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Persistent organic pollutants and mercury in a colony of Antarctic seabirds: Higher concentrations in 1998, 2001, and 2003 compared to 2014 to 2016

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Abstract

Over decades, persistent organic pollutants (POPs) and trace metals like mercury (Hg) have reached the remotest areas of the world such as Antarctica by atmospheric transport. Once deposited in polar areas, low temperatures and limited solar radiation lead to long environmental residence times, allowing the toxic substances to accumulate in biota. We investigated the load of polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDTs) and metabolites (DDEs, DDDs) in embryos from failed eggs of the smallest seabird breeding in Antarctica, the Wilson's storm-petrel (*Oceanites oceanicus*) at King George Island (Isla 25 de Mayo). We compared samples of different developmental stages collected in 2001, 2003, and 2014 to 2016 to investigate changes in pollutant concentrations over time. We detected eight PCBs including the dioxin-like (dl) congeners PCB 105 and 118 (Σ PCBs: 59-3403 ng g⁻¹ ww) as well as 4,4'-DDE, and 4,4'-DDD (Σ DDX: 19-1035 ng g⁻¹ ww) in the embryos. Samples from the years 2001 and 2003 showed higher concentrations of PCBs than those from 2014 to 2016. Concentrations of DDX was similar in both time intervals. Furthermore, we determined Hg concentrations in egg membranes from 1998, 2003, and 2014 to 2016. Similar to PCBs, Hg in egg membranes were higher in 1998 than in 2003, and higher in 2003 than in the years 2014 to 2016, suggesting a slow recovery of the pelagic Antarctic environment from the detected legacy pollutants. Embryos showed an increase in pollutant concentrations within the last third of their development. This finding indicates that contaminant concentrations may differ among developmental stages, and it should be taken into account in analyses on toxic impact during embryogenesis.

Keywords:

Wilson's storm-petrel, polychlorinated biphenyls (PCBs), DDX, Hg, ontogeny

Statements and Declarations:

The authors have no competing interests to declare that are relevant to the content of this article.

Data availability statement:

We declare that data archiving is not mandated but data will be made available upon reasonable request.

Author contribution:

NK, PQ, LB, and RD conceived and designed the research. NK, LB, and PB conducted or were involved in pollutant analyses. ML facilitated permits and access to the field station in the framework of our collaboration between Argentina and Germany. CB, ML, NK, and PQ collected samples. NK and LB analyzed data. NK wrote the manuscript. All authors reviewed and approved the manuscript.

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Introduction

Persistent organic pollutants (POPs) and trace metals like mercury (Hg) are known to affect the environment and living organisms for a long time (Eagles-Smith et al. 2018; Jacob 2013). This is especially relevant for legacy organochlorine compounds, which are still abundant in many places as a consequence of their low degradation rates, even though they have been banned in most countries for decades (UNEP 2018). Both, POPs and Hg, can travel far distances through global distillation (Choi et al. 2008; Kang et al. 2012; Wania and Mackay, 1996), hydrospheric transport (Fuoco et al. 2009; Wania and Mackay, 1993), and migrating animals (Braune et al. 2005; Fort et al. 2014). Thus, they can reach pristine polar environments such as Antarctica, where cold temperatures, circumpolar currents, snow, and ice capture them (Wania and Mackay 1996). Additionally, passive air sampling suggests that Arctic and Antarctic stations also emit pollutants to the environment (Choi et al. 2008).

Through food intake and bioconcentration, POPs and Hg accumulate in biota and biomagnify through the food webs (Fisk and Hobson 2001; Langis et al. 1999; Morel et al. 1998). Top predators are especially prone to concentrate high contaminant loads (Haraguchi et al. 2009; Krahn et al. 2009), and both mammals and birds are at risk of transferring part of their own load to the next generation (van de Merwe et al. 2011; Verboven et al. 2009). One non-invasive method of monitoring POPs in birds is to collect abandoned eggs. Within the egg, the yolk contains the highest amount of the highly lipophilic polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDTs) and the metabolites dichlordiphenyldichlorethen (DDEs) and dichlordiphenyldichlorethan (DDD; hereafter DDX is used to represent DDTs, DDEs and DDDs together) in an egg is found in the yolk. Only negligible amounts are found in the albumen that contains < 1% of the egg lipids (Drouillard and Norstrom 2001; Russel et al. 1999). The egg yolk, the main nutrient carrier for an embryo, is eventually consumed entirely by the embryo (Noble and Cocchi 1990), and hence, the full load of the yolk's POPs will be transferred from the egg to the hatchling. On the other hand, Hg accumulates majorly in the albumen proteins of an egg (Wolfe et al. 1998; Grajewska et al. 2015). Still, Hg concentrations of yolk and egg membrane closely correlate with Hg concentrations in albumen, which makes all tissues suitable to monitor Hg concentration in eggs (Brasso et al. 2012; Peterson et al. 2017).

Pollutants like PCBs, DDX, and Hg affect bird fitness and survival. DDX became infamous more than 50 years ago when it was linked to eggshell thinning (e.g. Tucker and Haegele 1970). Resulting eggshell breakage caused severe declines of whole bird populations (Ankley et al. 2002; Elliott et al. 1988; Johnstone et al. 1996; Vasseur and Cossu-Leguille 2006). Within the group of PCBs, dioxin-like PCBs (dl-PCBs) have properties similar to dioxins, and can cause endocrine disruptions in animals (Tanabe 2002). They seem to cause mal-development of the lymphatic system and embryo deformation in some bird species (Bosveld and van den Berg 1994). In female little auks (*Alle alle*), high Hg concentrations caused smaller eggs the following breeding season (Fort et al. 2014), but in mallards also caused deformation of embryos, early mortality, and brain lesions (Wolfe et al. 1998).

All these pollutants place a significant threat to wildlife (Goutte et al. 2014). They threaten the stability of bird populations due to their impact on reproductive success, especially of those at the top of the food chain (Fisk and Hobson 2001; Langis et al. 1999).

The Wilson's storm-petrel (*Oceanites oceanicus*) is a common predator breeding in subantarctic and Antarctic regions. Here, we investigated whether POP and Hg contamination for this species changed within the last decades around the Antarctic Peninsula. We collected eggs that were abandoned, e.g. due to prolonged adverse conditions such as snowstorms from the same colony in 2001, 2003, and from 2014 to 2016 (Quillfeldt 2001; Büber et al. 2004), as well as membranes of hatched eggs in 1998, 2003, and 2014 to 2016. As Wilson's storm-petrels collect all nutrients needed to form the egg in one location during the pre-laying exodus (Beck et al. 1972), an egg will be influenced by the pollutant concentration of this area. To evaluate differences of pollutant levels among years, it is important to be aware of potentially different nutrient origins. Both, the foraging area and the trophic position of prey species could influence pollutant concentrations in seabird eggs (Corsolini and Sará 2017; Braune et al. 2005; Carravieri et al. 2014, 2016; Cherel et al. 2018; Mills et al. 2020). To evaluate foraging habits and areas among years, we analyzed stable isotope values for carbon and nitrogen. In the Southern Ocean, $\delta^{13}\text{C}$ values are linked to the latitudes of foraging areas (Cherel and Hobson 2007; Quillfeldt et al. 2005, 2010). Hence, we investigated whether pre-exodus areas of Wilson's storm-petrels were similar among the studied time periods, or whether a transition to more northern or more southern feeding grounds took place. Through enrichment of ^{15}N relative to ^{14}N from prey to predator, $\delta^{15}\text{N}$ indicates the trophic position of an animal (Post 2002; Weiss et al. 2009). We used this to test whether prey of Wilson's storm-petrels ranged within similar trophic positions or whether trophic positions changed among the years. Additionally to temporal differences of pollutant exposure, we investigated whether embryos incorporate pollutants at a constant rate, as timing of toxic effects may be crucial for embryonic development, and analyzed different age groups of embryos. Explicitly, we addressed the following questions:

1. What are POP concentrations in embryos, and Hg concentrations in egg membranes of Wilson's storm-petrels?
2. Do POP and Hg concentrations in embryos and egg membranes, respectively, differ depending on embryo age? And can we, hence, learn when POPs are transferred from the egg to the embryo?
3. Do POP and Hg concentrations change over the years? In addition, do stable isotope analyses indicate differences in pre-laying exodus area and trophic position that may explain differences in pollutants?

We expected to find POP concentrations in the same range as eggs of seabirds with similar foraging preferences from the same area, like Adélie penguins (*Pygoscelis adeliae*; Cipro et al. 2010, Corsolini et al. 2011). Furthermore, we expected POP transfer to follow lipid transfer from yolk to embryo, but no variation of Hg concentrations in egg membranes through the development. If no change of pre-laying exodus area or trophic feeding level could be detected (Noble and Cocchi, 1990), we expected lower POP concentration in samples from more recent years due to the

extensive ban of those substances (UNEP, 2018), and no change in Hg concentrations among years, due to continuing input into the environment and transport to polar areas (Streets et al. 2017, Soerensen et al. 2012).

Material / Methods

Species and study site

The study took place at the “Tres Hermanos” hill about 1.5 km from Carlini Research Base (Fig. 1) on King George Island (Isla 25 de Mayo), South Shetland Islands (62° 14' S, 58° 40'W), where a research project on Antarctic storm-petrel species was set up in 1995. Breeding success and number of established nests were observed for more than 20 years at a colony of Wilson’s storm-petrels. Here, breeding takes place in the scree slopes underneath big rocks, where the depth of accessible nests varies from 20 to 60 cm. Wilson’s storm-petrels are small marine birds weighing on average 38 g (Fig. 1; Beck et al. 1972; Quillfeldt 2006). This common predator feeds mainly on Antarctic krill (*Euphausia superba*), squid, small fish, and amphipods (Quillfeldt 2002). Wilson’s storm-petrels spend their life at sea when they are not breeding, and can be found in all oceans except for Arctic waters (Quillfeldt 2006). Their breeding sites are in the Antarctic and on subantarctic islands. Breeding pairs establish their nesting burrow in cavities below rocks (Quillfeldt 2006; Roberts, 1941), before the females leave again prior to egg-laying on a pre-laying exodus. This foraging trip is used to accumulate nutrients to produce a single egg that contains the recently consumed pollutants, and hence, establishes the burden of pollutants for every surviving hatchling (Beck et al. 1972; Hobson et al. 1997, 2000).

