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POPs concentrations in cetaceans stranded along the agricultural coastline of SE Spain show lower burdens of industrial pollutants in comparison to other Mediterranean cetaceans

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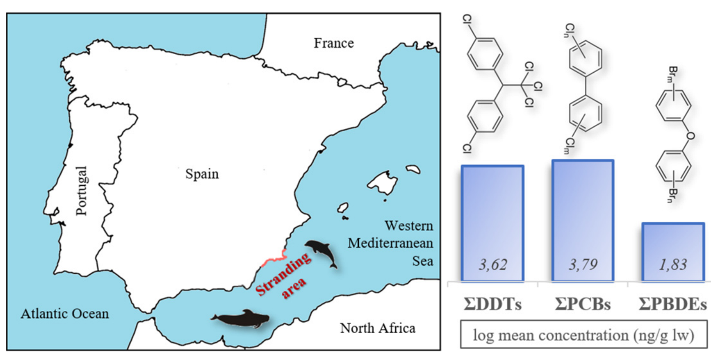
HIGHLIGHTS

- Various POPs are studied for first time in cetaceans stranded in SE Spain.
- Lower concentrations are reported compared to previous reports in NW Mediterranean.
- DDE/ ΣDDT ratio suggest no recent exposure to these chemicals.
- PCBs remains as one of the major concerns for NW Mediterranean cetaceans.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite the Mediterranean Sea being one of the world's marine biodiversity hotspots, it is a hotspot of various environmental pollutants. This sea holds eight cetacean with resident populations whose numbers are considered to decline in the last decades and which are particularly susceptible to POPs bioaccumulation due to their peculiar characteristics. In this work, we studied blubber concentration of various OCPs and several PCBs and PBDEs congeners in cetaceans stranded in the northern coast of the Gulf of Vera (Region of Murcia, SE Spain) between 2011 and 2018. Most compounds and congeners were above the limit of detection in most samples, although some pesticides like endosulfan stereoisomers or endrin were never detected. DDT and its metabolites, PCBs and metoxychlor appear as the dominant compounds while PBDEs shows concentrations of lower magnitude. Striped dolphin was the species accounting for higher concentrations of most pollutants. There were differences in concentrations and profiles between species which could be partially explained by differences on diet and feeding behavior. We also observed differences based on life history parameters suggesting maternal transfer for most POPs, in accordance with other works. DDE/ ΣDDT ratio suggest no recent exposure to these pesticides. Despite showing lower concentrations than some previous works, PCB concentrations accounted for higher total TEQ than many studies. According to toxicity thresholds in the literature, we cannot guarantee the absence of health consequences on populations studied, especially for those caused by PCBs. These findings are of major importance considering the relevance of the study area in the conservation of Mediterranean cetaceans.

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1. Introduction

Despite being considered as one of the world's marine biodiversity hotspots (Lejeusne et al., 2010), Mediterranean Sea is currently one of the most impacted regions in the world (Costello et al., 2010; Halpern et al., 2008). Climate change (Bianchi and Morri, 2000), overfishing (Bearzi et al., 2006; Gómez-Campos et al., 2011) and chemical pollution (Coll et al., 2010; Jepson et al., 2016; López-Berenguer et al., 2020a) are just some of the several hazards that Mediterranean marine biota faces constantly. Once persistent pollutants reach the oceanic water through aquatic or atmospheric transport, they usually remain for long periods, where they are available to the marine biota affecting population and individual's health. This matter becomes particularly relevant in semi-enclosed water bodies like the Mediterranean Sea, which is particularly susceptible for chemical pollution due to this geographical condition and the intense anthropogenic pressure to which it is subjected (Bacci, 1989; Castro-Jiménez et al., 2013; Marsili et al., 2018; Meadows, 1992).

The Gulf of Vera represents a transition zone between the Alborán Sea, which has a very strong influence of the Atlantic Sea through the Gibraltar Strait, and the rest of the basin with more distinctive Mediterranean character. This is eminently an agricultural area with a predominance of widely distributed irrigated crops and dotted with livestock farms, especially swine. Although industry is gradually spreading in some points along its eastern basin, there is only one industrial hotspot, around the historic port city of Cartagena, where several chemical industries, including one of the biggest oil refineries in Spain and a hydroelectric thermal power plant, are gathered. The Gulf of Vera has been recognized as an area of high importance for cetacean conservation in the Mediterranean Sea (ACCOBAMS, 2016), probably due to certain idiosyncratic characteristics which lead to cetacean's abundance such as an extremely narrow continental shelf, the presence of important submarine canyons or the occurrence of highly productive spring blooms (Cañadas and Vázquez, 2014; d'Ortenzio and d'Alcalà, 2009; Uitz et al., 2012). It is home of the eight cetacean endemic species that the Mediterranean Sea holds, whose populations – when there is enough information – are considered as '*vulnerable*' or '*endangered*' (IUCN, 2022). These species are particularly vulnerable to the side-effects of human activities because of several characteristics, including long lifespans, low reproductive rate, and marine food web dominance. Paradoxically, some of these human-resembling characteristics give their study an added value (Browning et al., 2017; Pérez and Wise, 2018). Direct study of alive cetaceans is often complicated due to the difficulties which entail aquatic nature, their size and both health and legal considerations. Thus, using stranded cetaceans as a source of toxicological information has shown to be extremely useful despite the occurrence of certain limitations (Geraci and Lounsbury, 2005).

Both agriculture and industry are responsible for releasing countless classes of chemicals to the marine environment, among which persistent organic pollutants (POPs) play a major role. Globally, countless efforts have been conducted to control the production, commercialization, and usage of those chemicals which have been probed to possess a higher risk for the environment, wildlife and human health. For example, several compounds once widely used, such as countless organochlorines (OCs) like organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs), or polybrominated diphenyl ethers (PBDEs), have been listed under the Stockholm Convention and are currently prohibited in most worldwide countries. However, their strong persistence makes them still to persist ubiquitously in all ecosystems. Furthermore, many of these compounds have continued being stored, commercialized, and used in some regions, and many of them still persist in countless products in homes, industries, etc. This is a potential hazard for wildlife, including cetaceans.

Since PCBs and OCPs were firstly reported in cetaceans from the Western Mediterranean Sea (Alzieu and Duguy, 1979), this region has been repeatedly considered as a global hotspot for these compounds (Aguilar et al., 2002; Jepson et al., 2016; Stuart-Smith and Jepson, 2017). After the prohibition, PCBs and especially DDT concentrations decreased for several years (Aguilar and Borrell, 2005); however, since some point between 2000 and 2010 the concentrations of many OCs have remained stable in Mediterranean cetaceans' tissues (Dron et al., 2022; Jepson et al., 2016), as well as in other Mediterranean marine biota, including fish and mollusks (Cresson et al., 2015; Dron et al., 2019; Bouchoucha et al., 2021). The environmental distribution from the sources of pollution, as well as the remobilization of these pollutants from contaminated soils, sediments and wastelands, leading to the input of POPs mainly through the rivers, has been pointed as one of the possible causes of this plateau (Gómez-Gutiérrez et al., 2006; Liber et al., 2019). At this moment there is scarce information for PCBs and OCPs in cetaceans from the Mediterranean Sea from the 2010s and many works considering that time period are being currently published. Most POPs, including OCs and PBDEs are lipophilic and thus they accumulate preferentially in fatty tissues like the blubber of cetaceans and other marine mammals (Dron et al., 2022; Lazar et al., 2012; Yordy et al., 2010a). OCs most well-known adverse effects in marine mammals include immunosuppression (Aguilar and Borrell, 1994a; De Swart et al., 1994, 1995, 1996; Simmonds and Mayer, 1997) and reproductive impairment (Béland et al., 1993; Helle et al., 1990; Reijnders and Brasseur, 1992) although they are also responsible for a number of adverse effects at other levels. In comparison, PBDEs adverse effects in marine mammals have been much less studied, although some studies have reported alterations in the thyroid hormone and the immune system (Hall et al., 2003; Rajput et al., 2018). Thus, POPs can have serious consequences on the health of cetacean's populations as well as on the welfare of the individuals. However, the lack of updated toxicological data makes difficult to draw conclusion about the current status of these pollutants on Mediterranean cetaceans.

