



Chemical threats for the sentinel *Pygoscelis adeliae* from the Ross Sea (Antarctica): Occurrence and levels of persistent organic pollutants (POPs), perfluoroalkyl substances (PFAS) and mercury within the largest marine protected area worldwide

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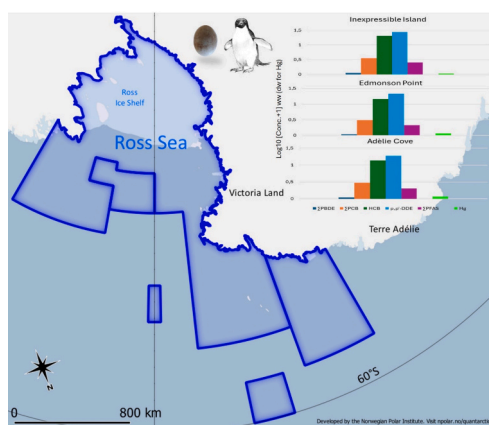
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HIGHLIGHTS

- PFAS were reported for the first time in Adèlie penguin from the Ross Sea.
- Long-chain PFCAs dominated the PFAS profile exceeding PFOS in penguin eggs.
- *p,p'*-DDE and HCB prevailed over PCBs, PFAS and PBDEs in penguin eggs.
- Penguin colonies from the same meta-population showed no significant differences.
- Legacy pollutants including mercury showed similar levels compared to previous studies.

GRAPHICAL ABSTRACT



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ABSTRACT

The Ross Sea Marine Protected Area (RS-MPA) hosts endemic species that have to cope with multiple threats, including chemical contamination. Adèlie penguin is considered a good sentinel species for monitoring pollutants. Here, 23 unhatched eggs, collected from three colonies along the Ross Sea coasts, were analysed to provide updated results on legacy pollutants and establish a baseline for newer ones. Average sum of polychlorinated biphenyls (Σ PCBs) at the three colonies ranged 20.9–24.3 ng/g lipid weight (lw) and included PCBs IUPAC nos. 28, 118, 153, 138, 180. PCBs were dominated by hexachlorinated congeners as previously reported. Hexachlorobenzene (HCB) and *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE) ranged between 134 and 166 and

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Brominated flame retardants
Mercury

181–228 ng/g lw, respectively. Overall, \sum PCBs was exceeded by pesticides, contrary to previous studies from the Ross Sea. Sum of polybrominated diphenyl ethers (\sum PBDEs) ranged between 0.90 and 1.18 ng/g lw and consisted of BDE-47 (that prevailed as expected, representing 60–80 % of the \sum PBDEs) and BDE-85. Sum of perfluoroalkyl substances (\sum PFAS) ranged from 1.04 to 1.53 ng/g wet weight and comprised five long-chain perfluorinated carboxylic acids (PFCAs), perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and perfluorooctanoic acid (PFOA); perfluorooctane sulfonamide (PFOSA) was also detected. The PFAS profile was dominated by PFCAs as already observed in Arctic seabirds. Mercury ranged from 0.07 to 0.15 mg/kg dry weight similarly to previous studies. Legacy pollutants confirmed their ongoing presence in Antarctic biota and their levels seemed mostly in line with the past, but with minor variations in some cases, likely due to continued input or release from past reservoirs. PFAS were reported for the first time in penguins from the Ross Sea, highlighting their ubiquity. Although further studies would be useful to increase the sample size and accordingly improve our knowledge on spatial and temporal trends, this study provides interesting data for future monitoring programs within the RS-MPA that will be crucial to test its effectiveness against human impacts.

1. Introduction

The Ross Sea is the largest shelf ecosystem in the Antarctic continent and one of the most productive areas south of the Antarctic Circle (Arrigo et al., 1998; Smith et al., 2007). Thus, despite the extreme environmental conditions (Corsolini, 2011), it represents an important foraging ground for many species (Ainley, 2002; Brooks, 2013). Its trophic web is based on few key species and thus considered fragile (Smith et al., 2007; Corsolini, 2009; Corsolini et al., 2017), however it still is mostly intact as demonstrated by the full suite of top and intermediate predators (Smith et al., 2007; Ballard et al., 2012). Due to its characteristics, the Ross Sea region provides a valuable context for ecological (Smith et al., 2007; Ballard et al., 2012) and ecotoxicological (Corsolini et al., 2017) studies and must be protected from the increasing threats it, and by extension the entire Antarctica, has to cope with. These include: increasing tourism, estimates for the 2022/2023 season indicated more than 100,000 incoming visitors (IAATO, 2022), increasing research activities connected with the 76 stations currently in operation on the continent (COMNAP, 2017), climate change (Chown et al., 2017; Convey and Peck, 2019), and industrial fishing (Ainley, 2010; Chown et al., 2015). Aiming at the protection of such a unique ecosystem, the Ross Sea Marine Protected Area (RS-MPA) entered into force in December 2017 (CCAMLR, 2016). The RS-MPA, covering 2.09 million km², is the largest protected area worldwide and with the restrictions applied should prevent this unique and still substantially preserved (Chown et al., 2015) environment from being overexploited (Brooks, 2013).

Adèlie penguin (*Pygoscelis adeliae* Hombron and Jaquinot, 1841) is an Antarctic ecosystem mesopredator (Ballard et al., 2012) and one of the most abundant penguin species (Ainley, 2002; Olmastroni et al., 2020; Sun et al., 2020) with a circumpolar distribution (Cusset et al., 2023). Adèlie penguin, being a resident species, lives year-round in the Southern Ocean (Corsolini et al., 2011) wintering on the sea ice where it can find better feeding conditions (Ainley, 2002; Ballard et al., 2010; Michelot et al., 2020), while nesting in colonies on the coastal free-ice areas during the breeding season (Olmastroni et al., 2020). Adèlie penguin is an indicator species used in the monitoring programs of the Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR) (Agnew, 1997; Lyver et al., 2014): being a key species in the short trophic web of the Ross Sea, it can help monitoring that ecosystem and detecting changes to its structure and responses to multiple stressors (Brooks and Ainley, 2022), thus improving the management of marine protected areas (Brooks and Ainley, 2022; Olmastroni et al., 2022).

