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Occurrence and distribution of hydrocarbons in the surface microlayer and subsurface water from the urban coastal marine area off Marseilles, Northwestern Mediterranean Sea

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ABSTRACT

Aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs) were analyzed in dissolved and particulate material from surface microlayer (SML) and subsurface water (SSW) sampled at nearshore observation stations, sewage effluents and harbour sites from Marseilles coastal area (Northwestern Mediterranean) in 2009 and 2010. Dissolved and particulate AH concentrations ranged 0.05–0.41 and 0.04–4.3 $\mu g\, l^{-1}$ in the SSW, peaking up to 38 and 1366 $\mu g\, l^{-1}$ in the SML, respectively. Dissolved and particulate PAHs ranged 1.9–98 and 1.9–21 $ng\, l^{-1}$ in the SSW, amounting up 217 and 1597 $ng\, l^{-1}$ in the SML, respectively. In harbours, hydrocarbons were concentrated in the SML, with enrichment factors reaching 1138 for particulate AHs. Besides episodic dominance of biogenic and pyrogenic inputs, a moderate anthropisation from petrogenic sources dominated suggesting the impact of shipping traffic and surface runoffs on this urbanised area. Rainfalls increased hydrocarbon concentrations by a factor 1.9–11.5 in the dissolved phase.

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1. Introduction

Hydrocarbons are among the most carcinogenic, mutagenic and toxic contaminants found in the aquatic systems (Kennish, 1992). In the marine environment, they may have a natural (pyrolysis, diagenesis, biosynthesis, natural seepage) or anthropogenic origin (industrial and urban wastes, maritime transport, oil plants and refineries). Hydrocarbons are introduced in the coastal marine waters mainly through dry (aerosols) and wet (heavy rains) atmospheric depositions, rivers, municipal/industrial effluents and surface runoffs (Tolosa et al., 1996; Lipiatou et al., 1997). Many studies on exchange processes at the air/sea interface have highlighted that a wide variety of organic contaminants concentrate in the surface microlayer (SML) because of their surfactant nature, hydrophobic properties, possible association with floatable particles, vertical diffusion mechanisms and bubble scavenging (Liss and Duce, 1997; CIESM Workshop, 1999). High concentrations of hydrocarbons have been recovered in the SML compared to the subsurface water (SSW) in various coastal environments (El Nemr and Abd-Allah, 2003; Wurl and Obbard, 2004; Manodori et al., 2006; Guitart et al., 2007).

Aliphatic hydrocarbons (AHs), which may be of biogenic or anthropogenic origin, consist of a series of resolved compounds (R) and of unresolved complex mixture (UCM) hump. Concerning the distribution of the resolved compounds, an elevated proportion of C15–C23 n-alkanes indicates that unburned lubricating oils from road traffic exhaust are a significant contributor to AHs (Simoneit, 1985; Colombo et al., 1989). Furthermore, the carbon preference index (CPI) in the range nC_{21}–nC_{33}, computed from the ratio of odd to even numbered n-alkanes, provides useful information about the AH origin. Indeed, high values of CPI_{21-33} (i.e. above 3–5) are characteristic of terrestrial higher plant debris. For instance, epicuticular waxes of higher plants typically have n-alkane maxima at C_{27}, C_{29} and C_{31} (Douglas and Eglinton, 1966; Eglinton and Hamilton, 1967; Giger and Schaffner, 1975; Rielley et al., 1991). On the contrary, lower CPI_{21-33} values are consistent with chronic petroleum inputs (Bouloubassi and Saliot, 1993; Wang et al., 1997). Pristane (Pr) to phytane (Phy) ratio is also of interest since high values are reliable indicator of the absence of petroleum and clearly indicate a marine biological origin (Cripps, 1989; UNEP/IOC/IAEA, 1992) although low values do not reflect the presence of petroleum (Humphrey et al., 1987). As for the unresolved compounds, the UCM hump is generally considered as to be a mixture of many structurally complex isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by capillary gas chromatography (GC) columns (Bouloubassi and Saliot, 1993). The presence of UCM is the sign of a petroleum input and/or the presence of biodegraded complex mixture of hydrocarbons. Its relative importance, expressed as the ratio of unresolved to resolved compounds (UCM/R), is commonly used

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as diagnostic criteria of pollutant inputs (Mazurek and Simoneit, 1984). The threshold value of UCM/*R* that confirms the widespread presence of petroleum-related residue is 4 according to Mazurek and Simoneit (1984) and Lipatou and Saliot (1991).

Polycyclic aromatic hydrocarbons (PAHs), which are almost exclusively of anthropogenic origin, are sensitive indicators of petrogenic (incombusted petroleum) and pyrogenic sources (incomplete combustion of fossil fuels) (see reviews by Wang et al., 1999; Wurl and Obbard, 2004). Petrogenic PAHs, which originate from low temperature alterations of organic matter, correspond to low molecular weight (LMW) 2–3 ring PAHs that have a large proportion of alkylated homologues. Conversely, pyrogenic PAHs, issued from high temperature combustions, correspond to high molecular weight (HMW) 4–6 ring PAHs with a low abundance of alkylated products (Wang et al., 1999). It is worth noting that in many environmental studies "total" PAH concentrations are reported as the sum of 2–6 ring parent (non alkylated) compounds. Albeit this facilitates comparisons, it may lead to underestimate the total petrogenic PAH concentrations in the samples (Bouloubassi and Saliot, 1993). In order to assess the contamination sources, previous studies have proposed two PAH ratios: phenanthrene (Phe)/anthracene (Ant) and fluoranthene (Flt)/pyrene (Pyr). When Phe/Ant < 10 and Flt/Pyr > 1, pyrogenic sources dominate. Alternatively, when Phe/Ant > 15 and Flt/Pyr < 1, petrogenic sources dominate (Mille et al., 1982; Budzinski et al., 1997; Readman et al., 2002; Lim et al., 2007). More recently, alkylated homologues/parent compounds (alk/parents) and LMW/HMW ratios have been used as indices of PAH sources because a predominance of alkylated and LMW compounds points out petrogenic inputs (Azimi et al., 2005).

Marseilles (Southern France) is the first Mediterranean harbour for goods traffic and the Marseilles-Fos petrochemical complex is the world's third oil port. Marseilles is also the second most populated city in France, and thus generates important industrial, shipping, nautical and tourism activities. Hence, the Marseilles coastal area is exposed to numerous potential sources of contamination such as urban and industrial wastes, petroleum inputs and atmospheric depositions from transports, pyrogenic residues, and industrial and harbour activities. A number of data are available about the distribution of hydrocarbons in the SML and/or SSW from neighbouring coastal areas, such as Catalan and Tyrrhenian Seas and Venice Lagoon (Dachs et al., 1997; 1999; Cincinelli et al., 2001; Manodori et al., 2006; Guitart et al., 2007). However, even though the concentrations of hydrocarbons in sediments from the Marseilles area are well documented (Lipiatou et al., 1997; Benlahcen et al., 1997; Le Dréau et al., 1997; Mille et al., 2007; Asia et al., 2008), the data dealing with hydrocarbons in the SML or SSW are scarce for this zone (Marty and Saliot, 1976; Siron et al., 1987; Bouloubassi and Saliot, 1991).

The objective of this study is to investigate the distributions of hydrocarbons (AHs and PAHs) in the SML and SSW from the Marseilles coastal area (Northwestern Mediterranean Sea). This work will allow implementing the data relative to hydrocarbon concentrations in both dissolved and particulate phases along the French Mediterranean coast, and to estimate, using several indices and ratios, the contamination sources and the impact of heavy rains on this highly urbanised coastal area.

