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# Evaluation of PCDD/Fs, PCBs and PBDEs in two penguin species from Antarctica

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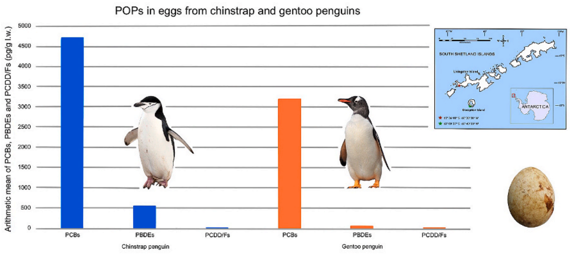
## HIGHLIGHTS

- POP levels were higher in chinstrap than in gentoo penguin eggs.
- PCBs are predominant POPs in chinstrap and gentoo penguin eggs.
- POP profiles in penguins suggest long-range transport as their main source.
- PBDE-209 was the predominant congener among PBDEs.
- TEQ values well below the threshold level for harmful effects.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Persistent Organic Pollutants (POPs) are a global threat, but impacts of these chemicals upon remote areas such as Antarctica remain unclear. Penguins can be useful species to assess the occurrence of POPs in Antarctic food webs. This work's aim was the evaluation of polychlorodibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in eggs of two penguin species, chinstrap (*Pygoscelis antarcticus*) and gentoo penguins (*Pygoscelis papua*), breeding in the South Shetland Islands. Results showed a common pattern in POP levels regardless of the species, characterized by a major abundance of PCBs (98 %), followed by PBDEs (1–2%) and PCDD/Fs (<1 %). Concentrations of POPs in chinstrap and gentoo penguin eggs were 482 and 3250 pg/g l.w., respectively. PCBs, PBDEs and PCDD/Fs were found at higher concentrations in chinstrap penguin eggs, being these differences significant for PBDEs. Interspecies differences in POP levels agree well with potential trophic position differences among species due to changes in prey composition and foraging areas. POP profiles were dominated by congeners with a low degree of halogenation. Our results therefore suggest similar sources of POPs in the food webs exploited by both species and in both cases attributable to the long-range transportation rather than to the presence of local sources of POPs. TEQs were found between 1.38 and 7.33 pg/g l.w. and followed the pattern non-*ortho* dl-PCBs > PCDFs > PCDDs > mono-*ortho* dl-PCBs. TEQ values were lower than the threshold level for harmful effects in birds of 210 pg/g WHO-TEQ/g l.w.

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## 1. Introduction

Environmental pollution remains as one of the several factors that currently threaten Earth's biodiversity and the global environment (WHO, 2005a). Particularly, chemical pollution is ranked within the main environmental problems due among others to the high number and large amounts of compounds discharged into the environment and their ubiquity (WHO, 2005b). Among them, Persistent Organic Pollutants (POPs) stand out because of the threat they represent to human health and to the environment (UNEP, 2001). In addition to their toxicity, physicochemical properties of POPs make them highly resistant to degradation, so they linger in the environment for prolonged time periods. Due to their lipophilic nature, they bioaccumulate into the tissues of organisms, and biomagnify through food webs. Also, they have the potential to be long range transported because of their semivolatility, being able to reach regions where they have never been produced or directly applied, such as the Antarctica (Wania and Mackay, 1996). Due to these characteristics, and in order to safeguard human health and the environment against POPs, the UN Environment Program (UNEP) has established international instruments to control and regulate the use and production of these compounds since 2004 through the Stockholm Convention (UNEP, 2001).

Long-range atmospheric transport (LRAT) mechanism of semi-volatile POPs mainly relays on their ability to migrate in successive volatilization-deposition jumps between the ocean or the earth and the atmosphere, a process called 'grasshopper migration' (Wania and Mackay, 1996). Thus, global distillation processes result in the atmospheric mobilization of these compounds from warmer to colder regions. In these areas, low temperatures prevent from re-volatilizations resulting in a general deposition and accumulation; thus, becoming part of the polar ecosystems (Wania and Mackay, 1993; Jones and De Voogt, 1999). For this reason, the remoteness and nature of the Antarctic region offer a valuable opportunity to investigate global pollution, transport mechanisms and effects of POPs like few places on Earth (Caroli, 2001). Although LRAT is thought to be the predominant mechanism by which POPs reach polar regions (Wania and Mackay, 1993; Kallenborn et al., 1998; Van den Brink et al., 1998), different investigations have suggested that other factors, such as human activity, transport through migratory birds and local bird activity also constitute mechanisms that amplify the occurrence of these pollutants in Antarctic ecosystems (Kennicutt et al., 1995). In fact, penguin colonies have been recognized as secondary sources of contamination with POPs (Roosens et al., 2007; Cipro et al., 2019). The study of surface-soil exchanges in Antarctica Peninsula by Cabrerizo et al. (2013) demonstrated that snow and soil are important secondary sources of POPs during the austral summer. Also, a reduction in glacial ice sheets may serve as a secondary source of legacy POPs (Nash, 2011).

Seabirds have been used in numerous studies as bioindicators to study the occurrence and distribution of environmental pollution (Furness and Camphuysen, 1997; Burger and Gochfeld, 2004), since, among other reasons, they tend to occupy high trophic positions in the food webs and reflect biomagnification processes (Roscales et al. 2010, 2019; Jerez et al., 2013; Mello et al., 2016). In Antarctica, *Pygoscelis* penguins are the most abundant vertebrates and have been pointed out as good bioindicators of POPs to evaluate their presence, distribution and dynamics (Corsolini et al., 2007; Mello et al., 2016; Montone et al., 2016; Rudolph et al., 2016; Cipro et al., 2019). Specifically, studies on POPs and other pollutants in penguins have used a wide variety of tissues for their determination (Cipro et al., 2010; Colabuono et al., 2015; Metcheva et al., 2017). Among them, eggs can be particularly useful (Mello et al., 2016; Schiavone et al., 2009; Corsolini et al., 2011; Cipro et al., 2013) because POPs tend to be transferred along with the lipid content during egg formation (Mineau et al., 1984; Leat et al., 2011). Accordingly, the concentration of POPs in eggs reflects the load of contaminants that the female had at the time of laying (Coulson et al., 1972; Becker, 1989; Wolschke et al., 2015; Mwangi et al., 2016). In addition, the use of unhatched eggs represents a minimally invasive and non-destructive method, ensuring a negligible impact on individuals and populations under study. Moreover, penguins are gregarious birds and during the austral summer, in the breeding season, they gather in large colonies up to several thousands of individuals to reproduce, which facilitates the collection of a representative quantity of biological samples for further examination. Also, during this period, penguins depend on local oceanic food sources to supply their offspring (Hinke et al., 2007; Colominas-Ciuró et al., 2021), so they reflect the local conditions of the environment where they are found. The different penguin species in this region usually feed on krill (*Euphausia superba*), followed by fish and squid, although the types and relative abundance of prey often vary between locations, years, during the season and between species (Kokubun et al., 2010; Rombola et al., 2010; Ratcliffe and Trathan, 2012; Herman et al., 2017; Colominas-Ciuró et al., 2021).

Although several studies have reported the occurrence of POPs in Antarctic birds, unfortunately, there is a dearth of consistent data to evaluate temporal trends (Corsolini, 2011; Van den Brink et al., 2011; Wolschke et al., 2015; Ellis et al., 2018). Also, there are few studies on the presence of dioxins and furans in Antarctica (Borghesi et al., 2008; Cincinelli et al., 2016). Therefore, additional data on these pollutants in the region are necessary to further investigate temporal, spatial or interspecific variability in their presence, especially from the perspective of possible adverse health effects.

This work's chief objective was to evaluate levels of polychlorodibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) as well as their congener profiles present in eggs of two species; namely, chinstrap penguin (*Pygoscelis antarticus*) and gentoo penguin (*P.papua*), assessing the influence of interspecific variations in trophic ecology (diet, trophic position or foraging areas) on POP content. In addition, this work aims to quantify the total toxic equivalents (TEQs) due to the presence of dioxin-like PCBs and PCDD/Fs, based on their corresponding toxic equivalency factors (TEFs).

## 2. Materials and methods

### 2.1. Study area and sample collection

10 and 20 infertile eggs from gentoo and chinstrap penguins, respectively, were collected in the following weeks after the hatching (between December 2016 and January 2017). Samples were collected during the 2016–2017 austral summer in the South Shetland Islands, located northwest of the Antarctic Peninsula. As shown in Fig. 1 the Vapour Col chinstrap penguin colony is located in Deception Island, and the Devil Point gentoo penguin colony is located on the Byers Peninsula, Livingston Island. Both colonies occupy areas free of ice during the austral summer, especially in the case of Deception Island due to its constant volcanic activity (Rosado et al., 2019). Eggs were kept at −20 °C during the campaign and transported to the lab, where they were kept at −80 °C until their subsequent analysis. Each whole egg content was used for chemical analysis.

### 2.2. Analytical procedure

After egg's homogenization and lyophilization, 3 g were weighed and subjected to matrix solid phase dispersion (MSPD) as previously described in Merino et al. (2005) with the modifications included in Roscales et al., (2016a). Briefly, egg contents were mixed and homogenized with 40 g of anhydrous sodium sulfate ($Na_2SO_4$) and 10 g of silica gel for residue analysis. Extraction was performed using 400 mL of a n-hexane:acetone (1:1) mixture in a glass column (3 cm diameter, 50 cm length). Each sample was spiked with a total of 20 μl of $^{13}C$-labeled standards including PCBs, PBDEs and PCDD/Fs prior to MSPD (detailed in Supplementary Information, SI, Table S1). Extracts were concentrated using a TurboVap® system (Zynmarck Inc., Hopkinton, Massachusetts,

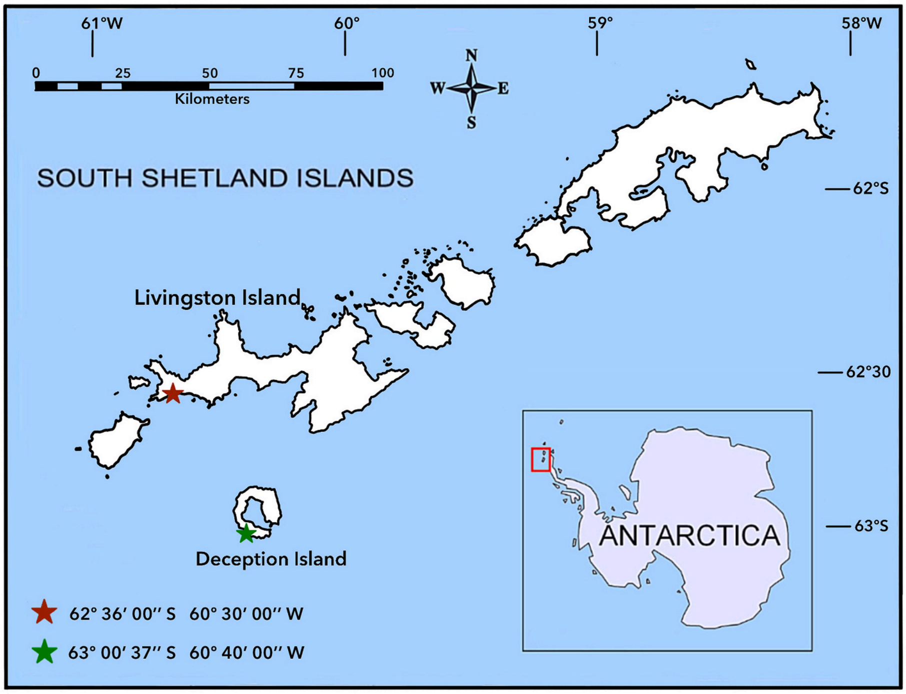

**Fig. 1.** Map of the two penguin breeding colonies located at the South Shetland Islands.

USA) and purified by means of the automated sample preparation system DEXTech+ (LCTech GmbH, Germany) as previously described in Bartalini et al., (2019). A TurboVap® system was used for the evaporation of extracts down to ~1 mL. Subsequently, they were transferred to vials, and dried under a gentle nitrogen stream using a Pasvial system (V3 Model, HiTC. S.A., Spain). Fractions were finally reconstituted in 5 µL of $^{13}$C-labeled injection standards (IS) of PCDD/Fs, PCBs and PBDEs prior to instrumental analysis. The lipid content of each egg was determined gravimetrically (Muñoz-Arnanz et al., 2011). Further details are comprehensively provided within the Supplementary Information (Annex).

### 2.3. Instrumental determination

Samples were analyzed for 17 2,3,7,8-susbtituted PCDD/Fs, 18 PCBs (including 12 dioxin like PCBs, dl-PCBs, and 6 indicator PCBs), and 26 PBDE congeners (all compounds detailed in Table 1). The use of isotopically labeled standards ($^{13}$C) allowed the identification and quantification by means of the isotopic dilution technique. Specifically, a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy) was used coupled to a high-resolution mass spectrometer (DFS, Thermo Fisher Scientific, Bremen, Germany) (GC-HRMS). One microliter of each final extract was injected in splitless injection mode at a temperature of 260 °C, with helium as carrier gas working in a constant flow mode. GC separation of PCDD/Fs and PCBs was carried out using a DB-5MS column (Agilent J&W, USA) with dimensions of 60 m × 0.25 mm x 0.25 µm, while GC separation of PBDEs proceeded on a 15 m × 0.25 mm x 0.10 µm Rxi-5Sil MS column (Restek, USA). Different oven temperatures programs and carrier flows used for each family of target compounds are shown in the Supplementary Information (Table S2). Positive electron ionization (EI+) at 45 eV was selected operating the HRMS in selected ion monitoring (SIM) mode working with two major ions of each analyte at a 10,000 resolving power, as it is described in Bartalini et al. (2019).

### 2.4. Quality assurance/quality control (QA/QC)

Throughout the entire analytical protocol, especial care was taken to minimize the exposure to UV light. All material (glassware and otherwise) was carefully cleaned by means of 3 high purity solvents of decreasing polarity; namely, acetone, dichloromethane and n-hexane. In order to check and control for possible contamination, one blank was included and analyzed within each batch of five samples. Whenever levels were found in blanks, they were subtracted from the corresponding samples in the batch. Identification was based on (a) retention times (±0.1 min with respect to theoretical times), and (b) ratio between the two monitored ions within ±15 % of theoretical values. Average surrogate recoveries of $^{13}$C-PCDD/Fs, $^{13}$C-PCBs and $^{13}$C-PBDEs were satisfactory, with average (and range) values of 70 % (58–92 %), 66 % (53–84 %) and 65 % (45–80 %), respectively (Tables S3–S8 SI). Limits of Detection (LOD) were obtained as blanks' mean plus 3 times the standard deviation of the blanks. Analytes with concentrations below their LODs were given a value of zero (PBDEs and indicator PCBs). In the case of PCDD/Fs, dl-PCBs and TEQs, the values were determined according to the "upper bound" (i.e. substitution of non-detected compounds for LOD values). Average LODs in chinstrap penguin ranged from 0.17 to 1.1 pg/g l.w. for PCBs, 0.01–0.4 pg/g l.w. for PBDEs and 0.05–0.13 pg/g l.w. for PCDD/Fs (Tables S3, S5 and S7 SI). In gentoo penguin eggs, average LODs ranged from 0.14 to 1.02 pg/g l.w. for PCBs, 0.008–0.87 pg/g l.w. for PBDEs and 0.04–0.12 pg/g l.w. for PCDD/Fs (Tables S4, S6 and S8 SI).

