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Organochlorine contaminants and polybrominated diphenyl ethers in eggs and embryos of Antarctic birds

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Abstract: Organochlorine contaminants (OCs) and polybrominated diphenyl ethers (PBDEs) were investigated in the eggs of five bird species from the South Shetland Islands. Additionally, OCs and PBDEs were also analysed in embryos of two species. The concentration ranges in eggs were (ng g^{-1} wet weight) 2.11 to 541 for polychlorinated biphenyls (PCBs), < 0.25 to 0.88 for PBDEs, 2.45 to 405 for *p,p'*-DDE and 1.50 to 603 for mirex. The PCBs were predominant in the eggs of *Macronectes giganteus*, *Catharacta antarctica* and *Larus dominicanus*, whereas hexachlorobenzene (HCB) was the major compound found in the eggs of *Pygoscelis antarcticus* and *Sterna vittata*. The PBDE congeners were detected only in the eggs of *C. antarctica* (PBDE 47 and 153) and *S. vittata* (PBDE 47). There were differences in OC concentrations of up to two orders of magnitude between *M. giganteus* embryos which were related to the development stage and OC concentrations in the respective eggs. Trophic ecology and post-breeding dispersal exerted an influence on contaminant patterns. Comparisons with data from the literature indicate an increase in the concentrations of some OCs over recent years.

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Key words: Antarctica, organic pollutants, seabirds, South Shetland Islands

Introduction

Many organic contaminants undergo long-range transport and can be found at relatively high concentrations in remote environments (Bustnes *et al.* 2007). Recent studies have demonstrated the presence of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the Antarctic marine food web (Schiavone *et al.* 2009, Taniguchi *et al.* 2009, Corsolini *et al.* 2011, Cipro *et al.* 2013). Monitoring such contaminants is important to gain a better understanding of the dynamics in polar regions and to assess the impact of these compounds on the environment.

Bird eggs have proven to be particularly useful as bioindicators of organohalogens in aquatic environments and have been used in environmental contamination studies at high latitudes (e.g. Braune *et al.* 2007, Schiavone *et al.* 2009, Vander Pol *et al.* 2009, Corsolini *et al.* 2011, Cipro *et al.* 2013). Contaminant concentrations in eggs may also assist in the assessment of hazards faced by adult birds, as the composition of these contaminants directly reflects that in maternal tissues (Russell *et al.* 1999).

Little data is available regarding contamination in developing embryos, which are often exposed to similar levels of organic contaminants as adults but exhibit greater toxicological sensitivity (Barron *et al.* 1995, Russell *et al.* 1999). Field and experimental studies have shown embryonic exposure during development due to the absorption of contaminants from yolk (Bargar *et al.* 2001, Zheng *et al.* 2014). Information on embryonic exposure to contaminants is important both to evaluate toxic effects in early life stages and in making ecological risk assessments.

Ecological patterns may influence the levels of contaminants in birds (Corsolini *et al.* 2011). Thus, the comparison of species in different trophic positions and with diverse distribution and/or migration patterns is useful in assessing the differences in exposure to contaminants. For example, species that forage or breed in Antarctica in the summer and migrate to lower latitudes may accumulate a greater amount of contaminants if they winter in polluted areas compared to birds that breed on the Antarctic continent or islands and overwinter in the Southern Ocean (Corsolini 2009).

This study assessed levels of OCPs, PCBs and PBDEs in the eggs of southern giant petrels (*Macronectes giganteus* (Gmelin)) and chinstrap penguins (*Pygoscelis antarcticus* (Forster)) breeding in the South Shetland Islands. These birds have distinct distribution ranges and feeding habits. In order to contribute to the scarce data relating to contamination levels in some bird species

in the area, organohalogen concentrations are also reported for a small number of eggs from brown skuas (*Catharacta antarctica* Lesson), kelp gulls (*Larus dominicanus* (Lichtenstein)) and Antarctic terns (*Sterna vittata* Gmelin), as well as for embryos of *M. giganteus* and *S. vittata*. These data provide a qualitative and quantitative indication of the impact of contaminants in the Antarctic ecosystem.