In the present study we evaluate the exposure of seven species of resident Mediterranean cetaceans to three main groups of organic pollutants OCPs, PCBs and PBDEs through the analysis of blubber tissue from stranded cetaceans on the Gulf of Vera, an area of low industrial and urban pressure, between 2011 and 2018. We hypothesize that despite previous apparent stabilization in the concentration of certain legacy pollutants and the apparent limited success of previous legal actions, POPs concentrations will eventually continue to decrease, and this will be especially noticeable in those areas far from high anthropogenic pressure. Additionally, we assess the reported concentrations regarding the species and previous reports in the literature, and we use striped dolphin as a model species to assess their pollutant burden in relation to life history parameters.

2. Material and methods

2.1. Sample collection

Blubber samples ($n = 51$) from different cetacean species were collected between 2011 and 2018 during standardized necropsies conducted by the staff of the wildlife recovery center "El Valle" (Dirección General de Medio Natural, CARM) in stranded animals along the coastline of the Region of Murcia (SE Spain), whose waters mainly corresponds to those of the Gulf of Vera. Once removed, all samples were stored separately and immediately frozen at −20 °C until their analysis. Several information including sex and morphometry was recorded during necropsies. Further information on sampling and data collection can be found at Martínez-López et al. (2019). Study species included seven cetaceans with resident populations in the Mediterranean Sea: striped dolphin *Stenella coeruleoalba* ($n = 33$), bottlenose dolphin *Tursiops truncatus* ($n = 8$), common dolphin *Delphinus delphis* ($n = 3$), long-finned pilot whale *Globicephala melas* ($n = 3$), Risso's whale *Grampus griseus* ($n = 1$), Cuvier's beaked whale *Ziphius cavirostris* ($n = 1$) and sperm whale *Physeter macrocephalus* ($n = 2$).

2.2. Analytes of interest, reagents, and standards solutions

Blubber samples were analyzed for different POPs, including OCPs, PCBs and PBDEs. 16 different OCPs, including certain isomers and metabolites, were analyzed in this work: alpha-hexachlorocyclohexane (α-HCH), beta-hexachlorocyclohexane (β-HCH), gamma-hexachlorocyclohexane (γ-HCH or lindane), delta-hexachlorocyclohexane (δ-HCH), hexachlorobenzene (HCB), heptachlor, α-endosulfan, β-endosulfan, aldrin, dieldrin, endrin, p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), metoxychlor and mirex. A set of 18 PCB congeners was analyzed as well, including congeners n° 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180 and 189. Lastly, eight PBDEs were analyzed, including congeners n° 28, 47, 85, 99, 100, 153, 154 and 183.

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). All the standards of the selected POPs were purchased from CPA Chem (Stara Zagora, Bulgaria) in commercial 4 mixes of 100 μg/ml, distributed in organochlorine pesticides (in acetone), PCBs (in isooctane) and PBDEs (in isooctane). An intermediate solution at 20 μg/ml, and a working solution at 1 μg/ml were prepared in acetone.

2.3. Extraction procedure

Samples were kept frozen until the time of the analysis. Prior to the analysis, blubber samples were thawed at room temperature. POPs 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. Additional information of QC and Recoveries for this technique can be found at Espín et al. (2010).

2.4. Instrument

Instrumental quantification was conducted by gas chromatography by using a GC System 7890B 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 union (PUU, Agilent Techonologies) 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 20.75 min. Injector and transfer line were set at 280 °C. The injection volume was 1 μl. All samples and standards were analyzed in the splitless 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 impact 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 SI.1) 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 in Acosta-Dacal et al. (2021). The chromatographic and mass spectrometric conditions used in this method are shown in Table SI.2.

2.5. Data handling and statistical analysis

All concentrations of OCPs, PCBs and PBDEs are given in ng/g, expressed in lipid weight (l.w.) basis. We used the estimation of a mean of 70 % of lipid content in blubber suggested by Tanabe et al. (1994) and used in other works (Aguilar et al., 2002) to transform our original results in a wet weight (w.w.) basis into l.w. This lipid estimation was in the range of previous analysis in our laboratory in other cetacean blubber samples. Statistical analyses were conducted by using SPSS v25.0 statistical package. We conducted descriptive statistic for all species and more detailed analyses only for striped dolphin due to its larger sample set. For intra-species comparation we considered adult males and females those striped dolphins aged twelve or longer than 187 cm (Calzada et al., 1996;

Table 1
Concentration of various OCPs, ΣPCBs and ΣPBDEs in blubber from different endemic cetacean species from the western Mediterranean Sea. Results are expresed as mean ± standard deviation; ng/g l.w.

Species	metoxychlor	Mirex	HCB	heptachlor	ΣHCH	ΣDrins	ΣDDTs	ΣOCPs	ΣPCBs	ΣPBDEs
S. coeruleoalba n = 33	2263 ± 2920	12.8 ± 15.2	32.9 ± 58.1	9.8 ± 13.0	133 ± 271	36.4 ± 78.7	4752 ± 7415	5973 ± 8253	6490 ± 9549	73.0 ± 103
calves & subadult *n* = 10; 2	2314 ± 2729	6.4 ± 7.2	25.9 ± 28.1	9.1 ± 11.5	131 ± 237	24.8 ± 28.6	3865 ± 4628	5886 ± 6004	4340 ± 7090	57.2 ± 55.4
adult females *n* = 6	1823 ± 2011	10.9 ± 8.6	15.9 ± 21.1	10.5 ± 10.9	75.4 ± 93.5	23.6 ± 36.4	2120 ± 1593	4079 ± 2732	2206 ± 1535	29.8 ± 17.2
adult males n = 6	1160 ± 2003	21.4 ± 27.6	41.5 ± 67.1	6.7 ± 16.4	242 ± 533	28.0 ± 68.5	9788 ± 15,030	11,287 ± 15,477	13,361 ± 18,208	70.2 ± 95.0
T. truncatus n = 8	1308 ± 1633	10.1 ± 3.88	18.6 ± 12.3	5.2 ± 7.8	73.4 ± 58.8	10.4 ± 15.9	2266 ± 1739	3691 ± 2786	6106 ± 5610	53.3 ± 42.0
D. delphis n = 3	2191 ± 3423	4.65 ± 4.45	5.2 ± 5.2	9.3 ± 16.1	104 ± 138	50.0 ± 71.0	2161 ± 694	4520 ± 3955	3860 ± 3536	24.8 ± 25.3
G. melas n = 3	1970 ± 1706	1.92 ± 3.32	24.6 ± 23.7	14.9 ± 3.8	46.7 ± 42.2	18.0 ± 23.6	841 ± 871	2917 ± 2428	1059 ± 1023	48.5 ± 56.4
G. griseus n = 1	376	5.76	2.68	<LoD	<LoD	<LoD	729	1114	1017	11.83
Z. cavirostris n = 1	2463	2,45	6.57	11.4	46	6.87	956	3493	956	15.3
P. macrocephalus n = 2	2666 ± 2108	2.33 ± 1.61	18.3 ± 13.6	15.6 ± 13.9	71.6 ± 22.7	24.7 ± 7.03	1715 ± 157	4514 ± 1968	1401 ± 78.4	25.6 ± 11.7

Marsili et al., 2014 and references therein). We estimated age from length following a model provided by Marsili et al. (2014) for the Mediterranean subpopulation. As Kolmogorov-Smirnov test probed POPs concentrations were not normally distributed, Mann-Whitney *U* test was used to study influence of sex on POPs concentration, and Spearman correlation coefficient was used to study influence of length/age. The significance level was set to $\alpha = 0.05$. Any result below the limit of detection (LoD) was considered as zero in all the statistical analyses to avoid an overestimation of the pollutant burden. We calculated toxic equivalent quantities (TEQ) for dioxin-like PCBs (dl-PCBs) using those toxic equivalency factors for mammals provided by Van den Berg et al. (2006).

