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High concentrations of persistent organic pollutants in adult killer whales (*Orcinus orca*) and a foetus stranded in Ireland

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ABSTRACT

Bio-accumulation of persistent organic pollutants including polychlorinated biphenyls (PCBs), brominated flame retardants and organochlorine pesticides continue to be of major concern for marine apex predators such as killer whales. The concentrations of 16 polychlorinated biphenyls, 7 poly-brominated diphenyl ethers (PBDEs), 1 poly-brominated biphenyl (PBB) and a range of 19 organochlorine compounds (OCs) was investigated in blubber samples from a mother-foetus pair, an adult female and an adult male killer whale stranded in Ireland between 2010 and 2017. Concentrations ranged from 1.5 mg/kg to 49.3 mg/kg lipid weight and 0.04–1.2 mg/kg lipid weight for $\Sigma 16$ PCBs and $\Sigma 7$ PBDEs respectively. Concentrations of organochlorine compounds were also investigated in the male killer whale; a $\Sigma 19$ OC concentration of 49.4 mg/kg lipid weight was recorded. This study shows high levels of persistent organic pollutants occur in this species of whales stranded in Ireland.

1. Introduction

The impact of persistent organic pollutants (POPs) in the marine environment has been of considerable concern since the 1970s as these compounds remain ubiquitous in the environment (Fiedler, 2001). Low vapour pressure, high thermal stability and the lipophilic nature of persistent organic pollutants including PCBs, PBDEs and OCs are the physico-chemical characteristics that allow them to travel and accumulate in the environment and biota respectively; even in remote areas of the globe with no previous direct anthropogenic contamination (Ikononou et al., 2002).

PCBs have been found to accumulate in waterways, aquatic systems and adsorb onto sediment. This accumulation can be attributed to run-off from the land application of PCBs, improper disposal of electrical equipment containing PCB transfer fluids and hydraulics, as well as seepage from accidental spills and sewage (Voogt and Brinkman, 1989; Beyer and Biziuk, 2009). Brominated flame retardants, specifically poly-brominated diphenyl ethers (PBDE) and poly-brominated biphenyls (PBBs) were largely used to confer flame resistant properties in the production of textiles, plastics and electrical equipment (De Wit, 2002; Hites, 2004). Organochlorines such as dichlorodiphenylchloroethane (DDD), dichlorodiphenylchloroethylene (DDE), dichlorodiphenyltrichloroethane (DDT),

hexachlorobenzene (HCB) as well as Dieldrin, Aldrin and Isodrin have a range of different chemical structures. The high degree of chlorination and aliphatic or aromatic cyclic structures of OCs led to their widespread use as pesticides from the 1950s–1970s (Shen and Wania, 2005), and consequently their environmental persistence and potential for long range transportation (Beyer et al., 2000).

The lipophilic nature of halogenated contaminants allows for bio-accumulation in the lipid-rich blubber of marine mammals, including killer whales, and is the cause of widespread concern not only in Europe, but on a global scale (Jepson and Law, 2016; Desforges et al., 2018). Killer whale populations in the UK and Ireland, were monitored by Beck et al. (2014) through the use of opportunistic photo-identification of individual animals over a 19 year period which suggested a slight decline of an isolated killer whale population around the Irish and British coasts had occurred. However, sparse data on this small population (n = 10) presented difficulties in defining the potential causes of this decline (Beck et al., 2014). Killer whales are apex predators, often feeding on species that occupy the highest trophic levels. This, coupled with high lipid content and a long life-span, places them at particular risk to bio-accumulation of ubiquitous POPs such as OCs, PCBs and PBDEs. These compounds pose an ongoing threat; the possible extinction of local populations has been suggested (Jepson et al., 2016;

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Desforges et al., 2018) as high concentrations of pollutants are consistent with reproductive and recruitment failure. A toxicity threshold of 17mg/kg in the blubber of marine animals has been suggested as leading to reproductive impacts (Kannan et al., 2000). It remains essential that concentrations of such contaminants in top predators are measured and reported. An expansion of monitoring contaminant concentrations may lead to a more holistic understanding of the impacts of such compounds and associated detriments to the species as a whole.

