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Trends of banned pesticides and PCBs in different tissues of striped dolphins (*Stenella coeruleoalba*) stranded in the Northwestern Mediterranean reflect changing contamination patterns

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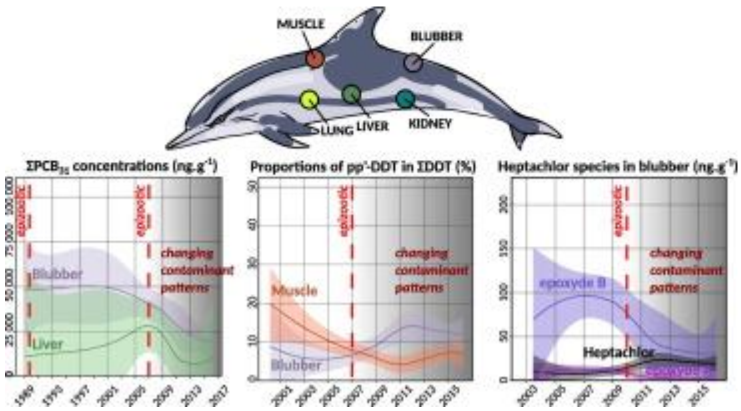
Abstract :

Although banned for years, organochlorine pesticides and PCBs continue to affect aquatic life, dolphins being particularly exposed. The concentrations of 31 PCB congeners, and 15 banned pesticides or metabolites were measured in 5 tissues of 68 striped dolphins stranded in the Northwestern Mediterranean coast in 2010–16. The results were compared to historical data (1988–2009) and, even though there is a slow decreasing trend, the levels in the 2010–2016 samples were still elevated based on common cetacean toxicological thresholds. A transition period in 2007–08, probably caused by a morbillivirus epizootic amplified the stranding, espacially of highly contaminated specimens. From 2010, higher proportions in parent compounds towards metabolites were observed yet again. These changing patterns were likely reflect the exposure of dolphins to the remobilization of pollutants from contaminated soils and sediments, with a prominent role of rivers. This should lead to an even slower decline of these contaminants that could last for decades, requiring new efforts to reduce their dispersal to aquatic ecosystems.

Graphical abstract



Highlights

► Banned organochlorine contaminants globally decreased in dolphins since 1988. ► Global levels remain elevated and still constitute a threat to dolphins. ► Levels of parent compounds towards metabolites reflect a shift in contaminants origin. ► Increasing parent compounds suggest diffusion from contaminated lands and sediment. ► Morbillivirus epizootic likely affected preferably highly multi-contaminated dolphins.

Keywords : PCBs, Organochlorine pesticides, Temporal trends, Striped dolphins, Morbillivirus, Contaminant remobilization

1. Introduction

Organochlorine (OC) contaminants such as PCBs, DDT and other pesticides are often persistent and particularly harmful to aquatic ecosystems (Agency for Toxic Substances and Disease Registry (ATSDR), 2000; Jayaraj et al., 2016). Several OC contaminants were banned around the world, starting with PCBs and DDT in the 1980s, and followed by other in the subsequent decades. However, these compounds continue to affect all the compartments of continental and marine waters (Williams et al., 2020; Kean et al., 2021) and eventually human health through fish consumption (Smith and Gangolli, 2002; Jiang et al., 2005; Jeanjean et al., 2021). Several works and surveys point out that banned OC contaminants are still brought to the sea, likely associated to remobilization from contaminated soils, sediments, and industrial or other wastelands (Sabatier et al., 2014; Li et al., 2018; Liber et al., 2019).

Since the Stockholm Convention on Persistent Organic Pollutants signed in 2001 (Stockholm Convention on POPs), international programs encourage to maintain strong monitoring efforts of these chemical contaminants in marine biota (European Commission (EC), 2000; OSPAR Assessment Portal, 2017; UNEP(DEPI)/MED IG.22/28, 2016). Long-term surveys thus inform on the fate and impacts of contaminants through the different compartments and the food chain, providing essential field data towards their degradation kinetics, their incidences on species reproductive and immuno-toxicity, or population dynamics (Beckmen et al., 2003; Jepson et al., 2016; Williams et al., 2020; Kean et al., 2021). Moreover, it enables to confront early predictions and adjust further modeling and monitoring, but also provides responses to stakeholders in the preparation of future regulations (Stuart-Smith and Jepson, 2017).

Cetaceans and especially odontocetes, while being emblematic, are particularly vulnerable to OC chemicals' contamination. Their bioaccumulation levels often reach extreme values, due to the high trophic level of dolphins which are top predators, their relatively long lifespan, fat blubber and melon tissues favoring the accumulation of hydrophobic compounds, and the transfer of contaminants to their offspring through gestation and lactation (Tanabe et al., 1982; Kawai et al., 1988; Wafo et al., 2005; Romanić et al., 2014; Jepson et al., 2016). The striped dolphin (*Stenella coeruleoalba*) is found in all oceans and is the most common cetacean in the Mediterranean Sea, which makes it particularly valuable for long-term surveys (Marsili et al., 2018). Also, its Mediterranean subpopulation is considered vulnerable by the IUCN red list (International Union for Conservation of Nature) with several threats, in particular chemical pollution from human activities (Aguilar and Gaspari, 2012) especially in the Pelagos Sanctuary (NW Mediterranean, Fossi et al., 2013).

Benefiting from the sampling of several tissues of stranded striped dolphins in the 2010–16 period, and of the historical background in the French NW Mediterranean coastline since 1988 (Wafo et al., 2005, 2012a, 2012b), the present study concerned extended temporal trends of PCBs, DDT and other banned OC pesticides such as aldrin, heptachlor, and endosulfan, with a particular focus on the variations of mother compounds towards their metabolites. The incidence of the documented 2007–08 morbillivirus epizootic is discussed, and more generally, the fate of the OC contaminants regarding their degradation products was investigated to provide new insights into the changing contaminantion patterns in marine top predators. Moreover, OC pesticides such as aldrin, heptachlor or endosulfan and their metabolites were rarely described in Mediterranean cetaceans and clearly required additional reporting (Wafo et al., 2012b; Romanić et al., 2014).

2. Materials and methods

2.1. Study area and sampling

The NW Mediterranean coastline in France (Supplementary Material S1) is characterized by highly urbanized areas (cities of Marseilles, Toulon and Nice) and intensive agriculture, mainly in the west. The Rhône river, which separates the east from the west parts, is one of the main river flowing into the Mediterranean Sea (1700 $m^3 \cdot s^{-1}$, in average) and is considered as a major input of contaminants to the sea (Cresson et al., 2015). Between the river mouth and the city of Marseilles also lies one of the main industrial harbor in Europe (Fos-Marseille). Previous studies reflected these contrasts with higher organochlorine pesticides levels in fish from the west and the Rhône river prodelta (Ribeiro et al., 2005; Dierking et al., 2009), as well as elevated PCB concentrations in fish and sediments by the Rhône river mouth (Salvadó et al., 2013; Cresson et al., 2015; Dron et al., 2019) and the urban centers of Marseilles, Toulon, and Nice (Garrigues et al., 1993; Wafo et al., 2006, 2016; Bouchoucha et al., 2021). The Rhône river still renders continuous organochlorine contaminants fluxes to the Mediterranean by their remobilization from river sediment, polluted soils or waste leaching (Sabatier et al., 2014; Liber et al., 2019), with a PCB input of 0.03 to 0.12 tons y^{-1} (sum of ICES-6 indicator PCBs) since 2001 while an earlier study estimated a flux 0.29 tons y^{-1} in 1994 (Launay, 2014; Poulier et al., 2018).

