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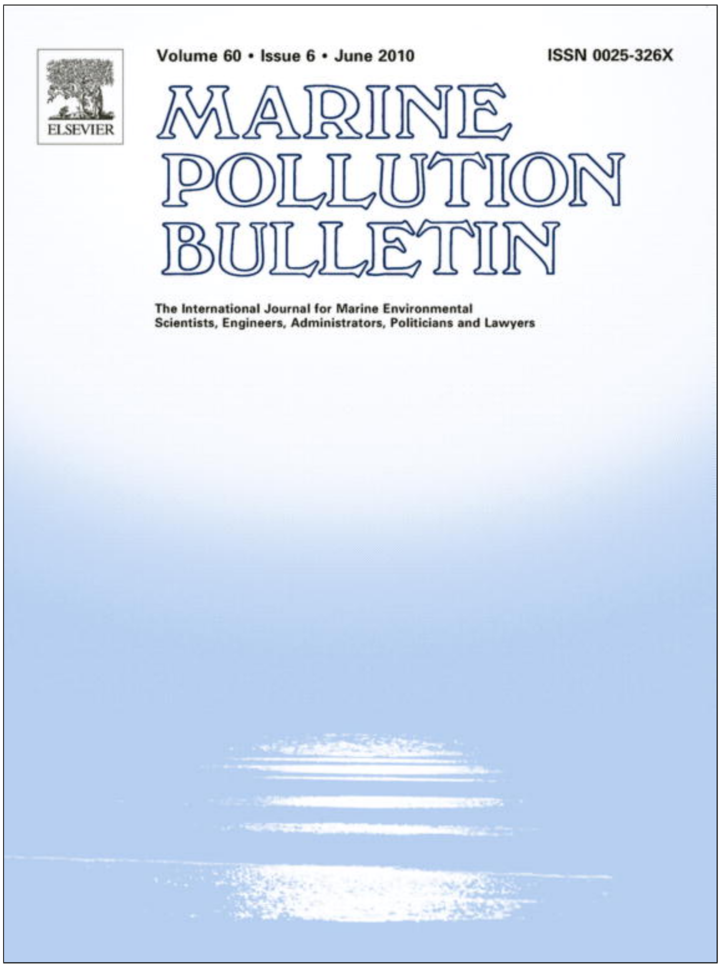

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PCBs and organochlorine pesticides in Hector's (*Cephalorhynchus hectori hectori*) and Maui's (*Cephalorhynchus hectori maui*) dolphins

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A R T I C L E I N F O

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A B S T R A C T

Polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticide levels were determined in blubber samples collected from stranded and incidentally by-caught Hector's (*Cephalorhynchus hectori hectori*) and Maui's (*Cephalorhynchus hectori maui*) dolphins from New Zealand waters between 1997 and 2009. PCBs (45 congeners) and a range of OC pesticides including dieldrin, hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), along with its metabolites DDE and DDD were determined. OC pesticides dieldrin, *p,p*′-DDE, *p,p*′-DDD and *p,p*′-DDT were present at the highest concentrations. Sum DDT concentrations ranged from 93.7 to 8210 (Mean = 1358, S.D = 1974) and 252.4 to 57,390 (Mean = 12,389, S.D = 18,161) µg/kg wet weight in females and males, respectively. Similarly, Σ45CB concentrations ranged from 45.5 to 981.3 (Mean = 333.2, S.D = 265.8) and 60.5 to 5574 (Mean = 1833, S.D = 1659) µg/kg wet weight in females and males, respectively. The transfer of ΣDDTs and summed PCBs (both as ΣICES7CBs and Σ45CBs) between a pregnant female and her unborn fetus was calculated at 5.7% and 4.3%, respectively. As the fetus was close to term, this likely represents the degree of placental transfer. Concentrations of OC pesticides determined in the present study are higher than those previously reported for Hector's dolphins. Sum DDT and DDE/ΣDDT levels calculated reveal New Zealand's legacy of DDT usage, particularly off the east coast of the South Island.

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1. Introduction

Marine mammals fill many diverse ecological roles, from primary consumers to top carnivores. Subsequently, they exhibit an extensive range of functional and morphological adaptations that may influence susceptibility or resistance to toxic substances (O'Hara and O'Shea, 2001). As apex predators, cetaceans can particularly accumulate high concentrations of contaminants, many of which vary with biological factors, for example, diet, body size, nutritive condition, gender and reproductive biology (Aguilar et al., 1999). Majority of contaminant burdens evident in dolphins reflect dietary sources, and are relative to inputs from both natural and anthropogenic inputs. The lipophilic nature of such chemicals facilitates their accumulation along food chains where, in the case of top predators, they may bio-accumulate to high concentrations. Many toxicological studies have focused on the pollutant burdens of cetaceans, particularly in small toothed (odontoceti) cetaceans (e.g., Kunito et al., 2004; Wafo et al., 2005; Hall et al., 2006; Borrell et al., 2001, 2007; Krahn et al., 2007; Lavery et al., 2008; Law et al., 2008; Pierce et al., 2008). The high metabolic rate and elevated trophic position of odontocetes within food webs increase their likelihood of accumulating persistent toxins, such as OC pesticides. These factors, in combination with the longevity and the large proportion of lipids present within cetaceans, facilitate bioaccumulation, a phenomenon that in some populations can result in high levels of toxicity (Reijnders and Aguilar, 2002).

Several studies have examined the biological effects of contaminants such as PCBs, and OC pesticides on marine mammal health and life history (e.g., Subramanian et al., 1987; Kuiken et al., 1994; Wells et al., 2005). Certain OCs (e.g., dieldrin, lindane) are known to be particularly toxic in the early developmental stages of life and have been identified as endocrine-disrupting chemicals. Such chemicals may interfere with the production and metabolism of hormones responsible for the maintenance of homeostasis and the regulation of reproduction processes (O'Hara and O'Shea, 2001). In marine mammals, persistent pollutants have also been

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associated with a variety of toxic effects including immune suppression and the development of infectious diseases (e.g., Kuiken et al., 1994; Jepson et al., 2005), reproductive impairment (e.g., Fujise et al., 1988; Schwacke et al., 2002; Wells et al., 2005) and the generation of tumors (e.g., De Guise et al., 1994; Martineau et al., 1999).

