Chemosphere 288 (2022) 132639

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polychlorinated biphenyl (PCB) concentrations and profiles in marine mammals from the North Atlantic Ocean

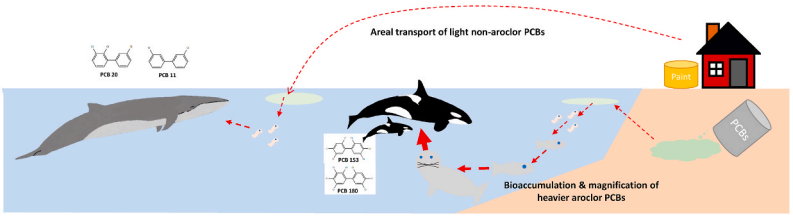
David Megson [a,b,*], Thomas Brown [c], Gareth Rhys Jones [d], Mathew Robson [e], Glenn W. Johnson [f], Guuske P. Tiktak [a], Courtney D. Sandau [b], Eric J. Reiner [e]

[a] Manchester Metropolitan University, Ecology & Environment Research Centre, Department of Natural Science, Manchester, UK
[b] Chemistry Matters, Calgary, AB, Canada
[c] Scottish Association for Marine Science (SAMS), Oban, Scotland, UK
[d] Waters Corporation, Manchester, UK
[e] Ontario Ministry of the Environment, Conservation and Parks. 125 Resources Road, Toronto, ON, M9P 3V6, Canada
[f] University of Utah, Salt Lake City, UT, 84108, USA

HIGHLIGHTS

- Over 145 different PCBs consistently detected in samples.
- PCBs continue to pose a significant risk to marine mammals.
- Inadvertent PCBs can contribute >5% of total PCB load.
- Unique atmospheric deposition PCB signature identified in sei whale.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Magali Houde

Keywords:
Polychlorinated biphenyls
PCBs
Enantiomer fractions
Marine mammal
Multivariate statistical analysis

ABSTRACT

Polychlorinated biphenyls (PCBs) can provide crucial information into the bioaccumulation and biomagnification of POPs in marine mammals. Muscle tissue samples were obtained for detailed PCB congener specific analysis of all 209 PCBs in 11 species of marine mammals stranded across the coast of the UK between 2010 and 2013. At least 145 PCB congeners were found in each individual. The highest concentrations of PCBs were recorded in a killer whale (318 mg/kg lipid) and the highest toxic equivalent in a Risso's dolphin (1687 pg/g TEQ_{2005} wet). Concentrations of PCBs in the majority of samples exceeded toxic thresholds (9 mg/kg lipid) for marine mammals, highlighting the health risk they face from PCB exposure. Many PCB profiles did not fit typical 'Aroclor' signatures, but instead indicated patterns of congeners that are resistant to biotransformation and elimination. However, this study identified a novel PCB signature in a sei whale that has not yet been previously observed in marine mammals. The whale had a PCB profile that included lighter and inadvertent PCB congeners such as PCB 11, suggesting that the main source of exposure was through atmospheric deposition, rather than terrestrial discharges. Seven subsamples were chosen for chiral analysis of PCB 95, 136 and 149. The enantiomer fractions (EFs) of C-PCBs 95 and 149 were non racemic suggesting there may be enantiomer selective metabolism in marine mammals. Although there has been a shift in the literature towards emerging pollutants, this study acts as a stark reminder that PCBs continue to pose a significant risk to wildlife.

* Corresponding author. Ecology and Environmental Research Centre, Manchester Metropolitan University, Manchester, UK.
E-mail address: d.megson@mmu.ac.uk (D. Megson).

https://doi.org/10.1016/j.chemosphere.2021.132639
Received 12 August 2021; Received in revised form 16 October 2021; Accepted 19 October 2021
Available online 20 October 2021

1. Introduction

Persistent organic pollutants (POPs) are a subset of chemicals that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. Polychlorinated biphenyls (PCBs) are some of the most widely studied POPs, they are ubiquitous in the environment, and as a result are routinely detected in marine environmental samples (Domingo and Bocio, 2007; Letcher et al., 2010). Health risks from PCBs and their bioaccumulation in the environment have been known for decades, which has helped lead to either voluntary restrictions in their use or bans on their production (ATSDR, 2000), however inadvertent or unintentionally produced sources of PCBs (u-PCBs) are staring to become of increased importance (Hu and Hornbuckle, 2010; Hu et al., 2011; Garmash et al., 2013; Guo et al., 2014; Vorkamp, 2016; Liu and Mullin, 2019; Megson et al., 2019b; Hermanson et al., 2020; Rodenburg et al., 2020).

Long range atmospheric transport of POPs has been widely documented and results in the accumulation of POPs in the Arctic with major source regions identified as North America and Western Europe (O'Sullivan and Sandau, 2013). The North Atlantic Ocean therefore presents an excellent study area for the presence of POPs as it boarders two major PCB source regions (N. America and Europe) and is a major global sink (Axelman and Gustafsson, 2002). The high lipophilicity and biomagnification of POPs results in the accumulation of high concentrations of these compounds in top predators, especially marine mammals with high blubber contents in Arctic and sub-Arctic areas (Tanabe et al., 1983, 1987; Aguilar et al., 1999; Arnot and Gobas, 2004; Kelly et al., 2007).

Many marine mammals such as whales, dolphins and seals are found in the North Atlantic Ocean and due to their varying habitats and diets can be good bioindicators of ocean health, as well as providing insight into the fate, breakdown and transport of POPs. Some species such as the bearded seal (*Erignathus barbatus)* and Risso's dolphin (*Grampus griseus*), live in localised colonies around the UK and have relatively small home ranges and so are good indicators of local contamination from source regions. Other species have much larger home ranges but predominantly feed in the deeper ocean depths far from the mainland, such as the long-finned pilot whale (*Globicephala melas*) and sperm whale (*Physeter macrocephalus*). These species are excellent indicators for the transport of POPs away from the major source and sink regions. Marine mammals with their high lipid contents and high tropic positions are some of the most at-risk species from contamination by POPs (Houde et al., 2005; Weijs et al., 2013; Jepson et al., 2016; Desforges et al., 2018; Jeong et al., 2020). Although PCB use has been phased out, PCB pollution continues to impact killer whales (*Orcinus orca*) and other dolphins in European waters (Jepson et al., 2016). Most research on marine mammals has focused on calculating total PCB concentrations and establishing health risks, with less research performed on identifying sources of PCBs or investigating the biological activity of chiral PCBs.

Polychlorinated biphenyls were originally produced as technical mixtures such as Arolcors (U.S.), Clophen (Germany), Phenochlor (France), Sovol (Sovjet). Although "Aroclor" PCBs are still found in the environment, an increasing importance is being placed on non-Aroclor (inadvertently produced) PCBs. Unlike Aroclor PCBs, inadvertently produced PCBs were never intentionally produced and were believed to be of minor concern as they were thought to only be present in small quantities in the environment. However, research using methods capable of determining all 209 PCBs have helped to identify that thy are of concern and in some cases are now significantly influencing PCB profiles in some samples (Hu and Hornbuckle, 2010; Hu et al., 2011; Garmash et al., 2013; Guo et al., 2014; Vorkamp, 2016; Bartlett et al., 2019; Liu and Mullin, 2019; Megson et al., 2019b; Hermanson et al., 2020; Rodenburg et al., 2020). Many PCBs studies only focus on a subset of PCBs such as the 7 indicator PCBs (which are relatively cheap to determine and easy to work with) or the WHO12 dioxin like PCBs (DL-PCBs) (that are commonly used to assess health risks). Whilst these can be useful when comparing PCB concentrations in different data sets, they are not as useful when attempting to establish sources of contamination or understand fate and transport mechanisms (Megson, 2019b). By undertaking comprehensive congener specific analysis, it is possible to identify and quantify the impact of inadvertent PCB sources and how they are impacting the marine environment.

Despite the relatively large number of studies undertaken on PCBs, chiral PCBs (C-PCBs) remain an understudied area. However, they can provide valuable insight into the different pathways and metabolism of PCBs in organisms and the wider environment (Serrano et al., 2000; Warner et al., 2005; Bordajandi and González, 2008; Kania-Korwel and Lehmler, 2016a). C-PCBs produced in technical mixtures and synthetic C-PCBs are present as a racemic mixture (i.e. ratio of 1:1, enantiomer fraction of 0.5). Enrichment of C-PCBs 95, 136 and 149 differs per organism, though in many marine mammals and sharks C-PCB 95 and 149 are found in racemic or nearly racemic mixtures. Studies suggest differences in enantiomer composition can be explained by diet, *in vivo* biotransformation and elimination of PCBs as well as trophic transfer (Blanch et al., 1996; Serrano et al., 2000; Warner et al., 2005; Lu et al., 2014).

This current study determines the concentrations of all 209 PCBs in 19 marine mammals from 11 different species. It aims to quantify total PCB concentrations in all samples and produce detailed PCB congener profiles. These profiles will be used to identify potential inadvertently produced PCBs and processed using multivariate statistics to establish if differences in PCB profiles can be distinguished based on geographical location and feeding habits of the marine mammals. Selected samples were also analysed to determine the enantiomer fractions of C-PCBs 95, 136 and 149 to investigate any enantioselective species-specific factors.

