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Polycyclic Aromatic Hydrocarbon Degradation and Sorption Parameters in Coastal and Open-Sea Sediment

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Abstract This work describes the experimental determination of the major degradation and sorption parameters of polycyclic aromatic hydrocarbons (PAHs) in a sensitive marine environment, the Northern Adriatic Sea (Mediterranean Sea). The persistence and sorption of complex PAH mixtures were analysed in the laboratory in conditions mimicking open-sea and coastal sediments, which differ in grain size and organic carbon content and are characterized by different oceanographic conditions including abiotic influences. The study investigated how sediment type and texture and salinity, temperature and solar irradiation conditions affect the partitioning of low molecular weight (LMW) and high molecular weight (HMW) PAHs into aqueous and solid phase, which critically influence their behaviour. With regard to the change from offshore to coastal conditions, HMW PAHs were found to be more sensitive to the increased salinity (from 21 to <37 parts per thousand), whereas LMW PHAs were more sensitive to the temperature increase (from 11 to 22 °C). HMW PAHs were more affected by sediment type changes in terms of distribution coefficient (K_d). Since the physicochemical properties of organic pollutants affect their distribution, transport, bioavailability and toxicity, analysing the accumulation and persistence of dissolved pollutants can provide useful information for environmental risk assessment and management.

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Keywords $t_{1/2}$ · K_d · K_{oc} · PAHs · Adriatic Sea · Coastal sediment · Open-sea sediment

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an ubiquitous class of pollutants that tend to persist in the environment. Due to their toxicity to humans, mutagenicity and carcinogenicity, 16 PAHs are included in the US Environmental Protection Agency (EPA) priority pollutant list (Laflamme and Hites 1978; Keith and Telliard 1979; Neff 1979; Elmquist et al. 2007; Honda et al. 2007; Parinos et al. 2013). These organic compounds are found in all environments. In marine water, they are found especially near the areas involved by intense human activity such as harbours, industrial site urban areas and close to river estuaries (Yunker et al. 2002; Kannan et al. 2005; Lucialli et al. 2007; Botsou and Hatzianestis 2012; Manzetti 2013). Along their route from their petrogenic or pyrogenic sources to the water column and coastal and open-sea sediments, PAHs undergo chemical and biological processes that affect their toxicity (e.g. photo-oxidation) and turn them into more reactive products that are more subject to bioaccumulation (Shor et al. 2004; Bihari et al. 2006; Parinos et al. 2013). The main processes are sorption and degradation (Neff et al. 2005; Celis et al. 2006; Sehili and Lammel 2007; Haritash and Kaushik 2009; Wu and Sun 2010). Particle-water interactions are among the most important mechanisms affecting the distribution and movement of hydrophobic organic chemicals in aquatic environments (Trevisan et al. 1995; Zhou et al. 1999; Xia and Wang 2008). Aqueous-phase PAHs are more available and therefore have a greater toxic potential, than solid-phase PAHs. Owing to their highly hydrophobic nature, PAHs show strong sorption to sediment organic matter and to fine combustion particles (like soot and/or char black carbon), which protect them from degradation during transport in water (Dachs et al. 2002; Yunker et al. 2002; Ravaioli et al. 2003; Neff et al. 2005; Parinos et al. 2013). The partitioning of organic compounds into solid and aqueous phase can be expressed by the distribution coefficient (K_d), a physicochemical parameter describing the ratio of solid phase (C_s, ng g^{-1} d.w.) to aqueous phase (C_w, ng ml^{-1}), where C is the concentration of the contaminant (Karickhoff et al. 1979; Trevisan et al. 1995; Yu et al. 2009). Moreover, the organic carbon (OC)/water partition coefficient (K_{oc}) can help select appropriate test parameters for sorption studies based on the equation $K_{oc}=K_d/f_{oc}$, where f_{oc} is the total OC (TOC, %) fraction of sediment. K_{oc} is similar to the octanol/water partitioning coefficient (K_{ow}), which is frequently used in modelling non-polar organic compound bioconcentrations (Neff et al. 2005). Substance persistence in marine sediment is usually defined by its half-life ($t_{1/2}$), i.e. the loss of 50 % of the initial concentration of the contaminant (Marini and Frapiccini 2013).