2. Material and methods

2.1. Study sites

Six sites were studied in the coastal Northwestern Mediterranean Sea according to their different potential sources of contamination: five sites located in the Marseilles coastal area and one site located in the Bay of Banyuls-sur-mer (Fig. 1 and Table 1). Sofcom (SOF) and Sola (SOL) are two nearshore observation sites of the Service d'Observation en Milieu LITtoral (SOMLIT; http://www.domino.u-bordeaux.fr/somlit_national/). They were selected as marine references by comparison to the other highly anthropogenically impacted sites. SOF, situated near the Frioul Islands (~5 km off Marseilles), is the observation station of the Oceanology Center of Marseilles and is sampled twice a month for 13 years for the

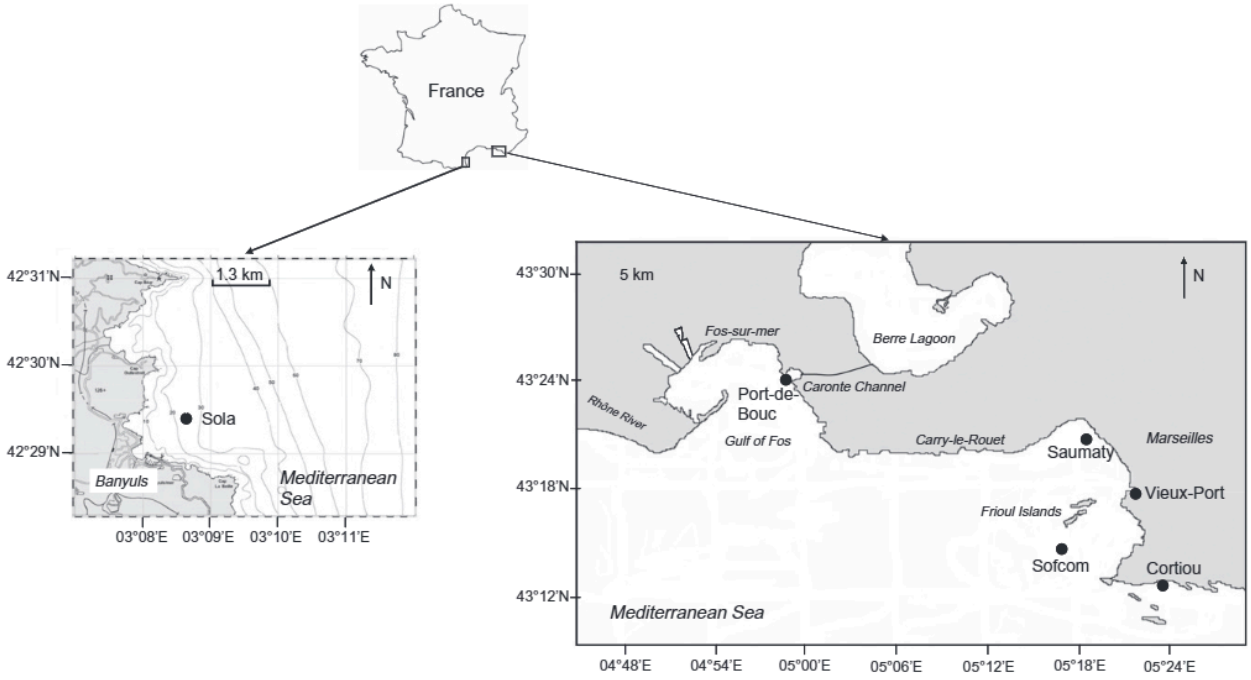

Fig. 1. Location of the six study sites in the coastal Northwestern Mediterranean Sea: five sites are located in the Marseilles coastal area (Sofcom, Cortiou, Port-de-Bouc, Saumaty, Vieux-Port) and one site in the Bay of Banyuls-sur-mer (Sola). The detailed characteristics of these sites are provided in Table 1.

Table 1
Characteristics of the study sites.

Name	Abbreviation	Water type	Position	Depth of the water column (m)	Date of sampling	Sampling depth
Sofcom	SOF	NW Mediterranean coastal water	43°14.3′N, 05°17.3′E	60	22/06/09	SSW
					03/02/10	SML and SSW
					08/06/10	SSW (BR)
					16/06/10	SSW (AR)
Sola	SOL	NW Mediterranean coastal water	42°29.3′N, 03°08.7′E	30	07/06/10	SSW
Cortiou	CO	Treated sewage effluent	43°12.8′N, 05°24.1′E	10	23/06/09	SML and SSW
					25/01/10	SML and SSW
					16/06/10	SSW (AR)
Port-de-Bouc	PB	Harbour water	43°24.1′N, 04°59.0′E	5	01/07/09	SML and SSW
					02/02/10	SML and SSW
					08/06/10	SSW (BR)
					15/06/10	SSW (AR)
Saumaty	SA	Harbour water	43°21.5′N, 05°19.5′E	4	25/06/09	SML and SSW
					01/02/10	SML and SSW
Vieux-Port	VP	Harbour water	43°17.8′N, 05°22.4′E	5	29/06/09	SML and SSW
					27/01/10	SML and SSW (AR)

NW: Northwestern; SML: surface microlayer; SSW: subsurface water; BR: before rain; AR: after rain.

measurement of hydrological and biogeochemical parameters. SOL, situated ~0.5 km off Banyuls, is the observation station of the Oceanology Observatory of Banyuls (Fig. 1 and Table 1).

Cortiou (CO), located in the Cortiou Cove (southern part of Marseilles Bay), is the discharge area of the secondary-treated sewage effluent (SE) from Marseilles and 15 surrounded municipalities. CO is positioned ~40 m from SE outflow (Fig 1; Table 1). The SE is composed by domestic sewages and storm waters. Its treatment consists in a (primary) physico-chemical procedure including solid removal and chemically-assisted (flocculation/coagulation) sedimentation followed by a (secondary) biological treatment based on the Biostyr® system. The secondary-treated SE is released in the Cortiou Cove at the surface, with a daily average flow rate of 2.3 $m^3 s^{-1}$ (by dry weather).

Port-de-Bouc (PB), Saumaty (SA) and Vieux-Port (VP) are three harbours of the Marseilles coastal area (Fig 1 and Table 1). PB is situated in the Gulf of Fos-sur-mer and is surrounded by the Marseilles-Fos petrochemical complex, which includes several chemical, petroleum and steel-work plants. The Gulf of Fos-sur-mer receives some freshwater inputs coming from the Rhône River and the Berre Lagoon (Ulses et al., 2005). Furthermore, PB is positioned on the route of oil cargo ships going to the Berre Lagoon through the Caronte channel. VP is a marina and is the main recreative harbour of Marseilles. During strong rainfalls, VP can overflow and receive large amounts of highly hydrocarbon-loaded freshwaters. SA is a dynamic fishing port that combines trawlers, tuna boats and wholesale trading centers.

2.2. Sampling strategy

Sampling was performed in summer 2009 (June–July), winter 2010 (January–February) and summer 2010 (June) aboard the R/V Antédon II. First, 5 sites (SOF, CO, PB, SA and VP) were investigated in June 2009 and January 2010 to study the seasonal distribution of hydrocarbons in the SML and SSW. Three of these sites (SOF, CO and PB) were sampled a third time in June 2010 to focus on the impact of heavy rains on the concentrations and distributions of hydrocarbons. Before rain (BR) samples were collected from 7 to 8 days before rainfalls and after rain (AR) samples were collected within 24 h following these events. SOL was sampled once in June 2010. Sampling was systematically made in the morning between 9:00 and 10:00 am.

Samples of (3–8 l) were collected under very low wind (<2 m s^{-1}) and calm sea conditions. SML samples were obtained with a stainless-steel screen (0.8 m × 0.6 m, 2 mm mesh) according to the method by Garret (1965). The metal screen, deployed from an inflatable boat, was selected as SML sampler because it provides adequate sample volumes in a reasonable time with regard to the determination of hydrophobic organic matter (Guitart et al., 2004). SML samples were poured into 4 l Nalgene® polycarbonate bottles by means of a precombusted (450 °C, 6 h) glass funnel. SSW samples were collected directly in the Nalgene® bottles at ~0.1 m below the water surface. The bottles were opened below the water surface to avoid the sampling of the SML. The Nalgene® polycarbonate bottles, previously washed with 1 M hydrochloric acid (HCl) and ultrapure water (i.e. Milli-Q water from Millipore system, final resistivity: 18.2 MΩ cm^{-1}), were rinsed three times with the respective sample before filling and placed in the dark after the sample collection. SML and SSW samples were used for AH and PAH measurements.