2. Materials and methods

2.1. Sample collection

Muscle tissue samples were obtained from the following 19 stranded marine mammals; bearded seal (*Erignathus barbatus*) (n = 1), Sowerby's beaked whales (*Mesoplodon bidens*) (n = 1), white-beaked dolphins (*Lagenorhynchus albirostris*) (n = 3), long-finned pilot whales (*Globicephala melas*) (n = 5), Risso's dolphin (*Grampus griseus)* (n = 1), sperm whale (*Physeter macrocephalus*) (n = 1), killer whale (*Orcinus orca*) (n = 1), sei whale (*Balaenoptera borealis*) (n = 1), minke whale (*Balaenoptera acutorostrata*) (n = 1), Atlantic white-sided dolphins (*Lagenorhynchus acutus*) (n = 3), and fin whale (*Balaenoptera physalus*) (n = 1). Samples were collected by the Scottish Marine Animal Stranding Scheme (SMASS), all samples were retrieved from stranded animals collected from the Scottish coast during 2010–2013. Sample locations are provided in SI1 and age group in SI2 approximately 1 g of sample was freeze dried and stored in the freezer prior to extraction.

2.2. Sample preparation

Samples were extracted using the method described in Megson et al. (2013) which was adapted from Brown et al. (2013). Lipid content was determined gravimetrically through solvent extraction on approximately 0.5 g of tissue. For PCB analysis approximately 0.5 g of sample was accurately weighed, then freeze-dried (−45 °C; 0.2 mbar; 72 h) and ground into a powder. Prior to extraction all samples were spiked with 20 μL of a recovery standard solution containing mass labelled PCBs from every level of chlorination (PCBs: 3,15,31,52,118,153,180,194, 206,209) (MBP-GC solution, Wellington Laboratories). Samples were then extracted by adding dichloromethane/methanol (2:1 v/v) and ultrasonicating (80 min). Extracts were filtered, dried and re-suspended in hexane before being separated into a non-polar fraction by column chromatography (SiO_2). Samples were blown down to incipient dryness using nitrogen and reconstituted with 50 μL of spiking solution

containing mass labelled BDE 79.

2.3. Congener specific analysis by GC-APCI-qqqMS

Analysis was undertaken using gas chromatography atmospheric pressure chemical ionisation triple quadrupole mass spectrometry (GC-APCI-qqqMS). An Agilent 7890 A GC was fitted with an Agilent DB-5MS column (60 m × 0.25 mm ID x 0.10 μm) coupled to Waters Xevo TQ-XS tandem quadrupole mass spectrometer with APGC source. Quantification of PCBs was performed by isotope dilution to enable trace level analysis of less abundant PCB congeners. Due to the high concentrations of PCBs present 1 μL of sample was injected at a split ratio of 10:1 and constant flow rate of 1.7 mL/min. Analysis was performed for all 209 PCBs, but only PCBs present above detection limits (10 fg on column) were reported. Further information on this method is presented in SI1 and concentration data for all PCBs presented in SI2.

2.4. Chiral analysis by GC-EI-HRMS

Enantiomer Fractions (EFs) of chiral PCBs (C-PCBs) 95, 136 and 149 were analysed according to the method of Robson and Harrad (2004), using an Agilent 7890 gas chromatograph fitted with a Chirasil-Dex column (25 m × 0.25 mm x 0.25 μm) coupled to a Micromass Auto-Spec Premier high-resolution mass spectrometer (GC-HRMS) tuned to greater than 10,000 mass resolution (10% valley definition). The two most abundant isotopes of each enantiomer were recorded in Selected Ion Recording Mode (SIR). These were *m/z* 325.8804 and 327.8775 for C-PCBs 95, and *m/z* 359.8415 and 361.8385 for C-PCBs 136 and 149. These PCBs were chosen because they are; (a) able to be baseline separated on the Chirasil-Dex column, (b) free from any co-eluting congeners that may bias the results and (c) normally present in the environment in high enough concentrations to be accurately measured.

Enantiomeric Fractions were calculated as per Harner et al. (2000) using the following formula:

$$EF = E1 / (E1 + \qquad E2)$$

Where E1 equals the first eluting of the (+) enantiomer and E2 the second eluting enantiomer.

2.5. Toxic Equivalents (TEQ)

Toxic Equivalents (TEQ_{2005}) were calculated for all dioxin-like PCBs (DL-PCBs) (non-ortho: 77, 81, 126, 169 and mono-ortho: 105, 114, 118, 123, 156, 157, 167 and 189) for 19 samples: Atlantic white-sided dolphins (n = 3), bearded seal (n = 1), fin whale (n = 1), killer whale (n = 1), long-finned pilot whales (n = 5), minke whale (n = 1), Risso's dolphin (n = 1), sei whale (n = 1), 1 Sowerby's beaked whale (n = 1), sperm whale (n = 1) and white beaked dolphins (n = 3) using the 2005 World Health Organisation's (WHO) Toxic Equivalency Factors (TEFs) (van den Berg et al., 2006).

2.6. Data quality

For congener specific analysis, instrument detection limits (excluding chiral analysis) were tentatively set at 10 fg on column as this represented the lowest concentration standard solution which could consistently be detected with a S:N ratio >10. Average recovery rates were for PCBs in each sample were generally between 60 and 80% with recovery rates for all levels of chlorination in all samples within the acceptable range specified by USEPA method 1668C. To measure precision calibration solution CS4 (Wellington WP-CVS) (containing 10 pg μL^{-1} of PCBs 81, 118, 167 and 189) was analysed after each batch of 10 samples. This resulted in a total of 3 measurements where the analytical precision (standard deviation) was 1.9%. There were low femtogram levels of several PCBs detected in the procedural blanks (1 per batch of 10 samples). PCBs detected in the procedural blanks were PCB11 (30 fg/μL), PCB18 (20 fg/μL), PCB31 (30 fg/μL), PCB 43 (15 fg/μL), PCB 48 (15 fg/μL), PCB 95 (15 fg/μL), PCB 101 (20 fg/μL), PCB99 (20 fg/μL), PCB 139 (30 fg/μL), PCB 118 (30 fg/μL), PCB 153 (50 fg/μL), PCB105 (10 fg/μL), PCB 138 (40 fg/μL), PCB 180 (30 fg/μL). As these levels were several orders of magnitude lower that the concentrations observed in the samples no blank correction was performed.

For chiral analysis, the chromatographic performance of the method was assessed prior to each run of 8 samples by analysis a 1:1:1 mixture of Aroclors 1248, 1252 and 1260. Samples where only accepted for quantitation if the enantiomeric fractions of the three atropisomers studied were 0.50 (±0.01) in the Aroclor mixture (results of 0.49,0.50, 0.51,0.51 and 0.50 were obtained from the 5 standards run throughout the experiment), the least abundant enantiomer of the pair had a signal to noise (S:N) ratio greater than 10:1, the isotope ratios were within 20% of their theoretical values and the analytical recovery of the sample was greater than 30%. The instrument LOD was estimated by analysing a standard mixture of C-PCB 95 and C-PCB 149, LODs were calculated at a concentration of 2.5 pg μL^{-1} per enantiomer. Procedural blanks were prepared for each batch of 8 samples; no chiral PCBs were detected in the blanks above the limits of detection.

2.7. Statistical analysis

The results for the marine mammal tissue samples were subjected to principal component analysis (PCA) following the general methodology outlined by Johnson et al. (2015). Data pre-processing included screening for non-detects. Congeners/coeluting peaks reported below detection limits (non-detects) in all 19 samples were removed from the data matrix, reducing the data matrix to 19 samples and 156 variables. Remaining non-detects in the matrix were substituted with zero. Before performing PCA the data were normalised by transformation to a percent metric to remove concentration/dilution effects. The data were then mean centred and scaled (autoscale transform) to prevent high concentration variables from dominating the analysis (Johnson et al., 2015). The PCA was conducted on this transformed matrix using the Matlab computational software package, using Matlab's the 'pca' function. The number of principal components was evaluated based primarily on evaluation of Miesch CD scatter plots (included in Supplementary Information (SI3). See also Johnson et al. (2015).

3. Results and discussion

3.1. Total PCB concentrations

Total concentrations of PCBs in the samples ranged from 1.9 to 318 mg/kg lipid (Fig. 1 & SI2), which is comparable to concentration data compiled by Jepson et al. (2016) for cetaceans in the North Atlantic. Whilst the Jepson et al. (2016) study focused on a subset of PCB congeners (18–25) this current study determined the presence (or absence) of all 209 congeners. On average 150 different PCB congeners were detected in the samples analysed, with at least 145 PCBs being detected in each sample. The greatest number of congeners were detected in the white beaked dolphin and Risso's Dolphin (155 different PCBs), which is amongst the greatest number of different PCBs ever detected in one environmental sample. The highest concentration of PCBs was detected in a killer whale (318 mg/kg lipid) with concentrations in dolphins generally greater than those in the whale species. This difference is most likely attributable to the different tropic positions that each species feed in. Filter feeders such as the sei whale and fin whale consume plankton as well as small fish and copepods (Flinn et al., 2002) whereas the dolphins and killer whale have a more varied diet including organisms that are higher in the food web and therefore contain greater PCB concentrations.