This study complements previous PAH research conducted by the authors in the Northern Adriatic Sea (Marini and Frapiccini 2013). In the present work, three key degradation and sorption parameters, $t_{1/2}$, K_d and K_{oc}, are calculated experimentally and compared in conditions mimicking coastal and open sea, to gain insights into PAH bioavailability in the marine environment and provide data on the mobility of solid- and aqueous-phase PAHs.

2 Materials and Methods

2.1 Study Area

The Northern Adriatic Sea receives important PAH inputs from the Po Valley, a major industrial and agricultural area with a dense population (Stracquadanio et al. 2007; Masiol et al. 2013). Several Alpine and Apennine rivers running through it discharge organic contaminants including PAHs into the Northern Adriatic Sea (Castellarin et al. 2011). Freshwater inputs generally form a coastal layer characterized by cyclonic circulation; since most of this water is discharged by the Po River, the layer is found mainly south of the Po River delta (Campanelli et al. 2004, 2011; Marini et al. 2008). In a previous study, we examined persistence in deep Northern Adriatic Sea sediment (Marini and Frapiccini 2013). The present study compared PAH persistence and sorption in coastal and open-sea sediment. Sediment samples were collected at the same sites as in the previous study: site A, a shallow water area close to Ravenna harbour, in the Po Valley (Fig. 1) and site B, an open-sea area along the Adriatic Sea midline, 50 km off Ancona (Fig. 1).

2.2 Sediment Collection and Characterization

Sediment samples (0–2 cm), two from site A and five from site B, were collected using a box corer (17×10×24.5 cm). After removal of gross material and debris, samples were stored in transparent glass jars at −18 °C until analysis. Particle size was classified according to Shepard (1954). TOC was measured in silver capsules using a FISONS NA2000 Element Analyzer (Tesi et al. 2006) after dissolving the sample in 1.5 N HCl to remove the carbonate fraction. Bottom water samples (one per site) were analysed for salinity and temperature by the CTD multiparameter probe (Campanelli et al. 2011). Sediment and water data are reported in Table 1.

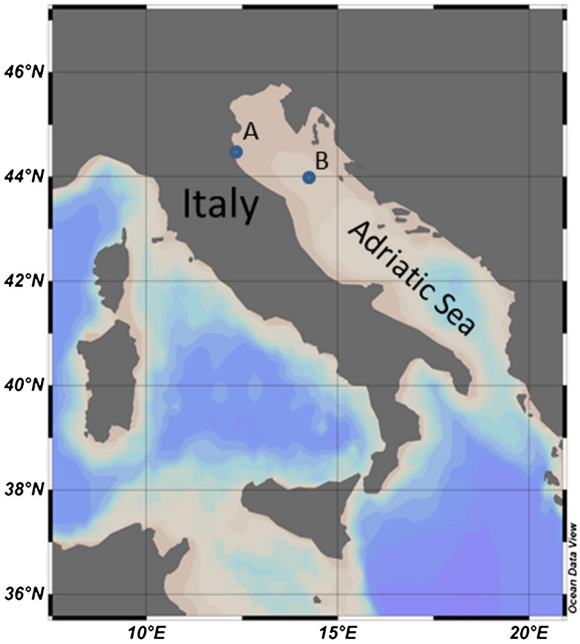

Fig. 1 Map of the Adriatic Sea and geographical localization of the two sampling sites

Table 1 Description of study area, temperature (°C), salinity (ppt), bathymetry (m), sediment characteristics (min, max, average, %) and sum of PAH total (ng g^{-1} dry weight) of site A and site B