2.3. Filtration

Back to the laboratory, the samples were immediately filtered under a low vacuum (<50 mm Hg) through precombusted GF/F (~0.7 μm) glass fibre filters (47 mm diameter, Whatman) using polysulfone filtering systems. The filters (for particulate hydrocarbons) were stored at −18 °C and filtered water (for dissolved hydrocarbons) was kept in 2 l SCHOTT® glass bottles with 50 ml dichloromethane (CH_2Cl_2) at 4 °C in the dark before solvent extraction. During the experiments and analyses, gloves were worn and care was taken to avoid contaminations. All the glassware was washed with 1 M HCl and ultrapure water and combusted at 450 °C during 6 h. All the materials that could not be baked were washed with 1 M HCl and ultrapure water and dried at 50 °C.

2.4. Solvent extraction and treatment for hydrocarbons

Dissolved hydrocarbons present in the fraction <0.7 μm were extracted from seawater by liquid–liquid extraction with CH_2Cl_2 (3 × 50 ml per litre). Particulate hydrocarbons present on the filters were extracted according to Bligh and Dyer (1959). Each filter was ground in a monophasic solvent mixture [CH_2Cl_2/methanol (CH_3OH)/H_2O, 1/2/0.8, v/v/v] and sonicated for 15 min. The mixture was then filtered and CH_2Cl_2 (1 v) and H_2O (1 v) were added to produce a biphasic mixture in a way that hydrophobic compounds were released in the organic phase. The latter phase was removed and the extraction of the aqueous phase was performed twice again. Then, the analytical steps were similar for both dissolved and particulate hydrocarbon extracts. Organic phases were combined and evaporated on a rotary evaporator. Prior to purification, solvent was changed to *n*-hexane. Hexane solubilised extracts were then purified to separate AHs (fraction 1, F1) from PAHs (fraction 2, F2). Extracts were fractionated on a 500 mg silica

column. Silica gel (extra pure, Merck) was activated at 450 °C for 6 h followed by partially deactivation with 4% water by weight. F1 was eluted with 2 ml *n*-hexane while F2 was eluted with 3 ml *n*-hexane/CH_2Cl_2 (3:1 v/v). Deuterated standard mixtures (C_{16}-d_{34}, C_{24}-d_{50}, C_{36}-d_{74} for AHs, and Naph-d_8, Phe-d_{10}, Ant-d_{10}, Per-d_{12} for PAHs) were introduced prior to extraction, as well as a supplementary deuterated standard before injection, and used as surrogates to assess the recoveries of analytical procedures and to perform quantitation accuracy. All solvents were of organic trace analysis quality (Rathburn, Interchim).

2.5. Analysis of hydrocarbons by gas chromatography (GC–FID and GC–MS)

Both F1 and F2 fractions were concentrated under a gentle stream of nitrogen and analyzed by gas chromatograph–flame ionization detector (GC–FID) (AutoSystem XL, Perkin Elmer, USA) equipped with a HP-5 column (25 m × 0.32 mm × 0.52 μm, J&W Scientific, Agilent Technologies, USA). The injector (used in splitless mode) and detector temperatures were 300 and 320 °C, respectively. The column temperature programme was that used by Díez et al. (2005). Compounds were identified by reference to the analysis of standard mixtures (04071, Fluka and 47543-U, Supelco among others). Dissolved and particulate phase blanks were run by analysing solvents and filters, respectively. All concentration values were blank and recovery corrected. F1 and F2 were further analysed by using a gas chromatograph–mass spectrometer (GC–MS) (TraceISQ, ThermoElectron) operating at an ionization energy of 70 eV for a *m/z* range of 50–400, using hydrogen as carrier gas at a flow rate of 1.2 ml min^{-1}.

2.6. Determination of indices and ratios

For AHs, we determined *R*, which corresponds to the sum of the concentrations of the resolved *n*-alkane series from nC_{16} to nC_{35} with two isoprenoids, Pr and Phy. We also determined the UCM concentrations by integrating the hump (when present) using the mean response factor of the resolved compounds. Then we calculated the enrichment factor of the SML (EF), given by *R* in the SML to *R* in the SSW ratio, as well as the CPI_{21-33} indices and the C_{16}–C_{23}/R, Pr/Phy and UCM/*R* ratios.

Concerning PAHs, we determined the concentrations of 17 parent PAHs ($PAHs\text{-}_P$), namely naphthalene (Naph), acenaphtylene (Acy), acenaphtene (Ace), fluorene (Flu), dibenzothiophene (DBT), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]-fuoranthene (BbF), benzo[*k*]fuoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BP), indeno[1,2,3-*cd*]pyrene (IndP), as well as the concentrations of alkylated (methyl, dimethyl, trimethyl) Naph, Flu, Phe, Pyr and Chr ($PAHs\text{-}_A$), which lead to a total of 32 PAHs ($PAHs\text{-}_{P+A}$). Naph, Acy, Ace, Flu, DBT, Phe and Ant are LMW compounds (2–3 rings) while Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BP and IndP are HMW compounds (4–6 rings). Thus, we calculated $EF\text{-}_P$, given by $PAHs\text{-}_P$ in the SML to $PAHs\text{-}_P$ in the SSW ratio, as well as LMW/HMW_P, LMW/HMW_{P+A}, alk/parents, Phe/Ant and Flt/Pyr ratios.

In addition, for both AHs and PAHs, we determined the load factor (LF), given by the concentration before rain (BR) to the concentration after rain (AR) in the SSW (i.e. only at SOF and PB during summer 2010).

2.7. Statistics

Analyse of variance (ANOVA) and Mann Whitney test (*U*-test) were used for the comparison of two independent data groups. *U*-test was employed when the number of observations in each group was low and/or when their distributions were non-normal (normality assessed with Kolmogorov–Smirnov test). Tests were carried out with StatView 5.0. The significance threshold was set at $p < 0.05$.

3. Results

Samples are named according to the location, water depth (SML or SSW) and sampling period. For instance, a SSW sample from Port-de-Bouc collected in summer 2009 is named PB-SSW-Sum09. A note for BR and AR is added when focussing on the rain event effects. AH and PAH data are presented in Tables 2 and 3, respectively.

3.1. Aliphatic hydrocarbons (AHs)

3.1.1. NW Mediterranean coastal waters (SOF, SOL)

For the dissolved phase, the concentrations of resolved alkanes (*R*) in the SSW ranged from 0.09 to 0.41 μg l^{-1} (summer and winter samples), while that measured in the SML was of 0.13 μg l^{-1} (winter sample), leading to an enrichment factor (EF) of 0.52 (winter samples) (Table 2). The *R* pattern was dominated by heavy compounds (C_{16}–$C_{23}/R < 0.5$). After the rain event (summer 2010), *R* concentration increased by a factor 4.6, *R* distribution got even more enriched in heavy compounds around nC_{29} (C_{16}–$C_{23}/R = 0.16$) and a light UCM (0.56 μg l^{-1}) appeared in the SSW. In the particulate phase, *R* concentrations of the SSW varied in the same range as in the dissolved phase from, 0.04 to 0.57 μg l^{-1}, whereas that of the SML was of 3.2 μg l^{-1} with a corresponding EF of 5.6. The distribution pattern was much more variable than in the dissolved phase (C_{16}–C_{23}/R ranged from 0.09 to 0.67). The presence of UCM was noticeable in the range 1.2–30 μg l^{-1} with UCM/*R* ratios >4, revealing the presence of petroleum-related residues. After the rain event (summer 2010), *R* concentration decreased by a factor 2.8, while *R* distribution was little affected.

3.1.2. Treated sewage effluent (CO)

In the dissolved phase, *R* concentrations in the SSW and SML ranged from 0.15 to 0.26 μg l^{-1} and from 0.32 to 0.63 μg l^{-1}, respectively, with EFs varying from 1.9 to 4.2 (Table 2). In the particulate phase, *R* concentrations ranged from 0.05 to 1.4 μg l^{-1} in the SSW and from 1.4 to 6.4 μg l^{-1} in the SML. The EFs varied from 4.2 in winter up to 128 in summer. R distributions were nearly the same for both phases, with C_{16}–C_{23}/R ratio varying from 0.26 to 0.46, indicating the predominance of heavy *n*-alkanes, except for 2 samples (dissolved and particulate CO-SML-Sum09) dominated by the contribution of short carbon chain AHs (C_{16}–$C_{23}/R = 0.58$ and 0.56, respectively). Contrary to what was observed at SOF, the UCM was present in the SML in both phases at both seasons, as well as in the particulate SSW after heavy rains, with UCM/*R* values widely above 4. Moreover, concerning heavy rain effects, particulate CO-SSW-Sum10 seemed to be widely affected with an increase in *R* concentration by 4- to 28-fold with respect to other SSW samples (particulate CO-SSW-Sum09 and CO-SSW-Win10), while dissolved sample was little affected regarding *R* and C_{16}–C_{23}/R values.