The total concentrations of PCBs detected in the majority of tissue samples exceed the "applied" marine mammal toxicity thresholds (lower

bound: 9 mg/kg lipid and upper bound: 41 mg/kg lipid, Fig. 1) (Helle et al., 1976; Kannan et al., 2000; Jepson et al., 2005, 2016). Onset of physiological effects in marine mammals are observed at concentrations as low as 9 mg/kg lipid, with extreme physiological effects such as reproductive impairments and immunosuppression occurring when the higher threshold of 41 mg/kg lipid is exceeded, and in some extreme cases lead to death (Alonso Farré et al., 2010; Murphy et al., 2010, 2018; Jepson et al., 2016). This is concerning as although PCBs have been banned their levels are still above toxicological thresholds. Concentrations of PCBs found in one killer whale and white beaked dolphin are almost eight times over the maximum toxic threshold for marine mammals which suggests that their health could be significantly impacted. Trophic level data obtained from Pauly et al. (1998) revealed that there was a significant positive correlation (Spearman's: $R = 0.57$, $p < 0.0103$) between the trophic level and total dioxin-like PCBs concentrations in marine mammals, though no significant correlation was observed for concentrations of total PCBs (Spearman's: $R = 0.408$, $p = 0.0828$). Marine mammals typically occupy high trophic levels, which in combination with their k-life strategies (e.g. few offspring, long lived and large size) makes them more susceptible to bioaccumulation of pollutants (Tanabe, 2002; Dorneles et al., 2013; Jepson et al., 2016; Chouvelon et al., 2018). Variations in total PCB concentration could in large part also be driven by variation in diets, for example killer whales feed at higher trophic levels compared to sei whales, Atlantic white sided dolphins and pilot whales (Desforges et al., 2018; Jourdain et al., 2019; Jourdain et al., 2020a, 2020b). Marine mammals also often have a high percentage of blubber which allows for the accumulation of lipophilic pollutants, such as organochlorines, PCDD/Fs and PCBs (Muir et al., 1988; Borrell and Aguilar, 1993; Jeong et al., 2020).

Dioxin like PCB (DL-PCB) concentrations and TEQ values (pg/g wet) are presented in Table 1. Total DL-PCB concentrations were the highest in the killer whale (6970 ng/g wet), followed by one long-finned pilot whale (1419 ng/g wet) and bearded seal (1312 ng/g wet). However, the highest TEQ value was observed in Risso's dolphin (1687 pg/g TEQ_{2005} wet), followed by the sperm whale (1339 pg/g TEQ_{2005} wet) and one white beaked dolphin (1100 pg/g TEQ_{2005} wet).

3.2. PCB profiles

The percent normalised congener profiles for the different samples are presented as bar-graphs in the Supplementary Information (SI4). These profiles were compared against existing Aroclor profiles which revealed a poor match for all samples. Even when considering a best fit mixture of Aroclors similarity metrics (Cosine theta and R^2) the data still displays a poor match. For the majority of samples, this deviation from a simple Aroclor mixture was due to elevated proportions of PCBs such as PCB 138 and 153 (Fig. 2a). These have previously been identified as congeners that are resistant to biotransformation and elimination in a wide range of different species (Safe, 1993; Hansen, 1998, 1999; Grimm et al., 2015). Several samples displayed a different congener profile enriched in many of the less chlorinated congeners in the Aroclor 1242 range, but with an elevated proportion of the inadvertent PCBs 11 and PCB 20&30 (Fig. 2b). Interestingly, nearly all samples displayed elevated proportions of PCB 139 which is only present in trace levels (<0.2%) in technical mixtures (e.g. A1254).

The PCB signature of the killer whale exhibits a congener profile typically found in most marine mammals (Fig. 2a), with elevated proportions of the metabolism-resistant congeners such as PCB 132 & 153 & 186. The signature of the sei whale, however, does not match this 'typical' profile (Fig. 2b). The PCB signature of the sei whale can be more closely compared to one commonly found in air or surface depositions, with higher concentrations of lighter PCB congeners such as PCBs 8, 11,

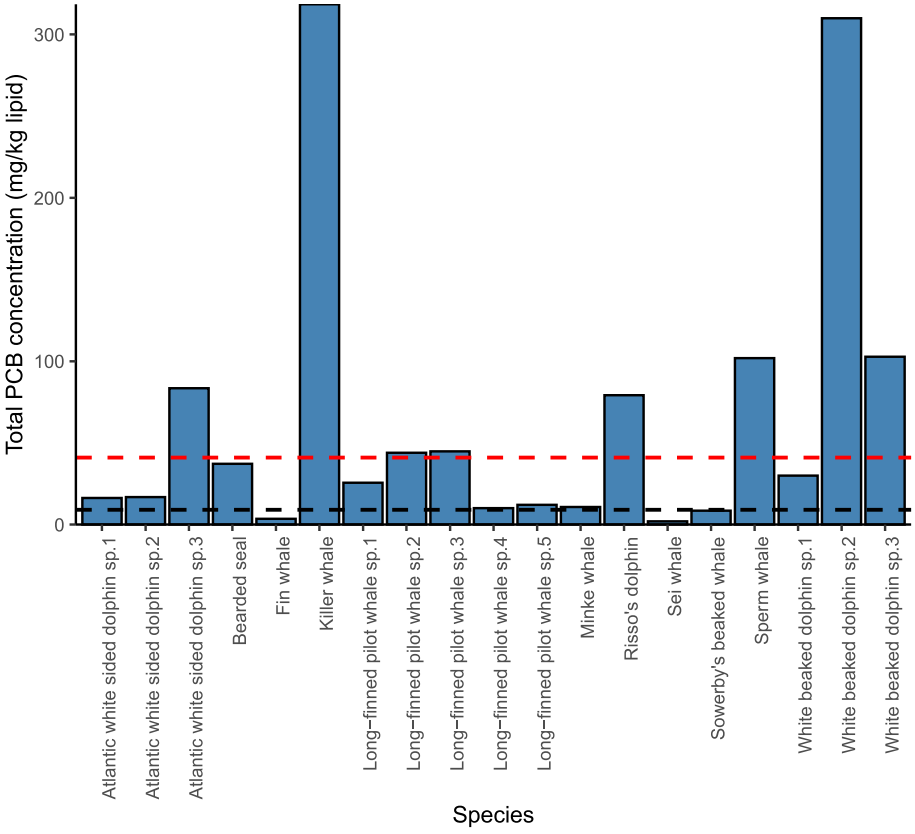


Fig. 1. Total PCB concentrations (mg/kg lipid) determined in each sample. The toxic threshold in marine mammals was indicated by a lower value of 9 mg/kg lipid (black dashed line) and a higher value of 41 mg/kg lipid (red dashed line) (approach adapted from (Jepson et al., 2016)). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Total dioxin-like-PCB (DL-PCB) concentrations (pg/g wet) and Toxic Equivalency Factors (TEQ) WHO 2005 (pg/g wet) in marine mammals from the North Atlantic Ocean.

Sample no.	Species	Non-ortho PCBs				Mono-ortho PCBs								Total DL-PCBs	Total PCBs	% DL-PCB	TEQWHO 2005
		77	81	126	105	114	118	123	156	157	167	169	189				
1	Atlantic white sided dolphin (Lagenorhynchus acutus)	828	94.4	68.2	24,200	1160	90,800	291	3870	5250	13,100	37.0	5160	1,45,000	73,20,000	2.0%	30.0
2	Atlantic white sided dolphin (Lagenorhynchus acutus)	551	61.0	69.7	25,200	1320	98,000	486	4610	5310	14,700	81.2	5110	1,55,000	92,10,000	1.7%	27.0
3	Atlantic white sided dolphin (Lagenorhynchus acutus)	1890	341	239	62,200	3770	2,34,000	5530	11,100	10,600	26,600	94.8	7240	3,64,000	1,40,00,000	2.6%	241
4	Bearded seal (Erignathus barbatus)	1820	227	2850	2,59,000	16,300	8,76,000	ND	80,600	35,700	34,900	106	5170	13,10,000	1,21,00,000	10.8%	1010
5	Fin whale (Balaenoptera physalus)	490	85.1	311	7240	1110	60,200	840	7410	2010	6880	30.9	840	87,400	18,20,000	4.8%	68.0
6	Killer whale (*Orcinus orca*)	4920	798	5490	11,90,000	75,500	41,70,000	31,500	5,69,000	2,61,000	5,23,000	5460	1,40,000	69,70,000	15,40,00,000	4.5%	1920
7	Long finned pilot whale (*Globicephala melas*)	2300	ND	344	1,66,000	8870	4,78,000	2800	31,300	16,400	34,300	516	4280	7,45,000	1,01,00,000	7.3%	188
8	Long finned pilot whale (*Globicephala melas*)	1600	572	482	2,75,000	18,900	9,39,000	5230	73,200	29,500	66,200	1040	8550	14,20,000	1,80,00,000	7.9%	305
9	Long finned pilot whale (*Globicephala melas*)	853	278	294	1,06,000	6450	3,57,000	4540	28,500	10,400	23,400	493	3190	5,41,000	68,70,000	7.9%	405
10	Long finned pilot whale (*Globicephala melas*)	896	443	228	35,500	2740	1,20,000	1760	12,200	4150	9890	209	1750	1,89,000	29,90,000	6.3%	124
11	Long finned pilot whale (*Globicephala melas*)	4120	1120	840	90,500	6280	2,98,000	3470	25,100	9850	15,800	324	2280	4,58,000	62,70,000	7.3%	220
12	Minke whale (Balaenoptera acutorostrata)	1550	516	669	18,600	1640	89,800	1540	8580	3070	7130	225	1260	1,35,000	23,00,000	5.9%	378
13	Risso's dolphin (Grampus griseus)	28,200	2980	13,800	2,02,000	11,600	6,98,000	7140	82,700	25,100	64,100	7860	14,100	11,60,000	1,10,00,000	10.5%	12,100
14	Sei whale (Balaenoptera borealis)	1040	189	88	4350	452	18,800	269	1140	383	932	25.6	137	27,900	8,67,000	3.2%	26.0
15	Sowerby's beaked whale (Mesoplodon bidens)	1280	465	1510	29,800	2780	1,31,000	2000	10,100	3070	4990	69.5	1390	1,89,000	27,10,000	7.0%	506
16	Sperm whale (Physeter macrocephalus)	13,400	2940	11,500	2,91,000	15,100	6,80,000	8330	85,700	27,900	48,900	4550	9510	12,00,000	2,07,00,000	5.8%	6600
17	White beaked dolphin (Lagenorhynchus albirostris)	994	ND	10,700	1,57,000	8980	5,42,000	ND	17,300	9390	23,300	146	4390	7,74,000	56,10,000	13.8%	5860
18	White beaked dolphin (Lagenorhynchus albirostris)	157	47.8	52.1	10,200	859	67,500	1110	3360	3160	10,000	32.7	3090	99,600	5,15,00,000	0.2%	570
19	White beaked dolphin (Lagenorhynchus albirostris)	15,200	ND	1640	1,62,000	8470	4,64,000	6690	4,66,000	20,200	46,800	1370	10,800	12,00,000	1,88,00,000	6.4%	1400