Data on levels of pollutants in marine mammals are more numerous in northern hemisphere cetaceans, particularly off western Europe, North America, Canada, Japan and Hong Kong (e.g., Minh et al., 1999; Hayteas and Duffield, 2000; Ross et al., 2000; Hobbs et al., 2001; Endo et al., 2003; Hobbs et al., 2003; Borrell and Aguilar, 2005; Mallory et al., 2005; Outridge et al., 2005; Roots et al., 2005; Hall et al., 2006; Hung et al., 2006; Borrell and Aguilar, 2007; Yang et al., 2007). However, only limited data exist for many other countries and regions (e.g., Africa, India). This is especially true of southern hemisphere waters such as the South Pacific (e.g., Kemper et al., 1994; Haynes et al., 2005; Lavery et al., 2008).

A range of organochlorine pesticides have historically been used in New Zealand including dichlorodiphenyltrichloroethane (DDT), dieldrin, heptachlor, hexachlorobenzene (HCB), chlordane, hexachlorocyclohexane (HCH) and aldrin (Buckland et al., 1998). However, few published data relating to such compounds or their effects on biological systems within New Zealand can be found in the literature (e.g., Buckland et al., 1990; Jones et al., 1996; Stockin et al., 2007). Presented here are data relating to PCBs and OC pesticide levels determined in Hector's (*Cephalorhynchus hectori hectori*, Van Bénéden, 1881) and Maui's (*Cephalorhynchus hectori maui*, Baker et al., 2002) dolphins.

Hector's dolphins are endemic to New Zealand, and are most concentrated along the west coast of the South Island (WCSI) between 41° 30′ and 44° 30′S. In particular, hotspots occur between Karamea and Makawhio Pt and around Banks Peninsula on the east coast of the South Island (ECSI). With a population estimate of 7240 (CV = 16.2%, Slooten et al., 2004), Hector's dolphins are listed as *endangered* by the International Union for Conservation of Nature (Reeves et al., 2008a). Maui's dolphin, a subspecies of Hector's dolphin (Baker et al., 2002), occur in a very small population (111, CV = 44%, Slooten et al., 2006) on the west coast of North Island (WCNI) between 36° 30′ and 38° 20′S and are considered *critically endangered* (Reeves et al., 2008b). Typically, *Cephalorhynchus* species occur within 8 km of the shoreline (Rayment et al., 2006), making them particularly vulnerable to point source pollutants. Here we describe pollutant levels in males and females, and examine for differences between individuals from different coastlines around New Zealand. Furthermore, we investigate parent-offspring pollutant transfer between a mother and her unborn fetus, and discuss pollutant levels and their implications at the population level.

2. Materials and methods

2.1. Sample collection and storage

Tissue sampling was undertaken on *Cephalorhynchus* that were recovered from stranding or net entanglements events around the New Zealand coast between 1997 and 2009 (Table 1). The majority of samples deemed suitable for toxicological analyses comprised Hector's dolphins ($n = 27$) recovered from individual strandings along ECSI and WCSI (Fig. 1). Of these, nine were from carcasses recovered from nets or confirmed as by-catch following post-mortem examination. A further subset of Maui's dolphin samples ($n = 3$) were also included. All carcasses were examined and subjectively divided into three categories (*fresh, mild* and *moderate*) based on the degree of post-mortem autolysis evident (Table 1). Prior to sampling, external measurements (cm) and body weight (kg) were recorded (Table 1).

Tissue samples were taken for PCB and OC analysis using standard protocols (e.g., Kuiken et al., 1994; Jepson et al., 2005). In summary, cross sectional samples of blubber adjacent to the dorsal fin were excised from each carcass using a stainless steel knife. Samples were contained in whirlpak bags and stored at −20 °C. In order to assess pollutant transfer between parent and offspring, the transfer rate of ΣDDTs and ΣICES7CBs between a mother and her unborn fetus was calculated using methods outlined in Borrell and Aguilar (2005).

2.2. Chemical analyses

Organochlorine pesticides and CBs were determined in blubber by high resolution gas chromatography–high resolution mass spectrometry (HRGC–HRMS). Extraction and quantification of hexachlorocyclohexanes; *alpha*-HCH, *beta*-HCH, *gamma*-HCH (lindane), dieldrin, heptachlor, heptachlor epoxide, *alpha*-chlordane, *gamma*-chlordane and DDT plus metabolites *p,p′*-DDE, *p,p′*-DDD (also known as *p,p′*-TDE), *o,p′*-DDT, *p,p′*-DDT and 45 chlorobiphenyl congeners (CB1, CB3, CB4/10, CB15, CB19, CB28, CB37, CB44, CB49, CB52, CB54, CB70, CB74, CB77, CB81, CB99, CB101, CB104, CB105, CB110, CB114, CB118, CB123, CB126, CB138, CB153, CB155, CB156, CB157, CB167, CB169, CB170, CB180, CB183, CB187, CB188, CB189, CB194, CB196/203, CB200, CB202, CB205, CB206, CB208 and CB209) was conducted as follows:

2.2.1. Lipid extraction

Samples were thawed and a portion of the blubber tissue (~10 g) was removed and chopped into small cubes (~1 cm). The sample was accurately weighed and placed into a blender with powdered Na_2SO_4 and blended until the mixture was free-flowing. Each sample was subsequently packed into a Soxhlet extraction thimble. The blender container was cleaned between samples by thorough scrubbing with hot water and detergent, and rinsing with hot water, followed by acetone, toluene and dichloromethane. Before extraction, a range of isotopically labeled internal standards was added to each sample. Each sample was Soxhlet extracted with dichloromethane:hexane (1:1 v/v) for at least 16 h. The sample extracts were evaporated to 100 ml on a rotary evaporator, from which portions were split out for the different analyses and the remainder kept for archival.

2.2.2. Lipid determination

A 10% split of each sample extract was evaporated to constant weight in a tared flask on a rotary evaporator. The lipid content was measured by difference.