3.1.3. Harbour waters (PB, SA, VP)

At the three harbour sites, except two samples, dissolved *R* concentrations varied from 0.05 to 0.38 μg l^{-1} in the SSW and from 0.31 to 1.7 μg l^{-1} in the SML, with EFs comprised between 0.95 and 11 (Table 2). In the other two samples, namely PB-SML-Sum09 and VP-SML-Win10, *R* concentrations reached 38 and 32 μg l^{-1} with EF of 190 and 356, respectively. The dissolved *R* distribution pattern was highly variable for PB and VP sites, with

Table 2
Aliphatic hydrocarbons: concentrations of *R* and UCM (μg l^{-1}), CPI_{21-33} index, EF, C_{16}-C_{23}/*R*, Pr/Phy and UCM/*R* ratios.

Sample	Dissolved							Particulate						
	R (μg l^{-1})	EF	C_{16}–C_{23}/*R*	CPI_{21-33}	Pr/Phy	UCM (μg l^{-1})	UCM/*R*	*R* (μg l^{-1})	EF	C_{16}–C_{23}/*R*	CPI_{21-33}	Pr/Phy	UCM (μg l^{-1})	UCM/*R*
SOF-SSW-Sum09	0.10		0.44	1.3	0.99			0.04		0.59	2.0	0.44	1.2	30
SOF-SML-Win10	0.13	0.52	0.25	0.29	0.93			3.2	5.6	0.67	1.5	0.26	30	9.4
SOF-SSW-Win10	0.25		0.28	0.29	1.6			0.57		0.09	1.1	0.70		
SOF-SSW-Sum10 (BR)	0.09		0.36	1.1	1.5			0.33		0.26	0.31	1.4	2.4	7.3
SOF-SSW-Sum10 (AR)	0.41		0.16	0.99	1.2	0.56	1.4	0.12		0.32	0.45	2.0		
SOL-SSW-Sum10	0.12		0.38	0.99	1.1			0.09		0.17	3.6	0.60		
CO-SML-Sum09	0.63	4.2	0.58	1.2	0.84	6.7	11	6.4	128	0.56	1.2	0.49	50	7.8
CO-SSW-Sum09	0.15		0.46	1.1	0.99			0.05		0.45	9.5	0.86		
CO-SML-Win10	0.32	1.9	0.40	0.88	0.82	4.1	13	1.4	4.2	0.41	1.2	0.84	43	31
CO-SSW-Win10	0.17		0.32	1.1	1.1			0.33		0.29	1.4	1.0		
CO-SSW-Sum10 (AR)	0.26		0.26	0.91	1.1			1.4		0.33	3.3	0.78	13	9.3
PB-SML-Sum09	38	190	0.57	1.1	14	288	7.6	14	50	0.71	1.3	0.36	687	49
PB-SSW-Sum09	0.20		0.50	1.2	1.1			0.28		0.54	1.2	0.66	3.5	13
PB-SML-Win10	0.31	1.3	0.22	0.88	0.99			2.7	0.63	0.49	1.2	0.44	30	11
PB-SSW-Win10	0.24		0.38	0.60	1.4			4.3		0.55	1.3	0.29	18	4.2
PB-SSW-Sum10 (BR)	0.05		0.38	0.98	0.90			0.16		0.58	1.3	0.61		
PB-SSW-Sum10 (AR)	0.34		0.27	1.2	0.64			0.22		0.43	1.2	0.89	3.2	15
SA-SML-Sum09	1.7	11	0.50	1.4	0.48	66	39	1087	453	0.57	1.3	0.43	47259	43
SA-SSW-Sum09	0.16		0.58	1.3	0.97			2.4		0.66	1.4	0.87		
SA-SML-Win10	0.36	0.95	0.62	0.99	0.57			43	17	0.80	1.5	0.47		
SA-SSW-Win10	0.38		0.54	0.77	1.2			2.5		0.16	1.2	0.66		
VP-SMLSum09	0.38	1.7	0.64	1.3	1.1	2.9	7.6	50	63	0.68	1.5	0.74	1371	27
VP-SSW-Sum09	0.23		0.29	1.2	1.3			0.79		0.75	1.5	0.63	1.2	1.5
VP-SML-Win10 (AR)	32	356	0.78	1.4	0.43	154	4.8	1366	1138	0.81	1.5	0.36	6527	4.8
VP-SSW-Win10 (AR)	0.09		0.43	0.60	0.57			1.2		0.65	1.5	0.45		

R: resolved aliphatic hydrocarbons (sum of *n*-alkanes from C_{16} to C_{35} with two isoprenoids, pristane and phytane); UCM: unresolved complex mixture; CPI_{21-33}: carbon preference index (ratio of odd number *n*-alkanes over even numbered *n*-alkanes between C_{21} and C_{33} *n*-alkanes); EF: enrichment factor of the surface microlayer (SML) with respect to the subsurface water (SSW); C_{16}–C_{23}/*R*: ratio between the sum of *n*-alkanes from C_{16} to C_{23} over resolved aliphatic hydrocarbon concentrations; Pr/Phy: pristane (Pr) over phytane (Phy) ratio; UCM/*R*: unresolved complex mixture over resolved aliphatic hydrocarbon concentration ratio.

Table 3
Polycyclic aromatic hydrocarbons: concentrations of PAHs-$_P$ and PAHs-$_{P+A}$ (ng l^{-1}), EF_P, LMW/HMW_P, LMW/HMW_{P+A}, alk/parents, Phe/Ant, Flt/Pyr ratios.