Material and methods

Sampling

The eggs of five seabird species [*C. antarctica* ($n = 2$), *L. dominicanus* ($n = 1$), *S. vittata* ($n = 3$), *M. giganteus* ($n = 8$) and *P. antarcticus* ($n = 7$)] from the South Shetland Islands (62°S, 58°W), Antarctica, were collected during the summers of 2011 and 2012. Sampling was opportunistic and only unhatched or deserted eggs were collected. Egg contents (yolk, albumen and embryos) were stored in glass vials (previously decontaminated at 450°C for 4 hours) and kept frozen at -20°C until analysis. In the case of eggs containing embryos, the residual yolk and albumen were carefully removed, stored and analysed separately from the embryos.

The incubation stage of the embryos was estimated based on Romanoff (1960), Hays & LeCroy (1971) and Freeman & Vince (1974) using morphological characters and the amount of yolk and albumen in the egg, which are consumed during embryo growth. Albumen is a reserve of protein and water that the embryo does not utilize in the early stages of incubation (Carinci & Manzoli-Guidotti 1968). In later development stages, the albumen and a portion of the yolk are consumed, which is the only source of lipids during embryo growth. Part of the yolk remains after hatching to provide immediate post-hatching energy to the chicks (Romanoff 1960, Freeman & Vince 1974).

Chemical analyses

The egg content (yolk and albumen) and whole embryos were homogenized in an Ultra-Turrax apparatus. The analytical procedure was optimized from the method described by MacLeod *et al.* (1986). Five grams of wet sample were extracted, after the addition of anhydrous Na_2SO_4, in a Soxhlet apparatus for 8 hours using 80 ml of n-hexane and methylene chloride (1:1, v/v). Before extraction, 2,2',4,5',6-pentachlorobiphenyl (PCB 103) and 2,2',3,3',4,5,5',6-octachlorobiphenyl (PCB 198) were added to all samples, blanks and reference material as surrogates for OCPs, PCBs and PBDEs. The extractable lipids were determined by gravimetric method using a 100 µl aliquot. The extracts were cleaned using column chromatography with 8 g of silica and 16 g of alumina, both 5% water deactivated, eluted with 80 ml of methylene chloride. The fraction was further purified by high-performance liquid chromatography using methylene chloride as the eluent, with a flow of 5 ml min^{-1}. The extract was concentrated to a volume of 0.9 ml in hexane. The internal standard 2,4,5,6-tetrachlorometaxylene (TCMX) was added before the gas chromatographic analysis. A procedural blank was included for each set of eight samples.

The OCP identification and quantification analyses were performed using an Agilent Technologies 6890 N gas chromatograph with an electron capture detector (GC-ECD) with a 30 m x 0.25 mm i.d. capillary column coated with a 5% phenyl-substituted dimethylpolysiloxane phase (0.25 µm film thickness). Automatic splitless injections of 2 µl were applied and the total purge rate was adjusted to 50 ml min^{-1}. Hydrogen was the carrier gas (constant pressure of 40 kPa at 100ºC) and nitrogen was the make-up gas at a rate of 60 ml min^{-1}. The PCBs and PBDEs were quantitatively analysed using a gas chromatograph (5973N Agilent Technologies) coupled to a mass spectrometer (GC-MS) in the selected ion mode (SIM 70 eV) with a 30 m x 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.25 µm film thickness). The volume injected was 1 µl in automatic splitless mode. Helium was used as the carrier gas (constant flow of 1.1 ml min^{-1}).

For the quality assurance/control, the analytical methodology was validated using a standard reference material (SRM) for PCBs, OCPs and PBDEs (SRM 1945; organics in whale blubber, www.nist.gov) purchased from the National Institute of Standards and Technology (NS&T). The recovery of analytes and surrogates in the SRM, spiked blanks and matrices produced satisfactory results within the range accepted by the NS&T (Wade & Cantillo 1994). Analytes in laboratory blanks were subtracted from the samples. Method quantification limit (QL) values were (ng g^{-1} wet weight): < 0.11 to 1.27 for OCPs, < 0.11 to 2.36 for PCBs, and < 0.25 to 1.29 for PBDEs. The quantification of analytes was performed using a nine-level analytical curve and followed the internal standard procedure.

The concentration of organochlorines was expressed on a wet weight basis. Fifty-one PCB congeners (International Union of Pure and Applied Chemistry (IUPAC) # 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 77, 81, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 201, 203, 206 and 209) and seven PBDEs (IUPAC # 28, 47, 100, 99, 154, 153 and 183) were analysed. The OCPs analysed were DDTs (*o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE and *p,p'*-DDE), HCHs (α, β-, δ- and γ-isomer), chlordanes (α-, γ-chlordane and oxychlordane), drins (aldrin, isodrin, dieldrin and endrin), heptachlor, heptachlor epoxide A and B, endosulfan I and II, methoxychlor, hexachlorobenzene (HCB), and mirex.