Sampled site	Study area description	Temperature[a]	Salinity[a]	Bathymetry	Sand	Silt	Clay	TOC	PAHs total
Site A (*n*=2)	Coastal Ravenna harbour	18–22	21–33	10	57.4[b] (56.4–58.3)	31.0[b] (27.7–34.2)	11.6[b] (9.3–13.9)	0.8	321.1
Site B (*n*=5)	Open-sea Adriatic Sea midline	<11	>37	76	7.9[b] (7.1–9.3)	34.9[b] (30.1–35.1)	57.2[b] (53.1–58.4)	3.4[b]	108.0[b]

[a] Measured by the CTD multiparameter probe

[b] In accordance with Marini and Frapiccini (2013)

2.3 Laboratory Conditions and PAH Subdivision

The characteristics of coastal (site A) and open-sea (site B) sediment were reproduced in the laboratory according to Artegiani et al. (1997) based on the laboratory conditions reported by Marini and Frapiccini (2013): 18–22 °C and sunlight for site A and <11 °C and darkness for site B. Salt concentrations, prepared with synthetic seawater, were 21–33 and >37 ppt (part per thousand, 1 ppt=1‰) for site A and site B, respectively.

$t_{1/2}$, K_d and K_{oc} were measured in PAH compounds and averaged on the basis of their molecular weight. PAHs with two and three aromatic rings (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) were considered as low molecular weight (LMW) PAHs (Bajt 2012) and those with four, five and six rings (fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benz[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) were considered as high molecular weight (HMW) PAHs.

2.4 Chemicals and PAH Extraction

The chemicals used were dichloromethane, acetonitrile for high-performance liquid chromatography (HPLC) gradient grade (VWR International, Fontenay-sous-Bois, France), and formaldehyde 40 % (Sigma-Aldrich, St. Louis, MO, USA). A standard PAH solution with dichloromethane (1 ml) containing the 16 priority pollutants (EPA 610 PAH Mix, Supelco, Bellafonte, PA, USA) was used as the inoculum for batch tests. PAH compounds were extracted from wet sediment samples (10 g) in an ultrasonic bath (Sun et al. 1998) (three 15 min cycles) using dichloromethane (20 ml). The solvent extracted was centrifuged, and the suspended fraction was gradually reduced by rotary evaporation (28±2 °C). The dry residue was recovered with acetonitrile (0.5 ml). In the sorption study, PAH was extracted only from the aqueous phase by liquid-liquid separation using dichloromethane (25 ml).

2.5 PAH Quantification and Recovery Test

PAH quantification was carried out by HPLC (Ultimate 3000, Thermo Scientific, Waltham, MA, USA) with Thermo Scientific fluorescence and diode array detectors. The 16 LMW and HMW PAHs were separated with a gradient programme (1.5 ml min^{-1}) on an analytical reverse-phase column C16 (4.6×150 mm, 3 μm, 120 Å). A mixture of acetonitrile and water (Mill-Q system, Millipore, Billerica, MA, USA) was used as the mobile phase. A calibration solution was prepared from the standard PAH solution by serial dilutions (1:50, 1:100 and 1:200). The wet weight of each sediment sample was corrected to dry weight, after determination of percent sediment humidity. Concentrations were expressed on a dry weight basis. The detection limit of the method was 0.04–0.4 ng g^{-1}, estimated as three times the background noise.

The methods employed were validated by the recovery test, which was carried out using certified sediments for PAHs (IAEA/MEL/65 1998; IAEA/MEL/67 1999) and wet marine sediments. Recovery rates were 65 % (LMW PAHs) and 82 % (HMW PAHs) in certified sediment and 59 % (LMW PAHs) and 100 % (HMW PAHs) in wet marine sediment.