3. Results and discussion

3.1. POPs concentration in blubber

Values in blubber from different species for OCPs, PCBs and PBDEs are summarized in Table 1 (detailed information for each individual compound and congener is reported at Tables SI.3, SI.4 and SI.5). Striped dolphin data are subdivided according to life history groups (i.e., calves and immature, adult females, adult males). The rest of the results are simply separated by species, as the small sample set did not allow for further divisions. Statistical analyses of time-trends were not conducted because of this reason.

Despite the worldwide reduction or prohibition on manufacture and usage of most chemicals considered in this work, their concentrations in cetacean tissues still reach the mg/kg level in many cases. Quantitatively, those chemicals reaching the highest levels in blubber were DDTs, PCBs and methoxychlor, ranking in different positions according to the species. DDTs and PCBs have demonstrated to be the most widespread organochlorines and, generally, those reaching the highest concentrations in animal tissues (Aguilar and Borrell, 2005). These compounds have traditionally received most of the attention in toxicological studies on marine mammals and are therefore those for which there is the most extensive literature, also in the Mediterranean basin. Mean ΣPCBs in our study species ranged between 6490 ± 9549 ng/g l.w. (striped dolphin) and 956 ng/g l.w. (Cuvier's beaked whale), while mean ΣDDTs ranged between 4752 ± 7415 ng/g l.w. (striped dolphin) and 729 ng/g l.w. (Risso's dolphin). We intended to gather the available information on POPs in blubber from Mediterranean cetaceans samples collected between 2000 and 2020 in Table 2. To our knowledge, Dron et al. (2022) conducted the most recent work considering PCBs and various OCPs in blubber and other tissues of striped dolphins stranded in the French Mediterranean coast between 2010 and 2016. Despite they reported comparable levels for ΣDDTs (mean 10,777 ng/g l.w.), they found four-fold higher concentrations for ΣPCBs (Σ31PCBs, mean 21,058 ng/g l.w.) in comparison to our data. However, it has to be noted that these authors analyzed a wider set of PCB congeners, which impairs further comparisons (18 vs 31 congeners).

Far below the aforementioned compounds, mean ΣPBDEs ranged between 73.0 ng/g l.w. (striped dolphin) and 11.8 ng/g l.w. (Risso's dolphin). In contrast to DDTs and PCBs, PBDEs became a matter of concern more recently and they have been scarcely studied in Mediterranean odontocetes. To our knowledge, eight works have been previously published on this topic (Barón et al., 2015a, 2015b; Bartalini et al., 2019; Capanni et al., 2020; Fossi et al., 2013; Pettersson et al., 2004; Pinzone et al., 2015; Zaccaroni et al., 2018), most of them focused on the western coast of Italy. Despite long-range atmospheric and oceanic transport are the major pathways of PBDEs to remote areas (Law et al., 2014), their hydrophobic and relatively low volatile nature probably makes soils and sediments the major pathways to the Mediterranean Sea. This input mainly comes from diffuse sources through the degradation of the matrixes in which the PBDEs are contained (EPA, 2014) although certain hotspots including electronic recycling facilities, landfills, and sewage treatment plants (Deng et al., 2015; Li et al., 2012) might play an important role as well. Mediterranean cetaceans are considered to carry lower burden of PBDEs in comparison to those from American waters, which is suggested to be related to a lesser use of these chemicals in Europe (Law et al., 2014; Bartalini et al., 2019). However, the concentrations reported in our study (Tables 1 & SI.4) are below the lower range of most of the concentrations reported in the last two decades in NW Mediterranean (Table 2). The northern coast of the Gulf of Vera (SE Spain) is scarcely urbanized and essentially agricultural in contrast with other the coastal areas such as the Iberian coast of the Balearic Sea. As PBDEs tend to appear in higher concentrations close to highly and industrialized and urbanized areas (Fair et al., 2010; Krahn et al., 2007; Lebeuf et al., 2004), this fact might partially explain the aforementioned results. However, it has to be noted that differences on the set of congeners analyzed in different works might also have influence on their results.

In this work we have found metoxychlor concentrations in blubber of cetaceans comparable to those of DDTs or PCBs. However, in comparison to these organochlorines, metoxychlor is seldom reported in toxicological studies in marine mammals. This compound was once used as a pesticide against a wide range of pests in the past and it has been banned in EU and USA since the beginning of the 2000s. Unlike in this work, Hansen et al. (2004), seldomly detected metoxychlor in blubber samples of bottlenose dolphin from the USA Atlantic coast. Other OCPs were detected at lower concentrations, while four of them were not detected in any samples (δ-hexachlorocyclohexane, two endosulfan stereoisomers, and endrin). Endosulfan is a pesticide which was manufactured as a mixture of two stereoisomers (α and β). Despite β-endosulfan has a longer half-life than α-endosulfan, none of them are considered persistent in warm-blooded animal tissues, where they are rapidly metabolized and excreted (Dorough et al., 1978). However, they have commonly been reported in worldwide cetaceans from other recent works, also in the Mediterranean Sea (Hansen et al., 2004; Dron et al., 2022). The fact that both stereoisomers were not detected would indicate absence of recent exposures in our study area. Similarly, α-, β-, γ- and δ-HCH are a group of hexachlorocyclohexane stereoisomers with different metabolization rates and tissue affinity and persistence. For instance, β-HCH accumulates more in blubber but less in brain than α-HCH (Kawai et al., 1988). Despite β-HCH is usually referred as more persistent than the other isomers, we observed the following pattern γ-HCH (lindane) > > β-HCH > α-HCH in all species. This is not in accordance with other works (Durante et al., 2016), where β stereoisomer was prevalent over the rest. However, in Spain γ-HCH production and usage were quantitatively more important than the technical product which contained higher proportions of the β stereoisomer (Fernández et al., 2013). This fact which could explain our results. On the other hand, aldrin, dieldrin and endrin are structurally similar compounds used in the past as pesticides against a number of plagues. In all our study species, dieldrin was detected at one or two orders of magnitude higher than aldrin, which was only detected in the 15 % of our samples. Dieldrin can be bioaccumulated either by its direct exposure of through its formation from its parent compound aldrin both abiotically and biotically through its epoxidation in the liver (reviewed by Zitko, 2003). On the other hand, endrin is a stereoisomer of dieldrin; however, unlike dieldrin, it is not clear whether endrin can also appear as a metabolite of aldrin (Purnomo, 2017; Zitko, 2003). Moreover, despite its persistence in abiotic matrixes, endrin is rapidly metabolized in the organism (reviewed by Zitko, 2003), so usually it is not detected at high concentrations except in recent exposures (Smith, 1991). These are probably the reasons for the non-detection of endrin and the detection of higher proportions of dieldrin than aldrin. Finally, HCB and Mirex mean concentrations in this study ranged between 2.68 and 32.9 and between 2.45 and 12.4 ng/g l.w., respectively, which are lower than those reported in other works (Durante et al., 2016; Alonso et al., 2014).

3.2. Chemical profiling

Frequently not only the concentration of a chemical but also its significance regarding the concentration of other chemicals may offer useful information. For example, high concentrations of parent compounds like DDT or aldrin with respect to their metabolites (i.e., DDE and dieldrin) would suggest recent exposures to undegraded forms of these compounds.

Table 2
ΣDDTs, ΣPCBs and ΣPBDEs (ng/g l.w.) in blubber samples from Mediterranean endemic species between 2000 and 2020. Data are expressed as mean ± standard deviation (when possible). Abbreviations; M: males; F: females; C: calves; I: immature; A: adults.; U: undetermined.