2.2.3. Organochlorine pesticides

A 10% split of each sample extract was subjected to further clean-up for the analysis of organochlorine pesticides. The extracts were evaporated to residual lipid level and mixed with 2 ml of toluene. Subsequently, 20 ml acetonitrile of was added to each sample, mixed and placed in a freezer overnight to freeze out some of the lipids. The extracts were filtered through a cotton wool plug and transferred into ethyl acetate:cyclohexane solvent (1:1 v/v). The remaining lipids were removed by gel permeation chromatography (GPC) on a Phenomenex Envirosep ABC 300 × 7.8 mm GPC column using ethyl acetate:cyclohexane (1:1 v/v). The GPC extracts were finally transferred to hexane and chromatographed on a 10 g column of florisil, the pesticides being eluted with hexane:diethyl ether (94:6 v/v). The solvent was removed by nitrogen blowdown and the solution reconstituted in 100 µl of toluene containing the recovery standard ($^{13}C_{12}$–CB) and analysed by HRGC–HRMS using the accurate mass ions described in USEPA Method 1699.

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Table 1
Specimen details for *Cephalorhynchus* stranded and by-caught in New Zealand waters between 1997 and 2009. Note: B = recovered from a net or diagnosed as a suspected by-catch at necropsy, S = Stranded/Beach cast, TBL = Total Body Length, F = Female, M = Male.

MU Ref	DOC Code	Sex	TBL (cm)	Stranding	Source	Location/Region	Condition	Latitude	Longitude
Cephalorhynchus hectori hectori									
WB00-23_31309	#250	F	120	27/11/1997	B	North Canterbury, South Island	Mild	43° 20′S	172° 57′E
W04-20_36528	H84/04	F	143	9/10/2004	S	New Brighton Beach, Christchurch, South Island	Mild	43° 30′S	172° 43′E
WB02-10_32950	H43/01	F	136	22/12/2001	B	Paroa Beach, Greymouth, South Island	Fresh	43° 33′S	172° 45′E
W07-17_40256	H145/07	F	141	29/04/2007	S	Punakaiki, Greymouth, South Island	Mild	42° 06′S	171° 20′E
W07-26_40850	H150/07	F	141	16/09/2007	S	Waikouaiti River, Dunedin, South Island	Mild	45° 38′S	170° 39′E
W07-24_40664	H149/07	F	139	27/07/2007	S	Buller Kawatiri, South Island	Fresh	41° 30′S	171° 56′E
W08-01_41223	H157/08	F	54	8/1/2009	S	Te Wae Wae Bay, South Island	Fresh	46° 09′S	167° 24′E
W08-20_42649	H167/08	F	136	3/10/2008	S	Ross Beach, Totara, Hokitika, South Island	Moderate	42° 52′S	170° 47′E
W08-18_42366	H168/08	F	142	7/10/2008	S	Waipara Rocks, Canterbury, South Island	Fresh	43° 08′S	172° 48′E
W08-21_42644	H169/08	F	133	7/11/2008	S	North of Hector Beach, Ngakawau, South Island	Mild	41° 36′S	171° 52′E
W08-10_42764	H163/08	F	136	2/8/2008	S	Paroa Beach, Greymouth, South Island	Mild	42° 30′S	171° 10′E
W09-01_42749	H176/09	F	137	21/01/2009	S	Keepers Beach, North otago, South Island	Mild	45° 23′S	170° 52′E
W07-16_39822	H133/07	F	143	6/1/2007	B	Gillespie Beach, South Westland, South Island	Fresh	43° 19′S	170° 00′E
W06-21_39484	H124/06	F	67	10/11/2006	S	Farewell spit, Golden Bay, South Island	Mild	40° 31′S	172° 51′E
W07-03_39794	H132/07	F	80	6/1/2007	B	Port Craig and Flat Beach, Otago, South Island	Severe	46° 13′S	167° 21′E
W07-05_39824	H130/06	M	78	7/12/2006	S	Gore Bay, Canterbury, South Island	Fresh	43° 51′S	173° 18′E
WB00-24_31311	#279	M	123	5/2/1999	B	Little Wanganui River, South Island	Mild	41° 23′S	172° 03′E
WB02-28_33351	H44/01	M	127	24/12/2001	B	Wasdyke, Timaru, South Island	Mild	44° 24′S	171° 15′E
WB02-09_32949	H42/01	M	121	1/12/2001	B	Karoro Beach, Greymouth, South Island	Moderate	43° 31′S	172° 44′E
WB01-15_32208	H36/00	M	122	19/12/2000	B	Leithfield Beach, Canterbury, South Island	Mild	43° 12′S	172° 45′E
WB01-14_32211	#316	M	121	25/02/2001	B	North Beach, Westport, South Island	Mild	41° 43′S	171° 34′E
W06-16_39380	H122/06	M	129	4/9/2006	S	Twin Beach, Buller, South Island	Mild	41° 15′S	172° 05′E
WS06-23_39548	H126/06	M	114	30/11/2006	S	Te Wae Wae Bay, South Island	Mild	46° 09′S	167° 25′E
W07-29_41362	H155/07	M	135	14/12/2007	S	Long Beach, Otago, South Island	Mild	45° 45′S	170° 39′E
W07-11_39860	H136/07	M	125	20/02/2007	S	Rarangi Beach, Blenheim, South Island	Fresh	41° 24′S	174° 02′E
W08-19_42428	H166/08	M	120	2/10/2008	S	Rapahoe Beach, Greymouth, South Island	Mild	42° 22′S	171° 14′E
W06-24_39587	H129/06	M	107	6/12/2006	S	Kaikoura, South Island	Fresh	42° 53′S	173° 21′E
Cephalorhynchus hectori maui									
W07-28_41043(A)	H153/07	F	70	10/11/2007	S	Manu Bay, Raglan, North Island	Fresh	37° 49′S	174° 48′E
W07-28_41043	H153/07	F	153	10/11/2007	S	Manu Bay, Raglan, North Island	Mild	37° 49′S	174° 48′E
W06-22_39485	H125/06	M	73	13/11/2006	S	Sunset Beach, Port Waikato, North Island	Mild	37° 23′S	174° 42′E

2.2.4. Polychlorinated biphenyls (PCBs)

A 50% split of each sample extract was subjected to further clean-up for the analysis of polychlorinated biphenyls. The extracts were transferred to hexane and partitioned with concentrated H_2SO_4, followed by distilled water. After drying through Na_2SO_4, the hexane extracts were chromatographed on a reactive multi-column containing sodium silicate and sulfuric acid/sodium hydroxide impregnated silica gel by elution with hexane. Finally the sample extracts were further cleaned on a Bond–Elut SPE cartridge, eluting with hexane. The hexane was removed by nitrogen blowdown and the residue reconstituted in 100 µl of nonane containing the recovery standards and analysed by HRGC–HRMS.