2.6 Determination of the Degradation Parameter ($t_{1/2}$)

The degradation parameters were calculated by tests carried out on all sediment samples from both areas in laboratory conditions reproducing the environmental conditions of coastal and open-sea sediments. The degradation parameters were determined according to Marini and Frapiccini (2013). A known quantity of standard PAH solution (dil. 1:10) was used to spike the samples (2 ml in 200 g). The total PAH concentration of the inoculum for each sediment sample was 597 μl g^{-1}. After an equilibration time of 24/48 h, PAH degradation rates were studied as described above for 50 days, to detect microbial degradation (Shuttleworth and Cerniglia 1995). A first-order degradation model with two fitting parameters was applied to fit the concentration data. The first-order rate constant (K) was obtained from the equation $C=C_0 \exp^{(-kt)}$, where C was the concentration of a target compound at time t and C_0 was the average initial concentration (Hinga 2003; Chen et al. 2014). $t_{1/2}$ was calculated using the formula $\ln 2/r= 0.693/r$, where r is the mean slope of the degradation curve over the period of observation (Viñas et al. 2009).

2.7 Determination of Sorption Parameters (K_d and K_{oc})

The sorption parameters were established by batch tests carried out to build the equilibrium sorption isotherms using five different initial concentrations of standard PAH solution (EPA 610, 1:10, 1:25, 1:50, 1:100 and 1:200) and dichloromethane as the solvent. Dry sediment (1 g) was used in each batch test with a final solution volume of 10 ml, with 0.4 % formalin to inhibit microbial activity (Means 1995; Marini and Frapiccini 2014). Samples were placed into glass centrifuge tubes, sealed, and then equilibrated in a shaking table (1000 rpm) in the dark at a temperature of 25±0.5 °C. Equilibrium was achieved in about 24 h (Means 1980; Barret et al. 2010; Soares et al. 2013). After equilibration, the solutions were centrifuged at 3000 rpm at a controlled temperature (25±0.5 °C) for 30 min, to separate the solid and aqueous equilibrium phases, then PAH were extracted as described above. Blank samples to calculate the PAH concentrations sorbed to the solid phase were prepared in the same way as the sediment samples, but without sediment. The PAH concentrations sorbed to the solid phase were calculated as the difference between blank and sediment samples (Kohl and Rice 1999).

3 Results and Discussions

3.1 Degradation Parameter ($t_{1/2}$)

The data regarding the degradation parameter ($t_{1/2}$) studied in the sediments mimicking coastal and open-sea environmental conditions are reported in Fig. 2a, b.

The experiments showed that the PAH mixtures degraded rapidly in 1–2 weeks in both conditions, as also reported in the previous study (Marini and Frapiccini 2013). A clear relationship was found between degradation rate and molecular weight, since HMW PAHs showed a longer $t_{1/2}$, owing to their lower aqueous solubility and greater incorporation to the organic fraction of sediment, which limited the access of degradation microorganisms (Lei et al. 2005; Achten et al. 2011).

It is well established that an increase in salinity affects the solubility of chemicals in water (Ni and Yalkowsky 2003). This was demonstrated by a slight difference in $t_{1/2}$ values between the two sites. The $t_{1/2}$ values of PAHs in sediment reproducing coastal salinity conditions were 3.8 and 4.6 days for LMW and HMW PAHs, respectively, whereas those of PAHs analysed in sediment mimicking open-sea salinity were respectively 4.8 and 6.7 days (Fig. 2a). The latter values were therefore slightly higher (by 1 and 2.1 day, respectively, for LMW and HMW PAHs) due to the higher salinity of