Sample	Dissolved								Particulate							
	PAHs-$_P$ (ng l^{-1})	EF_P	LMW/ HMW_P	PAHs-$_{P+A}$ (ng l^{-1})	LMW/ HMW_{P+A}	alk/ parents	Phe/ Ant	Flt/ Pyr	PAHs-$_P$ (ng l^{-1})	EF_P	LMW/ HMW_P	PAHs-$_{P+A}$ (ng l^{-1})	LMW/ HMW_{P+A}	alk/ parents	Phe/ Ant	Flt/ Pyr
SOF-SSW-Sum09	42		8.4	75	15	0.97	6.2	1.2	3.2		0.41	33	5.2	20	2.9	0.57
SOF-SML-Win10	68	4.3	1.4	129	3.2	1.4	21	1.2	6.0	2.9	0.76	29	3.6	7.4	7.2	0.80
SOF-SSW-Win10	16		0.91	23	1.6	0.72	5.4	1.6	2.1		0.92	13	4.0	9.6	6.6	0.72
SOF-SSW-Sum10 (BR)	4.2		5.2	14	13	3.3	22	0.96	3.0		3.8	11	12	3.5	12	0.66
SOF-SSW-Sum10 (AR)	8.1		1.9	22	4.1	2.7	30	0.70	2.6		1.4	9.5	4.8	4.6	27	0.86
SOL-SSW-Sum10	1.9		0.77	5.0	2.8	2.5	18	0.91	1.9		2.3	5.5	6.7	2.8	10	0.58
CO-SML-Sum09	176	15	0.18	1007	0.7	6.3	27	0.13	137	29	0.04	1726	0.4	18	28	0.12
CO-SSW-Sum09	12		0.72	52	1.7	5.3	15	0.38	4.7		1.2	20	1.3	4.9	14	0.42
CO-SML-Win10	127	17	0.30	156	0.6	0.67	1.9	1.0	6.4	0.70	1.2	20	2.2	3.3	14	0.72
CO-SSW-Win10	7.5		6.0	17	12	1.6	18	0.73	9.1		0.91	17	1.9	1.2	54	1.4
CO-SSW-Sum10 (AR)	5.7		0.87	42	10	9.5	13	0.86	21		0.22	33	0.6	1.6	8.3	1.0
PB-SML-Sum09	217	2.6	3.5	564	7.1	2.0	*	0.28	24	11	0.42	382	1.9	28	2.7	0.55
PB-SSW-Sum09	83		26	159	38	1.2	22	0.72	2.2		0.82	7.1	2.1	3.7	9.6	0.61
PB-SML-Win10	50	2.3	2.1	191	6.0	3.8	36	1.1	7.6	0.45	1.1	40	3.8	6.8	9.2	0.80
PB-SSW-Win10	22		3.8	49	8.4	1.6	22	0.96	17		0.54	82	3.5	7.8	8.2	0.87
PB-SSW-Sum10 (BR)	8.5		4.3	31	13	3.6	21	1.4	3.0		0.92	7.8	1.6	3.2	14	0.75
PB-SSW-Sum10 (AR)	98		0.26	145	0.6	1.2	28	1.4	6.0		1.0	21	3.7	4.5	5.9	0.83
SA-SML-Sum09	167	6.0	0.70	980	5.8	6.1	39	0.41	1597	84	0.36	37303	5.5	33	34	0.33
SA-SSW-Sum09	28		1.3	162	8.8	8.4	5.1	0.60	19		1.1	208	7.6	14	15	0.39
SA-SML-Win10	77	3.9	2.1	341	7.7	4.4	24	0.84	102	6.4	0.18	1566	3.6	28	17	0.61
SA-SSW-Win10	20		1.1	88	7.2	6.9	20	1.2	16		0.30	54	2.0	4.3	7.3	0.46
VP-SMLSum09	55	2.0	4.9	413	20	8.6	12	1.2	103	17	0.64	1710	8.3	24	23	0.94
VP-SSW-Sum09	28		4.7	74	13	2.7	10	1.4	6.0		0.33	16	1.7	4.4	4.3	0.74
VP-SML-Win10 (AR)	148	5.9	0.71	871	4.7	7.8	30	0.69	350	22	0.13	3081	3.1	19	12	0.66
VP-SSW-Win10 (AR)	25		0.84	75	3.8	3.8	5.1	1.0	16		0.42	42	1.9	4.0	2.4	0.81

PAHs-$_P$: 17 parent polycyclic aromatic hydrocarbons(PAHs); PAHs-$_{P+A}$: sum of 17 parents and 15 alkylated homologues PAHs; EF_P: enrichment of the surface microlayer (SML) with respect to the subsurface water (SSW) calculated from the PAHs-$_P$ concentrations; alk/parents: alkylated homologues over parent PAH concentrations ratio. Phe/Ant: phenanthrene (Phe) over anthracene (Ant) concentration ratio. Flt/Pyr: fluoranthene (Flt) over pyrene (Pyr) concentration ratio. LMW/HMW_P: low molecular weight over high molecular weight PAH concentration ratio calculated from parent PAHs. LMW/HMW_{P+A}: low molecular weight over high molecular weight PAH concentration ratio calculated from parent and alkylated homolog PAHs.

* Ant non detected.

C_{16}–C_{23}/*R* ranging from 0.22 to 0.78, showing an equal distribution between samples dominated by light and those dominated by heavy compounds. For SA site, C_{16}–C_{23}/*R* was systematically above 0.50, underlining a relatively high contribution of short carbon chain AHs. Furthermore, after the rain event, we noticed an increase by 7-fold of *R* concentration for PB-SSW-Sum10 (AR) with a slight enrichment in heavy compounds around nC_{29} and the second highest dissolved SML concentration value recorded for VP-SML-Win10 (AR). Otherwise, the systematic presence of UCM, to various extent of concentrations, was noticed in the SML at the three harbour sites during summer, as well as at VP in winter after heavy rains.

For the particulate phases at the three sites, *R* concentrations in the SSW ranged from 0.16 to 4.3 $\mu g\,l^{-1}$ when four of the six SML values ranged from 2.7 to 50 $\mu g\,l^{-1}$ with the EFs varying within two orders of magnitude (0.63–63). For SA-SML-Sum09 and VP-SML-Win10 (AR), *R* concentrations reached 1087 and 1366 $\mu g\,l^{-1}$ while EFs reached up to 453 and 1138, respectively. *R* distributions in the particulate phase were also quite variable with the range of C_{16}–C_{23}/*R* varying from 0.16 to 0.81. However, except for three samples dominated by heavy compounds, particulate phase was clearly dominated by light compounds, suggesting that unburned lubricating oils from road traffic exhaust were a significant contributor to AHs. For both SML and SSW and both phases, UCM were found in a majority of samples, especially for PB site where it appeared, in a wide extent, after the rain event during summer 2010. Only one UCM/*R* ratio value was below 4 (VP-SSW-Sum09), besides, all samples presented a high value of this ratio, up to 49. In addition, as in the dissolved phase after heavy rains, particles of PB-SSW-Sum10 (AR) got enriched in heavy compounds, the highest particulate SML concentration being recorded for VP-SML-Win10 (AR).

For almost all samples in both phases, CPI_{21-33} values were not far from the petrogenic signature of 1 (Table 2). However, three particulate samples from SOL and CO collected during summer [SOL-SSW-Sum10, CO-SSW-Sum09 and CO-SSW-Sum10 (AR)] exhibited CPI_{21-33} values >3 (3.6, 9.5 and 3.3, respectively). These higher values reflected an enrichment in odd carbon numbered nC_{27}–nC_{35} alkanes, pointing out terrestrial biogenic matter inputs. In the same way, Pr/Phy ratio values remained close to 1, except for PB-SML-Sum09 in the dissolved phase (Pr/Phy = 14), which might indicate some marine biogenic matter contributions to AHs.

3.2. Polycyclic aromatic hydrocarbons (PAHs)

In order to compare our results with previous studies, we decided to focus our data description on the total amount ($PAHs\text{-}_P$) and the distribution (LMW/HMW_P) of parent compounds (Table 3).

3.2.1. NW Mediterranean coastal waters

For dissolved and particulate phases, $PAHs\text{-}_P$ concentrations in the SSW ranged from 1.9 to 42 $ng\,l^{-1}$ and from 1.9 to 3.2 $ng\,l^{-1}$, respectively, while the concentrations in the SML in winter reached 68 $ng\,l^{-1}$ (EF = 4.3) and 6.0 $ng\,l^{-1}$ (EF = 2.9), respectively (Table 3). $PAHs\text{-}_P$ distribution patterns were characterized by rather light compounds (2–3 rings) in the dissolved phase with a majority of LMW/HMW_P values over 1, against a lack of dominance in the particulate phase. Then, as already observed for AHs, the rain event resulted in an increase (by 2-fold) of the total dissolved $PAHs\text{-}_P$ concentrations at SOF, and an enrichment in heavy molecular compounds (decrease in LMW/HMW_P values) in both phases.

3.2.2. Treated sewage effluent

For dissolved and particulate phases, $PAHs\text{-}_P$ concentrations of the SSW ranged from 5.7 to 12 $ng\,l^{-1}$ and from 4.7 to 21 $ng\,l^{-1}$, respectively, while the concentrations in the SML ranged from 127 to 176 $ng\,l^{-1}$ (EF = 15–17) and from 6.4 to 137 $ng\,l^{-1}$ (EF = 0.7–29), respectively (Table 3). $PAHs\text{-}_P$ distribution patterns were characterized by rather heavy compounds with a majority of LMW/HMW_P values below 1 in both phases. Moreover, according to what was observed for AHs, the rain event impacted mainly the particulate of CO-SSW-Sum10 (AR) with an increase in $PAHs\text{-}_P$ concentration by 2.3- to 4.5- fold with respect to other SSW samples but also, the highest $PAHs\text{-}_P$ concentration value (21 $ng\,l^{-1}$) of the whole particulate SSW dataset.