### 2.5. Data handling

Concentrations are expressed in pg/g lipid weight (l.w.) since significant interspecies differences in the lipid content (Student t-test; $t_{28} = -2{,}21$, $p < 0.05$) and a significant relationship between POP burdens and lipids in the eggs content of the samples (Pearson's correlation test; $r = -0{,}68$, $p < 0{,}001$ for PCBs; $r = -0{,}47$, $p{=}{<}0{,}01$ for PBDEs; $r = -0{,}44$, $p = 0{,}05$ for PCDD/Fs) were found. TEQs for PCDD/Fs and dl-PCBs in chinstrap and gentoo penguin eggs were calculated based on the toxic equivalency factors (TEFs) for birds provided by the World Health Organization (WHO) (Van den Berg et al., 2006). IBM SPSS Statistics 26 for Windows (SPSS Inc, Chicago, IL, USA) was used for statistical analyses. Normal distribution and homogeneity of variance of pollutant concentrations were analyzed using a Kolmogorov-Smirnov and Levene tests, respectively. In those cases, in which significant

**Table 1**

Arithmetic mean, geometric mean, median and range of total POPs, PCBs, PBDEs and PCDD/Fs in eggs from chinstrap and gentoo penguins (concentrations are expressed in pg/g l.w.).

| | Chinstrap penguin | | | | Gentoo penguin | | | | Interspecific Student t-test |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | Geometric mean | Median | Range | Mean | Geometric mean | Median | Range | |
| ∑POPs [a] | 4820 | 4160 | 4360 | 1660–11670 | 3250 | 3000 | 3590 | 1210–4930 | $t_{27} = 1.6$, $p = 0.12$ |
| ∑PCBs [b] | 4710 | 4080 | 4330 | 1610–11560 | 3200 | 2950 | 3550 | 1170–4870 | $t_{28} = 1.61$, $p = 0.12$ |
| ∑indicator PCBs [c] | 3660 | 3020 | 3050 | 1110–10370 | 2180 | 1980 | 2410 | 728–3250 | $t_{28} = 1.85$, $p = 0.07$ |
| ∑mono-*ortho* PCBs [d] | 990 | 941 | 957 | 478–1750 | 976 | 867 | 774 | 415. – 2390 | $t_{28} = 0.54$, $p = 0.6$ |
| ∑non-*ortho* PCBs [e] | 59.9 | 57.6 | 58.6 | 30.6–105 | 47.6 | 45.0 | 44.5 | 29.4–74.7 | $t_{28} = 2.02$, $p = 0.053$ |
| ∑PBDEs [f] | 123 | 89.6 | 75.5 | 35.7–473 | 48.8 | 42.6 | 42.1 | 20.1–105 | $t_{27} = 2.75$, $p < 0.05$ |
| ∑PCDD/Fs [g] | 3.87 | 3.31 | 3.23 | 1.19–8.50 | 3.89 | 3.16 | 2.54 | 1.36–7.67 | $t_{28} = 0.15$, $p = 0.88$ |
| ∑PCDDs [h] | 0.74 | 0.64 | 0.64 | 0.27–1.48 | 0.69 | 0.59 | 0.47 | 0.34–1.53 | $t_{28} = 0.36$, $p = 0.72$ |
| ∑PCDFs [i] | 3.13 | 2.63 | 2.4 | 0.92–7.02 | 3.2 | 2.55 | 2.08 | 1.02–6.3 | $t_{28} = 0.07$, $p = 0.95$ |

[a] Sum of ∑PCBs, ∑PBDEs and ∑PCDD/Fs.

[b] Sum of PCBs # 28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189.

[c] Sum of PCBs # 28, 52, 101, 138, 153, 180.

[d] Sum of PCBs # 105, 114, 118, 123, 156, 157, 167, 189.

[e] Sum of PCBs # 77, 81, 126, 169.

[f] Sum of PBDEs # 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209.

[g] Sum of PCDD/Fs 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF.

[h] Sum of PCDDs 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD.

[i] Sum of PCDFs 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF.

differences were found with respect to the normal distribution ($p < 0.05$), log transformation was followed to achieve the criterion of normality. Student t-test was used to assess interspecies comparisons. Additionally, Pearson's correlation analyses were applied to evaluate the relationship between concentrations of different pollutants and between pollutant concentrations and the eggs' volume.

## 3. Results and discussion

### 3.1. POP concentrations and congener profiles

The three POP families (PCDD/Fs, PCBs and PBDEs) were found in all analyzed samples (Table 1). PCBs were found at the highest concentration followed by PBDEs, which were at around one order of magnitude below (Table 1). The lowest concentrations were found in all cases for PCDD/Fs, around three orders of magnitude below PCBs (Table 1). No significant differences were detected in the total POP levels (∑PCDD/Fs + ∑PCBs + ∑PBDEs) in eggs between the studied species. However, concentrations for all POP families were higher in chinstrap compared to gentoo eggs (Table 1), with geometric mean values in chinstrap eggs that almost doubled those found in gentoo eggs in the case of PCBs and PBDEs.

Contribution of each POP family to total POPs did not show remarkable differences between penguin species. PCBs accounted for about 98 % of total POPs, namely indicator PCBs (~70 %) and mono-*ortho*-PCBs (~28 %), followed by PBDEs (1–2%) and PCDD/Fs (~1 %). These relative abundances agree with those reported in previous studies in eggs of other Antarctic penguin species, such as the emperor penguin *Aptenodytes forsteri* or the Adélie penguin *Pygoscelis adeliae* (Corsolini et al., 2007; Cipro et al., 2010; Mwangi et al., 2016), as well as in the same species in other Antarctic colonies (Corsolini et al., 2004; Mello et al., 2016), some of them studied more than 10 years ago.

No significant differences were detected in total concentrations of PCBs, although indicator PCBs and non-*ortho* PCB concentrations were higher in chinstrap than in gentoo penguins eggs (Table 1). All PCB congeners were measured in all samples of both species, except for PCB77, which was not found in one of the gentoo penguin samples (detailed in Supplementary Information, SI, Tables S3, S4, and S9). Among them, PCB28 (3 Cl) was the most abundant congener with an average contribution to total PCBs of 20 % in both species (Fig. 2), followed by PCB153 and 118 (19 % and 15 %, respectively in chinstrap eggs; 17 and 19 %, respectively in gentoo eggs). The great similarity found between species in the congener profiles suggests that the main sources of POPs in the food webs exploited by both species are similar. Major abundances of low chlorinated PCBs suggest that LRAT is the main cause of POPs' occurrence in the study area (Corsolini et al., 2002; Cipro et al., 2010). These congeners reach polar regions more efficiently than the more halogenated congeners due to their higher volatility (Wania and Dugani, 2003). Besides differences among the LRAT potential of studied congeners, other factors such as the biological pump also may contribute to increase the relative presence of PCBs with a low chlorination degree. The biological pump in the Antarctic Ocean is a flow of organic matter and therefore of hydrophobic pollutants associated with it, from the atmosphere to the deep waters of the water column (Galbán-Malagón et al., 2013). Most hydrophobic PCBs, which have the highest degree of chlorination, are most likely to partition into organic matter, and therefore to be dragged into deep water by deposition processes, making it difficult to transfer to higher trophic positions compared to lighter PCBs (Nizzetto et al., 2012).

In regard of PBDEs, total concentrations were significantly higher in the chinstrap penguin eggs than in gentoo penguin eggs (Table 1). Several PBDE congeners (7, 15, 17, 66, 77, 126,138, 156, 191) were not detected in any sample (detailed in Supplementary Information, SI, Tables S5, S6 and S10). PBDE congeners 119, 184, 196 and 197 were detected in less than 30 % of cases in both species. Congener PBDE 85 was found in 70 % of the gentoo penguin eggs, whereas it was only detected in 30 % of the chinstrap penguin ones. Contribution profiles were dominated by the same congeners in both species but PBDE 209 and 153 outlined clear differences in the profiles of the species (Fig. 3). PBDE 209 was the most abundant congener in chinstrap penguin eggs (29 %) and the second most predominant in gentoo eggs (16 %). In contrast, PBDE 153 dominated egg profiles of gentoo penguins (22 %) and represented a 7 % in the case of chinstraps'. Among the rest of congeners, PBDE 154, 100 and 47 were the main contributors in both species (Fig. 3). Previous studies have shown PBDE profiles similar to those described here in Antarctic food webs including penguin species (Mwangi et al., 2016).

Recent studies on Antarctic wildlife also have found major abundances of PBDE 153 in Antarctic seabirds and relate them to the high bioaccumulation and biomagnification potential of this congener compared to other PBDEs (Colabuono et al., 2015). Moreover, species-specific accumulation and excretion processes may play a role in

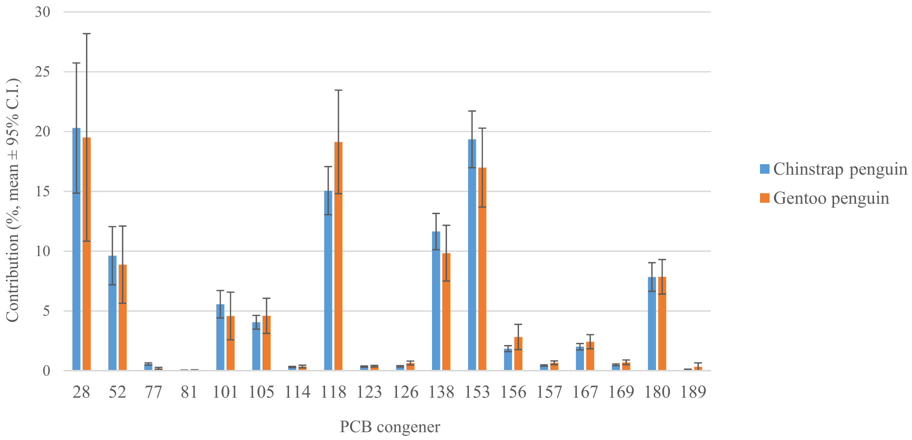

**Fig. 2.** Mean contribution of each congener to the total PCB content in chinstrap and gentoo penguin eggs. Error bars represent 95 % confidence interval.