Species	n (nM:nF)	Age group	Period	Region	ΣDDTs	ΣPCBs	ΣPBDEs	Reference
S. coeruleoalba	33 (12 M;13F;8 U)	All	2011–2018	Gulf of Vera, NW Mediterranean	4752 ± 7415	6490 ± 9549	73.0 ± 103	This study
S. coeruleoalba	12 (4 M;5F;3 U)	C & I	2011–2018	Gulf of Vera, NW Mediterranean	3865 ± 4628	4340 ± 7090	57.2 ± 55.4	This study
S. coeruleoalba	6(F)	A	2011–2018	Gulf of Vera, NW Mediterranean	2120 ± 1593	2206 ± 1535	29.8 ± 17.2	This study
S. coeruleoalba	6 (M)	A	2011–2018	Gulf of Vera, NW Mediterranean	9788 ± 15,030	4341 ± 7090	70.2 ± 95.0	This study
S. coeruleoalba	11 (8 M;3F)	All	2004–2011	Spanish coast, Alborán Sea			940 (100–2250)	Barón et al., 2015b
S. coeruleoalba	5 (M)	All	2015–2016	Thyrrenian and Ligurian Seas		2590 (1700-3840)	846 (406–1660)	Capanni et al., 2020
S. coeruleoalba	5 (F)	All	2015–2016	Thyrrenian and Ligurian Seas		1360 (474–1880)	371 (219–469)	Capanni et al., 2020
S. coeruleoalba	10 (5 M;5F)	All	2015–2016	Thyrrenian and Ligurian Seas		1980 (474–3840)	608 (219–1660)	Capanni et al., 2020
S. coeruleoalba	47 (26 M;21F)	U	2007	Pelagos Sanctuary, W Ionian Sea & Strait of Gibraltar	28,814	39,489	130	Fossi et al., 2013
S. coeruleoalba	45	I & A	2010–2016	French coast, NW Mediterranean Sea	10,777 (1240-38,723)	21,058 (5240-71,906)		Dron et al., 2022
S. coeruleoalba	33	All	2000–2003	French coast, NW Mediterranean Sea	17.036	37,460		Wafo et al., 2012
S. coeruleoalba	3	All	2000–2003	French coast, NW Mediterranean Sea	3.108	69,978		Wafo et al., 2005
T. truncatus	8 (3 M;3F;2 U)	All	2012–2018	Gulf of Vera, NW Mediterranean	2266 ± 1739	6106 ± 5610	53.3 ± 42.0	This study
T. truncatus	1 (M)	I	2004–2011	Spanish coast, Alborán Sea			850	Barón et al., 2015b
T. truncatus	20	U	2012	Gulf of Cádiz, Atlantic Ocean			813 (17.3–1947)	Barón et al., 2015a
T. truncatus	20		2012	Strait of Gibraltar			1184 (<LoD-2328)	Barón et al., 2015a
T. truncatus	14 (9 M;5F)	A	2013	Gulf of Ambracia; Ionian Sea	62,850 ± 99,920	26,770 ± 28,270		Gonzalvo et al., 2016
T. truncatus	12 (4 M;6F;2 U)	All	2000–2005	Croatian coast, Adriatic Sea	34,272 ± 48,351	66,812 ± 73,754		Romanić et al., 2014
T. truncatus	5 (2M3F)	I & A	2004–2006	Israel coast, E Medtieranean Sea	49,851 ± 85,303			Shoham-Frider et al., 2009
T. truncatus	2 (M)	I & A	2004–2006	Israel coast, E Medtieranean Sea		9000 ± 3233		Shoham-Frider et al., 2009
D. delphis	3 (2 M;1F)	A	2011–2015	Gulf of Vera, NW Mediterranean	2161 ± 694	3860 ± 3536	24.8 ± 25.3	This study
D. delphis	10 (7 M;3F)	All	2004–2011	Spanish coast, Alborán Sea			1000 (93–2040)	Barón et al., 2015b
D. delphis	15		2012	Gulf of Cádiz, Atlantic Ocean			203 (<LoD-422)	Barón et al., 2015a
D. delphis	2		2012	Strait of Gibraltar			199 (74,3–323)	Barón et al., 2015a
D. delphis	1 (M)	A	2004	Croatian coast, Adriatic Sea	9500	13,8100		Lazar et al., 2012
G. melas	3 (1 M;2 U)	I & A	2011–2018	Gulf of Vera, NW Mediterranean	841 ± 871	1059 ± 1023	48.5 ± 56.4	This study
G. melas	49 (26 M;23F)		2006–2013	NW Mediterranean Sea	46,081 ± 37,506	38,666 ± 25,731	712 ± 412	Pinzone et al., 2015
G. melas	3 (1 M;2F)	I & A	2004–2011	Spanish coast, Alborán Sea			390 (190–490)	Barón et al., 2015b
G. melas	10		2012	Strait of Gibraltar			240 (<LoD-423)	Barón et al., 2015a
G. melas	4 (2F;2 U)	A	2003–2009	French coast, NW Mediterranean Sea	35,380 ± 33,630	66.020 ± 57,910		Praca et al., 2011
G. griseus	1 (F)	A	2015	Gulf of Vera, NW Mediterranean	729	1017	11.83	This study
G. griseus	1 (M)	I	2004–2011	Spanish coast, Alborán Sea			370	Barón et al., 2015b
G. griseus	4 (M)	A	2003–2009	French coast, NW Mediterranean Sea	47,200 ± 25,210	114,240 ± 68,620		Praca et al., 2011
Z. cavirostris	1 (U)	U	2018	Gulf of Vera, NW Mediterranean	956	956	15.3	This study
P. macrocephalus	2 (M)	C & I	2011–2018	Gulf of Vera, NW Mediterranean	1715 ± 157	1401 ± 78.4	25.6 ± 11.7	This study
P. macrocephalus	43 (32 M;11F)		2006–2013	NW Mediterranean Sea	37,647 ± 38,518	22,849 ± 15,566	347 ± 173	Pinzone et al., 2015
P. macrocephalus	9 (M)	A	2009	Thyrrenian and Adriatic Seas		6420 ± 6150	612 ± 401	Bartalini et al., 2019
P. macrocephalus	3(F)	A	2014	Italian coast, Adriatic Sea			167 ± 13.9	Zaccaroni et al., 2018
P. macrocephalus	12 (U)	All	2003–2009	French coast, NW Mediterranean Sea	115.980 ± 112,350	107,810 ± 108,720		Praca et al., 2011
B. physalus	70 (35 M;35F)		2006–2013	NW Mediterranean Sea	6643 ± 5549	5721 ± 5180	177 ± 208	Pinzone et al., 2015

