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Assessment of polycyclic aromatic hydrocarbons (PAHs) in mediterranean top marine predators stranded in SE Spain

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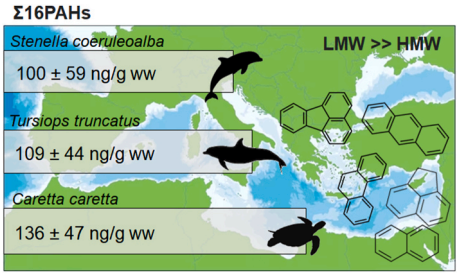
HIGHLIGHTS

- 16 PAHs were measured in fatty tissues from Mediterranean dolphins and marine turtles.
- Detectable concentrations of several PAHs are reported in marine top predators.
- The constant detection of the easily excretable PAHs demonstrates a constant exposure.
- The tissue pattern of PAHs suggests eminently a petrogenic origin.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Although they are not bioaccumulated in vertebrates, chronic exposures might still derive on serious toxic effects. We studied concentrations of 16 reference PAHs on blubber of two dolphin species (striped dolphin, n = 34; and bottlenose dolphin, n = 8) and one marine turtle (loggerhead turtle, n = 23) from the Mediterranean waters of SE Spain, an important or potential breeding area for these and other related species. Σ16 PAHs concentrations were relatively similar between the three species, but they were in the lower range in comparison to worldwide data. Of the six PAHs detected, fluoranthene was the only high molecular weight (HMW) PAH, so low molecular weight (LMW) PAHs predominated. Naphthalene and phenanthrene were invariably those PAHs with higher detection rates as well as those with higher concentrations. In accordance with the literature, sex and length did not have significant influence on PAHs concentrations, probably due to high metabolization rates which prevent for observation of such patterns. Despite LMW PAHs are considered less toxic, we cannot dismiss toxic effects. This is the first work assessing PAHs concentrations in cetaceans and sea turtles from the SE Spain, which could serve as the baseline for future research.

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1. Introduction

PAHs are a large group of organic compounds whose chemical structure is composed of hydrogen and carbon atoms organized in two or more fused benzene rings. Although they have not been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), they are persistent pollutants with long-range transport widely spread across the globe, with the ability of causing negative impacts in both wildlife and human health. Nevertheless, they differ from other POPs in that they can occur in the environment either by natural or anthropogenic sources, although these last are currently the most quantitatively significant [WHO et al., 2003]. They are characterized by a general low water solubility, variable volatility and moderate to high lipophilicity [Latimer and Zheng, 2003], which primary determines their distribution in the environment. However, their molecular weight influence to some degree these characteristics. Higher molecular weights lead to decreased aqueous solubility and vapor pressure, and increased fat solubility and resistance to degradation [Baumard et al., 1998a; Latimer and Zheng, 2003]. In the marine environment PAHs are ubiquitous pollutants; however, they appear at higher concentrations in shallower and coastal waters, especially in those areas highly subjected to anthropogenic inputs, i.e., river mouths, harbors, wastewater pipes, urban/industrial runoff, etc. [Baumard et al., 1998b; Berrojalbiz et al., 2011]. Atmospheric transport of volatilized PAHs is also a relevant marine input, especially in off-shore waters [Tsapakis and Stephanou, 2005, 2006]. According to the primary sources, marine inputs can be classified as petrogenic, when PAHs come from petroleum products (e.g., oil spills, discharges from vessels, urban runoff, or natural oil seeps), or pyrogenic, when they come from incomplete combustion of organic matter (e.g., internal combustion engines or forest fires) [Lawal, 2017]. Due to their high fat solubility, they are easily transferred to the marine food web from the abiotic compartment [Balcıoğlu, 2016]. However, while invertebrates have lower capacities for metabolizing PAHs, vertebrates are considered efficient metabolizers of these compounds [Jonsson et al., 2004; Meador et al., 1995]. They are generally able to degrade rapidly PAHs into more water-soluble molecules which are easily excreted. Therefore, unlike organochlorines and other POPs, PAHs do not biomagnify in the upper levels of the marine food chain [Broman et al., 1990; Takeuchi et al., 2009; Wan et al., 2007]. Nevertheless, PAHs can still cause a wide range of toxic effects in vertebrate biota, including cytotoxic, immunotoxic, reproductive and carcinogenic effects [Dejmek et al., 2000; NTP, 2000; Perera et al., 2012; Villeneuve et al., 2002].

The Mediterranean Sea is currently one of the most impacted marine regions in the world due to its semi-enclosed basin surrounded by several highly populated and industrialized riparian countries. Marine traffic, pollution, overfishing and climate change are worldwide threats which especially affect this region [Campana et al., 2015; Lejeusne et al., 2010; Pace et al., 2015]. While open seas and oceans dilute pollutants in worldwide seawaters, its narrow connection with the Atlantic Ocean through the Strait of Gibraltar makes the Mediterranean Sea particularly efficient at accumulating pollutants. For example, it has been previously probed to be a hotspot for several pollutants, including mercury, polychlorinated byphenils (PCBs) or per- and polyfluoroalkyl substances (PFASs) [Aguilar and Borrell, 1994; López-Berenguer et al., 2020; Martínez-López et al., 2019]. Despite these threats, the Mediterranean Sea holds a unique and rich set of ecosystems characterized by a high biodiversity with a strong endemism [Coll et al., 2010, 2012]. Its water holds endemic populations of various cetacean and sea turtle species which play a key ecological role maintaining the biodiversity and the good environmental status of the oceans [Azzellino et al., 2014; Coll et al., 2010; Moore, 2008]. However, their populations in the Mediterranean Sea are among the most affected by human threats [Coll et al., 2012]. According to IUCN, all Mediterranean cetacean populations for which enough information exist, are considered to be declining. On the contrary, loggerhead turtle Mediterranean population is considered of least concern; however, this status has been classified as conservation-dependent because the current population is the result of decades of intense conservation programs and it still faces severe problems including bycatch, ingestion of marine debris, and chemical pollution [Casale, 2015; Casale and Margaritoulis, 2010; Margaritoulis et al., 2003]. The western Mediterranean basin has localized coastal areas of high PAHs pollution interspersed with areas of low to moderate PAHs pollution, as it has been reported in several studies considering PAHs concentrations in sediments, seawater, or mussels [Barakat et al., 2011; Baumard et al., 1998a; b; Benlahcen et al., 1997]. These localized coastal areas are inexorably linked to harbors and industrial areas [Merhaby et al., 2019]. However, inshore-Mediterranean waters do not seem to be affected by coastal and localized sources of PAHs but by atmospheric deposition and biogeochemical cycles [Berrojalbiz et al., 2011]. Although many studies in the Mediterranean Sea have studied PAHs in mollusks, crustaceans, and fishes [Baumard et al., 1998a; Costa et al., 2016; Frapiccini et al., 2018; 2020], information regarding marine top predators' status is scarce. To our knowledge, only two works have been conducted regarding this issue in Mediterranean cetaceans, both along the Italian coast [Marsili et al., 2001, 2014], and there is not any previous report in turtles from the Mediterranean Sea. Considering the socio-geographical characteristics of the Mediterranean that make this sea an area of potential contamination by PAHs, we considered particularly important to evaluate how this situation may affect some of the most endangered species of this region.