Among the threats the Ross Sea ecosystem had and still has to face are toxic chemicals such as persistent organic pollutants (POPs) and mercury (Hg). Their occurrence has been reported in penguins since the late 1960s (George and Frear, 1966; Sladen et al., 1966; Risebrough et al., 1968) and 1980s (e.g. Schneider et al., 1985; Honda et al., 1986; Subramanian et al., 1986), and this species has been reported as a suitable bioindicator of these contaminants (e.g. Bargagli et al., 1998; Ancora et al., 2002; Smichowski et al., 2006; Corsolini et al., 2007;

Brasso et al., 2015; Carravieri et al., 2016; Mello et al., 2016; Montone et al., 2016; Padilha et al., 2022; Cusset et al., 2023; Gimeno et al., 2024).

Although legacy POPs such as polychlorinated biphenyls (PCBs), some organochlorine pesticides (OCPs), and Hg have been found in the Adèlie penguin for decades, recent data on their presence and levels in breeding individuals from East Antarctica and especially the Ross Sea are scarce. This trend becomes even more pronounced when considering new pollutants, such as polybrominated diphenyl ethers (PBDEs) or perfluoroalkyl substances (PFAS), which were restricted more recently or have not been restricted yet.

To collect data on chemical pollutants and define their baselines is crucial to be able to monitor changes and check the effectiveness of the restriction measures applied to the chemicals globally and within the MPAs, even more in the current changing scenario that poses the Ross Sea ecosystem under new and increasing threats that could act as confounding factors (Hung et al., 2016; Borgå et al., 2022).

In recent years more attention has been given to the use of non-destructive samples to monitor chemicals in biota (Mello et al., 2016; Morales et al., 2022) and abandoned and/or unhatched eggs represent a suitable option with this perspective (e.g. Court et al., 1997; Corsolini et al., 2002; Mello et al., 2016; Morales et al., 2022). Eggs are considered a useful tool to monitor both organic chemicals (Luke et al., 1989; Schiavone et al., 2009a; Mello et al., 2016; Morales et al., 2022; Padilha et al., 2022) and metals (Luke et al., 1989; Bargagli et al., 1998; Cipro et al., 2010) because they reflect the contamination status of the female during the pre-laying period (Bargagli et al., 1998; Mello et al., 2016).

In the present work legacy and newer POPs as well as PFAS and Hg have been analysed in Adèlie penguin eggs in order to provide recent data that could be useful in future monitoring studies connected with the RS-MPA management.

Specific objectives of this study were: i) to evaluate the levels of PCBs, hexachlorobenzene (HCB), *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE), PBDEs and Hg in the eggs of Adèlie penguins collected from colonies located within the RS-MPA, ii) to provide baselines for the less studied and not yet fully regulated PFAS few years after the establishment of the protected area and iii) to evaluate potential differences in levels of selected pollutants among different penguin colonies along the Ross Sea coasts. Stable isotope analysis was useful as a proxy to infer differences in trophic position ($\delta^{15}\text{N}$) and foraging ground ($\delta^{13}\text{C}$) among the colonies thus supporting the discussion on contamination burden. Expected results include consistent or lower levels of legacy POPs and mercury compared to the past decades, detectable levels of the ubiquitous PFAS, and no significant differences among colonies on a local scale.

2. Materials and methods

2.1. Sample collection and study area

Unhatched and abandoned eggs ($n = 23$) of Adèlie penguin were

collected during 2021/2022 and 2018/2019 austral summer in the framework of the XXXIV and XXXVII Italian Expedition of National Research Program in Antarctica (PNRA). Fifteen samples, five from each site, were collected at Inexpressible Island (74°54 S, 163°39 E), Adèlie Cove (74°46 S, 164°00 E) and Edmonson Point (74°20 S, 165°08 E) (Fig. 1) during the 2021/2022 austral summer; eight samples were collected at Adèlie Cove ($n = 3$) and Edmonson Point ($n = 5$) during the 2018/2019 campaign. Eggs were collected at the end of the hatching period (December and beginning of January) when found outside the nest, using polyethylene bags, where they were stored and kept at -20°C until laboratory procedures.

Sampling sites lie within or adjacent to Antarctic Specially Protected Areas (ASPAs). Edmonson Point (EP) is situated in the Wood Bay, a large embayment covered by fast ice year-round while Inexpressible Island (II) and Adèlie Cove (AC) are located in the Terra Nova Bay (TNB) overlooking a wind-driven polynya, about 75 km away from EP (Olmastroni et al., 2020). The three sites host Adèlie penguin colonies that together represent a cluster of colonies and constitute a meta-population (Ballerini et al., 2015). With around 24,000 and 11,000 breeding pairs respectively, II and AC are the larger colonies while EP hosts about 2000 breeding pairs (Lyver et al., 2014).

2.2. Chemicals and residue analysis

2.2.1. PCBs, OCPs and PBDEs

Samples were analysed for seven PCB congeners (IUPAC numbers 28, 52, 101, 118, 138, 153, 180), HCB, *p,p'*-DDE and twelve PBDE congeners (IUPAC numbers 17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 209).

Acetone and hexane, glass distilled grade, were purchased from Rathburn Chemicals Ltd., Walkerburn, Scotland. Aluminium oxide (Alumina B, Activity I) was purchased from Thermo Fisher Scientific, Bremen, Germany. Isooctane, sulfuric acid (95–97 %), sodium sulfate anhydrous EMSURE® grade and silica gel 60 (70–230 mesh) for column chromatography were purchased from Merck, Darmstadt, Germany. Among internal and recovery standards ($\geq 99\%$ purity), ^{13}C -labelled BDE-209 and BDE-71 were purchased from CIL, Tewksbury, MA, USA, CB-53 and CB-198 were provided by Ultra Scientific, North Kingstown,

Rhode Island, USA and CB-155 and CB-40 were provided by Prochem, Wesel, Germany and Dr. Ehrenstorfer, Augsburg, Germany, respectively.

Eggs were brushed externally to remove any debris (such as guano or soil residues) then opened to remove the shell and collect the content. Only eggs with a very low embryo development were selected for the analyses. Whole egg content was homogenized and approximately 2.50 g (2.40–2.80 g) (Table S1) were weighted into a 50 ml Falcon® tube, mixed with 8 g of anhydrous sodium sulfate and spiked with a known amount of the recovery standards CB-40 and CB-198. Extraction of the analytes was conducted by a solid-liquid protocol consisting of three sequential extraction (6 ml each) with a mixture of hexane:acetone (3:1, v:v). Then samples were rotary evaporated to 1 ml and cleaned-up with multilayer silica gel and alumina columns (Vorkamp et al., 2004), using 250 ml of hexane. Purified extracts were concentrated under a gentle nitrogen stream and internal standards (CB-55 and CB-155 for the analysis of PCBs and OCPs and BDE-71 for the analysis of PBDEs) were added prior to reaching the final volume of 1 ml. The extractable lipid content was determined gravimetrically evaporating 2.5 ml of the extract to dryness under nitrogen until a steady weight.

PCBs and OCPs were identified and quantified on an Agilent 7890A gas chromatography system coupled to a micro electron capture detector (Agilent, Palo Alto, CA, USA). Two microliters were injected in splitless mode and the separation of the analytes was performed by two Agilent J&W columns (DB-5 and DB-1701 both $60\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness) assembled with an Agilent glass Y-splitter.

PBDEs were analysed on an Agilent 7890B gas chromatography system coupled to a 5977B mass spectrometer (Agilent, Palo Alto, CA, USA). Two microliters were injected in pulsed splitless mode and the chromatographic separation was performed with an Agilent J&W capillary column model DB-5 ($60\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$ film thickness). BDE-209 was analysed with an Agilent 6890 GC, equipped with an Agilent J&W DB-1 model ($15\text{ m} \times 0.25\text{ mm i.d.} \times 0.10\text{ }\mu\text{m}$ film thickness), coupled with a 5973 N mass spectrometer (Agilent, Palo Alto, Ca, USA). The injection volume was 1 μl in pulsed splitless mode. Analysis was performed in selected ion monitoring (SIM) mode with electron capture negative ionization (ECNI). Details on instrumental

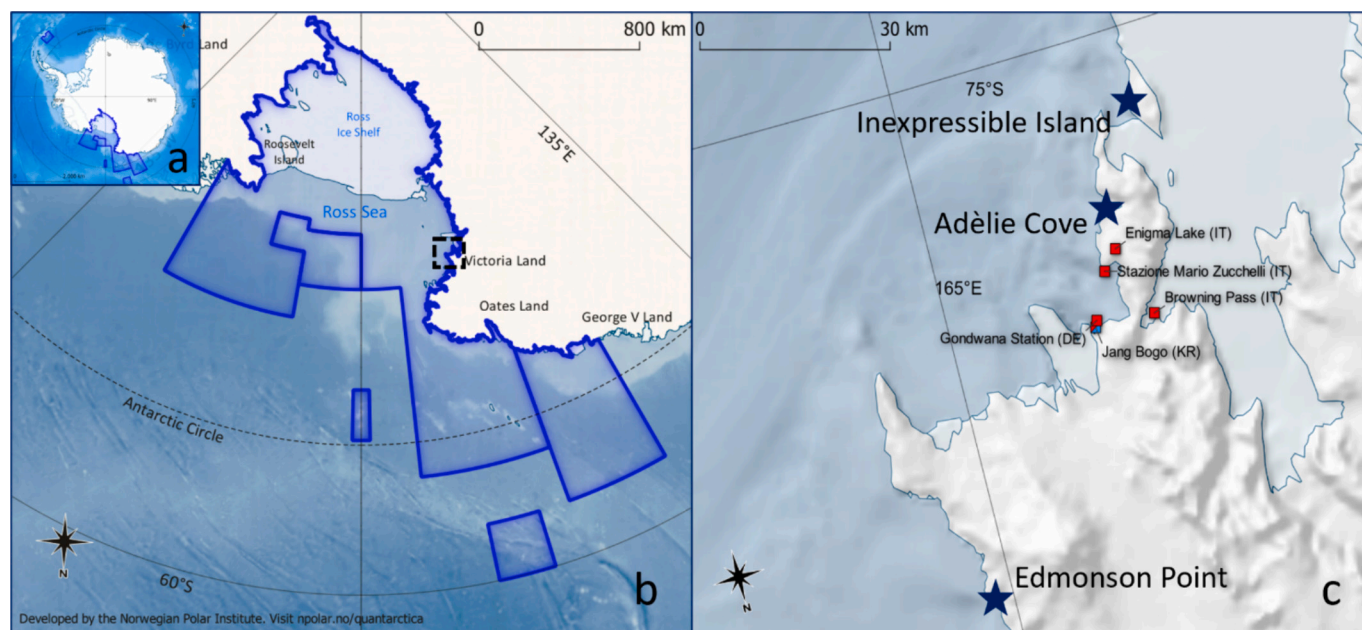


Fig. 1. a) Overview of the Antarctic continent with the indication of the Ross Sea Marine Protected Area (RS-MPA) in blue; b) Focus on the Ross Sea region with the RS-MPA area framed in blue and the study area indicated by a black-traced square; c) coastal area of Victoria Land in the Ross Sea. Blue stars show the sampling site. Red symbols indicate summer-only stations or facilities (e.g., Enigma Lake and Browning Pass airstrips) and blue-red symbol year-round station. The map was created using Quantarctica 3.2 (Matsuoka et al., 2021).

methods settings are provided in Supplementary Information (SI). Quantification was based on the construction of linear duplicate nine-point calibration curves for PCBs, OCPs and BDE-209 (ten-point for the other PBDEs).

All the target compounds showed a significant statistical correlation (Spearman's correlation test, $p < 0.05$) between wet weight concentrations and lipid content (PCBs: $p = 0.0347$, $r = 0.4997$; HCB: $p = 0.0107$, $r = 0.5854$; DDE: $p = 0.0427$, $r = 0.4260$; PBDEs: $p = 0.0281$, $r = 0.5653$). Thus, results were presented on lipid weight (lw) basis. Lipid contents are reported in Table S1.

Recoveries of CB-198 (for PBDEs) and CB-40 (for PCBs and OCPs) were satisfactory in all cases ranging from 85 to 101 % and from 82 to 106 %, respectively (Table S2). Each batch of samples included: one procedural blank, one duplicated sample and two duplicates of internal reference material spiked with all the target compounds to check the accuracy and precision of the method. Relative percentage difference between duplicates was always < 17 % showing good within-batch precision. Blank values were below the lowest quantifiable standards in all the samples. Method detection limits (MDLs) were defined as the lowest calibration standard that could be quantified with a deviation from the theoretical value < 20 % for PBDEs and < 7.5 % for PCBs and OCPs, related to the actual sample intake. The MDLs ranged from 0.28 to 0.56 ng/g lw for PBDEs and 0.58–0.85 ng/g lw for PCBs and OCPs (Table S3).

2.2.2. Ionic PFAS and PFOSA

Samples were analysed for perfluorooctane sulfonamide (PFOSA), five perfluorinated sulfonic acids (PFASs) namely, perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS) and ten perfluorinated carboxylic acids (PFCAs) specifically, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTDA).

Methanol, glass distilled grade, was purchased from Rathburn Chemicals Ltd., Walkerburn, Scotland. Methanol OPTIMA® LC/MS grade was purchased from Fisher Scientific, Bremen, Germany. Acetic acid (glacial) 100 % EMSURE® grade and Acetonitrile LiChrosolv® grade were purchased from Merck, Darmstadt, Germany. ^{13}C -labelled PFAS were purchased from Wellington Laboratories (Guelfh, ON, Canada).

PFAS analysis was based on the method described in Ahrens et al. (2009), with minor modifications. Aliquots of around 1 g (Table S1) of the previously homogenized whole egg content were weighted in polypropylene tubes and spiked with a mix of ^{13}C -PFAS as internal standards, listed in Table S4. Extraction was carried out by adding two times 5 ml of acetonitrile. Extracts were evaporated under nitrogen to 2 ml then cleaned-up using Supelclean™ ENVI-Carb™ cartridges (100 mg, 1 ml, 100–400 mesh, Supelco®, USA) conditioned with 2 ml of acetonitrile and 1 ml of glacial acetic acid 20 % in acetonitrile. After adding 50 μl of glacial acetic acid to the extracts, analytes were eluted with 3 ml of methanol. Cleaned-up extracts were evaporated to dryness under nitrogen and reconstituted with 500 μl of a methanol/2 mM ammonium acetate buffer (50:50, v:v).

Instrumental analysis was performed with a high-performance liquid chromatography (HPLC) system Agilent 1290 Infinity II, equipped with a C18 Kinetex column (2.6 μm particle size, 2.1 \times 100 mm; Phenomenex, Torrance, CA, USA), coupled with an Agilent 6495 triple quadrupole mass spectrometer (Agilent, Palo Alto, CA, USA). Details on the mobile phase gradient and instrumental parameters are provided in the SI. Injection volume was 10 μl and the analysis was performed in multi reaction monitoring (MRM) mode with negative electrospray ionization (ESI). Quantification was based on the construction of a five-point

calibration curve in duplicate. Monitored ions and their corresponding ^{13}C -labelled standards are reported in Table S4. Results are reported in ng/g ww. Overall quality of the method was monitored by participating in the QUASIMEME interlaboratory tests. Every batch of samples included: a procedural blank, at least one sample in duplicate and two QUASIMEME samples in duplicate to check the accuracy and precision of the method. Deviations from the assigned values were acceptable for all the compounds, except for PFTDA, that was accordingly excluded. Relative percentage difference between duplicates was < 10 % for the included compounds. Blanks did not show detectable values. MDLs for PFAS were calculated as three times the standard deviation of the certified (QUASIMEME) samples and ranged from 0.004 to 0.06 ng/g ww (Table S3).

2.2.3. Mercury

Aliquots of the whole egg content previously homogenized were lyophilized in a LIO 5Pascal for 48 h at 0.125 mbar and -53 °C. Then Hg analysis was performed by an inductively coupled plasma mass spectrometer (ICP-MS), NexION 300 \times (Perkin Elmer, Waltham, MA, USA) after acid solubilization with HNO_3 and H_2O (1:1, v:v) in a microwave digestion unit UltraCLAVEIII (MLS GmbH, Leutkirch im Allgäu, Germany). Concentrations are expressed as mg/kg on a dry weight (dw) basis.

Each sample batch included routine procedural blanks and certified reference materials (CRMs), namely DORM-4 fish protein and bovine liver no. 1577b (provided by National Research Council Canada and National Institute of Standards & Technology, USA, respectively). Rhodium ICP standard solution was used as internal standard. Before ICP-MS analysis, L-Cysteine was added to all standards, samples and rinse solution to prevent the memory effects of Hg. Results of each batch were accepted only if data obtained from the CRMs were within the uncertainty range of the certified values (intervals with 95 % confidence). Five replicates of CRMs, subjected to the same procedure as the samples, were analysed to check the analytical precision and the percentage relative standard deviation was 1.6 ± 0.8 %.

2.3. Stable isotopes

Samples were dried at 60 °C for 24 h and ground with a mortar (Abed-Navandi and Dworschak, 2005; Sarà, 2006), then analysed using a Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS). The carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope ratios were expressed as δ values in parts per thousand (‰) relative to Vienna Pee Dee Belemnite for $\delta^{13}\text{C}$ and atmospheric nitrogen (air) for $\delta^{15}\text{N}$, after being computed according to the following equation:

$$\delta X = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 10^3,$$

where X is ^{13}C or ^{15}N , and R represents the ratios $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$.

2.4. Data analysis

Statistical analyses were performed through Excel (Microsoft®) and GraphPad Prism 5.01 (GraphPad Software). Values below MDLs were substituted with zero in sum and average calculations. Compounds below the MDLs in all the samples were excluded. Concentrations were not blank corrected. Due to the available number of samples, it was not possible to test for parametric analysis of variance (ANOVA) assumptions (e.g. normality of data). Accordingly, concentration variation among sites and stable isotope values differences were evaluated through the non-parametric Kruskal-Wallis (KW) test (significance level: $p < 0.05$). Consistently, non-parametric tests were used to test the correlations between concentrations and lipid content (Spearman's correlation test, as above mentioned) and to test differences between years of sampling (Mann Whitney (MW) test). Samples were combined when

they were not significant. In the case of PCBs, PBDEs and PFAS results were combined only if none of the congeners or compounds showed significant differences. Moreover, the five available 2018/2019 samples from EP had already been freeze-dried for another study. An ad hoc experiment (described in SI) on control samples was run to determine if data obtained from dried and wet sample analyses could be combined. According to the described procedures the number of samples reported can vary among sites depending on the compounds.

3. Results and discussion

All the analysed groups of chemicals were found in the Adélie penguin eggs (Table 1). Individual sample concentrations on lipid and wet weight basis are reported in Table S5a and b, respectively.

3.1. Comparison among colonies

As expected, none of the studied pollutants varied significantly among the three sites (\sum PCBs: $p = 0.7961$; p,p' -DDE: $p = 0.6701$; HCB: $p = 0.4000$; \sum PBDEs: $p = 0.3296$; \sum PFAS: $p = 0.1013$; Hg: $p = 0.7900$). During winter penguins from the three colonies are likely to share the same foraging ground (Ballard et al., 2010; Ballerini et al., 2015) and presumably the same happens in late winter (late September – October), when they come back to their breeding areas (Ballard et al., 2010). That period, when they are still at sea, also overlaps with the starting of the egg formation (Astheimer and Grau, 1985; Meijer and Drent, 1999). Thus, the energy resources stored through diet and allocated for the egg formation should be the same for the three colonies as well as the pollutant intake, that will be accordingly transferred to the eggs. Regarding this, Ainley et al. (2003) also suggested that clustered colonies may have a similar diet. Furthermore, Corsolini et al. (2011) found no significant differences in chlorinated POP levels in Adélie penguin eggs collected between Coulman and Inexpressible Islands, thus on a similar spatial scale as our study.

3.2. Stable isotopes

Our results on lack of differences among colonies were further supported by $\delta^{13}C$ and $\delta^{15}N$ values (Table S6) that, on average, ranged from

–30.51 to –30.87 ‰ and from 9.89 to 10.15 ‰, respectively. In fact, no statistically significant differences were found among the three colonies ($\delta^{13}C$: $p = 0.3396$; $\delta^{15}N$: $p = 0.2699$), as expected. Thus, the foraging ecology was quantitatively confirmed to be similar among the three colonies both in terms of foraging ground ($\delta^{13}C$) and individual's trophic position ($\delta^{15}N$), resulting in a similar dietary contaminant exposure during the egg formation period, as previously discussed (Section 3.1).

3.3. POP abundance pattern

The POP abundance pattern, common for the three sites, was p,p' -DDE > HCB > \sum PCBs > \sum PFAS > \sum PBDEs with p,p' -DDE and HCB representing around 50 % and 40 % of the total burden, respectively. This pattern was different from most data reported for Adélie penguin contamination and especially from the Ross Sea in which PCBs always prevailed over p,p' -DDE and/or HCB (Focardi et al., 1993; Court et al., 1997; Corsolini et al., 2002, 2006, 2011, 2017). Instead, it was unexpectedly in line with the pattern generally found in the Antarctic Peninsula (Inomata et al., 1996; Van Den Brink, 1997; Van Den Brink et al., 1998; Schiavone et al., 2009a; Taniguchi et al., 2009; Corsolini et al., 2011; Mello et al., 2016), or in the Indian sector of the East Antarctica (Subramanian et al., 1986), although in most cases, HCB prevails over DDE, contrary to our study. Wild et al. (2022) reported the same pattern (pesticides > PCBs) from East Antarctic coasts (Mawson, Davis and Casey station regions), that generally shows the same pattern as the Ross Sea (Corsolini, 2009), but again showed the prevalence of HCB over p,p' -DDE. Thus, it seemed that these patterns could result from a complex combination of many factors such as site, year of sampling, matrix as well as the number of PCB congeners included in the sum calculation. In our study it could be due to the expected decline of the legacy PCB levels in combination with the steady levels of still in use DDTs, together with a remobilisation of the volatile HCB. It will be important to continue monitoring to understand how the pattern of accumulation of different classes could change and which will be the factors influencing them.

3.4. PCBs

Among the seven PCB indicators (nos. 28, 52, 101, 118, 138, 153,

Table 1

Concentrations of POPs, PFAS and Hg [mean, standard deviation (sd), median, minimum – maximum (min-max)] in the eggs of Adélie penguins collected at the three sampling sites along the Ross Sea coasts. Values are expressed in ng/g wet weight for PFAS, mg/kg dry weight for Hg and ng/g lipid weight for OCPs, PCBs and PBDEs. n = number of samples; *n = 5 for PFAS and PBDEs; **n = 10 for p,p' -DDE.

	Adélie Cove n = 8*				Edmonson Point n = 5**				Inexpressible Island n = 5			
	Mean	SD	Median	Min-max	Mean	SD	Median	Min-max	Mean	SD	Median	Min-max
CB-28	1.09	0.53	1.08	0.50–2.10	0.98	0.17	1.02	0.77–1.17	1.00	0.21	1.02	0.65–1.18
CB-118	3.90	1.25	3.94	2.32–5.53	4.67	1.23	4.99	2.58–5.77	4.46	1.82	4.22	2.51–6.50
CB-138	3.66	1.18	3.45	2.00–5.62	4.85	1.43	4.37	3.04–6.50	4.11	1.05	3.76	2.89–5.30
CB-153	8.94	3.32	8.71	4.51–13.4	10.6	3.07	11.6	5.50–13.7	9.92	4.35	9.22	5.65–16.3
CB-180	3.36	1.33	3.03	1.85–5.36	3.18	0.97	3.36	1.68–4.32	3.08	1.65	2.84	1.69–5.83
\sum PCBs	20.9	6.64	20.0	13.8–30.1	24.3	6.62	25.8	13.7–31.3	22.6	8.87	21.1	13.4–35.1
HCB	134	28.8	137	95.5–167	159	36.3	158	107–209	166	56.2	178	96.4–230
p,p' -DDE	181	44.9	184	132–257	191	68.1	175	106–294	228	90.2	198	128–346
BDE-47	0.67	0.16	0.73	0.51–0.86	0.72	0.21	0.74	0.38–0.92	0.71	0.22	0.71	0.40–0.92
BDE-85	0.36	0.22	0.42	<0.28–0.58	0.19	0.26	0.00	<0.28–0.53	0.47	0.13	0.52	0.28–0.59
\sum PBDEs	1.03	0.26	0.93	0.75–1.32	0.90	0.32	0.92	0.38–1.20	1.18	0.31	1.23	0.68–1.51
PFHxS	0.02	0.01	0.02	0.01–0.04	0.03	0.02	0.03	0.01–0.05	0.02	0.02	0.01	<0.02–0.05
PFOA	0.08	0.07	0.05	0.03–0.19	0.05	0.02	0.05	0.03–0.08	0.09	0.06	0.07	0.05–0.19
PFOS	0.27	0.04	0.27	0.21–0.31	0.25	0.07	0.27	0.14–0.30	0.35	0.10	0.36	0.24–0.45
PFNA	0.03	0.01	0.03	0.03–0.04	0.03	0.01	0.04	0.02–0.04	0.05	0.02	0.05	0.03–0.08
PFDA	0.07	0.01	0.07	0.06–0.09	0.07	0.02	0.07	0.04–0.09	0.11	0.04	0.12	0.07–0.16
PFUnDA	0.30	0.04	0.31	0.24–0.34	0.27	0.06	0.28	0.18–0.34	0.48	0.14	0.48	0.32–0.69
PFDoDA	0.12	0.04	0.14	0.07–0.15	0.16	0.06	0.16	0.08–0.25	0.16	0.05	0.16	0.10–0.22
PFTTrDA	0.16	0.03	0.16	0.11–0.19	0.25	0.16	0.23	0.08–0.45	0.27	0.09	0.24	0.18–0.41
\sum PFAS	1.04	0.11	1.06	0.87–1.17	1.12	0.33	1.15	0.62–1.45	1.53	0.39	1.63	1.05–2.04
PFOSA	1.18	0.26	1.13	0.86–1.46	0.98	0.25	0.91	0.80–1.41	0.96	0.25	1.07	0.64–1.21
Hg	0.13	0.08	0.10	0.06–0.28	0.15	0.08	0.11	0.09–0.26	0.07	0.07	0.08	<0.05–0.16

and 180), PCB-52 and CB-101 were < MDL in all the samples while the other congeners were always > MDL (Table 1).