2.2.5. Instrumental

The HRGC–HRMS analyses were performed on an Agilent 6890 gas chromatograph equipped with a Phenomenex Zebron ZB5 60 m × 0.25 mm id × 0.25 µm phase thickness column (for organochlorine pesticides) or an Agilent J&W DB1 30 m × 0.25 mm id × 0.25 µm phase thickness column (for polychlorinated biphenyls) using splitless injection, coupled to a Micromass AutoSpec Ultima high resolution mass spectrometer. All analyses were performed under the laboratory's IANZ accreditation (No. 131).

2.2.6. Quality assurance

The analyses were based on USEPA Methods 1668A (PCBs) and 1699 (Organochlorine pesticides). All QC/QC procedures employed were based on those described in the USEPA methods. This included analysis of a laboratory method blank and spiked control sample with every batch of 15 samples. The results of these QC samples were assessed against criteria set out in the USEPA methods. In addition, each sample was fortified with a range of isotopically labeled internal standards, and the recovery of the standards also assessed against criteria set out in the USEPA methods.

2.2.7. Data analyses

Samples were categorized based on species (Hector's or Maui's dolphin), coastline (WCNI, ECNI, WCSI or ECSI), sex (male or female) and age class (mature or immature). Due to species distribution, only Maui's dolphins were categorized along WCNI. Gender was typically determined directly via anatomy during a post-mortem examination. In females, sexual maturity was confirmed during necropsy by the presence of *Corpora lutea* or *Corpora albicantia* on either ovary (Slooten 1991). Male maturity was inferred via total body length (TBL) and gross examination of the testes. Males whose testes at macroscopic level appeared undeveloped and whose TBL <120 cm were considered immature. Males whose testes appeared developed and whose TBL exceeded 120 cm were considered mature (Slooten 1991). Regression analysis with binary predictors was used to assess pollutant loads observed in males and females examined from different regions of the New Zealand coastline. Sum DDT concentrations were calculated based on p,p'-DDE + p,p'-DDD + o,p'-DDT + p,p'-DDT). The ICES list of seven congeners were used to allow comparisons to be made across datasets in which, overall, different suites of congeners were determined. The seven CB congeners on the ICES7 list are CB28, CB52, CB101, CB118, CB138, CB153 and CB180.

3. Results and discussion

3.1. Samples

Thirty samples were analysed, comprising 13 males and 17 females (Table 1). Males and females ranged from 73 to 135 and 54 to 153 cm in TBL, respectively (Table 1). The sample set included 22 mature and 8 immature animals representing each gender and coastline. Majority of samples ($n = 21$) originated from carcasses that had been found beach cast. A further subset ($n = 9$)

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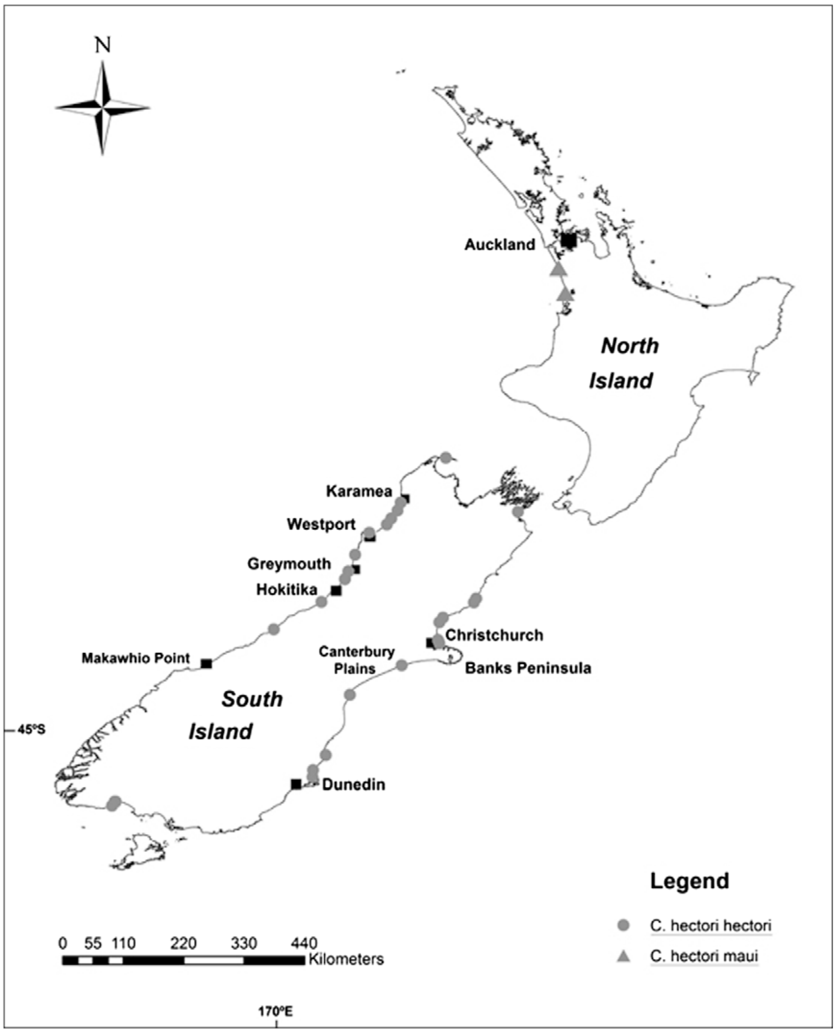

Fig. 1. Map of New Zealand showing origin of Hector's (circles) and Maui's (triangle) dolphins sampled for PCB and OC analyses between 1997 and 2009. Note: Each symbol may represent more than one individual.

were collected from individuals that had recovered from fishing nets and/or exhibited evidence of by-catch trauma during a post-mortem examination (Table 1).