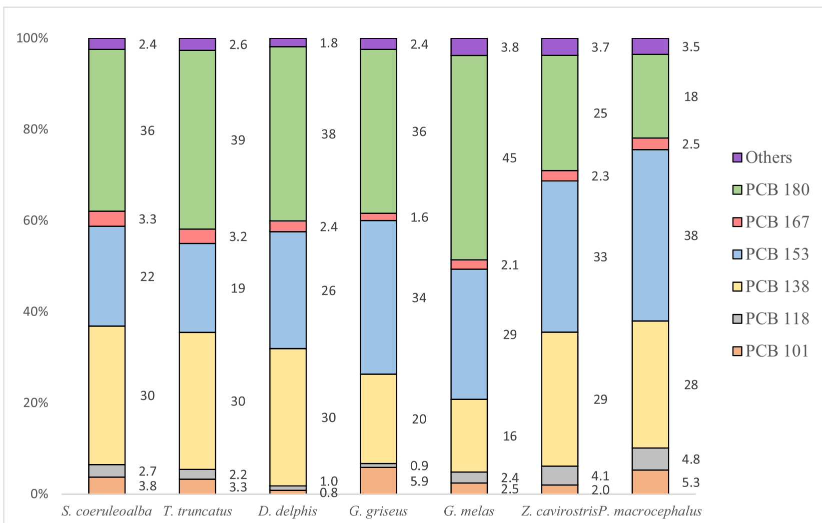
In this sense, DDE and DDD are metabolites of DDT commonly grouped together as ΣDDTs. DDE and DDD can be abiotically or biotically formed from DDT (Gold and Brunk, 1982), although both commonly appeared as impurities in DDT commercial mixtures (WHO, 1979). DDE is the most persistent metabolite naturally formed in the environment from DDT and it is commonly the most detected compound of the ΣDDTs in marine mammals (reviewed by Zitko, 2003). DDE/ ΣDDTs ratio in cetacean tissues is a commonly used indicator of recent exposures and therefore recent releases of DDT (Bachman et al., 2014; Borrell et al., 2001). High values would indicate high abundance of the metabolized form DDE and no recent usage or release of DDT to the environment. After the DDT ban in the UE, Borrell et al. (2001) observed that the DDE/ ΣDDTs ratio in NW Mediterranean common dolphins increased between 1984 and 1996. In our study, we found a consistent pattern in all species DDE > > DDD > DDT. Despite all species showed detectable concentrations of parent DDT, its composed <1 % of the ΣDDTs in all cases. DDE/ ΣDDTs mean ratio was 0.90 ± 0.15, which would suggest that the studied populations have not been recently exposed to DDT for a long time. The DDE/ ΣDDTs ratio in blubber from different Mediterranean cetacean species had been decreasing in time since the 1980s as a consequence of DDT prohibition in the EU (Aguilar and Borrell, 2005). For example, Aguilar and Borrell (2005) reported that the DDE percentage in blubber from Mediterranean striped dolphins increased from about 56 % in 1987 to 82 % in 2002. As ours is the first report in our study area, we cannot know whether previous DDE/ ΣDDTs ratios were higher or lower. However, our values are in accordance with the literature concerning this region.

On the other hand, we calculated PCBs and PBDEs patterns for each species, represented in (Fig. 1), as the percentage each PCB or PBDE congener represent of the total burden of PCBs (ΣPCBs) or PBDEs (ΣPBDEs) respectively. Of the set of 18 PCB congeners studied on this work, CB-180 (range 77.0–14,129 ng/g l.w.), CB-138 (range < LoD – 13,117 ng/g l.w.) and CB-153 (range < LoD – 20,930 ng/g lw.) were those detected at higher concentrations, whereas PCBs congeners n° 77, 81, 105, 114, 123 and 169 were below the detection limit for all the individuals studied. CB-180, CB-138 and CB-153 invariably dominated the PCB pattern in all studied species, accounting in all cases >80 % of the total. On average, CB-180 accounted for 33.9 % of the ΣPCBs, while CB-153 and CB-138 accounted for 28.6 % and 26.2 % respectively. These three congeners have been

	Penta	Penta	Hexa	Hexa	Hexa	Hepta	<2% individualmente
	PCB 101	PCB 118	PCB 138	PCB 153	PCB 167	PCB 180	Others
S. coeruleoalba	3.8	2.7	30	22	3.3	36	2.4
T. truncatus	3.3	2.2	30	19	3.2	39	2.6
D. delphis	0.8	1.0	30	26	2.4	38	1.8
G. griseus	5.9	0.9	20	34	1.6	36	2.4
G. melas	2.5	2.4	16	29	2.1	45	3.8
Z. cavirostris	2.0	4.1	29	33	2.3	25	3.7
P. macrocephalus	5.3	4.8	28	38	2.5	18	3.5

	Tetra	Penta	Penta	Penta	Hexa	Hexa
	BDE 47	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154
S. coeruleoalba	57	0.9	8.4	19	3.3	12
T. truncatus	62	0.6	5.1	23	0.6	8
D. delphis	47	2.1	1.6	23	7.9	19
G. griseus	65	0	15	20	0.0	0
G. melas	24	11	14	22	1.3	28
Z. cavirostris	65	0	13	8.9	0.0	13
P. macrocephalus	27	26	14	17	0.0	16
	49.5	5.8	10.1	19.0	1.9	13.7

a - PCBs



b - PBDEs

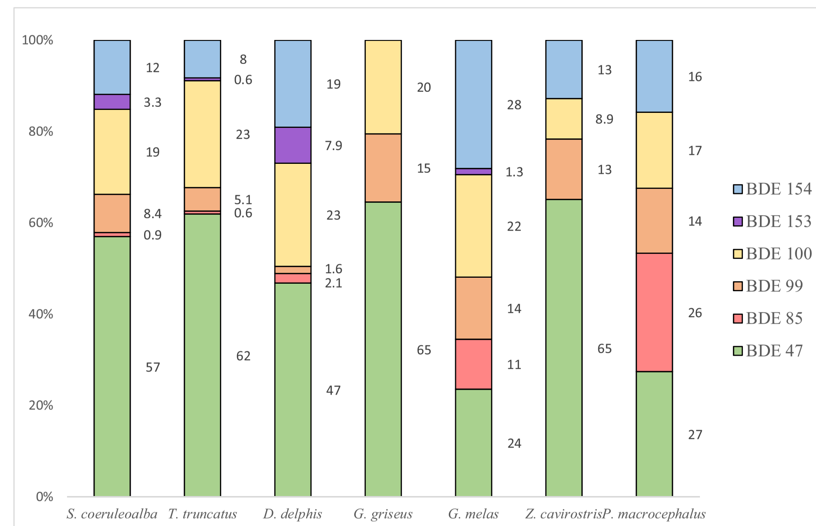


Fig. 1. PCBs (a) and PBDEs (b) profiles in blubber from different endemic cetacean species from the western Mediterranean Sea. Results are expressed as percentage of each congener with respect to total sum of congeners.

referred as being particularly resistant to metabolization by marine mammals (Boon et al., 1997, 2000, 2001), and they are constantly reported to dominate the PCB patterns of marine mammals and other marine species like loggerhead sea turtles *Caretta caretta* (Marsili and Focardi, 1997; Lazar et al., 2011; Storelli and Marcotrigiano, 2000). In all cases, higher chlorinated homologues were prevalent over those lower chlorinated. There was a direct relationship between the number of chlorine atoms within the PCB structure and its accumulation within blubber, following this scheme: PCB-7Cl ≥ PCB-6Cl > > PCB-5Cl > PCB-4Cl > PCB-3Cl, in accordance with other reports in Mediterranean dolphins elsewhere (Romanić et al., 2014; Storelli et al., 2007, 2012; Wafo et al., 2005). Higher persistence of those PCBs with more chlorine atoms is likely a possible explanation for this pattern. According to some authors, by the time PCBs' production peaked, PCB patterns in cetacean tissues reflected similar proportions of those PCB-containing commercial products (Brown et al., 2015; Wafo et al., 2005). For example, Aroclor 1260 was the most used technical product in France and other parts of Europe, and was composed of 38.5 % of PCB-7Cl, 43.4 % PCB-6Cl and 0.4 % PCB-4Cl. The PCB pattern can be useful to assess whether the pollution source has a local or a distant origin. As heavily chlorinated PCBs are less volatile than low chlorinated congeners, they appear in relative high concentrations in areas with local PCB pollution sources (Brown et al., 2015). However, according to this hypothesis, our results are not aligned with what we expected. Thus, while our study area is eminently agricultural and scarcely urbanized, the PCB profile of all species was dominated by highly chlorinated PCBs, which would virtually indicate a local source of PCBs.