The mean concentration for the \sum PCBs at the three sites (Table 1) was in line or lower than values reported in literature for penguin eggs (Table S7), both in the Ross Sea (Court et al., 1997; Corsolini et al., 2002, 2006, 2011; Kumar et al., 2002) and other regions (Subramanian et al., 1986; Schiavone et al., 2009a; Cipro et al., 2010; Corsolini et al., 2011; Mello et al., 2016). Lower levels (up to one order of magnitude) than reported by e.g. Corsolini et al. (2006) and Cipro et al. (2010), could be attributable to a complex sum of factors such as diet, local sources, sampling year, matrix, including the analytical technique used. In fact, there was no clear pattern considering only year of sampling or areas when comparing values. Nonetheless, the findings of levels consistent with the past or lower was overall expected for these legacy POPs banned decades ago. Other authors reported a slightly decreasing trend for PCBs in fish (Cincinelli et al., 2016) and penguins (Van Den Brink et al., 2011) until the 2010s.

The abundance of homologues (Fig. 2) was dominated by the hexaCBs (nos. 153 and 138), with PCB-153 showing by far the highest percentage (above 40 % of the \sum PCBs), followed in the order by penta-, hepta- and tri-CBs (nos. 118, 180 and 28, respectively). The pattern was the same at AC and II with a slight difference for EP in which CB-138 and CB-118 were inverted (Fig. 2). The prevalence of hexachlorinated congeners was in line with the results reported by Focardi et al. (1995), Court et al. (1997), Corsolini et al. (2006, 2011), with the predominance of PCB-153 in Court et al. (1997) and Corsolini et al. (2006, 2011), in Adèle penguin samples collected in the same area, as well as with findings by Wild et al. (2022) from the Eastern Antarctic sector. Adèle penguins from the northern Ross Sea colonies mainly prey on krill (*Euphausia superba* Dana, 1850, *E. crystallorophias* Holt & Tattersall, 1906) and fish (*Pleuragramma antarctica* Boulenger, 1902) (Olmastromi et al., 2020). The PCB pattern for those species in the same area was dominated by low chlorinated congeners (Corsolini et al., 2003, 2006) that prevail at the higher latitudes due to their chemical-physical properties (Wania and MacKay, 1996; Wania and Su, 2004). However, lighter congeners, once entered in the trophic web, can be more easily metabolised and thus found at lower percentage compared to heavier molecules in predators, e.g. the hexaCBs that are more resistant to biotransformation (Bengtson Nash et al., 2008; Corsolini et al., 2011; Wild et al., 2022).

3.5. OCPs

HCB and *p,p'*-DDE were found above MDL in all the samples with concentrations up to two orders of magnitude higher than the other POPs (Table 1). These compounds have been reported among the most abundant POPs in Antarctic trophic webs (Corsolini, 2009).

HCB was of the same order of magnitude or one order higher than reported previously for Adèle penguin eggs (Table S7), independently of being collected in the Ross Sea (Court et al., 1997; Corsolini et al.,

2002, 2006, 2011) or other regions (Luke et al., 1989; Schiavone et al., 2009a; Cipro et al., 2010; Corsolini et al., 2011; Mello et al., 2016); moreover, no clear spatial or time trend was observed, like for PCBs probably because of the high number of variables involved in the bioaccumulation process. A circumpolar study by Ellis et al. (2018) reported a declining HCB trend in penguin eggs, these results were not confirmed in our study. Some indirect effects of global warming such as the release from ice melting as suggested by Geisz et al. (2008) for DDE or remobilisation by benthic biota as suggested by Bates et al. (2017) for HCB, may explain such observation.

Regarding *p,p'*-DDE, concentrations found in our samples were always higher (Luke et al., 1989; Court et al., 1997; Corsolini et al., 2002, 2007, 2011) or in the same order of magnitude (Lukowski, 1983; Subramanian et al., 1986; Corsolini et al., 2006, 2011; Geisz et al., 2008; Schiavone et al., 2009a) than previously reported. Chemical-physical properties, volatility and persistence of the studied pesticides, together with their wide past usage (for HCB; Bailey, 2001) and still ongoing usage in the case of DDT (Poza et al., 2017; Zanardi-Lamardo et al., 2019), of which DDE is one of the main metabolite, could contribute to make their levels stable through time and the above-mentioned remobilisation mechanisms could lead to higher levels in marine organisms than measured in the past.

3.6. PBDEs

Among the twelve congeners analysed only BDE-47 and BDE-85 were detected, showing 100 % and 73 % of values > MDL, respectively (Table 1). This agreed with other studies reporting low detection frequency for many BDE congeners in Pygoscelids (Yogui and Sericano, 2009; Mello et al., 2016; Morales et al., 2022).

Very few data are available on concentrations of PBDEs in Adèle penguins (Corsolini et al., 2006, 2017) and more generally in Antarctic seabirds (Mello et al., 2016; Corsolini et al., 2017; Lewis et al., 2022) and to the best of our knowledge only two were conducted on eggs. \sum PBDEs was in line with the first report in penguins from the same area (Corsolini et al., 2006), conducted on samples collected almost thirty years before this study, and were two order of magnitude higher than values reported in Mello et al. (2016) in samples collected at Admiralty Bay (King George Is., South Shetland Islands). Our results were also one to two orders of magnitude higher than Chinstrap and Gentoo penguin eggs from the South Shetland Islands (Mello et al., 2016; Morales et al., 2022) although in the same order of magnitude as results in eggs of the same species from the same place reported in Yogui and Sericano (2009). However, the similarity of our results with those reported in the previous literature (Corsolini et al., 2006), also including those found in other tissues than eggs (Corsolini et al., 2007, 2017; Mwangi et al., 2016; Wild et al., 2022), was in line with the lack of a decreasing trend for PBDEs in Antarctic biota (Markham et al., 2018), contrary to what has been observed in the Arctic after PBDEs were phased out (Vorkamp et al., 2011; Braune et al., 2015).