The coastline was subdivided into sectors of 40 km named A to I from west to east (Supplementary Material S1). Sectors A and B were extended to 100 km and 50 km long, respectively, to cover the reduced number of individuals found stranded in this area, where the shallow waters of a broad continental shelf keeps striped dolphins away. Conversely, the eastern coast is characterized by steep slopes and regular upwelling currents (sectors D to I), partly located within the Pelagos Sanctuary (sectors F to I), and hosts a large population of striped dolphins (Panigada et al., 2017). The genetic structure of populations in this region showed significant differentiation between living areas and suggested distinct inshore and offshore populations and kinship (Gaspari et al., 2007; Gonzalvo et al., 2016). Even though migration may still occur especially under critical conditions (Meissner et al., 2012; Gaspari et al., 2019). The feeding habits of Mediterranean striped dolphins are opportunistic and largely composed of cephalopods which have only a limited and strictly vertical migration in the Mediterranean (Gannier, 1999; Öztürk et al., 2007), but also of bony fishes (Würtz and Marrale, 1993).

The sampling of 68 striped dolphins (*Stenella coeruleoalba*) found stranded from May 2010 to April 2016 was performed by the National Marine Mammals Stranding Network (RNE), coordinated by the Mediterranean Cetaceans Study Group (GECEM, today MIRACETI) over 41 locations (Supplementary Material S1). All details concerning specimens before 2010 were reported in previous publications (Wafo et al., 2005, 2012a, 2012b). Dolphins were weighted and measured, and up to 5 tissues and organs (blubber, liver, kidney, lung and muscle) were sampled and stored at −20 °C. They were freeze-dried, pulverized and homogenized prior to analysis. Their mean water contents were 45% in the blubber, 70% in the liver, and 75% in the other tissues. As in previous works, the newborn and calves ($n = 6$) were considered separately according to a total length below 120 cm (Wafo et al., 2005, 2012a, 2012b). From the length/age relation given by Marsili et al. (2004) for Mediterranean striped dolphins, this size corresponds to an age of 1.5 years, when calves feeding habits switches from lactation to solid food, affecting their exposure to pollutants (Miyazaki, 1977; Calzada et al., 1996). The other individuals were considered as adults ($n = 36$ males and $n = 25$ females), because the main differences in exposure were observed between calves feeding from maternal lactation and older dolphins, even though sexual maturity occurs at 9–12 years (Miyazaki, 1977; Calzada et al., 1996).

2.2. Chemical analyses

The PCB determination focused on 31 congeners (IUPAC 20, 31, 28, 18, 44, 52, 95, 92, 101, 60, 87, 151, 136, 149, 118, 105, 153, 141, 138, 187, 183, 128, 174, 177, 156, 180, 170, 201, 194, 195, and 196). Besides, 14 banned OC pesticides and related compounds were analyzed, pp′-DDT, pp′-DDD, pp.'-DDE, γ-HCH, heptachlor and epoxides (A and B isomers), dieldrin, aldrin, endrin, isodrin, *trans*-chlordan, endosulfan (-I and -II isomers). In addition, the organophosphorous pesticide diazinon was also determined (Supplementary Material S2). The sum of the 31 PCB congeners were referred as ΣPCB_{31} and the sum of pp′-DDT, pp′-DDD, and pp′-DDE, as ΣDDT.

The analytical method was fully described in previous works (Wafo et al., 2005, 2012a, 2012b). The freeze–dried samples (~1 g) were Soxhlet-extracted with hexane (Pestipur grade) in cellulose thimbles (pre-extracted for 12 h to remove any contamination) during 16 h. A part of the extract was used to determine lipid contents by gravimetry. The remaining was purified with concentrated sulfuric acid, followed by additional purification on a silica–alumina column and fractioning. The first fraction contained PCBs, aldrin, pp.'-DDE, and heptachlor (50%), while the following fractions contained heptachlor (50%) and epoxides, and the other pesticides. They were all analyzed by gas chromatography (Agilent 7890B) equipped with a Rxi-XLB column (60 m × 0.25 mm × 0.25 μm, Restek) coupled with a mass spectrometer (Agilent 5977A). Variation in the MS response was corrected by daily calibration with a mixture prepared from standard solutions of 30 PCB congeners and pesticides (AccuStandard). Quantification was performed in the MS SIM mode.

The detection limits were 0.01 $ng \cdot g^{-1}$ for PCB congeners, 0.2 $ng \cdot g^{-1}$ for dieldrin and endosulfan-I, 0.1 $ng \cdot g^{-1}$ for aldrin, diazinon, endosulfan-II, endrin, heptachlor, γ-HCH, pp′-DDT, pp′-DDE and pp′-DDD, and 0.01 $ng \cdot g^{-1}$ for heptachlor epoxides and chlordan. Each analysis sequence included blank and tuna homogenate certified material (IAEA-435) runs, which results were reported in Supplementary Material S3.

2.3. Statistical analyses

All the data treatment and analyses were performed with the R software version 3.6 (R Core Team, 2020). Comparisons of means were realized with the Tukey post-hoc test after an analysis of variance (aov and TukeyHSD functions, “stats” package), and correlation tests with the cor.test function from “stats” package. The significance of the temporal trends were evaluated by the Kwiatkowski–Phillips–Schmidt–Shin KPSS test (kpss.test function, “tseries” package), which allows for designating trend or level stationarity (Kwiatkowski et al., 1992). In the kpss.test function, the null hypothesis ($p > 0.1$) is stationarity, meaning an homogeneous trend (regular increasing or decreasing variation) when trend stationarity is tested, or no variations (homogeneous levels) in the case of level stationarity. Also, level stationarity was tested first, and when differences were revealed ($p < 0.05$), trend stationarity was additionnally tested. To enhance the visualization of temporal trends, the graphical outputs were supported by moving regression (geom_smooth function, “ggplot2” package) used with LOESS (locally estimated scatterplot smoothing) regression at a 0.9 span value and a 0.95 confidence interval.

