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Pelagic seabirds as biomonitors of persistent organic pollutants in the Southwestern Atlantic

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ABSTRACT

Persistent Organic Pollutants (POPs) are accumulated through time and can exert different effect on ecosystems. POPs and Chlorpyrifos, a current use pesticide, were assessed in body feathers of males and females of Black-browed albatross (*Thalassarche melanophris*, *BBA*) and Cape petrels (*Daption capense, CAP*) during their non-breeding seasons at the Patagonian Shelf, Argentina. Chlorpyrifos showed the highest values among all pollutants in both species (49.56–84.88 ng g^{-1}), resulting from current agricultural practices. The pattern OCPs > PCBs > PBDEs was observed in both species, and CAP showed higher concentrations than BBA probably as a consequence of higher lipid mobilization and pollutants availability during dispersion. Non-significant differences between sexes about POPs levels were found; however a slight tendency was observed, females > males in CAP, and males > females in BBA. More attention and further studies are needed to understand seabirds' physiology and its relationship with the pollutants distribution in their tissues and considering breeding season.

1. Introduction

Persistent Organic Pollutants (POPs), including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are anthropogenic chemicals extensively used globally for industrial and agricultural purposes (Wania and Mackay, 1996). OCPs have been extensively used in crops, for livestock treatments and for human protection, such as DDT which use is permitted for malaria control in affected regions. PCBs have been widely used in dielectric fluids, electrical transformers and capacitors and open applications as additives in several building materials (lubricating, cutting oils, paints, sealants and plastics) over the past 50 years, until their prohibition over two decades ago (UNEP 2004). PBDEs are a class of brominated flame retardants added to commercial and house hold products such as furniture foams, textiles and also to electronic components. These compounds are characterized by their hydrophobicity, ubiquity, volatility and environmental persistence, which allow them to be highly toxic, having considerable bioaccumulation potential in organisms and biomagnifications through the food web (Ondarza et al., 2014; Jaspers et al., 2006; Lohmann et al., 2007; Alharbi et al., 2018). POPs have been forbidden worldwide and regulated since 2001 under the Stockholm Convention (UNEP 2017). However, their occurrence in the environment has been reported in different matrices (Miglioranza et al., 1999, 2013a, 2013b;Gómez-Ramírez et al., 2012; Durante et al., 2016; Commendatore et al., 2018; Monclús et al., 2018; Qiu et al., 2019) as a result of their persistence in the environment and long-range transport. On the other hand, Chlorpyrifos, an organophosphate insecticide, is the most widely-used pesticide on crops, including corn, soybeans, apples, and is also widely used in non-agricultural settings like golf courses. The physical-chemical properties of Chlorpyrifos allowed it to be globally distributed through long-range atmospheric and oceanic transport mechanisms and thus it reaches environments where it has not been applied (Mackay et al., 2014). Previous studies have showed that Chlorpyrifos and several POPs can negatively impact the nervous, immune, cardiovascular, respiratory and endocrine systems of several groups of vertebrates, including birds, by impairing their behavior, physiology and reproduction (Fry et al., 1995; Mitra et al., 2011; Eng et al., 2017). Moreover, the interference of these pollutants with response elements on the genome and its effects depend on the stage of development of the exposed

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organisms and sex (Vasseur and Cossu-Leguille, 2006). Other important point is that there may be variation across the sexes, given that females may eliminate some of their contaminant loads during egg laying.

Among upper predators, pelagic seabirds (namely albatrosses and petrels) have been used as indicators of chemical pollution of aquatic ecosystems; given their trophic position in the food webs and the distant offshore feeding areas they used (Mallory et al., 2010; Seco Pon et al., 2011; Acampora et al., 2018). In birds, organic pollutants have been traditionally monitored through a range of internal tissues (Jaspers et al., 2006; Espín et al., 2010; Colabuono et al., 2012). However, during the last years, the use of feather samples for measuring organic pollutants has become preferred method over other tissues since it involves working with live organisms (Dauwe et al., 2005; Jaspers et al., 2007; Behrooz et al., 2009; Eulaers et al., 2011; García-Fernández et al., 2013a; Monclús et al., 2018). Pollutants in feathers may derive from endogenous or exogenous deposition (Dauwe et al., 2005). In the first case, organic pollutants can reach feathers via blood during the growth period thus producing internal contamination. When they mature, vascular connections undergo atrophy and thus pollutant concentrations remain stable (Burger and Gochfeld, 2004). On the other hand, exogenous contamination may derive from dust, precipitations or the uropygial gland depositions on the feather surface (Dauwe et al., 2005). Feathers can be easily obtained from a bird, providing a non-invasive matrix, they are easy to store, they also showed significant correlations with internal body burdens of contaminants, allowing the retrospective assessment of long-term contaminant exposure (Jaspers et al., 2006, 2007, 2011; Eulaers et al., 2011, 2013; García-Fernández et al., 2013b). This is particularly relevant considering that recent reviews show the rapidly worsening conservation status of a number of albatross and petrel populations (ACAP, 2012; BirdLife International, 2018).

According to the *Global Distillation and Effect and Cold Condensation* (Wania and Mackay, 1996), POPs tend to accumulate in ecosystems located at high latitudes, including polar ecosystems. Most of the studies focused in birds, including seabirds, were conducted in the northern hemisphere (Jaspers et al., 2006, 2011; Acampora et al., 2018; Monclús et al., 2018; Svendsen et al., 2018). Few reports are available for other regions like southern South America (Colabuono et al., 2012; Commendatore et al., 2018; Dias et al., 2018). The waters off Argentina and its shelf-break constitute a rich marine ecosystem of global importance with an outstanding biodiversity endemism and high biomass of certain species from warm, temperate and cold waters, offering plentiful food for a diverse number of local and migratory marine megafauna, including seabirds (Favero and Silva Rodriguez, 2005; Seco Pon et al., 2015). The main economic activities that take place on it and may pose a threat to seabirds include fishing and oil extraction and exploration (Anticamara et al., 2011; Seco Pon et al., 2015).