3.2. Organochlorines and PCBs

Concentrations of OC pesticides and summarized PCBs in blubber are listed in Table 2. Log ΣICES7CBs, Σ45CBs, dieldrin and ΣDDT by gender and age class are represented in Fig. 2. Contaminant ranges reported by region are further summarized in Table 3. Further discussion of OC and PCB levels refer to the *Cephalorhynchus* genus collectively, unless otherwise stated.

Of the organochlorines determined, *p,p′*-DDE (up to 53,000 μg/kg wet weight), *p,p′*-DDT (up to 2400 μg/kg wet weight), *p,p′*-DDD (up to 1200 μg/kg wet weight) and *o,p′*-DDT (up to 800 μg/kg wet weight) were present at the highest concentrations. Dieldrin (up to 490 μg/kg wet weight) and HCB (up to 90 μg/kg wet weight) were detected at considerably lower values. Alpha-HCH, aldrin and heptachlor were not detected in any of the samples examined. Sum DDT concentrations ranged from 93.7 to 57,390 μg/kg wet weight (Mean = 6138, S.D = 13,020). These values are considerably higher than the concentrations reported for New Zealand common dolphins (*Delphinus* sp.), whose ΣDDT concentrations ranged from 17 to 4430 μg/kg (Mean = 1302, S.D = 1263) wet weight, respectively (Table 4, Stockin et al., 2007). This represents a 6.9 and 9.7-fold increase in male and female *Cephalorhynchus*, respectively, based on mean ΣDDT values reported for *Delphinus* (Table 4, Stockin et al., 2007).

Organochlorine concentrations in the blubber of reproducing female dolphins are usually lower than those of adult males as a result of transplacental and lactational transfer of these lipophilic contaminants to the calves. In this case, ΣDDT concentrations in the blubber ranged from 93.7 to 8210 (Mean = 1358, S.D = 1974) and 252.4 to 57,390 (Mean = 12,389, S.D = 18,161) μg/kg wet weight in females and males, respectively. Similarly, Σ45CB concentrations, the sum of the 45 congeners determined, ranged from 45.5 to 981.3 (Mean = 333.2, S.D = 265.8) and 60.5 to 5574 (Mean = 1833, S.D = 1659) μg/kg wet weight in females and males, respectively. Mean Σ45CB values reported here for male and female *Cephalorhynchus* were 2.2 and 2.4 times higher than were previously recorded in male and female *Delphinus* from New Zealand waters, respectively (Table 4, Stockin et al., 2007). Similar patterns were observed in ΣICES7CBS which were 1.9 and 2.5 times higher in male and female *Cephalorhynchus*, respectively (Table 4, Stockin et al., 2007).

The transfer of organochlorine pesticides and chlorobiphenyls from a Maui's dolphin to her unborn fetus was estimated. In terms of blubber concentrations, ΣDDT and PCB levels (both as Σ45CBs and ΣICES7CBs) were approximately half of those in the mother (PCBs 0.45× lower; ΣDDT 0.6× lower). The mean transfer of

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Table 2
Lipid content, PCB and OC pesticide levels (μg/kg wet weight) determined in the blubber of *Cephalorhynchus* sampled from New Zealand waters between 1997 and 2009. Note: M = Male, F = Female, ND = Not Detected, NQ = Not Quantified.

MU Ref	DOC Ref	Sex	Lipid (%)	β-HCH	γ-HCH	HCB	Dieldrin	Heptachlor-epoxide	α-Chlordane	γ-Chlordane	p,p′-DDE	p,p′-DDD	o,p′-DDT	p,p′-DDT	ΣDDT	Σ45CBs	ΣICES7CB*
Cephalorhynchus hectori hectori																	
WB00-23_31309	–	F	90.5	4.6	0.54	61	140	14	39	1.6	7300	320	130	460	8210	937.8	700.1
W04-20_36528	H84/04	F	91.6	ND	ND	3.5	14	ND	2.8	0.6	420	38	3.9	24	485.9	301.4	208.9
WB02-10_32950	H43/01	F	96	1.2	ND	19	34	4	29	2.5	720	57	22	100	899	237.6	171.3
W07-17_40256	H145/07	F	67.2	2.2	ND	37	33	4.3	23	ND	630	32	14	80	756	238.1	170.4
W07-26_40850	H150/07	F	90.5	1.6	ND	33	43	5.4	12	ND	3200	150	80	270	3700	981.3	742.7
W07-24_40664	H149/07	F	59	4.2	ND	29	63	12	32	0.79	1400	75	26	89	1590	453	331.2
W08-01_41223	H157/08	F	95	–	ND	3.3	5.3	ND	1.5	ND	140	9.6	2.3	22	173.9	73.6	41.6
W08-20_42649	H167/08	F	82.6	–	ND	6	8.2	–	2.8	ND	130	14	3.4	26	173.4	83.3	52.3
W08-18_42366	H168/08	F	94	–	ND	2.7	5.7	ND	1.7	ND	500	30	6.2	33	569.2	291.5	193.8
W08-21_42644	H169/08	F	94.3	–	ND	43	69	–	31	–	800	48	23	110	981	287.3	203.4
W08-10_42764	H163/08	F	91.5	–	ND	5	11	ND	18	ND	600	22	16	72	710	266.9	180
W09-01_42749	H176/09	F	87.5	–	0.3	16	62	–	5.1	ND	1900	71	26	140	2137	343.2	225.8
W07-16_39822	H133/07	F	91.3	ND	ND	6.4	6	ND	2.7	ND	73	5.7	–	15	93.7	45.5	28.9
W06-21_39484	H124/06	F	87.2	–	ND	44	50	–	15	ND	880	25	14	37	956	211.4	165.4
W07-03_39794	H132/07	F	59.4	–	ND	17	41	–	4.2	ND	750	110	15	52	927	195.2	142.7
W07-05_39824	H130/06	M	86.2	ND	ND	7.1	6.2	ND	ND	ND	230	8.9	2.5	11	252.4	60.5	45.9
WB00-24_31311	–	M	80.5	7.2	0.26	67	150	31	89	3.7	4200	140	120	280	4740	826.5	640.3
WB02-28_33351	H44/01	M	90.1	7.7	0.58	55	490	32	120	4.4	53,000	1200	790	2400	57,390	5574	4276
WB02-09_32949	H42/01	M	82.5	9.9	ND	59	180	38	170	3	8500	230	150	320	9200	1510	1144
WB01-15_32208	H36/00	M	93.1	10	0.58	65	300	31	110	2.1	44,000	750	800	1700	47,250	3136	2315
WB01-14_32211	–	M	90.8	8.7	0.36	47	170	33	130	3.5	6700	220	130	350	7400	1126	851.1
W06-16_39380	H122/06	M	91.4	5.7	ND	45	82	18	96	1.3	5600	88	73	120	5881	1106	838.8
WS06-23_39548	H126/06	M	85.6	3.1	ND	48	140	6	19	1.3	2900	380	77	240	3597	820.4	604.6
W07-29_41362	H155/07	M	87.1	6.3	0.3	87	300	21	29	ND	6400	290	99	320	7109	4180	3238
W07-11_39860	H136/07	M	73	6.6	ND	48	100	18	78	ND	12,000	180	130	180	12,490	3081	2240
W08-19_42428	H166/08	M	94.6	–	ND	90	140	–	90	1.6	1900	77	42	180	2199	597.6	439.1
W06-24_39587	H129/06	M	95.1	–	0.19	61	47	–	7.1	ND	1300	46	11	53	1410	299.2	217.3
Cephalorhynchus hectori maui																	
W07-28_41043 (A)	H153/07	F	78.1	–	ND	6.3	7.7	ND	1.6	ND	230	17	3.8	22	272.8	192.4	140.1
W07-28_41043	H153/07	F	95.5	ND	ND	5.7	7.9	ND	–	ND	380	27	6.5	43	456.5	525.5	318.1
W06-22_39485	H125/06	M	66.1	–	0.27	15	110	–	11	ND	2000	100	9.6	41	2151	1516	1164