3. Results

3.1. PCB levels in 2010–16 and trends

The ΣPCB_{31} levels recorded in the tissues of the striped dolphins were summarized in Table 1. The ΣPCB_{31} concentrations in most tissues were significantly and positively correlated, except for lung which only correlated with liver ($R = 0.74, p < 0.01$). Muscle levels were best correlated with kidney ($R = 0.71$, $p < 0.001$) and liver ($R = 0.53$, $p < 0.001$), but more weakly with blubber ($R = 0.47$, $p < 0.05$). Finally, strong correlations were observed between kidney, liver and blubber ($R > 0.69$, $p < 0.001$). The average ΣPCB_{31} levels were systematically lower in dolphin females compared to calves and adult males (Supplementary Material S4). As documented elsewhere, this likely reflects the elimination of the organochlorine contaminants through placental and lactation transfer (Tanabe et al., 1982; Miyazaki et al., 1999; Storelli and Marcotrigiano, 2000).

The predominant congeners were CB153 (13.9% to 18.0% of ΣPCB_{31} among tissues), CB138 (10.7 to 13.1%), CB180 (9.1 to 11.6%) and CB187 (7.3 to 10.3%), but other (CB141, CB149, CB170 and CB201) occasionally contributed over 5%. An interesting difference in the relative contributions of the PCB classes, defined from the number of chlorine substituents, was observed between blubber and other tissues (Supplementary Material S5). The dolphins blubber contained higher proportions of low chlorine PCB-3Cl, -4Cl, and -5Cl congeners. On the other hand, PCB-6Cl, -7Cl and PCB-8Cl congeners were more elevated in lungs, and in a lesser measure, in other tissues.

Recently, “dioxin-like” DL-PCBs were measured in the blubber tissues of stranded striped dolphins in the Mediterranean Ligurian coast (Capanni et al., 2020), and the mean cumulated concentration of CB105, CB118 and CB156 (1635 $ng\cdot g^{-1}$ lipid weight l.w.) was higher than what determined here (903 $ng\cdot g^{-1}$ l.w.). To our knowledge, no other PCB data from striped dolphins samples collected since 2010 were available in the Mediterranean (Marsili et al., 2018), but comparable levels where found in Bottlenose dolphins (*Tursiops truncatus*) from western Greece in 2013 (Gonzalvo et al., 2016). In other parts of the world, the most recent data indicated lower ΣPCB_{30} levels in the blubber of male Australian snubfin (*Orcaella heinsohni*) and Australian humpback (*Sousa sahulensis*) dolphins while they were comparable in females (Cagnazzi et al., 2020). Lower concentrations of ΣPCB_{19} were also reported in Indo-Pacific humpback dolphins (*Sousa chinensis*) from the South China Sea (Gui et al., 2014). On the contrary, bottlenose dolphins from the English Channel presented much higher ICES-6 indicator PCBs concentrations (Zanuttini et al., 2019). The ΣPCB_{31} levels reported in the present study for blubber samples in 2010–16 were also lower than what reported in the 2000–10 period in the French Mediterranean coasts (Table 1) (Wafo et al., 2005, 2012a) as in Spanish Mediterranean waters (mean and median 59,114 and 49,140 $ng\cdot g^{-1}$ l.w., for striped dolphin data extracted from Jepson et al. (2016)).

The globally decreasing trends of ΣPCB_{31} in blubber and muscle tissues from 1988 were confirmed by KPSS tests indicating that data had a regular trend ($p < 0.01$ for level stationarity and $p > 0.1$ for trend stationarity). However, they may be possibly reaching a plateau from 2010 (Supplementary Material S6), supporting recent observations in the NW Mediterranean for mussel and fish (Cresson et al., 2015; Dron et al., 2019; Bouchoucha et al., 2021). The ΣPCB_{31} levels in liver, kidney and lung tissues were even significantly level stationary since 1988 (level KPSS tests $p > 0.1$), even though a limited number of observations before 2003 made the trends uncertain. Finally, extreme values were recorded in the 2007–08 years (Supplementary Material S6), during a well documented epizootic caused by a morbillivirus (Raga et al., 2008; Keck et al., 2010; Gaspari et al., 2019), this will be discussed in Section 4.1.

Table 1
Total PCB and DDT concentration statistics (expressed in $ng\cdot g^{-1}$[2, 3] l.w. -lipid weight- in blubber and $ng\cdot g^{-1}$ d.w. -dry weight- in other tissues) in the tissues of *Stenella coeruleoalba* stranded along the French Mediterranean coast from 1988 to 2016.

Period		Blubber	Liver	Kidney	Lung	Muscle
ΣPCB_{31}						
1988–90 [1]	Mean	45,200 (n = 5)	13,360 (n = 5)	NA	NA	4200 (n = 5)
	Median	62,200	3700			3600
	Range	2700–83,200	2700–30,400			1200–8500
2000–03 [1]	Mean	69,978 (n = 3)	16,200 (n = 5)	6299 (n = 6)	3103 (n = 6)	14,294 (n = 3)
	Median	55,754	10,863	6446	3484	4363
	Range	55,754–110,343	5810–39,444	1990–12,365	648–4118	4007–34,512
2003–09 [2]	Mean	37,460 (n = 33)	26,002 (n = 48)	8556 (n = 48)	4701 (n = 33)	5894 (n = 32)
	Median	31,360	5763	3493	2479	3020
	Range	1079–159,696	284–498,928	933–81,091	481–33,148	466–32,765
2010–16 [3]	Mean	21,058 (n = 45)	9923 (n = 56)	4564 (n = 52)	4601 (n = 18)	2692 (n = 64)
	Median	18,057	7340	3169	3411	2206
	Range	5240–71,906	1119–41,931	463–23,015	715–19,371	327–12,864
ΣDDT						
2000–03 [1]	Mean	3108 (n = 4)	990 (n = 5)	530 (n = 6)	337 (n = 6)	350 (n = 2)
	Median	2779	962	509	245	272
	Range	309–6566	503–1518	320–796	89–968	54–723
2003–09 [2]	Mean	17,036 (n = 33)	5317 (n = 47)	3272 (n = 47)	1472 (n = 32)	2462 (n = 31)
	Median	12,556	1859	1926	918	1423
	Range	600–55,174	61–51,150	205–31,294	114–10,122	112–16,630
2010–16 [3]	Mean	10,777 (n = 45)	3311 (n = 56)	1337 (n = 53)	1076 (n = 18)	1127 (n = 64)
	Median	10,128	1931	811	1005	642
	Range	1240–38,723	307–23,806	132–11,036	163–3682	98–8421

[1] ΣDDT and ΣPCB statistics calculated from data reported in Wafo et al. (2005), representing 104% in average of the ΣPCB_{31} measured in [2] and [3].
[2] ΣDDT and ΣPCB_{31} statistics from data reported in Wafo et al. (2012a).
[3] ΣDDT and ΣPCB_{31} in this study.

The average proportions of most PCB congener classes were globally stable over time in blubber. However, in 1988–90 ($N = 3$, Wafo et al., 2005), the PCB-4Cl and PCB-7Cl contributions to ΣPCB_{31} in blubber were slightly higher (2.6% and 34.6% in 1988–90, and 1.7% and 31.2% in 2010–16, respectively) and PCB-6Cl lower (43.6% and 49.5% in 1988–90 and 2010–16, respectively). These early values were closer to commercial mixtures (Aroclor 1260, 0.4%, 38.5%, and 43.4%, respectively).