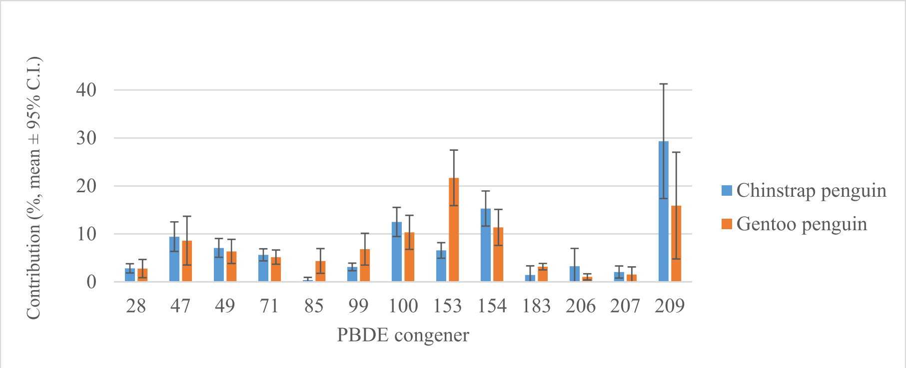

**Fig. 3.** Mean contribution of each congener to the total PBDE content in chinstrap and gentoo penguin eggs. Error bars represent 95 % confidence interval.

the accumulation differences found for this compound between the two penguin species (Borgå et al., 2004; Schiavone et al., 2009). In the case of PBDE 209, the great abundance of this congener could be explained by both LRAT and the potential presence of local sources. On one hand, previous studies have indicated that PBDE profiles dominated by PBDE 209 in Antarctica can be influenced by the presence of local PBDE sources (Hale et al., 2008; Lewis et al., 2020). This may explain the differences in the relative contribution of this congener found here between penguin colonies. However, although low brominated PBDEs can be expected to be predominant congeners due to their greater volatility (Oh et al., 2002; Wania and Dugani, 2003), medium brominated PBDEs (PBDE 47, 100, 153, 154) as well as highly brominated congeners (209) are transported mostly associated with particulate matter through the atmosphere, reaching Antarctica at similar concentrations (Dickhut et al., 2012). Results from Krasnobaev et al. (2020), and other studies (Goutte et al., 2013) indicate that PBDE-209 may be released in the Antarctic marine system by atmospheric deposition originated from LRAT, independently of local sources as suggested by Hale et al. (2018). Therefore, our work adds further evidence to the LRAT as source of this PBDE congener in Antarctic ecosystems.

No significant interspecies differences were found in total PCDD/F concentrations in penguin eggs (Table 1). Three PCDD congeners (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD) were not detected in any sample (detailed in Supplementary Information, SI, Tables S7, S8 and S11). Congeners 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD and 1,2,3,7,8,9-HxCDF were detected in less than 30 % of cases in both species. In chinstrap penguin eggs, the most abundant PCDD/Fs were 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF and OCDF, reaching average contributions of 20 %, 17 % and 13 %, respectively (Fig. 4). In the case of gentoo penguin eggs, 2,3,4,7,8-PeCDF (22 %), 1,2,3,4,7,8-HxCDF (13 %) and OCDF (12 %) accounted for the greatest contributions. Low concentrations of these compounds reflect the poor contribution of PCDD/Fs to POPs exposure in Antarctica, also consistent with the fact that they are unintentional POPs (UNEP, 2001). Congener profiles in the eggs of both penguin species were found to be dominated by low-chlorinated PCDF congeners such as 2,3,7,8-TCDF (4 Cl), 2,3,4,7,8-PeCDF (5 Cl), and 1,2,3,4,7,8-HxCDF (6 Cl). These profiles agree with those found in eggs of other penguin species (Kumar et al., 2002; Mwangi et al., 2016) in which, as in our case, the results suggest LRAT as the main source of these POPs. Similarly, higher concentrations of PCDFs compared to PCDDs are consistent with previous studies in polar species, such as Adelie penguins (Kumar et al., 2002). Regardless of these general patterns in the profiles, main interspecies differences found here are related to the markedly great contribution of 2,3,7,8-TCDF found in chinstrap penguin eggs, five times greater than that found in gentoo eggs, which to our knowledge has not been previously described in this or other penguin species. Therefore, this unexpected result could be related to local conditions that affect the studied colonies. For instance, the constant volcanic activity in Deception island where chinstrap penguins were sampled could represent a source of PCDD/Fs that influence the profiles found in these eggs (Takizawa et al., 1994; Feshin et al., 2006; Poberezhnaya, 2012; Szumińska et al., 2018).