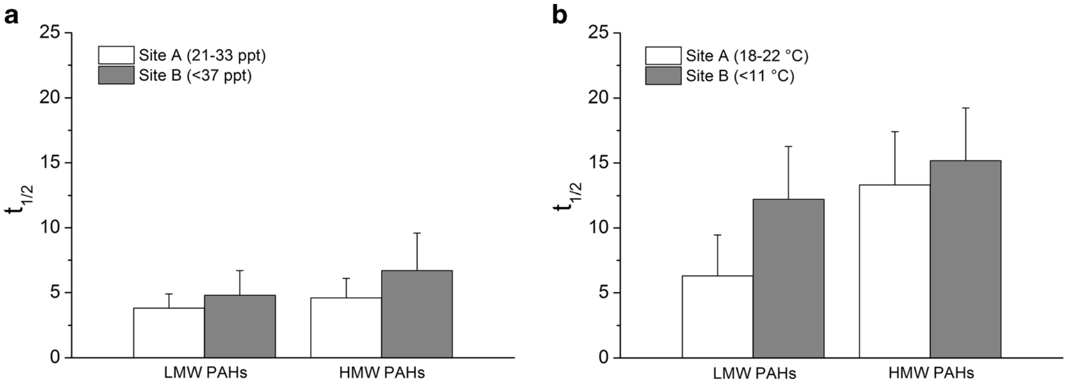

Fig. 2 **a** Half-lives of LMW and HMW PAHs studied in sediment reproducing site A (coastal) and B (open sea) salinity conditions. **b** Half-lives of LMW and HMW PAHs studied in sediment reproducing site A (coastal) and B (open sea) temperature conditions

open-sea water, which reduces non-polar PAH water solubility (Tremblay et al. 2005; Shukla et al. 2007). Oh et al. (2013) found that PAH water solubility decreased as salinity increased from 0 to 30 ppt in coastal sediments, resulting in enhanced PAH sorption. Our findings confirm their data, especially with regard to open-sea sediments, where salinity was higher (30 ppt). Thus, salinity increased the PAH sorption capacity of sediment and reduced PAH degradation rates. As demonstrated in our previous study (Marini and Frapiccini 2013), HMW PAHs were more sensitive to the salinity change (from 21 to <37 ppt) than LMW PAHs, resulting in a degradation rate of 30 % in presence of the higher ionic concentrations.

The $t_{1/2}$ values of the PAHs studied in conditions reproducing coastal temperature and sunlight were 6.3 and 13.3 days for LMW and HMW PAHs, respectively, whereas those of the PAHs studied in sediment mimicking open-sea temperature and darkness conditions were 12.2 and 15.6 days, respectively (Fig. 2b). As regards the influence of temperature and solar irradiation at the two sites, $t_{1/2}$ values were markedly higher in open sea compared with coastal sediments, due to lower temperature (<11 °C) and darkness. Enell et al. (2005) have demonstrated that temperature reduction affects PAH release and reduces desorption rates. In the present study, the temperature decrease (from 22 to 11 °C) reduced degradation rates; in particular, LMW PAH persistence increased by 48 % in conditions of low temperature and lack of solar irradiation. Temperature thus plays a significant role in controlling PAH bioavailability and toxicity, as also reported by Vieira and Gudhermino (2012) and as described by Marini and Frapiccini (2013) in laboratory conditions.

3.2 Sorption Parameters (K_d and K_{oc})

K_d values were determined by construction of linear adsorption isotherms, to estimate the sediment/water partitioning of LMW and HMW PAHs in marine sediments with different grain size and TOC. The K_d values were averaged on the basis of molecular weight and are reported in Fig. 3. K_d values in the sandier coastal sediments, which are poor in OC, were 10.3 and 16.7 for LMW and HMW PAHs, respectively, whereas in the clayey and OC-rich open-sea sediments, they were respectively 9.8 and 31.5. As expected, HMW PAH showed a greater solid-phase fraction than LMW PAHs. The K_d difference between site A and site B was particularly marked for HMW PAHs, whereas they were similar for LMW PAHs. This can be attributed to the fact that HMW PAHs, being more tightly bound to sediment particles due to their physicochemical properties, were more influenced in terms of K_d by sediment-

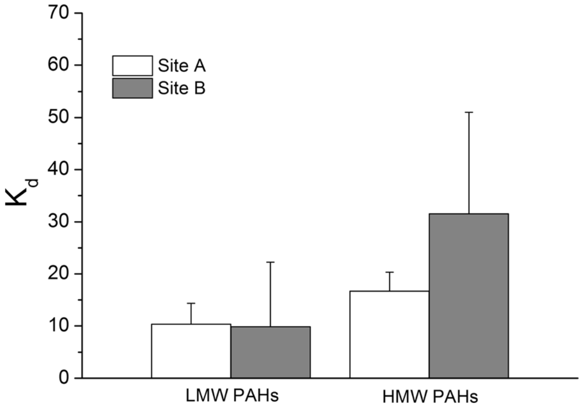

Fig. 3 Average K_d values based on PAH molecular weight at sites A and B

type variations compared with LMW PAHs. HMW PAHs were therefore associated with the clayey site (57.2 %) with high OC content (3.4 %), i.e. open-sea sediment.

