



Linking pollutant exposure of humpback whales breeding in the Indian Ocean to their feeding habits and feeding areas off Antarctica[☆]



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ABSTRACT

Humpback whales, *Megaptera novaeangliae*, breeding off la Reunion Island (Indian Ocean) undergo large-scale seasonal migrations between summer feeding grounds near Antarctica and their reproductive winter grounds in the Indian Ocean. The main scope of the current study was to investigate chemical exposure of humpback whales breeding in the Indian Ocean by providing the first published data on this breeding stock concerning persistent organic pollutants (POPs), namely polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), DDT and its metabolites (DDTs), chlordane compounds (CHLs), polybrominated diphenyl ethers (PBDEs), and methoxylated PBDEs (MeO-PBDEs). Analyses of stable isotopes $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in skin resulted in further insight in their feeding ecology, which was in agreement with a diet focused mainly on low trophic level prey species, such as krill from Antarctica. POPs were measured in all humpback whales in the order of $\text{HCB} > \text{DDTs} > \text{CHLs} > \text{HCHs} > \text{PCBs} > \text{PBDEs} > \text{MeO-BDEs}$. HCB (median: $24 \text{ ng g}^{-1} \text{ lw}$) and DDTs (median: $7.7 \text{ ng g}^{-1} \text{ lw}$) were the predominant compounds in all whale biopsies. Among DDT compounds, *p,p'*-DDE was the major organohalogenated pollutant, reflecting its long-term accumulation in humpback whales. Significantly lower concentrations of HCB and DDTs were found in females than in males ($p < 0.001$). Other compounds were similar between the two genders ($p > 0.05$). Differences in the HCB and DDTs suggested gender-specific transfer of some compounds to the offspring. POP concentrations were lower than previously reported results for humpback whales sampled near the Antarctic Peninsula, suggesting potential influence of their nutritional status and may indicate different exposures of the whales according to their feeding zones. Further investigations are required to assess exposure of southern humpback whales throughout their feeding zones.

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1. Introduction

Southern Hemisphere humpback whales (*Megaptera novaeangliae*) feed mainly on krill in circumpolar waters around Antarctica and migrate to specific breeding grounds in tropical waters where they reproduce during the austral winter (Clapham, 2009). For management purposes, the International Whaling Commission (IWC) separated the Southern Hemisphere in 7 breeding stocks

designated by the letters A–G (International Whaling Commission, 1998), which link to 6 putative feeding areas, designated as Areas I–VI (Fig. 1). In the south-western Indian Ocean, three main breeding sub-regions within the breeding region C (C1 to C3) have been described by the IWC based on historical whaling data and contemporary surveys, genetic studies, and photo-identification (Fleming and Jackson, 2011; Fossette et al., 2014; Jackson et al., 2014). A fourth breeding region C4 (Mascarene Islands) has been recently suggested, following the increase in the number of whales wintering around Reunion island (International Whaling Commission, 2011). Humpback whales wintering in the south-western Indian Ocean are presumed to feed mainly in Feeding

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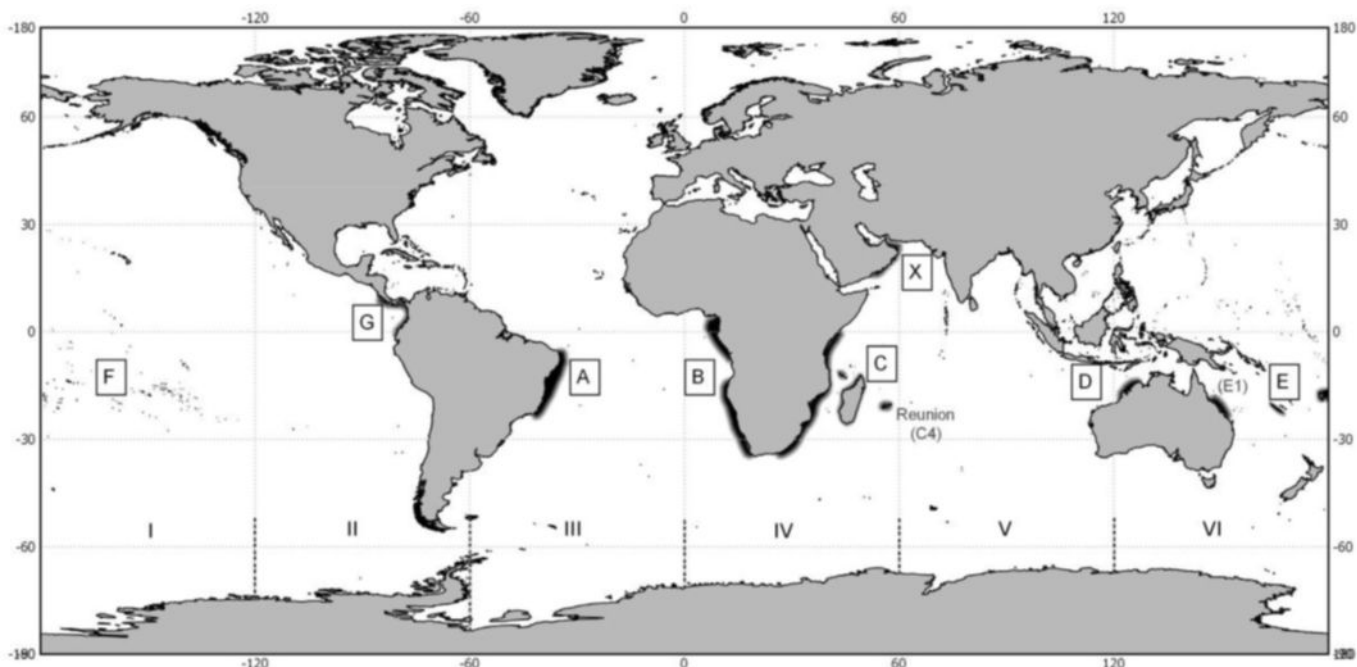


Fig. 1. Stocks and feeding grounds of humpback whales breeding off la Reunion Island (Stock C), off Australia (stock E), off Ecuador (stock G). Other stocks (A, B, X, D and F) as defined by the International Whaling commission are also presented. (International Whaling Commission, 1998).

Area III as confirmed by recent satellite tagging (Cerchio et al., 2013; Fossette et al., 2014). During their north- and southbound migration and on the breeding grounds, humpback whales, like most baleen whales, feed at a reduced rate and opportunistically (Cerchio et al., 2013; Fossette et al., 2014; Silva et al., 2013). The extensive fat accumulated during the summer feeding season in Antarctica support their reproduction and their migratory journeys (Silva et al., 2013). However, whales, and marine mammals in general, experience a high risk of accumulating toxic levels of highly lipophilic chemicals because of their metabolic requirements, extensive fat store and long life span (Bossart, 2011). Effects of migration and fasting on pollutant concentrations in humpback whales is poorly known, but seasonal mobilization of blubber fractions of pollutants during prolonged periods of lipid depletion may place humpback whales in a higher risk category than attributed by exposure alone (Bengtson Nash et al., 2013).

Persistent organic pollutants (POPs) are widely distributed compounds that can be transported to remote areas away from their production sites via long-range environmental transport (Wania and Mackay, 1993). The atmosphere is the dominant pathway for transport of POPs to polar regions, which act as environmental storage for such chemicals (Corsolini et al., 2006). First reports of POPs in Antarctic biota go back to the 1960s (George and Frear, 1966; Sladen et al., 1966; Tatton and Ruzicka, 1967). Current literature further documents the ubiquitous distribution of POPs throughout the Southern Ocean food webs (Bengtson Nash et al., 2008; Corsolini et al., 2006), including in the Antarctic krill *Euphausia superba*, which forms the base diet of several marine mammal species (Chiuchiolo et al., 2004; Corsolini et al., 2002).

For conservation purposes, it is of prime importance to better understand the feeding ecology of humpback whales and their current exposure to organic and inorganic pollutants. Over the past decade, stable isotope (SI) ratios ($^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ reported as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) have been widely used to study trophic ecology of marine mammals, allowing the assessment of their trophic position in the food web and their foraging habitat

(Newsome et al., 2010). The combined use of SI and POPs may also be used to trace feeding habits and thus to provide further insights into population structure and movement pattern of migratory species (Witteveen et al., 2009). Research efforts should further investigate the feeding strategies and ecology of Southern Hemisphere humpback whales, in order to boost the scarce information about the connection between populations, their dependency on local prey stocks as well as their exposure to contaminants.

The principal objective of the current study was to document the chemical exposure of humpback whales breeding in the Indian Ocean by providing the first quantitative data on POP concentrations in this breeding population. POPs measured in the blubber include polychlorinated biphenyls (ΣPCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), DDT and its metabolites (ΣDDX), chlordane compounds (CHLs), polybrominated diphenyl ethers (PBDEs), and methoxylated PBDEs (MeO-PBDEs). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values measured in skin of humpback whales were used to describe feeding habits of humpback whales presumably on their feeding ground in Antarctica. Unless whales undertook migratory feeding, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are expected to reflect accumulated energy stores from Antarctica.

2. Methodology

2.1. Sampling location

Reunion Island is a small oceanic island (2511 km²) located in the south-western Indian Ocean, 700 km east of Madagascar (Fig. 2) and 250 km west of Mauritius. The humpback whale is the cetacean species most frequently observed in shallow waters from June to November and is involved in breeding activity (Dulau-Drouot et al., 2012).

2.2. Sample collection

Skin and blubber biopsy samples from female ($n = 14$) and male

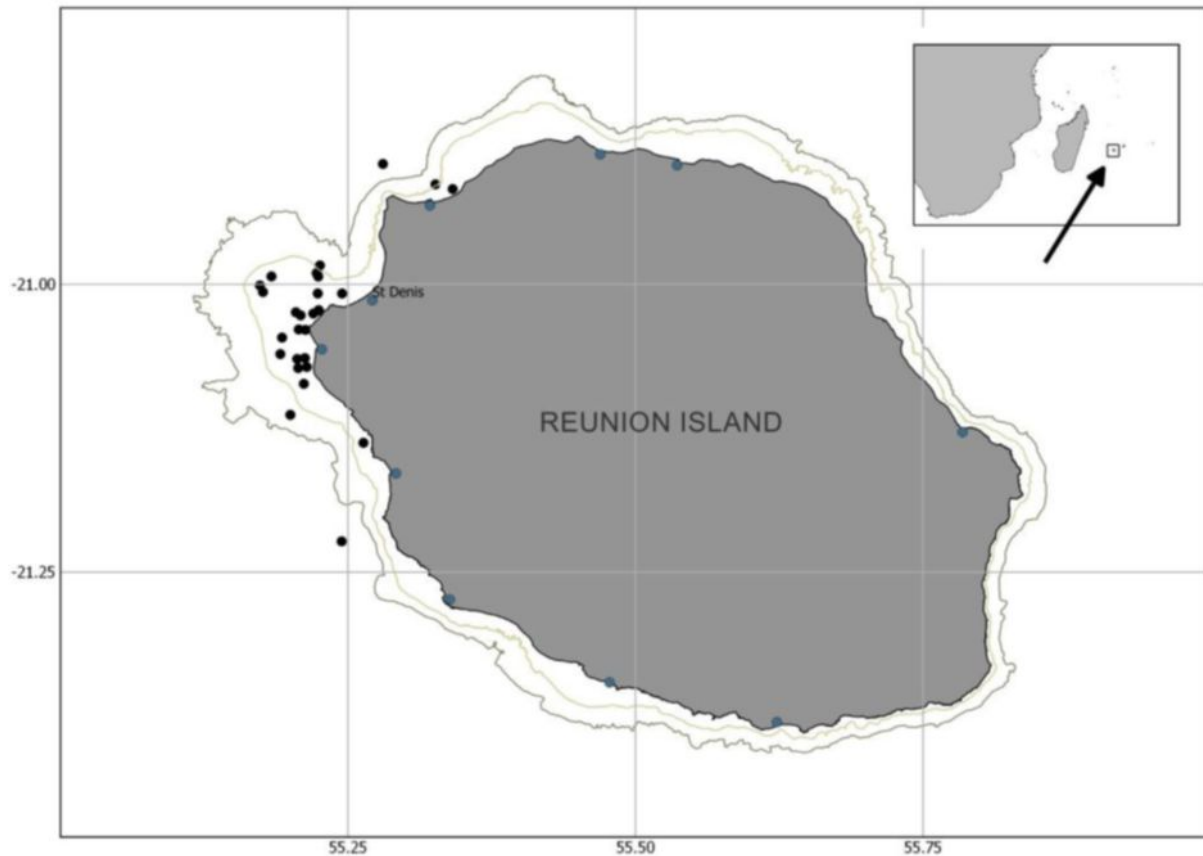


Fig. 2. Sampling location of humpback whales, *Megaptera novaeangliae* off La Reunion Island (Indian Ocean). Black dots correspond to sampled whales.

($n = 12$) humpback whales (*Megaptera novaeangliae*) were collected from Reunion Island during two breeding seasons: from the 3/09/2010 to the 20/10/2010 and from the 16/08/2011 to the 10/11/2011 (Fig. 2 and Table S1).

Biopsies were collected from a 7 m motor-boat, using a regular Barnett crossbow and aluminium darts as previously described (Dirtu et al., 2016; Lambertsen, 1987). A custom-made stainless steel tube tip (0.8 cm diameter, 2.5 cm length) was screwed at the end of the dart (Fig. S1). Before loading the dart into the crossbow, biopsy tips were sterilized in 92% ethanol and, after each shot, biopsy tips were cleaned and boiled for ten minutes, to minimize wound infection and contamination of the sample. Only adult-sized animals were sampled, chosen randomly, photo-identification data was systematically collected, by taking photographs of left and right side of the dorsal fin and, whenever possible, the ventral side of the whale fluke (Fig. S2). Photographs from each whale were compared in order to detect and remove any duplicate samples from the analysis.

2.3. Sex determination

Sex was determined genetically using DNA extracted from skin samples and Qiagen DNeasy kits by following the manufacturer's instructions. The ZFX/ZFY region of the sex chromosomes was amplified by polymerase chain reaction (PCR) (Berube et al., 1996). PCR products were separated by electrophoresis and detected under UV-light to distinguished the females (one product) from the males (two products).

2.4. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements

Skin was freeze-dried and ground to a powder with mortar and pestle. Skin was closely associated to subcutaneous lipids from the blubber. Since lipids are enriched in ^{12}C relative to bulk proteins in a given tissue, this results in a decrease in the $^{13}\text{C}/^{12}\text{C}$ and $\delta^{13}\text{C}$ values in the bulk tissue (DeNiro and Epstein, 1978; Ryan et al., 2012). Lipid content may be variable among samples and thus the potential influence of lipid content on $\delta^{13}\text{C}$ values in bulk tissue must be considered (Ryan et al., 2012). Therefore, lipid extraction is often recommended when the C:N ratio is too high (because of lipid content) to apply an equation for lipid normalization (Post et al., 2007; Ryan et al., 2012). However, chemical lipid extraction may affect $\delta^{15}\text{N}$ values and requires separate $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses (Lesage et al., 2010; Ryan et al., 2012; Sweeting et al., 2006). Lipids were discarded by rinsing skin samples with chloroform:methanol (2:1, v/v). Samples were analysed before and after defatting. Stable isotope ratios were measured using a mass spectrometer (VG Optima, Isoprime, UK) fitted with an elemental analyzer (Carlo Erba, Italy) for combustion and automated analysis. Carbon and nitrogen isotope ratios were expressed as δ values (‰) relative to the Vienna PeeDee Belemnite (vPDB) standard and to atmospheric N_2 respectively. IAEA-N1 ($\delta^{15}\text{N} = 0.4 \pm 0.2\text{‰}$) and IAEA CH-6 ($\delta^{13}\text{C} = -10.4 \pm 0.2\text{‰}$) were used as reference materials.

2.5. Organic pollutant analyses

Thirty PCB congeners (IUPAC numbers: CB 18, 28, 49, 52, 87, 95, 99, 101, 105, 110, 118, 128, 138, 146, 149, 153, 156, 170, 171, 172, 174, 177, 180, 183, 187, 194, 195, 199, 205, and 209), five DDTs (p,p' -DDD,

p,p'-DDE, *p,p'*-DDT, *o,p'*-DDD, and *o,p'*-DDT), chlordane compounds (CHLs) (*cis*-chlordane (CC), and *trans*-chlordane (TC), *trans*-nonachlor (TN), *cis*-nonachlor (CN), oxychlordane (OxC)), three hexachlorocyclohexane (HCH) isomers (α -HCH, β -HCH and γ -HCH), hexachlorobenzene (HCB), as well as 7 PBDEs (IUPAC numbers: BDE 28, 47, 99, 100, 153, 154, and 183), were analysed. Additionally, two MeO-PBDEs (2'-MeO-BDE 68 and 6-MeO-BDE 47) were also measured. All used solvents were of pesticide-grade (Merck, Darmstadt, Germany). Silica and sodium sulphate were washed with *n*-hexane prior to use. Extraction thimbles were washed for 45 min with the solvent mixture used for extraction of samples and dried overnight at 100 °C.

Measurements of POPs in blubber samples were done as described elsewhere (Weijs et al., 2013). Blubber samples (~150 mg) were weighed, mixed with anhydrous Na₂SO₄ and spiked with internal standards (CB 143, BDE 77, BDE 128, and ϵ -HCH). The samples were extracted by hot Soxhlet for 2 h with 100 mL hexane/acetone (3:1, v/v). The lipid content was measured gravimetrically on an extract aliquot (105 °C, 1 h), while the rest of the extract was subjected to clean-up on ~8 g acidified silica (44%, w/w). Analytes were eluted with 20 mL hexane and 15 mL dichloromethane. The cleaned extract was evaporated to near dryness and re-dissolved in 100 μ L *iso*-octane. Quantifications of POPs were performed using GC-MS (Weijs et al., 2013).

The extraction and clean-up had good absolute recoveries of the internal standards PCB 143 and BDE 77 (mean \pm SD 86 \pm 6% and 93 \pm 10%, respectively). The peaks were properly identified as target analytes if: (1) their retention time matched that of the corresponding reference standard within \pm 0.1 min and (2) their signal-to-noise ratio (S/N) was >3:1. Procedural blanks were included in every batch of seven samples to control interferences and/or contamination from solvent and glassware. Procedural blanks were stable (RSD < 30%) and therefore the mean value for each compound was subtracted from the values measured in the samples. After blank subtraction, we calculated the limit of quantification (LOQ) as 3*SD of the procedural blanks. The analysis was further validated through the replicate analysis of certified material SRM 1945 (organic contaminants in whale blubber) for which measured values of POPs deviated with less than 10% from the certified values.

2.6. Data analysis

Statistical analyses were performed with the SPSS software (SPSS for Windows: SPSS Inc., 2001). Before starting the statistical analysis, outliers were removed, while values <LOQ were assigned a value equal to df^*LOQ , where df is the detection frequency of each compound. Mann-Whitney *U* test (non-parametric distribution of the data) and paired *t*-test (parametric distribution of the data) were used to compare the groups. Correlations between compounds and lipid contents were tested with Spearman's rank correlation. Results are presented as averages, medians with minimum and maximum values. Parameters with a probabilistic value of <0.05 were considered as having significant relationship with contaminant level. The concentrations of POPs were expressed in ng g⁻¹ lipid weight (lw), unless otherwise specified.

3. Results

Lipid content in blubber of humpback whales varied widely for males from 6 to 67% (median value: 32%) and for females from 11 to 75% (median values: 41%), without any significant difference between sexes (Table 1). $\delta^{13}C$ and $\delta^{15}N$ values differed significantly from lipid and non-lipid extracted samples (paired *t*-test, *p* < 0.05; Table 1). $\delta^{13}C$ values in lipid-extracted samples and $\delta^{15}N$ in non-lipid extracted samples were used for further statistical tests

Table 1

Lipid percentage and concentrations of PCBs, HCB, DDTs, chlordanes, HCHs, PBDEs, and MeO-PBDEs in blubber samples from male and female humpback whales *Megaptera novaeangliae* biopsied off La Reunion Island (Indian Ocean).

	Females <i>n</i> = 14	Males <i>n</i> = 11	<i>p</i> -value
Lipid %	40 (41) \pm 18 11–75	33 (32) \pm 18 6–67	ns
Σ PCBs	2.7 (1.95) \pm 2.3 0.64–7.8	4.2 (2.3) \pm 5.1 0.6–16	ns
HCB	17 (15) \pm 9.4 6.6–36	44.0 (43) \pm 14 23.0–67	<i>p</i> < 0.001
Σ DDX	6.0 (5.3) \pm 3.4 2.4–12	13.9 (10.4) \pm 6.7 3.6–26	<i>p</i> < 0.005
Σ CHLs	6.3 (3.9) \pm 6.4 1.4–26	10.2 (8.0) \pm 6.3 2.6–24	ns
Σ HCHs	3.9 (2.2) \pm 4.1 0.4–12.2	3.0 (2.8) \pm 2.2 0.4–6.6	ns
Σ PBDEs	1.1 (0.68) \pm 1.1 0.19–3.9	1.9 (0.97) \pm 3.4 0.24–12	ns
Σ MeO-PBDEs	<LOQ – 0.5	<LOQ – 2.5	ns

p-value resulting from Mann-Whitney *U* test to compare male and female blubber concentrations. POP concentrations are expressed as mean (median) \pm sd; min – max in ng.g⁻¹ lw. ns: not significant.

(Table 2) as recommended in previous studies (Ryan et al., 2012; Sweeting et al., 2006). $\delta^{13}C$ values in lipid extracted samples ranged from –25.7 ‰ to –23.4‰. $\delta^{15}N$ values in non-lipid extracted samples ranged from 7.2 to 9.0 ‰ and were similar between females and males and between sampling years (Mann-Whitney *U* test, *p* = 0.08 and *p* = 0.2 respectively).

POPs were measured in variable quantities in all blubber samples in the order of HCB > DDTs > CHLs > HCHs > PCBs > PBDEs > MeO-PBDEs (Table 1). The predominant compound for male and female within each chemical class were: HCB; *p,p'*-DDE; *cis*-chlordane; γ -HCH; PCB-153; BDE-99, and 6-MeO-BDE47. HCB and DDTs were the dominant POPs in all whale samples accounting for 52% and 17% respectively, of all analysed organohalogen compounds. *p,p'*-DDE was the predominant DDT metabolite in both male and female samples (Fig. 3). The major chlordane compound was *cis*-chlordane (CC) followed by *trans*-nonachlor (TN), oxychlordane (OxC) and *cis*-nonachlor (CN) (Fig. 3). PBDEs had the lowest contribution to the POPs measured in the current study (Fig. 2). Only 6-MeO-BDE 47 was detected in the blubber samples (range <0.1–2.5 ng g⁻¹ lw). $\delta^{13}C$ values were not correlated to any organohalogen compound (*p* > 0.05) and $\delta^{15}N$ values were only correlated to Σ DDX (Fisher Transformation Test, *p* = 0.016, Fig. 4).

One whale was sampled twice within a time interval of a little more than 7 weeks between biopsies, i.e., on September 7th, 2011 and on November 1st 2011 (female Mn 18, Table S2, Supplementary data). Lipid percentage dropped from 75 to 55%. $\delta^{15}N$ values increased from 7.7 to 8.1 ‰. A slight increase of HCB, CHLs, HCHs, and PBDEs was noticed while other compounds were similar between the two samples.