We designed this study to assess for first time in the literature PAHs concentrations in two odontocetes and loggerhead turtles from the Spanish Mediterranean Sea. We used blubber from stranded individuals to determine concentrations of 16 priority PAHs defined by the EPA in order to characterize the pollution exposure of these species in the study area.

2. Materials and methods

2.1. Sample collection

Blubber samples were obtained from two dolphin species, striped dolphin *Stenella coeruleoalba* (n = 34) and bottlenose dolphin *Tursiops truncatus* (n = 8), and loggerhead sea turtle *Caretta* (n = 23), stranded along the Mediterranean coast of the Region of Murcia (SE Spain; Figure SI1) between 2011 and 2018, within the stranding program carried out by the wildlife recovery center of the Region of Murcia "El Valle" (Dirección General del Medio Natural, CARM). We chose these species as they accounted for a higher number of strandings in comparison to other cetaceans and sea turtles and blubber was the tissue of choice as it accumulates the highest concentration of PAHs and it reflects longer-term accumulation of lipophilic pollutants in comparison to other tissues [Storelli et al., 2012]. Samples from dolphins were devoid of skin, while those from sea turtles included it. Sampling was conducted during standardized necropsies and samples were stored separately in plastic bottles and immediately frozen at −20 °C. Sex and total length were recorded during necropsies. Further information on sampling and data collection for both cetaceans and sea turtles can be found at Martínez-López et al., [2019] and Martínez-López et al., [2021], respectively. Samples were kept frozen until the time of the analysis.

2.2. Analytes of interest

Blubber samples were analyzed for the set of 16 priority PAHs identified by the United States Environment Protection Agency [1987]; i.e., acenapthene, acenapthylene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene, dibenz[ah]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene and pyrene. Limits of detection can be found in Table SI1.

For the extraction procedure, analytical grade hexane, acetone, diethyl ether and petroleum ether were acquired from J.T.Baker

(Phillipsburg, NJ, USA) and analytical grade sodium sulfate anhydrous was obtained from Panreac AppliChem (Ottoweg, Darmstadt, Germany). For instrumental analysis, analytical-grade cyclohexane (CHX) and acetone were obtained from Honeywell (Morristown, NJ, USA). The standards of the selected PAHs were purchased from CPA Chem (Stara Zagora, Bulgaria) in a commercial mix of 100 μg/mL in iso-octane. An intermediate solution at 20 μg/mL, and a working solution at 1 μg/mL were prepared in acetone.

2.3. Extraction procedure and instrumental analysis

Samples were kept frozen until the time of the analysis. Prior to the analysis, blubber samples were thawed at room temperature. PAHs were extracted from the tissue by using a mixture of organic solvents. Briefly, a subsample of 0.2 g was taken and homogenized for 5 min in a plastic tube with 20 ml of acetone:hexane 5:15 (v/v). The resultant mixture was passed through a porous plate funnel with 5 g of anhydrous sodium sulfate to a glass flask. 5 ml of extra hexane were passed through the porous plate funnel to the glass flask to drag the maximum target compounds. The resulting extract was evaporated at 35 °C in a rotatory evaporator and redissolved in 5 ml of hexane. For clean-up Florisil® cartridges (Thermo Fisher Scientific, Waltham, MA, USA) were used. 2 ml of hexane were used for conditioning the cartridges. Immediately, the sample extract was passed through the cartridge, followed by 25 ml of petroleum ether:diethyl ether 21:4 (v/v). Both the sample extract and the eluent were collected in a glass flask and again evaporated. Finally, the dry extract was redissolved in 1 ml of hexane and passed to a glass vial.

Instrumental quantification was conducted by gas chromatography by using a GC System 7890 B equipped with a 7693 Autosampler (Agilent Technologies, Palo alto, CA. USA). The separation was performed using two 15 m columns (Agilent J&WHP-5MS, 0.25 mm inner diameter and 0.25 μm film thickness each) joined together using a purged un-ion (PUU, Agilent Technologies) to allow the use of the backflushing technique. Helium (99.999%) was used as the carrier gas and the flow rate was adjusted using retention time (tR) lock function. Temperatures of the oven were programmed as follows: Initial temperature of 60 °C held for 1 min, ramped at 40 °C/min to 170 °C and then at 10 °C/min to 310 °C with 3 min hold time. Total run time was 20 min. Injector and transfer line were set at 280 °C. The injection volume was 1 μL. All samples and standards were analyzed in the split-less mode using a 4-mm ultra-inert liner with glass wool (Agilent Technologies).

The GC was interfaced with a Triple Quad 7010 mass spectrometer (Agilent Technologies), which was used for the detection of all the analytes in a single run. Nitrogen (99.99%) was used as the collision gas. Collision gas flow was set at 1.5 ml/min. The QqQ mass spectrometer was operated under the following conditions: ionization with electron im-pact at 70 eV in multiple-reaction monitoring (MRM) with an emission current of 100.0 μA. The ionization source temperature was set at 230 °C. A filament multiplier delay of 3.7 min was fixed was programmed to allow the solvent front to pass. The electron multiplier voltage was set at 900 V. The dwell time was set at 10 for all the analytes.