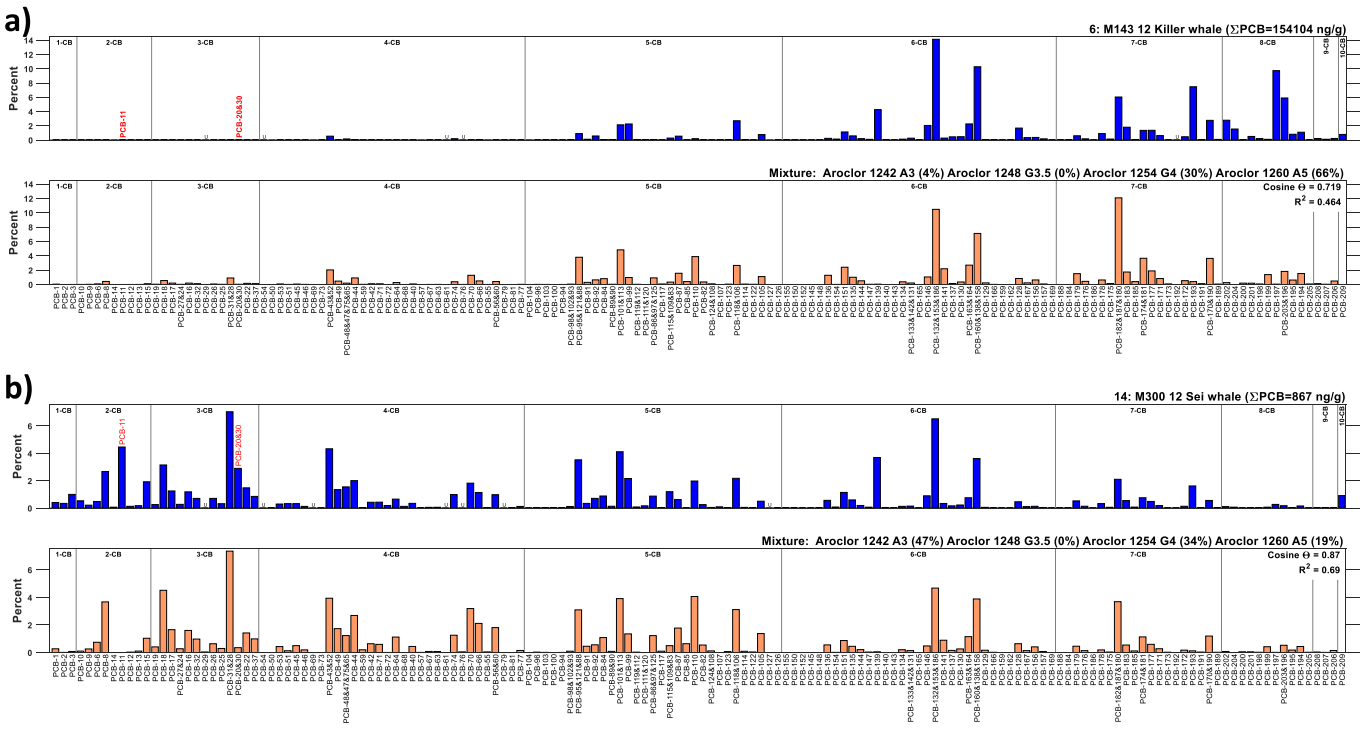


Fig. 2. Congener profiles with associated (poor) best fit matches to technical PCB mixtures for two marine mammals; (a) killer whale and (b) sei whale.

15, 20&30 (Bartlett et al., 2019; Hermanson et al., 2020). Note in particular the presence of PCB 11 and PCB 20&30 (annotated in red text on Fig. 2b) in sei whale sample M300. These congeners have been reported in sediments and birds and thought to be inadvertent PCB congeners, rather than from technical mixtures, as is discussed in more detail in Section 3.3. Sei whales are filter feeders (Cooke, 2018) that predominantly feed at the top of the water column that is directly exposed to atmospheric deposition. They do not consume animals from higher trophic positions that will have experience PCB bioaccumulation and biomagnification. This may explain the unusual pattern seen in this sei whale and why it differs from the other marine mammals.

Principal component analysis (Fig. 3) revealed a general two end member continuum between the two congener profiles displayed in Fig. 2. Sei whale sample M300 (which exhibits higher proportions of lower chlorinated congeners) plots to the far right. Killer whale sample M143 (with higher proportions of higher chlorinated, metabolism-resistant congeners) plots towards the left of Fig. 3. The point at the base of the plot that is located away from the main data cluster is the bearded seal sample, which is the only non-cetacean in the dataset. The majority of the mammals display a congener profile that is commonly observed in wildlife, with PCBs 153 and 138 being most abundant. This is evident by inspection of individual sample bar-graphs, which are included in SI4. Similar profiles have been recorded in killer whales, ringed, elephant and harbor seals (Ross et al., 2000; Muir et al., 2003;

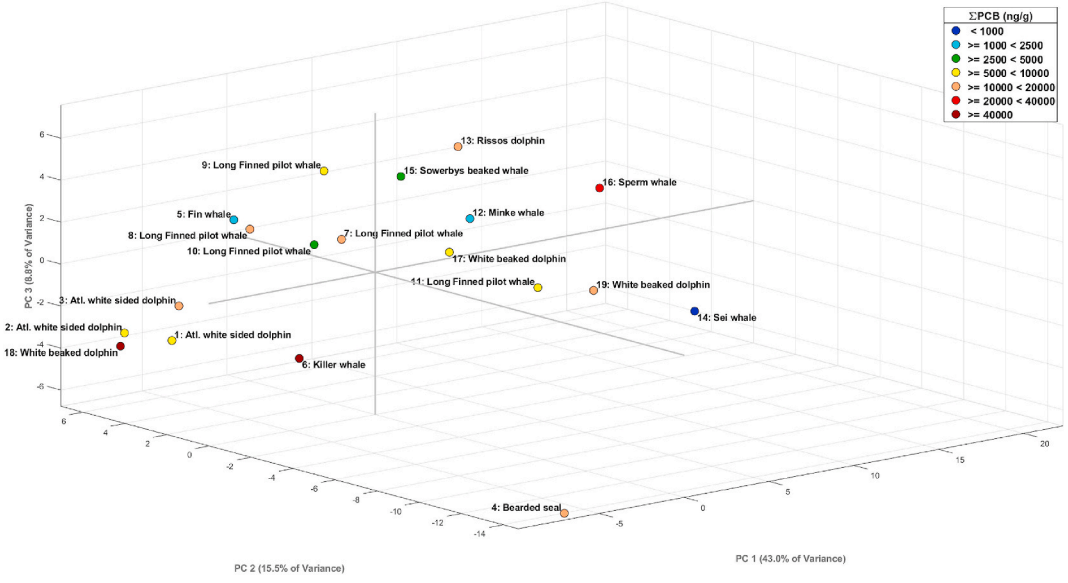


Fig. 3. Scores plot from principal components analysis (PCA) of 19 samples, 156 variable data set. Samples are color-coded by total PCB concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Wolkers et al., 2004; Debier et al., 2006). Many of the animals that displayed this signature are in fairly advanced levels of the trophic scale (e.g. killer whale, white beaked dolphin, sperm and log finned pilot whale) and therefore are at positions where biomagnification of congeners that are resistant to biotransformation and elimination is able to occur (Muir et al., 2003).

