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Wide range of metallic and organic contaminants in various tissues of the Antarctic prion, a planktonophagous seabird from the Southern Ocean

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HIGHLIGHTS

- Trace elements and POPs were measured in various tissues of 10 Antarctic prions.
- Residue diversity was notable given the species' small size and low trophic position.
- Cd, Se, BDE 183 and 209 showed noticeably high internal tissue concentrations.
- Several POPs showed inter- and intra-tissue correlations, indicating co-exposure.
- Blood was validated as a good bioindicator of internal tissue As and Hg levels.

GRAPHICAL ABSTRACT

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ABSTRACT

Trace elements (n = 14) and persistent organic pollutants (POPs, n = 30) were measured in blood, liver, kidney, muscle and feathers of 10 Antarctic prions (*Pachyptila desolata*) from Kerguelen Islands, southern Indian Ocean, in order to assess their concentrations, tissue distribution, and inter-tissue and inter-contaminant relationships. Liver, kidney and feathers presented the highest burdens of arsenic, cadmium and mercury, respectively. Concentrations of cadmium, copper, iron, and zinc correlated in liver and muscle, suggesting that uptake and pathways of metabolism and storage were similar for these elements. The major POPs were 4,4′-DDE, mirex, PCB-153 and PCB-138. The concentrations and tissue distribution patterns of environmental contaminants were overall in accordance with previous results in other seabirds. Conversely, some Antarctic prions showed surprisingly high concentrations of BDE-209. This compound has been rarely observed in seabirds before, and its presence in Antarctic prions could be due to the species feeding habits or to the ingestion of plastic debris. Overall, the study shows that relatively lower trophic level seabirds (zooplankton-eaters) breeding in the remote southern Indian Ocean are exposed to a wide range of environmental contaminants, in particular cadmium, selenium and some emerging-POPs, which merits further toxicological investigations.

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1. Introduction

Trace elements and persistent organic pollutants (POPs) are commonly found in terrestrial and aquatic ecosystems worldwide (Walker et al., 2012). These environmental contaminants come from both natural and anthropogenic sources, and can exhibit toxic properties causing endocrine dysfunction, mutagenesis, or reproductive and behavioural disturbances (e.g., Scheuhammer, 1987; AMAP, 2004; Walker et al., 2012). Although polar marine environments are isolated from the major emission sources, they are reached by trace elements and POPs through atmospheric and oceanic transport (Fitzgerald et al., 2007; Galbán-Malagón et al., 2013). Many contaminants, such as mercury (Hg) and POPs bioaccumulate in organisms and biomagnify in food webs (Morel et al., 1998; Fisk et al., 2001). