Science of the Total Environment 518–519 (2015) 605–615

Contents lists available at ScienceDirect

Science of the Total Environment

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

# Organochlorine pesticides and PCBs in Southern Right Whales (*Eubalaena australis*) breeding at Península Valdés, Argentina

P. Torres [a], K.S.B. Miglioranza [b], M.M. Uhart [c], M. Gonzalez [b], M. Commendatore [a,d,*]

[a] Universidad Nacional de la Patagonia San Juan Bosco (UNPSJB), Bv. Brown 2915, U9120ACD Puerto Madryn, Chubut, Argentina
[b] Instituto de Investigaciones Marinas y Costeras (CONICET), Universidad Nacional de Mar del Plata (UNMdP), Funes 3350, 7600 Mar del Plata, Argentina
[c] One Health Institute, School of Veterinary Medicine, 1089 Veterinary Medicine Dr., University of California, Davis, Davis 95616, CA, USA
[d] Centro Nacional Patagónico (CONICET), Bv. Brown 2915, U9120ACD Puerto Madryn, Chubut, Argentina

## HIGHLIGHTS

- Organochlorine pesticides and PCBs were found in Southern Right Whales.
- OCP levels were slightly higher than PCB in all individuals.
- Samples showed a predominance of recent endosulfan and aged DDT.
- Prevalence of lower chlorinated congeners indicates atmospheric global transport.

## ARTICLE INFO

*Article history:*
Received 13 December 2014
Received in revised form 6 February 2015
Accepted 18 February 2015
Available online 24 March 2015

Editor: D. Barcelo

*Keywords:*
PCBs
OCPs
South West Atlantic
Southern Right Whales
Bioaccumulation
Península Valdés

## ABSTRACT

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were assessed in blubber from 35 dead Southern Right Whales (SRW — *Eubalaena australis*) stranded at Península Valdés, Argentina. The life cycle includes a feeding period in high productivity areas of the South West Atlantic and a reproductive period in coastal template waters of Argentina. Organochlorine pesticides showed higher concentrations (22.6 ± 13.8 ng·g$^{-1}$ ww) than PCBs (7.5 ± 10 ng·g$^{-1}$ ww). Among pesticides, HCHs, DDTs, endosulfans, dieldrin, chlordans, heptachlor epoxide, and trans-nonachlor were detected. *p,p′*-DDE and *p,p′*-DDT were present in 69% and 26% of samples, respectively. *p,p′*-DDT/*p,p′*-DDE ratio showed low values (<0.33) as a result of aged DDT inputs. However, the occurrence of only *p,p′*-DDT in some samples suggests a recent pesticide input. α-HCH/γ-HCH ratio (<DL-0.37) indicated no recent contribution of technical HCH mixture and/or current use of lindane. Dieldrin was present in 77% of the samples and endosulfan was detected in all samples with predominance of α- (75%) over β-endosulfan (19%) and scarce contribution of endosulfan sulphate (7%), suggesting a recent input of this insecticide to the environment in the SRW foraging area. A predominance of pentachlorobiphenyls was observed. In 21 samples at least one PCB indicator was found and PCB #118, highly toxic, contributed in 5% to total PCBs. Although all these organochlorine compounds are forbidden they were bioaccumulated in the blubber of SRW with a predominance of endosulfans, the more recently used pesticide. The absence of data on chemical pollutants in stranded dead whales is highlighted as a priority for research. This is the first study on levels, compositional patterns, and organochlorine sources in SRW. Moreover, more research including milk, and other tissues/organs is recommended considered that in the studied specimens, mostly calves, pollutants are likely transferred from the mother during pregnancy and nursing.



## 1. Introduction

Persistent organochlorine pollutants (POPs) are ubiquitous, toxic chemicals released around the world and transported to polar regions primarily via air masses according to global distillation and fractionation processes (Wania and Mackay, 1996; Bengtson Nash et al., 2008). As volatility decreases markedly with falling temperatures, the colder areas at higher latitudes act as major sinks for these compounds (Aguilar et al., 2002). Most organochlorine pesticides (OCPs) and all polychlorinated biphenyls (PCBs) are included in the Stockholm Convention list (2009), and despite their prohibition some years ago in many countries, they persist globally at considerable levels (Fowler, 1990; Sarkar et al., 1997; Pazi et al., 2011). These pollutants which enter into the environment from anthropogenic sources (industrial and agricultural) are highly persistent, bioaccumulative, and transferable through the trophic chain, and they have contributed significantly

* Corresponding author at: Centro Nacional Patagónico (CONICET), Bv. Brown 2915, U9120ACD Puerto Madryn, Chubut, Argentina.
*E-mail address:* commenda@cenpat-conicet.gob.ar (M. Commendatore).

http://dx.doi.org/10.1016/j.scitotenv.2015.02.064
0048-9697/

to environmental pollution (Tolosa et al., 2010). POPs were first detected in Antarctic biota and snow in the late 1960s, contributing further evidence towards the long range environmental transport of these compounds (Riseborough et al., 1968). However there are few reports on POPs in Antarctica in comparison to the Arctic (Bengtson Nash et al., 2008). POP occurrence in animal tissues has been associated to several deleterious effects on all hierarchical levels of biological organization (organism, population, community, and ecosystem) including damage to reproduction, endocrine disruption, immune suppression, and cancer (UNEP, 2012). Although accumulation in males and females of different species and trophic level is expected to be similar, female mammals can transfer a large part of their POP burden to their calves through the placenta and during lactation (Marsili and Focardi, 1995).

Southern Right Whales (*Eubalaena australis*) inhabit the southern hemisphere (Bastida and Rodriguez, 2009). They are an emblematic species in Patagonia (Argentina) and a regional resource that sustains important tourism activities linked to whale-watching. The life cycle of the population of SRW which breed in Península Valdés includes a feeding period in areas of high biological productivity in the South West Atlantic and a reproductive period in coastal and temperate waters (Bastida and Rodriguez, 2009). Specifically, SRWs migrate annually between mid-latitude areas (Península Valdés, Argentina; Uruguay; and southern Brazil) where they winter (Payne, 1986; Santos et al., 2001), returning to high latitudes to feed during the summer (Best et al., 1993; Valenzuela et al., 2009). When in the breeding areas in Peninsula Valdés, SRWs ingest almost no food (Payne, 1986), although opportunistic feeding has been reported when zooplankton patches with adequate composition and high density are present in the spring (Hoffmeyer et al., 2010). While outside the breeding season they feed mostly on krill (*Euphausia superba*) at high latitudes of the Southern Atlantic Ocean (Valenzuela et al., 2009), and thus likely incorporate organochlorines via prey ingestion. According to the International Union for the Conservation of Nature (IUCN), SRWs are currently classified as "least concern" (http://www.iucnredlist.org/details/8153/0). SRWs are protected internationally by the International Whaling Commission, the Convention on International Trade in Endangered Species of Wild Fauna and Flora (http://www.cites.org/esp/app/appendices.php), and the Convention on Migratory Species (http://www.cms.int/es/). In Argentina, SRWs are also protected as a National Natural Monument (Law No 23,094) and by laws from Chubut Province. The last SRW population estimate for PV was near 4000 individuals, including the calves born in 2010 (IWC, 2012). Contrary to other whale populations, the SRWs that use PV as their breeding grounds are increasing; however, over the last decade the growth rate has decreased from near 7% (Cooke et al., 2001) to 5% (IWC, 2012). This fact may be in part due to recurrent mortalities, primarily affecting newborn calves, recorded since 2005 (Rowntree et al., 2013).

The assessment of chemical pollutants in dead whales was recently highlighted as a priority for research (IWC, 2010). Whales coming to PV have been studied since the 1970s particularly with a biological focus (Payne, 1986; Best et al., 1993; Santos et al., 2001; Valenzuela et al., 2009). Health studies are more recent (2003) and started with the Southern Right Whale Health Monitoring Program (SRWHMP). Particularly, metals were assessed by Rosas et al. (2012) and Martino et al. (2013) in SRW tissues, but there is no available information on organochlorine levels. The aim of this research is to contribute to understanding the role of SRWs as sink of POPs in the marine environment and the relation of organochlorine compounds with mortality factors providing a useful baseline for future comparisons.

## 2. Materials and methods

### 2.1. Study area and sample collection

The study area included coastal zones of Península Valdés (PV), specifically gulfs Nuevo and San José (42° 42′ 0″ S, 64° 36′ 0″ W) (Fig. 1), where SRWs remain between May and December of each year for parturition, lactation and reproduction. Blubber samples were collected from dead stranded SRWs by the SRWHMP. Most were from 2011 (n = 12), and 23 samples collected in previous years (2003, 2004, 2005, 2006, 2007, 2009, 2010), and preserved at −20 °C, were also analyzed. General data recorded during sampling included: date, hour, site, body condition, age category, sex and size. Age categories were defined as follows: calves (less than 1 year of age), head length 15–16% of total body length (TBL), up to 9 m total length; juveniles (less than 10 years of age), head length 17–19% of TBL, 9 to 12 m total length; and adults (up to 70 years), head length 20% or more of TBL, longer than 12 m. Samples of dorsal blubber were wrapped in previously calcinated aluminum foil (450 °C/4 h), placed inside a Ziploc bag with an identification label, and then conserved frozen at −20 °C until analysis.