3.2.3. Harbour waters

For dissolved and particulate phases, $PAHs\text{-}_P$ concentrations of the SSW ranged from 8.5 to 98 $ng\,l^{-1}$ and from 2.2 to 19 $ng\,l^{-1}$ while the concentrations in the SML ranged from 50 to 217 $ng\,l^{-1}$ (EF = 2.0–6.0) and from 7.6 to 1597 $ng\,l^{-1}$ (EF = 0.45–84), respectively (Table 3). For the dissolved phase, the distribution pattern was dominated by light compounds (mean LMW/HMW_P = 4.0 ± 1.9) excluding samples collected after heavy rains, while the distribution pattern in the particulate phase was dominated by heavy compounds (mean LMW/HMW_P = 0.58 ± 0.17). The rain event particularly affected the dissolved phase at PB site where PB-SSW-Sum10 (AR) got highly enriched in $PAHs\text{-}_P$ (by a factor 12) and displayed a decrease in LMW/HMW_P (by a factor 16) with respect to PB-SSW-Sum10 (BR). In the same way, PAH concentration values recorded for both phases of VP-SML-Win10 (AR) were the highest among the sites for the season (winter 2010). Furthermore, at VP site, between summer 2009 and winter 2010, LMW/HMW_P decreased from ~4.8 to ~0.8 (both dissolved SML and SSW) and from 0.6 to 0.1 (particulate SML). This decreasing reflected an enrichment in heavy compounds.

At all sites, for dissolved and particulate phases, Phe/Ant ratio ranged from 1.9 to 39 and from 2.4 to 54, respectively, whereas Flt/Pyr ratio ranged from 0.13 to 1.6 and from 0.12 to 1.4 respectively (Table 3). The variation range of these ratio values, around 10 and 1 for Phe/Ant and Flt/Pyr ratios, respectively, suggested both petrogenic and pyrogenic origin for PAH contaminations. A crossover comparison of these ratios is presented later to assess the relative importance of these two origins. In addition to parent PAH concentration values, $PAHs\text{-}_{P+A}$ concentrations allowed to evaluate the range of potential enrichment in aromatic compounds of both phases ($PAHs\text{-}_{P+A}/PAHs\text{-}_P$: 1.2–7.6 and 1.6–23.4 for dissolved and particulate phases, respectively) due to alkylated homologues. Moreover, alk/parent and LMW/HMW_{P+A} were generally highly >1 for the set of samples (mean particulate values: 11 ± 9.6 and 3.7 ± 2.6, *n* = 25, respectively; mean dissolved values: 3.9 ± 2.7 and 8.4 ± 8.0, *n* = 25, respectively). Thus, the widespread presence of alkylated homologues in Marseilles coastal area clearly suggested dominating petrogenic signatures in almost all samples. However, pyrogenic contributions might have been detected in some of these samples with regard to parent compounds (Phe/Ant < 10 and Flt/Pyr > 1 ratio values).

4. Discussion

4.1. Potential enrichment of the SML (EFs)

The SML represents the interface between the ocean and the atmosphere where the transfer of material is controlled by complex physico-chemical processes and which can serves as both a sink and a source of anthropogenic compounds. EF provides an estimation of the degree of enrichment in lipophilic compounds of the SML with respect to the SSW. Recently, a review paper dealing with the levels of contaminants in the SML reported that the concentration and EF values published so far were rather contradictory (Wurl and Obbard, 2004). Indeed, EF variability must be interpreted with caution. It may be due to the thickness of the

SML depending on the sampling device and on a number of external factors. Except for 5 of 36 values (all 5 recorded in winter and ranging from 0.45 to 0.95; Tables 2 and 3), EFs showed that higher hydrocarbon concentrations were found in the SML, up to 84 and 1138 for PAHs-$_P$ and *R* respectively, underscoring the high enrichment potential of the air–sea exchange microlayer. If our lowest EF values are in the range of the literature for low or moderately anthropised environments (Witt, 2002; El Nemr and Abd-Allah, 2003), our highest values, especially for AHs, are closer to ones usually encountered in strongly contaminated areas (Hardy et al., 1990; Burns and Codi, 1999; Cincinelli et al., 2001). In areas contaminated by petroleum, the surface film can be enriched by a factor of 1000 (Marty and Saliot, 1976; Hardy et al., 1987) and up to 2000 (Guitart et al., 2008) with hydrocarbons as a result of slick formation. This suggests that in urban Mediterranean harbours, the SML may be strongly impacted by shipping traffic. Besides, no statistically significant differences were found for EF values, neither with reference to season (summer *versus* winter) nor to sites, nor to phase partitioning (dissolved *versus* particulate), nor to hydrocarbons (AHs *versus* PAHs) (*U*-test, $p > 0.05$). In addition to the low number of SML samples, this lack of correlation may be explained by SML formation processes in the Marseille areas (tensio-active properties of organic compounds and low wind intensity) which are not controlled by seasonality.

4.2. Distribution of aliphatic hydrocarbon (AHs), biogenic versus anthropogenic sources

As expected from AH hydrophobic properties, *R* concentrations (a series of resolved C_{16}–C_{35} *n*-alkanes and 2 isoprenoids) were significantly lower in the dissolved phase (0.13–38 and 0.05–0.41 μg l^{-1} in SML and SSW, respectively) than in the particulate phase (1.4–1366 and 0.04–4.3 μg l^{-1} in SML and SSW, respectively) (*U*-test, $p < 0.05$) in agreement with Cincinelli et al. (2001) and Stortini et al. (2009) and contrary to the results observed by Marty and Saliot (1976) and Marty et al. (1988). The variability of *R* concentrations in the particulate phase was greater than in the dissolved one. The dissolved *R* concentration levels reported in this paper, except for three SML harbour water samples, can be compared to levels recorded in Antarctic water between 1998 and 2001: 0.11 to 0.30 μg l^{-1} for the SSW and from 0.15 to 0.53 μg l^{-1} for the SML (Cincinelli et al., 2005; Stortini et al., 2009). The three highest SML values, one in each harbour (1.7, 32 and 38 μg l^{-1}) were in the range of values recorded by Marty and Saliot (1976) in the NW Mediterranean (Nice offshore waters, France) and by Cincinelli et al. (2001) in the highly contaminated harbour of Leghorn (Italy), where dissolved SML values ranged from 0.2 to 43.9 μg l^{-1}. More than half of particulate *R* concentration levels reported here (0.04–0.33 μg l^{-1}) for the SSW were up to one order of magnitude higher than levels reported by Dachs et al. (1999) for the Catalan Sea (NW Mediterranean) but were still in the range of Antarctic expedition data cited above (0.16–0.32 μg l^{-1}). However, the rest of the SSW (>0.32 μg l^{-1}) and all SML concentration values were in the range of values obtained in more contaminated areas (Cincinelli et al., 2001). Because of this high variability and as regards the relatively low number of samples, no statistically significant differences were found for *R* concentrations with reference to season. Furthermore, no significant differences were observed in dissolved *R* concentrations between sites (*U*-test, $p > 0.05$). By contrast, we found that particulate *R* concentrations were significantly lower at the two nearshore stations (SOF and SOL) than in SA and VP harbours, and significantly lower in the sewage effluent area (CO) than in SA harbour (*U*-test, $p < 0.05$).