Of the eight PBDE congeners considered in this work, only PBDE-183 was below the detection limit in all samples. Meanwhile, BDE-47 (mean contribution 49.5 %.), BDE-100 (mean contribution 19.0 %), BDE-154 (mean contribution 13.7 %.) and BDE 99 (mean contribution 10.1 %) were the dominant congeners. This pattern remained constant among most of our study species, which would indicate either exposure to similar PBDEs sources and/or similar distribution and metabolization pathways among these species. However, PBDEs burden and profile do not necessarily reflect either the original PBDEs released to the environment or the PBDEs to which the studied species were originally exposed, but it may also reflect the debromination of highly brominated congeners into other lower brominated. Thus, understanding the dynamics of the PBDEs in the environment and biota become essential to assess their profile in the tissues. For example, while decaBDE mixtures were the most demanded commercial mixtures and they were phased out several years after penta- and octaBDEs they are generally not detected in cetaceans, with few exceptions (Aznar-Alemany et al., 2019). Highly-brominated BDEs included in the decaBDEs commercial mixtures – mainly BDE-209 and nonaBDes – debrominate abiotically very rapidly due to sunlight (reviewed by De Wit, 2002) and they are also poorly bioaccumulated and easily debrominated in biota (He et al., 2006; Kierkegaard et al., 2007; Stapleton et al., 2006) to form less brominated PBDEs. For example, Stapleton et al. (2004b) probed in juvenile carps *Cyprinus carpio* the debromination of BDE-209 (the main constituent of decaBDEs commercial mixtures) mainly into penta- to octa-BDEs, causing the depletion of BDE-209 in the tissues. Several authors have reported that animal tissue usually accumulate higher concentrations of those PBDEs containing four (BDE—4Br) and five (BDE—5Br) bromine atoms and possessing physicochemical properties similar to other POPs as PCBs or DDT (Rahman et al., 2001; Tittlemier et al., 2002). Our findings are partially in agreement with these previous observations as BDE-183 (BDE—7Br) and BDE-28 (BDE—3Br) were either never or rarely detected respectively. However, BDE-154 (BDE—6Br) was quantitatively the second congener contributing to the PBDE profile, which would disagree with the previous statement. BDE-153 and BDE-154 were intermediate components (≈ 1–10 %) of various commercial penta- and octaBDEs commercial mixtures (La Guardia et al., 2006). Although BDE-153 accounted for higher percentages in technical mixtures than BDE-154, the former can be biotransformed from various higher brominated BDEs in liver microsomes, including BDE-183 and BDE-209 (Stapleton et al., 2004a, 2004b, 2006). Moreover, BDE-154 has much longer half-life (35 ± 18 days in carp liver) than BDE-153 (13.6 ± 9 days) (Stapleton et al., 2004b). These factors could explain that BDE-154 was, on average, a constituent ten times more important quantitatively than BDE-153 in cetaceans' blubber. Similarly, BDE-47 and BDE-99 were the major components (35–45 %) of the most common pentaBDE commercial mixtures produced in USA and EU while BDE-100 was an intermediate component (7–15 %) (La Guardia et al., 2006). Higher contributions of BDE-47 to the profile might be explained as well by its formation through the debromination of various higher brominated BDEs, including BDE-99 (Stapleton et al., 2004a). In turn, BDE-47 debrominates to BDE-28 (Bhavsar et al., 2008); however, this BDE was not detected in most samples, perhaps due to its rapid metabolization or excretion. The PBDEs patterns described in this work are in accordance with most works, not only in Mediterranean cetacean species (Pettersson et al., 2004), but also in other worldwide cetacean species like beluga whales *Delphinapterus leucas* from Canada (Lebeuf et al., 2004) or different odontocetes from the Indian Ocean (Aznar-Alemany et al., 2019) or the Atlantic Ocean (Dorneles et al., 2010).

3.3. Sources of variation: inter- and intraspecific differences

In those species coexisting in the same area, most interspecific differences on POPs concentrations can be explained by diet and trophic position, as pollutants primarily reach the organism through the digestive system (Aguilar et al., 1999; Bachman et al., 2014). For instance, Aguilar and Borrell (2005) found levels of DDT and PCBs in striped dolphins from their study to be higher than those found in other cetaceans from the same region, which they attributed to differences on diet. Similarly, in their work with 16 species of cetaceans from the Pacific Ocean, Bachman et al. (2014) suggested that those species feeding at higher trophic positions accounted for higher accumulation of pollutants. On the other hand, as major POPs sources come from the inland, cetaceans inhabiting coastal and shallower waters are expected to be exposed to higher burdens of pollutants in comparison with those species breeding and feeding away from the continental shelf and in deeper waters (Fair et al., 2007; López-Berenguer et al., 2020b). For example, Litz et al. (2007) reported higher levels of PCBs, DDTs and PBDEs, in those bottlenose dolphin populations living closer to areas with greater urbanization and industrialization along the U.S.A. southeast coast.

As the species considered in this work have strongly differentiated diets, feeding behaviors and home-ranges (Astruc and Beaubrun, 2005; Cañadas and Hammond, 2008; Natoli, 2004), it is to be expected a reflection of these differences in their pollutants burden. According to their differences on diet and habitat in the Gulf of Vera, we could separate our study species within two groups: a first group of epipelagic/shallow-mesopelagic opportunistic feeders and a second group of mesopelagic/bathypelagic teuthopagous feeders. The first group includes striped dolphin, bottlenose dolphin and common dolphin, which are opportunistic feeders whose main prey mainly include fishes and cephalopods. The bottlenose dolphin populations in our study area are the most coastal of all species. They feed on demersal prey along and in the edge of the continental shelf, on waters 200–400 m depth, mainly on hake *Merluccius merluccius* and other fishes, but also on other species like octopuses (Blanco et al., 2001; Canales et al., 2008; Wells and Scott, 1999). NW common dolphins and striped dolphins, in contrast, feed in the water column of deeper waters out of the continental shelf. While striped dolphin feed on a range of fish species (e.g., families Gadidae, Sparidae, and Gonostomiatidae) and various cephalopods in waters between 900 and 1500 m depth (Blanco et al., 1995; Gómez de Segura et al., 2008; Gómez-Campos et al., 2011; Meotti and Podestà, 1997), common dolphins feed in slightly shallower waters, between the continental slope and 1000 m depth, also on fish (e.g., families Clupeidae and Gadidae) and cephalopods (Bearzi et al., 2003; Cañadas and Hammond, 2008; Natoli, 2004). These three species generally accumulated higher POPs concentrations (Table 1) than the others according to the following pattern: striped dolphin > bottlenose dolphin > common dolphin. In contrast, the second group includes long-finned pilot whales, Risso's dolphin, sperm whale and Cuvier's beaked whale, whose NW Mediterranean populations mainly feed on bathypelagic cephalopods of the Histioteuthidae and Ommastrephidae families (Astruc and Beaubrun, 2005; Praca and Gannier, 2008; West et al., 2017). Risso's dolphin, long-finned pilot whale and sperm whale usually prefer waters with >1000 m and with a pronounced slope, although some of them can also be sporadically found in shallower waters of 500 m depth (Azzellino et al., 2008; Cañadas et al., 2002; Gómez de Segura et al., 2008; Praca and Gannier, 2008). Among them, sperm whale is able to feed on bigger and deeper prey due to its superior diving capacity and increased length (Drouot et al., 2004; Praca and Gannier, 2008). Finally, Cuvier's beaked whale is also usually found in steep slopes as well and deeper waters (> 2000 m). It is particularly associated with submarine canyons, where they forage on various cephalopods between 600 and 1500 m depth (Podestà et al., 2016; Schorr et al., 2014). For this second group of mesopelagic/bathypelagic teuthopagous feeders, the accumulation pattern was more variable according to each compound. Although these species generally accumulated lower concentrations of most chemicals, exceptionally sperm whale was the species accumulating the highest amounts of metoxychlor and heptachlor, with remarkable concentrations of DDTs as well. This fact might be explained by their position as the largest species of all odontocetes, which probably allows for hunting larger and more contaminated prey in comparison with their counterparts. This hypothesis could be supported by the fact that, on the contrary, Risso's dolphin, which is the smallest of the four diving species, generally showed lower concentrations for most POPs. It has to be noted that other physiological interspecific differences could also have influence on pollutant uptake and accumulation, including their detoxification capacity or life-span.