In an Irish context, there is limited knowledge regarding concentrations of OCs, PCBs and PBDEs in most marine mammal species including killer whales. A limited number of studies of organochlorine concentrations in some odontocete species in Irish waters have been published, such as on bottlenose dolphins (*Tursiops truncatus*) (Berrow et al., 2002), white-sided dolphins (*Lagenorhynchus actus*), (McKenzie et al., 1997), common dolphins (*Delphinus delphis*) and harbour porpoises (*Phocoena phocoena*) (Smyth et al., 2000) as well as one mysticete, the humpback whale (*Megaptera novaeangliae*) (Ryan et al., 2013). There is only one known sample from a killer whale from the Irish coast analysed to date in which concentrations of PCBs and a suite of organochlorines were reported (McHugh et al., 2007).

The aim of this study was to contribute to the limited knowledge of PCB, OC and PBDE contamination levels in killer whales stranded in Ireland. A pregnant female stranded in County Mayo and an adult female stranded in Waterford were analysed for a suite of 16 PCBs, and 7 PBDEs, while samples from an adult male stranded in 2017 were also analysed for a range of OCs, in addition to PCBs and PBDEs.

2. Analytical methods

All killer whale blubber samples were obtained through the Irish Whale and Dolphin Group (IWDG) Cetacean Stranding Scheme. Samples were collected from 1. Doohoma, County Mayo (54°18'35.0"N 9°58'47.8"W); 2. Roundstone, County Galway (53°23'06.2"N 10°01'37.0"W) and 3. Tramore, County Waterford (52°09'33.8"N 7°04'48.1"W) (Fig. 1, Table 1). Samples were initially stored at -20°C , before transfer to -80°C freezer storage at the Marine Institute Laboratories in Rinville Oranmore before analysis. Samples from killer whales stranded in Doohoma and Tramore, both adult females and the foetus, were analysed for a suite of 16 PCBs (Ballschmitter and Zell notation used: Congeners 18, 31, 28, 52, 44, 101, 149, 118, 153, 105, 138, 156, 180, 170, 194, 209) and 7 PBDEs (Congeners 28, 47, 100, 99, 154, 153, 183). The sample from Roundstone was analysed for the same 16 PCBs, 4 PBDEs (Congeners 47, 100, 99, 153), PBB 153 as well as 19 OCs. A post-mortem was carried out on the pregnant female killer whale, which was not in an advanced state of decay. It was discovered that the foetus was female and in cranial presentation (Ryan and Pierini, 2013). No cause of death was established for any of the samples. The adult female from Tramore was in excellent condition, however the male from Roundstone was in poor condition with its skin lost to weathering and scavenging. No length measurement was taken of the male but it was estimated at around 7 m.

The Smedes method of extraction was used for the extraction of the lipid component of the blubber samples (Smedes, 1999). This involved homogenization using an Ultra Turrax (IKA T25) and a solvent mix of 16 ml Isopropanol, 20 ml Cyclohexane and 18 ml deionized water. 100 mg of ^{13}C isotopically labelled internal standards was added prior to total lipid extraction and was used in the quantification of all analytes.

After centrifugation and separation of the organic layer, the remaining precipitate was re-extracted with an 87:13 mix of cyclohexane/isopropanol. Extracts were evaporated using a Turbo Evaporator (TurboVap LV) at 35°C under a uniform nitrogen stream of 7.5 psi. Column chromatography was utilized as a clean-up phase to remove any remaining interferants. Glass wool ($\sim 0.5\text{ cm}$) plugged columns were packed with hexane washed sodium sulphate ($\sim 0.5\text{ cm}$), 6 g

