study
Western Mediterranean Sea					
coastal area					
Marseilles (April '73)	2.38	7.18	15	1214	Marty and Saliot (1976)
offshore waters					
Ligurian Sea (April '81)	20.6	0.52			Saliot et al. (1985)
Rhone delta (April '81)	0.05	0.18			Saliot et al. (1985)
English Channel					
coastal waters					
Roscoff (May '72)	0.11	0.28	17.71	97.99	Marty and Saliot (1976)
Northern Adriatic Sea					
offshore waters					
Transect from Rovinj to the Po river delta (July '80, October '82)	0.177–0.386	0.031–0.049	0.139–1.073	0.097–1.0	Marty et al. (1988)

found in polluted coastal waters off Marseilles (France).

Literature values for the enrichment factor of dissolved and particulate *n*-alkanes range from 0.3 to 3–4 for both coastal and open sea waters (Marty et al., 1979; Boehm, 1980; Ho et al., 1982).

In areas contaminated by petroleum, the surface film can be enriched by a factor of 1000 with hydrocarbons as a result of slick formation (Marty and Saliot, 1976; Hardy et al., 1987). Sometimes, higher EF values for dissolved *n*-alkanes with respect to particulate hydrocarbons have been reported (Marty and Saliot, 1976). According to our results, the EF values of *n*-alkanes in the particulate phase are always higher than those dissolved.

The concentrations of total PAHs in the particulate phase of SML suggest that almost all the sites near Leghorn coast contain large quantities of these pollutants compared with other contaminated areas such as Chesapeake Bay (USA) (Hardy et al., 1990) and San Diego Bay (California, USA) (Zeng and Vista, 1997). In such zones, the highest concentra-

tions of particulate PAHs in SML are about 10 μg/l.

Much lower values for PAHs were found in the dissolved phase of SML and SSL from different water masses of various oceans. For example, dissolved aromatics represent a small fraction ($\sim$ 10%) of the total at each of the sites analysed in Chesapeake Bay (USA) (Hardy et al., 1990).

According to Saliot et al. (1985), concentrations of dissolved and particulate PAHs in the Ligurian Sea ranged from 0.03 to 0.11 μg/l, and are comparable to those determined in pristine and scarcely polluted Antarctic marine environment. The mean value in the Bransfield Strait (Southern Ocean) was 0.23 μg/l (Cripps, 1990) and similar levels were estimated by Desideri et al. (1989) in the Terra Nova Bay (Ross Sea). Far greater values (9.4 μg/l) of particulate PAHs were measured in polluted waters of the Weddell Sea (Comes et al., 1987).

As regards our data, it should be noted that two- or three-ring PAHs, such as naphthalene and acenaphthylene, represent almost all the PAHs, and that

in some samples the concentration of acenaphthylene is quite high.

At station 6 (see Table 5), the concentration of dissolved PAHs in the surface film (333 μg/l) is greater than that of particulate hydrocarbons (226 μg/l) and this behaviour is in contrast with the observation that most of the PAHs are associated with particles, particularly in polluted samples (Hardy et al., 1987). These results can be attributed to the presence of petroleum slicks, which dissolve PAHs and allow these compounds to reach unusual concentration levels in water.

About 7000 ships enter the Port of Leghorn per year and this traffic can be responsible for the high levels of low molecular weight PAHs found in the study area.

According to toxicological information, exposure of fish eggs or larvae to concentrations of petroleum hydrocarbons greater than about 100 μg/l results in harmful effects (Hardy and Word, 1986). Toxic effects are expected in seawater solution at fluoranthene and benzo(a)pyrene concentrations ranging from 50 to 500 ng/l and from 10 to 100 ng/l, respectively (OSPAR, 1993). Reduced or abnormal larval hatch of fish eggs can result from exposition

to concentrations of benzo(a)pyrene as low as 0.1 to 0.2 μg/l (Hardy and Word, 1986). These limits are often exceeded in the study area, in particular at stations 6, 8 and 9 in the Port of Leghorn and at Meloria's Tower. In addition, at stations 2 and 7, benzo(a)pyrene concentrations in the particulate phase are greater than 0.01 μg/l pointing out a "high degree of pollution" according to Shabad and Smirnov (1973).

4.1.2. Phathalates

Phthalate esters have become widely spread contaminants of the aquatic environment because of their large use in industrial, agricultural and domestic applications and as non-reactive plasticizers improving the flexibility and workability of polymeric materials (Turner and Rawling, 2000).