Table I. Concentration range (ng g^{-1} wet weight) of organochlorine and brominated contaminants in bird eggs and embryos from Antarctica.

	Σ PCBs	Σ PBDEs	HCB	γ-HCH	Oxychlordane	Dieldrin	*p,p'*-DDE	*p,p'*-DDT	*p,p'*-DDD	Mirex	Lipids %
Eggs											
Catharacta antarctica	492.00	0.33	139.00	<0.18	31.60	4.61	270.00	13.76	3.97	603.00	11.30
Catharacta antarctica	541.00	0.88	44.20	<0.18	13.70	3.61	144.00	7.63	1.99	351.00	6.40
Macronectes giganteus	201.00	<0.25	84.10	<0.18	19.20	2.51	148.00	<0.47	<0.27	35.10	7.32
Macronectes giganteus	241.00	<0.25	214.00	<0.18	26.20	<0.12	101.00	<0.47	<0.27	2.69	11.00
Macronectes giganteus	220.00	<0.25	162.00	<0.18	24.30	1.89	160.00	<0.47	<0.27	8.38	11.50
Macronectes giganteus	96.60	<0.25	80.80	<0.18	14.40	1.77	62.50	<0.47	<0.27	1.50	9.22
*Macronectes giganteus**	7.80	<0.25	3.35	0.45	1.38	<0.12	11.90	<0.47	<0.27	25.20	13.10
*Macronectes giganteus**	112.00	<0.25	54.30	<0.18	11.40	1.83	90.80	6.51	<0.27	104.00	7.78
Macronectes giganteus	148.00	<0.25	105.00	<0.18	20.60	2.59	167.00	13.30	<0.27	259.00	7.62
*Macronectes giganteus**	138.00	<0.25	49.00	<0.18	17.40	1.98	143.00	9.05	<0.27	272.00	8.10
Larus dominicanus	74.20	<0.25	34.56	<0.18	4.57	0.43	45.83	<0.47	<0.27	17.95	7.80
Sterna vittata	25.80	0.65	36.10	1.20	1.68	<0.12	17.70	<0.47	<0.27	12.20	14.30
Sterna vittata	8.23	<0.25	10.70	<0.18	<0.67	<0.12	10.00	<0.47	<0.27	3.38	7.48
*Sterna vittata**	11.90	0.31	20.10	<0.18	0.87	<0.12	16.50	<0.47	<0.27	6.15	10.50
Pygoscelis antarcticus	2.11	<0.25	18.70	<0.18	1.19	1.11	12.40	0.91	<0.27	4.03	6.06
Pygoscelis antarcticus	2.84	<0.25	14.70	<0.18	1.03	0.94	15.90	1.45	<0.27	3.39	5.60
Pygoscelis antarcticus	5.16	<0.25	30.00	0.60	0.96	1.54	16.80	<0.47	<0.27	4.12	7.39
Pygoscelis antarcticus	3.09	<0.25	34.60	<0.18	1.24	1.47	18.00	1.17	<0.27	4.64	7.90
Pygoscelis antarcticus	2.57	<0.25	19.30	0.26	1.06	1.05	15.10	0.88	<0.27	2.15	8.24
Pygoscelis antarcticus	3.89	<0.25	29.40	0.75	1.06	0.80	17.40	0.75	<0.27	3.43	8.32
Pygoscelis antarcticus	3.14	<0.25	15.20	0.31	<0.67	0.68	10.60	0.59	<0.27	2.35	8.24
Embryos											
Macronectes giganteus	344.00	<0.25	199.00	<0.18	43.80	3.29	405.00	16.00	<0.27	495.00	0.66
Macronectes giganteus	5.33	<0.25	2.83	<0.18	1.02	<0.12	7.21	0.72	<0.27	17.60	0.36
Macronectes giganteus	4.10	<0.25	2.66	<0.18	1.27	<0.12	11.00	0.86	<0.27	13.70	0.42
Sterna vittata	2.63	<0.25	2.49	<0.18	<0.67	<0.12	2.45	<0.47	<0.27	1.98	1.22

*Eggs containing an embryo.