The Black-browed albatross (BBA, *Thalassarche melanophris*), with Malvinas Islands comprising almost 70% of the global population (ACAP, 2012), is the most abundant Procellariiform species in this ecosystem and also one of the species with greater rates of bycatch in a number of South West Atlantic fisheries (Seco Pon et al., 2015). Tracking data showed that adult birds use waters within the Patagonian shelf year round (Grémillet et al., 2000; Copello et al., 2013). BBAs are essentially surface-seizers and shallow divers preying on fish, cephalopods, and crustaceans, and to some extent fishery discards while breeding (Prince, 1980). However, the species have been reported attending fishing vessels throughout the year, taking advantage of fishery byproducts (Seco Pon, 2014), fact that was also became evident through molecular analyses. On the other hand, the Cape petrel (CAP, *Daption capense*), with colonies spreading along the Southern Oceans, is also an abundant species in this area regularly attending fishing vessels at least during the time off breeding (Seco Pon et al., 2015). During the breeding season the species feeds mainly on cephalopods, crustaceans and fish (Hodum and Hobson, 2000). However, the analysis of stable isotopes during the non-breeding season have revealed the contribution of demersal fish species to CAPs diet, particularly discards from trawler and demersal long liners fleets (Mariano-Jelicich et al., unpublished data).

The aim of this study was to determine persistent organic pollutants and Chlorpyrifos concentrations in feathers from Black-browed albatross and Cape petrel in order to relate concentrations of pollutants in two species with different dispersion areas, and, to test possible contaminant accumulation differences between sexes.

2. Materials and methods

2.1. Sample collection

A sample entailing 23 BBAs and 19 CAPs was analyzed. Birds were captured at sea from fishing vessels around 42° S near the shelf-break off Argentina in winter of 2011 (Copello et al., 2013). From each individual, 3 to 5 body feathers were collected immediately after the capture. Birds were sexed by DNA techniques (chain reaction of the DNA polymerase), with blood samples taken from the tarsal vein and absorbing a small droplet of it onto a commercial filter paper (Quintana et al., 2008). Feathers samples – consisting of a random pinch of body feathers plucked from the right side of the breast of the individuals, were stored in paper envelopes and maintained in room temperature until analysis.

2.2. Extraction and analyses

The sample preparation was adapted from Dauwe et al. (2005). Body feathers were washed with deionized water to remove exogenous materials, then wrapped with filter paper and dried overnight at room temperature. After drying, feathers samples were cut into 1 mm pieces, weighted (approximately BBA: 150 mg; CAP: 80 mg) and transferred to glass recipients. Feather pieces were covered with 5 ml of HCl (4 M) and 3 ml of hexane:dichloromethane (4:1, v/v), spiked with 10 ul of internal standard (PCB 103) and incubated at 40 °C for approximately 12 h. After incubation, 4 ml of hexane:dichloromethane (4:1, v/v) mixture was added to each sample before analytes extraction by a liquid–liquid procedure. This process was carried out twice. The combined fractions (two extractions) of organic solvents were concentrated to 1 ml under nitrogen stream and purified by using column chromatography with activated silica (200 °C for 24 h). The final eluate was concentrated to 1 ml and kept in vials at −20 °C prior to gas chromatography analysis (Metcalfe and Metcalfe, 1997; Miglioranza et al., 2003). All solvents were residue analysis grade and other reagents were obtained from Merck Co. (Darmstadt, Germany).

Compounds were analyzed according to Miglioranza et al. (2003). Briefly, samples were screened for OCPs (α-, β-, γ- and δ-HCH, α- and β-endosulfan, endosulfan sulfate, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, α- and γ-chlordane, aldrin, dieldrin, endrin, endrin ketona, heptachlor, heptachlor epoxide, metoxichlor), Chlorpyrifos, PCBs (#8, #18, #31 + 28, #33, #52, #49, #44, #70 + 95, #66, #56 + 60, #101, #99, #97, #87, #110, #118, #105, #151, #123 + 149, #153 + 132, #141, #138, #158, #128, #156, #187, #183, #174, #177 and #180), and PBDEs (#28, 47, 99, 100, 153, 154, and 138). All compounds were analyzed on a Shimadzu gas chromatograph GC-17A with electron capture detector (ECD), equipped with a fused-silica SPB-5 capillary column (30 m, 0.25 mm i. d.,0.25 μm film thickness, Supelco, Bellefonte, PA, USA). The ECD was kept at 310 °C. The oven temperature program started at 100 °C, held for 1 min, followed by an increase of 5 °C/min up to 150 °C, held for 1 min, followed by an increase of 1.5 °C/min up to 240 °C, and then by an increase of 10 °C/min up to 300 °C, and held for 10 min.

The group of DDT and its metabolites (ΣDDTs) accounted the sum of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD. Hexaclorocyclohexanes (ΣHCHs) included α, β, and δ isomers. ΣEndosulfan encompassed α- and β-endosulfan, and endosulfan sulfate. ΣChlordanes included α- and γ-

isomer. ΣDrins involved aldrin, dieldrin, endrin, and endrin ketone, and ΣHeptachlors included heptachlor and heptachlor epoxide. ΣPCBs and ΣPBDEs represented the sum of the 35 and 7 congeners above referred, respectively.

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

Laboratory and instrumental blanks were analyzed throughout the procedure and results indicated that there were no contaminants or interferences of the samples during laboratory handling. Recoveries, calculated by a spiking matrix and surrogate recovery (PCB #103) were > 90%. Method detection limits was calculated according to Keith et al. (1983) and ranged between 0.03 and 0.5 ng ml^{-1} for HCHs and between 0.08 and 0.33 ng ml^{-1} for the remaining compounds.

2.4. Statistical analysis

A value of DF x LOQ was assigned to samples with levels below the LOQ, where DF was the detection frequency, or the proportion of measurements with levels above the LOQ, while LOQ was the limit of quantification. As previously done in other studies, only compounds detected in > 50% of the measurements above LOQ were included in further statistics analysis (e.g. Chlorpyrifos, α-endosulfan and endrin) (Voorspoels et al., 2002; Constantini et al., 2017; Svendsen et al., 2018; Monclús et al., 2018). For some compounds (β- and γ-HCHs) the detection frequencies resulted different between studied species, for example, CAP showed DFs higher than 50% in β-HCH, while BBA showed DFs higher than 40%in γ-HCHs; still none of those compounds were included in the analysis. The effect of predictor variables (gender and species) on the concentrations of POPs and Chloryrifos was tested with Generalized Linear Models (GLM) with Gamma error distribution and log link function (Crawley, 2007). Gender (male and female) and species (BBA and CAP) were included as categorical variables. All statistical analyses were performed using R software version 2.5.1 (R Development Core Team, 2012). The level of significance in all tests was set to $P < 0.05$. Pollutant concentrations are expressed as ng g^{-1}, dry weight and as mean ± two SD.

3. Results and discussion

3.1. Pollutant levels

3.1.1. Chlorpyrifos

This pesticide was the main pollutant found in feather samples of both seabird species analyzed (Table 1; BBA, mean concentration: 57.69 ± 23.82 ng g^{-1}; CAP, mean concentration: 84.66 ± 47.97 ng g^{-1}). Chlorpyrifos has an environmental half-life, ranging between 2 weeks and 1 year depending on soil type, climate and other environmental conditions (Chai et al., 2013). Therefore, the presence of Chlorpyrifos in body feathers of both species may reflect a recent birds' exposure to this contaminant. This result is in line with the fact that Chlorpyrifos is the main insecticide used in the region, including Argentinean, Uruguayan and Brazilian markets for soybean, wheat and corn crops (CASAFE, 2012; Mugni et al., 2012). It is known that a big proportion of agricultural pesticide application never reaches its target organisms; rather it disperses through the air, soil, and water (Aktar et al., 2009). Several studies have previously detected insecticides such as Chlorpyrifos in oceanic air and surface seawater from different ocean basins, mainly in the northern hemisphere (Zhong et al., 2011; Wania et al., 2010). Moreover, only a few studies regarding Chlorpyrifos residues in feathers have been reported (Gervais et al., 2000). Given the main physico-chemical properties of Chlorpyrifos (e.g. low degradation in seawater, intermediate vapor pressure, short environmental half-life), the occurrence of Chlorpyrifos in feathers of pelagic seabirds was expected considering that this pesticide can potentially undergo long-range transport as was previously demonstrated by Giesy and Solomon (2014) in other areas of the world. Still, both studied species seldom attend coastal waters of the Patagonian Shelf during their non-breeding seasons (Huin, 2002; Copello et al., 2013), though the entire area is used year-round by these species (Grémillet et al., 2000). There are few studies reporting accumulation of Chlorpyrifos in marine fish or cephalopods in the study area (Chierichetti M.A. 2015). In this sense, additional research is needed to address the relative contribution of natural prey and fishery discards in BBA and CAP diets and the effect that diet has upon Chlorpyrifos concentrations considering sex and age.

3.1.2. Persistent organic pollutants

The mean concentration of PCBs, OCPs and PBDEs in feathers of BBA and CAP are summarized in Fig. 1. The total POPs levels in body feathers of BBA and CAP was 25.78 ng g^{-1} and 66.96 ng g^{-1} feathers, respectively (overall genders combined, Fig. 1). There is scarce information about levels of POPs in feathers from pelagic seabirds inhabiting the Southwestern Atlantic. Regional comparisons are feasible for some POPs analyzed in this study as information is available for other seabird species, mainly from northern Europe (Sagerup et al., 2009; Acampora et al., 2018; Svendsen et al., 2018) and from South Shetland Islands and Western Antarctica (Metcheva et al., 2017). The POPs distribution pattern obtained in this study for both seabird species was similar, being OCPs > PCBs > PBDEs (BBA: mean = 16.30, 7.23, and 2.25 ng g^{-1} feathers, respectively; CAP: mean = 48.06, 9.60, and 9.31 ng g^{-1}feathers, respectively) (Fig. 2).

Other reports from northern Europe have shown different distribution pattern of POPs for feathers, with a predominance of PCBs followed by OCPs and PBDEs (Jaspers et al., 2009; Acampora et al., 2018; Svendsen et al., 2018). Acampora et al. (2018) reported mean levels of POPs in European storm petrels (*Hydrobates pelagicus)* breeding in Ireland. However, the ΣOCPs concentrations in CAP (mean: 48.06 ng g^{-1} feathers) were higher than those reported for the European storm petrel (mean: 17.9 ng g^{-1} feathers), while in BBA similar concentrations were observed (mean: 16.30 ng g^{-1} feathers). The mean ΣPCBs concentrations found in European storm petrels ranged between 4.23 and 136.7 ng g^{-1} while mean ΣPBDEs levels were between 1.96 and 15.9 ng g^{-1}. Thus, these PBDEs values were similar to those found in this study (mean BBA and CAP: 2.25 and 9.31 ng g^{-1} feathers, respectively). In the case of ΣPCBs, the levels observed in this study (BBA: mean = 7.23 ng g^{-1} feathers, CAP: mean = 9.60 ng g^{-1} feathers) were lower than those reported for *H. pelagicus* (mean ± SD: 27.26 ± 1.52 ng g^{-1}). The occurrence of POPs in feathers may be derived from endogenous or exogenous origin. Thus, the levels of contaminants in BBA and CAP feathers would also reflect the impact of the habitats on contaminant profiles, and also the role of the atmospheric pollution on contaminant deposition. In this sense, our results are in line with previous studies from South America showing the predominance of agricultural over industrial and urban pollutants in different matrixes (Barra et al., 2006; Miglioranza et al., 2013a, 2013b; Ondarza et al., 2014; Silva Barni et al., 2014; Neves et al., 2018).