The quantification was based on peak areas using 10-point calibration curves in CHX 1% olive oil that ranged between 0.195 and 100 ng/ml. Limits of detection (LoD; Table S1) were determined as the lowest point of the calibration curve having a S/N ratio above and acceptable accuracy (80–120%). More detailed information can be found at Acosta-Dacal et al., [2021].

2.4. Data handling and statistical analysis

Statistical analysis was conducted using SPSS® for Windows® (version 24.0; SPSS, Chicago, IL, USA) and Microsoft Excel 2013. Data management was carried out for both individual compounds and their sum (Σ16 PAHs). PAHs concentrations are expressed on a wet weight (ww) basis and detection rates were expressed for each compound. Values under the limit of detection (LoD) were considered as non-detected. Descriptive analyses (mean, standard deviation, median, and range) were carried out and the normality of the data set was assessed using the Kolmogorov-Smirlov test. The Kruskal-Wallis and Mann-Whitney non-parametric tests were used afterwards to analyze the influence of the study variables i.e., species, length, sex. However, these two latter variables were only considered for striped dolphin, the species accounting for a larger sample set. Spearman's correlation rank was used to assess potential relationships between PAHs concentrations and body length. The significance level was set at 0.05 for all tests.

3. Results and discussion

3.1. Concentrations of PAHs in western mediterranean marine top predators

Concentration of each individual PAHs as well as the sum of the whole set for each species is graphically represented in Fig. 1. Summarized numerical values, including detection rates, can be found at Table S2, while detailed information for each individual can be found at Table SI3.

Generally, vertebrates and other upper trophic web organisms have demonstrated to possess efficient metabolisms mechanisms which allow to transform PAHs into more water soluble and therefore easily excretable species [Collier and Varanasi, 1991; Varanasi et al., 1989]. Thus, several works have demonstrated that PAHs in marine trophic web undergo trophic dilution [Nakata et al., 2003; Takeuchi et al., 2009; Wan et al., 2007]. However, in marine mammals and turtles, PAHs are commonly reported at detectable concentrations, usually of the same magnitude or even higher than those observed in lower trophic level organisms (e.g., mollusks [Baumard et al., 1998a; León et al., 2013]). This situation probably arises from the constant exposure of these species to high burdens of PAHs which overwhelm their detoxification systems, causing permanent high concentrations of PAHs within their tissues despite their constant elimination. Notwithstanding, HAPs concentrations in marine top predators has been a scarcely studied topic in worldwide environmental toxicology studies. Mean Σ16 PAHs in the three study species showed relatively similar values. In striped dolphin this value accounted for 100 ± 59.0 ng/g ww, in bottlenose dolphin 109 ± 44.1 ng/g ww, and in loggerhead sea turtle 136 ± 46.7 ng/g ww. Loggerhead turtle accounted for significantly higher concentration of acenaphthene and naphthalene, and slightly lower values for phenanthrene and fluoranthene in comparison to the other species. We never detected fluorene in this species. Meanwhile, striped dolphin and bottlenose dolphin showed very similar concentrations for all compounds. Despite sea turtles tend to accumulate lower concentrations of anthropogenic pollutants in comparison to marine mammals [D'ilio et al., 2011; Finlayson et al., 2016], loggerhead turtle had on average higher PAHs concentrations than the two dolphin species in our study. However, it should be noted that our limited sample set could have influence on these results.

Most marine species can incorporate PAHs from the marine environment either through respiration or feeding. Nevertheless, cetaceans and sea turtles are lunged animals, which obligates them breath atmospheric oxygen instead the one dissolved in the sea water. Accordingly, diet is not only the main route of marine PAHs into their organism but practically the only possible [Formigaro et al., 2014]. The three species included in this study are opportunistic species whose populations are easily adaptable to the environmental conditions of the habitats they use. However, they present very differentiated feeding behaviors affecting not only the prey the consume but also the habitats they use for foraging. While striped dolphin and bottlenose dolphin feeds mainly on fish and cephalopods in oceanic (>1000 m depth) and coastal (200–400 m depth) waters, respectively, loggerhead turtles feeds on both pelagic-oceanic and neritic-benthic prey of more diverse taxa including tunicates, jellyfish, crustaceans and sessile mollusks, but also from