High concentrations of phthalates from ppb to ppm levels (Fatoki and Ogunfowokan, 1993; Preston and Al-Omran, 1989; Long et al., 1998; Tan, 1995; Vitali et al., 1997) were found in freshwaters from various rivers in central Italy. The content of bis-(2-ethylhexyl)phthalate, one of the most important phthalates, accounting for nearly 90% of European plasticizer use (Giam et al., 1984), ranged in coastal
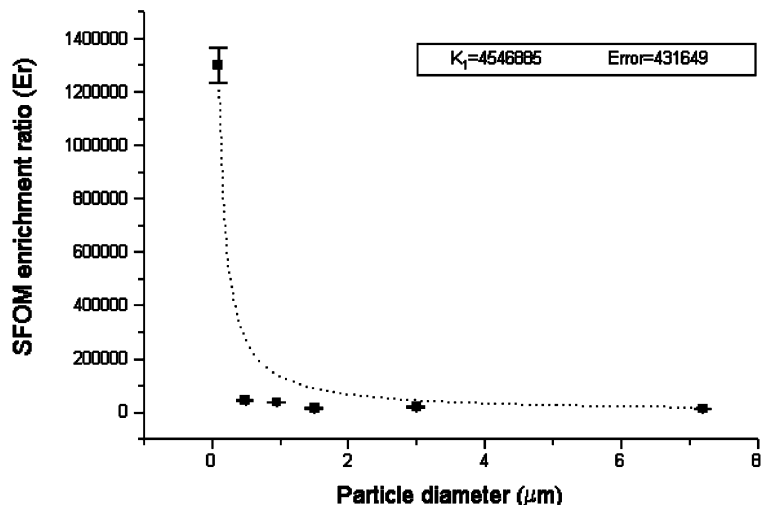

Fig. 2. Experimental values of the enrichment ratio of SFOM as a function of fractionated particle aerosol. The vertical bars represent the maximum error in Er. The curve represents the SDAM fitting with $\Delta r = 0.01$ and 0.1 μm for the smallest class of particles. The evaluation of the constant K_1 and the corresponding error are also reported.

waters from 0.13 μg/l in the Gulf of Mexico (Giam et al., 1978) to 0.1–2.2 μg/l in Tees Bay and Plymouth Sound in the UK. (Law et al., 1991). Ppt levels were reported in open waters of Atlantic Ocean (Giam et al., 1978).