Egg and egg membrane collection

In all years, active nests (incubating adult or egg) were identified during the incubation period from mid-December to the end of January; all accessible eggs were measured once in the absence of adult birds (length, width, weight) using calipers and a digital balance. With these measurements, we estimated the chicks’ hatching dates by density loss over time according to Quillfeldt (2001). We looked for hatched chicks five days after this estimated date and monitored nestlings regularly afterwards until they fledged, or the end of the season. Eggs that did not hatch until the estimated date were checked at most four more times, approximately every five days. Whenever possible nest checks were done at sight to reduce possible disturbance of incubating adults. After a chick hatched, its nest was searched for the eggshell to collect the egg membrane. Membranes were freed from shell parts and dirt by rinsing them with tap water, air dried at the field station, and stored at room temperature in 2003, and from 2014 to 2016. In 1998, eggshells were collected, transported and stored frozen (-20° C) until needed. Membranes were then separated from the shell, rinsed under tap water, air dried, and stored at room temperature until further analyses took place.

Snowstorms and the resulting blocking of nest entrances regularly cause failure of hatching of chicks (e.g. Büßer et al. 2004). These eggs and all other abandoned and accessible eggs were collected at the end of the season (i.e., end of March) when no further hatching could be expected. As the

inaccessibility of the nests for parents and, hence, hypothermia was the main reason for embryos to die before hatching, we expect pollutant concentrations found in this study to be representative for eggs that hatched. In 2001, embryos were dissected at the research station. In 2003 and 2014 to 2016, collected eggs were preserved whole, and egg membrane and embryo samples were prepared during egg dissection after leaving the field station. All samples were stored at -20°C until preparation of samples.

Selection and preparation of samples

We used embryos to analyze POPs, and conducted stable isotope and Hg analyses on egg membranes. To compare pollutant loads from 2014 to 2016 to earlier years, we used available, stored samples from the same colony from 1998 (only egg membranes), 2001 (only embryos), and 2003 (egg membranes and embryos) (Table 1).

Eggs from 2003 and 2014 to 2016 were thawed and opened to extract the embryos. The embryos were weighed, frozen again, and then freeze-dried to mass consistency. Storage time of frozen embryos varied by up to 15 years. Resulting wet weight (ww) was not equally reliable for all samples due to water sublimation. To correct this, ww was calculated backwards from dry weight (dw) using the average percentage of mass loss during drying from the newest samples from 2016 (81.8%, n = 6; compare Leat et al. 2011).

Preliminary trials on other bird material with the below described method, and literature research (compare Online Resource 8) led us to the expectation that POP concentrations in individually analyzed embryos would be below the limit of detection (LOD) or limit of quantification (LOQ) for all but two samples from 2016. All embryos but those two were therefore pooled into eight groups, clustered into two time periods of sampling (2001 and 2003, and 2014 to 2016) and for each time period into four age groups, to learn more about the temporal transfer of organic pollutants to the embryo. We estimated embryo age from ww following the equation for embryonic growth of birds described by Ricklefs (2010). Detailed calculations can be found in Online Resources 1–3. We divided the available embryos as equally as possible into four similar age groups for both time intervals, with the aim of covering a wide range of developmental steps. It is biologically relevant to be able to differentiate between the first two third of development (0–33 days) and the last third of development (34–50 days), as the major amount of lipids and, hence, lipid soluble pollutants are expected to be taken up by the embryo in the last third of development (Noble and Cocchi 1990). Age group one includes embryos with an approximate age up to 25 days, age group two includes embryos aged 26 to 30 days, age group three includes embryos of the ages 31 to 33 days, and age group four includes embryos of the ages 34 to 40 days (Online Resource 3). Group 5 contained only two embryos approximately 1–2 days before hatching from 2016 with an embryonic age of approximately 48 days (Online Resources 3 and 2). No comparable embryos for group 5 were available from 2001 or 2003. Dried embryos were ground as fine as possible first using a stainless steel blade grinder (Severin, 140 W) for approximately 2 min and then using an agate mortar and pestle.

POP extraction and analysis

Chemicals

All analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The indicator congeners PCB 28, 52, 101, 138, 153, and 180 were purchased as standard mix together with PCB 118 in methanol solution ("PCB Mix 3", 10 µg mL⁻¹). The PCB congeners 49, 77, 99, 105, 110, 156, 170, 183, and 187 as well as the six DDX dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD), and dichlorodiphenyldichloroethylene (DDE), each as 2,4'- and 4,4'-chlorinated isomers, as well as 1,2,3,4-tetrachloronaphthalene for use as internal standard, were purchased as pure substances in powder form. The PCB 132 was purchased dissolved in iso-octane. The PCB set contains four dl-PCBs, i.e. PCBs 77, 105, 118, and 156. All substances were prepared and used dissolved in methanol.

Extraction procedure

POP extraction from dried, pulverized, and pooled embryos was performed by microwave assisted extraction (MAE) adapted from Düring and Gäth (2000), followed by sulfuric acid purification adapted from Murphy (1972). Extraction was followed by concentration of extracts by rotary evaporator followed by N₂ flow, and then transfer to an aqueous solution for measurement by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography-mass spectrometry (GC-MS). For extraction, 400 ± 1 mg of dried and pulverized embryos were weighed to polyfluoralkoxy (PFA) MAE vessels. Then, heat transformer disks (Weflon® disks, MLS Corp., Leutkirch, Germany) and 15 mL *n*-hexane (≥99 %, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) were added before closing the vessels. Two types of control vessels were prepared, either with 15 mL *n*-hexane or with 15 mL *n*-hexane and 2.5 µL of a 10 ng µL⁻¹ PCB standard solution (PCB Mix 3, Dr. Ehrenstorfer GmbH, Augsburg, Germany). 1,2,3,4-tetrachloronaphthalene was added to all samples as an internal standard (4 µL of a 5 ng µL⁻¹ solution). The MAE was performed at 120 °C with 250 W for 1 min followed by 1000 W for 15 min. After passive cooling and opening of the vessels, aliquots of 12 mL were removed from the supernatant and transferred to 20-mL glass vials. For purification from greasy components, aliquots were treated with 2 mL concentrated sulfuric acid (95.0-98.0 %, Sigma-Aldrich, ACS reagent), and shaken by hand for 1 min. After centrifugation (20 min at 210 RCF, Hettich Rotanta 460 R), the acidic solution was carefully removed by glass Pasteur pipettes. This procedure was repeated once with 1 mL of sulfuric acid. Afterwards, 10-mL aliquots of the acid treated *n*-hexane extracts were transferred to rotary evaporator flasks followed by their careful reduction to volumes of 200 µL. Solvent reduction was accelerated by using a water bath (40 °C), rotating the flask (150 rpm), and by applying negative pressure with a vacuum pump (350–400 mbar). Remaining extracts were transferred to fresh 20-mL headspace vials. The flasks were flushed twice with 150 µL *n*-hexane each that was also transferred to the 20-mL headspace vials afterwards. The resulting *n*-hexane volume (~500 µL) was largely reduced by a gentle N₂ stream. Once only a few drops remained, the vials were passively air dried. The target substances were redissolved with 100 µL of solubilizing

methanol (p.a. quality, Carl Roth GmbH, Karlsruhe, Germany), followed by the addition of 10 mL NaCl solution (1g 10 mL⁻¹) for salting out of POPs to the headspace.

Instrumental and data analysis:

Measurement of POPs was performed by HS-SPME coupled to GC-MS. Basics of the performed process are given in Böhm et al. (2017) and Wiltshcka et al. (2020). In the present study, the following parameters were used for automated SPME: fiber with 100 µm PDMS coating (Sigma-Aldrich), heating of the fiber prior to extraction to eliminate cross contamination: 10 min, pre-equilibration before extraction: 10 min, extraction: 60 min at 90 °C while shaking the sample vial at 250 rpm. Samples were processed by a CombiPAL autosampler (CTC-Analytcs, Zwingen, Switzerland) with thermodesorption of the fiber in the injector of the GC-MS for 3 min at 270 °C. Chromatographic separation and mass detection were performed with a GC-ion trap MS (Trace GC Ultra/ITQ 900, Thermo Fisher Scientific) equipped with a XLB-type capillary column (Thermo TG-XLBMS, 60 m, 0.25 mm, 0.25 µm). Semi-quantitative screening of a sample aliquot in full-scan mode of the MS (m/z 50–500) was used to identify concentration ranges of target PCB congeners as well as to identify further PCB congeners by chlorine pattern. For quantification, the MS was used in selected ion storage (SIS) mode (designated as “selected ion monitoring”, SIM, in Thermo Xcalibur software) with respective segments for the analytes. Quantification was performed based on six-point calibrations for PCBs in the range of 0.01 to 0.75 µg L⁻¹ and for DDX in the range of 0.01 to 2 µg L⁻¹. For samples that exceeded this range, an extended 12-point calibration from 0.01 to 3.25 µg L⁻¹ was used. For all analytes LODs and LOQs were determined analog to IUPAC (1997), using the numerical factor $k = 3$ or $k = 10$, respectively (Online Resource 6). Processing of GC-MS data was performed with the software ‘Xcalibur’ (Thermo Fisher Scientific) combined with a manual verification of peak integration. Data for all analytes were corrected based on TCN as internal standard. Concentrations from SPME-GC-MS measurements were recalculated considering aliquoting and initial sample weight of embryos. Final POP concentrations in embryos are given in ng g⁻¹ dw. Detailed parameters on GC-MS conditions (i.e. oven program and parameters for MS detection) are given in the Online Resources 4 and 5.

Analysis of mercury

We determined total Hg (the sum of inorganic and organic Hg, thereafter called Hg) concentrations in egg membranes from 1998, 2003, and 2014 to 2016 (Table 1). Whenever possible, analysis was conducted with membranes from the same eggs of which embryos were used for POP analysis. Additional samples were used from hatched chicks for all years. Surface contaminants were removed from egg membranes in ultrasonic baths. Each sample was individually sonicated for 3 min in a bath filled with a 2:1 volume ratio of chloroform and methanol. Subsequently, they were rinsed twice in consecutive methanol baths and dried for 48 hours at 45 °C. Clean egg membranes were cut with stainless steel scissors into tiny fragments to produce a homogeneous powder. Aliquots of 2–11 mg powdered egg membrane were used to determine Hg concentrations with an Advanced Mercury Analyzer spectrophotometer Altec AMA-254. To evaporate Hg, aliquots were heated

progressively until 800 °C under an oxygen atmosphere and Hg was amalgamated on a gold-net during 3 min (Bustamante et al. 2006). Then, the net was heated to liberate the collected Hg, which was finally measured by atomic absorption spectrophotometry (Bustamante et al. 2006). Measurements were repeated two or three times for each sample until having a relative standard deviation (SD) <10%. Accuracy and reproducibility for each set of samples were tested by analytical blanks and replicate measurements of certified reference material (DOLT-5, dogfish liver, National Research Council of Canada; certified concentration: $0.44 \pm 0.18 \mu\text{g g}^{-1} \text{ dw}$). Measured Hg concentrations for the certified reference material were: $0.33 \pm 0.00 \mu\text{g g}^{-1} \text{ dw}$ ($n = 7$). The detection limit of the AMA was 0.05 ng. Hg concentrations were expressed in $\mu\text{g g}^{-1}$ dry weight (dw).