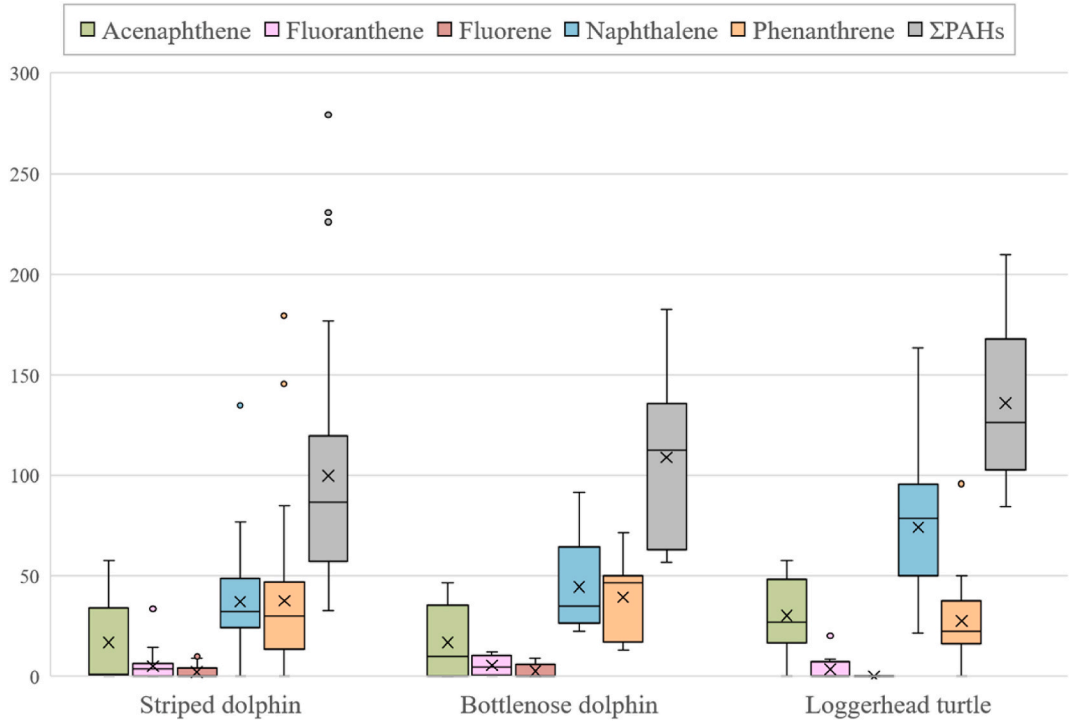

Fig. 1. Boxplot for individual PAHs and total PAHs (Σ16 PAHs) concentrations (ng/g ww) in striped dolphin, bottlenose dolphin and logger-head turtle. Upper and lower limit border of the box represent third and first quartile respectively while the end of upper and lower whisker represents maximum and minimum values (excluding outliers). Dots represent outliers (<Q1 - 1.5·IQR or > Q3 + 1.5·IQR) and crosses represent mean values.

discharged by-catch of fish and cephalopods [Blanco et al., 2001; Blasi et al., 2018; Canales et al., 2008; Cardona et al., 2012; Gómez-Campos et al., 2011; Gómez de Segura et al., 2008; Tomas et al., 2001].

In sea water there is usually a concentration gradient increasing from offshore water to coastal waters [Latimer and Zheng, 2003]. In fact, 50% of Mediterranean PAHs are estimated to accumulate in the 0–200 m water depth area, i.e., over the continental shelf [Lipiatou et al., 1997]. Besides, marine sediments lying in the bottom act as a reservoir of PAHs highly protected against degradation and available for benthic organisms [Baumard et al., 1998a]. Thus, organisms feeding closer to the coast and or benthic organisms should be expected to accumulate higher PAHs concentrations than those feeding in oceanic waters on pelagic prey. On the other hand, as fish and other upper trophic web marine organisms are efficient at metabolizing PAHs, their concentrations are usually low [Lawrence and Weber, 1984; Takeuchi et al., 2009]. On the contrary, marine organisms with lower trophic position like mollusks usually accumulates higher concentrations of PAHs in their tissues [Baumard et al., 1998a; León et al., 2013; Takeuchi et al., 2009]. Therefore, consuming low trophic organism should also contribute to higher PAH uptake.

Although PAHs concentrations in the three studied species were quite similar, we found significant differences between striped dolphin and loggerhead turtle for acenaphthene (Mann-Whitney $U = 257.5$, $p < 0.05$), naphthalene (Mann-Whitney $U = 163$, $p < 0{,}001$) and Σ16 PAHs (Mann-Whitney $U = 190$, $p < 0{,}001$). Contrarily, we did not find any significant difference between PAHs concentrations in bottlenose dolphin and the other species for any compound. These results, together with the similar burden of PAHs in the three species, might suggest that diet and feeding behavior would not influence the overall accumulation of these pollutants as much as they do for other pollutants. We hypothesize that their lesser bioaccumulation might be at least partially responsible for this situation. Thus, their rapid metabolism and excretion in vertebrates, including marine mammals and sea turtles, might lead to a rapid turnover in their tissues which partially dissociate those PAHs acquired while foraging from those PAHs concentrations in their tissues.

In the same vein, the rapid turnover of PAHs in their tissues might be also the reason underlying the absence of sex- or age-related differences of these compounds, as it has been previously reported in several works [Gui et al., 2018; Lourenço et al., 2016; Marsili et al., 2001; Moon et al., 2011]. Our results in striped dolphin, the species accounting for a higher number of samples, are mostly in accordance with this fact, as we did not find significant correlation for length (Spearman correlation test, $p > 0.05$) and we only detected significant differences between sexes for phenanthrene (Kruskal-Wallis $H = 0.240$, $p < 0.05$), which we likely attribute to a low sample size (only twelve samples included for this analysis). Exceptionally, although they did not find significant correlation between length and blubber PAHs concentrations, Gui et al., [2018] reported significant higher concentrations of PAHs between different age groups (calves and juvenile/adults) of Indo-Pacific humpback dolphins *Sousa chinensis*, which they attributed to an incomplete development of detoxifying mechanisms in calves. We could neither find significant differences among different stranding location within the coastline of Region of Murcia. In this regard, Gui et al., [2018] demonstrated that even within a small sampling area (~150 km length coastline), the stranding site of Indo-Pacific humpback dolphins had a strong influence on PAHs blubber concentration, with an increasing gradient towards those areas more affected by anthropogenic pollution. These authors hypothesized that PAHs concentrations in stranded dolphins could reflect the contaminant status in the surroundings of the stranding site. To our knowledge, there is no information about PAHs half-life in marine mammals or turtles. However, half-life of most parent PAHs after oral administration is of around 10 days in fish [Meador et al., 1995; Niimi and Palazzo, 1986] and of a few hours in humans [Motorykin et al., 2015]. Thus, it is possible that PAHs concentrations detected in marine mammals or turtles' tissues only reflect those PAHs ingested during the foraging activities occurred in the very close past prior to the death of the animal, so the detected concentrations could be representative of the existing pollution in the surroundings of the sampling area. However, several factors including starvation, distance

between death and sampling sites, or long movements prior to death, could influence PAHs concentrations as well. In the study area considered in this work there is a potential hotspot for PAHs pollution, the port city of Cartagena, with a large industrial and commercial harbor and a high industrial development dominated by petrochemical and energy industries. This area contrasts with the general depopulation and scarce industrialization of the rest of the coastline, which is characterized by a rural and agricultural environment with few urban settlements of relative low population outside the summer period. However, these differences were not reflected in the PAHs concentrations of the sample set.