3.3. Non-Aroclor sources

The presence of non-Aroclor sources of PCBs in the environment has been gaining more attention over the last decade. Significant inputs of PCBs such as PCB11 and PCB209 have been reported in sediments and birds (Hu and Hornbuckle, 2010; Hu et al., 2011; Grimm et al., 2015; Vorkamp, 2016; Megson et al., 2018; Bartlett et al., 2019; Hermanson et al., 2020; Rodenburg et al., 2020). There are a variety of different processes that can create PCBs and this results in the production of many different PCB congeners including PCB11 and PCB209 (Grimm et al., 2015). These are often used as indicators of inadvertent PCB sources as they were not present in high proportions in technical PCB mixtures (although PCB 209 was used a major congener some technical mixtures that were not widely used e.g. A1268, 1270, A1271, A1272). Other potential indicators for inadvertent PCB sources include PCBs 21, 68, 90 and 169, which are also produced by inadvertent PCB sources but not found in technical mixtures. An additional layer of complexity comes from PCBs that are abundant in both inadvertent and Aroclor sources (such as PCBs 28 and 52). Identifying non-Aroclor contributions from these congeners is much more of a challenge, however Bartlett et al. (2019) and Hermanson et al. (2020) attributed elevated levels of PCB 28 in Arctic samples to non-Aroclor sources. Whilst we appreciate PCBs can be degraded and biotransformed in the environment, to provide a conservative "lower bound" estimate of the contribution of inadvertent sources, the sum of PCBs 11, 209, 21, 68, 90 and 169 are presented as ∑u-PCBs and converted to a percentage total in each sample (Fig. 4). These are presented alongside (a conservatively high) "upper bound" estimate of ∑u-PCBs which includes contributions from an additional 38 PCBs identified in Megson et al. (2019b) which are present in both inadvertent sources and technical products (Fig. 4). These include PCBs; 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 13, 15, 18, 20, 26, 28, 31, 33, 34, 35, 40, 47, 48, 51, 52, 56, 64, 72, 77, 99, 101, 109, 118, 126, 146, 153, 206, 208.

The results show that the conservative estimates of the proportion of uPCBs is relatively low for most samples, however contributions of greater than 5% of the total were observed in the sei whale (Fig. 4). Notable contributions conservative estimates of uPCBs were also found in white beaked dolphin (3.0%), sperm whale (2.8%) and minke whale (2.3%). When these values are compared against the upper uPCB estimations they become much more significant, with estimates between 20 and 50% of the total PCB content and total concentrations of over 100 mg/kg lipid in a white beaked dolphin. In most cases we assume 100% of these additional 38 PCBs have arisen from Aroclor sources. These are not minor congeners and so this research shows that it may be important to not jump to this assumption as inadvertently produced PCBs could be making up a larger proportion of the total PCB values than we previously anticipated. More research is needed to help deconvolute the proportions of PCBs that are found in both inadvertent sources and technical mixtures. Specific research is also required to identify the potential source of PCB 139 as this was common across most samples but is not present in high proportions in technical mixtures.

White beaked dolphins are continental species that feed predominantly on fish as well as squid, octopus and crustaceans (Canning et al., 2008; Jansen et al., 2010). Sperm whales are often found in deeper waters, feeding on cephalopods and fish in mesopelagic and benthic habitats (Spitz et al., 2011). Minke whales are found in all oceans and have a broad diet that includes schooling and demersal fish, krill and copepods (Haug et al., 2002). Although these species have higher proportions of inadvertent PCBs, they don't share similar diets or habitat. They may be exposed to these PCBs at lower depths, through their diet or when they contact the surface of the water. The killer whale had high concentrations of PCBs but lower proportions of inadvertent PCBs. This difference could be explained by the diet of killer whales as they target marine mammals (e.g. seals), sea turtles, sea birds, cephalopods and bony fish (e.g. herring and lumpfish) (Jourdain et al., 2019). Their generalist diet means they may be exposed to higher concentrations of PCBs with less volatile PCBs. These differences highlight how little we know about the magnitude of different pathways for animal exposure to

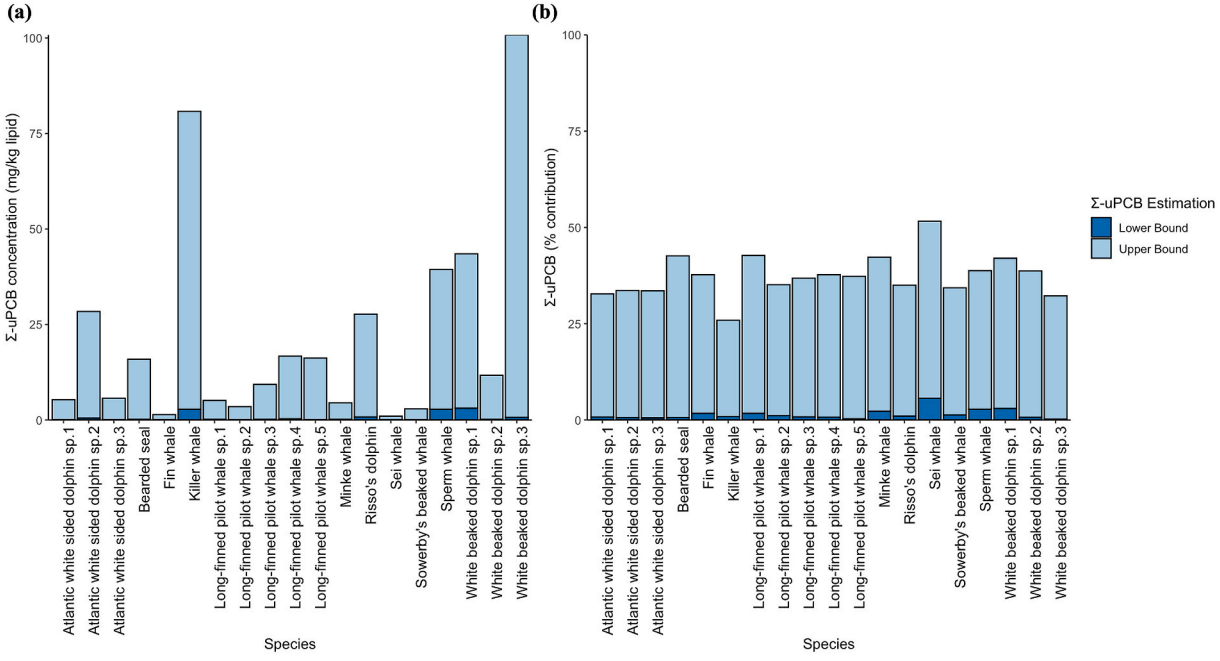


Fig. 4. (a) Total concentrations of u-PCBs determined in each sample along with the (b) percentage of Aroclor and inadvertent PCBs. "Lower bound" is a conservative estimate of the contribution of inadvertent sources, the sum of PCBs 11, 209, 21, 68, 90 are presented as (a) ∑u-PCBs and (b) converted to a percentage total in each sample, and "upper bound" is a ∑u-PCBs which includes contributions from an additional 38 inadvertently produced PCBs identified in Megson et al. (2019).

inadvertent PCBs.

3.4. Enantiomer fractions (EF)

There has been limited research in the environmental behaviour and enantioenrichment of chiral PCBs (C-PCBs). C-PCBs are produced as a racemic mixture (EF = 0.5) and due to various biological process, the biotransformation and elimination of these compounds may be enantioselective (Blanch et al., 1996; Serrano et al., 2000; Chu et al., 2003; Harrad et al., 2006; Bordajandi and González, 2008; Megson et al., 2015; Zheng et al., 2016).

A subset of 7 samples (1 sperm whale, 1 Sowerby's beaked whale, 1 minke whale, 1 long-finned pilot whale, 1 fin whale, 1 killer whale and 1 sei whale) were selected for chiral analysis to cover a wide range of different species, the EFs for PCB 95, 136 and 149 in these samples are presented as Fig. 5. For C-PCB 95 and C-PCB 149 all species had EF values = /< 0.5 (EF values ranged from 0.41 to 0.5 for C-PCB 95 and 0.4–0.5 for C-PCB 149), whereas all samples for PCB136 were close to racemic (0.47–0.53). The long-finned pilot whale showed the largest enrichment of C-PCB 95 and C-PCB 149 with an EF value of 0.41. The Sowerby's, minke and long-finned pilot whale showed the largest enrichment of C-PCB 149 with EF values ranging from 0.40 to 0.41. These results are similar to those reported previously by Megson et al. (2015) and Zheng et al. (2016) for human serum but contradict some of the other existing literature (Blanch et al., 1996; Serrano et al., 2000). PCB 95 (236–2′5′-CB) and 149 (236–2′4′5′-CB) possess free chlorine in either the *meta* or/& *para* (4/4' & 5/5′) positions, whereas PCB 136 (236–2′3′6′-CB) does not. This has led others to conclude that lower biotransformation rates occur with C-PCB 95 and C-PCB 149 relative to C-PCB 136 which resulted in hardly detectable changes of enantiomeric composition of these two PCBs in the liver of Portuguese dogfish (*Centroscymnus coelolepis*) (Blanch et al., 1996). Similar findings were also reported by Serrano et al. (2000) who reported racemic or nearly racemic results for C-PCB 95 and C-PCB 149 in almost all of the groupers (*Epinephelus marginatus*) and sharks.

Our data was assessed to establish if there was a link between PCB concentrations and EFs. There was a weak positive trend between total PCB concentrations and EF, as well as DL-PCB concentrations and EF (Fig. 5). As concentrations of PCBs increased the EF of C-PCB 95 and C-PCB 136 increased, but conflicting evidence was observed for C-PCB 149. Despite the slight positive trends in Fig. 5 no significant correlations were observed between the EF for C-PCBs 95, 136 and 149, and the total PCB concentration (a-c). Similarly, no significant correlations were observed between the EF for C-PCBs 95, 136 and 149, and the total DL-PCB concentration (d-f) (See SI for test output) so it is still unclear what is driving these changes in EFs of C-PCB 95 and PCB 149.