Bulk stable isotope analysis

Stable isotope analysis (SIA) was conducted using subsamples of egg membranes from the same eggs that were used for Hg analysis. An amount of 0.32 to 0.50 mg (mean \pm sd: $0.40 \text{ mg} \pm 0.04 \text{ mg}$) of egg membrane was weighed in tin cups. Carbon and nitrogen ratios were determined with a continuous-flow mass spectrometer (Delta V Plus, Thermo Scientific, Bremen, Germany) coupled to an elemental analyzer (Flash EA 1112 [37 samples] or Flash 2000 [16 samples], both Thermo Scientific, Milan, Italy). Results are expressed in the δ notation as parts per thousand (‰) deviation from the international standards Vienna Pee Dee Belemnite ($\delta^{13}\text{C}$) and atmospheric N_2 ($\delta^{15}\text{N}$). The used formula is $\delta^{13}\text{C}$ or $\delta^{15}\text{N} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3$, where R is $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$, respectively. To assess the quality of the analytical procedures, measurements of internal laboratory standards were conducted using acetanilide (Thermo Scientific) and peptone (Sigma- Aldrich) or two types of caffeine (USGS-61 and USGS-62; Reston stable isotope laboratory, United States Geological Survey) and indicated a standard deviation for analyzed samples of $< \pm 0.06 \text{ ‰}$ for $\delta^{13}\text{C}$ and $< \pm 0.09 \text{ ‰}$ for $\delta^{15}\text{N}$.

Statistical analyses

Only POPs with concentrations above LOQ (Online Resource 6) were included in the following analyses. Pollutants above LOD but below LOQ were presented in this paper, but were not included in any statistical analyses. Pollutants below LOD are given in the Online Resource 6, but were not considered beyond this. As the small sample size did not meet necessary requirements for non-parametric testing, we used parametric tests for statistical analyses on POPs.

Concentration differences among PCB congeners were tested with a Kruskal-Wallis rank sum test followed by Dunn's test for post hoc pairwise comparisons with Bonferroni correction (Haynes 2013), concentration differences between DDT metabolites were tested using Wilcoxon rank sum test.

To test concentration differences of PCBs and DDX among age groups in embryos, the parametric Friedman rank sum test was used with data paired for individual pollutants. For post hoc analyses between single age groups, Wilcoxon signed rank exact tests with paired samples and p -values corrected according to Bonferroni were used. If ties occurred Wilcoxon signed rank tests with continuity correction were used. To test if there was a correlation between Hg concentration of egg

membranes and age of the embryo, we used a Spearman's rank correlation with the embryo's dw as a proxy for embryo age. To compare Hg concentrations from samples of hatched vs. unhatched eggs, we used a Wilcoxon signed rank sum test with continuity correction.

We analyzed differences of pollutant concentrations for POPs between the available years 2001 and 2003, and 2014 to 2016 using a Wilcoxon signed rank exact test. Samples were paired for pollutants, and differences between early and recent years were tested over all samples, as well as for embryos younger than 34 d or older than 33 d separately. The p -values for these post-hoc tests were adjusted using Bonferroni corrections. In analyses using individual age groups, pollutant concentrations in the years 2014 to 2016 were averaged for age group 4 (31–33 d) and 5 (> 33 d) to allow comparisons with years 2001 and 2003 where only 4 age groups could be analyzed. Further, PCB 170 was excluded from age comparisons, as only one sample showed concentrations > LOD for this substance. To test differences of Hg concentrations among the available years 2001, 2003, and 2014 to 2016 we used a Kruskal-Wallis rank sum test followed by pairwise Wilcoxon tests for post hoc pairwise comparisons with Bonferroni correction (Haynes 2013).

The ratio of 4,4'-DDE to the total sum of DDX was calculated as an indicator for differentiating between recent or ancient input (Borrell and Aguilar 1987; Fries et al. 1969; Yogui et al. 2003). Values above 0.7 are considered to show an origin from ancient sources, while values below 0.7 show a more recent input of commercial DDX into the environment.

Stable isotope patterns were analyzed for inter-annual differences (for post-hoc analysis with Bonferroni correction) for the years 1998, 2003 and 2014 to 2016 using the Wilks' Lambda test and a One-way MANOVA (Bartlett Chi²). Trophic positions (TP) for Wilson's storm-petrels (TP_{ocea}) were calculated according to Weiss et al. (2009), using the formula

$$TP_{ocea} = TP_{prey} + (\delta^{15}N_{ocea} - \delta^{15}N_{prey}) \times 3.4 \text{ ‰}^{-1}$$

where TP_{prey} is 2.3, the estimated TP of the main prey, Antarctic krill (Hodum and Hobson 2000), $\delta^{15}N_{prey}$ is 5.3 ‰, the average $\delta^{15}N$ of krill in the northern Antarctic Peninsula (Seyboth et al. 2018), and 3.4 ‰ is the assumed enrichment factor as estimated by Post (2002). Samples that clearly originated from non-Antarctic waters ($\delta^{13}C > -21 \text{ ‰}$; 1998: $n = 1$; 2015: $n = 3$) were excluded for the calculation of trophic positions. We tested if Hg concentrations were linked to $\delta^{13}C$ or $\delta^{15}N$ values using Pearson's product-moment correlations.

All statistical analyses and figures were conducted in R 4.0.5 (R Core Team 2021). Map of study site was composed using QGIS 3.24 (QGIS Development Team, 2022) and the Quantarctica data set (Matsuoka et al. 2018).

Results

Pollutant concentrations

In Wilson's storm-petrel embryos, eight PCBs and two DDT metabolites could be quantified (Table 2, Fig. 2). Concentrations of PCBs differed significantly among congeners (Kruskal-Wallis rank sum

test, $\chi^2 = 27.28$, $p < 0.001$). The highest values among the PCBs were reached for PCB 153 with more than 1400 ng g⁻¹ ww. Compared to PCBs 99 and 183, concentrations of PCB 153 were significantly higher (Dunn's Post-hoc test with Bonferroni correction, PCB 99 vs. PCB 153; $Z = -3.44$, $p = 0.016$; PCB 153 vs. PCB 183: $Z = 4.57$, $p < 0.001$; results of all pairwise comparisons are presented in Online Resource 7). The sum of all detected PCBs ranged from 59 ng g⁻¹ to 3403 ng g⁻¹ within the samples. Among quantified PCBs, two dl-PCBs (PCBs 105 and 118) were found in sum concentrations between 12-549 ng g⁻¹ ww. Among the DDX, 4,4'-DDE reached the highest concentrations with more than 350 ng g⁻¹ ww, and was in general significantly higher than 4,4'-DDD (Wilcoxon rank sum test, $W = 11$, $p = 0.008$). The ratio of the 4,4'-DDE concentration to the total concentration of all DDX was on average 0.88 ± 0.21 , and only one sample had a ratio below 0.7 with 0.36.

Additionally, PCBs 49, 52, 77, 101, 156, and 187 could be qualified, but concentrations were below LOQs (Online Resource 6). Out of these, PCBs 77 and 156 are dl-PCBs. The PCBs 28, 110, and 132 could not be detected in any sample.

Concentrations of Hg in egg membranes ranged from 0.006 to 0.436 $\mu\text{g g}^{-1}$ dw (Table 2).

Pollutant concentrations and embryo age

The pollutant concentration of PCBs in embryos differed among ages in the years 2001 and 2003 compared to those from 2014 to 2016 (Fig. 3, Friedman rank sum test; 2001 and 2003: $\chi^2 = 20.0$; $df = 3$; $p < 0.001$; 2014 to 2016: $\chi^2 = 26.1$; $df = 3$; $p < 0.001$) with significantly higher concentrations in embryos aged 34 days or older compared to younger embryos (Wilcoxon signed rank exact test for eight pollutants and Bonferroni adjusted p -values; 2001 and 2003: $V = 0$; $p = 0.031$; 2014 to 2016: $V = 0$; $p = 0.031$, Fig. 3). No significantly different PCB concentrations could be found in embryos older than 40 days and embryos between 34 and 40 days of age in recent years (Wilcoxon signed rank exact test for eight pollutants and Bonferroni adjusted p -values; 2014 to 2016: $V = 5$; $p = 0.313$). No significant differences among ages could be found for DDT metabolites (Friedman rank sum test for two DDT metabolites, 2001 and 2003: $\chi^2 = 5.4$; $df = 3$; $p = 0.145$; 2014 to 2016: $\chi^2 = 6.7$; $df = 3$; $p = 0.107$). We found no significant correlation of higher Hg concentrations in egg membranes when embryos were older (Spearman's rank correlation, $r_s = 1232$, $p = 0.066$, $\rho = 0.39$), but Hg concentrations of membranes from hatched eggs were significantly higher than those from unhatched eggs (Wilcoxon signed rank sum test with continuity correction; $W = 105.5$; $p < 0.001$).

Temporal differences of pollutant concentrations and foraging behavior

The overall load of PCBs was higher in 2001 and 2003 than in 2014 to 2016 (Wilcoxon signed rank exact test, $V = 50$, $p < 0.001$). For DDT metabolites, no significantly higher concentrations in 2001 and 2003 were found compared to 2014 to 2016 (Wilcoxon signed rank exact test, $V = 5$, $p = 0.078$). Also, PCB concentrations were higher in 2001 and 2003 compared to 2014 to 2016 in the group of younger ages (0-33 d; Wilcoxon signed rank exact test for eight PCBs and Bonferroni adjusted p -values, $V = 50$, $p = 0.048$) and the group of older ages (≥ 34 d; Wilcoxon signed rank exact test for

eight PCBs and Bonferroni adjusted p -values, $V = 0$, $p = 0.031$) tested separately. For DDT metabolites, there were no difference in younger or older embryos from 2001 and 2003 compared to 2014 to 2016 (Wilcoxon signed rank exact test for two DDX, 0-33 d: $V = 5$, $p = 0.313$; ≥ 34 d: $V = 0$, $p = 0.5$).