All OCPs analyzed were detected in feathers of both seabird species (Table 1). The distribution pattern of OCP groups in BBA was HCHs > drins > DDTs > Endosulfan > heptachlors = chlordanes > metoxichlor; while in CAP was drins > HCHs > endo > heptachlors > chlordanes > metoxichlor. Thus, the predominance of HCHs and drins (particularly endrin and endrin ketone) for both species showed mean values of HCHs: 4.92 ± 6.01 ng g^{-1}, drins: 3.62 ± 10.51 ng g^{-1} for BBA; and in the case of CAP, the HCHs and drins levels were: 11.73 ± 15.47 ng g^{-1} and 24.34 ± 31.19 ng g^{-1} feathers, respectively (Table 1). Martínez-López et al. (2015) reported similar OCPs distribution pattern in feathers of three species of terrestrial scavenger birds from northern Patagonia in the Rio Negro Province, Argentina, with a mean concentration of HCHs: 1.31 ± 1.34 ngg^{-1} feathers and drins 1.33 ± 1.52 ng g^{-1} feathers. Moreover, the occurrence of HCHs is consistent with the fact that this group of

Table 1
Concentrations of POPs and Chlorpyrifos (ng g^{-1} feathers) in sexes of Black-browed albatross (BBA) and Cape petrel (CPA). Values are presented as mean ± standard deviation. < dl: below detection limit.

Compounds	BBA		CPA	
	Male	Female	Male	Female
Pesticides				
Chlorpyrifos	58.64 ± 27.31	49.56 ± 18.45	84.88 ± 50.57	75.98 ± 47.97
α-HCH	0.11 ± 0.29	0.23 ± 0.39	0.05 ± 0.18	0.20 ± 0.46
β-HCH	1.31 ± 1.98	1.47 ± 1.75	7.62 ± 10.39	11.25 ± 20.14
γ-HCH	4.42 ± 7.54	2.6 ± 0.39	2.37 ± 3.38	2.15 ± 3
α–chlordane	0.13 ± 0.23	0.55 ± 0.87	0.64 ± 1.78	0.76 ± 1.75
γ-chlordane	0.43 ± 0.61	0.18 ± 0.30	0.45 ± 0.87	0.19 ± 0.58
α–endosulfan	2.08 ± 2.64	1.94 ± 2.37	3.86 ± 3.18	4.70 ± 3.99
β–endosulfan	0.18 ± 0.41	0.32 ± 1	< dl	1.89 ± 2.86
Endosulfan sulfate	0.2 ± 0.72	0.79 ± 1.69	1.39 ± 3.01	< dl
Heptachlor	0.39 ± 0.93	0.12 ± 0.39	< dl	< dl
Heptachlor epoxide	0.4 ± 0.94	0.64 ± 1.37	0.88 ± 1.87	4.38 ± 7.10
Dieldrin	1.16 ± 1.7	0.85 ± 2.37	3.61 ± 10.25	0.97 ± 1.66
Endrin	< dl	5.98 ± 15.86	8.21 ± 11.84	16.56 ± 30.76
Endrin ketone	< dl	< dl	4.75 ± 10.59	13.59 ± 31.16
p,p′-DDD	0.85 ± 2.17	< dl	0.50 ± 1.58	< dl
p,p′-DDE	1.7 ± 2.33	3.68 ± 6. 68	0.58 ± 1.84	0.52 ± 1.75
p,p′-DDT	0.21 ± 0.54	0.44 ± 1.4	1.48 ± 4.67	< dl
Metoxichlor	0.49 ± 1.06	< dl	0.44 ± 1.4	1.48 ± 4.44
PCBs congeners				
18	0.44 ± 1.03	< dl	< dl	< dl
31 + 28	0.03 ± 0.11	< dl	< dl	< dl
33	0.66 ± 2.15	1.09 ± 2.89	1.83 ± 5.49	< dl
52	0.23 ± 0.82	< dl	< dl	< dl
49	0.04 ± 0.15	0.33 ± 1.06	< dl.43 ± 1.29	< dl
44	1.88 ± 4.11	0.91 ± 2.53	< dl	< dl.41 ± 1.24
70 + 95	0.07 ± 0.18	0.03 ± 0.09	< dl	< dl
66	0.03 ± 0.11	0.07 ± 0.23	0.06 ± 0.17	0.23 ± 0.68
56 + 60	0.44 ± 1.58	< dl	< dl	0.34 ± 1.03
101	0.29 ± 0.72	< dl	< dl	< dl
99	< dl	0.1 ± 0.32	0.48 ± 1.45	< dl
97	0.23 ± 0.45	0.3 ± 0.95	< dl	< dl
87	0.06 ± 0.23	0.45 ± 1.43	< dl	< dl
110	0.85 ± 1.57	0.41 ± 1.28	0.35 ± 0.94	0.72 ± 2.17
118	< dl	< dl	< dl	0.3 ± 0.9
105	0.98 ± 2.63	< dl	< dl	< dl
151	0.17 ± 0.43	0.36 ± 0.8	2.49 ± 7.48	
149/123	0.34 ± 0.67	< dl	< dl	0.51 ± 1.52
153 + 132	0.2 ± 0.5	0.15 ± 0.32	< dl	1.07 ± 3.23
141	0.61 ± 1.2	< dl	< dl	< dl
138	0.69 ± 1.49	< dl	< dl	< dl
128	0.19 ± 0.47	< dl	< dl	< dl
156	0.11 ± 0.41	< dl	1.5 ± 4.51	0.63 ± 1.89
187	0.13 ± 0.33	< dl	< dl	1.09 ± 3.29
183	0.27 ± 0.78	0.33 ± 0.76	2.72 ± 3.55	1.43 ± 4.29
174	< dl	< dl	0.29 ± 0.86	0.37 ± 1.09
177	0.03 ± 0.11	0.12 ± 0.39	< dl	< dl
180	0.18 ± 0.38	0.05 ± 0.17	1.35 ± 2.41	1.24 ± 2.89
PBDEs congeners				
47	1.38 ± 4.02	< dl	< dl	7.28 ± 23.02
100	< dl	0.05 ± 0.16	2.61 ± 5.75	< dl
99	1.45 ± 3.57	1.16 ± 2.47	0.42 ± 1.26	3.89 ± 11.13
153	0.49 ± 1.76	< dl	< dl	< dl