Not only the overall concentrations varied among species but also the contribution of each pollutant or set of pollutants. For example, while in those species feeding closer to the coast and/or in shallower waters PCBs were those chemicals detected at highest concentrations, in those species feeding deeper and further from the continental shelf methoxychlor was found at higher concentrations. PCBs pattern (Fig. 1a) was relatively similar between species. In all cases CB-180, CB-153 and CB-138 were the main congeners; however, while in most species CB-180 was the dominant congener, in Cuvier's beaked whale and sperm whale CB-153 and CB-138 contributed, by decreasing order, with higher proportions. Regarding PBDEs pattern (Fig. 1b), it remained constant among the coastal/shallower feeders (BDE-47 > BDE-100 > BDE-154) but the deeper feeders shower slight variations. For example, all these species had remarkable and higher concentrations of BDE-99. Particularly, included BDE-85 (besides BDE-47) as a dominating compound over BDE-100, BDE-154 and BDE-99. NW Mediterranean sperm whales considered in other works, however, have reported a pattern similar to the other species included in these studies, dominated by BDE-47 > BDE-99 ≈ BDE-100 and with negligible concentrations of BDE-85 (Bartalini et al., 2019; Pinzone et al., 2015; Zaccaroni et al., 2018).

As many other authors, we hypothesize that most of the reported interspecific differences are based on diet and habitat preferences. Thus, common patterns are reported among those species which share common behaviors in this regard. Due to the scarce literature existing on Mediterranean populations of all the aforementioned species, we considered important to include any information in this work, even when only one or two samples were available. However, we are aware of the difficulties of discuss and understand these data, in that the excessively limited number of samples probably has a significant effect on the results, as can be observed in the S.D., among others. This fact does not only lead to a potential underrepresentation of reality, but also magnify the influence of sex and age of the individuals in the results. Ideally only individuals of the same condition (sex and age group) should be used for interspecific comparisons. Unfortunately, the small sample sets available for most species didn't allow for further divisions of the results other than the species.

As striped dolphin is the most common cetacean in the Mediterranean Sea (Aguilar, 2000) they account for more strandings than the other species. The larger sample set for this species in our study ($n = 33$) allowed for a more detailed analysis based on the division on the results by sex and age group, which are those variables with higher influence within a same population on POPs accumulation in cetacean tissues. Both variables affect uptake, bioaccumulation, metabolization, and excretion of pollutants, not only based on inner physiological differences but also because of indirect differences, e.g., diet, blubber thickness, etc. (Aguilar et al., 1999). For example, males are frequently able to feed on bigger, deeper, or more offshore prey in comparison with females or subadults. Countless works have described sex- or age-based differences on POPs burden in several cetacean species both for organochlorines (Aguilar et al., 1999; Borrell et al., 2001; Hansen et al., 2004; Yordy et al., 2010b) and PBDEs (Dorneles et al., 2010; Pettersson et al., 2004; Litz et al., 2007). Generally, age is positively correlated with POPs accumulation (Aguilar et al., 1999). POPs are bioaccumulative and lipophilic, which males blubber a tissue where these compounds accumulate for long periods, often at a higher rate than they are eliminated. Moreover, POPs are biomagnifiable, so adult cetaceans feeding at higher trophic positions in the marine food web than calves and subadults leads to higher uptake of pollutants (Aguilar and Borrell, 1994b; Borrell et al., 2001). However, age-based increase on POPs uptake and accumulation is frequently masked by sex-based processes. Organochlorine compounds and PBDEs are passed from adult females to their offspring both through placental and lactational transfer (Borrell et al., 2001; Dorneles et al., 2010). This is such an effective process that can cause females to lose up to 90 % of their total organochlorines body burden (Borrell and Aguilar, 2005; Tanabe et al., 1982). These interaction between age- and sex-related influencing factors usually leads to the following pattern of POPs accumulation in marine mammals' populations: adult males ≥ nulliparous females > calves ≥ subadults > primiparous and multiparous females, which is roughly the pattern observed in our work and many others (Aguilar and Borrell, 1994b; Bachman et al., 2014; Dron et al., 2022; Hansen et al., 2004; Krahn et al., 2009; Pettersson et al., 2004; Zaccaroni et al., 2018).

Adult males of striped dolphin accumulated more ΣDDTs (mean 9788 ng/g l.w.), ΣPCBs (mean 13,361 ng/g l.w.), and ΣPBDEs (mean 70.2 ng/g l.w.), than calves and subadults (mean ΣDDTs, 3865 ng/g l.w.; mean ΣPCBs 4340 ng/g l.w.; mean ΣPBDEs 57.2 ng/g l.w.), which on turn showed higher concentrations than adult females (mean ΣDDTs, 2120 ng/g l.w.; mean ΣPCBs 2206 ng/g l.w.; mean ΣPBDEs 29.8 ng/g l.w.). This pattern is usually constant among different studies even if they consider different species or different regions; however, occasionally these trends are not observed in some populations of study. For example, Dron et al. (2022) reported higher DDT concentrations in males and calves of NW Mediterranean striped dolphins in comparison to adult females, but no significant differences for PCBs and other OCPs as aldrin or heptachlor. Also, Lebeuf et al. (2004) did not find any significant different on PBDE levels between males and females of belugas *Delphinapterus leucas* from St. Lawrence Estuary (Canada). There are no simple explanations for these observations the former work suggested extremely high exposures and accumulation rates masking elimination processes as a possible cause. Other causes might include small sample sets, sample sets from long or different periods, or inclusion of diseased or emaciated animals, etc. According to the statistical analyses, any of our variables (i.e., sex and length/age) had a significant effect on the blubber concentration of OCPs, PCBs or PBDEs; however, we attribute this situation to the scarce amount of samples included within our sample set as there was easily observable differences among groups.

On the other hand, maternal transfer is not equally efficient for all pollutant; for example, Borrell et al. (2001) suggested a higher transference for DDTs in comparison to PCBs. In the same sense, the process have suggested to be more effective for DDT than for DDE (Borrell et al., 2001; Tanabe et al., 1982; Borrell et al., 1995; McKenzie et al., 1997) as well as for those less halogenated PCB and PBDE congeners (Cadieux et al., 2015; Dorneles et al., 2010), probably due to their lower hydrophobicity and molecular size in comparison with highly halogenated congeners. This fact would result in lower concentrations of DDT and highly chlorinated or brominated PCBs or PBDEs in adult females in comparison to adult males and calves, as well as in higher concentrations of DDE and lower halogenated congeners in calves with respect to their mothers. However, some authors have not reported such differences between adult males and females (Borrell et al., 2001; Salata et al., 1995) or have reported similar patterns between mothers and calves (Zaccaroni et al., 2018). In our study, PCB pattern was similar among the three sex/age groups and especially between calves and subadults (Fig. SI.1a). On the contrary, it was possible to observe more variability in PBDEs pattern (Fig. SI.1b). In this case, adult males had higher proportions of BDE-47 (BDE—4Br) and much lower proportions – 10 time less – of BDE-154 (BDE—6Br) in comparison with adult females, while calves and subadults where in between these two. This could suggest that, as aforementioned, lower brominated PBDEs are more easily transferred to the offspring highly brominated PBDEs, causing a progressive accumulation of these formers in adult females along their reproductive life.

According to Lebeuf et al. (2004), some POPs, like mirex and γ-HCH do not seem to be significantly affected by maternal transfer; however, in our study these two chemicals followed the general scheme, appearing in lower concentrations in adult females than in calves, subadults and adult males. On the contrary, the compounds which deviated from the norm were heptachlor, which was higher in adult females than in the other groups, and aldrin, which was higher in calves and immature followed by adult females. CB-28, CB-101, CB-156 and BDE-74 were higher in calves and subadults and, except CB-28, they appeared at higher concentrations in adult females than in males.