The C_{16}–C_{23}/R and CPI_{21-33} ratios allowed us to discriminate biogenic, anthropogenic or mixed (anthropogenic and biogenic) sources since C_{16}–$C_{23}/R > 0.5$ and $CPI_{21-33} < 3$ indicates petroleum inputs while C_{16}–$C_{23}/R < 0.5$ and $CPI_{21-33} > 3$ indicates terrestrial biogenic inputs. Fig. 2 shows the relationship between these two ratios. Data indicated that AHs were of mixed origin in most dissolved SSW samples, at all stations except SA, while in the SML, and especially in particles, they were mainly of anthropogenic origin. In particulate SSW samples, more various inputs were identified, strictly anthropogenic (mainly in harbours), strictly biogenic (at CO and SOL sites) and mixed origin, which points out the view that suspended matter in the water column is the site of both biological production and hydrocarbon adsorption. Although Fig. 2 gives a global picture of the contamination origin, the distribution of other ratios (Pr/Phy and UCM/*R*) may bring some relevant information about additionnal sources. A large UCM hump (UCM/*R* > 4; Mazurek and Simoneit, 1984) has been related to the presence of biodegraded petroleum wastes. Thus, while particulate AHs of CO-SSW-Sum10 (AR) were considered of biogenic nature according to Fig. 2, UCM/*R* value (9.3) indicated a high anthropogenic contribution to inputs. The complex contamination pattern of this sample exhibiting distinctly both strong biogenic and anthropogenic inputs was probably due to heavy rain effects draining large amounts of mixed origin hydrocarbons. Indeed, on one hand the Cortiou Cove is located very close to land and it could be widely influenced by terrestrial inputs as we can observe for particulate CO-SSW-Sum09. On the other hand, this site could receive large amounts of biodegraded petroleum wastes (dissolved and particulate SML) from the sewage treatment plant, especially after heavy rains. Actually, when it rains, the SE flow rate significantly rises. Above 12 m^3 s^{-1}, the treatment plant cannot process the SE anymore, which is directly (untreated) discharged into the Cortiou Cove. Alternatively, high values of Pr/Phy ratios show marine biogenic sources (Wang et al., 1999). Therefore, in Port de Bouc harbour during summer 2009 (PB-SML-Sum09), while dissolved AHs were considered of anthropogenic nature according to the dominance of short chain aliphatic hydrocarbons and carbon preference index clues (Fig. 2), the very important Pr/Phy ratio value (14; Table 2) points out a strong marine biogenic feature to hydrocarbon distribution at this site. PB is situated in the Gulf of Fos-sur-mer and is surrounded by the Marseilles-Fos petrochemical complex, which includes several chemical, petroleum and steelwork plants. In addition, the Gulf of Fos-sur-mer receives some freshwater inputs coming from the Rhône River and the Berre Lagoon (Ulses et al., 2005; Pairaud et al., 2011) which might stimulate autochthonous phytoplankton production (Para et al., 2010; Pairaud et al., 2011).

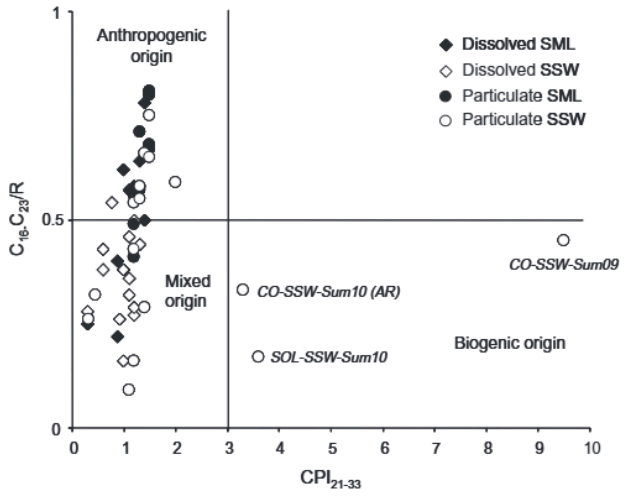

Fig. 2. Cross plot of C_{16}–C_{23}/R *versus* CPI_{21-33} values for SML and SSW at all sites.

4.3. Distribution of polycyclic aromatic hydrocarbons (PAHs), petrogenic versus pyrogenic origins

Shipping activity is known to increase PAH concentrations in harbour areas, in the SML in particular. For instance, the total (dissolved and particulate) concentrations of PAHs-$_P$ in the SML reached up to 6 μg l^{-1} in the Chesapeake Bay (Hardy et al., 1990), 56 μg l^{-1} in the harbour of Los Angeles (Cross et al., 1987) and 170 μg l^{-1} in Leghorn (Cincinelli et al., 2001). In this study (Marseilles coastal area and SOL site), the parent PAH concentrations (50–217 and 6.0–1597 ng l^{-1} in dissolved and particulate SML, respectively, 1.9–98 and 1.9–21 ng l^{-1} in dissolved and particulate SSW, respectively) showed a moderate contamination of the area when compared to marine areas cited above. Except for particulate SA-SML-Sum09 (1597 ng l^{-1}; Table 3), the concentration levels were comparable to previous concentrations measured in this area (Bouloubassi and Saliot, 1991; Tedetti et al., 2010) or in other Mediterranean coastal areas (El Nemr and Abd-Allah, 2003; Manodori et al., 2006). However, for Barcelona (Spain), Guitart et al. (2007) reported lower values, up to one order of magnitude for both SML and SSW, either in the dissolved or in the particulate phases. Like AHs, no significant differences were observed in PAHs-$_P$ concentrations between the sites for the dissolved phase (U-test, $p > 0.05$). On the contrary, we found that particulate PAHs-$_P$ concentrations were significantly lower at the two nearshore stations (SOF and SOL) than in the sewage effluent area (CO) or than in SA and VP harbours (U-test, $p < 0.05$). Otherwise, alkylated homologue concentrations have to be taken into consideration for assessing the global content and distribution of PAHs as well as the acute incidence in mortality of aquatic biota. Our PAHs-$_{P+A}$ concentrations could not be easily compared with literature due to a lack of available data of alkylated homologue concentrations in the water column. Nevertheless, Gonzales et al. (2006) reported concentrations of 25 PAHs-$_{P+A}$ for offshore Galicia coast (NW Spain) after the Prestige oil spill. For the SSW, they measured dissolved + particulate concentrations ranging from 250 to 5800 ng l^{-1} and from 350 to 580 ng l^{-1} just after spillage and several months later, respectively. In our study, dissolved + particulate PAHs-$_{P+A}$ ranged from 11 (SOL) to 370 ng l^{-1} (SA) and from 158 (SOF) to 38,283 ng l^{-1} (SA) for SSW and SML, respectively. Therefore, it is worth noting that some of our SML PAH-$_{P+A}$ values were in the range of the media lethal concentration (LC50) for standardized test species, calculated on 26 and 40 PAHs-$_{P+A}$ (2200–245,000 ng l^{-1}; French, 1998; Barron et al., 1999).

As for AHs, no significant seasonal differences were observed. However, contrary to AHs, PAHs-$_P$ concentration values depicted a preferential accumulation in the dissolved phase with respect to the particulate one (U-test, $p < 0.05$). This behavior is in contrast with the observation that most of PAHs are associated with particles, particularly in polluted environments (Hardy et al., 1987) but