The congener contribution to the \sum PBDEs was similar at II and AC; BDE-47 was approximately 60 % in samples from II and AC, and ca. 80 % in those collected at EP. BDE-47 is often the most abundant BDE congener in penguins (Corsolini et al., 2006, 2007; Mello et al., 2016; Wild et al., 2022) and in other Antarctic organisms (Markham et al., 2018); interestingly, BDE-85 was detected in our samples. Few authors reported BDE-85 in Adèle (Corsolini et al., 2006) and Gentoo (Morales et al., 2022) penguins in concentrations one (blood) and two (eggs) orders of magnitude lower, respectively. Wolschke et al. (2015) reported BDE-85 in the same order or one order of magnitude lower than our study in Gentoo penguin egg white and yolk (converted assuming 10 % of lipids), respectively. BDE-47 was one of the main congeners of the commercial-pentaBDE mixture (La Guardia et al., 2006), where BDE-85 was also present, although in a very low percentage (La Guardia et al., 2006). Thus, like the other low-mid brominated congeners it can be easily transported to polar regions through long range atmospheric

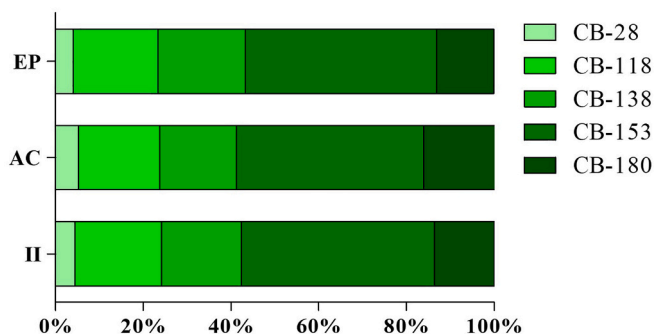


Fig. 2. PCB homologue pattern (%) in eggs from the three sites (Edmonson Point (EP), Adèle Cove (AC), Inexpressible Island (II)).

transport (Wania and Dugani, 2003). Vecchiato et al. (2015a,b) found BDE-85 in lake water and surface snow in Northern Victoria Land. The same congener was also reported in krill (Bengtson Nash et al., 2008) as well as the other constituent of the penta-formulation, mainly BDE-47 and BDE-99 (Bengtson Nash et al., 2008; Markham et al., 2018). Thus, although found rarely or in low concentrations in penguins (compared to the other studied congeners), its biomagnification in the Antarctic trophic web can be suggested.

3.7. Ionic PFAS and PFOSA

Nine out of sixteen compounds were detected and all of them with a detection frequency of 100 % except PFHxS that was < MDL in one sample (detection frequency of 93 %) (Table 1).

Very few studies are available about PFAS in Adèle penguins and among them our results were in line with Schiavone et al. (2009b) and Padilha et al. (2022) (assuming a water content of 70 % (Cipro et al., 2017)). In both cases, Adèle penguin eggs were collected on King George Island (South Shetland Islands). The only previous study from the Ross Sea exclusively investigated PFOS and it was reported as below detection limits (Tao et al., 2006) in Adèle penguin eggs collected in 1995–1996. An increase in concentrations across years could be hypothesised, however, it should be considered that our MDL was ten times lower than the reported detection limit at that time.

The contribution of individual ionic PFAS was nearly the same at the three sites (except PFOA > PFDA at AC and vice versa at the other sites) (Fig. 3) and was dominated by PFUnDA (C₁₁) (24–32 %) followed by PFOS (C₈) (22–25 %). PFCAs dominated the profile with the \sum PFCAs representing >70 % of the \sum PFAS and among them the long-chain (\geq C₉) compounds prevailed. PFSAs were dominated by PFOS over the short-chain PFHxS (C₆), representing >90 % of the \sum PFSAs.

The prevalence of long-chain PFCAs in Adèle penguin samples was in line with other studies (Schiavone et al., 2009b, in eggs; Alfaro Garcia et al., 2022, in chick's plasma; Padilha et al., 2022, in eggs). The occurrence of PFCAs in polar regions was suggested to be a consequence of the atmospheric transport of the fluorotelomer alcohols (FTOHs) being neutral and volatile precursors of PFCAs (Braune and Letcher, 2013; Roscales et al., 2019). The odd > even chain pattern observed by other authors in birds (Tao et al., 2006; Braune and Letcher, 2013; Vorkamp et al., 2019) was confirmed, however, just in the upper part of the profile (C₁₁ > C₁₂). This pattern could be due to the combination of the atmospheric degradation pathway of the FTOHs with the higher bioaccumulation potential of the long-chain compounds (Braune and Letcher, 2013; Bossi et al., 2015; Vorkamp et al., 2019). PFOS has been reported as the prevailing compound in biota worldwide (Butt et al., 2010; Braune and Letcher, 2013). However, our pattern showed that it has been passed by long-chain PFCAs in penguins. PFOS started to be voluntarily phased out in the beginning of the millennium thus, our result may be due to those actions together with the effectiveness of the following restriction measures. Furthermore, long-chain PFCAs,

currently under review by the Stockholm Convention (UNEP, 2021), have been recently reported as increasing in birds and other Arctic species (Butt et al., 2010; Ahrens et al., 2011; Braune and Letcher, 2013; Vorkamp et al., 2019). Finally, PFCAs have been reported as preferentially accumulating in protein rich matrices such as eggs (Gebbink and Letcher, 2012; Braune and Letcher, 2013).

In the literature, PFOSA was detected with a low frequency (Schiavone et al., 2009b) or not detected (Roscales et al., 2019; Wild et al., 2022) in penguins. However, this study showed PFOSA values comparable to those of \sum PFAS and a 100 % detection frequency. PFOSA is a neutral and volatile PFOS precursor (Braune and Letcher, 2013) that can be transported via the atmosphere (Ellis et al., 2003, 2004; Martin et al., 2004; Ahrens et al., 2010; Butt et al., 2010) and reach remote regions where it can be degraded abiotically or by organisms (Martin et al., 2004; Ahrens et al., 2010; Butt et al., 2010).