Table 2

$\delta^{13}C$ and $\delta^{15}N$ values (‰) and C:N ratio in skin from humpback whales *Megaptera novaeangliae* from Reunion Island (Indian Ocean).

	$\delta^{13}C$	$\delta^{15}N$	C:N
Lipid non extracted	–29.1 (–29.0) \pm 1.1 (–31.3/–26.5) <i>n</i> = 25	7.8 (7.8) \pm 0.4 (7.2–9.0) <i>n</i> = 25	5.5 (5.7) \pm 0.9 (3.7–7.2) <i>n</i> = 25
Lipid extracted	–24.8 (–25.1) \pm 0.6 (–25.7/–23.4) <i>n</i> = 22	7.9 (7.9) \pm 0.5 (6.8–8.8) <i>n</i> = 22	3.1 (3.1) \pm 0.1 (2.9–3.3) <i>n</i> = 22

Results are expressed as mean (median) \pm sd; (min – max), *n*: number of analysed samples.

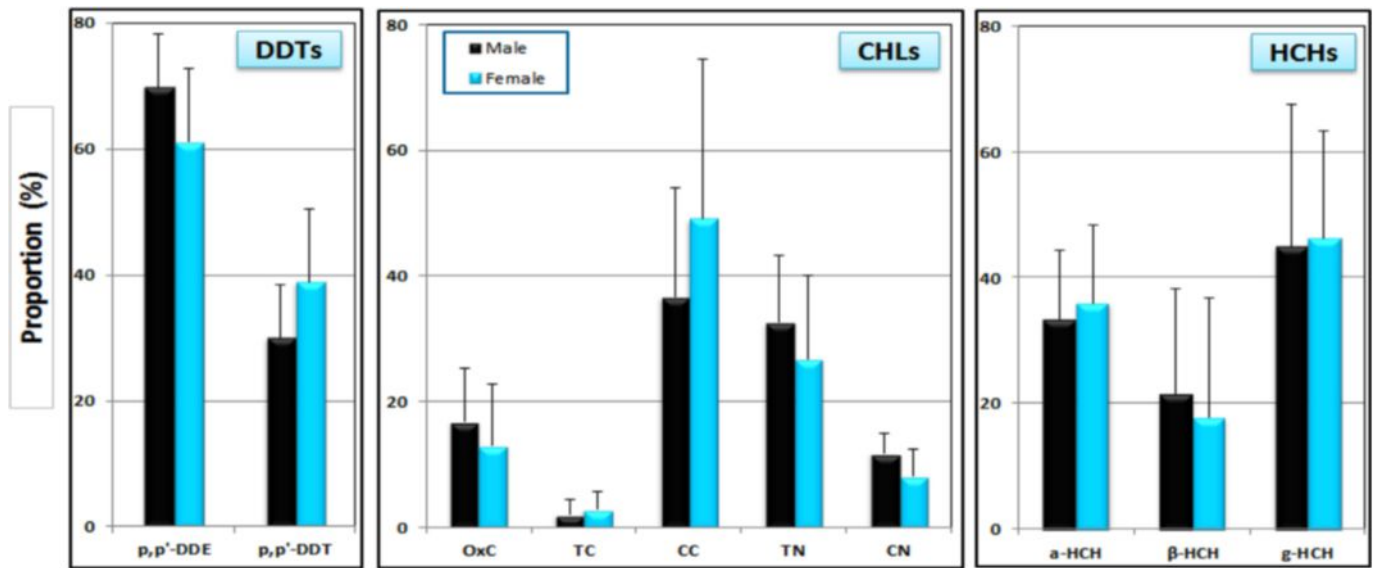


Fig. 3. Profile (%) of DDTs, CHLs and HCH compounds in the blubber of humpback whales, *Megaptera novaeangliae* off la Reunion Island.

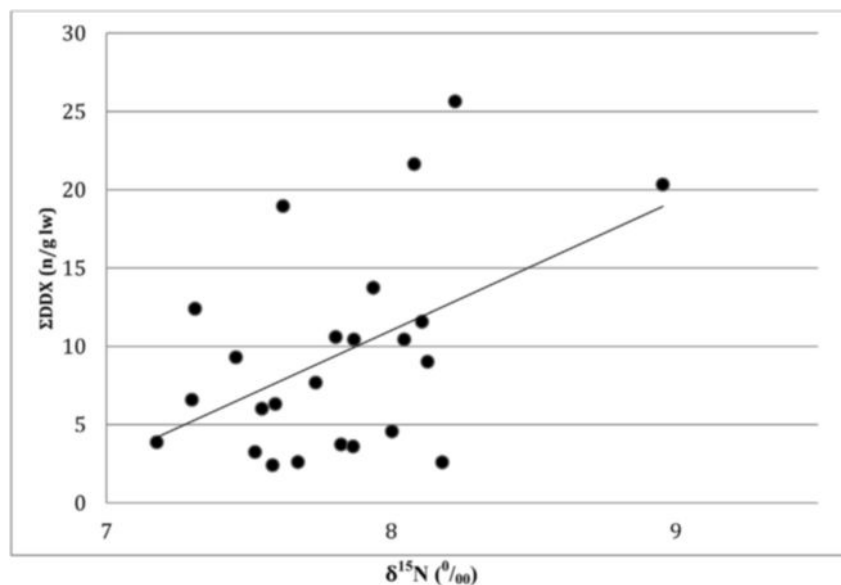


Fig. 4. Relationship between $\delta^{15}\text{N}$ values in skin and ΣDDX in blubber of humpback whales, *Megaptera novaeangliae* off la Reunion Island.

3.1. Sex-related differences

Significantly higher concentrations of HCB and DDTs were found in male than in female blubbers samples (Mann-Whitney U Test, $p < 0.001$; Table 1). Concentrations of PCBs, CHLs, HCHs, PBDEs, and MeO-PBDEs were similar between females and males ($p > 0.05$) (Table 1). Significant positive correlations between most classes of contaminants was mainly obtained for female samples, while very few could be observed for samples collected from males (Table S3).