* The seven CB congeners included on the list developed by the ICES7 for comparative purposes are CB28, CB52, CB101, CB118, CB138, CB153 and CB180.

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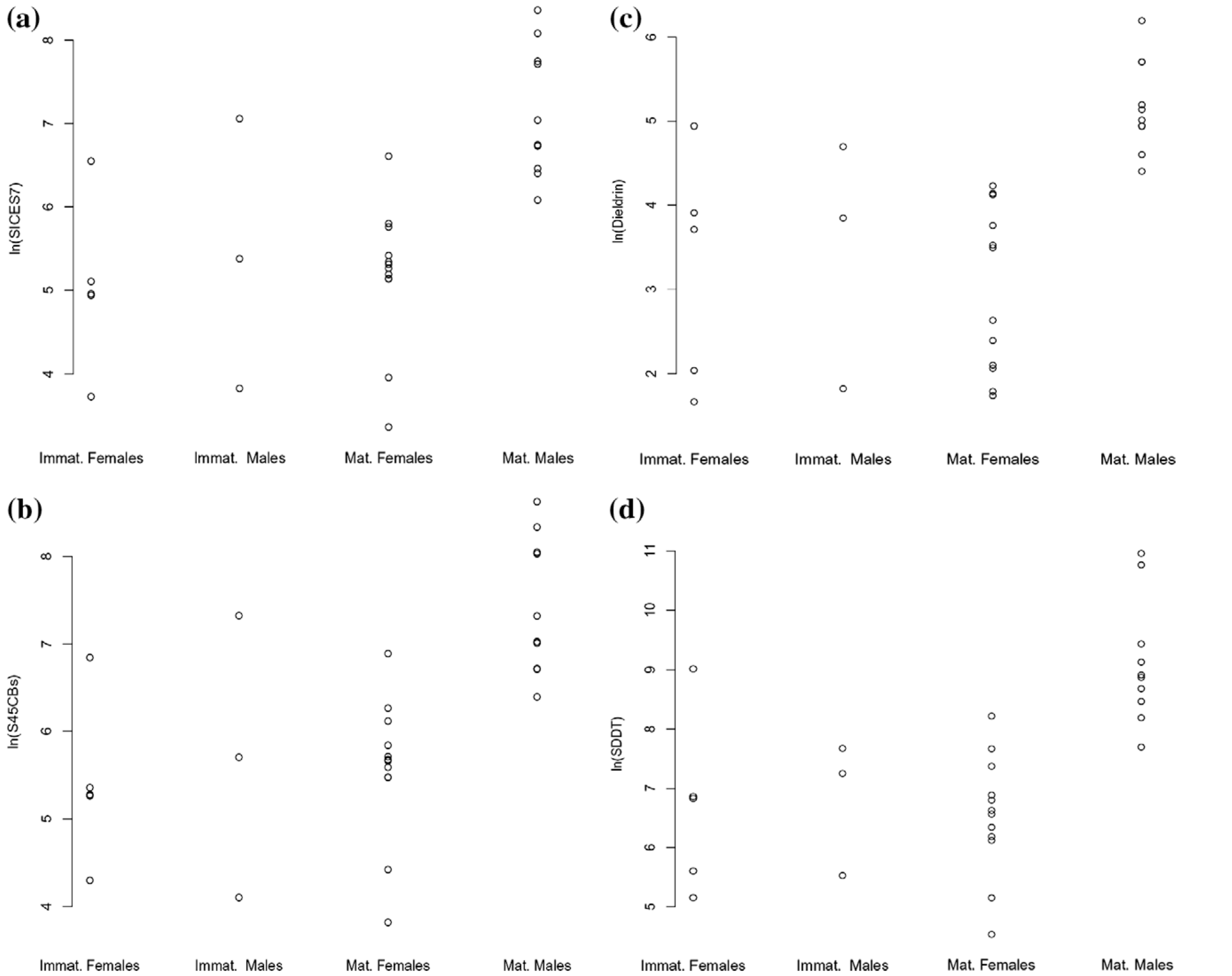

Fig. 2. Log (a) ΣICES7CBs, (b) Σ45CBs, (c) dieldrin and (d) ΣDDT in *Cephalorhynchus* by sex and age class from specimens sampled in New Zealand between 1997 and 2009.