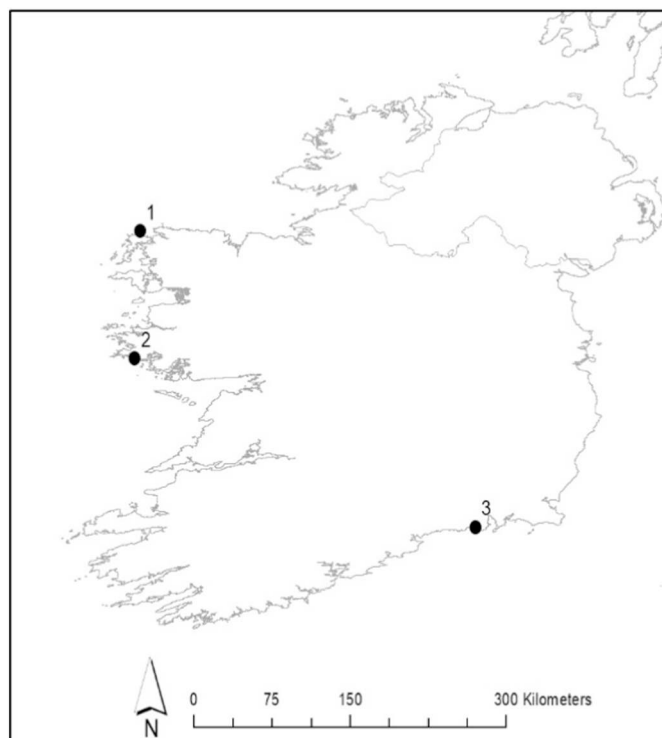


Fig. 1. Map showing sites of stranding and whale blubber sampling.

($\pm 0.1\text{ g}$) deactivated alumina [5% w/w] and 1.5 g ($\pm 0.1\text{ g}$) deactivated silica [5% w/w].

An Agilent GC-MS equipped with a 60 m HT8 capillary column was used for the analysis. Oven temperature programming was employed to achieve resolution of analyte peaks. A concentrated stock was run using Scan mode for the identification of contaminant ions and fragmentation spectra. Single ion monitoring (SIM) mode was used for the quantification of PCB, PBDE and OC analytes. Electron ionization methods were employed in negative ion mode. SIM parameters used for the analysis can be found in the *Supplementary Information*. Analysis of all samples and standards in SIM mode allowed for increased specificity and sensitivity.

3. Quality control

Analyses of PCBs and PBDEs for both adult female killer whales as well as the foetus sample were carried out at the Marine Institute, ISO 17025 accredited for the analysis of PCBs. NIST 1947 Lake Michigan tissue was used as a certified reference material (CRM) and was analysed alongside samples. LOQs across all analytes ranged from 0.05 to 0.2 ng/g, a full list of LOQs can be found in the *Supplementary Information*. Procedural blanks were also run, and samples were analysed in triplicate. NIST 1947 Lake Michigan tissue was used as a CRM for this analysis. The adult male killer whale was analysed for PCBs, PBDEs and OCs in the Galway-Mayo Institute of Technology. Due to lack of sample availability, only two replicates could be carried out for this sample. Standard deviations for PCBs, PBDEs and OCs were calculated and are also reported alongside contaminant concentrations in Tables 2–4 respectively.

4. Results

Individual contaminant analytes were detected across all replicates from all samples. The Tramore female was found to contain a sumPCB concentration of 1.5 mg/kg on a lipid weight (lw) basis and sumBDE concentration of 0.04 mg/kg lw. The pregnant female from Doohoma

Table 1
Record of killer whales stranded on the coast of Ireland from 2010 to 2017.

Animal	KW Adult Female	KW Foetus	KW Adult Female	KW Adult Male
Matrix	Blubber	Blubber	Blubber	Blubber
Stranding Location	Doohoma, Mayo	Doohoma, Mayo	Tramore, Waterford	Roundstone, Galway
Date collected	4th October 2010	4th October 2010	30th January 2015	15th July 2017
Length (m)	5.12	2.09	5.12	~7
Reference	Ryan and Pierini (2013)	Ryan and Pierini (2013)	Hernandez-Milian et al., 2017	O'Connell and Berrow, 2019

was found to contain a sumPCB concentration of 49.3 mg/kg lw and a sumBDE concentration of 1.2 mg/kg. The foetus had a sumPCB concentration of 10.6 mg/kg lw and a sumBDE concentration of 0.3 mg/kg lw. SumPCB and sumBDE concentrations in the Roundstone male were found to be 13.9 mg/kg lw and 0.27 mg/kg lw. The sumOC concentrations for the Roundstone male was found to be 49.4 mg/kg lw. The Σ DDTs and Σ HCHs were also calculated as 48.7 mg/kg lw and 0.03 mg/kg lw respectively. Results for individual contaminant analytes are outlined in Tables 1 and 2 for PCBs and PBDEs respectively. Fig. 2 shows a direct comparison of specific PCB congener concentrations and Fig. 3 shows a direct comparison of specific BDE congener concentrations across the four individuals sampled. SumPCB and sumBDE ratios of 21.57% and 23.82% respectively were calculated for the mother-foetus pair.