3.4. Risk assessment

All the Mediterranean cetacean species whose populations have been assessed in this work are considered to be declining (IUCN, 2022). Cetaceans inhabiting the Mediterranean Sea are exposed to a number of stressors including habitat degradation, fishing interactions (prey depletion and by-catch), infectious diseases (e.g., morbillivirus pandemic) and chemical and acoustic pollution (Costello et al., 2010; Halpern et al., 2008). Although POPs concentrations reported in cetacean tissues are not usually considered directly responsible for their death, their toxic effects on endocrine, immune, reproductive, or nervous system have certainly harmful consequences on organism survival. Scientists have been reporting high levels of pollutants in worldwide cetaceans since many decades ago; however, direct causal links of health impairments have rarely been demonstrated. Martineau et al. (1994, 1999) observed an apparent link between a high prevalence of tumors in a beluga whale *Delphinapterus leucas* population in a highly polluted area and high presence of PAHs and PCBs. Similarly, association between PCBs and mortality caused by infectious diseases was established in harbor porpoises *Phocoena phocoena* from the British islands (Jepson et al., 2005) or striped and bottlenose dolphins from the Mediterranean Sea during the morbillivirus epidemic in the 1990s (Aguilar and Borrell, 1994a; Evans et al., 2008). In these cases, an increase of death rate was observed in those individuals showing high PCB levels, which was attributed to the ability of these compounds for immunosuppression. However, despite examples like these, the biological significance and nature of effects caused by chemical pollution exposure in cetaceans usually remains uncertain.

The lack of knowledge on the subject, the difficulty of studies on these species and the interspecific variability in the response to contaminants (Boon et al., 1997; Kannan et al., 2000) make it extremely difficult to carry out exhaustive and accurate assessments on the risk to which free-living cetaceans are exposed by their exposure to environmental pollutants. However, several works have adopted different strategies to try to establish useful toxicity thresholds which would allow for rigorous assessments of such risk. Generally, PCBs are considered the major hazard for Mediterranean cetaceans (reviewed by Jepson and Law, 2016), as well as for most worldwide cetacean species, which has resulted in a greater number of studies focusing on this class of contaminants. This particular attention has resulted in a range of PCB toxicity thresholds depending on the methodology used and the toxic effect to be assessed. These thresholds range from a LOAEL of 17 mg/kg l.w. established by Kannan et al. (2000) based on primary data on minks *Mustela vison*, to 41 mg/kg l.w. derived by Helle et al. (1976, adjusted by Jepson et al., 2016) based on important reproductive impairments in ringed seals *Phoca hispida*. It has to be noted that any of them derives from cetaceans. As for our results, PCB concentration in tissue of three striped dolphins (one calf) and one bottlenose dolphin exceeded the lowest threshold, but none of them approached the highest one. On the other hand, dioxin-like PCBs are considered to be more toxic for biota in comparison to other congeners. Their toxicity is also commonly assessed by the toxic equivalent quantity (TEQ) approach, which consider the overall toxicity of a mixture of dioxin-like PCBs based on their potential toxicity in relation to that of the reference chemical 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; TEF = 1). We analyzed all dioxin-like PCBs (dl-PCBs), including non-ortho and mono-ortho PCBs; however, some of them were not detected in any sample (i.e., congeners 77, 81, 105, 114, and 123). Depending on the species, % of dl-PCBs ranged between 4.0 and 10.1 % with respect to ΣPCBs. Median total TEQs (Table SI.6) was 365 pg TEQ/g l.w., although all species except Risso's dolphin accounted for >290 pg TEQ/g l.w., with a maximum of 976 pg TEQ/g l.w. for striped dolphin. Despite our dl-PCBs concentrations are below those of other works (e.g., Bartalini et al., 2019), our TEQ values are as high or higher than those reported by these works. These results are strongly influenced by some specimens showing detectable concentrations of CB-126 ($n = 27$; range 2.21–157 ng/g l.w.), which has assigned a TEF value of 0.1 in contrast to TEF values of 0.00003 for the other detectable congeners in our study. Thus, our TEQ results remark a difference of three or four orders of magnitude between those individuals with detectable concentrations of CB-126 and those individuals without detectable concentrations of these congener. Ross et al. (1995) proposed a toxicity threshold of 210 pg TEQ/g l.w. in blubber based on the onset of immunotoxic effects in harbor seals. Accordingly, approximately half of the individuals considered in this study ($n = 26$) would be at risk of immunotoxic alterations. To our knowledge, no similar thresholds have been established in marine mammals' species for DDTs or other organochlorine pesticides, and there is only one toxicity threshold for PBDEs in these species. In this case, Hall et al. (2003) reported alterations of the thyroid hormones when ΣPBDEs in blubber of grey seals *Halichoerus grypus* ranged between 61 and 1500 ng/g l.w. Despite our highest ΣPBDEs concentrations is 480 ng/g l.w. (striped dolphin) and the median ΣPBDEs concentration is of 27.8 ng/g l.w., there are 17 individuals whose concentrations surpass the lower limit.

Usage of thresholds derived from data from laboratory animals or from other species to assess the risk to which cetacean species are subjected facing POPs accumulation within their tissues is risky and inaccurate. Nevertheless, despite the limitations of this approach, given the difficulties involved in the management and study of these species, the use of these toxicity thresholds can be a practical and useful tool. It is thought that cetaceans do not detoxify efficiently some classes of pollutants, including organochlorines and PBDEs, in comparison with other species (Boon et al., 2000, 2001; Letcher et al., 2009; Tanabe, 2002). Therefore, some of these limits established for the onset of different toxic harms might be underestimating the consequences of the reported concentrations on the health of the studied populations. On the other hand, while OCPs, PCBs and PBDEs are known to affect countless tissues and organic systems in marine mammals, the existing endpoints only reflect some of them. Moreover, new effects of pollutants on cetaceans' health are continuously being reported in the literature. For example, PBDEs are known to impair the immune response and alter the cytokine response in spotted dolphin *Stenella attenuate* cells (Rajput et al., 2018), and PCBs have been reported to be correlated with lower testes weights in harbor porpoises *Phocoena phocoena* (Williams et al., 2021).

3.5. Conclusions

Long-term monitoring of persistent pollutants is useful to understand the dynamics, fate, and impacts of these chemicals on the biota and their potential risk to the environment, wildlife and human health. Moreover, generating high-quality spatial and temporal data result essential to assess whether human actions (e.g., prohibitions, changes in production, use or storage, etc.) or the environmental fate (e.g., transport, deposition, degradation, etc.)

of these chemicals have impact on their burden on marine mammals' tissues in relatively closed areas. This information can be used by national and international agencies, organizations, and regulators to assess the impact of their recommendations and legislation and correctly address their future efforts.

Potential health risks for cetaceans chronically exposed to POPs include a number of toxic effects. Despite the fact that more than fifty years have passed since first organochlorine chemicals were reported in cetacean tissues, information on their effects on marine mammals' health, either on individuals or populations, remain extremely scarce. This fact is far more worrying when chemicals of more recent concern, like PBDEs, are considered. Although we have reported lower concentrations of PBDEs in comparison with other reports in others relatively close areas, and PCB and DDT concentrations are far below from those reported two or three decades ago, our results suggest that various resident cetacean populations inhabiting the NW Mediterranean might be undergoing health consequences from their exposure to environmental pollutants. Moreover, little is known regarding the combined effect of these and other pollutants which might be negatively affecting these species. Despite the almost global ban on those compounds considered in our study, their persistence in cetacean tissues, their coexistence with other significant hazards, and the alarming status of several of the cetacean populations in the NW Mediterranean Sea, make it difficult to foresee a promising future for its conservation in this area. Moreover, the continuous development of new chemicals (brominated flame retardants, halogenated norbornenes…) in order to substitute those which become regulated leaves little hope for the elimination of chemical pollution as a risk for oceanic wildlife in the near and medium term.

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CRediT authorship contribution 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.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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