By contrast, the proportions of PCB-3Cl strongly decreased from 2010 in all the other tissues, from 2.2%–3.3% in 2003–09 to 0.3%–0.6% in 2010–16, while they remained stable (0.8%) in the blubber (Fig. 1). The proportions of PCB-3Cl first measured in 1988–90 were only 0.2%–0.3% in the blubber and other tissues as in commercial mixtures (0.2%) (Wafo et al., 2005), except for lung (1.5%). Other PCB classes were either stable or slightly decreasing over time in liver, kidney, lung and muscle, except for PCB-7Cl (Fig. 1). The proportions in PCB-3Cl showed a peak in 2007–08, coinciding with the ΣPCB_{31} trend (Supplementary Material S6), and were homogeneous among dolphin size.

3.2. Organochlorine pesticides 2010–16 levels

The ΣDDT concentrations were reported in Table 1, along with previous data from the French Mediterranean in the 2000–10 decade. The correlations of ΣDDT between dolphin tissues were very significant in 2010–16, except for blubber with liver and kidney ($R < 0.3$, $p > 0.05$). Similarly to PCBs, the ΣDDT levels in the muscle were best correlated with kidney ($R = 0.64$, $p < 0.001$) and liver ($R = 0.80$, $p < 0.001$), and less with blubber ($R = 0.45$, $p < 0.05$). Significant correlations were observed for ΣDDT between levels in kidney, liver and lung ($R > 0.5$, $p < 0.001$), as well as between blubber and lung ($R = 0.93$, $p < 0.001$). Even though calves and males had higher ΣDDT levels than females in all tissues, significant differences were only found in kidney tissues (Supplementary Material S4), consistently with the preceding decade (Wafo et al., 2012a). No recent data were found for DDTs in Mediterranean striped dolphins. Gui et al. (2014) and Cagnazzi et al. (2020) reported higher blubber levels of ΣDTT in Indo-Pacific humpback dolphins from the South China Sea and Australian snubfin and Australian humpback dolphins, respectively, while Zanuttini et al. (2019) indicated significantly lower ΣDTT concentrations in blubber samples of bottlenose dolphins from the English Channel. Oppositely, dolphins from the East-Pacific seas presented higher ΣDDT but lower ΣPCB levels than French Mediterranean striped dolphins, while dolphins from the English Channel had more elevated PCB but lower ΣDDT concentrations.

The average concentration levels of the other pesticides studied here were reported in Table 2. Despite the recent ban of diazinon (2008), its homogeneous distribution across the different tissues may be explained by its lower K_{ow} and higher water solubility (Supplementary Material S2). The pesticides levels were golably higher in blubber but poorly correlated with other tissues, except for endosulfan-II in all tissues ($R = 0.43$ to 0.74, $p < 0.05$), and isodrin, heptachlor and epoxide-A in liver ($R = 0.36$ to 0.59, $p < 0.05$). On the other hand, the pesticides concentrations in liver were always significantly correlated with kidney, possibly indicating analogous physiological functions in striped dolphins towards these compounds ($R = 0.32$ to 0.57, $p < 0.05$). The amounts recorded in muscle tissues were also significantly correlated with those in liver and kidney ($R = 0.29$ to 0.48, $p < 0.05$), except for isodrin, aldrin, dieldrin, endosulfan-I and diazinon ($p > 0.05$).

No significant differences were observed between males, females and calves for these pesticides in blubber (Tukey tests, $p > 0.05$), except for heptachlor epoxide-A which was one order of magnitude higher in calves ($p < 0.001$). Neither were found between males and females in other tissues, except for muscle (heptachlor, chlordan, endosulfan-II, higher in males) and kidney (dieldrin higher in males). Calves

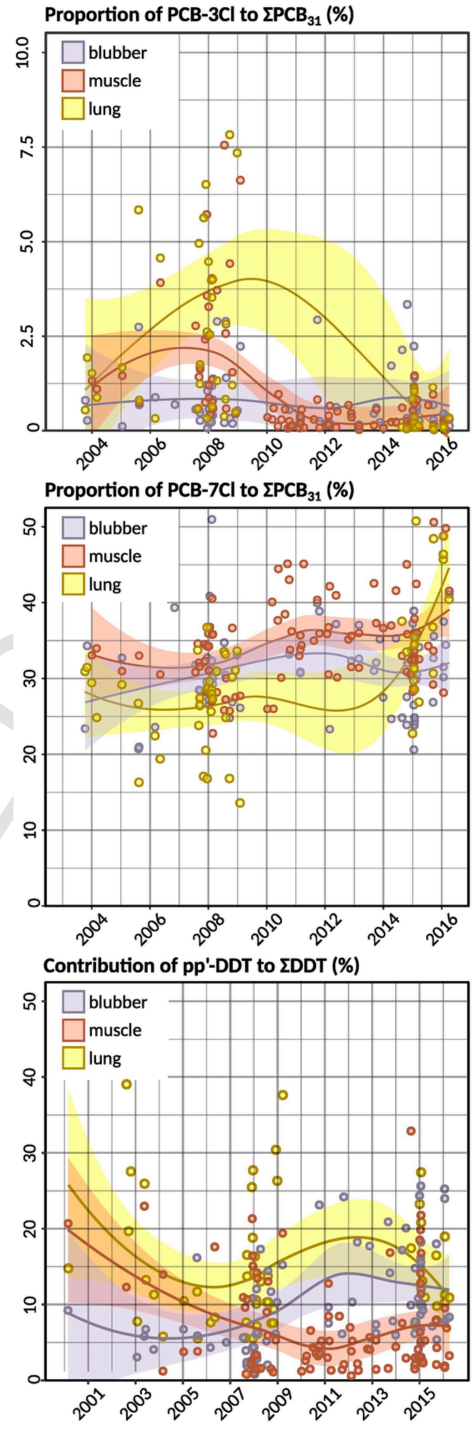


Fig. 1. Evolution of the PCB-3Cl and PCB-7Cl proportions (% of ΣPCB_{31}) in the blubber, lung and muscle tissues of *S. coeruleoalba* stranded in NW Mediterranean from 2003 to 2016, and of pp′-DDT (% of ΣDDT) in blubber, lung and muscle from 2000 to 2016. The curves and shaded areas are the results of LOESS smoothing with a 95% confidence interval.

presented also higher levels than females in liver (heptachlor epoxide-A, chlordan, endosulfan-II), kidney (chlordan, endosulfan-II, diazinon), lungs (γ-HCH, heptachlor and epoxides-A and -B, endosulfan-I, diazinon), and muscles (endrin, endosulfan-I). Finally, calves exhibited significantly higher concentrations than males in kidney (chlordan) and lungs (heptachlor and epoxide-B, endosulfan-I, diazinon). Among the studied tissues, the pesticides concentrations were the most contrasted

Table 2
Concentration mean levels (and standard deviations) of banned organochlorine pesticides and diazinon (expressed in ng·g^{-1} l.w. in blubber and ng·g^{-1} d.w. in other tissues) in the tissues of *Stenella coeruleoalba* stranded along the French Mediterranean coast from 2010 to 2016.