ΣDDTs and PCBs between mother and offspring, as defined by Borrell and Aguilar (2005) was calculated at 5.7% and 4.3%, respectively. Slooten (1991) indicates that the body length at birth for Hector's dolphin is 70–80 cm. In this instance, the fetus body length was 70 cm, indicating that it was close to term. We may, therefore, assume that around 5% represents the level of transplacental transfer in this mother-fetus pair. The major transfer likely occurs postpartum via lactation e.g., Stockin et al. (2007) reported overall transmissions of over 40% for both sets of organochlorines between a common dolphin mother-calf pair in Auckland's Hauraki Gulf, New Zealand. In the present study, examination of the female's ovaries revealed only one corpora scar (Massey University, unpubl. data), suggesting this likely represents her first pregnancy. This is significant since the offloading of contaminants is typically greater for the first born than for subsequent offspring (Borrell and Aguilar, 2005).

Dose-response relationships, based on experimental studies of PCB-induced immunological and reproductive effects in mammals have led to a proposed blubber total PCB (based on the Aroclor 1254 formulation) threshold concentration for adverse health effects in all marine mammals of 17 mg/kg lipid weight (Kannan et al., 2000). As analyses are now conducted on a congener basis, a conversion factor of three times the ΣICES7CB congeners (Table 4) and the total PCB concentration has been established to allow comparisons (Jepson et al., 2005). Applying the conversion factor to the data for *Cephalorhynchus*, the overall range of total PCB concentrations is from 0.1 to 14 mg/kg lipid weight (Mean = 2.6 mg/kg lipid weight), i.e., below the threshold concentration derived by Kannan et al. (2000).

In the present study, the ΣICES7CB concentrations ranged from 28.9 to 742.7 (Mean = 236.3, S.D = 200.1) and 45.9 to 4276 (Mean = 1385, S.D = 1267) μg/kg wet weight in females and males, respectively. There are a limited number of other data available for Hector's dolphins, from an earlier investigation by Jones et al. (1999). In that study, ΣICES7CB concentrations in six Hector's dolphins ranged from 447 to 706 (Mean = 577, S.D = 130) and 319 to 1916 (Mean = 887, S.D = 355) μg/kg wet weight in females and males, respectively. This represents a 2.4 and 1.6-fold increase in the present study compared with the mean levels previously reported in female and male Hector's dolphins. An earlier study by Baker (1978) reported ΣDDT 45 μg/kg and a DDE/ΣDDT ratio of 0.47 for a single male Hector's dolphin from the Banks Peninsula in the mid-1970s.

Data available for other members of the *Cephalorhynchus* genus exhibit lower contaminant burdens. de Kock et al. (1994) reported ΣDDT levels in Heaviside's dolphins (*Cephalorhynchus heavisidii*) off South Africa ranging from 0.78 to 4.77 (Mean = 3.26, S.D = 1.52) and 0.25 to 4.21 (Mean = 1.88, S.D = 2.07) μg/kg wet weight for males and females, respectively. DDT and PCB levels observed in the melon of Commerson's dolphin (*Cephalorhynchus*

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Table 3
A summary of ΣDDT and Σ45CBs levels (μg/kg wet weight) determined in male and female *Cephalorhynchus* stranded and by-caught within New Zealand waters between 1997 and 2009 by region. Note: *n* = Sample Size, TBL = Total Body Length (cm), S.D = Standard Deviation.

ΣDDT by region	Male						Female					
Coast	*n*	TBL Range	TBL Mean	ΣDDT Range	ΣDDT Mean	S.D	*n*	TBL Range	TBL Mean	ΣDDT Range	ΣDDT Mean	S.D
West Coast, North Island	1	73–73	73	2151–2151	2151	–	2	70–153	54	272.8–456.5	364.7	272.8
East Coast, South Island	6	78–135	115.7	252.4–57,390	20,983	24,871	6	80–158	127.2	485.9–8120	2671	927
West Coast, South Island	5	120–129	122.8	2199–9200	5884	2654	8	133–143	137.7	93.7–1590	743.8	507.6
South Coast, South Island	1	114–114	114	3597–3597	3597	–	1	54–54	54	173.9	173.9	–
Σ45CBs by region	**Male**						**Female**					
Coast	*n*	TBL Range	TBL Mean	Σ45CBs Range	Σ45CBs Mean	S.D	*n*	TBL Range	TBL Mean	Σ45CBs Range	Σ45CBs Mean	S.D
West Coast, North Island	1	73–73	73	1516–1516	1516	–	2	70–153	54	192.4–525.5	359	235.5
East Coast, South Island	6	78–135	115.7	60.5–5574	2722	2169	6	80–143	127.2	195.2–981.3	508.4	353.1
West Coast, South Island	5	120–129	122.8	597.6–1510	230.2	344.2	8	133–143	137.7	45.5–453.0	820.4	135.4
South Coast, South Island	1	114–114	114	820.4–820.4	820.4	–	1	54–54	54	73.6–73.6	73.6	–

Table 4
A summary of OC and PCB levels (μg/kg wet weight) determined in male and female (a) *Cephalorhynchus* (*n* = 30) stranded and by-caught within New Zealand waters between 1997 and 2009 and (b) *Delphinus* (*n* = 19) stranded and by-caught in New Zealand waters between 1999 and 2005 (source Stockin et al., 2007). Note: S.D = Standard Deviation.

	Male			Female		
	Range (*n* = 13)	**Mean**	**S.D**	**Range (*n* = 17)**	**Mean**	**S.D**
ΣDDT	252.4–57,390	12,389	18,161	93.7–8210	1358	1974
Dieldrin	6.2–490	170.4	128	5.3–140	33.7	34.8
HCB	7.1–90	53.4	23.6	2.7–61	19.9	18
ΣICESCB7	45.9–4276	1385	1267	28.9–742.7	236.3	200.1
Σ45CBs	60.5–5574	1833	1659	45.5–981.3	333.2	265.8
	Range (*n* = 12)	**Mean**	**S.D**	**Range (*n* = 7)**	**Mean**	**S.D**
ΣDDT	654–4430	1775	1217	17.0–337	140	114.4
Dieldrin	19.0–100	51.8	25.1	4.2–21.0	9.7	6.3
HCB	8.6–130	28.5	32.7	3.1–16.0	8.3	4.8
ΣICESCB7	192–1183	609.7	337.6	29.2–289	96.1	95.3
Σ45CBs	268–1634	851.3	466.4	48.9–386	141.4	126.5

commersonii) from the Kerguelen Islands (southern Indian Ocean) were reported as 1150 (±650) and 1150 (±770) μg/kg lipid weight, respectively (Abarnou et al., 1986). Previous HCB levels reported for Heaviside's dolphins ranged from 0.01 to 0.08 (Mean = 0.04, S.D = 0.03) and 0.01 to 0.06 (Mean = 0.04, S.D = 0.03) μg/kg for males and females, respectively (de Kock et al., 1994), while a value of 500 (±300) μg/kg was reported for Commerson's dolphin in the Kerguelen Islands (Abarnou et al., 1986).