pesticides, in addition to DDTs were the agrochemicals most frequently reported in human food in Argentina (Villaamil Lepori et al., 2013). HCHs isomers pattern differed between BBA and CAP with a prevalence of γ-HCH (lindane) in BBA, and β-HCH in CAP samples. Lindane was widely used as domestic pesticide and also for lice control and has a shorter half-life in the environment than other organochlorine compounds. Therefore, our results probably reflect recent exposure to lindane and also its release into the bloodstream by fat mobilization during differential at-sea distribution. The occurrence of β-HCH in CAP feathers suggests a previous exposure to HCHs technical mixture and/or a biomagnification process through the diet of sampled individuals. It is known that β-HCH has the lowest water solubility and vapor pressure, and the largest half-life in the environment among others isomers. Moreover, it is the main isomer among HCHs found in sediments due to high persistence and stability.

The composition of endosulfan isomers can reveal their historical or recent inputs into the environment (Weber et al., 2010). In this study, the ratios α/β-endosulfan found in both species were higher to 1, which indicate relatively fresh inputs of technical endosulfan (α/β = 2.33). Nevertheless, isomers ratio may be affected by metabolic processes occurring into the organisms. Both α- and β-endosulfan are converted to endosulfan sulfate, but the α-isomer is degraded faster than the β-endosulfan modifying the original isomer composition. Endosulfan did not show a significant contribution to the total OCPs levels (range between 2.47 and 6.60 ng g^{-1}) in this study. Nevertheless, other studies have reported endosulfan levels in different matrixes of Argentina

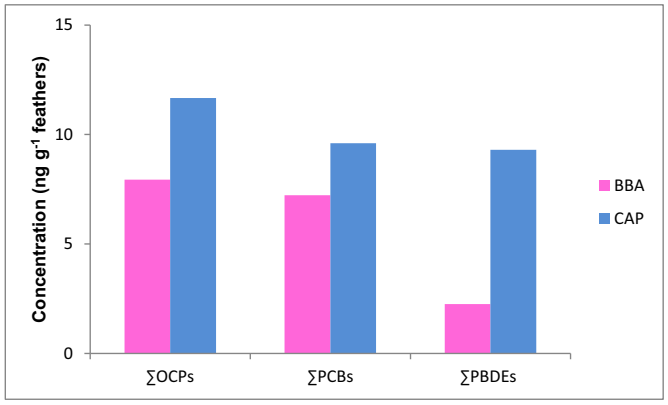

Fig. 1. Total concentrations of OCPs, PCBs, and PBDEs in body feathers of Black-browed albatrosses (BBA) and Cape petrels (CAP).

(Menone et al., 2000, Miglioranza et al., 2013a, 2013b, Ondarza et al., 2014, Silva Barni et al., 2014, Commendatore et al., 2018), indicating high concentrations of this contaminant in soil, fish, crabs, birds eggs and air. Endosulfan was the most widely used OCP in Argentina, with high persistence in the environment and capacity to be transferred long distances from the application sites, until its prohibition in July 2013 (SENASA, 2013). However, in warm-blooded organisms endosulfan is rapidly metabolized and easily excreted. Despite this fact, the results of this study showed a ratio α-/β-endosulfan > 1 for both species, suggesting an exposure to commercial technical mixtures (α-/β-isomers 70:30) during the sampling period that is coincident when the time this insecticide in use.

Regarding DDTs, both studied species showed a DDE + DDD/DDT ratio > 1. This relationship between metabolites and parental compound, could be used as proxy of the time since the application of the commercial mixture *p,p′*-DDT. The historic use of DDT in Argentina has been evidenced in different matrixes such us fish, soils, crabs and birds (Commendatore et al., 2018; Miglioranza et al., 2013a, 2013b; Ballesteros et al., 2014) denoting also a predominance of metabolites. Consequently, in this study, the ratios DDE + DDD/DDT were 9.81 for BBA and 2.69 for CAP, and are in line with those previous studies, and the historical application of this insecticide in the region. Technical DDT was globally used for agricultural purposes until its banning (Argentina in 1990), but it was still allowed to be used in tropical and subtropical countries, such as Brazil for malaria control. Due to its high volatility, *p,p′*-DDT is deposited in lower latitudes through air currents from warm areas (Wania and Mackay, 1996). This process, known as long-range transport, was previously described in Argentina (Miglioranza et al., 2013b) highlighting the coastal areas of Buenos Aires province as a receptor region. Particularly, *p,p′*-DDE was the most frequently detected metabolite in both species and its concentration ranged between < LOQ and 21.40 ng g^{-1} feathers. The predominance of this metabolite in this study may be explained by its high chemical stability and persistence in the environment. Moreover, the occurrence of DDE in seabirds may be due to both dietary accumulation and DDT metabolism. The high detection frequency of *p,p′*-DDE has already been reported in feathers of seabirds and raptor birds from Belgium, Iran and Ireland (Jaspers et al., 2007; Rajaei et al., 2011). Additionally, in other matrices from Argentine Patagonia, like the Rio Negro watershed, *p,p′*-DDE was also the main pesticide found among the DDT group in fishes, soils, pine needles and macrophytes (Miglioranza et al., 2013a). The past use and the persistence of DDT in the region in addition to its high volatility, may explain the presence of *p,p′*-DDT in analyzed samples. In addition, fresh DDT in the environment could be related to Dicofol use. In Argentina Dicofol has been used as pesticide since 1960s. Dicofol undergoes long range atmospheric transport, despite many countries from Latin America have forbidden its use. Dicofol is synthetized from technical DDT and therefore DDT is an impurity in technical Dicofol reaching values as high as 20% (Qiu et al., 2005).