Although the relative importance of oceanic and atmospheric long-range transport for ionic PFAS and their precursors is still unknown (Bengtson Nash et al., 2010; Roscales et al., 2019; Padilha et al., 2022), PFOSA detection, may suggest atmospheric transport as a source of PFAS to the Ross Sea ecosystem. Besides, PFAS have been previously reported in the atmosphere of polar regions (Dreyer et al., 2009; Cai et al., 2012), further supporting the hypothesis of long-range atmospheric transport as a possible contribution to their occurrence. However, an oceanic input of the ionic PFAS such as PFOS and PFOA, that are the most present PFAS in seawater (Ahrens et al., 2010), cannot be excluded. In fact, although the Antarctic Circumpolar Current (ACC) has been suggested to protect Antarctic ecosystem from oceanic input of PFAS (Bengtson Nash et al., 2010), their long half-lives in water (Falandysz et al., 2022) could make their transport with seawater possible even if delayed. Furthermore, scientific Antarctic stations were also suggested as local sources of PFOS (Wild et al., 2015) to the marine environment. Interestingly, PFHxS (C₆) was also found, even though with a low contribution to the \sum PFAS and was also the only sulfonate together with PFOS. This result highlighted the persistence and bioaccumulation of this recently restricted compound (UNEP, 2022).

3.8. Mercury

Mercury (Hg) was detected in Adèle penguin eggs content with a detection frequency of 89 % with values < MDL only at Inexpressible Island (Table 1).

Our results were in line with values reported for the Ross Sea in Adèle penguin egg content (Calizza et al., 2021) as well as in the albumen (Bargagli et al., 1998) where on average, 92.0 % of the total egg mercury is sequestered as reported for Gentoo penguin (Brasso et al., 2012b). Assuming 70 % of water content, as indicated in Cipro et al. (2017), our results were also of the same order of magnitude as those reported from other sites in East Antarctica (Honda et al., 1986; Luke et al., 1989). Cipro et al. (2017) found a concentration lower than our study in egg content of the same species from King George Island (Antarctic Peninsula). The Ross Sea showed higher Hg concentrations compared to other Antarctic regions, as previously reported (Bargagli et al., 1998; Brasso and Polito, 2013; Cusset et al., 2023) and this finding was attributed to the naturally occurring Hg sources like volcanic atmospheric emissions along the Ross Sea coasts (Bargagli et al., 1998; Cusset et al., 2023) and upwelling dynamics (Bargagli et al., 1998; Ancora et al., 2002). Moreover, Bargagli et al. (1998) highlighted that Hg concentrations in krill, collected in the open waters of the Ross Sea, were two-three times higher than in West Antarctica. However, a recent study from the Antarctic Peninsula (Padilha et al., 2023) reported an Hg mean value nearly twice as much compared to our results, thus further studies are needed to be able to explain this difference. Other studies on egg-related matrices reported Hg levels detected in egg membrane and eggshell, thus hampering further direct comparisons (Dos Santos et al., 2006; Brasso et al., 2012a; Brasso et al., 2014; McKenzie et al., 2021; Jarzynowska et al., 2023) (Table S7).

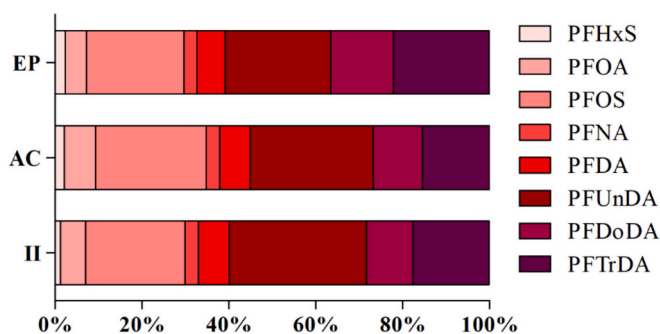


Fig. 3. Individual PFAS contribution (%) to the \sum PFAS in eggs from the three sites (Edmonson Point (EP), Adèle Cove (AC), Inexpressible Island (II)).

Hg maternal transfer to the eggs is well known (Bargagli et al., 1998; Brasso et al., 2012b, 2015), and as reported in Honda et al. (1986) eggs may reach Hg levels similar to the female body burden. Accordingly, although feathers are considered the major excretion route for penguins (Honda et al., 1986; Ancora et al., 2002; Souza et al., 2020; Cusset et al., 2023), and reflect a different exposure time, the period between two moulting episodes (almost one year, Cusset et al., 2023) versus from late winter to the pre-breeding period (Brasso et al., 2012a; Mello et al., 2016; Padilha et al., 2022), eggs seemed to show an important Hg load, as also suggested previously by Calizza et al. (2021).

4. Conclusions

This is the first study reporting the occurrence of some of the most widespread legacy pollutants, i.e. POPs and Hg, after the establishment of the RS-MPA in 2017. PCBs, PBDEs, OCPs, PFAS, and Hg were analysed in unhatched eggs of Adélie penguins collected from three colonies of the same metapopulation along the Ross Sea coasts. No statistically significant differences were found in the contamination levels, as expected from their feeding and reproductive habits, suggesting the three colonies as being equally representative of the MPA ecosystem. As expected, Hg and legacy POPs mostly showed similar levels compared to the past, but PCBs are not more abundant than OCPs suggesting that some changes could have occurred involving climate-driven remobilisation mechanisms for these semi-volatile compounds. Moreover, PFAS levels in penguins from the Ross Sea were reported for the first time, confirming their widespread distribution and suggesting volatile precursors as the main source. Further efforts in the future would be useful to overcome the limitations of the study and obtain larger sample sizes, thus increasing the power of the applied statistical tests and improving our ability to detect differences within colonies or years. These data, obtained analysing eggs of the most studied and iconic species of the Antarctic Region, provide an overall update of the chemical contamination of the Ross Sea ecosystem, and will represent a starting point for future monitoring to evaluate the effectiveness of the restriction measures applied with the institution of the RS-MPA and with regulation of chemicals of concern.

CRediT authorship contribution statement

Nicolas Pala: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Katrin Vorkamp:** Writing – review & editing, Supervision, Resources. **Rossana Bossi:** Writing – review & editing, Supervision, Resources, Methodology, Formal analysis. **Stefania Ancora:** Writing – review & editing, Supervision, Formal analysis. **Nicoletta Ademollo:** Writing – review & editing, Supervision, Conceptualization. **Davide Baroni:** Writing – review & editing, Supervision. **Gianluca Sarà:** Writing – review & editing, Formal analysis. **Simonetta Corsolini:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.174562>.

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