5. Discussion

There are a wide range of factors that may have affected our results, including age, sex, and reproductive status. Diet has also been shown to be important with transient killer whales accumulating increased concentrations of contaminants due to their diet of other marine mammals in contrast to sympatric resident ecotypes which have a mainly fish-based diet (Ross et al., 2000; Krahn et al., 2007). In this study, the stranded pregnant killer whale was found to have the highest concentration of contaminants presented here and was way above the toxicity threshold of 17 mg/kg contaminants for blubber in marine mammals established by Kannen et al. (2000). It is well established in the literature (Haraguchi et al., 2009; Krahn et al., 2009; Ross et al., 2000), that female cetaceans, including killer whales, have the ability to offload some of their POP burdens through gestation and lactation.

Lower concentrations in sexually mature females would be expected in comparison to their male counterparts of the same age, though this is largely dependent on whether or not females have successfully parturated, as well as the number of calves born (Lundin et al., 2016). The high concentrations in the pregnant female presented here may reflect its reproductive status; this was likely her first calf and thus had not the opportunity to offload through lactation. POPs were transferred through gestation as evidenced by the concentrations of 10.6 mg/kg lw and 0.3 mg/kg for PCBs and PBDEs in the foetus; concentrations which were comparable to the adult male in this study. The foetus was near term at a length of 2.09 m, another factor for the level of contaminants presented; a less developed foetus would have had a shorter gestation period and would likely have had a lower contaminant burden. The diet of killer whales in Ireland is not known. Killer whales elsewhere are known to eat pelagic prey such as mackerel *Scomber scombus* and herring *Clupea harengus* but also seabirds and mammals (Samarra et al., 2018; Bolt et al., 2009). All stranded individuals examined had work teeth consistent with type 1 killer whales which are thought to be mainly fish eaters as well as belonging to older individuals (Foote et al., 2009). Killer whales in Ireland have been reported feeding on Atlantic salmon and mullet *Chelon labrosus* (Ryan and Wilson, 2003), while the female killer whale stranded in Doohoma had remains of a sunfish, *Mola mola*, in its stomach (Ryan and Holmes, 2012).

SumPCBs and sumBDEs in the adult male sampled in this study had relatively lower concentrations of contaminants than expected compared to females analysed, with concentrations (13.93 mg/kg lw for PCBs and 0.06 mg/kg for PBDEs) similar to that of the foetus. Males tend to accumulate larger concentrations of pollutants with age due to their inability to transfer via reproduction, however the Roundstone male analysed in this study had much lower concentrations than

Table 2
Mean PCB concentrations and (standard deviations) in blubber from killer whales (*Orcinus orca*) stranded in Ireland. Values reported in ng/g lipid weight (lw).

Sample Location	KW Adult Female		KW Foetus		KW Adult Female		KW Adult Male	
	Doohoma	Mayo	Doohoma	Mayo	Tramore	Waterford	Roundstone	Galway
% Lipid	66.33	(3.16)	22.81	(6.55)	67.56	(12.32)	56.50	(6.22)
PCB 18	16.57	(1.16)	4.47	(0.46)	0.48	(0.15)	8.38	(2.04)
PCB 31	32.83	(1.32)	8.98	(0.59)	1.22	(0.39)	11.01*	(0.06*)
PCB 28	53.98	(1.75)	10.22	(0.55)	2.10	(1.24)	-	-
PCB 52	465.16	(28.80)	141.29	(11.47)	16.35	(1.74)	204.66	(3.69)
PCB 44	48.90	(11.43)	18.11	(2.63)	1.57	(0.39)	40.25	(17.95)
PCB 101	1910.90	(72.77)	589.97	(49.41)	55.78	(5.30)	1115.80	(3.60)
PCB 149	3619.63	(419.65)	988.47	(124.65)	64.04	(9.43)	1344.57	(20.44)
PCB 118	2251.08	(153.93)	699.11	(36.04)	91.74	(9.37)	1354.54	(41.82)
PCB 153	17397.71	(2421.36)	3951.07	(411.92)	518.71	(86.83)	4365.04	(154.03)
PCB 105	534.99	(47.03)	177.73	(4.53)	26.23	(3.37)	163.17	(5.03)
PCB 138	12296.49	(1085.82)	2450.10	(154.50)	321.71	(72.37)	3752.98	(120.39)
PCB 156	284.63	(16.05)	56.49	(5.97)	10.17	(3.38)	74.22	(3.93)
PCB 180	7576.83	(130.85)	1134.35	(114.04)	301.46	(65.03)	842.53	(385.43)
PCB 170	2163.16	(122.03)	364.04	(29.88)	73.43	(14.56)	514.46	(15.87)
PCB 194	648.90	(29.35)	41.59	(2.98)	33.89	(4.52)	129.55	(11.07)
PCB 209	16.95	(2.22)	2.57	(0.64)	2.28	(0.64)	6.59	(0.47)
Σ 16PCB	49318.71	(3100.25)	10638.57	(866.17)	1521.15	(273.28)	13927.74	(434.08)
%PCB153	35.17	(2.91)	37.11	(1.44)	34.17	(0.98)	31.4056	(2.0847)