Although interspecific differences in total POP concentrations were not significant, the concentrations of some POP families showed significant differences between both species with higher values in chinstrap than in gentoo eggs that could be related to factors influencing bioaccumulation of the studied POPs. Trophic ecology (e.g., diet, trophic position, foraging areas), migration, and species-specific accumulation and excretion processes (Borgå et al., 2004; Schiavone et al., 2009) may explain differences in POP concentrations found here among penguin

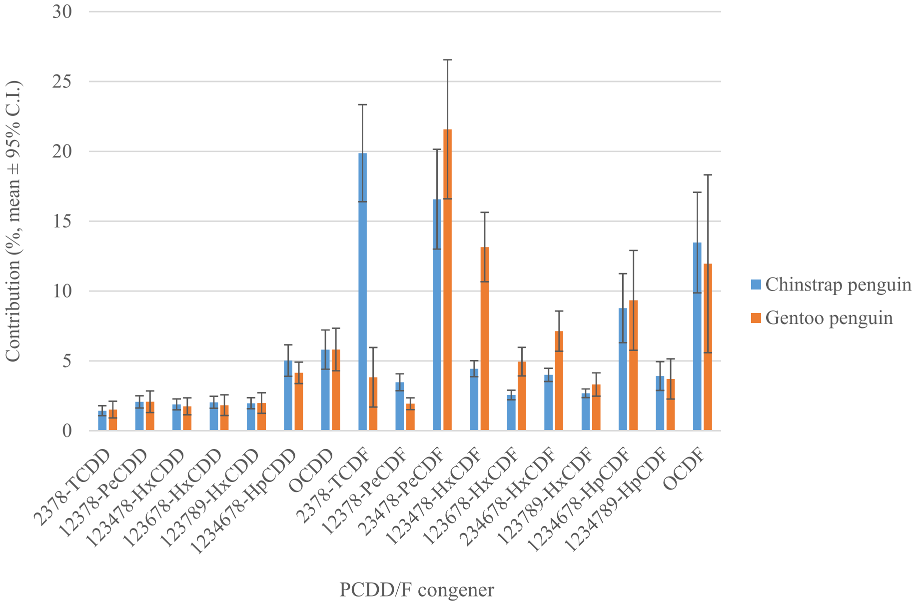

**Fig. 4.** Mean contribution of each congener to the total PCDD/Fs content in chinstrap and gentoo penguin eggs. Error bars represent 95 % confidence interval.

eggs. Diet and therefore trophic level, as well as the state of feeding areas, have been described as the main factors that explain POP levels in seabirds (Borgå et al., 2004; Roscales et al. 2016b, 2019). Thus, the small interspecific variations found in this study in POP concentrations could be linked to differences in the species' trophic ecology. There are great differences in the literature about diet composition in chinstrap and gentoo penguins (Ratcliffe and Trathan, 2012; Herman et al., 2017). This may be due to the trophic plasticity of these species, as Antarctica is characterized as a region where extreme climatic conditions impose a strong variability in food availability (Trivelpiece et al., 2011; Polito et al., 2011; Negrete et al., 2017). Prior studies on POPs and stable isotopes in these species suggested differences in the feeding and foraging habits for chinstrap and gentoo penguins that agree with the interspecific trends in POPs found here (Mello et al., 2016). Specifically, this study suggests a slightly higher trophic position of chinstrap penguin, as well as some degree of spatial segregation in the foraging areas. Although most studies performed in our study area point out that this species mainly forages on krill showing a lower trophic position than gentoo penguin (Colominas-Ciuró et al., 2021; Masello et al., 2021), such studies were conducted during chick rearing which could show differences with respect to the period of egg formation. In addition, studies based on stable isotopes have related the differences in the feeding areas of penguins with higher levels of POPs in chinstrap penguin (Mello et al., 2016). Previous studies in our study area have shown that both species show clear differences in the foraging niche that could also explain some of the differences found in POP levels. More specifically, gentoo penguins usually dive deeper into the benthic layer to capture their prey, while chinstrap penguins use the pelagic area of the water column, thus avoiding interspecific competition for common prey (Colominas-Ciuró et al., 2021; Masello et al., 2021). Moreover, gentoo penguins tend to feed near the coast during the day, while chinstrap penguins usually forage further from the coast, in the open sea, both during the day and night (Miller et al., 2010). Finally, both species also show differences in habitat use after the breeding season (Ratcliffe and Trathan, 2012) that could contribute to explain the differences, with the chinstrap penguin performing longer and northward displacements along the Southern Ocean during the non-breeding period and the gentoo remaining close to the place of the breeding colonies (Hinke et al., 2015).

This study highlights the current presence of POPs in Antarctic species, although, compared with other studies, our results suggest lower concentrations than those described in eggs of chinstrap and gentoo penguins from the South Shetland Islands in previous years. Although PCB production decreased or ceased after the 1970s, their presence in penguin eggs continued being detected during the 2000s. Cipro et al. (2010) analyzed PCBs in 26 chinstrap penguin eggs and 9 gentoo penguin eggs during the breeding periods 2004–2005 and 2005–2006. Later, Mello et al. (2016) analyzed PCBs and PBDEs in 20 chinstrap penguin eggs and 16 gentoo penguin eggs collected in the austral summers of 2010–2011 and 2011–2012. In all of them, the levels of PCBs and PBDEs were approximately one or two orders of magnitude greater than those found in this study. These trends are consistent with those found by other authors (Ellis et al., 2018), and possibly reflect the importance and effectiveness of implementing long-term control and regulation measures for POPs in the environment. An alternative explanation is based on differences of human activities between both study areas considering that previous studies were carried out in King George Island where there is a high concentration of research stations and an airport carrying more human impact than in our study areas.