The phthalate concentrations measured in our samples are generally comparable with those reported for coastal waters with the exception of those measured in stations 6 and 9 where greater levels were found.
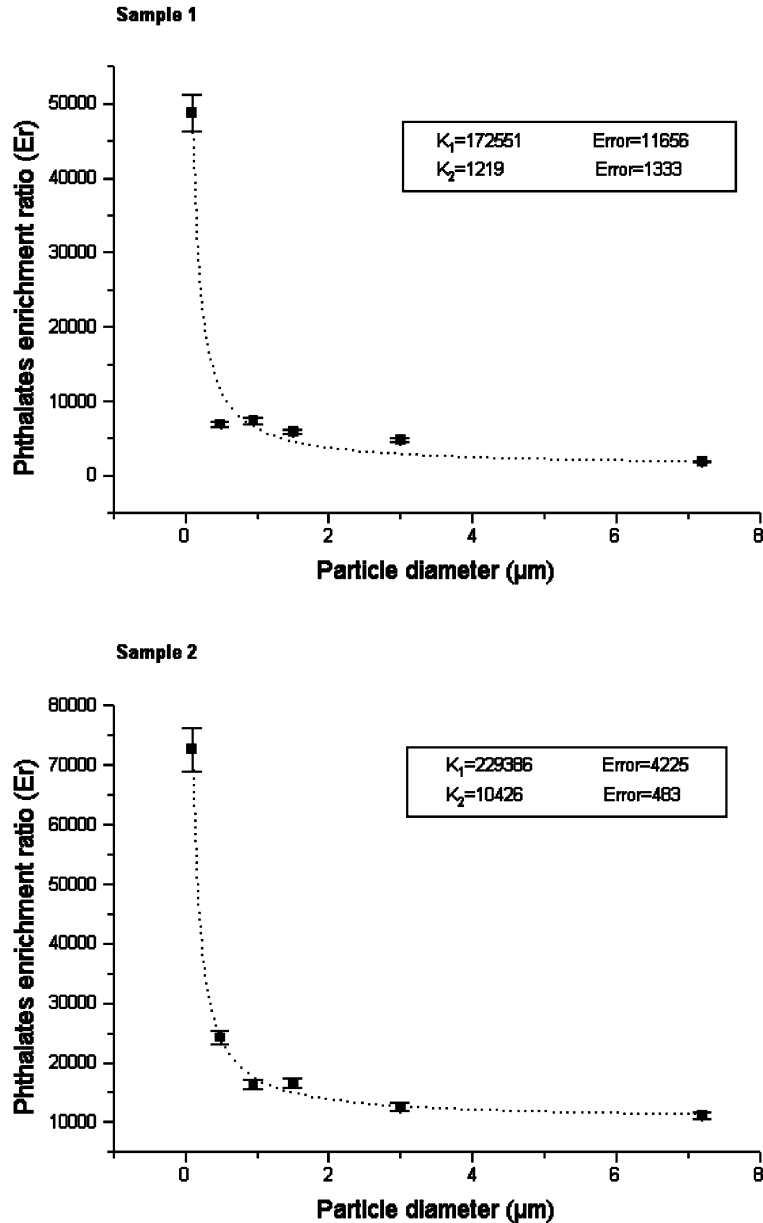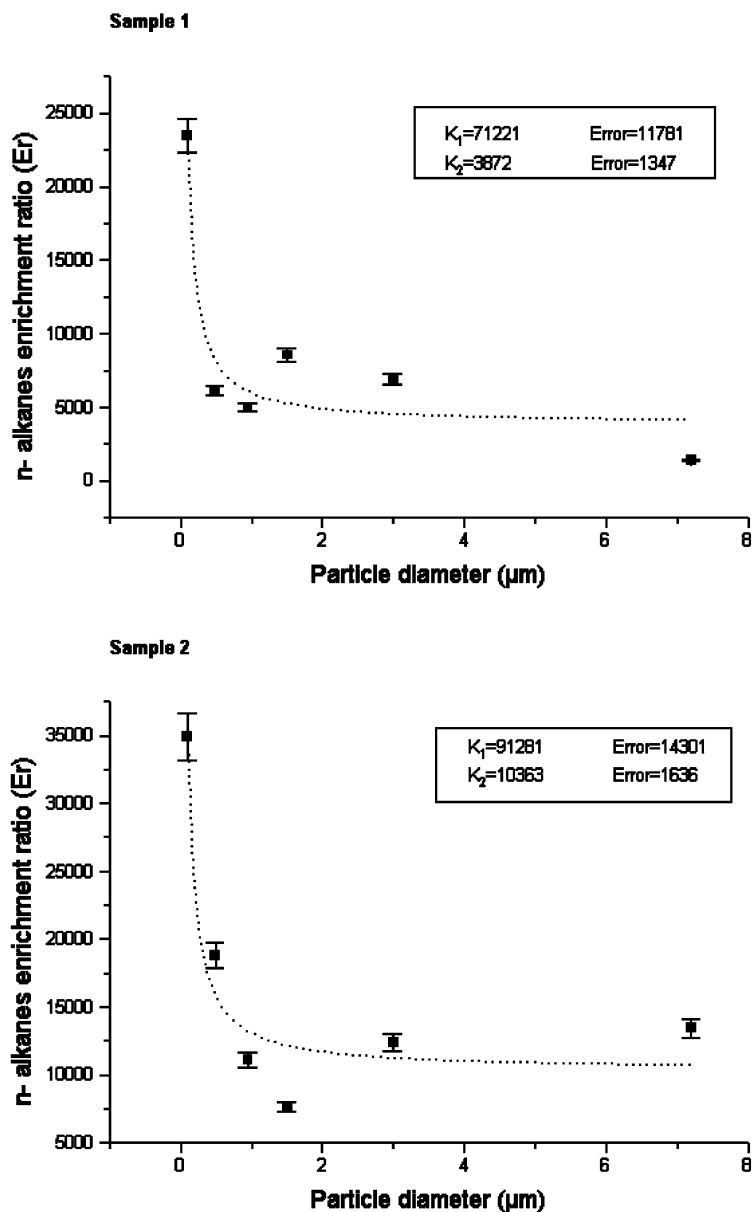

Fig. 3. Experimental values of the enrichment ratios of phthalates as a function of fractionated particle aerosol. The vertical bars represent the maximum error in Er. The curve represents the SDAM fitting with $\Delta r = 0.01$ and 0.1 μm for the smallest class of particles. The evaluation of the constant K_1, K_2 and the corresponding error are also reported.