The large variation in the enantiomer composition of different organisms suggests that the PCBs are biotransformed and eliminated in different ways, i.e. through cytochrome P450 metabolism, which increases as the meta-para hydrogen atoms increase (Bordajandi and González, 2008; Kania-Korwel and Lehmler, 2016b; Zheng et al., 2016). There could also be variation due to trophic level and geography, for

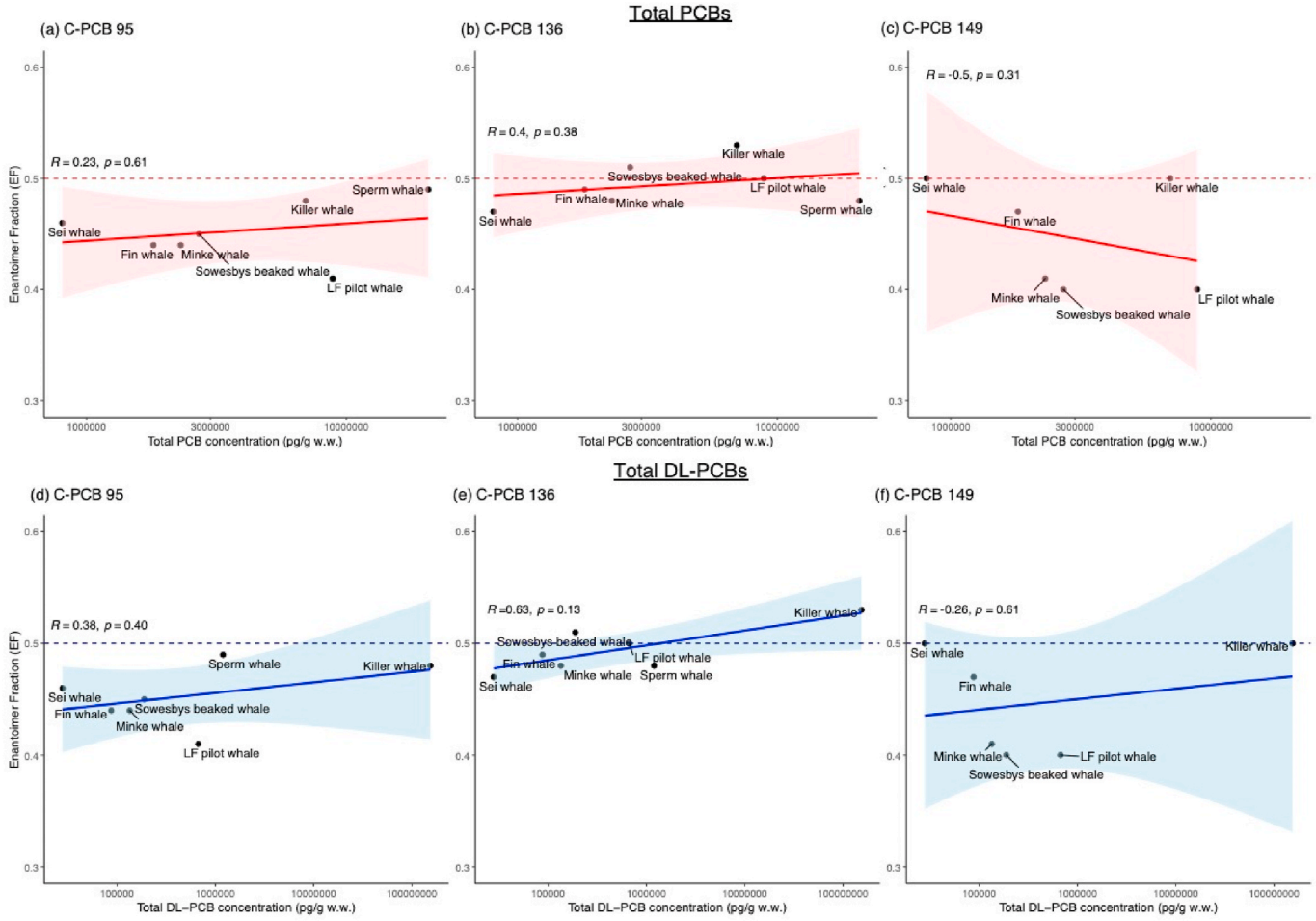


Fig. 5. Enantiomer fraction of C-PCB 95 (Fig. 5a and d), C-PCB 136 (Fig. 5b and e) and C-PCB 149 (Fig. 5c and f), and their relationship with total PCB (a–c) and DL-PCB (d–f) concentrations. The dashed line (dark red for total PCBs and dark blue for total DL-PCBs) on the scatter plots represents an EF of 0.5 (i.e. a racemic composition). C-PCB 149 was not detected in the sperm whale. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

example the Sowerby's, minke and long-finned pilot whale showed the largest variation from the racemic composition for C-PCB 149, all enriched with the second eluted enantiomer. Both species have higher trophic positions (4.3 and 4.4 respectively) (trophic level ranges obtained from Pauly et al., 1998), although the killer whale has the highest trophic position and shows the least variation from the racemic mixture. Kania-Korwel and Lehmler (2016b) suggested that the toxicokinetics of C-PCBs is congener specific as well as being species dependant. They found that trophic levels may play an important role, where species at lower trophic levels have more abiotic process that are involved in the breakdown of C-PCBs. This may explain the large variation from racemic for the minke whale and fin whale for C-PCB 95. The sei whale shows the least variation from the racemic mixture which could be explained by the PCB signature that contains a high proportion of lighter PCB congeners, or because it had the lowest total PCB concentrations and so may have therefore have had the least active cytochrome P450 system. Despite the few samples in this study, the variation of EF in C-PCB 95 and 149 indicate that there may be biotransformation processes occurring in the organism themselves (i.e. CP450) or along the food chain (dechlorination, weathering and microbial decomposition).

4. Conclusions

This study performed comprehensive congener specific PCB analysis in 11 different species of marine mammals. In total 19 samples were collected from mammals that had been stranded across the coast of the UK. As this study made use of opportunistic sampling from stranded animals in the UK there are some limitations that are discussed in SI1.

Total and dioxin like concentrations of PCBs found in this study were comparable with those found in the existing literature, however our study identified some of the highest number of different PCBs ever identified in environmental samples. At least 145 different PCBs were detected in each sample, with an average of 150 and maximum of 155 different PCBs (observed in the white beaked dolphin and Risso's Dolphin). The majority of the samples had concentrations exceeded the toxic threshold for marine mammals. Killer whales had the highest total PCB concentrations (318 mg/kg), as well as having the highest concertation of DL-PCBs (6970 ng/g wet) which highlights the significant risk that PCBs still pose in the marine environment.

Detailed congener profiles allowed us to identify a novel PCB profile in sei whales which was dominated by volatile and inadvertent PCBs. The PCB profiles in many of the other species were generally consistent with bioaccumulation profiles and technical mixtures found in other marine mammals. These PCB profiles suggest that the contribution of inadvertent PCBs to the total PCB burden in some marine mammals may be greater than 5% for some species (sei whale). Further research is recommended to identify better ways to differentiate sources of inadvertent PCBs from PCBs found in technical mixtures.

Seven subsamples were selected for chiral analysis of C-PCBs 95, 136 and 149. For C-PCB 95 and 149 all species had EF values $= /< 0.5$, whereas all samples for C-PCB 136 were close to racemic (0.47–0.53). These results contradict some existing literature which found racemic or almost racemic mixtures of C-PCB 95 and 149 in groupers and sharks, and supports existing literature that suggests C-PCB 136 enantioselective elimination of this PCB does not occur in mammals.

Author contributions statement

David Megson: Conceptualization, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Supervision, **Thomas Brown:** Resources, Formal analysis, **Gareth Rhys Jones:** Formal analysis, Writing - Review & Editing, **Mathew Robson:** Formal analysis, Writing - Review & Editing, **Glenn Johnson:** Formal analysis, Resources, Writing - Review & Editing, Visualization, **Guuske P. Tiktak:** Formal analysis, Writing - Original Draft, Writing - Review & Editing, **Court Sandau:** Writing - Review & Editing, **Eric Reiner:** Writing - Review & Editing.

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.

Acknowledgements

The authors would like to thank all those responsible for collecting samples under the Scottish Marine Animal Stranding Scheme (SMASS) and transporting them to T. Brown. The authors would also like to thank Thomas Hughes and Xaali O'Reilly Berkeley for drawing the killer whale and sei whale in the graphical abstract.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.132639.

References

Aguilar, A., Borrell, A., Pastor, T., 1999. Biological factors affecting variability of persistent pollutant levels in cetaceans. Journal Cetacean Resource Management 1, 83–116 (Special Issue.

Alonso Farré, J.M., González, A.F., Guerra, A., García-Hartmann, M., Lockyer, C., Boon, J.P., 2010. Assessing the effect of persistent organic pollutants on reproductive activity in common dolphins and harbour porpoises. J. Northwest Atl. Fish. Sci. 42, 153–173.

Arnot, J.A., Gobas, F.A.P.C., 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environ. Toxicol. Chem. 23 (10), 2343–2355.

ATSDR, 2000. Agency for toxic substance and disease registry (ATSDR). Toxicological Profile for Polychlorinated Biphenyls (PCBs). US Department of Health and Human Services, Atlanta, Georgia.

Axelman, J., Gustafsson, Ö., 2002. Global sinks of PCBs: a critical assessment of the vapor-phase hydroxy radical sink emphasizing field diagnostics and model assumptions. Global Biogeochem. Cycles 16 (4), 58-1.