Results

Eggs

Generally, PCBs were predominant in the eggs of *C. antarctica*, *L. dominicanus* and *M. giganteus* (followed by *p'p*-DDE and HCB). Among OCs, mirex had the highest concentration in some *C. antarctica* and *M. giganteus* eggs. In *P. antarcticus* and *S. vittata* eggs, HCB was the major compound (Table I). The PBDE congeners were detected only in eggs of *C. antarctica* (PBDE 47 and 153) and *S. vittata* (PBDE 47), but at concentrations close to the QL.

The eggs of *C. antarctica* and *M. giganteus* had the highest concentrations of OCs, which were from one to two orders of magnitude higher than those found in the eggs of *P. antarcticus* and *S. vittata*. Intermediate levels of OCs were exhibited by *L. dominicanus*, lower than *C. antarctica* and *M. giganteus* but higher than *P. antarcticus* and *S. vittata* (Table I). The only *M. giganteus* egg that showed low concentrations of OCs (two orders of magnitude lower than the other eggs) contained an embryo in an advanced stage of development.

The PCB profiles in the eggs of *C. antarctica*, *M. giganteus* and *L. dominicanus* were very similar, with

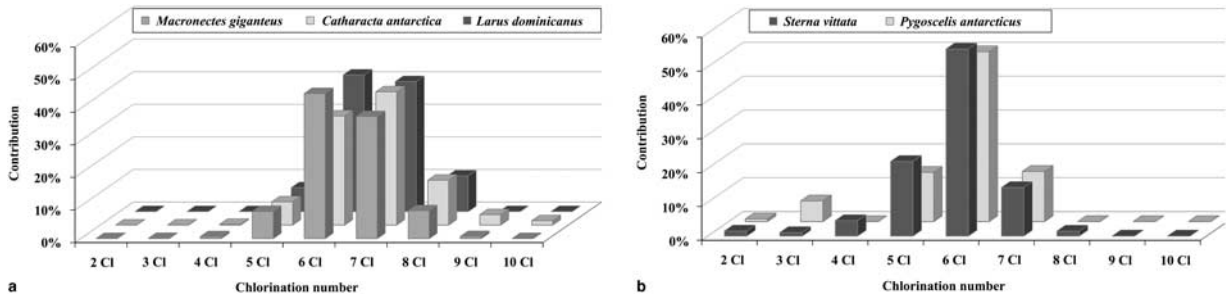

Fig. 1. Contribution of polychlorinated biphenyl (PCB) congeners, according to chlorination number, in the eggs of **a.** brown skuas (*Catharacta antarctica*), southern giant petrels (*Macronectes giganteus*) and kelp gulls (*Larus dominicanus*), and **b.** chinstrap penguins (*Pygoscelis antarcticus*) and Antarctic terns (*Sterna vittata*).

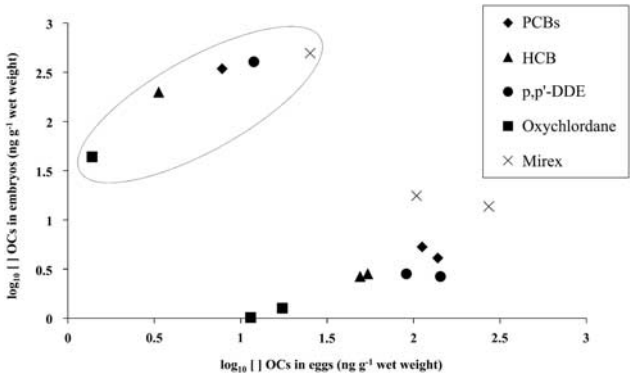

Fig. 2. Concentrations of the major organochlorine (OC) compounds found in the embryos of southern giant petrels (*Macronectes giganteus*) and their respective eggs. Circled markers correspond to the values detected for the egg/embryo in later development stage, while the remaining markers show the values for the eggs/embryos in earlier development stage.

a predominance of hexa- and heptachlorobiphenyls and the presence of congeners with eight and nine chlorine atoms. In contrast, in the eggs of *P. antarcticus* and *S. vittata* hexachlorobiphenyls were clearly the predominant congeners and PCBs with a lower chlorination number were also detected (Fig. 1).

Embryos

Three out the eight *M. giganteus* eggs contained embryos. The incubation time of this species is *c*. 60 days. Based on the presence of few external structures (wings, beak) and a large quantity of albumen and yolk, two embryos were thought to be in the early stages of development. One embryo was in a later development stage, with well-defined external structures (claws, toes, culmen, wings and eyes) and the egg contained only a small portion of yolk and no albumen.