Concentrations of POPs relative to each other were comparable among age groups (Fig. 4). The pollutants with the highest (PCB 153, 4,4'-DDE) or lowest concentrations (PCB 183) per sample were the same among samples. One exception was embryos aged 34–40 d from 2001 and 2003, which had a very high concentration of 4,4'-DDD. Interestingly, this value was even higher than that of 4,4'-DDE, which is dominating over 4,4'-DDD in all other samples.

In egg membranes, Hg concentrations were significantly higher in 1998 than in 2003 and in 2014 to 2016, and also higher in 2003 than in 2014 to 2016 (Kruskal Wallis rank sum test: $\chi^2 = 25.1$, $df = 2$, $p < 0.001$; Fig. 5). Between 1998 and 2003, a significant decrease of medians was observed: 59 %, and between 2003 and 2014 to 2016, medians decreased by 66 % (Post-hoc Analyses: Wilcoxon rank sum test with Bonferroni correction: 1998 and 2003: $W = 66$, $p = 0.004$; 1998 and 2014 to 2016: $W = 349$, $p < 0.001$; 2003 and 2014 to 2016: $W = 203$, $p = 0.036$; Fig. 5). Values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ differed significantly among 1998, 2003, and 2014 to 2016, and were significantly different between 2003 and 1998. Between 1998 and 2014 to 2016, or between 2003 and 2014 to 2016 no significant differences were found (1998 and 2003: Wilks' $\lambda = 0.437$, $\chi^2 = 11.58$, $df = 2.0$, $p = 0.009$; 1998 and 2014-2016: Wilks' $\lambda = 0.875$, $\chi^2 = 5.76$, $df = 2.0$, $p = 0.168$; 2003 and 2014-2016: Wilks' $\lambda = 0.864$, $\chi^2 = 5.86$, $df = 2.0$, $p = 0.160$; Fig. 6). Variation within time period of trophic positions was higher than between time periods (medians (ranges) for 1998: 3.2 (3.1 – 3.4); 2003: 3.0 (2.9 – 3.2); 2014 – 2016: 3.2 (2.9 - 3.4)). Neither values of $\delta^{13}\text{C}$ nor of $\delta^{15}\text{N}$ correlated with Hg loads (Pearson's product-moment correlation: $\delta^{13}\text{C}$: $t = -1.269$, $df = 51$, $p = 0.210$, $r = -0.17$; $\delta^{15}\text{N}$: $t = 0.734$, $df = 51$, $p = 0.466$, $r = 0.10$).

Discussion

Pollutant concentrations

The sum concentrations of all eight PCB congeners quantified in embryos in this study reached values as high as 3403 ng g⁻¹ ww in 2001 and 2003, and 565 ng g⁻¹ ww in 2014 to 2016. In both time periods, these sum PCB concentrations were higher than in other seabirds' eggs like penguins, gulls or petrels from the Antarctic Peninsula during the austral summer seasons 2003/2004 to 2005/2006 (Cipro et al. 2010; Corsolini et al. 2011; Online resource 8). It is worth to note that some of these studies included from eight and up to 81 PCBs (Cipro et al. 2010; Corsolini et al. 2011; Online resource 8). Similar levels were found only in skua eggs (*Stercorarius* spp.), for a total of 51 PCB congeners (Online resource 8, Cipro et al. 2013). The underlying reasons for species differences are difficult to determine. Among others, different foraging areas or trophic position of prey items are two possibilities that may explain higher concentrations when averaged for one congener (Σ PCB concentrations / number of congeners) in Wilson's storm-petrel eggs than in skua eggs (Corsolini and Sará 2017; Braune et al. 2005; Carravieri et al. 2014). However, even compared to Adélie penguins that are similar in habitat and prey preferences, Wilson's storm-petrel embryos showed higher concentrations (Cipro et al. 2010; Corsolini et al. 2011; Online resource 8). A study on PCB concentrations in Arctic birds suggested that higher metabolic rate, and hence feeding rate, may be a reason for higher pollutant concentrations in birds (Borgå et al. 2005). Wilson's storm-petrels have an almost threefold higher basal, and more than threefold higher field metabolic rate than Adélie penguins (adjusted for body mass). Therefore, a higher food, and hence, pollutant uptake relative to their body mass could explain higher PCB concentrations (Ellis and Gabrielsen 2001).

In the present study, the highest total concentration of PCBs was 3403 ng g⁻¹ ww. Adverse effects of sum concentration of PCBs in other birds' eggs occurred at 2100 ng g⁻¹ ww, for example, in eggs of the Great blue heron (*Ardea herodias*), resulting in induced enzymatic reactions (Bosveld and van den Berg 1994). An increase of morphological deformations of embryos appeared in Caspian terns (*Hydroprogne caspia*) at an egg PCB concentration of 4000 ng g⁻¹ ww compared to normal living embryos with egg PCB concentrations of 3600 ng g⁻¹ ww (Yamashita et al. 1993). Hence, sum concentrations of PCBs in Wilson's storm-petrel embryos reaching up to 3403 ng g⁻¹ could already pose a threat to the developing bird, especially during the sensitive embryonic phase. Next to 17 analyzed PCBs in the present study, up to 192 other congeners not explicitly looked for could add up to a potentially even higher PCB load. Yet, quantified sum concentrations of the years 2014 to 2016 were lower, with a maximum value of 565 ng g⁻¹ ww, suggesting the toxic threat linked to PCBs was lower in more recent years. However, toxic effects clearly differ among species and some may suffer severe alterations at levels that show no effect in others. No study so far evaluated impacts of PCBs on development or fitness in Wilson's storm-petrels. While levels of PCBs detected in Wilson's storm-petrels should be observed with caution, more studies evaluating the impact on this species' health are needed.

Among PCBs, dl-PCBs are especially toxic and can bind to the aryl hydrocarbon-receptor, a ligand dependent transcription factor (Poland et al. 1976; Safe 1994). This binding can cause interference with the immune system, cell migration, or the differentiation of cells of the nervous system (Barouki et al. 2012). In this study, we detected the dl-PCBs 77, 105, 118, and 156 above LOD, of which PCBs 105 and 118 were found above LOQ. Their exact adverse potential in Wilson's storm-petrels without species-specific studies is hard to assess. The fact that in this study even the lowest concentrations of dl-PCBs 105 and 118 together were more than 500-fold higher than European limits for consumable food (eel: 0.010 ng g⁻¹ ww, fish liver: 0.020 ng g⁻¹ ww; European Union 2011) shows how severe those pollutant loads are in Antarctic wildlife.

The patterns of PCB congeners in Wilson's storm-petrel embryos were similar to those found in eggs of other fish- and krill-eating birds (Bosveld and van den Berg 1994; Corsolini et al. 2011; Goutte et al. 2013). Patterns of PCBs differ due to species-specific metabolism of congeners between species and their prey species (Bodin et al. 2008; Na et al. 2017; Koenig et al. 2012). Certain PCB congeners with structures like meta-para vicinal H-atoms in at least one phenyl ring could be metabolized and accumulated less in fish liver and fish-eating seabirds than other congeners (Borlakoglu and Walker 1989; Zell et al. 1978). Excretion paths of PCBs for birds include preen oil, feces or maternal transfer to eggs (Barron et al. 1995; Rudolph et al. 2016; Solheim et al. 2016). While patterns of PCBs differed only to small extents in black-legged kittiwakes (*Rissa tridactyla*) between liver, feather, and preen oil samples, small differences could be seen for certain congeners (Solheim et al. 2016), which could add to species specific PCB patterns due to differentiation in excretion paths. In this study, observed patterns are in line with those of Adélie penguins or Common terns (*Sterna hirundo*; Bosveld and van den Berg 1994; Corsolini et al. 2011; Goutte et al. 2013).

The peak level of 4,4'-DDE, a potent endocrine disruptor and androgen receptor antagonist (Xu et al. 2006; Burgos-Aceves et al. 2021) that is even more persistent in animals than its parent compound (Burgos-Aceves et al. 2021), was from a sample from 2001–2003 (372 ng g⁻¹ ww). It reached a concentration still well below the critical concentration of reproductive failure in the sensitive brown pelican (*Pelecanus occidentalis*, 3000 ng g⁻¹, Blus 1982). Several other bird species could withstand higher DDE levels before their ability to reproduce was critically impaired such as the peregrine falcon (*Falco peregrinus*) and the osprey (*Pandion haliaetus*; Ratcliffe 1967; Johnson et al. 1975). Hence, we do not expect severe impacts on reproduction on Wilson's storm-petrels due to the comparatively lower DDE concentrations alone.

In all other samples, 4,4'-DDE concentrations were much lower, but with one exception always higher than the other detected DDX, 4,4'-DDD. Neither 2,4'-DDT nor 4,4'-DDT, the main components of commercial DDT mixes, could be detected in our samples. The ratio of 4,4'-DDE concentration to the total concentration of all DDX in those samples was higher than 0.6. DDE is only an impurity of commercial DDT production, and occurs only in low concentrations in the commercial mix. Hence, its occurrence in the wild is almost exclusively due to degradation of DDT. Both, the absence of DDT as well as the DDE/ΣDDX ratios are indicators for old input (Borrell and Aguilar, 1987; Yogui et al.

2003). This result is consistent with other studies on Antarctic seabirds such as the Antarctic petrel *Thalassoica antarctica* whose 4,4'-DDT concentrations in the plasma were very low, or even below LOD (Carravieri et al. 2021). However, at a larger spatial scale, other investigations on seabirds from the Southern Ocean revealed a recent use of DDT, likely for the fight against mosquitos, which are vector of malaria (Carravieri et al. 2014). Such contrasting results reveal the importance of on-going monitoring of contamination in subantarctic and Antarctic environments to evaluate if a new increase of DDX from recent input can be observed.

In one sample, 4,4'-DDD had the highest concentrations compared to the other DDX. To the best of our knowledge, this ratio between 4,4'-DDD and 4,4'-DDE has not yet been reported in biota feeding in Antarctic waters. The reason of this high occurrence of 4,4'-DDD remains unclear. It could be a sign of an uncommon food source, as 4,4'-DDD is the main degradation product of reductive dechlorination reactions of 4,4'-DDT (Yu et al. 2011; Zhang et al. 2015). Hence, prey items like lanternfish (Myctophidae) that spend part of the day at zones of minimal oxygen and use anaerobiosis to cope with these conditions, may explain this finding (Torres et al. 2012). As we did not have stable isotope information for all eggs from this pooled sample, we could not verify whether food items for these eggs were from different trophic positions than other analyzed samples. No 2,4'-DDT, 2,4'-DDD, or 2,4'-DDE was found. This is in accordance with other studies, where these components were below detection levels or had concentrations that were orders of magnitude lower than 4,4'-DDE, which was found in highest concentrations in seabirds (Cipro et al. 2010; Corsolini et al. 2011).

Mean Hg concentrations found in egg membranes of Wilson's storm petrels were in the same range as those of *Pygoscelis* penguins from the South Shetland Islands (Brasso et al. 2012). It is difficult to establish thresholds for lowest observed adverse effect levels for detrimental effects of Hg in eggs, e.g. due to different thresholds among species, and threshold often refer to whole-egg Hg levels (Dietz et al. 2013, Evers et al. 2003). In bird eggs, concentrations of Hg are closely linked to different egg compartments; former studies found that mean Hg concentrations for whole egg contents are 6.5 to 7.8 times higher than in egg membranes for Gentoo penguins (*Pygoscelis papua*) or American avocets (*Recurvirostra americana*), respectively (Brasso et al. 2012, Peterson et al. 2017). When estimating comparable Hg concentrations for whole-eggs (dw) with these values, only one sample from 1998 (0.436 $\mu\text{g g}^{-1}$ dw for egg membrane, estimate for whole-eggs: 2.8 – 3.4 $\mu\text{g g}^{-1}$ dw) is considered to reach a concentration that poses a moderate hazard for reproduction in several bird species (0.6 – 1.3 $\mu\text{g g}^{-1}$ ww, equals about 2.8 – 6.1 $\mu\text{g g}^{-1}$ dw, Evers et al. 2003). Impacts of high Hg concentrations in eggs include reduced hatchability, malformations of the embryos or reduced nestling survival (Burger and Gochfeld 1997; Heinz et al. 2009; Scheuhammer et al. 2007). However, if nestlings survive long enough, birds will be able to reduce their Hg load during feather growth and molt (Bond and Diamond, 2009; Falkowska et al. 2013; Albert et al. 2019). Especially very young birds can benefit from this excretion pathway as the example of common loon chicks (*Gavia immer*) shows (Fournier et al. 2002).

Pollutant concentrations and embryo age

In our samples, PCB concentrations were relatively constant for the first two thirds of the embryonic development (Fig. 3). After an embryonic age of 34 days, PCB concentrations were significantly higher. This concentration increase happened within the same time frame than in domestic chicken (*Gallus gallus domesticus*) embryos use yolk lipids for embryonic development; embryos took up only about 20% of lipids stored in the yolk during the first two thirds of their development, but more than another 65% of yolk lipids until briefly before hatching (Noble and Cocchi 1990). The investigated POPs, PCBs and DDX, have a very high affinity to lipids, and are, hence, mainly transferred to the embryos through lipids. While the domestic chicken is considered to belong to the developmental category of precocial birds, storm-petrels are considered by most researchers semi-precocial birds. However, independently of their developmental mode, birds undergo the same structurally defined developmental stages, and growth curves do not differ between precocial and altricial species, once egg size and incubation period is taken into account (Ricklefs and Starck 1998). It is therefore likely that also non-precocial birds show the lipid metabolism described by Noble and Cocchi (1990), which largely explains the observed POP increase during embryonic development.

We found a tendency of elevated Hg concentration in egg membranes of more developed embryos. Eggshells, known to become thinner during embryonic development (Karlsson and Lilja 2008; Orłowski and Hałupka 2015), were observed to have decreasing Hg concentrations with increasing embryonic age (Peterson et al. 2017). In Peterson et al.'s study, no relationship was described between Hg concentrations in egg membranes and embryonic age. As eggshells are thinning, Hg could be transported with calcium to the embryo. This way, part of Hg may not pass through the egg membrane and accumulate here. However, this could only lead to a small increase of Hg concentrations and further studies are needed to evaluate potential pathways of Hg within the egg during embryonic development.

Temporal differences of pollutant concentrations and foraging behavior

Concentrations of PCBs were higher in 2001 and 2003 than in 2014 to 2016. The global ban of many POPs by the Stockholm Convention led to a decline in worldwide, and therefore Antarctic, atmospheric contamination (Pozo et al. 2017). However, melting glaciers represent a potential source of pollutants trapped in the ice for decades (Geisz et al. 2008; Bogdal et al. 2009). Once released into the sea, their accumulation seems currently to primarily take place in benthic environments, where increases in pollutant levels can still be seen (van den Brink et al. 2009, 2011). Whether this will also have an impact on pelagic food webs is yet to be determined. Data from several studies confirm the general trend of pollutant decline in pelagic seabirds, which indicates a lower input for biota feeding in pelagic habitats (van den Brink et al. 2009; van den Brink et al. 2011). While concentrations change, no obvious change in substance relations can be observed. The reduction seen here and in several studies on pelagic seabirds is consistent with known half-life values for organic pollutants (compare Galbán-Malagón et al. 2013).

For DDX, we did not find significantly different concentrations between time periods among all age groups. A study comparing several penguin species showed that DDX concentrations in adult fat tissue were lower around 2010 than they were in the 1980s and 1990s (Ellis et al. 2018). Lower 4,4'-DDT/4,4'-DDE ratios 2000 to 2009 than in 1960 to 1969 suggest that more recently found DDX concentrations are from DDX that reached the Antarctic through long-distance transportation and is persistent to the environment now (Ellis et al. 2018). In this study, we neither detected 2,4'- or 4,4'-DDT in 2001 and 2003, nor in 2014 to 2016, which is in accordance with the suggestion that detected concentrations do not originate from recent input, and reflect persistent concentrations in the Antarctic environment. Similar concentrations between the two time intervals could hint to an equilibrium between transfer to Antarctic waters and sedimentation of DDX, but additional studies are needed to delineate whether this could be a time trend.

In the present study, egg membrane Hg concentrations were highest in 1998, and were higher in 2003 than in 2014 to 2016. In Adélie penguins, feather Hg concentrations were significantly lower in 2007 than in museum specimen from the 1950s (Carravieri et al. 2016), and prey animals like Southern Ocean squids from subantarctic waters showed decreasing Hg concentrations over a decade of monitoring (Seco et al. 2020). Other species feeding in Antarctic waters like emperor penguins (*Aptenodytes forsteri*) showed no change of Hg feather concentrations compared to museum samples (Carravieri et al. 2016). However, emissions in the southern hemisphere were at best stable or even increased within the past years (Streets et al. 2017, Soerensen et al. 2012). High emissions originate from artisanal small-scale gold mining that is increasing with rising gold prices. Gold mining is for example found in Ghana or Peru, and hence, no decrease of emissions in the southern hemisphere is expected in the near future (Eagles-Smith et al. 2018). In subantarctic regions, increasing atmospheric Hg concentrations are also reflected in Hg concentrations in feathers of several seabird species compared to years or decades earlier (Carravieri et al. 2016; Mills et al. 2020). Interestingly, even with decreasing atmospheric Hg concentrations, animals may not reflect these trends, because several environmental factors, e.g., warming climate, and biogeochemical processes, may promote Hg methylation and its subsequent incorporation in food webs (Wang et al. 2019). Hence, even though our results showed higher Hg concentrations in the early 2000s than in 2014 and 2016, caution is necessary, as due to atmospheric Hg deposition in oceanic waters (Krabbenhoft and Sunderland 2013, Cossa et al. 2011) an increase of Hg concentrations in seabirds like the Wilson's storm-petrel should not be excluded (Carravieri et al. 2016).

Foraging behavior of wildlife can often explain diverging pollutant concentrations, because of prey from different trophic positions or geographic areas (Corsolini and Sará 2017; Braune et al. 2005; Carravieri et al. 2014, 2016; Cherel et al. 2018; Mills et al. 2020). We used stable isotope $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values to analyze if differences of pollutant concentrations among time periods could be caused by foraging behavior. Stable isotope values of the years 2014 to 2016 did not differ from 1998 or 2003, while 1998 and 2003 were significantly different from each other. Specifically, there is a high divergence of $\delta^{15}\text{N}$ values, but a high overlap of $\delta^{13}\text{C}$ values that can be used as a proxy for latitude

(Fig. 5; Cherel and Hobson 2007; Quillfeldt et al. 2010). However, trophic positions calculated from $\delta^{15}\text{N}$ values differed in all years more within than among years. Additionally, Hg concentrations did not correlate to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. Hence, we think that observed concentration differences in this study of Hg in 1998, 2003 and 2014 to 2016, and of PCBs in 2001 and 2003 compared to 2014 to 2016, are unlikely to be caused by diverging pre-laying exodus latitudes or prey trophic positions, and rather reflect a decrease of the pollutants in the environment over time. However, our available data covered only a small number of breeding seasons, and more data are needed to delineate a significant decreasing trend of POPs and Hg concentrations in Wilson's storm-petrel eggs (Rigét et al. 2011; Bignert et al. 2004).

Conclusions and outlook

Overall, the pollutants in embryos and egg membranes of Wilson's storm petrels were similar to those often reported for biota in Antarctic waters. Concentrations of Hg in the egg membranes were in similar ranges than those of seabirds with similar diets like Adélie penguins, but POP concentrations measured in embryo samples were higher than those of the larger seabird. In general, concentrations of POPs and Hg decreased over the observed decade, and POP concentrations increased with advancing embryonic development. Our study established a first basis of pollutant concentrations found in embryos and egg membranes of Wilson's storm-petrels breeding in the Antarctic. Also, our results show the importance of considering the developmental stage of the embryo when analyzing pollutants. Further studies are needed to investigate potential impacts of these pollutants, e.g., on reproductive success and toxicity effects on nestlings. It is important to examine whether the low concentrations during the first weeks of embryonic development are negligible in terms of toxic impact on embryo development compared to higher pollutant loads transferred in later stages of development, or whether even low concentrations could be detrimental in sensitive phases of development. With melting ice masses due to climate change, trapped pollutants may be released into coastal Antarctic waters and incorporated in the food chain, likely increasing the toxicity risks for seabirds.