The first report of PAHs in tissues of cetaceans dates back from 1988, when Martineau et al., [1988] analyzed benzo[*a*]pyrene DNA adducts in brain tissue of three stranded beluga whales *Delphinapterus leucas* in St. Lawrence Estuary, Canada. Since then, few works reporting PAHs concentrations in tissues of cetaceans have been published in comparison to other legacy contaminants, probably because PAHs are thought not to bioaccumulate in these species. We compiled some of the worldwide information available for PAHs in blubber of cetaceans in Table 1. To our knowledge, only two papers reporting PAHs in Mediterranean cetacean tissues have been previously published [Marsili et al., 2001, 2014]. While those PAHs concentrations reported in blubber of striped dolphins from in our study (100 ± 59.0 ng/g ww) could be considered in the lower range of worldwide concentrations, paradoxically the only previous work for this species in the Mediterranean (median 29,455 ng/g ww, range 199.4–198,368 ng/g ww [Marsili et al., 2001]) reported one of the highest concentrations for any cetacean species on history. In that

Table 1
ΣPAHs concentration (ng/g) in blubber samples from worldwide cetacean species endemic species. When all information is available data were expressed as mean ± standard deviation (first line) and median (range) (second line). For comparison, results can be easily transformed from l.w. Basis to w.w. Basis and vice versa by applying a mean estimation of 70% of lipids in blubber tissue from cetaceans [Aguilar et al., 2002; Tanabe et al., 1994].

Species	*n*	Period	Sampling area (Region)	Sample type	Concentration (ng/g)	Basis	n PAHs	Reference
Striped dolphin *Stenella coeruleoalba*	34	2011–2018	SE Spain (NW Mediterranean Sea)	stranding	100 ± 59.0 78.8 (38,7–230)	w.w.	16	This study
Bottlenose dolphin *Tursiops truncatus*	8	2011–2018	SE Spain (NW Mediterranean Sea)	stranding	109 ± 44,1 112 (56.6–183)	w.w.	16	This study
Striped dolphin *Stenella coeruleoalba*	25	1993	Ligurian & Ionian Seas (NW Mediterranean Sea)	biopsy	36,205 ± 41,107 29,455 (199–198,368)	w.w.	14	Marsili et al. (2001)
Fin whale *Balaenoptera physalus*	23	1993–1996	Ligurian Sea (NW Mediterranean Sea)	biopsy	9053 ± 21,304 1974 (229–83,662)	w.w.	14	Marsili et al. (2001)
Sperm whale *Physeter macrocephalus*	7	2009	Adriatic Sea (NW Mediterranean Sea)	stranding	329 ± 136 310 (136–551)	l.w.	14	Marsili et al. (2014)
Indo-Pacific humpback dolphin *Sousa chinensis*	18	2009–2010	Great Barrier Reef, Australia (Coral Sea)	biopsy	51,035 ± 5227	l.w.	14	Cagnazzi et al. (2013)
Australian snubfin dolphin *Orcaella heinsohni*	17	2009–2010	Great Barrier Reef, Australia (Coral Sea)	biopsy	32,296 ± 3152	l.w.	14	Cagnazzi et al. (2013)
Bottlenose dolphin *Tursiops truncatus*	64	2003–2011	Canary Islands (NE Atlantic Ocean)	biopsy	15,932 ± 10,233 13,598 (1394–42,577)	l.w.	16	García-Álvarez et al. (2014a)
Bottlenose dolphin *Tursiops truncatus*	25	1997–2011	Canary Islands (NE Atlantic Ocean)	stranding	1168 ± 1409 789 (75.3–5761)	l.w.	16	García-Álvarez et al. (2014b)
Indo-Pacific humpback dolphin *Sousa chinensis*	37	2012–2017	Pearl River Estuary, China, (S China Sea)	stranding	2400 (17,6–6080)	w.w.	16	Gui et al. (2018)
Indo-Pacific finless porpoise *Neophocaena phocaenoides*	52	2003	Korean coast (South Sea & Yellow Sea)	by-catch	160 (4.8–432)	l.w.	16	Moon et al. (2011)
Common minke whale *Balaenoptera acutorostrata*	27	2006	Korean coast (South Sea & Yellow Sea)	by-catch	220 (66–555)	l.w.	16	Moon et al. (2012)
Short-beaked common dolphin *Delphinus capensis*	22	2006	Korean coast (South Sea & Yellow Sea)	by-catch	164 (63–269)	l.w.	16	Moon et al. (2012)
Indo-Pacific humpback dolphin *Sousa chinensis*	8	2016–2017	Pearl River Estuary, China (S China Sea)	stranding	3541 (2181–10,343)	w.w.	16	Sun et al. (2020)
Bottlenose dolphin *Tursiops truncatus*	28	2003–2005	FL & SC coasts, USA (SE Atlantic Coast)	biopsy	2345 (<10–9140)	l.w.	57[a]	Fair et al. (2010)
Brydes whale *Balaenoptera edeni*	6	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	4773 ± 5071	l.w.	16	Fossi et al. (2014)
Blue whale *Balaenoptera musculus*	6	2010	Gulf of California (NE Pacific Ocean)	biopsy	17,662 ± 7096	l.w.	16	Fossi et al. (2014)
Fin whale *Balaenoptera physalus*	8	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	12,741 ± 13,704	l.w.	16	Fossi et al. (2014)
Short-beaked common dolphin *Delphinus capensis*	12	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	10,762 ± 6493	l.w.	16	Fossi et al. (2014)
Killer whale *Orcinus orca*	5	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	25,742 ± 32,912	l.w.	16	Fossi et al. (2014)
Bottlenose dolphin *Tursiops truncatus*	13	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	23,485 ± 12,040	l.w.	16	Fossi et al. (2014)
Sperm whale *Physeter macrocephalus*	14	2008–2009	Gulf of California (NE Pacific Ocean)	biopsy	30,114 ± 29,282	l.w.	16	Fossi et al. (2014)

[a] 45 parents, including 16 EPA PAHs, and 12 metabolites.