Differences in OC concentrations were up to two orders of magnitude in the *M. giganteus* embryos (Table I). The embryos in initial growth stage had lower concentrations than their respective eggs (albumen and yolk). The embryo in the more advanced stage of development had the highest OC concentrations and its egg had the lowest concentrations of all OCs detected (Fig. 2).

The incubation time of *S. vittata* is *c*. 24 days. An *S. vittata* embryo found in one of the eggs was estimated to be 9–12 days old, with down just breaking out along dorsal tract and tail, wings, toes and claws visible, but still with a significant amount of yolk and albumen (approximately half of the internal space of the egg). In the *S. vittata* embryo, PCBs, HCB, *p'p*-DDE and mirex were detected but at lower concentrations relative to the *M. giganteus* embryos (Table I).

The *S. vittata* embryo had a predominance of hexachlorobiphenyls (also seen in the eggs of this species), but also a contribution of tri-, tetra- and pentachlorobiphenyls. Whereas *M. giganteus* embryos had a predominance of hexa- and heptachlorobiphenyls and the presence of heavier congeners (octa- and nonachlorobiphenyls) (Fig. 3).

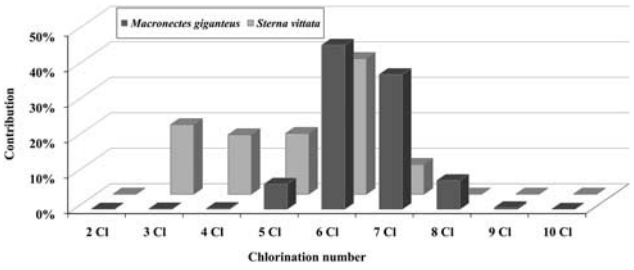

Fig. 3. Contribution of polychlorinated biphenyl (PCB) congeners, according to chlorination number, in the embryos of southern giant petrels (*Macronectes giganteus*) and Antarctic terns (*Sterna vittata*).

Discussion

The OC concentrations in the eggs of *M. giganteus* and *P. antarcticus* reflect the trophic ecology of these birds and the differences in post-breeding dispersal. *Macronectes giganteus* is a migratory species and its females have a greater dependence on marine prey, such as fish and cephalopods, although they also feed on carrion of other birds and marine mammals (Hunter 1983, Forero *et al.* 2005). On the other hand, *P. antarcticus* forages only in the Southern Ocean and feeds mainly on krill and small fish (Volkman *et al.* 1980), which explains the lower concentrations of contaminants in the eggs of this species.

Despite the small number of samples, the OC levels found in the eggs of the other Antarctic birds included in this study also indicated the influence of trophic status on contaminant patterns (*C. antarctica* > *L. dominicanus* > *S. vittata*). *Catharacta antarctica* feeds mainly on carrion, eggs and chicks of penguins and Procellariiformes (Pietz 1987, Phillips *et al.* 2004). *Larus dominicanus* feeds on a variety of prey, from carrion to amphipods, but the Antarctic limpet (*Nacella concinna* (Strebel)) is its primary food in the breeding season (Favero *et al.* 1997). *Sterna vittata* represents the lower trophic level among the three species, with a diet similar to *P. antarcticus* (Volkman *et al.* 1980, Casaux *et al.* 2008).

Mirex is one of the most stable and persistent pesticides, which was primarily used as an insecticide in many countries of South America and South Africa (Ritter *et al*. 1995). It was banned under the Stockholm Convention on Persistent Organic Pollutants in 2001. During the non-breeding season, *M. giganteus* and *C. antarctica* travel to these areas to feed (Del Hoyo *et al.* 1996, Sander *et al.* 2010). Thus, the higher concentrations of

mirex in the eggs of both species are probably associated with their migration habits, additional to biomagnification.

Hexachlorobenzene is a semi-volatile compound that reaches the coldest regions of the planet by long-range atmospheric transport (Simonich & Hites 1995). An increase in HCB concentrations in recent years is evident through a comparison with data reported in previous studies (Zhang *et al.* 2007, Schiavone *et al.* 2009, Corsolini *et al.* 2011). In the present investigation, HCB levels were up to one order of magnitude higher relative to levels reported in the eggs of *P. antarcticus* collected between 2003 and 2005 in the same region (Schiavone *et al.* 2009). *Macronectes giganteus* eggs also had higher HCB concentrations than those reported in eggs collected in 2001 and 2002 on the Fildes Peninsula (Zhang *et al.* 2007). A similar increase in PCBs and *p,p'*-DDE has also occurred in the eggs of *M. giganteus* in comparison to data reported by Zhang *et al.* (2007), whereas *P. antarcticus* eggs exhibited very similar concentrations to those described by Schiavone *et al.* (2009). This could be an indication of a rise in the levels of some contaminants at lower latitudes of the Southern Hemisphere, as well as the Southern Ocean.