4. Discussion

4.1. Feeding habits through stable isotope measurements

To the best of our knowledge, this study investigates for the first time POPs and stable isotopes in humpback whales breeding in the Indian Ocean. It completes works recently conducted on fish and

dolphins sampled off La Reunion (Dirtu et al., 2016), and increases the knowledge related to the southern Indian Ocean sector. Our results provide the first published records of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in skin biopsies from humpback whales from the Southern hemisphere and these data reflect their dietary sources. Although there are no measurements for the turnover rate of humpback whale skin, the turnover rate measured for the beluga whale *Delphinapterus leucas* and the common bottlenose dolphin *Tursiops truncatus* suggested that skin integrates the diet of the last 8–10 weeks prior to sampling (Hicks et al., 1985; St. Aubin et al., 1990). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values analysed in the skin of humpback whales off La Reunion Island reflect their diet more than two months prior to sampling, presumably on their feeding zone near Antarctica (Feeding zone 3, Fig. 1). During their migration and during the time spent on their breeding area, humpback whales feed at a reduced rate and their maintenance is occurring mainly from stored energy reserves during their feeding near Antarctica (Silva et al., 2013).

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were determined recently in baleen plates from the two Australian humpback whales breeding populations (Eisenmann et al., 2016). Evidence of feeding in temperate waters and during partial migration was suggested in some individual whales from East Australian breeding population, pointing to some plasticity in prey selection (Eisenmann et al., 2016).

The low trophic position of humpback whales breeding in the Indian Ocean, reflected by their low $\delta^{15}\text{N}$ values, are in agreement with previous observations describing humpback whales feeding on euphausiids near Antarctica (Cotté and Guinet, 2011; Ware et al., 2011). The range of $\delta^{13}\text{C}$ is relatively narrow (from -25.7 to -23.4 ‰), in agreement with $\delta^{13}\text{C}$ defined in particulate organic matter (POM) collected in Antarctic waters (Francois et al., 1993) and in baleen plates of West Australian breeding population of humpback whales feeding mainly in Antarctica (-26.2 to -23.3 ‰; Eisenmann et al., 2016). Furthermore, $\delta^{15}\text{N}$ comparison with existing data on krill and other krill-eating marine mammals from Antarctica is consistent with a diet focused mainly on krill (Fig. 5). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data in krill covered a broad range of values reflecting previously described geographical gradient and seasonal variations. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of baleen whales and crab-eater seal are lower than values previously described for fish-eating and mammal-eating mammals, including the Ross seal *Ommatophoca rossii* (Zhao et al., 2004), the Weddell seal *Leptonychotes weddellii* (Burns et al., 1998; Zhao et al., 2004), Type C killer whale *Orcinus orca* (Krahn et al., 2008), and the leopard seal *Hydrurga leptonyx* (Hall-Aspland et al., 2005; Zhao et al., 2004) (Fig. 5). Although feeding grounds for these marine mammal species are widely dispersed around Antarctica, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of various krill and krill-eater species are rather comparable.

The future of humpback whales from southern hemisphere is

tightly linked to the abundance of their main prey, the Antarctic krill (Herr et al., 2016). The effects on baleen whales induced by the krill variability are unclear because parallel long-term data on krill abundance and whale condition do not exist (Braithwaite et al., 2015). However, global changes are resulting in ecosystem scale changes in the Antarctica (Walther et al., 2002) which, together with expanding krill fisheries, may result in, among others, a dramatic reduction in the krill biomass available to whales (Nicol, 2003). Other krill-dependant species can also be impacted. Increasing temperature and reduction in sea ice in some Antarctica areas (Scotia Sea and adjacent West Antarctic Peninsula) have changed the physical environment needed to sustain large krill populations, already affecting Adélie penguin (*Pygoscelis adeliae*) populations (Trivelpiece et al., 2011). Braithwaite et al. (2015) reported that krill abundance varies with the ice extent in the Southern Ocean foraging grounds of humpback whales that breed off western Australia. The authors indicated a strong correlation between krill abundance and humpback whale condition. Since humpback whales breed and migrate on limited energy stores acquired during summer foraging in Antarctica, simultaneous changes in the krill abundance may have long-term implications for their condition and reproductive success (Braithwaite et al., 2015).

4.2. Chemical exposure of humpback whales from la Reunion Island

Long-range atmospheric transport of POPs is the main vector for the introduction of these chemicals to Antarctica. Even though the concentrations in Antarctica are low, there is evidence of local hotspots of contamination. POPs can be emitted from local primary sources (research stations, old equipment, etc.) and from migratory biota (Cabrerizo et al., 2012; Hale et al., 2008; Negoita et al., 2003;