Table 3Mean BDE concentrations (standard deviation) in blubber in killer whale (*Orcinus orca*) stranded in Ireland. Values reported in ng/g lipid weight (lw).

Sample Location	KW Adult Female		KW Foetus		KW Adult Female		KW Adult Male	
	Doohoma	Mayo	Doohoma	Mayo	Tramore	Waterford	Roundstone	Galway
% Lipid	66.33	(3.16)	22.81	(6.55)	67.56	(12.32)	56.50	(6.22)
BFR 28	9.84	(3.75)	2.17	(0.10)	0.71	(0.19)	–	–
BFR 47	689.65	(69.33)	210.04	(40.64)	16.60	(1.57)	174.54	(21.26)
BFR 100	312.36	(107.14)	45.95	(12.76)	13.12	(0.68)	64.79	(8.43)
BFR 99	126.65	(44.18)	30.99	(5.00)	2.99	(0.81)	29.39	(7.29)
BFR 154	95.97	(13.53)	11.52	(2.73)	4.46	(1.60)	–	–
BFR 153	42.54	(10.82)	4.01	(0.27)	1.55	(0.15)	1.33	(0.40)
PBB 153	–	–	–	–	–	–	6.83	(0.89)
BFR 183	4.17	(3.57)	0.57	(0.19)	0.32	(0.08)	–	–
ΣBDE	1281.18	(252.32)	305.24	(61.70)	39.74	(5.09)	270.06	(37.39)
%BDE 47	53.83	(363.92)	68.81	(123.29)	41.76	(9.99)	64.78	(1.09)

Table 4

Mean OC concentrations (standard deviation) in an adult male killer whale stranded in Roundstone, Galway in 2017. Concentrations are reported in ng/g lipid weight (lw).

OC	Mean (SD)
% Lipid	56.495 (6.21547)
α-HCH	11.23 (0.62)
γ-HCH	5.86 (0.55)
HCB	186.73 (8.75)
δ-HCH	15.17 (1.05)
Aldrin	1.26 (0.46)
Isobenzan	1.65 (0.39)
Isodrin	3.33 (0.71)
Heptachlor epoxide	65.19 (33.69)
o,p'-DDE	0.43 (0.17)
Endosulphan A	57.27 (14.69)
Dieldrin	272.65 (124.38)
p,p'-DDE	42239.14 (2721.04)
o,p'-DDD	1654.14 (10.35)
Endrin	0.00 (0.00)
Endosulphan B	4.61 (1.52)
p,p'-DDD	4434.08 (413.78)
p,p'-DDT	184.63 (68.58)
o,p'-DDT	280.88 (20.82)
Endosulphan II	5.26 (7.44)
Σ19OCs	49423.50 (3210.80)
ΣDDTs ^a	48793.297 (2146.25)
ΣHCHs ^b	32.253 (1.57)

^a Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, p,p'-DDT and o,p'-DDE.^b Sum of α-HCH, γ-HCH and δ-HCH.

expected. The adult female from the Tramore stranding had the lowest total concentrations for both PCBs and PBDEs. This result is consistent with other studies reporting lower amounts of persistent organic pollutants in females compared to males (Hayteas and Duffield, 2000; Lundin et al., 2016). It is possible that the Roundstone male was a young individual that had less time to bio-accumulate, and that the Tramore female may have recently reproduced and offloaded contaminants, or had feeding grounds in a less contaminated ecosystem, but little is known about the life history of these individuals sampled.