Heptachlor is an insecticide extensively used in Argentina for pest control mainly on potato and cotton crops until its prohibition in 1998; this pesticide breaks down rapidly in the environment to its metabolite heptachlor epoxide. In this study, levels of heptachlor ranged between 0.76 and 4.38 ng g^{-1} feathers (both studied species combined). BBA samples showed both the parental compound and the metabolite, heptachlor epoxide; however only the occurrence of heptachlor epoxide was found in CAP, despite the highest pesticide levels reported in this species. A secondary source of heptachlor could be wet deposition from atmosphere. In this sense, heptachlor, heptachlor epoxide and γ-chlordane was previously detected in air from Bahia Blanca, an area belonging to the northern Patagonia Argentina, despite its use was banned fifteen years ago (Tombesi et al., 2014). The chlordane levels found in both studied species were below 1 ng g^{-1}, most likely as a consequence

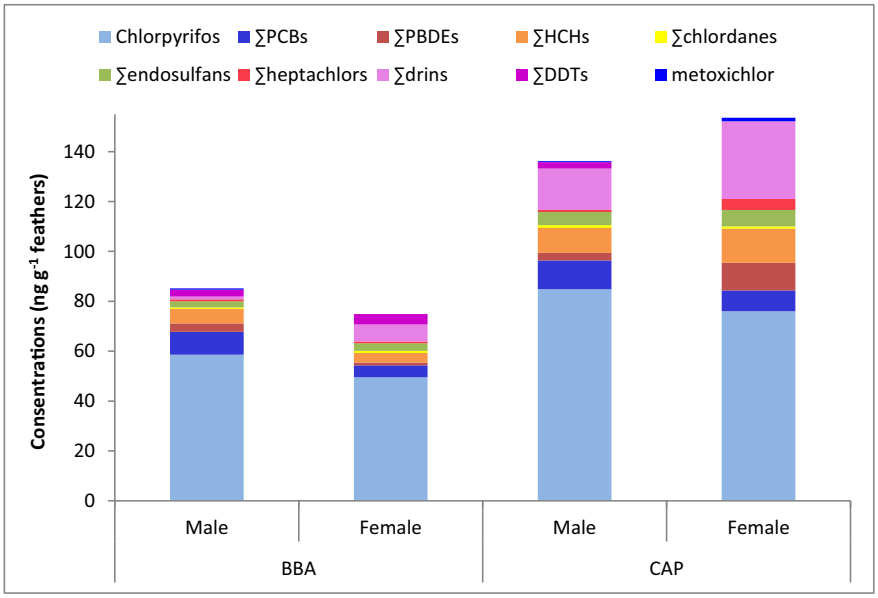

Fig. 2. Total concentrations of Chlorpyrifos, PCBs, PBDEs, HCHs, chlordanes, endosulfans, heptachlors, drins, DDTs and metoxichlor in males and females of Black-browed albatross (BBA) and Cape petrel (CAP).

of past use in the region.

Aldrin is rapidly transformed in the environment to dieldrin, which is more resistant to biodegradation. Additionally, endrin is an isomer of dieldrin and may be metabolized by animals. Endrin was primarily used as an insecticide and has been also employed as a rodenticide, avicide and on some fish farms had been used as a piscicide. In the environment, high temperature or intense sunlight leads to a more rapid breakdown of endrin into endrin ketone and endrin aldehyde, and consequently they can be found mainly in bottom sediments of aquatic environments. Endrin and endrin ketone were found in all CAP samples, whereas in the case of BBA only endrin was found in females. In all cases both pesticides were at higher concentrations than dieldrin. Colabuono et al. (2012) previously reported the occurrence of drins in wet tissues from albatrosses and petrels attending the South Atlantic marine environment of Brazil, with lower concentrations in muscle, < 1.24–20 ng g^{-1} ww and < 1.24–8.78 ng g^{-1} ww, for petrels and albatrosses, respectively. These results are in line with those reported in this study where drins were also found at highest levels in CAP. This fact would suggest differences in the exposure to or metabolism of these compounds.