Low chlorinated PCBs are expected to reach polar regions faster due their greater volatility in comparison to highly halogenated congeners (Wania & Dugani 2003). The PCBs with low chlorination levels are reported to be predominant in key species from the base of the Antarctic marine food web, such as silverfish (*Pleuragramma antarcticum* Boulenger) and krill (*Euphasia superba* Dana), although heavier PCB congeners have also been found (Corsolini *et al.* 2002, Cipro *et al.* 2010). Species that feed at lower trophic positions, *P. antarcticus* and *S. vittata*, exhibited low chlorinated PCBs (although these compounds were not predominant). Higher chlorinated PCBs were prevalent in the eggs of *M. giganteus*, *C. antarctica* and *L. dominicanus* as a result of bioaccumulation and biomagnification. High chlorinated PCBs are usually predominant in long-living predators that feed at high trophic positions (Corsolini *et al.* 2011, Cipro *et al.* 2013) due to the easier transformation and elimination of PCB congeners of a low molecular weight, which results in the accumulation of compounds with a greater number of chlorines (Maervoet *et al.* 2004).

Generally, PBDEs are found at lower concentrations in comparison to other organic contaminants, such as PCBs and DDTs (Corsolini *et al.* 2006, Yogui & Sericano 2009). However, PBDE 47, which was detected in the eggs of both *S. vittata* and *C. antarctica*, has greater volatility and water solubility and is the most abundant congener in krill and fish in Antarctica (Corsolini *et al.* 2006). Similar to some high halogenated PCBs, PBDE 153 is more resistant to biotransformation and tends to accumulate at higher trophic positions, which explains its occurrence only in the eggs of *C. antarctica*.

The inverse association between concentrations in the residual egg contents and in the embryos of *M. giganteus* in different development stages may be an indication of the transfer of contaminants during embryo growth. Custer *et al.* (1997) reported the transfer of contaminants from yolk to the embryo, but suggest that no metabolic changes appear to occur during embryo growth and lipid mobilization. Yolk is a lipid-rich energy source that remains in the embryo (*c.* 30%) after hatching (McLaughlin *et al.* 1963) and contains up to 60% of the total concentrations of OCs (Custer *et al.* 1997). Most of the contaminant load in the egg may be transferred to the embryo, but not readily absorbed and metabolized.

As was observed in the eggs, the PCB profiles in embryos of *M. giganteus* and *S. vittata* also reflect the differences associated with trophic status. In comparison to *M. giganteus*, *S. vittata* has a lower trophic status and exhibited a predominance of tri- (19.6%), tetra- (16.7%), penta- (17.1%) and hexachlorobiphenyls (38.2%), which accounted for 91.6% of total PCBs, whereas 92.2% of total PCBs in *M. giganteus* were constituted by hexa- (46.2%), hepta- (37.9%) and octachlorobiphenyls (8.1%).

Conclusions

The present analysis of bird eggs and embryos demonstrates the influence of ecological factors, such as dispersal and diet, on contaminant levels and patterns. These factors should be carefully considered when comparing contamination data between different species and populations. Despite the small number of samples, long-range migratory species, such as *M. giganteus* and *C. antarctica*, exhibited contamination from both breeding and migration areas, whereas OCs in resident birds mainly reflected the compounds found at higher concentrations in the Antarctic environment due to atmospheric transport, such as HCB. In agreement with data found in the literature, lower levels of PBDEs were found in comparison to OCs. Comparisons with data from previous studies indicate an increase in concentration of some contaminants, such as HCB, PCBs and *p,p'*-DDE. The use of eggs (regardless the incubation stage) as bioindicators is an easy, efficient method for the continuous monitoring and evaluation of changes in contaminant concentrations in the Antarctic environment.

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Author contribution

All authors authorize the publication of the final version of this manuscript. Fernanda I. Colabuono led the study design, chemical analysis, data analysis and manuscript preparation, and also contributed to fieldwork. Satie Taniguchi contributed to chemical analysis and manuscript development. Maria V. Petry led the fieldwork and contributed to the manuscript preparation. Rosalinda C. Montone contributed to data interpretation and manuscript elaboration.

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