6. POP concentrations

This study found sumPCB concentrations in the range of 1.5 mg/kg to 49.3 mg/kg on a lipid weight basis across all samples, values that conform to concentrations previously reported (Hayteas and Duffield, 2000; Ross et al., 2000; Kajiwara et al., 2006; Wolkers et al., 2007). To the authors' knowledge there is only one other published account of

pollutant concentrations from a killer whale sampled in Ireland; that individual, stranded at Roches Point, County Cork in 2001, was reported to have sumPCB level equal to 25.38 mg/kg lw, under one-half the concentrations reported here (McHugh et al., 2007). However, the same study of killer whales from British waters reported sumPCB between 1.45 and 248.20 mg/kg lw.

Total PBDE concentrations of 0.04–1.2 mg/kg lw were found across all samples and conform to the concentrations reported in the literature (Kajiwara et al., 2006; Wolkers et al., 2007; Haraguchi et al., 2009). Samples analysed by Law et al., 2005 from UK waters showed BDE concentrations of 0.27–11.06 mg/kg lw. A similar range of 0.67–2.93 mg/kg lw and 0.20–2.75 mg/kg lw was reported by Krahn et al. (2009) in their analysis of male and female killer whales.

ΣDDT and ΣHCHs were determined and levels reported here are lower than those in the literature (Hayteas and Duffield, 2000; Kajiwara et al., 2006; Krahn et al., 2007; Haraguchi et al., 2009). Aguilar (1984) suggested comparing the ratio between DDE and ΣDDT as a rudimentary indicator of historical pollution. A ratio value of > 0.6 was proposed as an indicator that contamination levels may stem from a historical source (Aguilar, 1984). Here a DDE/ΣDDT ratio of 0.86 was found, where ΣDDT equals the sum of Sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, p,p'-DDT and o,p'-DDE. This gives a crude indication that ΣDDT concentrations are a result of legacy emissions. Here, a p,p'-DDE concentration of 42.2 mg/kg lw was recorded; over double the 19.60 mg/kg lw from the killer whale stranded at Roches Point (McHugh et al., 2007). From a global perspective however, these results are relatively low, particularly in comparison to the highly contaminated transient killer whales from coasts along the north-east Pacific Ocean (Krahn et al., 2007).

7. Effects of contaminants

Ethical, legal and logistical challenges preclude controlled exposure and therefore cause-effect studies into the effects of contaminants on killer whales. However, immune, endocrine and reproductive system dysfunction has been linked to PCB contamination in a number of other odontocetes. In harbour porpoises, Jepson et al. (2005) observed a significant difference in the concentrations of PCBs between two groups of harbour porpoises. One group consisted of animals that died from acute physical trauma, the other of infectious disease. This study found that the group with infectious disease as the cause of death had a higher concentration of total PCBs, often exceeding the toxicity threshold of 17 mg/kg. It was also observed that this relationship was no longer significant where this threshold was not met (Jepson et al., 2005). Considering the challenges associated with gathering empirical data on remote species such as killer whales, models provide an important foundation in the association of contaminant concentrations and

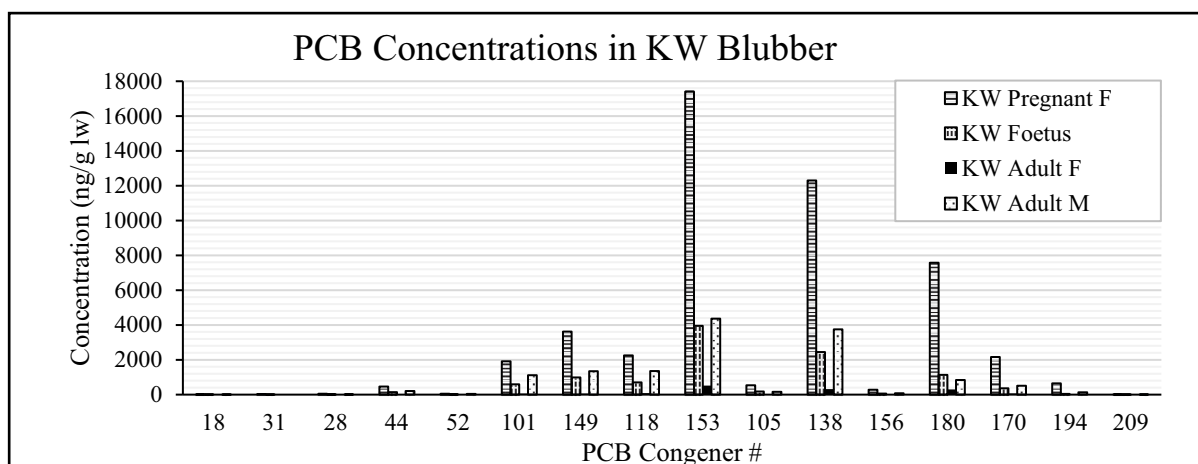


Fig. 2. Direct comparison of congener specific PCB concentrations (ng/g lw) per individual.