### 3.2. *Toxicity assessment*

Calculated Toxic Equivalent Quantity (TEQ) ranged from 1.38 to 7.33 pg/g l.w. (Table 2), being its average concentration higher in the case of the chinstrap penguin eggs than in the case of the gentoo penguin ones, although the difference was not significant. Both penguin species presented the same TEQ profiles, with non-*ortho* dl-PCBs and PCDFs being the compounds with the highest mean TEQ value, followed by PCDDs and mono-*ortho* dl-PCBs. Accordingly, the compounds with the greatest contribution to total toxic potential were non-*ortho* dl-PCBs and PCDFs, followed by PCDDs and mono-*ortho* dl-PCBs. Similar TEQ values were calculated for chinstrap and gentoo penguin eggs in previous studies (Corsolini et al., 2007). TEQ values in penguin eggs found here were lower than 210 pg TEQ/g l.w., the generic limit above which harmful effects have been reported in birds (Hart et al., 1996). The fact that the non-*ortho* dl-PCBs were the compounds with the highest average TEQ value is due to the fact that these compounds present a higher toxicity than mono-*ortho* PCBs (Marzocchi et al., 2011). In this line, Mwangi et al. (2016) described TEQ values for PCBs 2 to 14 times higher than those of PCDD/Fs in the case of other penguin species, such as the emperor and the Adelie penguins.

**Table 2**

Mean, median and range of total TEQ for each family of analyzed compounds in eggs of chinstrap and gentoo penguins (concentrations are expressed in pg/g l.w.).

| | Chinstrap penguin | | | Gentoo penguin | | | Interspecific Student t-test |
|---|---|---|---|---|---|---|---|
| | Mean | Median | Range | Mean | Median | Range | |
| $\sum$TEQ [a] | 4.15 | 4.24 | 1.37–7.33 | 3.49 | 3.32 | 2.06–5.46 | $t_{28} = 1.2$, $p = 0.24$ |
| $\sum$TEQ mono-*ortho* PCBs [b] | 0.03 | 0.03 | 0.002–0.06 | 0.03 | 0.03 | 0.01–0.09 | $t_{28} = -0.21$, $p = 0.83$ |
| $\sum$TEQ non-*ortho* PCBs [c] | 2.74 | 2.65 | 0.15–5.08 | 2.42 | 2.24 | 1.74–3.91 | $t_{28} = 0.61$, $p = 0.55$ |
| $\sum$TEQ PCDDs [d] | 0.12 | 0.12 | 0.07–0.17 | 0.11 | 0.11 | 0.09–0.13 | $t_{28} = 0.98$, $p = 0.34$ |
| $\sum$TEQ PCDFs [e] | 1.26 | 1.26 | 0.64–2.29 | 0.93 | 0.92 | 0.48–1.38 | $t_{28} = 1.98$, $p = 0.057$ |

[a] Sum of $\sum$TEQ for dl-PCBs and $\sum$TEQ for PCDD/Fs.

[b] Sum of TEQs for PCBs # 105, 114, 118, 123, 156, 157, 167, 189.

[c] Sum of TEQs for PCBs # 77, 81, 126, 169.

[d] Sum of TEQ for PCDDs 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD.

[e] Sum of TEQ for PCDFs 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF.

## 4. Conclusions

This study shows PCBs, compared to other POPs studied, as the chemical class with the greatest concentrations in gentoo and chinstrap penguin eggs. Although no significant differences were found in the total levels of POPs between the penguin eggs, the levels were generally higher in chinstrap eggs, which is compatible with differences in the diet composition, trophic position and feeding areas of both penguin species.

The results obtained suggest long-range transport as the main source of the analyzed POPs in both penguin species. Due to their greater capacity for transport through the atmosphere, PCBs with a lower degree of halogenation are the compounds with the greatest presence in the Antarctic penguin eggs and are the most likely to accumulate in these trophic networks. On the other hand, the particular abundance of PBDE-209 found in the present work, adds further evidence to the LRAT as source of this PBDE congener in Antarctic ecosystems.

Calculated Toxic Equivalents for PCBs and PCDD/Fs in penguin eggs were below threshold levels of toxicity and lower than those reported previously in both species. Despite their prohibition and regulation on a global scale, chemical contamination by POPs persists and continues to reach remote regions such as Antarctica. Therefore, further studies to ensure clear temporal tendencies of legacy and emerging POPs in such a remote and valuable region, as well as to better understand and identify the factors driving accumulation patterns among the species that compose Antarctic ecosystems are encouraged. On the other hand, studies on the metabolism and accumulation capacity of chemical pollutants in penguins and in the species that make up their Antarctic trophic networks would be useful to determine physiological characteristics that influence the specific-dependent processes of bioaccumulation and biomagnification of POPs and their significance within Antarctic ecosystems.

## Credit author statement

Patricia Morales: Methodology, Formal Analysis, Investigation, Data Curation, Writing-Original draft preparation, Writing - Review & Editing, Jose Luis Roscales: Conceptualization, Formal analysis, Methodology, Investigation, Data Curation, Visualization, Writing-Original draft preparation, Writing - Review & Editing, Juan Muñoz-Arnanz: Methodology, Data Curation, Writing - Review & Editing, Andrés Barbosa: Conceptualization, Resources, Writing - Review & Editing, Funding acquisition, Begoña Jiménez: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

## Declaration of competing interest

The authors have no conflicts of interest to disclose.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131871.

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