Bartlett, P.W., Isaksson, E., Hermanson, M.H., 2019. "New" unintentionally produced PCBs in the Arctic. Emerging Contaminants 5, 9–14.

van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93 (2), 223–241.

Blanch, G.P., Glausch, A., Schurig, V., Serrano, R., González, M.J., 1996. Quantification and determination of enantiomeric ratios of chiral PCBs in sharks. J. High Resolut. Chromatogr. 19 (7), 392–396.

Bordajandi, L.R., González, M.J., 2008. Enantiomeric fraction of selected chiral polychlorinated biphenyls in cow, goat, and Ewe milk and dairy products by heart-cut multidimensional gas chromatography: first results. J. Dairy Sci. 91, 483–489.

Borrell, A., Aguilar, A., 1993. DDT and PCB pollution in blubber and muscle of long-finned pilot whales from the Faroe Islands. Rep. Int. Whaling Comm. Spec. Issue 14, 351–358.

Brown, T.A., Belt, S.T., Ferguson, S.H., Yurkowski, D.J., Davison, N.J., Barnett, J.E.F., Jepson, P.D., 2013. Identification of the sea ice diatom biomarker IP25 and related lipids in marine mammals: a potential method for investigating regional variations in dietary sources within higher trophic level marine systems. J. Exp. Mar. Biol. Ecol. 441, 99–104.

Canning, S.J., Santos, M.B., Reid, R.J., Evans, P.G., Sabin, R.C., Bailey, N., Pierce, G.J., 2008. Seasonal distribution of white-beaked dolphins (Lagenorhynchus albirostris) in UK waters with new information on diet and habitat use. J. Mar. Biol. Assoc. U. K. 88 (6), 1159–1166.

Chouvelon, T., Cresson, P., Bouchoucha, M., Brach-Papa, C., Bustamante, P., Crochet, S., Marco-Miralles, F., Thomas, B., Knoery, J., 2018. Oligotrophy as a major driver of mercury bioaccumulation in medium-to high-trophic level consumers: a marine ecosystem-comparative study. Environ. Pollut. 233, 844–854.

Chu, S., Covaci, A., Van De Vijver, K., De Coen, W., Blust, R., Schepens, P., 2003. Enantiomeric signatures of chiral polychlorinated biphenyl atropisomers in livers of harbour porpoises (Phocoena phocoena) from the southern North Sea. J. Environ. Monit. 5, 521–526.

Cooke, J.G., 2018. Balaenoptera Borealis (Sei Whale). IUCN Red List.

Debier, C., Chalon, C., Le Bœuf, B.J., de Tillesse, T., Larondelle, Y., Thomé, J.P., 2006. Mobilization of PCBs from blubber to blood in northern elephant seals (Mirounga angustirostris) during the post-weaning fast. Aquat. Toxicol. 80 (2), 149–157.

Desforges, J.P., Hall, A., McConnell, B., Rosing-Asvid, A., Barber, J.L., Brownlow, A., De Guise, S., Eulaers, I., Jepson, P.D., Letcher, R.J., Levin, M., Ross, P.S., Samarra, F.,