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Tables

Table 1 Number and type of Wilson's storm-petrel samples used in this study for each year. All samples were collected at the study site at "Tres Hermanos" hill, close to Carlini Base

	1998	2001	2003	2014	2015	2016
embryos	0	30	10	10	10	3
egg membranes	10	0	7	9	15	12

Table 2 Means \pm standard deviation (SD) and concentration ranges of single organic pollutants and pollutant groups as well as mean \pm SD and concentration range of Hg of all investigated samples. Σ PCB^a: sum of 8 individual PCB congeners that are listed in the present table, Σ dl-PCB: sum of PCBs 105 and 118, Σ PCB (indicator)^b: sum of indicator PCBs, Σ DDX: sum of 4,4'-DDD and 4,4'-DDE

Pollutant	All samples		2001, 2003		2014 to 2016	
	Mean \pm SD	range	Mean \pm SD	range	Mean \pm SD	range
PCB concentrations (ng g ⁻¹) ww of embryo samples						
PCB 99	23 \pm 43	2-136	38 \pm 65	4-136	10 \pm 9	2-24
PCB 105	20 \pm 22	4-74	28 \pm 31	8-74	14 \pm 11	4-28
PCB 118	76 \pm 151	8-475	135 \pm 226	16-475	28 \pm 25	8-65
PCB 138	88 \pm 186	6-579	158 \pm 281	10-579	32 \pm 31	6-67
PCB 153	242 \pm 456	29-1437	395 \pm 695	29-1437	119 \pm 104	31-267
PCB 170	< LOD	< LOD-127	< LOD	< LOD	< LOD	< LOD
PCB 180	85 \pm 169	7-527	143 \pm 256	9-527	39 \pm 48	7-117
PCB 183	8 \pm 15	1-48	14 \pm 23	2-48	4 \pm 3	1-7
Σ PCBs ^a	556 \pm 1082	59-3403	944 \pm 1640	78-3403	246 \pm 227	59-565
Σ dl-PCBs	96 \pm 172	12-549	163 \pm 257	24-549	42 \pm 36	12-93
Σ PCBs (indicator) ^b	491 \pm 961	52-3018	832 \pm 1458	64-3018	218 \pm 205	52-516
DDT concentrations (ng g ⁻¹) ww of embryo samples						
4,4-DDD	80 \pm 219	< LOD-663	168 \pm 330	2-663	11 \pm 19	< LOD-43
4,4-DDE	110 \pm 108	18-372	144 \pm 153	44-372	82 \pm 58	18-146
Σ DDX	190 \pm 321	19-1035	312 \pm 482	46-1035	93 \pm 72	19-182
Hg concentrations (μ g g ⁻¹) dw of egg membranes						
Hg	0.062 \pm 0.086	0.006-0.436	1998:	1998:	2014-2016:	2014-2016:
			0.165 \pm 0.124	0.050-0.436		
			2003:	2003:		
			0.055 \pm 0.030	0.019-0.104		

^a PCBs 49 and 187, indicator PCBs 52 and 101, as well as dl-PCBs 77 and 156, were detected below LOQ and were not added to the sum of PCBs given in the present table.

^b Indicator PCBs that were detected in this study above LOQ were PCBs 138, 153, and 180.

Figures and figure captions:

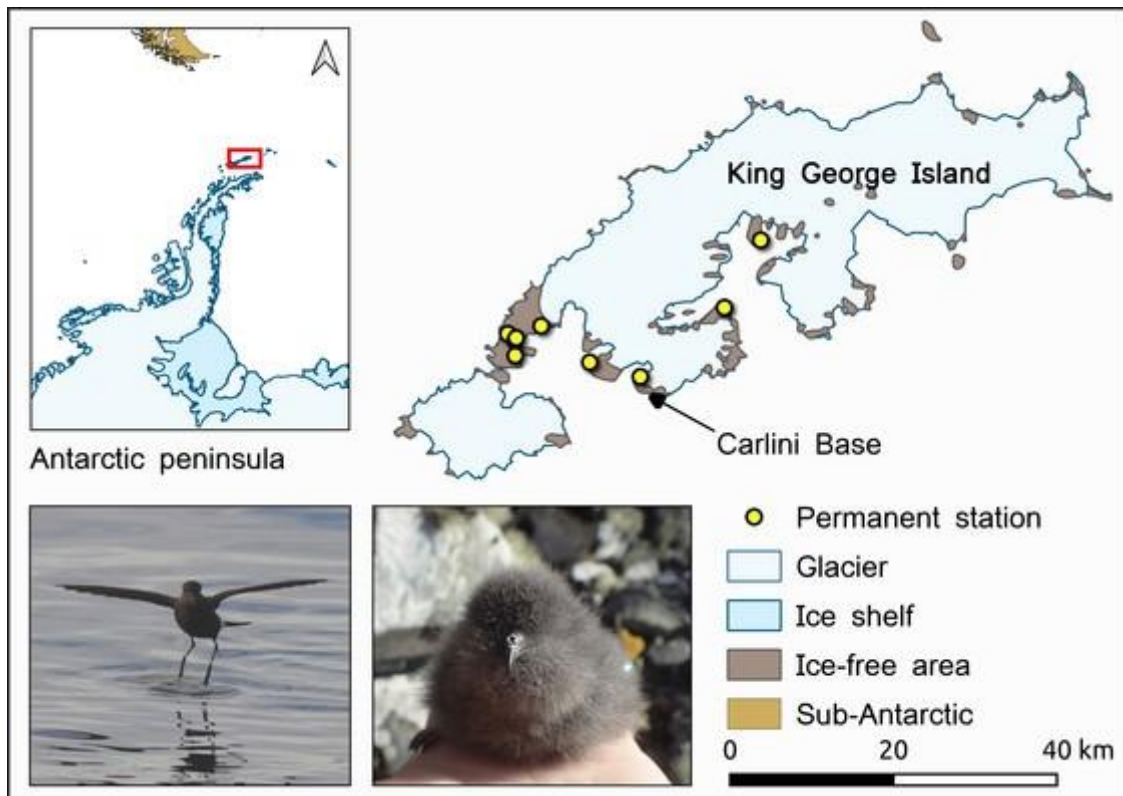


Fig. 1 Study area at Carlini Base on King George Island (map data from Quantarctica; Matsuoka et al. 2018), and adult and nestling of the study species Wilson's storm-petrel (*Oceanites oceanicus*).

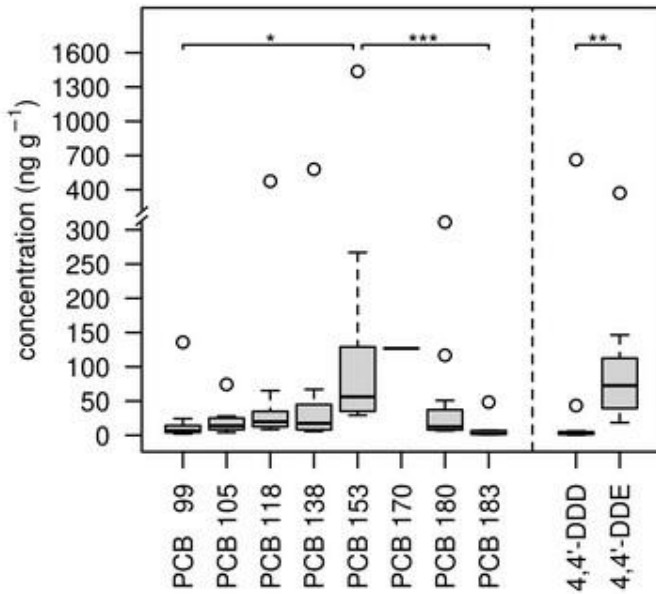


Fig. 2 Concentration ($\text{ng g}^{-1} \text{ ww}$) for eight quantified PCBs and two DDX in embryo samples of Wilson's storm-petrels. All PCBs were found in $n = 10$ samples, except for PCB 170, that was only detected in one sample. Significant differences between congeners are indicated by brackets and asterisks: *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$. Black bars represent median of samples, the box marks 25% respectively 75% quantiles. Whiskers show the point closest to but within 1.5-fold distance of interquartiles

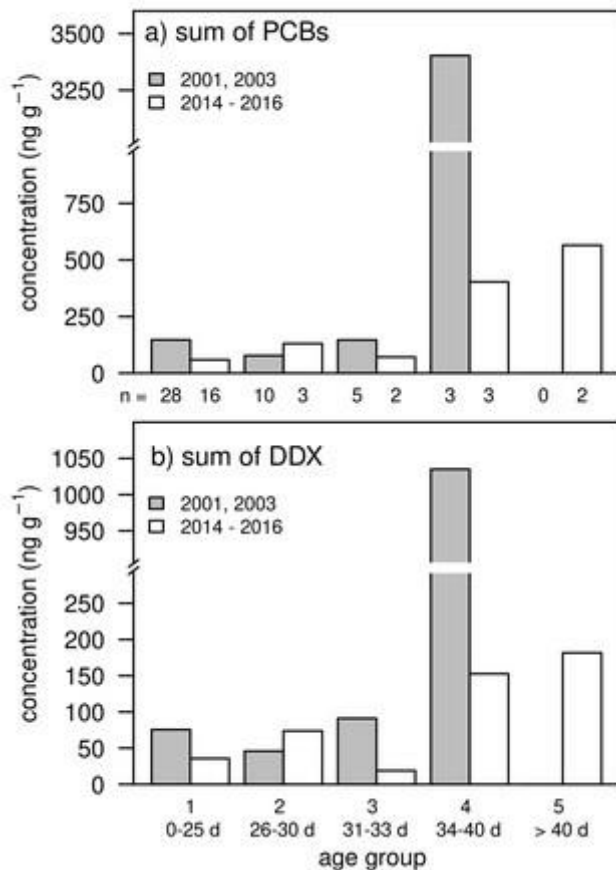


Fig. 3 Concentrations of ΣPCBs and ΣDDX from Wilson storm-petrel embryos for the years 2001 and 2003, as well as for 2014 to 2016 for each pooled age group. Embryo ages and according age groups for both figures are given below the x-axis. Each bar presents one pooled sample, n refers to number of embryos in a pooled sample, which is similar for both figures