Compound	Blubber (N = 45)	Liver (*N* = 56)	Kidney (*N* = 53)	Lung (*N* = 18)	Muscle (*N* = 64)
γ-HCH	9.8 (4.0) a	5.3 (3.8) b	4.9 (3.3) bc	3.0 (2.0) c	3.6 (2.1) c
Aldrin	11.6 (9.6) a	2.2 (1.8) b	2.0 (1.8) b	1.8 (1.8) b	1.8 (1.4) b
Isodrin	11.4 (7.6) a	2.0 (1.7) b	1.5 (1.1) b	1.8 (1.6) b	1.2 (0.8) b
Dieldrin	8.6 (7.6) a	2.6 (1.9) b	2.6 (2.1) b	2.3 (1.5) b	1.7 (1.1) b
Endrin	26.7 (13.7) a	18.4 (10.4) b	15.3 (6.7) bc	15.3 (9.5) bc	12.0 (7.7) c
Heptachlor	21.1 (17.7) a	10.7 (9.8) b	8.3 (7.4) b	7.5 (5.2) b	6.6 (6.1) b
Heptachlor-epoxA	2.1 (2.7) a	2.5 (3.0) a	2.1 (2.2) ab	1.0 (0.8) ab	0.9 (1.0) b
Heptachlor-epoxB	34.8 (27.6) a	9.8 (9.6) b	9.6 (7.9) b	9.0 (6.4) b	7.9 (7.7) b
Chlordan	33.1 (16.9) a	10.7 (9.8) b	5.2 (5.0) c	2.9 (1.7) c	3.4 (3.2) c
Endosulfan-I	23.8 (20.3) a	10.6 (11.0) b	8.2 (7.6) b	6.2 (7.0) b	5.0 (4.9) b
Endosulfan-II	91.4 (82.9) a	73.7 (62.2) a	39.7 (32.9) b	37.3 (29.2) b	33.8 (30.8) b
Diazinon	25.5 (16.9) a	33.9 (22.4) ab	27.5 (15.1) ab	26.2 (18.6) ab	21.4 (16.5) b

Letters following standard deviations represent the results of post-hoc Tukey tests between tissues.

in lungs towards age and in muscle towards gender, while blubber levels remained homogeneous among both gender and age.

No recent data was found in the literature for these compounds in striped dolphins. In bottlenose dolphins' blubber from the English channel, chlordan, endosulfan and dieldrin concentration levels were lower (1–25 ng·g^{-1} l.w.), comparable (62–405 ng·g^{-1} l.w.) and higher (180–1860 ng·g^{-1} l.w.), respectively (Zanuttini et al., 2019). Dieldrin and endrin were also much more elevated in blubber of Indo-Pacific humpback dolphins (59–2703 ng·g^{-1} l.w. and 109–991 ng·g^{-1} l.w., respectively), but heptachlor (17–143 ng·g^{-1} l.w.) and aldrin (12–40 ng·g^{-1} l.w.) were in comparable concentrations (Sanganyado et al., 2018). To our knowledge, Romanić et al. (2014) provided the only data in the Mediterranean, for bottlenose dolphins from the Adriatic Sea sampled in 2000–05. The γ-HCH levels were then much more elevated in all studied tissues (46 ng·g^{-1} l.w. in blubber, for instance).

3.3. Organochlorine pesticides trends

The mean levels of ΣDDT in the striped dolphins stranded from 2010 to 2016 were lower than in 2000–09, but the median levels remained stable in blubber, liver and lung tissues (Table 1). Statistically, the KPSS tests indicate stationarity for ΣDDT in all tissues (level KPSS $p > 0.05$). In the blubber, the average contribution of pp′-DDT to ΣDDT was higher after 2008 (12.7%) compared to 2000–07 (7.1%), deriving from both increasing levels of pp′-DDT and decreasing pp′-DDE (Fig. 1 and Supplementary Material S7). Both genders followed this trend, which was significant for females (level KPSS $p < 0.05$ and trend KPSS $p > 0.1$), but not for males (level KPSS $p > 0.1$). In other tissues, the contribution of pp′-DDT to ΣDTT was stable over the whole 2000–16 period (level KPSS $p > 0.1$).

In 2010–16, nearly all the other pesticides were lower in all tissues compared to 2003–09 (Wafo et al., 2012b), except heptachlor. A pronounced peak in dieldrin, endrin, heptachlor epoxide B, endosulfan-I and -II, as well as DDT and DDE was observed in the 2007–08 years (Fig. 2 and Supplementary Material S7), coinciding with the morbillivirus epizootic previously mentioned for PCBs.

The levels of the heptachlor epoxides globally decreased in all tissues, while the former heptachlor remained stable or even slightly increased (Fig. 2). The metabolism of aldrin leads primarily to dieldrin, and possibly also to endrin (Zitko, 2003; Purnomo, 2017). Similarly to heptachlor species, endrin and dieldrin strongly decreased but aldrin remained stable from 2003 (Fig. 2). Finally, the endosulfan-I to -II (endosulfan-I/II) ratio increased slowly in all dolphin tissues, simultaneously with declining concentrations. It was below 0.25 in striped dolphins before its ban in 2007, but afterwards an increasing number of