Víkingson, G., Sonne, C., Dietz, R., 2018. Predicting global killer whale population collapse from PCB pollution. Science 361 (6409), 1373–1376.
Domingo, J.L., Bocio, A., 2007. Levels of PCDD/PCDFs and PCBs in edible marine species and human intake: a literature review. Environ. Int. 33 (3), 397–405.
Dorneles, P.R., Sanz, P., Eppe, G., Azevedo, A.F., Bertozzi, C.P., Martínez, M.A., Secchi, E. R., Barbosa, L.A., Cremer, M., Alonso, M.B., Torres, J.P.M., Lailson-Brito, J., Malm, O., Eljarrat, E., Barceló, D., Das, K., 2013. High accumulation of PCDD, PCDF, and PCB congeners in marine mammals from Brazil: a serious PCB problem. Sci. Total Environ. 463, 309–318.
Flinn, R.D., Trites, A.W., Gregr, E.J., Perry, R.I., 2002. Diets of fin, sei, and sperm whales in British Columbia: an analysis of commercial whaling records, 1963–1967. Mar. Mamm. Sci. 18 (3), 663–679.
Garmash, O., Hermanson, M.H., Isaksson, E., Schwikowski, M., Divine, D., Teixeira, C., Muir, D.C.G., 2013. Deposition history of polychlorinated biphenyls to the lomonosovfonna glacier, Svalbard: a 209 congener analysis. Environ. Sci. Technol. 47, 12064–12072.
Grimm, F.A., Hu, D., Kania-Korwel, I., Lehmler, H.J., Ludewig, G., Hornbuckle, K.C., Duffel, M.W., Bergman, Å., Robertson, L.W., 2015. Metabolism and metabolites of polychlorinated biphenyls. Crit. Rev. Toxicol. 45 (3), 245–272.
Guo, J., Capozzi, S.L., Kraeutler, T.M., Rodenburg, L.A., 2014. Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments. Environ. Sci. Technol. 48, 8573–8580.
Hansen, L.G., 1998. Stepping backward to improve assessment of PCB congener toxicities. Environ. Health Perspect. 106 (Suppl. 1), 171–189.
Hansen, L.G., 1999. The ortho Side of PCBs. The Ortho Side of PCBs. Kluwer Academic Publishers, Boston, MA.
Harner, T., Wiberg, K., Norstrom, R., 2000. Enantiomer fractions are preferred to enantiomer ratios for describing chiral signatures in environmental analysis. Environ. Sci. Technol. 34 (1), 218–220.
Harrad, S., Ren, J., Hazrati, S., Robson, M., 2006. Chiral signatures of PCBs 95 and 149 in indoor air, grass, duplicate diets and human faeces. Chemosphere 63 (8), 1368–1376.
Haug, T., Lindstrøm, U., Nilssen, K.T., 2002. Variations in minke whale (Balaenoptera acutorostrata) diet and body condition in response to ecosystem changes in the Barents Sea. Sarsia N. Atl. Mar. Sci. 87 (6), 409–422.
Helle, E., Olsson, M., Jensen, S., 1976. PCB levels correlated with pathalogical changes in seal uteri. Ambio 5 (5/6), 261–262.
Hermanson, M.H., Isaksson, E., Divine, D., Teixeira, C., Muir, D.C.G., 2020. Atmospheric deposition of polychlorinated biphenyls to seasonal surface snow at four glacier sites on Svalbard, 2013–2014. Chemosphere 243, 125324.
Houde, M., Hoekstra, P.F., Solomon, K.R., Muir, D.C.G., 2005. Organohalogen contaminants in delphinoid cetaceans. Rev. Environ. Contam. Toxicol. 184, 1–57.
Hu, D., Hornbuckle, K.C., 2010. Inadvertent polychlorinated biphenyls in commercial paint pigments. Environ. Sci. Technol. 44, 2822–2827.
Hu, D., Martinez, A., Hornbuckle, K.C., 2011. Sedimentary records of non-aroclor and aroclor PCB mixtures in the great lakes. J. Great Lake. Res. 27 (2), 359–364.
Jansen, O.E., Leopold, M.F., Meesters, E.H., Smeenk, C., 2010. Are white-beaked dolphins Lagenorhynchus albirostris food specialists? Their diet in the southern North Sea. J. Mar. Biol. Assoc. U. K. 90 (8), 1501–1508.
Jeong, Y., Lee, Y., Park, K.J., An, Y.R., Moon, H.B., 2020. Accumulation and time trends (2003–2015) of persistent organic pollutants (POPs) in blubber of finless porpoises (Neophocaena asiaeorientalis) from Korean coastal waters. J. Hazard Mater. 385, 121598.
Jepson, P.D., Bennett, P.M., Deaville, R., Allchin, C.R., Baker, J.R., Law, R.J., 2005. Relationships between polychlorinated biphenyls and health status in harbor porpoises (Phocoena phocoena) stranded in the United Kingdom. Environ. Toxicol. Chem. 24 (1), 238–248.
Jepson, P.D., Deaville, R., Barber, J.L., Aguilar, À., Borrell, A., Murphy, S., Barry, J., Brownlow, A., Barnett, J., Berrow, S., Cunningham, A.A., Davison, N.J., Ten Doeschate, M., Esteban, R., Ferreira, M., Foote, A.D., Genov, T., Giménez, J., Loveridge, J., Llavona, Á., Martin, V., Maxwell, D.L., Papachlimitzou, A., Penrose, R., Perkins, M.W., Smith, B., De Stephanis, R., Tregenza, N., Verborgh, P., Fernandez, A., Law, R.J., 2016. PCB pollution continues to impact populations of killer whales and other dolphins in European waters. Sci. Rep. 14 (6), 1–17.
Johnson, G.W., Ehrlich, R., Full, W., Ramos, S., 2015. Chapter 18: principal components analysis and receptor models in environmental forensics. In: Morrison, R., Murphy, B. (Eds.), An Introduction to Environmental Forensics, third ed. Elsevier, Amsterdam, pp. 609–653.
Jourdain, E., Karoliussen, R., de Vos, J., Zakharov, S.E., Tougard, C., 2020a. Killer whales (Orcinus orca) feeding on lumpfish (Cyclopterus lumpus) in northern Norway. Mar. Mamm. Sci. 36 (1), 89–102.
Jourdain, E., Andvik, C., Karoliussen, R., Ruus, A., Vongraven, D., Borgå, K., 2020b. Isotopic niche differs between seal and fish-eating killer whales (Orcinus orca) in northern Norway. Ecology and Evolution 10 (9), 4115–4127.
Kania-Korwel, I., Lehmler, H.-J., 2016a. Chiral polychlorinated biphenyls: absorption, metabolism and excretion – a review. Environ. Sci. Pollut. Control Ser. 23 (3), 2042–2057.
Kania-Korwel, I., Lehmler, H.-J., 2016b. Toxicokinetics of chiral polychlorinated biphenyls across different species - a review. Environ. Sci. Pollut. Control Ser. 23 (3), 2058–2080.
Kannan, K., Blankenship, A.L., Jones, P.D., Giesy, J.P., 2000. Toxicity reference values for the toxic effects of polychlorinated biphenyls to aquatic mammals. Human and Ecological Risk Assessment 6 (1), 181–201.
Kelly, B.C., Ikonomou, M.G., Blair, J.D., Morin, A.E., Gobas, F.A.P.C., 2007. Food web-specific biomagnification of persistent organic pollutants. Science 317 (5835), 236–239.
Letcher, R.J., Bustnes, J.O., Dietz, R., Jenssen, B.M., Jørgensen, E.H., Sonne, C., Verreault, J., Vijayan, M.M., Gabrielsen, G.W., 2010. Exposure and effects assessment of persistent organohalogen contaminants in Arctic wildlife and fish. Sci. Total Environ. 408 (15), 2995–3043.
Liu, X., Mullin, M., 2019. Inadvertent polychlorinated biphenyls (PCBs) in consumer products. The 2019 ISEE & ISIAQ joint conference. In: ISES-ISIAQ 2019, Kaunas, Lithuania.
Lu, Z., Fisk, A.T., Kovacs, K.M., Lydersen, C., McKinney, M.A., Tomy, G.T., Rosenburg, B., McMeans, B.C., Muir, D.C.G., Wong, C.S., 2014. Temporal and spatial variation in polychlorinated biphenyl chiral signatures of the Greenland shark (Somniosus microcephalus) and its Arctic marine food web. Environ. Pollut. 186, 216–225.
Megson, D., 2019a. Polychlorinated biphenyls. In: Encyclopedia of Analytical Science. Elsevier, pp. 318–327.
Megson, D., Benoit, N.B., Sandau, C.D., Chaudhuri, S.R., Long, T., Coulthard, E., Johnson, G.W., 2019. Evaluation of the effectiveness of different indicator PCBs to estimating total PCB concentrations in environmental investigations. Chemosphere 237, 124429.
Megson, D., Brown, T.A., O'Sullivan, G., Robson, M., Ortiz, X., Worsfold, P.J., Comber, S., Lohan, M.C., Reiner, E.J., 2018. Changes to polychlorinated biphenyl (PCB) signatures and enantiomer fractions across different tissue types in Guillemots. Mar. Pollut. Bull. 131, 174–179.
Megson, D., Focant, J.F., Patterson, D.G., Robson, M., Lohan, M.C., Worsfold, P.J., Comber, S., Kalin, R., Reiner, E., O'Sullivan, G., 2015. Can polychlorinated biphenyl (PCB) signatures and enantiomer fractions be used for source identification and to age date occupational exposure? Environ. Int. 81, 56–63.
Megson, D., Kalin, R., Worsfold, P.J., Gauchotte-lindsay, C., Patterson, D.G., Lohan, M.C., Comber, S., Brown, T.A., Sullivan, O., 2013. Fingerprinting polychlorinated biphenyls in environmental samples using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. J. Chromatogr. A 1318, 276–283.
Muir, D.C.G., Norstrom, R.J., Simon, M., 1988. Organochlorine contaminants in arctic marine food chains: accumulation of specific polychlorinated biphenyls and chlordane-related compounds. Environ. Sci. Technol. 22 (9), 1063–1071.
Muir, D., Savinova, T., Savinov, V., Alexeeva, L., Potelov, V., Svetochev, V., 2003. Bioaccumulation of PCBs and chlorinated pesticides in seals, fishes and invertebrates from the White Sea, Russia. Sci. Total Environ. 306 (1–3), 111–131.
Murphy, S., Pierce, G.J., Law, R.J., Bersuder, P., Jepson, P.D., Learmonth, J.A., Addink, M., Dabin, W., Santos, M.B., Deaville, R., Zegers, B.N., Mets, A., Rogan, E., Ridoux, V., Reid, R.J., Smeenk, C., Jauniaux, T., López, A., Farré, J.M.A., González, A.F., Guerra, A., García- Hartmann, M., Lockyer, C., Boon, J.P., 2010. Assessing the effect of persistent organic pol- lutants on reproductive activity in common dolphins and harbour porpoises. NAFO/ICES/NAMMCO symposium the Role of Marine Mammals in the Ecosystem in the 21st Century. J. Northwest Atl. Fish. Sci. 42, 153–173.
Murphy, S., Law, R.J., Deaville, R., Barnett, J., Perkins, M.W., Brownlow, A., Penrose, R., Davison, N.J., Barber, J.L., Jepson, P.D., 2018. Organochlorine contaminants and reproductive implication in cetaceans: a case study of the common dolphin. In: Fossi, M.C., Panti, C. (Eds.), Marine Mammal Ecotoxicology. Academic Press, Cambridge, pp. 3–38.
O'Sullivan, G., Sandau, C., 2013. Environmental forensics for persistent organic pollutants. Environmental Forensics for Persistent Organic Pollutants. Elsevier B.V, Amsterdam, The Netherlands.
Pauly, D., Trites, A.W., Capuli, E., Christensen, V., 1998. Diet composition and trophic levels of marine mammals. ICES (Int. Counc. Explor. Sea) J. Mar. Sci. 55 (3), 467–481.
Robson, M., Harrad, S., 2004. Chiral PCB signatures in air and soil: implications for atmospheric source apportionment. Environ. Sci. Technol. 38 (6), 1662–1666.
Rodenburg, L.A., Hermanson, M.R., Sumner, A.L., 2020. Sources of polychlorinated biphenyl blank contamination and their impact on fingerprinting. Environ. Forensics 21 (1), 99–112.
Ross, P.S., Ellis, G.M., Ikonomou, M.G., Barrett-Lennard, L.G., Addison, R.F., 2000. High PCB concentrations in free-ranging Pacific killer whales, Orcinus orca: effects of age, sex and dietary preference. Mar. Pollut. Bull. 40 (6), 504–515.
Safe, S., 1993. Toxicology, structure-function relationship, and human and environmental health impacts of polychlorinated biphenyls: progress and problems. Environ. Health Perspect. 100, 259–268.
Serrano, R., Fernández, M., Rabanal, R., Hernández, M., González, M.J., 2000. Congener-specific determination of polychlorinated biphenyls in shark and grouper livers from the northwest African Atlantic Ocean. Arch. Environ. Contam. Toxicol. 38, 217–224.
Spitz, J., Cherel, Y., Bertin, S., Kiszka, J., Dewez, A., Ridoux, V., 2011. Prey preferences among the community of deep-diving odontocetes from the Bay of Biscay, Northeast Atlantic. Deep-Sea Res. Part I Oceanogr. Res. Pap. 58, 273–282.
Tanabe, S., 2002. Contamination and toxic effects of persistent endocrine disrupters in marine mammals and birds. Mar. Pollut. Bull. 45 (1–12), 69–77.
Tanabe, S., Kannan, N., Subramanian, A., Watanabe, S., Tatsukawa, R., 1987. Highly toxic coplanar PCBs: occurrence, source, persistency and toxic implications to wildlife and humans. Environ. Pollut. 47 (2), 147–163.
Tanabe, S., Mori, T., Tatsukawa, R., Miyazaki, N., 1983. Global pollution of marine mammals by PCBs, DDTs and HCHs (BHCs). Chemosphere 12 (9–10), 1269–1275.
Vorkamp, K., 2016. An overlooked environmental issue? A review of the inadvertent formation of PCB-11 and other PCB congeners and their occurrence in consumer products and in the environment. Sci. Total Environ. 541, 1463–1476.
Warner, N.A., Norstrom, R.J., Wong, C.S., Fisk, A.T., 2005. Enantiomeric fractions of chiral polychlorinated biphenyls provide insights on biotransformation capacity of Arctic biota. Environ. Toxicol. Chem. 24 (11), 2763–2767.

Weijs, L., Tibax, D., Roach, A.C., Manning, T.M., Chapman, J.C., Edge, K., Blust, R., Covaci, A., 2013. Assessing levels of halogenated organic compounds in mass-stranded long-finned pilot whales (Globicephala melas) from Australia. Sci. Total Environ. 461, 117–125.

Wolkers, H., Lydersen, C., Kovacs, K.M., 2004. Accumulation and lactational transfer of PCBs and pesticides in harbor seals (Phoca vitulina) from Svalbard, Norway. Sci. Total Environ. 319 (1–3), 137–146.

Zheng, J., Yu, L.H., Chen, S.J., Hu, G.C., Chen, K.H., Yan, X., Luo, X.J., Zhang, S., Yu, Y. J., Yang, Z.Y., Mai, B.X., 2016. Polychlorinated biphenyls (PCBs) in human hair and serum from E-waste recycling workers in southern China: concentrations, chiral signatures, correlations, and source identification. Environ. Sci. Technol. 50 (3), 1579–1586.