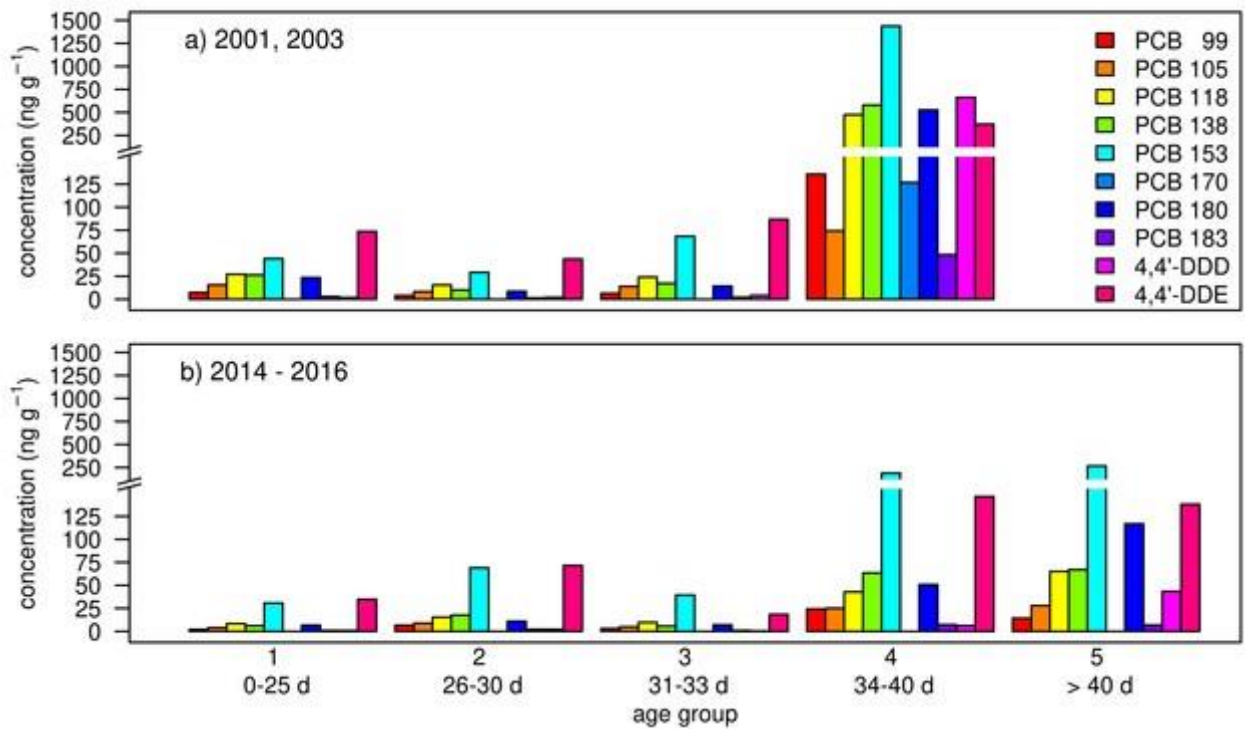


Fig. 4 Concentrations of POPs from Wilson's storm-petrel embryo samples for different age groups for a) 2001 and 2003, and b) among 2014 and 2016. Embryo ages and according age groups for both figures are given below the x-axis. The y-axis is scaled differently below and above the axis-break

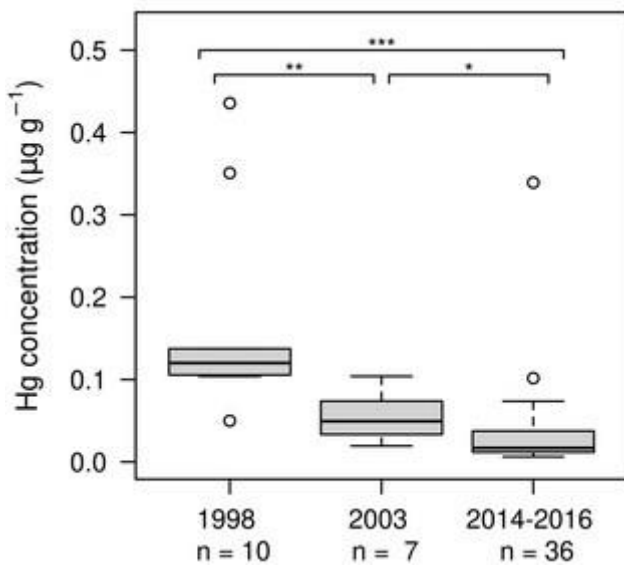


Fig. 5 Concentrations for Hg ($\mu\text{g g}^{-1}$ dw) from Wilson's storm-petrel egg membrane samples for 1998, 2003, and 2014 to 2016. Significant differences between years are indicated by brackets and asterisks: *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$

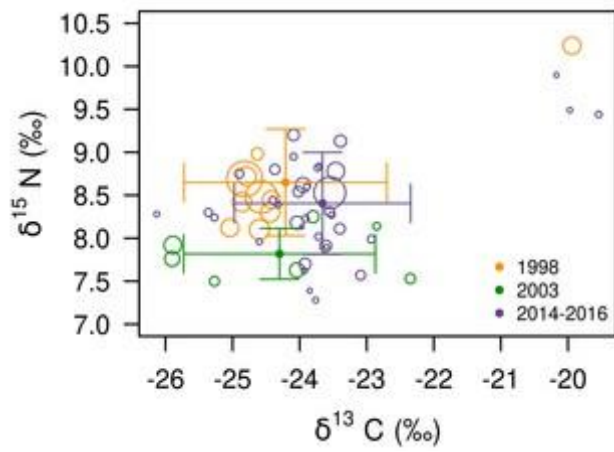


Fig. 6 Egg membrane $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for Wilson's storm-petrel eggs from King George Islands from 1998 to 2016. Bubble size is relative to Hg value of the same sample. Colors indicate the collection year of the sample. Solid points show means with error bars for 1998, 2003, and 2014 to 2016

Electronic supplementary material

Persistent organic pollutants and mercury in a colony of Antarctic seabirds: Higher concentrations in 1998, 2001, and 2003 compared to 2014 to 2016

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Calculation of embryonic ages

Embryonic ages were calculated following the formula evaluated by Ricklefs (2010):

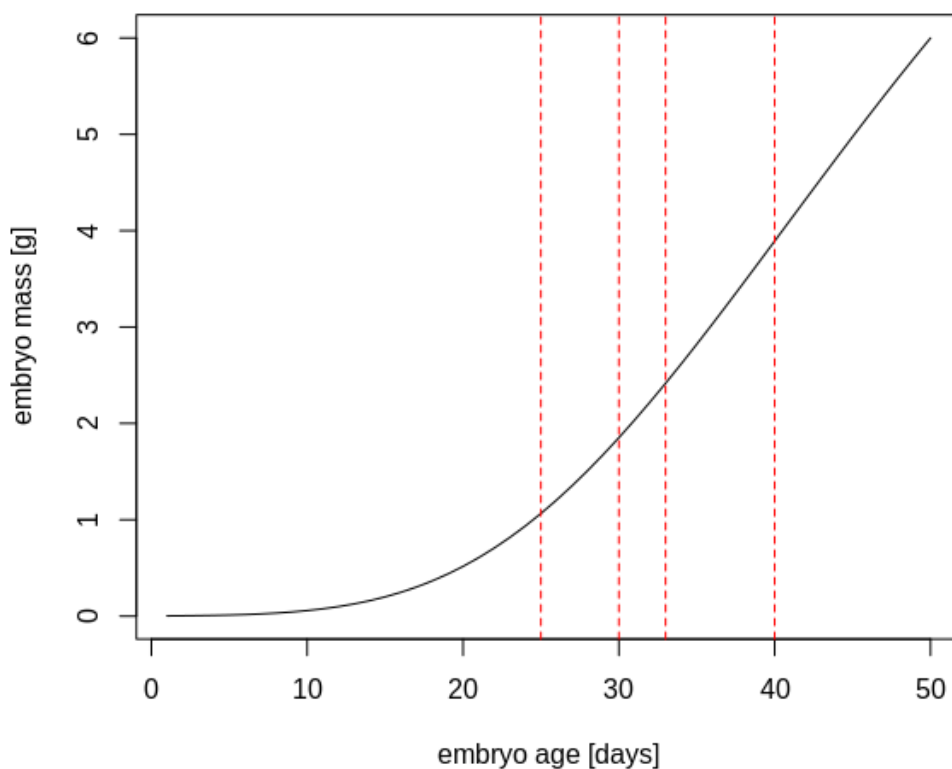
$$\frac{\ln(b) - \ln\left(\ln\left(\frac{A}{M}\right)\right)}{k} = t$$

where: b is the scaling parameter for the exponent of the Gompertz function; A is the fitted asymptote (g); M is the embryo's mass (g); k is the embryo's Gompertz growth rate (days⁻¹); t is the embryo age (days). To match our species, we used values for the related species, the Leach's storm-petrel (*Oceanodroma leucorhoa*, Ricklefs, 2010) and adjusted the values to fit *Oceanites oceanicus* based on own data (Online Resource 1).

Online Resource 1 Parameters used for embryo age determination in *Oceanodroma leucorhoa* (Ricklefs, 2010) and *Oceanites oceanicus*

Species	lnA	k	M ₀	Adult	IP	IEM
<i>Oceanodroma leucorhoa</i>	2.225	0.066	0.00133	39.8	41.8	11.2
<i>Oceanites oceanicus</i>	2.394	0.054	0.00133	38	50	11.8

lnA = natural log of the fitted asymptote (g); k = Gompertz growth rate of embryo (days⁻¹); M_0 = fitted initial embryo mass at age 0 (g); Adult = adult mass (g), primarily from Dunning (1993); IP = incubation period (days), from various sources; IEM = initial egg mass (g).



Online Resource 2 Approximate mass growth curve for *Oceanites oceanicus* embryos adjusted analogue to Ricklefs (2010). Dashed red lines show separation of age groups

As preliminary trails with material from other bird species suggested POP concentrations <LOD for individual samples, several embryos of similar ages were pooled together to one sample (Online Resource 3).