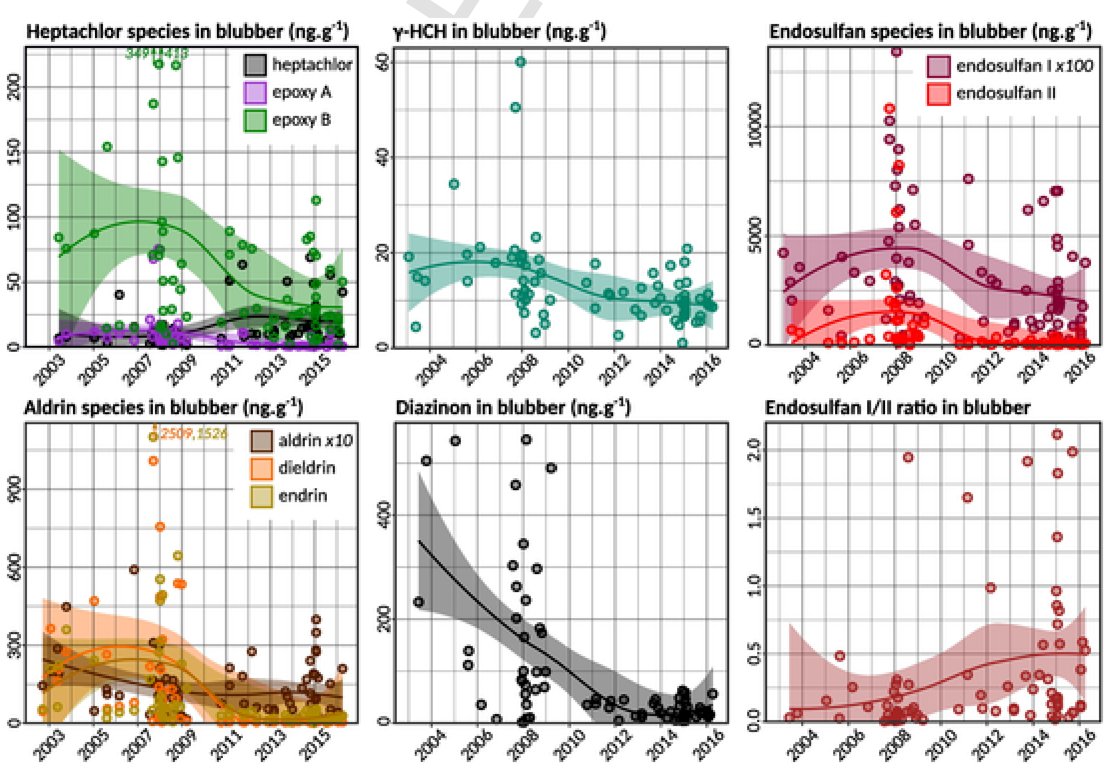


Fig. 2. Evolution of OC pesticides levels in blubber (ng·g^{-1} l.w.) samples of striped dolphins stranded in the NW Mediterranean, from 2003 to 2016.

specimens presented endosulfan-I/II ratios similar to the initial commercial mixtures (Fig. 2), *i.e.* 2.0 to 2.3 (Weber et al., 2010).

3.4. Evolution of spatial distributions

Considering the lack of knowledge on the extent of the living areas of striped dolphins, and the distances potentially covered by the drifting carcass or weakened animals, the spatial results are described but further interpretation will remain uncertain as long as these movements are not better understood.

In 2010–16, the concentrations in blubber were homogeneous across the study area with mean levels ranging between 20,000 and 26,000 ng·g^{-1} l.w., except for sectors G and H (13,789 and 31,296 ng·g^{-1} l.w., respectively). In other tissues, higher levels were noticed in the sector C covering the Rhône river mouth and the industrial zone of Fos. When comparing these results with 1988–2009, it revealed that ΣPCB_{31} levels decreased everywhere but remained stable in sector C (Supplementary Material S8). The proportions of the PCB classes in blubber were also homogeneous among geographical sectors, but not in other tissues, as observed on a temporal point of view (see Section 3.4). In muscle samples, higher contributions of PCB-3Cl (Fig. 3), PCB-4Cl and PCB-5Cl and lower proportions of PCB-6Cl and PCB-7Cl were measured in sectors B and C in 1988–2009. It reversed in 2010–16 for PCB-3Cl which lowest proportion was in sector C (Fig. 3), while other PCB classes were comparable along the coastline.

All pesticides concentrations in blubber before 2010 were higher in the east coast, except for ΣDDT higher in the west (Supplementary Material S9). In other tissues, many pesticides (ΣDDT, diazinon, endosulfan, dieldrin, endrin) were also higher in the eastern shores in 2000–09, except that sector C was a hot spot for γ-HCH, aldrin and heptachlor in muscle tissues with concentrations one order of magnitude higher. In the following 2010–16 period, the highest levels of OC pesticides in muscle, kidney and liver remained in the east part. Only the highest blubber concentrations switched to the west for γ-HCH, endosulfan, and diazinon (Supplementary Material S9).

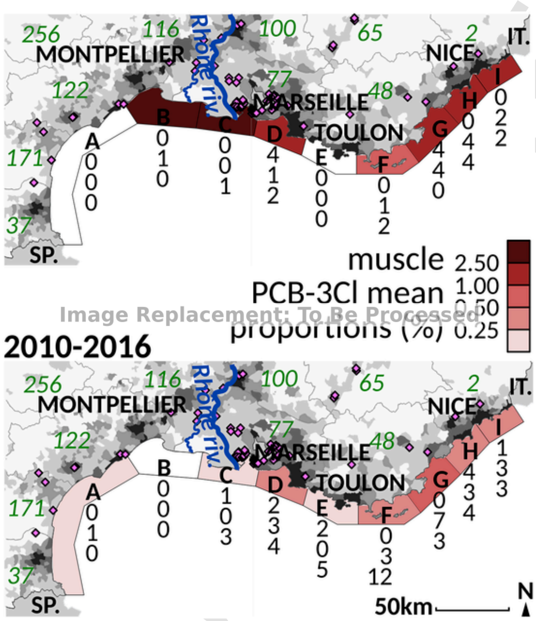


Fig. 3. PCB-3Cl proportions (%) among the geographical sectors in the 1988–2007 (data from Wafo et al., 2005 and Wafo et al., 2012a) and 2010–16 (present study) stranded striped dolphins muscle samples. Numbers below the sector lettering indicate the corresponding number of calves, females and males (top to bottom). Grey scale, green numbers and pink diamonds refer to population, agriculture surfaces, and industrial facilities classified under the Seveso-3 European directive, respectively (see Supplementary Material S1 for details). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The contributions of pesticides parent compounds towards their metabolites increased between 2000–09 and 2010–16 in all geographical sectors homogeneously and for all tissues. Only several exceptions were found in sector C, where the endosulfan-I/II ratio and the heptachlor proportion to its epoxides decreased in muscle tissues (0.59 to 0.11, and 36% to 8%, respectively), and heptachlor (32% and 37%) and aldrin (16% and 19%) proportions remained stable in blubber towards their metabolites.

4. Discussion

4.1. OC contaminant levels and morbillivirus epizootic

Despite a global reduction of nearly all the OC contaminants studied here, several specimens exhibited high concentration levels in 2007–08 for PCBs, DDT and DDE (Supplementary Material S6 and S7), endosulfan, heptachlor epoxides, dieldrin and endrin (Fig. 2). This period corresponds to a well documented epizootic caused by a morbillivirus affecting the cetaceans of the Mediterranean Sea (Raga et al., 2008; Keck et al., 2010; Dhermain et al., 2011; Gaspari et al., 2019). This event lead to an increase of the number of stranding of striped dolphins along the French Mediterranean coast, 78 and 115 ind·yr^{-1} in 2007 and 2008, respectively, compared to the 1997–2006 yearly average of 41 ind·yr^{-1} (Dhermain et al., 2011). In the studied area, 10 stranded striped dolphins were positive to morbillivirus in 2007–08 (among 36 tested) (Keck et al., 2010), while they were all negative in the previous and following periods (36 tested in 2010–16) ((Dhermain, 2012); Dhermain, 2016; Dhermain et al., 2015). It is noteworthy that the ΣPCB_{31} concentrations were comparable among dolphin size during this event. The dolphins mean size with ΣPCB_{31} above median value was 155 cm (range 100–221 cm) and dolphins mean size with ΣPCB_{31} below median value was 163 cm (range 90–220 cm). Males were predominant (9 males and 3 females above ΣPCB_{31} median), consistently with the global gender discrepancy (Supplementary Material S4). During that period, no significant variations were recorded for other common diseases (*Brucella*, *Toxoplasmosis*…) but there was only a very few data available.