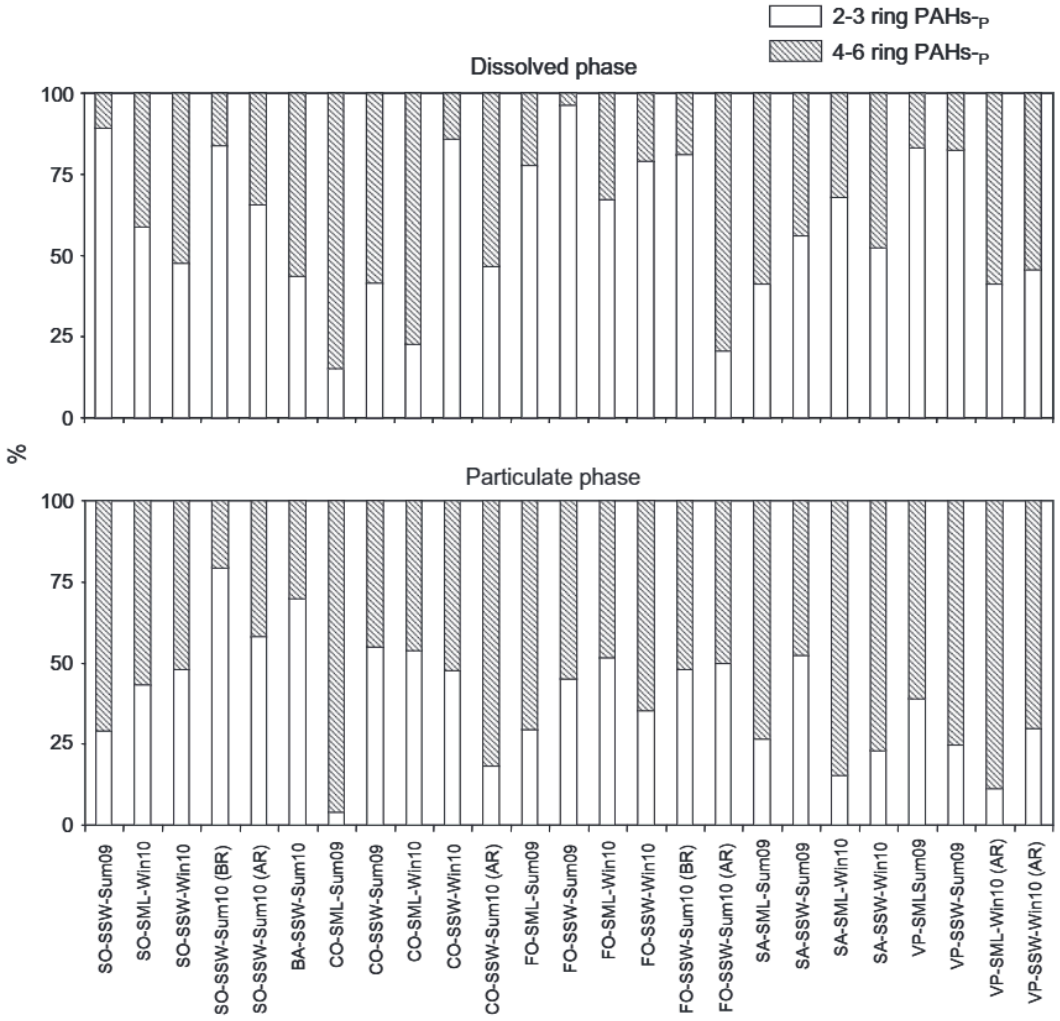

Fig. 3. Relative abundance of parent PAHs in the dissolved and particulate phases of SML and SSW samples.

it is in agreement with Bouloubassi and Saliot (1991), who demonstrated that the greatest PAH fraction was found in the dissolved phase in the Rhone delta waters. These latter authors also stipulated that dissolved PAHs might be as important as or even more important than the corresponding particulate pool, especially in the systems with low suspended matter load. Tedetti et al. (2010) also reported higher concentrations of PAHs in dissolved than in particulate phase in Marseilles coastal waters. As suggested by Cincinelli et al. (2001), these observations can be also attributed to the presence of slicks, which dissolve PAHs and allow these compounds to reach unusual concentration levels in water. Furthermore, the PAH distribution between the particulate and dissolved phases is strictly related to their octanol–water constant (K_{ow}). As reported in Fig. 3, while the LMW PAHs (2–3 rings) were predominant in the dissolved phase (60 ± 23%), the HMW PAHs (4–6 rings) dominated with particulate associated material (61 ± 18%) (ANOVA, $p < 0.05$). These findings are in line with those of Stortini et al. (2009). Nevertheless, due to this partitioning of LMW and HMW compounds between the two phases, directly related to their difference of solubility, the LMW/HMW ratio could be used to assess the nature of contaminants featuring each phase independently, but would not be very relevant to identify and compare the origin of the contamination for the whole sample set (dissolved and particulate samples). Hence, to identify the contamination sources of PAHs, it seems more appropriate to use indices that are not affected by the dissolved/particulate partitioning, such as the ratios between isomer compounds (Phe/Ant and Flt/Pyr) (Mille et al., 1982; Readman et al., 2002; Lim et al., 2007). Fig. 4 presents the cross plot between these two ratios. Clearly, PAHs in the Marseilles coastal area were mainly of strictly petrogenic or mixed origin. SML samples were rather of strictly petrogenic origin and only two (from dissolved SSW) over the set of samples were of strictly pyrogenic origin, corroborating the idea that the Marseilles coastal area was rather impacted by release of unburned petroleum from shipping traffic and surface runoffs.

4.4. Heavy rain effects

The load factors (LFs) were calculated for samples collected before (BR) and after (AR) rain in the SSW (i.e. at SOF and PB only). In the particulate phase, the LFs of R and $PAHs_{-P}$ concentrations ranged from 0.36 to 1.4 and from 0.87 to 2, respectively, while in the dissolved phase they ranged from 4.6 to 6.8 and from 1.9 to 11.5, respectively. Even though calculating a LF for CO and VP sites was not possible because of sampling sequences, high hydrocarbon concentrations recorded for particulate CO-SSW-Sum10 (AR) and for both phases of VP-SML-Win10 (AR) might be attributed to rain effects. The LF values for both aliphatic and aromatic compounds were significantly higher for the dissolved phase than for the particulate one (*U*-test, $p < 0.05$). In the Singapore harbour, for SSW samples, Lim et al. (2007) found most LF values closed to 1 for both phases, but one value of 38.5 for the particulate phase. They observed that the LF value was dependent on rainfall intensity and that a higher wash-out of atmospheric particulate resulted in the higher enrichment of particulate-associated hydrocarbon contaminations in the SML and the SSW. Otherwise, Witt (2002) observed that if the equilibrium between dissolved and particulate phases is disturbed, PAHs can desorb from particles into the dissolved phase, which could explain the lowest LF values recorded at SOF site (0.36 and 0.87). On the other hand, after heavy rains there would be a higher deposition of rainwater-dissolved PAHs directly to the surface waters as well as increased runoffs (rivers, sewages, road surfaces) as suggested by King et al. (2004) for the Brighton marina (UK). In addition, due to their relatively high water solubility, these two effects (desorption from the particulate and rainwater-dissolved PAHs deposition) would be expected to be greater for the LMW compounds, leading to the 2–3 ring compound enrichment of the dissolved phase (Manoli et al., 2000; Park et al., 2002; King et al., 2004). Contrasting with this latter assumption, the heavy rains in the present study led to enrichments in heavy compounds, which is in agreement with results by Lim et al. (2007).

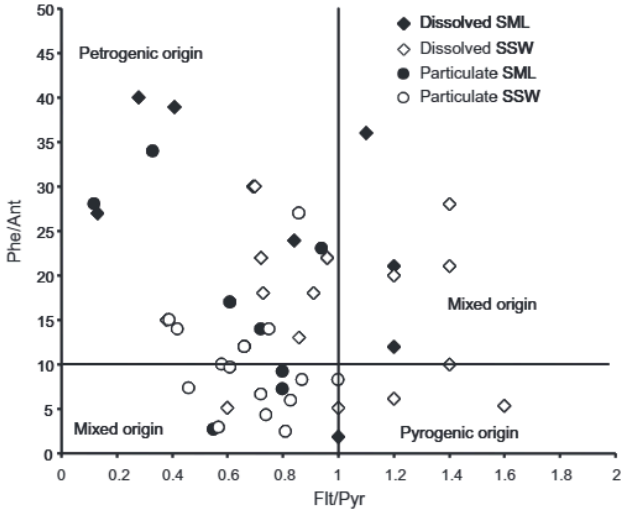

Fig. 4. Cross plot of Phe/Ant *versus* Flt/Pyr values for SML and SSW at all sites.

5. Conclusions

This study highlights that the Marseilles costal area was moderately contaminated with regard to the AH and PAH concentrations compared to other coastal environments, although some SML values in harbours (Saumaty, Vieux Port) and in treated sewage effluent (Cortiou) could reach toxic levels for marine biota. In the SML, AHs were essentially of anthropogenic origin, whereas a mixed origin and a strictly biogenic origin also appeared in the SSW. The biogenic matter signatures might be due to allochthonous terrestrial contributions and/or autochthonous plankton production. In both SML and SSW, PAHs were mainly of petrogenic and mixed origins, while the strictly pyrogenic source was revealed only for two SSW samples. This emphasises the anthropogenic pressures on the Marseilles area, with hydrocarbons very likely derived from shipping traffic, spillage incidents, surface runoffs and urban/industrial wastes, surimposed on terrestrial and marine biological sources. The variability and spatial differences in term of concentration were more visible in the particulate phase than in the dissolved one. By contrast, this study emphasises the interest of the dissolved phase for recording background contamination levels in low molecular weight PAHs in coastal areas. Otherwise, we pointed out the importance of SML enrichment factors (exacerbated for the particulate phase and for AHs) and of heavy rains on hydrocarbon concentrations and distributions. This work also underlined the importance to take into account alkylated homologues for accurately assessing the levels of PAHs in the coastal environments, and to use indices/ratios that are not affected by the phase partitioning when studying the origins of dissolved and particulate compounds.

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