study, the authors used biopsy samples collected between 1993 and 1996 in the Ligurian and Ionian Seas (Italian coast). At that time, they reported very high concentrations both in striped dolphins and fin whales *Balaenoptera physalus* (9053 ± 21,304 ng/g ww). However, in a second study with a sample set from a pod of sperm whales stranded in the Adriatic coast in 2009, they detected concentrations (329 ± 136 ng/g lw) slightly above the range reported in our study. According to the authors, those concentrations observed in the 1990s could have been influenced by the incident of the tanker *Haven*, which spilled about 144, 000 tons of crude oil in the Ligurian Sea in 1991. As PAHs are not bioaccumulated by cetaceans and PAHs pollution is strongly influenced by local sources, it is difficult to compare our results with those from the Italian coast, even though both sampling areas fall within the north coast of the western Mediterranean basin. However, more recent results may show a temporal decline of PAHs pollution in this region. Accordingly, we hypothesize that the results reported in this study might represent either a decrease on the PAHs pollution in the whole western Mediterranean region or the comparatively lesser pollution of our specific study area, or both. On a global scale, PAHs concentrations in blubber of cetaceans oscillate between the hundreds of nanograms per gram and tens of micrograms per gram, with a range of concentrations of three orders of magnitude. Our results are at the lower end of this range, which could support a low pollution scenario for our study area. In comparison to other legacy organic pollutants, PAHs have received much less attention in marine mammals and turtles, probably because they are thought not to persist in their tissues. Gaps between regions and years make difficult to deepen into regional and temporal variations of these pollutants on cetacean and turtle tissues. On the contrary, we did not find globally any work assessing PAHs concentrations in skin or blubber of loggerhead turtle or any other sea turtle species. Worldwide studies about PAHs in this species, including a few references from the Mediterranean, focused on plasma or whole blood concentrations rather than other tissues [Bucchia et al., 2015; Casini et al., 2018; Cocci et al., 2018], although we also found one work using eggs [Alam and Brim, 2000]. PAHs were not reported in Mediterranean sea turtles until 2015, when Bucchia et al., [2015] reported two-to-three-fold higher concentrations in plasma of Adriatic Sea turtles in comparison to NE Atlantic (13.39 vs 4.91 ng/ml). Our results (Σ16 PAHs, 136 ± 46.7 ng/g ww) in blubber were higher to those reported in liver of green sea turtle *Chelonia mydas* from Brazil (maximum 33.98 ng/g ww [Vilca et al., 2018]) and similar to those reported in liver of visibly oiled Kemp's ridley turtle *Lepidochelys kempii* collected in the Gulf of Mexico after the *Deepwater Horizon* oil spill (n = 10, Σ53 parent and alkylated PAHs, 140 ± 46.7 ng/g ww [Ylitalo et al., 2017];). However, the difference in the matrix prevents for further interpretation of these results.

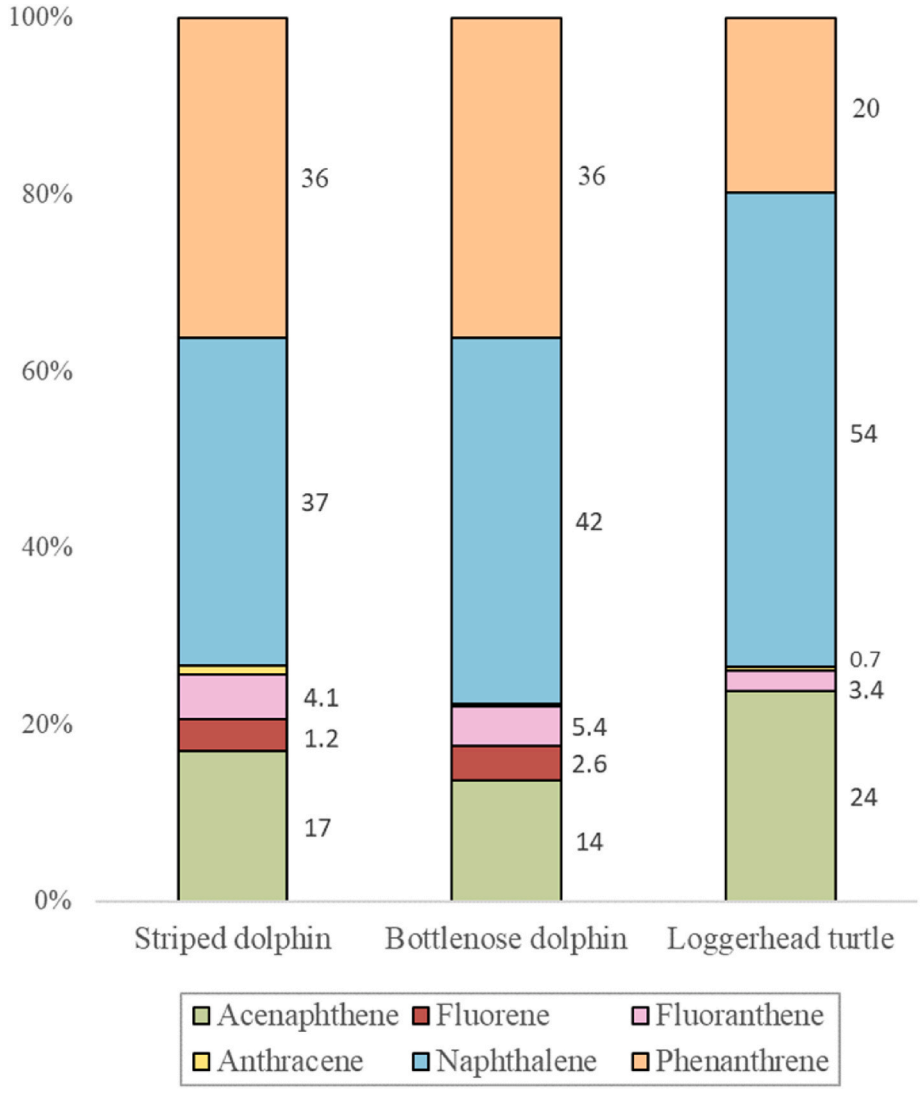

Fig. 2. PAHs pattern in blubber of western Mediterranean dolphins and logger-head turtles. Results are expressed as percentage of each individual PAH with respect to total sum of PAHs.