### 2.2. Analytical procedures

Subsamples of blubber (1.5 g) were homogenized with anhydrous $Na_2SO4$ and spiked with 20 ng of PCB #103 as surrogate. Compounds were extracted according to Metcalf and Metcalf (1997), with modifications of Miglioranza et al. (2003). They were Twisselmann extracted (8 h) with a mixture of hexane–dichloromethane (50:50), and then concentrated under vacuum and nitrogen flow to a final volume of 2 mL. Lipid content was removed by gel permeation chromatography (GPC) using Bio-Beads S-X3 (200–400 mesh, Bio-Rads Laboratory, Hercules, CA, USA) followed by lipid percentage calculation. Purification of the contaminant fraction was performed by silica gel chromatography previously activated at 200 °C during 24 h and extracts were concentrated to 1 mL and kept in sealed vials at −20 °C prior to chromatographic analyses. Identification and quantification were performed using a Gas Chromatograph, Shimadzu GC-17-A equipped with a $^{63}$Ni Electron Capture Detector (GC-ECD) and a capillary column SPB-5 [(5% phenyl)-methyl polysiloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness; Supelco Inc.]. One microliter was injected on a splitless mode (275 °C) and the detector was kept at 290 °C. The oven temperature program starts at 100 °C and held for 1 min, followed by an increase of 5 °C $min^{-1}$ up to 150 °C, held for 1 min, then 1.5 °C $min^{-1}$ up to 240 °C, and then 10 °C $min^{-1}$ up to 300 °C for 10 min. Ultra-high purity Helium was used as carrier gas (1.5 mL $min^{-1}$) and nitrogen as make-up gas (Miglioranza et al., 2003). A pesticide mixture from Ultra Scientific, RI, USA and PCB mixture from Accustandard Absolute Standards, INC, CT, USA were used for identification and quantification of single compounds, while PCB #103 from Ultra Scientific, USA. Analytes determined were (a) OCPs: α-, β-, γ-, and δ-HCH, heptachlor, heptachlor epoxide, α- and γ-chlordane, trans-nonachlor, *p-p′*-DDT, *p-p′*-DDD, *p-p′*-DDE, aldrin, dieldrin, endrin, α-endosulfan, β-endosulfan and endosulfan sulphate, and methoxychlor and (b) PCB congeners (24): IUPAC #8, 18, 28/31, 52, 44, 66, 101, 110, 123/149, 118, 153, 105, 138, 187, 128, 156, 180, 170, 189, 195, 206, and 209, including the six indicators IUPAC #28, 52, 101, 138, 153, and 180 PCBs (EFSA, 2005; EFSA, 2010; Stenberg and Andersson, 2008).

### 2.3. Quality control and quality assurance (QA/QC)

Laboratory and sampling glassware were washed with appropriate solvents to avoid interferences. The QA/QC included regular analysis of matrix blank, duplicated samples and instrumental and procedural blanks. Results indicate that there were no contaminations or interference during laboratory handling. Concentrations in the samples were based on surrogate standards added. Analyte concentrations were calculated using the PCB #103 as surrogate. The internal standard (TCMX) was used to calculate surrogate recoveries being greater than 85% and the results were not corrected for recovery efficiency. Recoveries, calculated from spiked matrixes, were greater than 90%. PCB #103 was also used for peak identification through relative retention time.

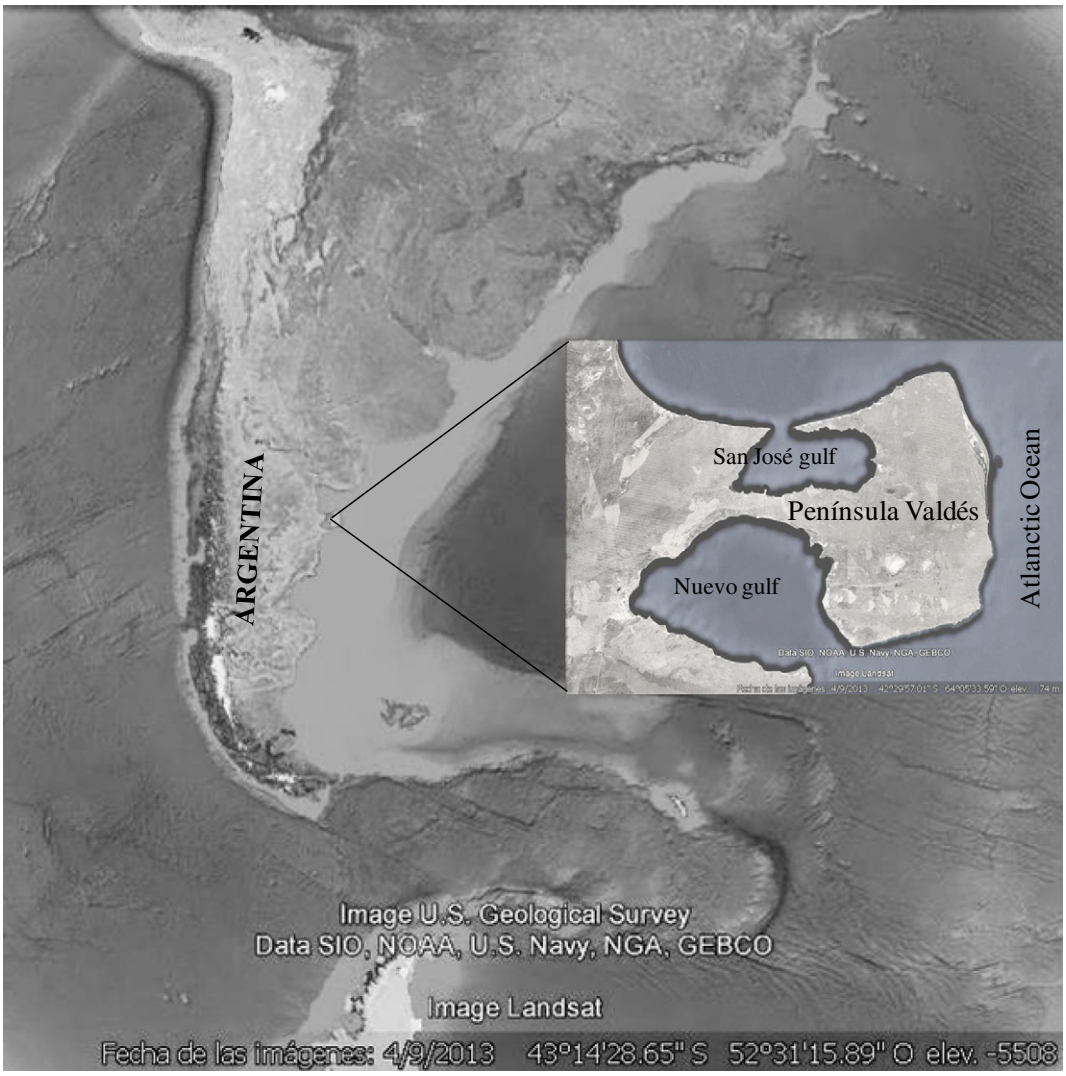


**Fig. 1.** Study area showing the San José and Nuevo gulfs where SRWs were sampled.

Detection limits (DLs) were calculated according to Keith et al. (1983) and ranged between 0.03 and 0.05 ng·mL$^{-1}$ for HCHs (α-, β-, γ- and δ-isomers) and between 0.08–0.33 ng·mL$^{-1}$ for the rest of chlorinated compounds [Chlordanes (α- and γ-isomers and trans-nonachlor), DDTs (pp′-DDE, pp′-DDD and pp′-DDT), endosulfans (α- and β-isomers and endosulfan sulfate) and PCBs (IUPAC #8, 18, 28/31, 52, 44, 66, 101, 110, 123/149, 118, 153, 105, 138, 187, 128, 156, 180, 170, 189, 195, 206, 209)].

## 3. Results

### 3.1. Sample characterization

A total of 35 blubber samples from calves (C) (n = 30); 3 juveniles (J) and 2 adults (A), were assessed (Table 1). Calves constituted 86% of total samples and their average length was 6.5 ± 1.55 m. The length of juveniles was 11.4 ± 0.9 m; and both adult females were 12.54 m each. Among calves, the male average length was 6.47 ± 2.57 m (n = 15) which was similar to females 7.57 ± 2.57 (n = 14). Two of the juveniles sampled were females and 1 of unknown sex (Table 1). The mean Total Lipid Content (TLC) was 28.4 ± 14.5% (n = 35).

### 3.2. Organochlorines

HCHs (α-HCH, β-HCH, and γ-HCH), DDTs (*p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD); endosulfans (α-endosulfan, β-endosulfan, and endosulfan sulphate); and dieldrin, α- and γ-chlordane, trans-nonachlor, and heptachlor epoxide were detected (Table 2); as well as PCB congeners (Table 3). Total levels of OCPs and PCBs in SRW blubber were in the ranges of 2.9–53.6 and <DL–42.2 ng·g$^{-1}$ ww, respectively. OCP levels were slightly higher than PCBs for all age categories and both sexes. Although it is not possible to make a straight comparison of organochlorine concentrations for the different sampling years because the number of samples was highly variable for calves, a stable trend in OCP values from 2004 to 2011 (Fig. 2a) and in PCB values from 2005 to 2011 (Fig. 2b) was observed. OCP and PCB concentrations showed a slightly positive correlation ($R^2$ = 0.180; $p < 0.05$; n = 35) that increased to $R^2$ = 0.651 when eight extreme values were removed. In addition, correlations between TBL and organochlorine levels at 95% confidence were not found (OCPs, $R^2$ = 0.070; PCBs, $R^2$ = 0.024; n = 35).

Among pesticides, endosulfans contributed 44% to the total concentration measured in all samples, DDTs 24%, other cyclodienes 23%, and HCHs 9% (Fig. 3a). Methoxychlor was not detected in any sample. Other cyclodiene distributions followed the order:

**Table 1**
Sample description and sampling year for Southern Right Whale blubber specimens collected at Peninsula Valdes, Argentina.

| Year/sample | 2003_1 | 2003_2 | 2004_3 | 2005_4 | 2005_5 | 2005_6 | 2006_7 |
|---|---|---|---|---|---|---|---|
| Age | C | C | C | C | C | C | C |
| Sex | M | M | M | F | F | M | F |
| Length (m) | 3.8 | 6.2 | 5.0 | 4.9 | 5.4 | 6.6 | 5.7 |
| Year/Sample | 2006_8 | 2006_9 | 2006_10 | 2007_11 | 2009_12 | 2009_13 | 2009_14 |
| Age | C | C | A | C | C | C | C |
| Sex | F | M | F | UK | M | M | F |
| Length (m) | 5.4 | 7.7 | 12.5 | 5.3 | 6.1 | 6.7 | 6.6 |
| Year/sample | 2009_15 | 2009_16 | 2009_17 | 2010_18 | 2010_19 | 2010_20 | 2010_21 |
| Age | C | C | C | C | A | C | C |
| Sex | F | M | F | M | F | M | F |
| Length (m) | 6.3 | 7.3 | 6.4 | 7.3 | 12.5 | 7.4 | 7.1 |
| Year/sample | 2010_22 | 2010_23 | 2011_24 | 2011_25 | 2011_26 | 2011_27 | 2011_28 |
| Age | C | J | J | C | C | C | C |
| Sex | F | F | F | F | F | M | M |
| Length (m) | 7.8 | 11.9 | 10.5 | 6.4 | 4.6 | 7.4 | 6.4 |
| Year/sample | 2011_29 | 2011_30 | 2011_31 | 2011_32 | 2011_33 | 2011_34 | 2011_35 |
| Age | J | C | C | C | C | C | C |
| Sex | UK | F | F | M | F | M | M |
| Length (m) | 10.7 | 7.9 | 6.5 | 5.2 | 7.8 | 8.3 | 5.8 |

Abbreviations: C (calf); J (juvenile); A (adult); M (male); F (female); UK (unknown).

Dieldrin > α-chlordane > heptachlor epoxide > γ-chlordane > trans-nonachlor. Among the 25 PCB congeners assessed in *E. australis*, only the congeners 8, 18, 28, 44, 52, 66, 101, 110, 118, 123/149, 138, 153, and 180 were found, and the contribution of each to the total PCBs concentration is showed in Fig. 3b.

Ratios DDT/DDE and αHCH/γHCH were assessed in order to identify possible fresh pesticide inputs. DDE metabolite was present as a unique representative of the DDT group in 57% of all samples whilst in 14% of them a prevalence of DDE over DDT was observed. Particularly, DDT was present as the sole representative of the group in 2 samples (6%) and the DDT/DDE ratio was >1 in 7 samples (20%). DDD was present as trace levels (0.1 $ng \cdot g^{-1}$ ww) only in one specimen. Among HCH isomers, the highest values were found for γ-HCH (Lindane) which accounted for 50 to 100% of the total HCHs; in fact, values for the αHCH/γHCH ratio ranged from <DL to 0.37. According to the number of chlorine atoms, penta-chlorinated biphenyls represented near 59% of the total PCBs analyzed whilst tri-chlorinated was 18%, tetra-chlorinated 12%, di-chlorinated 5%, hexa-chlorinated 5%, and hepta-chlorinated 2% (Fig. 4). $\sum$IndPCBs varied between <DL and 6.2 $ng \cdot g^{-1}$ ww and there was at least one indicator PCB in 60% of all samples. In addition, PCB #118, considered carcinogenic, was present in 43% of total samples.

## 4. Discussion

The background concentrations obtained in this study indicate organochlorine bioaccumulation in SRW blubber tissue. In mammals, exposure to organochlorines (OCs) is exclusively linked to a contaminated diet (Kleivane and Skaare, 1998). When in the breeding areas in Peninsula Valdés SRWs ingest almost no food (Payne, 1986). Beyond the breeding season they feed mostly on krill at high latitudes in the Southern Atlantic Ocean (Valenzuela et al., 2009), and thus likely incorporate organochlorines via prey ingestion. Although organochlorines have not been assessed in krill from SRW foraging grounds, POP occurrence has been reported in krill from Antarctic areas (Corsolini et al., 2002; Bengtson Nash et al., 2008). Given the distance from potential pollutant sources, the presence of organochlorines in SRW tissues should not be expected. However, the volatility of these compounds facilitates atmospheric global transport mainly from southern hemisphere countries, leading to their presence in higher latitudes and remote places. Antarctic krill transfers organic matter produced by nanoplankton and diatoms up the food chain to cephalopods, fish, seabirds, seals, and baleen whales. OCs such as HCHs, DDTs, and PCBs reported from 1988 to 2008 in Antarctic krill suggested the potential role of krill in POP transfer both in baleen whales and in higher levels of the Antarctic trophic web (Fuoco et al., 2009).

Although whale calves sampled in this study died before they left the waters of PV, they likely acquired contaminants through the placenta during gestation and later from their mother's milk while nursing. The gestation period is around one year and calves have a prolonged lactation period that may vary between 6 and 12 months (Bastida and Rodriguez, 2009). In cetaceans, the relative abundance of various toxic compounds is affected by reproductive and/or gestation processes. In the reproductive stage the transference of less lipophilic compounds is higher than the more lipophilic ones (Aguilar et al., 2002). In various dolphins for example, the transference of *p,p′*-DDE is higher than *p,p′* DDT during lactation, and higher for DDT than PCBs (Borrel et al., 1995; Tanabe et al., 1988). This could explain the higher DDE levels in calf blubber found in this study. This differential transfer has in turn effects on relationships such as DDE/DDT for ecotoxicological determinations (Aguilar et al., 2002). In general, OC accumulation depends on animal age and occurs during the growth stage, being higher in older animals, in both sexes. However, females present lower levels than males after sexual maturity. This pattern has been explained by the transfer of OCs, in considerable quantities, during lactation to their calves (Tanabe et al., 1994; Borrel et al., 1995).

Bengtson Nash et al. (2008) found 18 PCB congeners and various OCPs in *E. superba* krill sampled in the eastern Antarctic sector. These authors reported organochlorine total levels (expressed as $pg \cdot g^{-1}$ ww) in the range of <LOQ-66 for PCBs (36); <LOQ-52.4 for HCHs; 16.30–371.4 for DDTs; <LOQ-38.8 for dieldrin; 3–23.6 for heptachlor epoxide; 2.40–26.6 for trans-nonachlor; and <LOQ-25.2 for α-endosulfan. In SRW, PCB ($7.5 \pm 10$ $ng - g^{-1}$ ww) and OCP ($22.6 \pm 13.8$ $ng \cdot g^{-1}$ ww) levels were up to three and two orders of magnitude higher than reported levels for krill, respectively, suggesting POP accumulation through the whales' diet. In addition, average concentration

**Table 2**
Pesticide levels in Southern Right whale blubber collected at Peninsula Valdes, Argentina, expressed as $ng \cdot g^{-1}$ ww.

| Year/sample | Organochlorine pesticide | | | | | | | | | | | | | | | | | | | ΣOCPs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | α HCH | β HCH | γ HCH | ∂ HCH | Aldrin | Dieldrin | Endrin | Endrin-Ket | Heptachlor | Hep-ep | t-Nonac | α Chlord | γ Chlord | DDT | DDE | DDD | Endo α | Endo β | Endo S | Methoxychlor | |
| 2003_1 | <LD | 0.4 | 0.7 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.1 | 0.1 | <LD | 1.5 | 0.3 | <LD | <LD | 3.2 |
| 2003_2 | <LD | 0.6 | <LD | <LD | <LD | 0.3 | <LD | <LD | <LD | <LD | <LD | <LD | 0.1 | <LD | 0.3 | <LD | 1.0 | 0.7 | <LD | <LD | 3.0 |
| 2004_3 | <LD | <LD | 1.0 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.7 | <LD | <LD | 26.6 | <LD | 2.5 | 0.3 | <LD | <LD | 31.0 |
| 2005_4 | <LD | <LD | 0.7 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.1 | 0.3 | 0.7 | 0.6 | <LD | 4.1 | 1.3 | <LD | <LD | 8.0 |
| 2005_5 | <LD | 0.4 | 1.5 | <LD | <LD | 1.1 | <LD | <LD | <LD | 0.2 | <LD | <LD | <LD | <LD | 25.1 | <LD | 7.1 | 0.5 | <LD | <LD | 35.8 |
| 2005_6 | <LD | <LD | 3.5 | <LD | <LD | 5.6 | <LD | <LD | <LD | <LD | <LD | 1.1 | <LD | <LD | 5.5 | <LD | 13.6 | 2.4 | <LD | <LD | 31.7 |
| 2006_7 | <LD | 0.3 | 0.4 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.2 | 0.5 | <LD | 5.8 | <LD | 3.6 | <LD | <LD | <LD | 10.9 |
| 2006_8 | <LD | 0.4 | 0.7 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.3 | <LD | <LD | 50.1 | 1.5 | <LD | <LD | 53.0 |
| 2006_9 | 0.5 | <LD | 1.3 | <LD | <LD | 1.4 | <LD | <LD | <LD | <LD | <LD | 0.3 | 1.1 | 0.7 | 0.7 | <LD | 10.6 | 1.4 | <LD | <LD | 18.0 |
| 2006_10 | <LD | 0.8 | 1.6 | <LD | <LD | 4.6 | <LD | <LD | <LD | 0.4 | <LD | 1.1 | 0.4 | 1.4 | 2.1 | <LD | 10.7 | 1.6 | 6.1 | <LD | 30.6 |
| 2007_11 | <LD | <LD | <LD | <LD | <LD | 2.2 | <LD | <LD | <LD | <LD | <LD | 0.9 | 0.3 | <LD | 1.9 | 0,0 | 2.5 | 2.5 | <LD | <LD | 10.3 |
| 2009_12 | <LD | 0.4 | 0.5 | <LD | <LD | <LD | <LD | <LD | <LD | 2.1 | <LD | 2.0 | 0.7 | <LD | <LD | <LD | 4.0 | 0.4 | 1.4 | <LD | 11.5 |
| 2009_13 | 0.1 | <LD | 1.1 | <LD | <LD | 3.7 | <LD | <LD | <LD | 0.5 | <LD | <LD | <LD | <LD | 1.9 | <LD | 2.0 | <LD | <LD | <LD | 9.3 |
| 2009_14 | 0.1 | <LD | 0.6 | <LD | <LD | 3.8 | <LD | <LD | <LD | 0.2 | <LD | 2.9 | <LD | <LD | 2.7 | <LD | 1.8 | 2.8 | <LD | <LD | 14.9 |
| 2009_15 | <LD | <LD | 1.5 | <LD | <LD | 2.1 | <LD | <LD | <LD | <LD | <LD | 5.2 | 1.3 | <LD | 1.2 | <LD | 22.5 | 4.5 | <LD | <LD | 38.3 |
| 2009_16 | <LD | <LD | <LD | <LD | <LD | 1.2 | <LD | <LD | <LD | 0.3 | <LD | 1.1 | 0.2 | <LD | 1.9 | <LD | 1.0 | 0.4 | <LD | <LD | 6.1 |
| 2009_17 | 0.1 | 0.8 | 1.7 | <LD | <LD | 10.4 | <LD | <LD | <LD | 1.3 | <LD | 6.4 | 0.6 | <LD | 6.7 | <LD | 6.7 | 1.1 | <LD | <LD | 35.7 |
| 2010_18 | <LD | 0.5 | 0.8 | <LD | <LD | 1.2 | <LD | <LD | <LD | 0.5 | <LD | <LD | <LD | <LD | 0.6 | <LD | 2.0 | 0.8 | <LD | <LD | 6.3 |
| 2010_19 | 0.1 | <LD | 0.5 | <LD | <LD | 5.8 | <LD | <LD | <LD | 0.6 | <LD | 8.4 | 0.4 | 8.6 | 4.5 | <LD | 4.5 | 1.7 | 4.4 | <LD | 39.3 |
| 2010_20 | <LD | 0.4 | 1.3 | <LD | <LD | 1.2 | <LD | <LD | <LD | 0.1 | <LD | 0.9 | 0.2 | <LD | 2.8 | <LD | 11.0 | 1.6 | <LD | <LD | 19.6 |
| 2010_21 | <LD | 0.5 | 3.2 | <LD | <LD | 4.8 | <LD | <LD | <LD | 2.8 | <LD | 1.3 | <LD | <LD | 5.3 | 0,1 | 10.6 | 2.5 | 2.2 | <LD | 33.3 |
| 2010_22 | <LD | 0.6 | 3.2 | <LD | <LD | 6.5 | <LD | <LD | <LD | 0.5 | <LD | 10.2 | 0.5 | 7.1 | <LD | <LD | 8.1 | 14.9 | <LD | <LD | 51.7 |
| 2010_23 | <LD | 0.4 | 0.4 | <LD | <LD | 2.2 | <LD | <LD | <LD | 1.0 | <LD | <LD | 0.2 | 1.4 | 1.4 | <LD | 6.5 | 1.7 | 3.4 | <LD | 18.7 |
| 2011_24 | 0.1 | <LD | 6.6 | <LD | <LD | 4.3 | <LD | <LD | <LD | 2.2 | <LD | 1.3 | <LD | 1.0 | 5.5 | <LD | 12.7 | 1.6 | 0.7 | <LD | 35.9 |
| 2011_25 | 0.1 | <LD | 2.0 | <LD | <LD | 3.5 | <LD | <LD | <LD | <LD | <LD | 5.8 | <LD | <LD | 3.1 | <LD | 6.2 | 1.5 | 1.9 | <LD | 24.0 |
| 2011_26 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.1 | 0.2 | 0.3 | 3.1 | <LD | 0.3 | 0.3 | <LD | <LD | 4.3 |
| 2011_27 | <LD | <LD | 1.9 | <LD | <LD | <LD | <LD | <LD | <LD | <LD | <LD | 0.1 | <LD | 0.1 | 0.5 | <LD | 3.5 | 2.2 | <LD | <LD | 8.3 |
| 2011_28 | <LD | 1.1 | 2.9 | <LD | <LD | 5.0 | <LD | <LD | <LD | 2.9 | <LD | <LD | <LD | <LD | 13.7 | <LD | <LD | 0.6 | <LD | <LD | 26.2 |
| 2011_29 | 0.1 | <LD | 1.1 | <LD | <LD | 1.5 | <LD | <LD | <LD | 0.2 | <LD | 2.9 | 0.1 | <LD | 2.2 | <LD | 2.1 | 2.3 | <LD | <LD | 12.3 |
| 2011_30 | <LD | <LD | 2,7 | <LD | <LD | <LD | <LD | <LD | <LD | 0.7 | <LD | 5.7 | 1.0 | <LD | 7.2 | <LD | 12.2 | 3.4 | <LD | <LD | 33.0 |
| 2011_31 | <LD | <LD | 0,5 | <LD | <LD | 4.7 | <LD | <LD | <LD | 0.8 | <LD | 4.8 | 0.6 | 6.2 | 3.3 | <LD | 3.4 | 0.1 | 3.8 | <LD | 28.2 |
| 2011_32 | <LD | <LD | 2,4 | <LD | <LD | 1.7 | <LD | <LD | <LD | <LD | 0.3 | 2.7 | <LD | <LD | 4.3 | <LD | 0.4 | 0.5 | 0.3 | <LD | 12.7 |
| 2011_33 | <LD | <LD | 8,5 | <LD | <LD | 1.5 | <LD | <LD | <LD | <LD | 0.3 | 0.1 | 0.6 | <LD | <LD | <LD | 24.0 | 2.8 | <LD | <LD | 37.8 |
| 2011_34 | <LD | <LD | 2,2 | <LD | <LD | 3.5 | <LD | <LD | <LD | <LD | 0.4 | <LD | <LD | 1.2 | 10.1 | <LD | 0.8 | 2.6 | <LD | <LD | 20.9 |
| 2011_35 | <LD | <LD | 2,5 | <LD | <LD | 6.2 | <LD | <LD | <LD | 0.9 | 0.4 | <LD | <LD | <LD | 9.9 | <LD | 5.2 | 1.1 | <LD | <LD | 26.2 |

**Table 3**
PCB levels in Southern Right Whale blubber collected at Peninsula Valdes, Argentina, expressed as ng·g$^{-1}$ ww.

| Year/Sample | PCB congener # | | | | | | | | | | | | | | | | | | | | | | ΣPCBs | ΣI-PCBs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 8 | 18 | 28/31 | 52 | 44 | 66 | 101 | 110 | 123/149 | 118 | 153 | 105 | 138 | 187 | 128 | 156 | 180 | 170 | 189 | 195 | 206 | 209 | | |
| 2003_1 | <DL | 0.7 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.7 | <DL |
| 2003_2 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| 2004_3 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 38.6 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 38.6 | <DL |
| 2005_4 | <DL | 1.4 | <DL | <DL | <DL | <DL | <DL | <DL | 0.8 | 0.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 2.6 | <DL |
| 2005_5 | <DL | <DL | <DL | 2.2 | 0.7 | <DL | <DL | 39.3 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 42.2 | 2.2 |
| 2005_6 | <DL | 3.3 | <DL | <DL | <DL | <DL | <DL | 0.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 3.8 | <DL |
| 2006_7 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.9 | <DL | <DL | <DL | <DL | <DL | 0.9 | 0.9 |
| 2006_8 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.1 | 0.7 | 0.4 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.2 | <DL |
| 2006_9 | <DL | 1.1 | <DL | 0.1 | <DL | 1.0 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 2.2 | 0.1 |
| 2006_10 | <DL | 2.0 | 0.2 | <DL | 1.5 | <DL | <DL | <DL | 0.9 | 1.1 | <DL | <DL | 0.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 5.7 | 0.3 |
| 2007_11 | <DL | <DL | 2.0 | <DL | <DL | <DL | <DL | <DL | 0.6 | <DL | <DL | <DL | 0.2 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 2.8 | 2.1 |
| 2009_12 | 2.4 | <DL | <DL | <DL | <DL | 0.5 | <DL | <DL | 0.3 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 3.2 | <DL |
| 2009_13 | <DL | <DL | 1.2 | <DL | <DL | <DL | <DL | <DL | 0.5 | 0.6 | 5.0 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 7.2 | 6.2 |
| 2009_14 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.5 | <DL |
| 2009_15 | 2.1 | <DL | 6.1 | <DL | <DL | 0.5 | <DL | <DL | <DL | 0.7 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 9.4 | 6.1 |
| 2009_16 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.7 | 0.1 | 0.3 | <DL | <DL | <DL | <DL | <DL | 0.1 | <DL | <DL | <DL | <DL | <DL | 1.1 | 0.4 |
| 2009_17 | 1.5 | <DL | <DL | 1.0 | <DL | 0.9 | <DL | 2.1 | <DL | 0.6 | <DL | <DL | <DL | <DL | <DL | <DL | 1.5 | <DL | <DL | <DL | <DL | <DL | 7.6 | 2.5 |
| 2010_18 | <DL | <DL | <DL | <DL | 1.5 | <DL | <DL | 5.1 | 0.9 | 0.9 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 8.3 | <DL |
| 2010_19 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.6 | 1.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.7 | <DL |
| 2010_20 | 1.2 | 1.5 | <DL | <DL | 0.9 | 0.3 | <DL | <DL | 0.8 | 0.8 | 1.5 | <DL | 0.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 7.2 | 1.6 |
| 2010_21 | 3.4 | 4.3 | 0.3 | <DL | 1.3 | 1.3 | <DL | 11.4 | 0.6 | 0.7 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 23.3 | 0.3 |
| 2010_22 | 2.0 | 3.1 | 2.7 | <DL | 1.6 | 0.5 | <DL | <DL | 0.3 | 1.2 | <DL | <DL | <DL | <DL | <DL | <DL | 1.5 | <DL | <DL | <DL | <DL | <DL | 12.9 | 4.1 |
| 2010_23 | <DL | <DL | <DL | <DL | <DL | 0.4 | <DL | <DL | 0.5 | <DL | <DL | <DL | 0.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.0 | 0.1 |
| 2011_24 | <DL | <DL | <DL | <DL | 1.4 | <DL | <DL | 2.0 | <DL | <DL | 0.5 | <DL | 0.1 | <DL | <DL | <DL | 0.5 | <DL | <DL | <DL | <DL | <DL | 4.5 | 1.1 |
| 2011_25 | <DL | <DL | <DL | <DL | <DL | 0.3 | <DL | 4.6 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 0.4 | <DL | <DL | <DL | <DL | <DL | 5.4 | 0.4 |
| 2011_26 | <DL | <DL | <DL | <DL | <DL | <DL | 0.5 | 0.6 | <DL | <DL | 0.5 | <DL | 0.3 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 2.0 | 1.3 |
| 2011_27 | <DL | 1.5 | <DL | <DL | <DL | 0.1 | <DL | 0.2 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.7 | <DL |
| 2011_28 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.5 | 1.6 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 3.1 | <DL |
| 2011_29 | <DL | 0.3 | 1.1 | <DL | <DL | <DL | <DL | 1.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 2.5 | 1.1 |
| 2011_30 | <DL | 2.7 | <DL | <DL | <DL | <DL | <DL | 3.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 6.1 | <DL |
| 2011_31 | <DL | <DL | 1.2 | 0.2 | 0.1 | <DL | <DL | 2.1 | 0.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 1.0 | <DL | <DL | <DL | <DL | <DL | 5.0 | 2.4 |
| 2011_32 | <DL | <DL | <DL | <DL | 0.4 | <DL | <DL | 4.2 | <DL | <DL | 1.1 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 5.7 | 1.1 |
| 2011_33 | <DL | 7.4 | <DL | <DL | 4.5 | <DL | <DL | 7.2 | 0.8 | 1.4 | 2.8 | <DL | 0.5 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 24.5 | 3.3 |
| 2011_34 | <DL | 1.5 | <DL | <DL | <DL | <DL | <DL | 2.2 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 3.7 | <DL |
| 2011_35 | <DL | <DL | <DL | 0.5 | 5.6 | 1.0 | <DL | 4.9 | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | 12.0 | 0.5 |

Abbreviation: <DL (value lower than detection limit).

of PCBs in SRW blubber was one order of magnitude lower than OCPs. Coincidentally, Bengtson Nash et al. (2008) reported that in contrast to the Arctic, where PCBs dominate biotic and abiotic persistent organohalogen chemical profiles, PCBs did not feature prominently in Antarctic krill sampled in the eastern Antarctic sector.

HCHs were composed of 87% γ-HCH (Lindane), 11% β-HCH, and 1.5% α-HCH, while δ-HCH was not detected. Technical degree HCHs, used in agricultural activities, generally contains 55–80% α-HCH, 5–12% β-HCH, 8–15% γ-HCH, and 2–16% δ-HCH (Lee et al., 2001). According to Kim et al. (2002), the value of the ratio α-/γ- isomers between 4 and 7 in the technical commercial mixture is relatively stable and can be used as an indicator of degradation degree or as signal of current use of commercial HCH. In this study, the value of α-HCH/ γ-HCH ratios was lower than 0.37 indicating degradation processes of α-HCH; in fact, α-HCH was only detected in 8 of the 35 assessed specimens. In addition to technical commercial mixture, lindane was commonly used in pure form. In Argentina for example, lindane was utilized in this way at least up to three years ago, which could justify its predominance over the other HCH isomers. The use and commercialization of γ-HCH in Argentina were suspended in 2011 by disposition N° 617/2011 (Administración Nacional de Medicamentos, Alimentos y Tecnología Médica, ANMAT). According to Muir and de Wit (2010), previous studies of the Arctic Monitoring and Assessment Program (AMAP) have highlighted Lindane (γ-HCH) as a current use pesticide (CUP) that was ubiquitously present in the Arctic.

Both DDE and DDT were found in SRW blubber tissues. Bengtson Nash et al. (2008) reported *p,p′*-DDE in 78% of Antarctic krill samples in concentrations that ranged from <LOQ to 348 pg·g$^{-1}$ ww, and DDT levels of 10.8–27.6 pg·g$^{-1}$ ww. In the present study DDE was detected in 71% of the samples with an average concentration of 5.5 ± 6.5 ng·g$^{-1}$ ww (n = 29) and DDT with 2.85 ± 3.14 ng·g$^{-1}$ ww (n = 10), suggesting DDT bioaccumulation through the whale's diet. In addition, the ratio *p,p′*-DDT/*p,p′*-DDE was lower than 0.33 indicating a past DDT input in SRW (Strandberg et al., 1998). Likewise, Bengtson Nash et al. (2008) reported DDT:DDE ratios of 0.073 to 0.322 noting that these low values reflected the legacy of DDT in the Southern Ocean ecosystem as well as distance from fresh source inputs. However, recent DDT incorporation by the whales was suggested by the exclusive occurrence of this compound in two specimens as well as its prevalence over DDE in some samples (n = 8). The study by Bengtson Nash et al. (2008) in Antarctic krill provided information regarding DDT and its degradation products in the Southern Ocean ecosystem at a critical historical time point highlighting the persistence of these compounds despite 30 years of prohibition. On the basis of these reports, the levels of DDTs found in SRW would be a consequence of ongoing exposure to these contaminants through their diet. A potential current source of DDT could be malaria control, following recommendations from the World Health Organization for its use in indoor residual spraying (IRS) applications, until the development of alternative products and methods (WHO, 2011). In countries from the southern hemisphere DDT is still used for this purpose (UNEP/WHO, 2012). Moreover the use of Dicofol as an acaricide is a common practice at worldwide level and impurities of DDT (10%) are a consequence during manufacturing processes of Dicofol. Therefore, the use of this acaricide could represent another fresh input source of DDT to the environment.

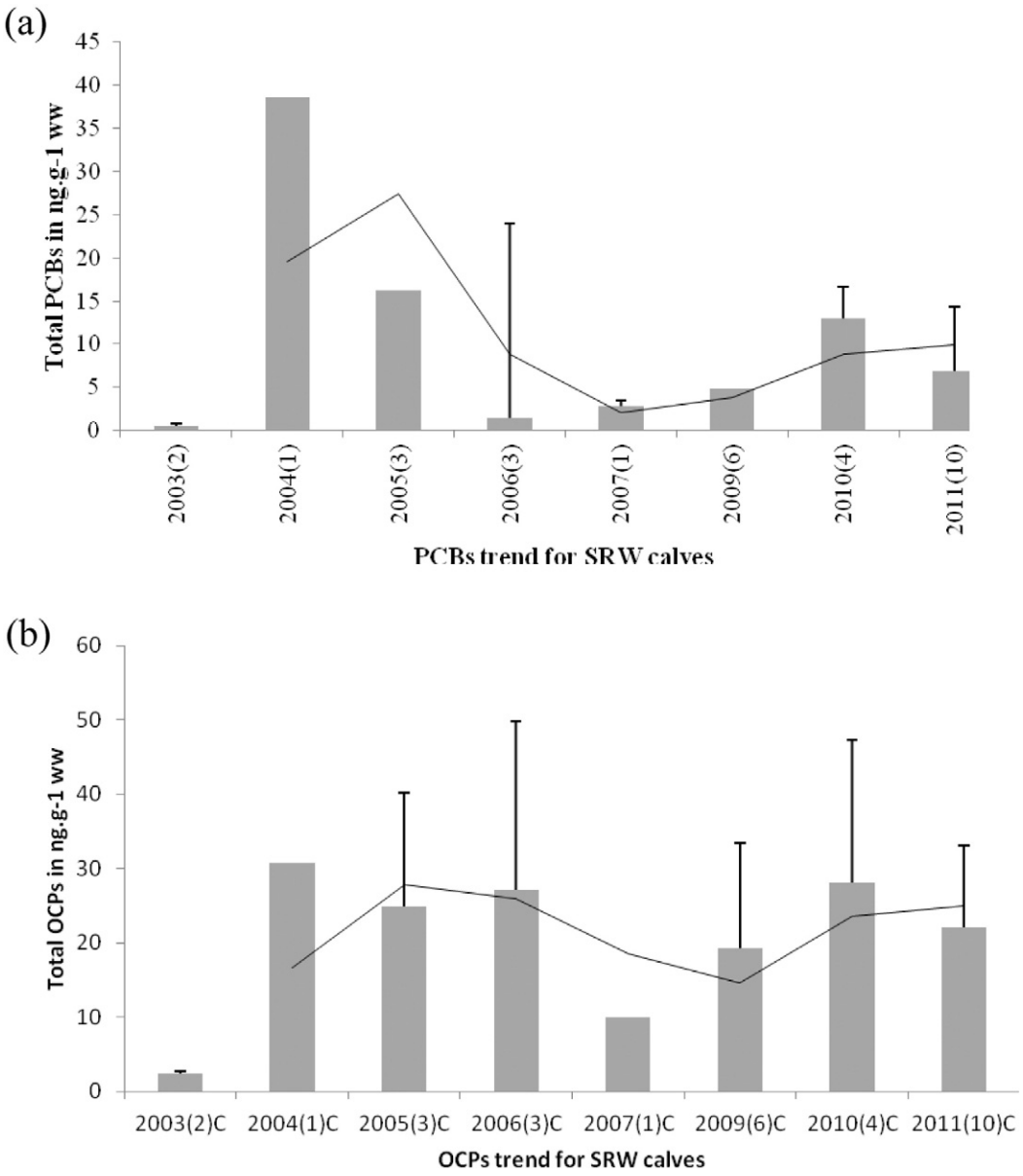


**Fig. 2.** PCB (a) and OCP (b) trends for SRW calves. Bars represent 1 positive standard deviation.

Endosulfan was detected in all SRW specimens. α-Endosulfan was the predominant compound contributing in 75% to the total endosulfan concentration ($\sum \alpha + \beta +$ endosulfan sulphate); while the β-isomer contributed in 19%. Lower levels were found for the metabolite endosulfan sulphate. In the commercial product α- and β-isomers are present approximately in a ratio 7:3. The predominance of α- over β-isomer indicates a recent input of the insecticide to the South West Atlantic (SWA). In addition, Schmidt et al. (2001) reported that α-endosulfan is the more thermodynamically stable of the two isomers; thus β-endosulfan could convert irreversibly to the α-form, although the conversion is slow. According to Muir and de Wit (2010), endosulfan is still in use as an insecticide in many parts of the world including circumpolar countries. Particularly in Argentina, endosulfan has been banned since July 1st, 2013 (Resolution No 511/11, Servicio Nacional de Sanidad Animal, SENASA). While overall global use has remained relatively constant at around 12,000 t/y from the mid-1990s to 2004, quantities produced in China increased over the same period (Jia et al., 2009). Despite the special focus placed on endosulfan in the Arctic environment due to its being the most abundant current use pesticide (CUP) (Weber et al., 2010), nothing is known about its presence in the biotic and abiotic matrixes of the Antarctic area. This is the first report of endosulfan in a baleen whale from the southern hemisphere feeding in the SWA near Antarctica. Among the other cyclodienes assessed, the levels of aldrin, endrin and endrin ketone were below the detection limit, while dieldrin was present in 77% of samples. It is known that aldrin is quickly transformed to the much more toxic and persistent dieldrin (Falandysz et al., 1998). Unfortunately there is no information about the aldrin's group in other substrates of the SWA environment. A few studies in Argentina's watersheds and coastal areas have demonstrated the occurrence of dieldrin in the environment (i.e. Colombo et al., 2011) suggesting sources for this compound. Heptachlor (banned in Argentina in 1993) was not present in SRW blubber tissues, but its degradation product heptachlor epoxide was found, suggesting no recent input of heptachlor in the analyzed samples.

$\sum$PCBs varied between <DL and 42.2 ng·g$^{-1}$ ww and higher concentrations were found for congener 110. Corsolini et al. (2007), reported sumPCB concentration ranging from 85.27 to 282.29 ng·g$^{-1}$ ww in krill from the Ross Sea, up to one order of magnitude higher than the

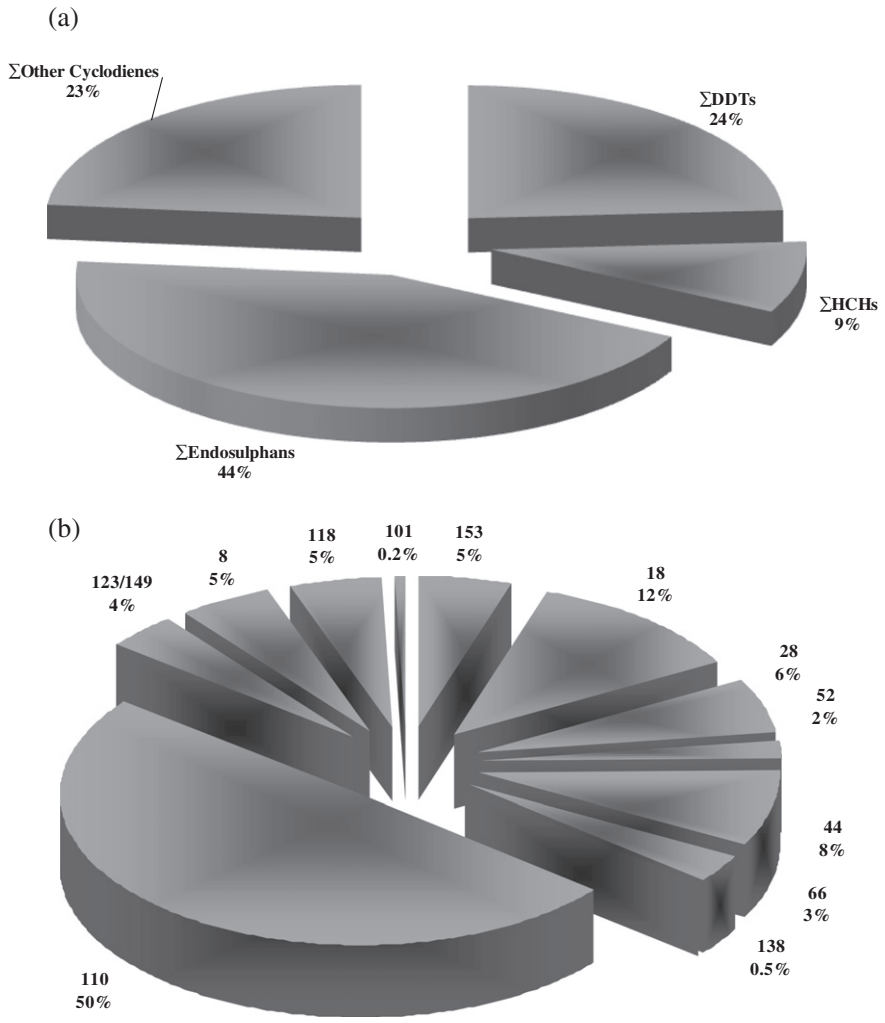


**Fig. 3.** Contribution of OCP groups (a) and PCB congeners (b) to the total concentrations found in SRW blubber.

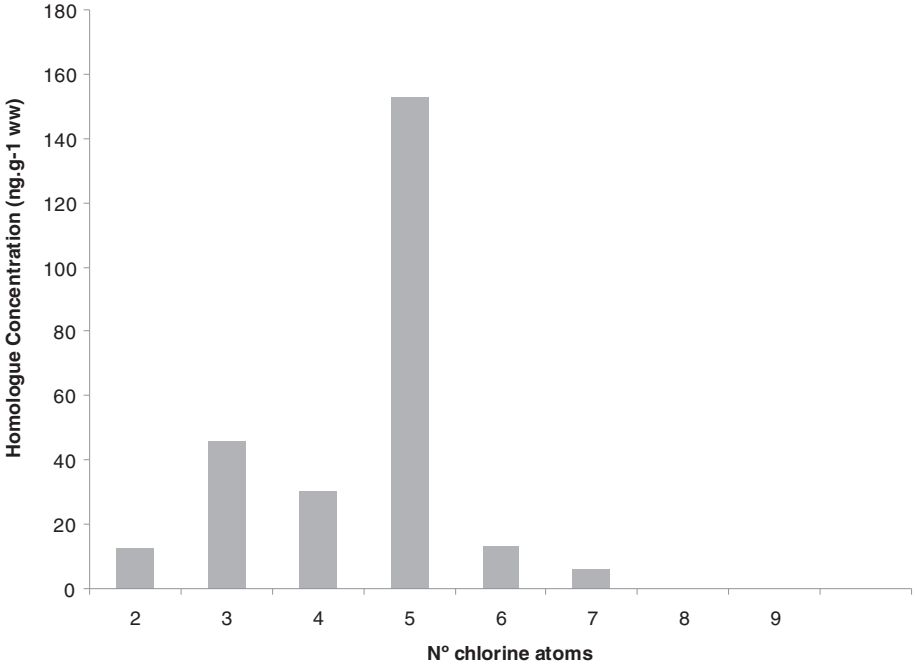


**Fig. 4.** PCB congener homologue concentrations.

values determined in SRW in this study. These facts, as well as those indicated in other reports (i.e. Kajiwara et al., 2004; Kock et al., 1994), point to the occurrence of PCBs in the Southern Ocean. The presence of these compounds may also be linked to the rapid melting of packed-ice in which POPs, carried through atmospheric transport during the 8–9-month winter season, are trapped and consequently released in the surrounding water. It is during this period that lower organisms of the marine food web abound (Corsolini et al., 2002).

Bengtson Nash et al. (2008) also evaluated PCB levels in Antarctic krill finding that they rarely exceeded several hundred pg·g$^{-1}$ lipid. In SRW, $\sum$PCB normalized by the lipid content ranged from <DL to almost 400 ng·g$^{-1}$ lipid, indicating bioaccumulation processes in the whales, at least partially, through krill ingestion. In SRW, penta-chlorinated predominated over other PCB congeners, showing a similar distribution pattern than for Antarctic krill in which penta-chlorinated congeners were also dominant (Bengtson Nash et al., 2008). Lower chlorinated congeners, with relatively higher vapor pressures and thus longer atmospheric residence times are expected to reach higher latitudes in greater quantities. This phenomenon is supported by the analysis of soil samples from the eastern Antarctic sector by Negoita et al. (2003). Thus, soil samples were analyzed for 28 PCB congeners being the lower chlorinated tri-, tetra- and penta-chlorinated biphenyls (penta-CBs) the main PCBs found in the profiles. Similarly Corsolini et al. (2003) found a predominance of lower chlorinated PCBs at low trophic levels (e.g. silverfish and krill). This pattern differs from findings at low and mid-latitudes in different organisms since many volatile congeners are prevalent at higher latitudes due to global fractionation. In silverfish larvae and krill, tetra-CBs were the main PCB group found. Moreover, tri-, tetra- and penta-CB congeners constituted more than 50% of the total residue in krill and larvae and less than 50% in adult silverfish (Corsolini et al., 2003). In 21 samples of SRW at least one indicator PCB was found and among them the dominant compounds were the congeners 28 (39%), 153 (31%), 180 (15%), and 52 (11%). In Antarctic krill the six indicator congeners were all represented among the three most dominant congeners at each site (Bengtson Nash et al., 2008). In addition, PCB #118, considered carcinogenic, was determined in 43% of SRW samples. Congener #118, a mono-ortho PCB, was determined in the range of <DL-1.6 ng·g$^{-1}$ ww. This congener is part of the list that the International Agency for Research on Cancer of the World Health Organization (IARC, http://www.iarc.fr/) re-categorized to group 1 "carcinogenic to humans". Various POPs may interact with the endocrine system of marine mammals affecting their health. Specifically, several organochlorines assessed in this study such as DDTs and PCBs are endocrine disruptors. These substances can interfere with the normal hormonal pathways producing harmful effects principally associated with a decrease in fertility and impaired reproduction in polar bears, cetaceans, and pinnipeds (Fossi and Marsili, 2003). Although endocrine disruption was not assessed in this study, the presence of the like-dioxin-PCB (LD-PCB) congener #118 is of concern, and this information can be useful for future assessment of these compounds in SRW. Other congeners found, in the group of non-dioxin-PCBs (ND-PCBs), are considered less toxic due to the chlorine positions in the molecule which hamper the interaction with the AhR (ATSDR, 2000; Elnar et al., 2012).

According to Méndez-Fernandez et al. (2014), reliable toxicity data for predatory marine mammals are scarce. The harmful consequences of the bioaccumulation of POPs in marine mammals include depression of the immune system (e.g. de Swart et al., 1996) and increased risk of infection and reproductive failure. Specifically, a total PCB concentration of 17 μg g$^{-1}$ lipid wt has been reported as a threshold level above which there are health effects in mammals (Kannan et al., 2000). In the current study, PCB levels in no case exceeded this toxic threshold. According to Bengtson Nash et al. (2014), baleen (filter feeding) whales are commonly attributed to a lower chemical risk category than their odontoceti (toothed whales) counterparts due to their lower trophic level. In fact, the principal route of POP accumulation in SRW would be the ingestion of large quantities of copepods and euphausiids (krill) while feeding in sub-Antarctic waters. In addition, POPs can accumulate on superficial natural oil layers and thus be available to organisms that live and eat in the more superficial strata of the water column. Therefore, the incorporation of these compounds in SRW tissues could happen through food, water, and/or suspended particulate material, substrates with which the whales interact, mainly when feeding.