As outlined by Aguilar (1984), the ratio of the concentration of *p,p′*-DDE to the sum of the concentrations of *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE (the DDE/ΣDDT ratio) can be used to identify recent inputs of DDT as it degrades to DDE over time. In the New Zealand *Cephalorhynchus*, this ratio ranges from 0.75 to 0.95 and 0.83 to 0.93, for Hector's and Maui's dolphins, respectively, indicating that these contaminants result from historic usage of DDT in New Zealand agriculture. Jones and Geisy (2000) suggest such use has resulted in many agricultural soils in New Zealand having higher concentrations of pesticides (particularly DDT) than those seen in "background" soils. A higher DDE/ΣDDT ratio was observed in the present study compared to that of a single male Hector's dolphin reported by Baker (1978) from Banks Peninsula, Canterbury, in the mid-1970s. Carcasses examined as part of the present study indicate approximately 10% (range 1.4–16%) of DDT residues within the tissues detected in *Cephalorhynchus* blubber remain as DDT, rather than the DDT metabolites DDD and DDE. During the earlier study by Baker (1978), this was estimated to be 32%, reflecting New Zealand's legacy of banned DDT metabolites within its marine environment.

A number of samples examined during the present study originated from carcasses retrieved from Canterbury beaches, along the ECSI (Fig. 1). The hinterland to Banks Peninsula (Canterbury Plains) is cited as being one of the most intensively agricultural areas of New Zealand (Baker 1978). Currently, two contaminants are considered to be of significance for soil conservation within this region, one of which is DDT and its residues DDD and DDE (Environment Waikato, 2004). Historically, DDT was applied widely to pasture in treatment of grass grub (*Costelytra zealandi*) and porina (*Wiseana* sp.) caterpillars. A subsequent legacy of DDD and DDE now persists in these soils as a result of extensive historical use. Cadmium accumulation from the past and present widespread use of phosphate fertilizers is of additional concern for this region.

Other regions of notable importance for Hector's dolphins examined during the present study include WCSI beaches between Karamea and Hokitika (Fig 1). Since the 1870s, the west coast has been considered New Zealand's most important mineral region, producing coal, gold and various aggregates, including cement, limestone and pounamu (greenstone). Mining and quarrying operations in this area include a mix of underground and opencast mines, quarries and operations that extract minerals from river beds. However, the extent of such activities on *Cephalorhynchus* inhabiting these coastal waters remains unclear, since trace elements were not investigated during the present study. An examination of OCs and PCBs in individuals sampled from the ECSI did exhibit higher levels of ΣDDT (up to 57,390 μg/kg wet weight) compared with dolphins from the WCSI, (9200 μg/kg wet weight). Indeed, a regression model of ln(ΣDDT) in mature individuals, controlling for differences in males and females, indicated ΣDDT was 3.0 times higher in individuals examined from ECSI compared with those examined from the WCSI ($p = 0.017$, Fig. 2). This was despite

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similar mean TBL for each region (Table 3). A similar pattern was observed in Σ45CBs, with the estimated burdens in ECSI adults being 2.9 times higher than that reported for WCSI adults ($p = 0.001$, Fig. 2). The observed difference between coasts was more pronounced in males than in females (Table 3), possibly owing to pollutant offloading in the mature females (Table 4), however this effect was not statistically significant.

Meaningful comparisons involving Maui's dolphins (WCNI) were not possible owing to the small sample size of this subspecies. However, trends in Σ45CBs revealed in male Maui's dolphins were on average over six times higher than WCSI Hector's dolphins but half than that recorded in ECSI animals. This is likely conservative given that the Maui's sub-sample comprised two females, one of which was a fetus. While values reported here indicate pollutant burdens to be generally higher on the ECSI, the potential impacts of leaching minerals from mining and quarrying activities remain unexamined for west coast individuals. Furthermore, the temporal scale and relatively small sample size used to represent the differing areas restrict conclusions being drawn from the data presented here.

Confounding factors are known to alter toxin loads and require consideration when examining the containment burdens of animals that have stranded, possibly due to ill health. We acknowledge toxin levels in specimens are variable with age and gender, and may change as a result of several different mechanisms, including decomposition (Borrell and Aguilar, 1990) and depletion of lipid reserves with disease or starvation (O'Shea, 1999). However, the examination of apparently healthy by-caught specimens, and our consideration of lipid content and body condition in the present study, alleviates many of these concerns. Consequently, the authors believe the toxicity levels reported herein fairly represent pollutant levels in *Cephalorhynchus* within New Zealand waters.

While it is widely acknowledged that coastal dolphins living within inshore waters close to agricultural and industrial activity tend to accumulate higher concentrations of toxins (O'Shea, 1999), few pollutant data are available for New Zealand marine mammals. This study reflects high similar pollutant burdens in Hector's and Maui's dolphins, thus highlighting the potential vulnerability of this genus to coastal anthropogenic impacts. However, no animal examined as part of this study revealed total PCB concentrations over the threshold concentration considered to have immunological and reproductive effects. Consequently, these pollutants alone unlikely explain the failing recovery of *Cephalorhynchus* within New Zealand waters. However, it should be noted that trace elements in addition to other emerging contaminants (e.g., brominated flame retardant PBDEs, perfluorinated chemicals) were not examined within the present study. As such, it is not possible to comment upon the potential impacts of these chemicals without further investigation.

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