Phthalates tend to concentrate along the aquatic food chains (Mayer et al., 1972; Russel et al., 1985; Shanker et al., 1985) and, recently, have been in-

cluded in the list of suspect environmental endocrine disrupters (EED) (Keith, 1997). Therefore, the significant concentrations of phthalate esters and, par-

Sample 1

Sample 2

Fig. 4. Experimental values of the enrichment ratios of *n*-alkanes as a function of fractionated particle aerosol. The vertical bars represent the maximum error in Er. The curve represents the SDAM fitting with $\Delta r = 0.01$ and 0.1 μm for the smallest class of particles. The evaluation of the constant K_1, K_2 and the corresponding errors are also reported.
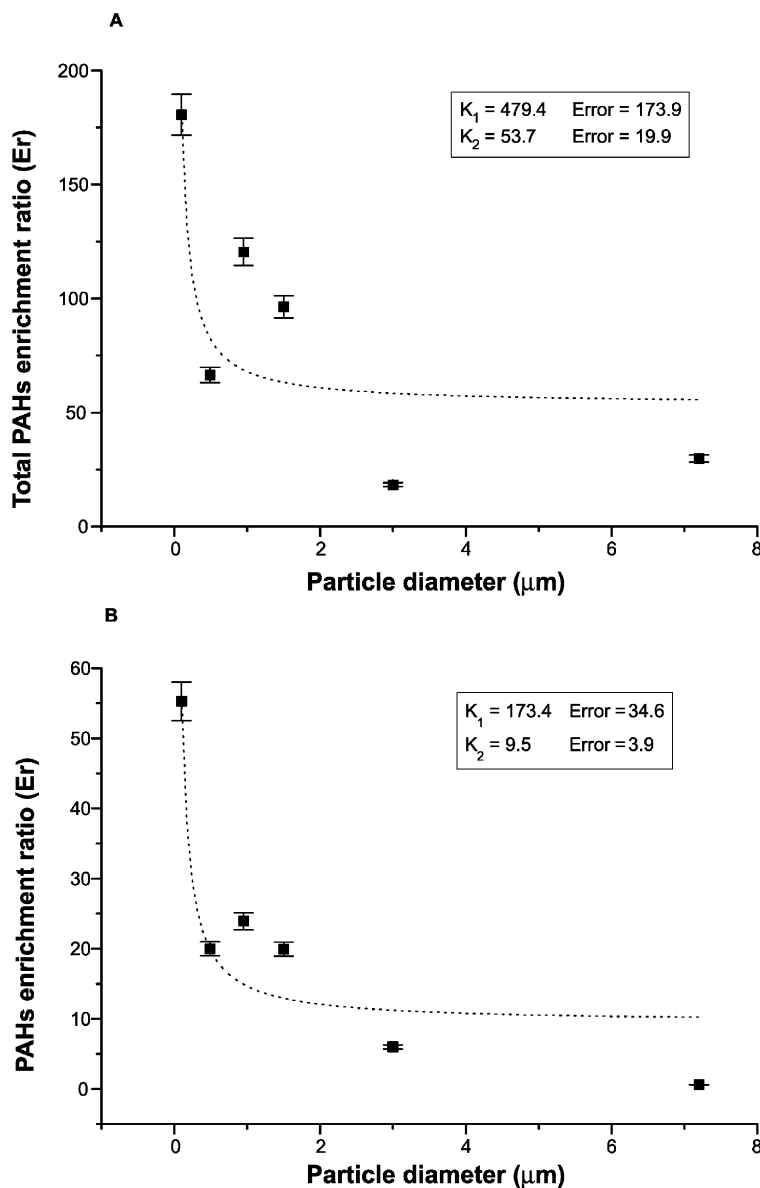
A