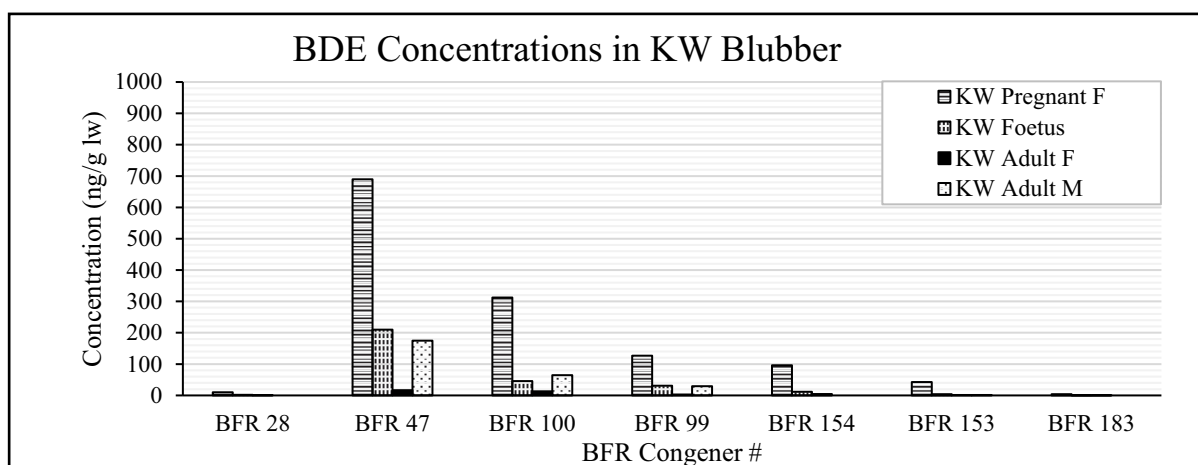


Fig. 3. Direct comparison of congener specific BFR concentrations (ng/g lw) per individual.

potential risks to the species. A recent toxicity study into the immunotoxic effect of contaminant cocktails on marine mammals, including killer whales, confirmed that PCB exposure impacted immunity (Desforges et al., 2017). In their 2018 study, Hall et al. (2018) developed models incorporating PCB effects on immune function and population growth rates. This study predicted that high exposure to PCBs, accumulation of > 5 mg/kg lipid per annum coupled with high concentrations in female blubber, would impact calf survival (Hall et al., 2018). While accumulation rates of the mother-calf pair in this study are unknown, the high concentrations found in the mother raises questions regarding the viability of the foetus. Reproductive effects of PCBs have also been investigated in bottlenose dolphins in a probability-based study by Schwacke et al. (2002). Here models suggested it was likely that high PCB concentrations negatively affected successful reproduction. However, there was a large degree of uncertainty associated with models which incorporated parameters related to other marine mammalian species such as mink (*Mustela vison*) (Schwacke et al., 2002; Witting, 2018).

8. Conclusion

Concentrations of persistent organic pollutants from four killer whales stranded in Ireland were investigated. One killer whale, the Doohoma female, exceeded the suggested toxicity threshold of 17 mg/kg. The role high concentrations of persistent pollutants may have played, if any, in its possible cause of death is not known. Although this

whale exceeded the toxicity threshold, the high concentration of contaminants did not appear to affect the fecundity of this animal as it was pregnant with a near term foetus. It is vital that concentrations of legacy pollutants are continually monitored and reported in order to add to the knowledge of pollutants across the entire range of this species. In addition to monitoring concentrations of pollutants, insight into the life history of individual animals under examination may allow for a better interpretation of the complex interactions between contaminants and their effects on marine mammals. Additional information and empirical data surrounding killer whale populations is required in order to accurately predict the fate of this species. (Desforges et al., 2018; Witting, 2018).

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2019.110699>.

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