It is likely that the virus affected preferably the specimens that were impaired by high contamination levels, known to induce a depressed immunological system (Beckmen et al., 2003). Consistently, Fig. 4 shows that the specimens stranded in 2007–08 were predominantly associated to the highest levels of ΣPCB_{31}, together with highest ΣDDT and other pesticides concentrations. This was particularly obvious in muscle. It showed that the suspected vulnerability to the disease would be favored by a multiple contamination involving at least also organochlorine pesticides, and not only PCBs. Surprisingly and for an unexplained reason, the east coast was particularly concerned by the stranding of strongly multi-contaminated specimens (sectors F, G, H).

After that epizootic, the concentrations dropped back to their previous levels or even below for PCBs, endosulfan, heptachlor epoxides, dieldrin and endrin, especially in blubber. It particularly impacted the metabolite concentrations such as PCB-3Cl, DDE (Fig. 1 and Supplementary Material S7), heptachlor epoxides, dieldrin and endrin (Fig. 2), and probably favored the emergence of new contamination patterns in dolphin tissues through the elimination of highly contaminated specimens. However, it confirms that the determination of morbillivirus and more generally of the cause of death is essential and needs to be further supported. In particular, cross-linking interdisciplinary interpretations such as virology and bioaccumulation, would improve our knowledge of the links between epizootic and pollutant levels (Berio et al., 2020).

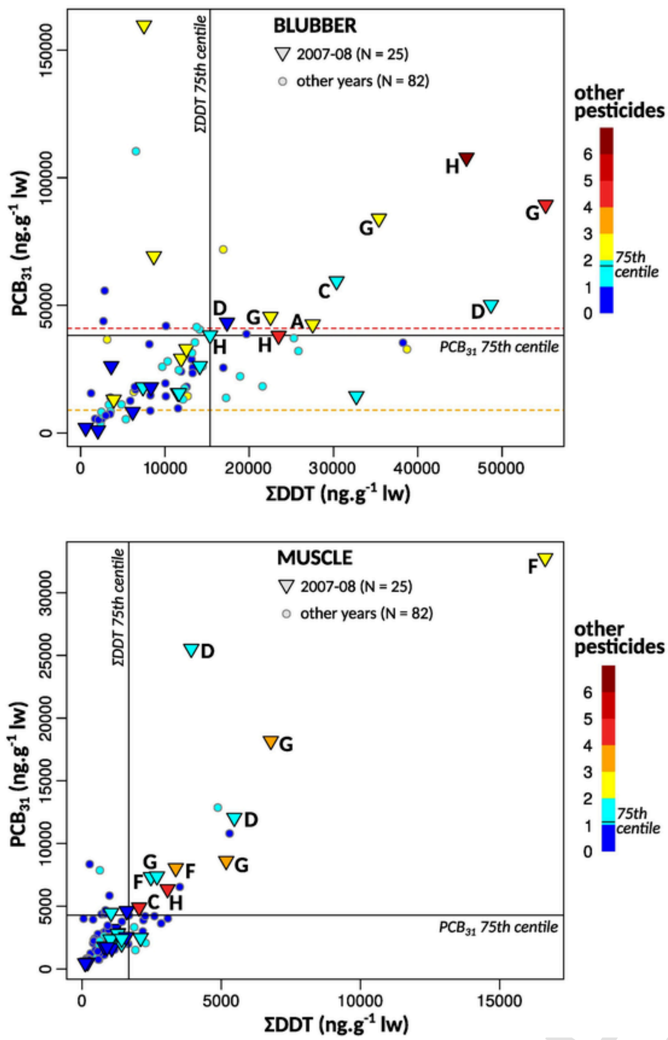


Fig. 4. Relationships between the concentration levels of ΣPCB_{31}, ΣDDT and other pesticides (cumulated normalized values) in blubber and muscle samples of *S. coeruleoalba* stranded along the French Mediterranean coast from 2000 to 2016 with and emphasis on 2007–08 years. Dotted lines in the blubber figure indicate the low (9000 $ng \cdot g^{-1}$ l.w.) and high (41,000 $ng \cdot g^{-1}$ l.w.) toxicity thresholds admitted for PCBs in cetaceans (Helle et al., 1976; Kannan et al., 2000).

4.2. Evolution of OC contaminant patterns and fate

At the time of the PCB ban in the late 1980s, their environmental levels were at the highest, and their profiles similar to the main commercial mixtures (Aroclor1260 in France) as reflected by measurements in early 1988–90 dolphin tissues (Wafo et al., 2005). At these high concentration levels, dechlorination processes (anaerobic biodegradation and photolysis) could have been predominant, as suggested by several early studies (Wafo, 1996; Agency for Toxic Substances and Disease Registry (ATSDR), 2000). These pathways lead to increasing proportions of low chlorine number congeners in 2003–09, as highlighted by the higher PCB-3Cl proportions during this period in all dolphin tissues, except for blubber (Fig. 1). Then, considering lower total PCB levels and higher proportions of low chlorinated congeners, the volatilization and aerobic degradation processes could have in turn became the dominant pathways, explaining the strong decline of PCB-3Cl in dolphin tissues from 2010 (Fig. 1). These variations were particularly noticeable in muscle, lung, kidney and liver, but smoothened in blubber due to its longer integration time (Yordy et al., 2010; Romanić et al., 2014).

Recently, it has been suggested that patterns dominated by congeners with a high degree of chlorination would reflect an incidence from fresh and local inputs, while a higher contribution of congeners with a low chlorine degree would indicate aged or long-ranged PCB mixtures (Brown et al., 2015). In the present study, this would indicate a transition from long-range to local sources, and support the hypothesis of an incidence of the remobilization of PCBs from sediment and soils which were less subjected to degradation because they remained deeper in the substrates. It is particularly interesting to note that this applies here on a temporal basis, while Brown et al. (2015) referred to a spatial aspect. Fresh (or more exactly non-degraded) inputs originating from remobilization, would then have overcome the contribution from the aged PCB (equivalent to long-range) contamination remaining in the aqueous system.

As of PCBs, the concentrations of several OC pesticides and their metabolites presented a shift in dolphin tissues from 2009. While pp′-DDE declined in all dolphin tissues, pp′-DDT levels increased in blubber, leading to higher pp′-DDT proportions (Fig. 1 and Supplementary Material S7). Interestingly, this observation was chronologically consistent with the recent (post-2005) sediment deposition observed in the lower Rhône river containing high proportions of pp′-DDT, which was attributed to recent use of DDT technical formulation (Liber et al., 2019). The precise origin of the DDT release may be also explained by the remobilization in the 2000–10 period of pp′-DDT from contaminated soils (vineyards, industrial wastelands) located along the Rhône river watershed, as shown by Sabatier et al. (2014) in the vicinity of a tributary. More intense and numerous flooding events of the Rhône river than usual occurred in the 2000–06 period, potentially reinforcing these mechanisms (Cresson et al., 2015).