B
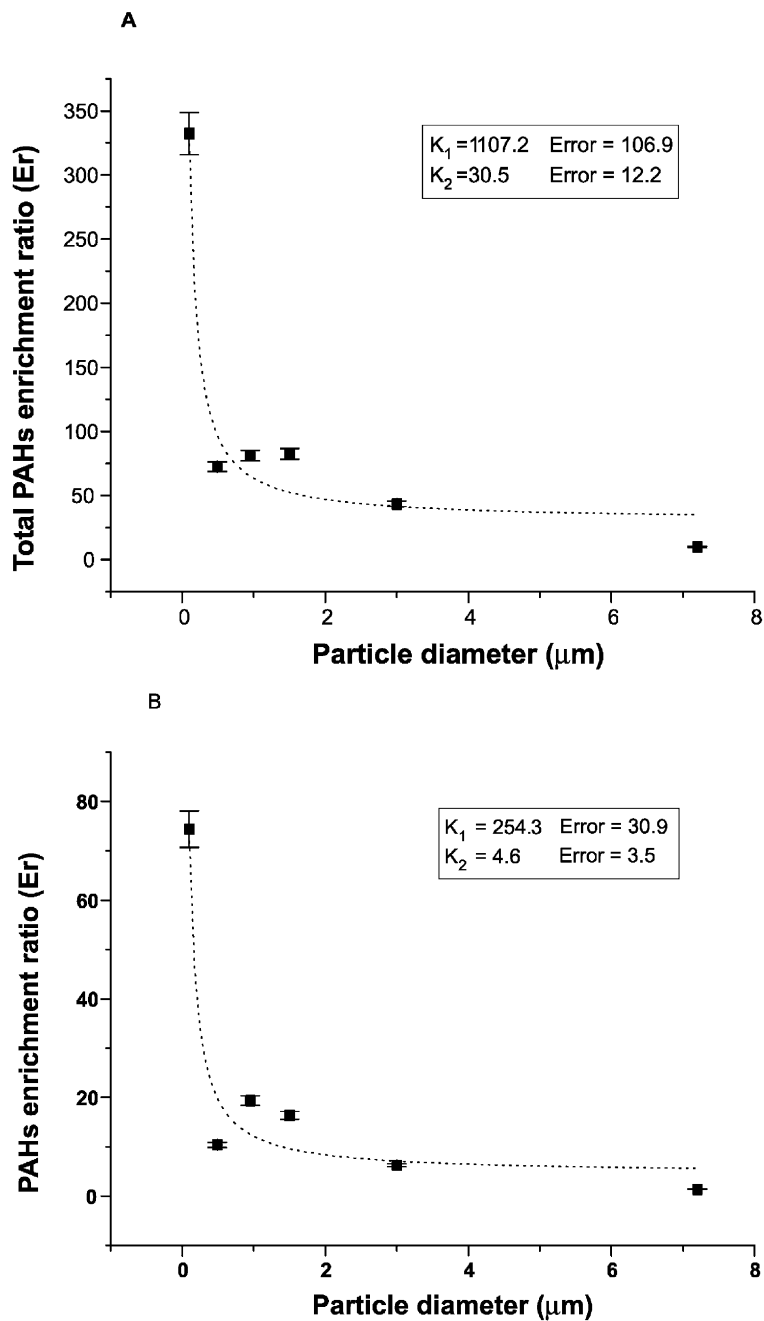
Fig. 5. Experimental values of the enrichment ratios of total PAHs (A) and PAHs with four or more rings (B) as a function of fractionated particle aerosol (sample 1). The vertical bars represent the maximum error in Er. The curve represents the SDAM fitting with $\Delta r = 0.01$ and 0.1 μm for the smallest class of particles. The evaluation of the constant K_1, K_2 and the corresponding error are also reported.

ticularly, of bis-(2-ethylhexyl)phthalate determined not only in samples 6 and 9 (Leghorn harbour) but even at station 8 (Meloria's Tower) and, although to a lesser extent, at the remaining sites indicate that the study area is on the whole contaminated.

4.2. Aerosol samples

In the Mediterranean area, studies on the composition of size fractionated aerosols have concerned aliphatic hydrocarbons (particularly *n*-alkanes), fatty

Fig. 6. Experimental values of the enrichment ratios of total PAHs (A) and PAHs with four or more rings (B) as a function of fractionated particle aerosol (sample 2). The vertical bars represent the maximum error in Er. The curve represents the SDAM fitting with $\Delta r = 0.01$ and 0.1 μm for the smallest class of particles. The evaluation of the constant K_1, K_2 and the corresponding error are also reported.

alcohols, fatty acids esters and PAHs (Sicre et al., 1987a,b, 1990). The n-alkane concentrations found by these authors were one order of magnitude lower than those measured in this study. In addition, their composition consisting of n-alkanes C_{20} to C_{45} appeared to be typical of terrestrial source inputs and of anthropogenic hydrocarbons predominantly carried by submicron particles (Sicre et al., 1990).