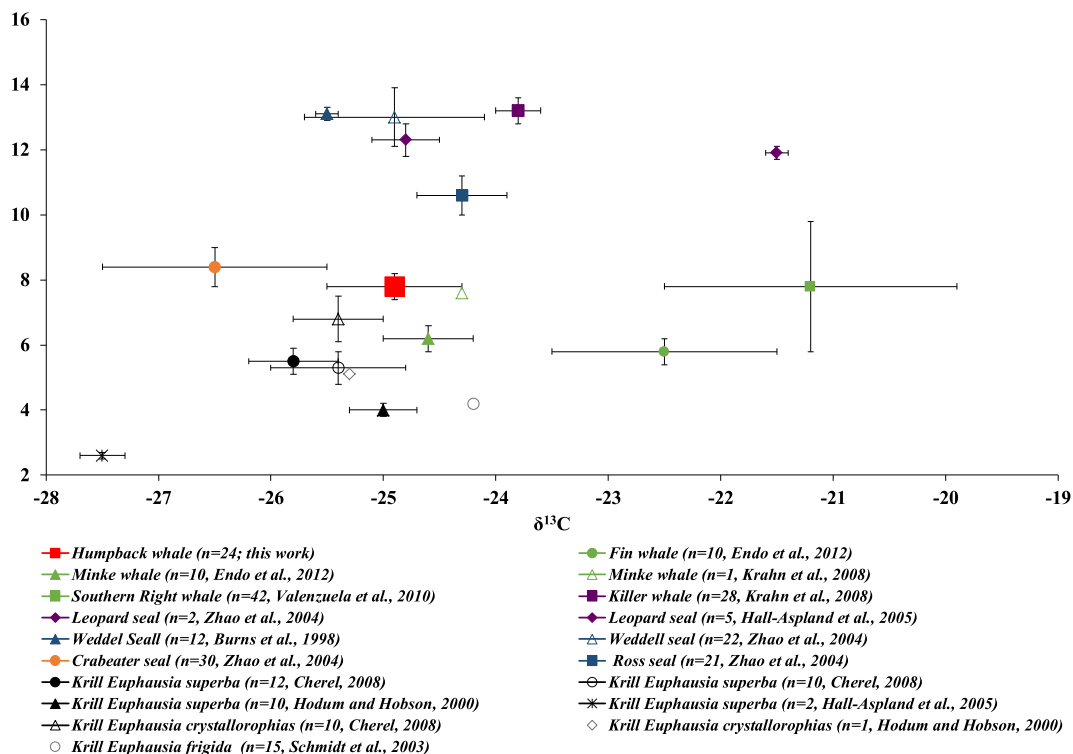


Fig. 5. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (‰) values in humpback whales, *Megaptera novaeangliae* off la Reunion Island (this work) compared to other krill and mammal species from the Antarctic: krill species sampled in Antarctica (black marks), in baleen whales including the fin whale, the minke whale and the southern right whale (green marks), the crab-eater seal (orange mark), other marine mammal species from Antarctica such as the killer whale, the leopard seal, the Weddell Seal and the Ross Seal (Burns et al., 1998; Chereil, 2008; Endo et al., 2012; Hall-Aspland et al., 2005; Hodum and Hobson, 2000; Krahn et al., 2008; Schmidt et al., 2003; Valenzuela et al., 2010; Zhao et al., 2004). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Roosens et al., 2007; Vanden Berghe et al., 2013; Wild et al., 2015).

Due to a lower trophic position, low POP concentrations are measured in most baleen whales compared to toothed whales (Dirtu et al., 2016; Kunito et al., 2002; Pinzone et al., 2015). POP concentrations in the tissues of humpback whales would vary according to the environmental contamination but also to many other factors including the sex, the diet and their nutritional status (Bengtson Nash et al., 2013; Dorneles et al., 2015; Waugh et al., 2012).

Lower POP concentrations were recently described in humpback whales from the Southern Hemisphere (Bengtson Nash et al., 2013; Dorneles et al., 2015; Waugh et al., 2012) compared to humpback whales from the Northern Hemisphere (Elfes et al., 2010; Gauthier et al., 1997; Metcalfe et al., 2004; Ryan et al., 2013), probably due to the greater historical usage of POPs and the higher trophic position of humpbacks whales in the Northern Hemisphere (Ryan et al., 2014). Low $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values combined with low POP concentrations measured in the present study confirm a diet mainly focused on krill for humpback whales breeding off La Reunion.

Great variations of blubber POP concentrations were also observed within the Southern hemisphere whale populations. PCB concentrations analysed in humpback whales from La Reunion were up to 40 times lower than those described for humpback whales feeding near the Western Antarctic Peninsula waters (Dorneles et al., 2015), but similar to those described in humpback whales migrating through Moreton Bay Marine Park, off eastern Australia (Bengtson Nash et al., 2013; Waugh et al., 2012) (Table 3). Other compounds including as HCHs and HCB were also lower in the blubber of humpback whales sampled in the Indian Ocean (Table 3).

These differences can be related to punctual contamination in Antarctica, foraging locations sampling periods and related nutritional status (Bengtson Nash et al., 2013; Dorneles et al., 2015; Waugh et al., 2012). Dietary differences between male and female were recently suggested based on chlorinated and brominated dominant profiles in humpback whales from Antarctic Peninsula (Dorneles et al., 2015).

Assuming that exposure to POPs occur primarily via the food chain (Corsolini et al., 2006), the available data suggest different contaminant load and input sources of POPs around the circum-polar waters of Antarctica, and thus likely among humpback whale feeding areas. We suggest a lower level of exposure of humpback whales from the western Indian Ocean and the Pacific Oceans (breeding stocks C and E respectively), compared to other stocks feeding around the Antarctic Peninsula (Feeding Area I). ΣDDX was correlated to $\delta^{15}\text{N}$ (Fig. 4) and no POP compound correlated to $\delta^{13}\text{C}$,

suggesting that other factors are likely to explain the variability of POP concentrations, such as the age and number of reproductive cycles for females.

Migration, fasting, and lactation obviously affect POP concentrations in tissues of marine mammals leading to an increase of concentrations of some compounds, such as PCBs, that are less easily mobilised from blubber than lipids (Debier et al., 2003). Maternal transfer of lipophilic contaminants have been widely described in marine mammals, resulting in males being generally more contaminated than females (Abarnou et al., 1986; Kajiwara et al., 2008; Pinzone et al., 2015). In the present study, males displayed significantly higher HCB and ΣDDX concentrations compared to females. Other compounds were similar between sexes, while previous studies describing higher POP concentrations in blubber biopsies sampled on males compared to females. The reason is unclear, but this could be an artefact of low sample size, low concentrations of pollutants, and high individual variability among females, since maternal transfer of POPs to offspring is negatively impacted by the age of the female and the number of reproductive cycles (Borrell et al., 1995; Weijs et al., 2013).