Σ_{28}PCBs were detected in feathers samples of both species (Table 1). Different patterns were observed between BBA and CAP. Body feathers of CAP showed higher levels of hexa- (3.1 ng g^{-1}) and hepta-CBs (4.24 ng g^{-1}) than congeners with lowest chlorination degree (Table 1). The high concentration of several congeners (#151, 153, 156, 180 and 183) may be due to the historical usage of Aroclor 1254 and 1260 mixtures, which have enrichment composition in penta and hexa-CBs (Schulz et al., 1989). The predominance of hexa- and penta-CBs in the region would reflect the use of those technical mixtures as was already reported by Commendatore et al. (2018), Miglioranza et al. (2013a, 2013b) and Ondarza et al. (2014). In line with our results, Behrooz et al. (2009) and Monclús et al. (2018) reported the predominance of high-chlorinated PCB congeners (#138, #153 and #180) in feathers from different bird species from Iran and Spain. Those authors indicated that the predominance of high-chlorinated PCBs congeners was due to the spatial exposure, in urbanized and industrial areas. Particularly, the levels of congeners #153 and #180 in feathers of Cinereous vultures (*Aegypsius monachus*) (mean: 0.67 ng g^{-1} and 0.6 ng g^{-1} dw, respectively), reported by Monclús et al. (2018) were similar to those reported for CAP in this study (mean: 0.54 ng g^{-1} and 1.3 ng g^{-1}, respectively). It is well known that the birds' capacity to metabolize PCBs decreases with increasing degree of PCB chlorination (Maervoet et al., 2004; Rajaei et al., 2011). On the contrary, in body feathers of BBA, the most abundant congeners included the tetra- (1.35–2.69 ng g^{-1}) and penta-CBs (1.26–2.42 ng g^{-1}) groups. Among them, the higher levels were found for congeners #33, 44, 110 and 105. The predominance of lighter PCBs might be explained by external deposition, as lower chlorinated PCB congeners are supposed to contribute more to contamination from the air than congeners with high degree of chlorination. Similar results were obtained by Dauwe et al. (2005) for feathers of the Great tit (*Parus major*) where higher levels of tetra- and penta-CBs congeners were found in feathers when compared to other tissues such as fat. In line with this fact, Jaspers et al. (2007) attributed the presence of low chlorinated PCB congeners in feathers of Common moorhens (*Gallinula chloropus*) to external contamination. Moreover, Vorhees and Altshul (1997) indicated that atmospheric deposition of organic pollutants may be important in modifying contaminant feather profiles, and it is expected that more volatile compounds could contribute mostly to this kind of external pollution. Thus, in this study the high concentrations of lower chlorinated congeners in feathers from BBA can also be explained by their presence in blood during molting.

Concentrations of PBDEs measured in feathers from BBA and CAP are summarized in Table 1.The higher concentrations of total PBDEs was found in CAP (7.1 ng g^{-1}), showing similar levels than those reported for the Herring Gull (*Larus argentatus*) with mean values of 11 ng g^{-1} (Jaspers et al., 2007). Moreover, a similar congener pattern was found in both seabird species, with a predominance of BDE-47, BDE-99 and BDE-100 (Table 1). These compounds have been previously detected in feathers from others top predators including birds around the globe (Jaspers et al., 2007; Eulaers et al., 2011; Acampora et al., 2018; Monclús et al., 2018).The BDE-47 showed the highest values in CAP (< LOD - 72.8 ng g^{-1}) followed by BDE-99 and BDE100. These results are in line with those reported by Acampora et al. (2018) (mean: 0.35 ng g^{-1}; 0.46 ng g^{-1}; 1.17 ng g^{-1} feathers, for BDE-47, BDE-99 and BDE-100, respectively). The highest levels of BDE-47 observed in this study is in agreement with other literature where the levels of BDE-47are higher in aquatic than in terrestrial species, probably due to this congener is the most ubiquitous BDE found in the environment as a result of atmospheric transport (Jaspers et al., 2006; Jaspers et al., 2007). Nevertheless, other studies in biotic and abiotic matrixes have attributed the PBDEs pattern with a predominance of BDE 47, 99 and 100 to the use of the penta-BDE commercial mixture (Peng et al., 2018), since such mixture contains between 75 and 98% of tetra + penta-BDE. In line with these studies, our results might also be explained by the use of technical mixtures of penta-BDE. There are three types of commercial PBDE mixtures, including penta bromodiphenyl ether (pentaBDE), octa bromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). DecaBDE is the most widely used PBDE globally. Because of their ubiquitous presence, bioaccumulation, and toxicity, penta- and octa-BDE mixtures have been restricted in some regions of the world, such as the European Union and some States the United States from 2004, with both PBDEs mixtures entering the Stockholm Convention in 2008. (Markham et al. 2018), reported PBDEs analyses for a set of > 200 biotic samples from the Antarctic including phytoplankton, krill, fish, and fur seal milk, spanning several sampling seasons over 14 years. Particularly, BDE-47 and BDE-99 were the dominant congeners found in all samples, constituting > 60% of total PBDEs, as was observed in this study for both birds species. Miglioranza et al. (2013a) and Commendatore et al. (2018) associated the high PBDEs concentration found in patagonian sediments with the presence of an urban garbage dump, where plastics and electronic waste were disposed, as well as the use of plastics in fishing activities. These urban and industrial activities in addition to atmospheric transport, could contribute to PBDEs levels in CAPs and BBAs feathers.

3.2. Intraspecific differences: differences between genders

Few studies concerning sex differences about persistent organic pollutant concentrations in birds are available in the literature (Bustnes et al., 2008; Sagerup et al., 2009; Svendsen et al., 2018). A study carried out in non-breeding Arctic seabirds such as the Glaucous Gull (*Larus hyperboreus*) and kittiwakes (*Rissa* sp.) from northern Europe, did not find significant differences between sexes when POPs were evaluated in the birds' feathers, plasma and liver (Sagerup et al., 2009; Svendsen et al., 2018). In this study, despite there was no significant differences between sexes (GLM, all values > 0.05), a slight tendency of higher concentrations in females (mean: 152.25 ng g^{-1}) than in males (mean: 139.63 ng g^{-1}) of CAP was observed; however in BBA an inverse tendency was detected, with slightly higher POPs levels in males (mean: 85.33 ng g^{-1}) than in females (mean: 74.51 ng g^{-1}) (Fig. 2). Likewise, Dauwe et al. (2005), found no significant differences for PCBs and OCPs levels between genders in feathers of the Great Tit and Razorbills (*Alca torda*). Pollutants load are suspected to vary in those species with differential diet and/or foraging areas or even with body-size differences between sexes. However, dietary analyses based on stable isotopes showed that during the non-breeding season both sexes of BBA and CAP forage at the same trophic level (Mariano-Jelicich et al., 2014; Mariano Jelicich et al., unpublished data). Otherwise, a certain degree of spatial segregation was observed between sexes in satellite-tracked BBA during the non-breeding period (Paz et al., unpublished data). Moreover, biometric measurements revealed significant body-size differences between sexes in BBA from different areas in the South Atlantic (Phillips