Online Resource 3 Defined age groups, their according dw, estimated ww equivalents, and embryonic age estimates (altered after Ricklefs, 2010) for embryos from 2001 and 2003 (N = 40), and 2014 to 2016 (N = 23)

Age group	Dry weight (g)	Wet weight (g)	Age (days)
1	0-0.25	0.0-1.2	0-25
2	0.25-0.40	1.2-2.0	26-30
3	0.40-0.50	2.0-2.5	31-33
4	0.50-0.80	2.5-4.0	34-40
5	> 0.80	> 4.0	> 40

Parameters of POP analysis

Online Resource 4 Temperature program of the GC oven

Rate (°C min ⁻¹)	Temperature (°C)	Hold (min)
-	60	3
10	200	0
2	270	0
40	290	17.5

Online Resource 5 Parameters of test substances for MS detection

Substance	Function	Structure	CAS RN	Molar mass (g mol ⁻¹)	Retention time (min)	Target ions (amu) ^a
PCB 28	Analyte	C ₁₂ H ₇ Cl ₃	7012-37-5	257.54	27.56	186, 256
PCB 52	Analyte	C ₁₂ H ₆ Cl ₄	35693-99-3	291.99	29.05	220, 257, 292
PCB 49	Analyte	C ₁₂ H ₆ Cl ₄	41464-40-8	291.99	29.35	220, 257, 292
TCN	IS	C ₁₂ H ₆ Cl ₄	20020-02-04	265.95	30.70	194, 266
2,4'-DDE	Analyte	C ₁₄ H ₈ Cl ₄	3424-82-6	318.03	34.02	246 , 318
PCB 101	Analyte	C ₁₂ H ₅ Cl ₅	37680-73-2	326.43	34.67	256, 291, 326
PCB 99	Analyte	C ₁₂ H ₅ Cl ₅	38380-01-7	326.43	35.06	256, 291, 326
4,4'-DDE	Analyte	C ₁₄ H ₈ Cl ₄	72-55-9	318.03	36.72	246, 318
2,4'-DDD	Analyte	C ₁₄ H ₁₀ Cl ₄	53-19-0	320.04	37.37	165, 235
PCB 110	Analyte	C ₁₂ H ₅ Cl ₅	38380-03-9	326.43	37.40	256, 291, 326
PCB 77	Analyte	C ₁₂ H ₆ Cl ₄	32598-13-3	291.99	38.42	220, 292
2,4'-DDT	Analyte	C ₁₄ H ₉ Cl ₅	789-02-6	354.49	39.66	165, 235
PCB 118	Analyte	C ₁₂ H ₅ Cl ₅	31508-00-6	326.43	39.84	256, 291, 326
4,4'-DDD	Analyte	C ₁₄ H ₁₀ Cl ₄	72-54-8	320.04	40.72	165, 235
PCB 153	Analyte	C ₁₂ H ₄ Cl ₆	35065-27-1	360.88	40.94	290, 325, 360
PCB 132	Analyte	C ₁₂ H ₄ Cl ₆	38380-05-1	360.88	41.05	290, 325, 360
PCB 105	Analyte	C ₁₂ H ₅ Cl ₅	32598-14-4	326.43	41.89	256, 291, 326
4,4'-DDT	Analyte	C ₁₄ H ₉ Cl ₅	50-29-3	354.49	43.10	165, 235
PCB 138	Analyte	C ₁₂ H ₄ Cl ₆	35065-28-2	360.88	43.20	290, 325, 360
PCB 187	Analyte	C ₁₂ H ₃ Cl ₇	52663-68-0	395.32	44.05	324, 359, 394
PCB 183	Analyte	C ₁₂ H ₅ Cl ₅	52663-69-1	395.32	44.51	324, 359, 394
PCB 156	Analyte	C ₁₂ H ₄ Cl ₆	38380-08-4	360.88	47.91	290, 360
PCB 180	Analyte	C ₁₂ H ₅ Cl ₅	35065-29-3	395.32	48.57	324, 359, 394
PCB 170	Analyte	C ₁₂ H ₅ Cl ₅	35065-30-6	395.32	50.97	324, 359, 394

1 ^a bold: masses used for quantification

Online Resource 6 Calculated LOD and LOQ values for all test substances in ng g⁻¹ ww. Used numerical factors are $k = 3$ (LOD), and $k = 10$ (LOQ)

Analyte	LOD	LOQ
PCB 28 ^b	27.0	83.1
PCB 52	0.3	0.8
PCB 49	0.4	1.1
2,4'-DDE	0.1	0.2
PCB 101	0.4	0.9
PCB 99	0.3	0.7
4,4'-DDE	0.1	0.2
2,4'-DDD	0.2	0.5
PCB 110	2.7	8.3
PCB 77	0.1	0.4
2,4'-DDT	0.2	0.3
PCB 118	0.4	0.9
4,4'-DDD	0.2	0.6
PCB 153	0.6	1.6
PCB 132	1.0	2.8
PCB 105	0.3	0.7
4,4'-DDT	0.2	0.4
PCB 138	0.2	0.4
PCB 187	0.1	0.3
PCB 183	0.1	0.2
PCB 171	0.1	0.3
PCB 156	0.2	0.5
PCB 180	0.1	0.3
PCB 170	0.1	0.2

^b high background noise levels at RT for PCB 28

Statistical comparisons between individual PCB concentrations

Online Resource 7 results of pairwise Dunn's post-hoc testing of concentrations differences between all possible pairs of PCB congeners with the test statistic Z , the unadjusted p value, the adjusted p value after Bonferroni correction, and the significance indication by asterisks: *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$

Comparison	Z	p	adjusted p	significance
PCB 99 vs. PCB 105	-0.8	0.411	1	
PCB 99 vs. PCB 118	-1.9	0.059	1	
PCB 105 vs. PCB 118	-1.1	0.288	1	
PCB 99 vs. PCB 138	-1.6	0.105	1	
PCB 105 vs. PCB 138	-0.8	0.425	1	
PCB 118 vs. PCB 138	0.3	0.79	1	
PCB 99 vs. PCB 153	-3.4	< 0.001	0.016	*
PCB 105 vs. PCB 153	-2.6	0.009	0.246	
PCB 118 vs. PCB 153	-1.6	0.119	1	
PCB 138 vs. PCB 153	-1.8	0.068	1	
PCB 99 vs. PCB 170	-1.8	0.074	1	
PCB 105 vs. PCB 170	-1.4	0.155	1	
PCB 118 vs. PCB 170	-0.9	0.344	1	
PCB 138 vs. PCB 170	-1.1	0.287	1	
PCB 153 vs. PCB 170	-0.2	0.803	1	
PCB 99 vs. PCB 180	-1.5	0.132	1	
PCB 105 vs. PCB 180	-0.7	0.494	1	
PCB 118 vs. PCB 180	0.4	0.704	1	
PCB 138 vs. PCB 180	0.1	0.909	1	
PCB 153 vs. PCB 180	1.9	0.053	1	
PCB 170 vs. PCB 180	1.1	0.265	1	
PCB 99 vs. PCB 183	1.1	0.26	1	
PCB 105 vs. PCB 183	1.9	0.051	1	
PCB 118 vs. PCB 183	3	0.003	0.072	
PCB 138 vs. PCB 183	2.7	0.006	0.168	
PCB 153 vs. PCB 183	4.6	< 0.001	< 0.001	***
PCB 170 vs. PCB 183	2.3	0.022	0.612	
PCB 180 vs. PCB 183	2.6	0.008	0.237	

Overview of pollutant levels found in other studies

Online Resource 8 Overview of PCB and DDT concentrations in eggs of different bird species across the Antarctic Peninsula. Congener numbers refer to the considered number of congeners, year of sampling indicates breeding season when eggs were collected

pollutant group	scientific name	common name	number congeners	Σ concentration, (range) (ng g ⁻¹ ww)	References (year of sampling)
PCB	<i>Sterna vittata</i>	Antarctic tern	51	133	Cipro et al. 2013 (2004/05, 2005/06)
PCB	<i>Pygoscelis adeliae</i>	Adélie penguin	27	32.5 (2.53–41.9)	Cipro et al. 2010 (2004/05, 2005/06)
PCB	<i>Pygoscelis antarcticus</i>	Chinstrap penguin	27	37.3 (3.11–78.7)	Cipro et al. 2010 (2004/05, 2005/06)
PCB	<i>Pygoscelis papua</i>	Gentoo penguin	27	26.0 (4.58–42.2)	Cipro et al. 2010 (2004/05, 2005/06)
PCB	<i>Stercorarius</i> spp.	skuas	51	228 (11.2–649)	Cipro et al. 2013 (2004/05, 2005/06)
PCB	<i>Daption capense</i>	Cape petrel	51	19.6 (13.7–25.4)	Cipro et al. 2013 (2004/05, 2005/06)
PCB	<i>Larus dominicanus</i>	Kelp gull	51	79.9 (64.5–95.3)	Cipro et al. 2013 (2004/05, 2005/06)
PCB	<i>Stercorarius antarcticus lonnbergi</i>	Brown Skua	54	53.41±19.61 (31.28-68.62)	Corsolini et al. 2011 (2003/04, 2004/05)
PCB	<i>Pygoscelis adeliae</i>	Adélie penguin	54	12.03±3.91 (7.26-16.81)	Corsolini et al. 2011 (2003/04, 2004/05)
DDX	<i>Sterna vittata</i>	Antarctic tern	6	76.6	Cipro et al. 2013 (2004/05, 2005/06)
DDX	<i>Pygoscelis adeliae</i>	Adélie penguin	6	6.29 (2.07–8.93)	Cipro et al. 2010 (2004/05, 2005/06)
DDX	<i>Pygoscelis antarcticus</i>	Chinstrap penguin	6	15.8 (2.67–38.0)	Cipro et al. 2010 (2004/05, 2005/06)

DDX	<i>Pygoscelis papua</i>	Gentoo penguin	6	5.47 (3.10–9.95)	Cipro et al. 2010 (2004/05, 2005/06)
DDX	<i>Stercorarius</i> spp.	skuas	6	26.3 (13.2–37.7)	Cipro et al. 2013 (2004/05, 2005/06)
DDX	<i>Daption capense</i>	Cape petrel	6	9.68 (6.42–12.9)	Cipro et al. 2013 (2004/05, 2005/06)
DDX	<i>Larus dominicanus</i>	Kelp gull	6	94.3 (52.4–136)	Cipro et al. 2013 (2004/05, 2005/06)
DDX	<i>Larus dominicanus</i>	Kelp gull	N.A.	no unit	Lukowski 1983 (1977/78)
DDX	<i>Macronectes giganteus</i>	southern giant petrel	N.A.	no unit	Lukowski 1983 (1977/78)

Literature

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