The recovering of other parent compounds (heptachlor, aldrin) with respect to their metabolites in the dolphins tissues, as well as endosulfan-I towards endosulfan-II, also suggest an impact from remobilization reaching Mediterranean cetaceans. Even though geographical aspects must be taken with care, the individuals from the Rhône river mouth area showed high proportions of heptachlor and aldrin in blubber already before 2009, and comparable proportions were reached in the other sectors in 2010–16. On the other hand, diazinon strictly showed a strongly decreasing trend (Fig. 2), probably due to its less lipophilic character, but its metabolites were not studied here.

These results all highlight the central role of rivers in the fate of contaminants in marine ecosystems, which still needs additional research, for instance regarding contaminants remobilization (Cresson et al., 2015).

4.3. Implications of changing contamination patterns

The main source of OC contaminants accumulating in striped dolphins likely shifted to diffuse inputs from contaminated lands and river sediments, possibly also from coastal areas, while industrial discharges have progressively vanished since the ban of these compounds. This will probably imply a slowdown in future decreasing trends for many OC contaminants due to their long lifetime. The numerous potential sources, among which many remain probably unknown, makes it particularly difficult to manage when aiming to minimize their incidence. However, stakeholders should primarily focus on identified highly contaminated sites, such as landfill, industrial wasteland or former agricultural lands playing a significant role in OC contaminants diffusion (Hou et al., 2013; Brown et al., 2015).

Considering the PCB thresholds in blubber tissues generally admitted for toxicological effects on cetaceans, the latest period under study (2010–16) showed a significant decrease in strongly contaminated dolphins with only 4 out of 46 specimens (8.7%) above the highest threshold (41,000 $ng \cdot g^{-1}$ l.w., Helle et al., 1976) while they were 34.3% in the 2003–09 period. Even though, a high and persistent contamination remains, with 37 out of 46 (80.4%) specimens above the lower threshold

(9000 ng·g^{-1} l.w., Kannan et al., 2000) in 2010–16, comparable to the 2003–09 period (85.7%). This high PCB level, that would possibly last for several decades considering the slowdown expected in contamination decrease, is particularly alarming regarding the recent works relating PCBs with rates of infectious disease mortality. It was thus estimated an increase in risk of 5% for each 1000 ng·g^{-1} l.w. of PCBs in blubber (Hall et al., 2006; Williams et al., 2020). In the present study, the median PCB level was 18,057 ng·g^{-1} l.w., corresponding to an increase in risk of 90%, which may threaten the striped dolphin population for years in the French Mediterranean coast. Brown et al. (2014) also demonstrated recently that comparable toxicological thresholds should be considered for PCBs, down to 1370–1680 ng·g^{-1} l.w. in Canadian ringed seals blubber.

Since the ban of the studied OC pesticides, most of their metabolites (DDE, dieldrin, endrin, heptachlor epoxides) showed a significant decline, as well as less lipophilic compounds such as diazinon. On the other hand, parent compounds reached a plateau. OC pesticides and metabolites should still be jointly monitored to investigate future evolution.

4.4. Monitoring strategy

In the present study, only 18.0% (68) out of the 377 striped dolphins stranded in 2010–16 along the French Mediterranean ((Dhermain, 2012); Dhermain, 2016; Dhermain et al., 2015) benefited from the determination of OC contaminants in one or more tissues.

Due to practical reasons such as logistical issues and a lack of appropriate facilities, the volunteers from the RNE (National Marine Mammals Stranding Network) in the Mediterranean generally realize less extended samplings and investigations on carcass in an advanced decomposition state (decomposition condition categories DCC-4 and -5, Jauniaux et al., 2002; IJsseldijk et al., 2019). Thus, the sampling rate decreased from 52% in very fresh DCC-1 to 32% in intermediate categories DCC-2 and -3 and finally 8% in decomposed carcasses (DCC-4 and -5).

Also, including a larger number of the stranded cetaceans for contaminant monitoring would undoubtedly improve the quality of the results and interpretations, and allow superior modeling capabilities. This aspect is being considered by the RNE and currently improved. Regarding the sampling limitations on a large part of individuals (DCC-4 and -5 represent 40% of stranding) that would require strong efforts in the availability of adapted sampling facilities, it appears recommended to promote primarily the determination of contaminants in blubber. It remains a reference material, because of its storage function, concentrating lipophilic contaminants and revealing long term exposure. Moreover, it is the most accessible tissue, possible to sample on free-ranging cetaceans (Jepson et al., 2016; Zanuttini et al., 2019), and has the richest historical data (Wafo et al., 2005, 2012a, 2012b; Jepson et al., 2016; Sanganyado et al., 2018). Considering the great benefit of monitoring other tissues, significant efforts should also be carried out to determine OC contaminants in at least a second material. In that respect, muscle tissues could be appropriate, reflecting a shorter integration time compared to blubber. It may be better conserved over time in deriving animals compared to organs such as kidney or lungs, and above all, easier to sample. However, when possible, the sampling of multiple tissues should still be encouraged, but not a limiting point. The present work also showed the advantages of monitoring the metabolites of parent compounds and a large set of PCB congeners, to provide essential information towards the origins and fate of OC contaminants in the environment, and further steer actions of protection. Finally, this work could support the reinforcement of environmental quality grids, ideally together with data from other Mediterranean and European regions.

5. Conclusion

The levels of OC contaminants globally decreased since 1988 in NW Mediterranean striped dolphins, but many of them seemed to reach a plateau from 2010, even though this must be confirmed by further data. The analysis of metabolites towards parent compounds shows that the sources of contaminants probably changed to more diffuse inputs from contaminated lands and sediments. This situation induces that further decrease of OC contaminants in striped dolphins is expected to be much slower, and needs to be considered in future management policies and projections. It is of particular concern since the present levels of OC contaminants in striped dolphins remain high and may lead to severe threats such as a greater sensibility to infectious disease mortality. In fact, the study of the historical trends also highlighted the incidence of the 2007–08 morbillivirus epizootic in the French Mediterranean coast, that likely affected preferentially the most contaminated specimens, not only designating PCBs but also DDT and most OC pesticides as aggravating factors. These considerations encourage to monitor multiple contaminants, when possible in several tissues, and in combination with the cause of death.

Uncited references

CRediT authorship contribution statement

Julien Dron: Writing – original draft, Writing – review & editing, Formal analysis, Data curation, Investigation. **Emmanuel Wafo:** Writing – original draft, Writing – review & editing, Formal analysis, Data curation, Project administration, Investigation, Conceptualization. **Pierre Boissery:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Frank Dhermain:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization, Investigation, Resources. **Marc Bouchoucha:** Writing – review & editing, Project administration, Conceptualization. **Philippe Chamaret:** Project administration, Resources. **Daniel Lafitte:** Project administration, Resources.

Declaration of competing interest

All authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2021.113198.

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