### 4.1. Comparison with previous studies of organochlorines in whales from the Southern Hemisphere

Various studies reported bioaccumulation and biomagnification of organochlorine compounds in marine mammals which feed on prey of higher trophic levels than krill (Weisbrod et al., 2000; Mossner and Ballschmiter, 1997). Conversely, very little information is known about species which prey on lower trophic level organisms, such as SRW. Woodley et al. (1991) analyzed concentrations of DDT, heptachlor epoxide, dieldrin, chlordane, and PCBs in Northern Right Whales (*Eubalaena glacialis*). These authors sampled blubber from dead adult males (n = 6) and females (n = 6), juveniles (n = 3), and calves (n = 2), and found contaminant concentrations one to three orders of magnitude higher than those reported in this study for *E. australis* (Table 4). Kock et al. (1994) reported ΣDDT, HCB, and PCBs in cetaceans from the southern hemisphere, including two male specimens of SRW sampled in 1984 and 1986. Values reported by Kock et al. (1994) for DDTs and PCBs in SRW were around 10 ng·g$^{-1}$ ww, similar or lower than trace levels found by Woodley et al. (1991). In the current study, performed 30 years later, the levels of DDTs and PCBs in SRW ranged from <DL to 27 ng·g$^{-1}$ ww and PCBs from <DL to 42 ng·g$^{-1}$ ww, two and four fold higher, respectively, than the concentrations recorded by Kock et al. (1994). Comparisons of organochlorine compound levels between previous and current studies are useful to assess trends over the years, particularly since their use was banned. However, some

**Table 4**
Comparison of OC concentrations (DDT, heptachloro-epoxide, dieldrin, chlordane, and PCBs) in Northern Right Whale (*E. glacialis*) (Woodley et al., 1991) and Southern Right Whale (*E. australis*) (this study).

| OCs ng·g$^{-1}$ ww | | | | | |
|---|---|---|---|---|---|
| Individuals | Total DDT | Heptachlor epox. | Dieldrin | Chlordane | PCBs |
| *Adult males* | | | | | |
| M1 | 210 | TR | 40 | TR | 900 |
| M2 | 440 | nd | 50 | TR | 700 |
| M3 | 30 | nd | TR | nd | 100 |
| M4 | 470 | nd | 50 | nd | 1900 |
| M5 | 80 | nd | 20 | nd | ND |
| M6 | 20 | nd | 20 | nd | 300 |
| *Adult females* | | | | | |
| F1 | TR | nd | nd | nd | 100 |
| F2 | 60 | nd | TR | TR | 700 |
| F3 | 20 | nd | TR | TR | 500 |
| F4 | 20 | nd | TR | nd | 400 |
| F5 | 20 | nd | 20 | TR | 400 |
| F6 | 30 | nd | 20 | nd | 400 |
| F, this study (n = 2) | 3.5–13 | 0.4–0.6 | 4.6–5.8 | 1.1–8.8 | 1.7–5.5 |
| *Juveniles* | | | | | |
| J1 | 70 | 20 | 40 | TR | 1400 |
| J2 | 30 | TR | 30 | TR | 600 |
| J3 | 110 | 20 | 40 | 0.02 | 800 |
| J, this study (n = 3) | 3.8 ± 2.3 | 1.09 ± 1.06 | 2.7 ± 1.5 | 1.5 ± 1.5 | 2.6 ± 1.7 |
| *Pups* | | | | | |
| P1 | TR | nd | TR | TR | 100 |
| P2 | 20 | nd | 20 | TR | 400 |
| C, this study (n = 30) | 5.4 ± 6.7 | 0.5 ± 0.9 | 2.4 ± 2.6 | 2.0 ± 2.8 | 8.2 ± 11.0 |

Abbreviations. nd: not detectable; TR: trace levels from 50 and 100 ng·g$^{-1}$ for PCBs and from 5 and 10 ng·g$^{-1}$ ww for OCPs.

parameters should be considered such as: (a) number of years elapsed (30 or more) between assessments; (b) advances in methodologies and equipment leading to improved detection limits; and (c) pollution by organochlorine compounds is higher in the northern than in the southern hemisphere due to greater development in northern countries. The latter issue is sustained by many studies at worldwide level (Borrel et al., 1995; Weisbrod et al., 2000; Kajiwara et al., 2004; Tanabe et al, 1986; Elfes et al., 2009).

## 5. Conclusions

Southern Right Whales presented organochlorine compounds in their blubber which are likely incorporated while feeding in sub-Antarctic waters. OCP and PCB levels determined in SRW were relatively low and similar to those reported for other cetaceans from the southern hemisphere. The prevalence of pesticides indicated the contribution of agricultural activities to oceanic pollution through watersheds. Interestingly, samples showed a predominance of recent endosulfan and aged DDT, coincident with the history of pesticide uses. These results constitute the first comprehensive report on organochlorine compounds in *E. australis* and provide an update on the status of DDT and PCB exposure since they were banned. Research on chemical contaminants in SRW has been highlighted as a need to better assess the potential causes contributing to recent high calf mortalities. Given that SRW is a species of both local and global relevance, the data reported in this study establishes a baseline for future studies and can contribute to management decisions.

## Acknowledgements

We are grateful to the Southern Right Whale Health Monitoring Program (SRWHMP) for samples and the government of Chubut, Argentina for work permits. We thank M. Di Martino and L. Beltramino for their assistance with sample collection in 2011, and L. La Sala, L. Pozzi, L. Musmeci, N. Mohamed, J. Andrejuk, J.E. Sala, L. Bandieri and A. Chirife for samples collected in previous years. Bomke and Puerto Madryn Municipality provided financial support to this study. The Laboratory of Ecotoxicology and Environmental Pollution of Mar del Plata University funded the organochlorine analysis. The SRWHMP has been funded by the US National Marine Fisheries Service, the US Marine Mammal Commission, the Island Foundation, Inc., The Lawrence Foundation, Wildlife Conservation Society, Fondo para la Conservación Ambiental del Banco Galicia, and Association of Zoo Veterinary Technicians. We specially thank V. Rowntree, M. Sironi, V. Rago and D. McAloose for their major contributions to the SRWHMP over the years.