In humpback whales sampled off Australia, two major pollutants, *p,p'*-DDE and HCB, exhibited a significant increase at the end of the breeding season, when whales are migrating back south to Antarctica, while other compounds showed similar concentration between north- and southbound migration legs (Bengtson Nash et al., 2013; Waugh et al., 2012). One humpback whale from the present study was sampled twice (Table S2), in September and in November 2011 and exhibited an increase of HCB, ΣCHLs , ΣHCHs and ΣPBDEs in a two-month period combined to a decrease of lipid content in the blubber. However, the significance of such increase for the population should be assessed on a larger sampling size. These periods of extreme food deprivation have to be taken into account when assessing chemical exposure of humpback whales as a reduction of the blubber lipid content can lead to a redistribution of organochlorine contaminants in the body (Bengtson Nash et al., 2013).

4.3. Contamination profile of humpback whales off la Reunion Island

Percentage contribution of organohalogenated POPs in blubber of humpback whales differed among humpback whales from southern hemisphere (Bengtson Nash et al., 2013; Dorneles et al., 2015; Waugh et al., 2012). PCBs accounted for 44% of all analysed organohalogenes in whales sampled in western Antarctic Peninsula waters (Dorneles et al., 2015), while the percentage contribution was only 6% in the present study, consistent with profiles described

Table 3
 Σ PCBs, Σ HCHs and HCB concentrations (ng g^{-1} lw) in humpback whales *Megaptera novaeangliae* from the Southern Hemisphere.

Sampling location	Year of sampling	Σ PCBs	ΣHCHs	HCB	Mean lipid percentage in the blubber	Reference
La Reunion Island Indian Ocean Breeding Stock C4 n = 25	2010–2011	3.4 \pm 3.8 0.6–16 Σ_{30} PCBs	3.6 \pm 4.4 0.4–12	29 \pm 18 7–67	37%	This study
Moreton Bay Marine Park, Australia Breeding Stock E n = 41	2008–2011	3.1 \pm 0.7 n = 41 Σ_{32} PCBs	13.9 \pm 0.3 n = 41	64 \pm 8	50%	Waugh et al., 2012; Bengtson Nash et al., 2013
Western Antarctic Peninsula Stock G (females) n = 15	2000–2001	131 \pm 192 4.4–761 Σ_{30} PCBs	11.5 \pm 11 2.2–44	35 \pm 20 6.8–74.5	40%	Dorneles et al., 2015

Data are expressed as mean \pm sd; (min – max), n: number of analysed samples.

in humpback whales sampled along the East coast of Australia (Waugh et al., 2014). *p,p'*-DDE was the major DDT metabolite in Reunion's samples (Fig. 3), which is in agreement with data from other Antarctic aquatic species, including krill, fish and penguins (Corsolini et al., 2006). *p,p'*-DDE is the most persistent metabolite of DDT, which bioaccumulates in Antarctic krill (Bengtson Nash et al., 2008). It has been shown that the Antarctic environment still receives input of *p,p'*-DDE via redistribution of previously deposited DDT in soil and snow/ice and from ongoing DDT usage in parts of the Southern Hemisphere for, e.g., vector control (Poulsen et al., 2012).

The major chlordane was *cis*-chlordane followed by *trans*-nonachlor, oxychlordane and *cis*-nonachlor. This is because chlordanes are transformed into *trans*-nonachlor, *cis*-nonachlor or oxychlordane, which persist in the tissues of mammals, fish, and birds (Kawano et al., 1988).

Hexachlorocyclohexanes (α -HCH and γ -HCH isomers) were detected in all samples. HCHs are less bioaccumulative than other organochlorine POPs, such as CHLs, DDTs, or HCB, due to their lower lipophilicity and shorter half-lives in biota. While β -HCH is more stable in biotas, it is less volatile than α -HCH and γ -HCH, thus it reaches the Polar Regions slower than the other HCHs, due to the global fractionation (Wania and Mackay, 1993). β -HCH concentration in Arctic air (Li et al., 2003) and in some animal species (Willett et al., 1998) is lower in comparison with the more volatile α - and γ -HCH. Due to their chemical properties, HCHs are easily volatilized and transported by air and water currents for long distances (Iwata et al., 1993; Wania and Mackay, 1993). Although Canada, Europe, and the U.S. have banned HCHs since the 1970s, several tropical countries still used lindane (pure γ -HCH) until the 1990s (Li et al., 2003; Senthilkumar et al., 2001, 1999), influencing thus the occurrence of γ -HCH in Antarctic food webs. Humpback whales feeding in the Antarctic Peninsula region displayed a high percent contribution of lindane (γ -HCH) to the Σ HCH, as a consequence of lindane use in South America close to the Peninsula (Dorneles et al., 2015).

CB-153 was the major PCB congener, followed by CB-187, CB-180 and CB-118. CB-153 has been reported as the most abundant PCBs in marine mammals from different parts of the globe (Reijnders and Aguilar, 2002). The higher contribution of these compounds is related to their predominance in commercial mixtures (e.g. Aroclor) and to their resistance to degradation.

BDE-99, -154, and -47 were the predominant PBDE congeners, similar to the composition reported in the literature in the Antarctic keystone species (Bengtson Nash et al., 2008). The PBDE detection in polar regions is due to their widespread usage as flame retardant in many consumer products. While PBDEs have been banned in the EU and the US, they are still widely used in many countries, especially in Asian developing countries (Möller et al., 2012). The presence of PBDEs and organochlorine POPs in Antarctic organisms confirms that these compounds are widely distributed in the environment via long-range transport and can reach remote area, such as Antarctica (Wania and Dugani, 2003).

The 6-MeO-BDE 47 congener was detected in the blubber samples of humpback whales from La Reunion. MeO-PBDEs have probably a natural origin, being formed by sponges or algae (Dorneles et al., 2015; Vetter, 2006). Currently, there is a lack of literature on MeO-PBDE concentrations in krill, the dominant prey species of whales from the Southern Hemisphere (Dorneles et al., 2015). The trophic transfer of MeO-PBDEs in Antarctic food chain definitely deserves further investigation.

Our study emphasizes the need of further investigations on the exposure of Southern Hemisphere humpback whale populations foraging in different circumpolar regions. Our findings, as indicated by blubber contaminant levels, gender and seasonal differences,

suggest significant heterogeneity in foraging ground exposure among southern hemisphere breeding stocks.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.11.032>.

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