Calculation of K_{oc}, where PAH partitioning was normalized with f_{oc}, demonstrated that PAH distribution was affected by geographical site as well as sediment grain size. Log K_{oc} values were higher at site A than that at site B for all 16 PAHs. This work, by comparing two very different sites, lends support to the data reported by Neff et al. (2005), who often found higher log K_{oc} values in urban estuaries or harbour sites. Moreover, the log K_{oc} values determined experimentally in our laboratory (Table 2) were comparable to those predicted by Chu and Chan (2000) and to those calculated experimentally in situ by Yu et al. (2009). Our finding that LMW PAH log K_{oc} values correlated linearly with log K_{ow} values at both sites are in line with the data of Karickoff et al. (1979), who showed a strong correlation between log K_{oc} and log K_{ow}. These correlations were significant both for site A (r=0.936, p<0.01) and for site B (r=0.846, p<0.05). The lack of a correlation between log K_{oc} and log K_{ow} for HMW PAHs—not significant at site A (r=0.629, p>0.05) and negative at site B (r=−0.298)—may be explained by their very low aqueous solubility (Yu et al. 2009).

4 Conclusions

The present study examined the three major degradation and sorption parameters of the 16 PAHs included in the EPA priority pollutant list. The three parameters, $t_{1/2}$, K_d and K_{oc}, were calculated in laboratory conditions mimicking coastal and open-sea sediment under different temperature, salinity and sunlight conditions. The PAHs associated with open-sea sediments exhibited a lower degradation rate, resulting in greater PAH accumulation in sediment particles also as a consequence of their finer grain size and salinity, temperature and sunlight conditions; such conditions reduced the aqueous solubility of PAHs, shifted their partitioning towards the sorbed phase, and limited their biodegradation. Partitioning of the more hydrophobic HMW PAHs involved a greater amount of solid phase and varied according to the grain size and OC content of sediment to a greater extent compared with LMW PAHs. Establishing the values of these parameters allows

Table 2 Log K_{oc} of PAHs in both studied sites (site A and site B) compared with other studies

	Log K_{oc} Site A	Log K_{oc} Site B	Log K_{oc} Yu et al. (2009)	Log K_{oc} Chu and Chan (2000)	Log K_{ow} Karickoff et al. (1979)
Naphthalene	4.75	3.22	3.58	3.11	3.37
Acenaphtylene	5.00	3.21	3.71	3.39	4.00
Acenaphtene	5.06	3.62	3.41	3.66	3.92
Fluorine	5.21	n.d.	3.61	n.d.	4.18
Phenanthrene	5.24	4.80	4.08	4.14	4.57
Anthracene	5.19	4.87	3.70	4.14	4.54
LMW PAHs	5.07	3.94	3.68	3.68	4.10
Fluoranthrene	5.11	4.80	4.33	4.57	5.22
Pyrene	5.21	4.92	4.13	4.57	5.18
Crysene	5.19	4.90	4.17	5.3	5.91
benz[a]anthracene	5.35	4.94	3.79	6.13	5.86
benzo[b]fluoranthene	5.27	4.84	3.80	5.74	5.80
benzo[k]fluoranthene	5.37	5.26	3.66	5.74	6.00
benz[a]pyrene	5.36	5.32	4.40	6.74	6.04
dibenz[a.h]anthracene	5.31	4.81	3.47	6.51	7.04
indeno[1,2,3 c.d]pyrene	5.33	4.42	3.67	6.20	6.75
benzo[ghi]perylene	5.44	4.82	3.46	6.20	6.50
HMW PAHs	5.29	4.90	3.88	5.77	6.03

n.d. not determined

predicting PAH mobility and the bioavailability of PAHs contained in sediments, providing useful data for environmental risk assessment and management.

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