## References

Agency for Toxic Substances and Disease Registry (ATSDR), 2000. U.S. Department of Health and Human Services. Public Health Service Agency for Toxic Substances and Disease Registry.
Aguilar, A., Borrel, A., Reijnders, P.J.H., 2002. Geographical and temporal variation in levels of organochlorine contaminants in marine mammals. Mar. Environ. Res. 53, 425–452.
Bastida, R., Rodriguez, D., 2009. In: Mazzini, Vázquez (Ed.), Mamíferos marinos. Patagonia y Antártida, p. 227.
Bengtson Nash, S.M., Poulsen, A.H., Kawaguchi, S., Vetter, W., Schlabach, M., 2008. Persistent organohalogen contaminant burdens in Antarctic krill (*Euphausia superba*) from the eastern Antarctic sector: a baseline study. Sci. Total Environ. 407, 304–314.
Bengtson Nash, S., Dawson, A., Burkhard, M., Waugh, C., Huston, W., 2014. Detoxification enzyme activities (CYP1A1 and GST) in the skin of humpback whales as a function of organochlorine burdens and migration status. Aquat. Toxicol. 155, 207–212.
Best, P., Payne, R., Rowntree, V., 1993. Long-range movements of South Atlantic Right Whales (*Eubalaena australis*). Mar. Mamm. Sci. 9 (3), 227–234.
Borrel, A., Bloch, D., Desportes, G., 1995. Age trends and reproductive transfer of organochlorine compounds in long finned pilot. Environ. Pollut. 88, 283–292.
Colombo, J.C., Cappelletti, N., Williamson, M., Migoya, M.C., Speranza, E., Sericano, J., Muir, D.C.G., 2011. Risk ranking of multiple-POPs in detritivorous fish from the Río de la Plata. Chemosphere 83, 882–889.
Cooke, J., Rowntree, V., Payne, R., 2001. Estimates of demographic parameters for southern right whales (*Eubalaena australis*) observed off Peninsula Valdes, Argentina. In: Best, P.B., Bannister, J.L., Brownell, R.L., Donovan, G.P. (Eds.), Right Whales: Worldwide Status. Journal of Cetacean Research and Management Special Issue 2, pp. 125–132.
Corsolini, S., Kannan, K., Imagawa, T., Focardi, S., Giesy, J., 2002. Polychloronaphthalenes and other dioxin-like compounds in Arctic and Antarctic marine food webs. Environ. Sci. Technol. 36, 3490–3496.
Corsolini, S., Ademollo, N., Romeo, T., Olmastroni, S., Focardi, S., 2003. Persistent organic pollutants in some species of a Ross Sea pelagic trophic web. Antarct. Sci. 15 (01), 95–104.
Corsolini, S., Borghesi, N., Schiamone, A., Focardi, S., 2007. Polybrominated diphenyl ethers, polychlorinated dibenzo-dioxins,-furans, and-biphenyls in three species of antarctic penguins. Environ. Sci. Pollut. Res. Int. 14 (6), 421–429.
De Swart, R.L., Ross, P.S., Vos, J.G., Osterhaus, A.D.M.E., 1996. Impaired immunity in harbour seals (*Phocavitulina*) exposed to bioaccumulated environmental contaminants: review of a long-term feeding study. Environ. Health Perspect. 104 (4), 823–828.
Elfes, C., Blaricom, V., Boyd, D., Calambokidis, J., 2009. Geographic variation of persistent organic pollutant levels in humpback whale (*Megaptera novaeangliae*) feeding areas of the North Pacific and North Atlantic. Environ. Toxicol. Chem. 29 (4), 824–834.
Elnar, A.A., Diesel, B., Desor, F., Feidt, C., Bouayed, J., Kiemer, A.K., Soulimani, R., 2012. Neurodevelopmental and behavioral toxicity via lactational exposure to the sum of six indicator non-dioxin-like-polychlorinated biphenyls ( 6 NDL-PCBs) in mice. Toxicology 299, 44–54.
European food safety authority, 2005. Opinion of the scientific panel on contaminants in the food chain on a request from the commission related to the presence of non dioxin-like polychlorinated biphenyls (PCB) in feed and food. EFSA J. 284, 1–137.
European Food Safety Authority, 2010. Scientific report of EFSA. Results of the monitoring of non dioxin-like PCBs in food and feed. EFSA J. 8 (7), 1701 (online: http://www.efsa.europa.eu).
Falandysz, J., Strandberg, B., Strandberg, L., Bergqvist, P.-A., Rappe, C., 1998. Concentrations and spatial distribution of chlordanes and some other cyclodiene pesticides in Baltic plankton. Sci. Total Environ. 215 (3), 253–258.
Fossi, M., Marsili, L., 2003. Effects of endocrine disruptors in aquatic mammals. Pure Appl. Chem. 75 (11–12), 2235–2247.
Fowler, W., 1990. Critical review of selected heavy metal and chlorinated hydrocarbon concentrations in the marine environment. Mar. Environ. Res. 29, 1–64.
Fuoco, R., Capodaglio, G., Muscatello, B., Radaelli, M., 2009. Persistent organic pollutants (POPs) in the Antarctic environment. A Review of Findings by The SCAR Action Group on Environmental Contamination in Antarctica (Cambridge, CB2 1ER, UK.ISBN 978-0-948277-23-8).
Hoffmeyer, M., Lindner, S., Carribero, A., Fulco, V., Menéndez, M., Fernández Severini, M., Diodato, S., Berasategui, A., Biancalana, F., Barrier, E., 2010. Planktonic food and foraging of *Eubalaena australis* on Peninsula Valdes (Argentina) nursery ground. Rev. Biol. Mar. Oceanogr. 45 (1), 131–139.
International Whaling Commission (IWC), 2010. Report of the Southern Right Whale Die-off Workshop. Centro Nacional Patagónico, Puerto Madryn, Argentina, p. 39 (15-18 March).
International Whaling Commission (IWC), 2012. A Draft Conservation Management Plan for Southwest Atlantic Southern Right Whales (IWC/64/CC7 Rev 1).
Jia, H., Li, Y.-F., Wang, D., Cai, D., Yang, M., Ma, J., Hu, J., 2009. Endosulfan in China 1—gridded usage inventories. Environ. Sci. Pollut. Res. 16, 295–301.
Kajiwara, N., Matsuoka, S., Iwata, H., Tanabe, S., Rosas, W., Fillmann, G., Readman, J., 2004. Contamination by persistent organochlorines in cetaceans incidentally caught along Brazilian coastal waters. Environ. Contam. Toxicol. 46, 124–134.
Kannan, K., Blankenship, A.L., Jones, P.D., Giesy, J.P., 2000. Toxicity reference values for the toxic effects of polychlorinated biphenyls to aquatic mammals. Hum. Ecol. Risk. Assess. 6 (1), 181–201.
Keith, L.H., Crummett, W., Deegan, J., Libby, R.A., Taylor, J.K., Wentler, G., 1983. Principles of environmental analysis. Anal. Chem. 55, 2210–2218.
Kim, S., Oh, J., Shim, W., 2002. Geographical distribution and accumulation features of organochlorine residues in bivalves from coastal areas of South Korea. Mar. Pollut. Bull. 45, 268–279.
Kleivane, L., Skaare, U., 1998. Organochlorine contaminants in northeast Atlantic minke whales (*Balaenoptera acutorostrata*). Environ. Pollut. 101, 231–239.
Kock, A., Best, P., Cockcroft, V., Bosma, C., 1994. Persistent organochlorine residues in small cetaceans from the east and west coasts of southern Africa. Sci. Total Environ. 154, 153–162.
Lee, K.T., Tanabe, S., Koh, C.H., 2001. Distribution of organochlorine pesticides in sediments from Kyeongii Bay and nearby areas, Korea. Environ. Pollut. 114, 207–213.
Marsili, L., Focardi, S., 1995. Organochlorine levels in subcutaneous blubber biopsies of fin whales (*Balaenoptera physalus*) and striped dolphins (*Stenella coeruleoalba*) from the Mediterranean Sea. Environ. Pollut. 91 (1), 1–9.
Martino, J., Wise, S.S., Perkins, C., Sironi, M., Wise, J.P., 2013. Metal Levels in Southern Right Whales (*Eubalaena australis*) from Península Valdés, Argentina. J. Environ. Anal. Toxicol. 3 (6), 1–6.
Méndez-Fernandez, P., Webster, L., Chouvelon, T., Bustamante, P., Ferreira, M., González, A.F., López, A., Moffat, C.F., Pierce, G.J., Read, F.L., Russell, M., Santos, M.B., Spitz, J., Vingada, J.V., Caurant, F., 2014. An assessment of contaminant concentrations in toothed whale species. Sci. Total Environ. 484, 196–205.
Metcalf, T.L., Metcalf, C.D., 1997. The trophodynamics of PCBs, including mono- and non-ortho congeners, in the food web of North-Central Lake Ontario. Sci. Total Environ. 201, 245–272.
Miglioranza, K., Aizpun de Moreno, J., Moreno, V., 2003. Dynamic of organochlorine pesticides in soils from a southeastern region of Argentina. Environ. Toxicol. Chem. 22 (4), 712–717.
Mossner, S., Ballschmiter, K., 1997. Marine mammals as global pollution indicators for organochlorines. Chemosphere 34 (5–7), 1285–1296.
Muir, D.G.C., de Wit, C.A., 2010. Trends of legacy and new persistent organic pollutants in the circumpolar arctic: overview, conclusions, and recommendations. Sci. Total Environ. 408 (15), 3044–3051.

Negoita, T.G., Covaci, A., Gheorghe, A., Schepens, P., 2003. Distribution of polychlorinated biphenyls (PCBs) and organochlorine pesticides in soils from the east Antarctic Coast. J. Environ. Monit. 5, 281–286.

Payne, R., 1986. Estudios a largo plazo sobre el comportamiento de la ballena franca austral (*Eubalaena australis*). Reports of the International Whaling Commission, pp. 161–167 (Special Issue 10).

Pazi, I., Kucuksezgin, F., Gonul, L.T., 2011. Distribution and sources of organochlorinated contaminants in sediments from Izmir Bay (Eastern Aegean Sea). Mar. Pollut. Bull. 62, 1115–1119.

Riseborough, R.W., Reiche, P., Peakall, D.B., Herman, S.G., Kirven, M.N., 1968. Polychlorinated biphenyls in the global ecosystem. Nature 220, 1098–1102.

Rosas, C.L., Gil, M.N., Uhart, M.M., 2012. Trace metal concentrations in Southern Right Whale (*Eubalaena australis*) at Península Valdés, Argentina. Mar. Pollut. Bull. 64, 1255–1260.

Rowntree, V.J., Uhart, M.M., Sironi, M., Chirife, A., Di Martino, M., La Sala, L., Musmeci, L., Mohamed, N., Andrejuk, j, McAloose, D., Sala, J.E., Carribero, A., Rally, H., Franco, M., Adler, F.R., Brownell Jr., R.L., Seger, J., Rowles, T., 2013. Unexplained recurring high mortality of southern right whale *Eubalaena australis* calves at Península Valdés, Argentina. Mar. Ecol. Prog. Ser. 493, 275–289.

Santos, M., Siciliano, S., Pacheco de Souza, S., Altmayer Pizzorno, J., 2001. Occurrence of southern right whales (*Eubalaena australis*) along south eastern Brazil. J. Cetac. Res. Manage. 2, 153–156 (special issue).

Sarkar, A., Nagarajan, R., Chaphadkar, S., Pal, S., Syngbal, S.Y.S., 1997. Contamination of organochlorine pesticides in sediments from the Arabian sea along the west coast of India. Water Res. 31 (2), 195–200.

Schmidt, W.F., Bilboulian, S., Rice, C.P., Fettinger, J.C., McConnell, L.L., Hapeman, C.J., 2001. Thermodynamic, spectroscopic, and computational evidence for the irreversible conversion of b to a-endosulfan. J. Agric. Food Chem. 49, 5372–5376.

Stenberg, M., Andersson, P.L., 2008. Selection of non-dioxin-like PCBs for in vitro testing on the basis of environmental abundance and molecular structure. Chemosphere 71, 1909–1915.

Strandberg, B., Strandberg, L., van Bavel, B., 1998. Concentrations and spatial variations of cyclodienes and other organochlorines in herring and perch from the Baltic Sea. Sci. Total Environ. 215, 69–83.

Tanabe, S., Miura, S., Tatsukawa, R., 1986. Variations of Organochlorine Residues With Age and Sex in Antarctic Mink Whale. 44. National Institute of Polar Research, pp. 174–181 (Spec. Issue).

Tanabe, S., Watanabe, S., Kan, H., 1988. Capacity and mode of PCB metabolism in small cetaceans. Mar. Mamm. Sci. 4 (2), 103–124.

Tanabe, S., Iwata, H., Tatsukawa, R., 1994. Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. Sci. Total Environ. 154, 163–177.

Tolosa, I., Mesa-Albernas, M., Alonso-Hernandez, C., 2010. Organochlorine contamination (PCBs, DDTs, HCB, HCHs) in sediments from Cienfuegos bay, Cuba. Mar. Pollut. Bull. 60, 1619–1624.

United Nations Environment Programme and the World Health Organization, 2012. State of the Science of Endocrine Disrupting Chemicals — 2012. In: Bergman, A., Heindel, J.J., Jobling, S., Kidd, K.A., Zoeller, R.T. (Eds.), (ISBN: 978-92-807-3274-0 (UNEP) and 978 92 4 150503 1 (WHO)).

Valenzuela, L., Sironi, M., Rowntree, V., Seger, J., 2009. Isotopic and genetic evidence for culturally inherited site fidelity to feeding grounds in southern right whales (*Eubalaena australis*). Mol. Ecol. 18, 782–791.

Wania, F., Mackay, D., 1996. Tracking the distribution of persistent organic pollutants. Control strategies for these contaminants will require a better understanding of how they move around the globe. Environ. Sci. Technol. 30 (9), 390–396.

Weber, J., Halsall, C.J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., 2010. Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Sci. Total Environ. 408 (15), 2966–2984.

Weisbrod, A., Shea, D., Moore, M., 2000. Organochlorine exposure and bioaccumulation in the endangered northwest Atlantic right whale (*Eubalaena glacialis*) population. Environ. Toxicol. Chem. 19 (3), 654–666.

Woodley, T., Brown, M.W., Kraus, D., Gaskin, E., 1991. Organochlorine levels in North Atlantic Right Whale (*Eubalaena glacialis*) blubber. Environ. Contam. Toxicol. 21, 141–145.

World Health Organization (WHO), 2011. Global Malaria Programme. The Use of DDT in Malaria Vector Control Position Statementp. 16.