et al., 2004; Gandini et al., 2009; Ferrer et al., 2016) and in CAP (Weidinger and van Franeker, 1998). Unfortunately, there is no information regarding the spatial distribution between sexes of the CAP in the South Atlantic based on tracked individuals. Other key point to be considered as a possible cause of differences between sexes is related to differences in the extent or timing of the molt (Booke, 2004). Future studies are need to address the relative contribution of sexual segregation in CAP use of space and the influence spatial use and interaction with environmental and anthropogenic activities has upon pollutant concentrations in sexes of this species. Moreover, it is recommended to continue this type of study through the species annual cycles in order to understand the dynamics of these pollutants during other periods, such as the breeding seasons, where an important load of contaminants are expected to be depressed in females during egg laying.

3.3. Interspecific differences: CAP vs BBA

Significant differences were found between feathers of BBA and CAP for Chlorpyrifos, α-endosulfan, β- and γ-HCH concentrations (Table 1), being all pollutant levels higher in feathers of CAP than BBA. Previous studies dealing with different bird species have attributed the observed differences in pollutant loads to dietary habits and location of breeding areas (Rajaei et al., 2011; Behrooz et al., 2009; Jaspers et al., 2006). The diet of both studied species is mostly comprised of fish, cephalopods and crustaceans (Prince, 1980; Hodum and Hobson, 2000; Fijn et al., 2012; Mariano-Jelicich et al., 2014). Besides, both species feed on discards and offal while attending commercial fishing vessels in the study area during their non-breeding seasons (Seco Pon et al., 2015), and have relative similar nesting areas; i.e. remote sites far away from urban and industrialized areas in the Southern Ocean. Though both species coexist in same breeding grounds in the sub-Antarctic, colonies of BBA and CAP are mainly located in mid-latitudes and Antarctica, respectively (Booke, 2004; Shirihai, 2008). Other important factor to be considered is the dilution effect suggesting a concentrations dilution together body size increase. Thus there is a big difference between body sizes of both species (mean BBA wingspan and mass: 107 cm and 3.06 kg; mean CAP wingspan and mass: 54.3 cm and 0.47 kg; Booke, 2004). Considering that both species are exposed to similar sources, such as diet and nestling areas, the dilution effect by growth could be a key point in those differences, as was previously reported by other authors (Silva Barni et al., 2014). However, migratory habits and molting may also play a significant role in the level of pollutants accumulated in feathers (Furness et al., 1993; Perkins and Barclay, 1997), since feathers stop receiving blood supply once they stop growing, hence at that moment they are completely grown, during which the blood supply and the internal input from contamination ceases. Procellariiformes are known to molt primarily during the non-breeding season (Warham, 1990); and in the case of albatrosses it has been suggested that species such as BBA may have multiple molt series throughout their wings (Edwards and Rohwer, 2005). Less information is related to the molting sequence of body feathers in pelagic seabirds attending the Southwestern Atlantic. However, body feathers are known to be most representative of concentrations in plumage as a whole (Burger and Gochfeld, 2004). This study was based on body feathers which were fully grown at the moment of sampling; this means that feathers analyzed in this study were not receiving contaminants via blood supply when both species were sampled. In periods that require a great expenditure of energy reserves, such as migrations, subcutaneous fat tissue is metabolized (Colabuono et al., 2012). Consequently, lipophilic pollutants such as POPs, would be mobilized and distributed through the blood stream, which in turn can result in a concentration increase of these contaminants in molted feathers (Rajaei et al., 2011), as it seems to be the case for CAP. During the non-breeding season (austral winter), the CAP is widely distributed in the South Atlantic, and can be commonly found in areas near the Equator (Harrison, 1983; Shirihai, 2008), while the distributional range of the BBA reaches the southeastern corner of Brazil (Harrison, 1983; Copello et al., 2013). A presumably increased lipid mobilization due to high energy expenditure in CAP dispersion could be a possible explanation for the higher concentrations of contaminants observed in CAP when compared to BBA.

4. Conclusions

This is the first study reporting POPs and Chlorpyrifos concentrations in feathers of two pelagic seabirds from the Southwestern Atlantic during their non-breeding seasons. Both studied species –the Black-browed albatross and the Cape petrel- showed a similar pollutant distribution pattern: Chlorpyrifos > OCPs > PCBs > PBDEs; although significant differences between sexes were not observed. The occurrence of POPs and Chlorpyrifos in feathers from non-breeding adult of BBA and CAP resulted from exposure to agricultural practices and industrial activities. Nevertheless, the predominance of Chlorpyrifos and OCPs over industrial and urban contaminants would indicate the influence of agriculture, over other activities in the region, highlighting the higher levels of Chlorpyrifos intensively used in Argentina and also in other countries of South America. Differences in contaminant levels between species could be related to differential at-sea distribution movements and dispersion strategies. Since both species were sampled during their non-breeding seasons; the difference between dispersal distances and the lipids mobilization with their consequent release of pollutants into the bloodstream would lead to a greater load of contaminants in the Cape petrel feathers formed during the last molting period. It is recommended a long-term monitoring of contaminants levels in pelagic seabirds involving different tissues which will provide insights about the dynamics of POPs and exposure pathways in marine ecosystems and therefore bring tools for the development of conservation strategies of seabirds inhabiting the Southwestern Atlantic.

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