3.2. PAHs profiles in western mediterranean marine top predators

We calculated PAHs profile as the percentage each individual PAH accounted in relation to Σ16 PAHs, which is represented in Fig. 2. Of the 16 PAHs analyzed, only six were detected: acenaphthene, anthracene, fluoranthene, fluorene, naphthalene, and phenanthrene. Detection rates for the other compounds in each species can be observed in Table S2. Naphthalene (94.1–100%) and phenanthrene (91.3–100%) were those compounds with higher detection rates in all species. On the contrary, fluorene (0–44.1%) and anthracene (8.7–14.7%) were those compounds with lower detection frequencies. Particularly, fluorene was never detected in loggerhead sea turtle. In all species, while fluoranthene was the only 4-ring PAH detected, acenaphthylene was the only 3-ring that was not detected. Thus, the profile was essentially composed by low molecular weight (LMW; ≤3 aromatic rings) PAHs, while high molecular weight (HMW; ≥4 aromatic rings) PAHs – uniquely represented by fluoranthene – only accounted for 2–5% of Σ16 PAHs. Predominance of LMW in tissues of marine mammals and sea turtles has been as well reported in other works [Camacho et al., 2014; Marsili et al., 2001; Moon et al., 2011]. PAHs distributes differently in the marine environment according to their molecular weight, which condition their vertical distribution in the seas. The Mediterranean seawater is dominated by LMW, which are more water-soluble. Thus, they appear in higher concentrations than HMW PAHs in the water column both in the dissolved and the particulate phase, making them more bioavailable [León et al., 2013]. On the contrary, HMW PAHs appear essentially linked to organic and inorganic particles which mainly accumulates in the marine bottom and to a lesser extent suspended in the water column [Berrojalbiz et al., 2011; Lourenço et al., 2016]. However, LMW PAHs concentrations in the Mediterranean water column decrease with depth at higher rates than HMW PAHs, so the proportion of the last increases with depth [Dachs et al., 1997]. As none of our study species is characterized by deep dives, other marine top predators hunting deeper might be exposed to PAHs mixtures with major fractions of HMW compounds. However, this does not seem either the case for the sperm whales [Marsili et al., 2014], which are usually considered a diving model among marine mammals. On the other hand, laboratory and field studies in fish and birds have demonstrated LMW PAHs are less efficiently metabolized than HMW PAHs, which could also explain their higher contribution for these and other species [Jonsson et al., 2004; Troisi et al., 2006].

Naphthalene was the compound detected at higher concentrations in all species, followed by phenanthrene and acenaphthene. However, while naphthalene and phenanthrene concentrations were similar in both striped and bottlenose dolphins, in loggerhead turtle anthracene concentrations doubled those of phenanthrene. Depending on the study, either naphthalene or phenanthrene are almost invariably those PAHs detected at higher concentrations in marine mammals and turtles [Camacho et al., 2014; Cocci et al., 2018; García-Álvarez et al., 2014a, 2014b; Gui et al., 2018]. Berrojalbiz et al., [2011] and Dachs et al., [1997] reported phenanthrene as the most abundant PAHs in the water column of the Mediterranean Sea, including the seawater, the suspended particulate matter or even the plankton. León et al., [2013] reported as well phenanthrene as the prevalent compound in mussel samples from the Mediterranean Spanish coast, including in various sampling sites coinciding with our sampling area and adjacent areas. However, none of these works considered naphthalene in their study set. The latter work attributed phenanthrene prevalence over other PAHs to its relative hydrophilicity and volatility, which allows it to be transported through atmospheric or oceanic transport for longer distances than other PAHs. As naphthalene is the simplest and the lightest of all PAHs, it is also the most water soluble and volatile [Latimer and Zheng, 2003], so the aforementioned statements are equally valid for this compound. This would explain their prevalence in cetaceans, which are extremely mobile animals that move over vast areas, generally far from local coastal sources of pollution, where other source-related PAHs could predominate [León et al., 2013]. Studies on PAHs pollution in sediments including naphthalene also report higher concentrations of these compound followed by phenanthrene [Berto et al., 2009]. On the other hand, reports of other individual PAHs in cetaceans seem to be more variable. Acenaphthene, fluoranthene, fluorene and pyrene and other PAHs commonly reported in works with cetaceans whose concentrations tend to be lower than those of anthracene and phenanthrene [Cagnazzi et al., 2013; Gui et al., 2018; Moon et al., 2012]. However, occasionally abnormally higher proportions of some of these compounds are reported, e.g., acenaphthene in sperm whales [Marsili et al., 2014]; or pyrene in Pacific or NE Atlantic dolphins [García-Álvarez et al., 2014a]. Probably these variations rely on the specific sources to which each region is specifically subjected. Other PAHs of higher molecular weights – most of them with carcinogenic properties – are by contrast more rarely detected than the others, and when they are detected, they tend to appear in very low concentrations compared to the aforementioned [Lourenço et al., 2021; Moon et al., 2012].

Composition of PAHs mixtures released to the environment varies according to the source [Barakat et al., 2011]. Petrogenic origins are usually source of LMW PAHs and their alkylated homologues while pyrogenic origins tend to release non-alkylated HMW PAHs [Collier et al., 2013]. This differentiation has led to the usage of various ratios to assess the origin (pyrogenic or petrogenic) of the pollutant inputs, including LMW/HMW (>1 petrogenic; <1 pyrogenic), phenanthrene/anthracene (<10 pyrogenic; >10 petrogenic), and fluoranthene/pyrene (<1 petrogenic; >1 pyrogenic) [Baumard et al., 1998a; 1998b]. While these ratios have been widely used in abiotic samples i.e., sediments, particulate suspended material, or seawater, their utilization in marine mammals is incipient [Lourenço et al., 2021]. PAHs sources and inputs to the marine environment can vary greatly within a same area [Baumard et al., 1998b] so long-ranging species like cetacean are probably exposed to complex mixtures from countless sources. Once in the environment, PAHs psychochemical characteristics determines their distribution, their persistence, and their availability for biota [Latimer and Zheng, 2003]. Biotic metabolism will be also affected by number of aromatic rings and molecular weight of each individual PAH [Neff, 2002]. When a PAHs mixture is detected in the tissue of a marine predator, each individual compound has undergone a long journey from its original source passing through the abiotic environmental compartment and the marine trophic web. As a consequence, a number of unknowable factors may have affected in countless manners the primary PAHs released to the environment from their release until their accumulation in tissues. Therefore, these ratios do not necessarily indicate which type of sources predominate in the global environment but in the tissues of the studied species. Moreover, as PAHs are supposed to be as rapidly metabolized and excreted in our study species as it happens in other vertebrates [Collier and Varanasi, 1991; Varanasi et al., 1989], we can only infer this information from a short period before the death of each individual. Our data showed very low detection rates for anthracene and non-detectable values of pyrene. LMW/HMW ratio provided a mean result higher than 100 in all species. Despite usually a minimum of two ratios are used to conduct such estimations [Baumard et al., 1998b], the practical absence of HMW in blubber samples from our work would point to an almost exclusive petrogenic origin for the reported concentrations. According to [Polinov et al., 2021], it is estimated that 53% of all petroleum reaching the marine environment is of anthropogenic origin. Despite accidental tanker oil spills receive the focus of public attention, they only account for 8% of the oil entering in the oceans, so the major fraction comes from deliberate and small but continuous discharges and natural seeps [GESAMP, 2007], which could be virtually responsible of the results.