Differently, our data on marine aerosol show anthropogenic n-alkanes with a carbon atom number included between C_{16} and C_{34} distributed over the whole particle size spectrum.

To explain the different amounts of the various compounds found in the six fractions of marine aerosol, it is useful to compare their enrichment ratios (Er) with those expected on the basis of SDAM (Oppo et al., 1999). The experimental Er of a compound X was calculated using the procedure previously described (Desideri et al., 1998), according to

$$Er_{exp}(X) = \frac{[X]_a/[Na^+]_a}{[X]_w/[Na^+]_w}$$

where the symbols a and w refer to aerosol and sea-water, respectively.

The calculation of the theoretic Er was performed according to the equation given by Oppo et al. (1999):

$$Er_{theor} = K_1\left(3\Delta r/R - 3\Delta r^2/R^2 + \Delta r^3/R^3\right) \qquad (1)$$

Δr = adsorption film thickness; R = drop radius.

Fig. 2 shows the experimental Er values of dissolved SFOM vs. the particle diameter together with the SDAM fitting for $\Delta r = 0.01$ μm. A hyperbolic-like trend is observed in agreement with the SDAM theory, although the I_n values referred to 0.49, 0.95 and 1.5 μm particles appear lower than expected. I_n is an index of SFOM and can be considered as a tracer to evaluate the distribution of surfactant organic matter in the size spectrum of marine aerosols.

The plots of the experimental Er values for phthalates, n-alkanes and PAHs vs. the particle diameter of marine aerosol fractions are reported in Figs. 3–6.

A better fit of data was obtained using the following equation:

$$Er_{theo} = K_1\left(3\Delta r/R - 3\Delta r^2/R^2 + \Delta r^3/R^3\right) + K_2$$

which presents the additional parameter K_2 compared to Eq. (1). K_2 represents the "systematic effect" which takes into account the enrichment observed for specific classes of organic compounds in the largest particles of aerosol.

Er values for phthalates increase with the decrease of the size fractions of the aerosol and, consequently, with the decrease of the size jet-microdrops (see Fig. 3). This behaviour is in perfect agreement with SDAM which predicts the enrichment of non-volatile surfactants as a function of the decrease in the size of the aerosol particle. According to this model, a hyperbolic-like function is obtained for non-volatile phthalates, which are surface active agents.

The behaviour of n-alkanes (see Fig. 4) is more complicated and difficult to explain. Alkanes are not surfactants, but these compounds, which have different volatilities, can be partly transported into the liquid aerosol owing to their affinity towards the air bubbles and the jet-drops (Cini et al., 1994a). In addition, they can strongly interact with SFOM present in the aerosol, predominantly fulvic acids, and have a similar fate. This could explain alkane patterns in Fig. 4 which partially agree with the SDAM model; the Er values referred to classes of particles > 1 appear larger or lower than what is expected on the basis of the model. Such a scattered behaviour could be due to the presence of greater or lesser amounts of fulvic acid colloidal micelles floated in these fractions.

The same explanations given for n-alkanes also improve our understanding of patterns shown in Figs. 5 and 6 for total PAHs and PAHs with four or more aromatic rings; however, the transport of PAHs into the liquid aerosol is partially connected to their different structures (Cini et al., 1994a). Larger differences from the theoretical behaviour were observed for sample 2 with respect to sample 1.

5. Concluding remarks

The results give a picture of aquatic surface contamination in a coastal zone of the Tyrrhenian sea, near Leghorn, during September–October 1999. Signals of pollution from chemicals of petrogenic origin are evident in SML samples collected in the harbour of Leghorn and at various distances from the Port.

The SML is enriched with *n*-alkanes, phthalates, PAHs, suspended matter and SFOM with respect to sub-surface waters. The presence of slicks gives rise to unusual dissolved concentrations of these organic compounds as shown in the sample taken in an inner zone of the harbour of Leghorn.

Chemicals found in the SML are transferred to the atmosphere by marine aerosol and enriched particularly in the finest particles, which can be involved in the long range transport of pollutants. Not only SFOM, but also phthalates, *n*-alkanes and PAHs show a behaviour which can be predicted by the SDAM model.

Acknowledgements

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