3.3. Potential toxicological implications

Despite environmental concern of PAHs arose several decades ago, their toxicity has been less studied in marine mammals and turtles in comparison with other substances. Moreover, studies on their effects on

these species have been generally more focused in the physical consequences of oiled animals during exceptional but noteworthy large oil spill (e.g., Prestige in the NE Atlantic Ocean) [Albers and Loughlin, 2003].

Many PAHs are known to be carcinogenic to humans and animals [IARC, 2022]. However, most of them need a previous metabolization by the enzymes of the CYP1 family, which transform parent PAHs into active metabolites which develop their carcinogenic activity once they bind covalently with the DNA to form DNA adducts [Baird et al., 2005; Miller and Miller, 1981; Varanasi et al., 1989]. Based on in vitro experiments with several cell lines of sperm whale *Physeter macrocephalus*, this metabolic pathway has also been suggested for cetaceans [Godard et al., 2004]. As molecular weight increases, the carcinogenicity of PAHs also increases with reducing acute toxicity. Thus, four to six-rings PAHs are more carcinogenic than two- and three-rings PAHs [Eisler, 2000] and, among them, benzo[*a*]anthracene, benzo[*a*]pyrene and dibenz[ah] anthracene has been identified as the most potent carcinogens [Armstrong et al., 2004; Bach et al., 2003]. Despite the literature on PAHs toxic effects in cetaceans and marine turtles is brief, various works have found linkages between PAHs exposure and cancer in these species [Marsili et al., 2014 Webb et al., 2014; Whitlock, 1999; Wilson et al., 2005]. For example, Vilca et al., [2018] observed a significant influence of hepatic PAHs and fibropapilomatosis in green sea turtles while. Parallelly, Martineau et al. [Martineau et al., 1994, 2002] found clues of a possible relation about high benzo[*a*]pyrene concentrations in blubber of belugas from St. Lawrence Estuary (Canada), overexpression of cytochrome P450 1A1 (CYP1A) and 2 N (CYP2B) and high cancer prevalence. On the other hand, despite carcinogenicity is most recognized adverse effect caused by PAHs, other effects derived from PAHs exposure have been described, including immunotoxicity, dioxin-like estrogenic responses or alterations in fetal and postnatal development after prenatal expositions [Dejmeck et al., 200; Perera et al., 2012; Villeneuve et al., 2002]. In cetaceans, Godard et al., [2006] observed in vitro clonogenic cytotoxicity in north Atlantic right whale *Eubalaena glacialis* testis, skin, and lung primary fibroblast cell lines exposed to benzo[*a*] pyrene. In loggerhead turtles, significant correlations have been described between plasma PAHs concentrations and diverse gene biomarkers for stress response (HSP60) and estrogenic activity (ERα), and DNA fragmentation and methylation [Casini et al., 2018; Cocci et al., 2018]. In our work we did not detect benzo[*a*]pyrene nor other carcinogenic HMW PAHs, which would indicate a lower risk of these effects in our study species. However, despite its carcinogenic potential is considered to be lower in comparison to the aforementioned [Nisbet and Lagoy, 1992], naphthalene, which composed the major fraction of the Σ16 PAHs, is classified as possible carcinogenic for animals (group 2 B) by the IARC [2022] and it has probed to induce cancer in the upper and lower respiratory tracts of rodents in laboratory studies [NTP, 1992, 2000]. Moreover, we cannot dismiss the occurrence of non-carcinogenic toxic effects derived from the exposition to the PAHs that we have reported in this work.

4. Conclusions

Unlike it happened for other pollutant classes (i.e., PCBs, DDTs, PBDEs), few measures have been taken against PAHs pollution, probably due to the difficulty to face their sources. Although the detected concentrations of these compounds are generally lower in magnitude, they still might exert potential negative effects in the biota. This works provides novel information about PAHs concentrations in three species of Mediterranean marine top predators. Total PAHs concentrations in blubber of dolphins and sea turtles were at a relative low level in comparison to other works and LMW PAHs predominated over more carcinogenic HMW PAHs, which were not detected in any sample. However, information about the possible toxic effects caused by the detected LMW PAHs is scarce so we might not dismiss other effects derived from chronic exposures to this set of PAHs and, considering the short half-lives of PAHs within the organism, we cannot ensure that our study species have not been exposed to carcinogenic HMW PAHs. The waters surrounding our study area are considered an important breeding area for striped dolphin and other cetacean species. Besides, loggerhead turtles seem to have started to spawn again in this and adjacent areas in the previous years. Moreover, preserving Mediterranean biodiversity does not only entail an ecological value, but it is essential to ensure the welfare and the survival of the human populations inhabiting this region, especially of those segments of the population which directly depend on the marine resources.

Credit author statement

G. López Berenguer: formal analysis, methodology, writing-original draft and review; A. Acosta-Dacal: formal analysis, and review; OP Luzardo: resources, methodology, supervision and review; J. Peñalver: Data Curation, resources and review; E Martínez-López: Conceptualization, Data Curation, resources, methodology, funding acquisition, supervision, writing - review & editing.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Andrea Acosta-Dacal reports financial support was provided by Regional Ministry of Economy, Knowledge, and Employment of the Canary Islands Government and the European Social Fund.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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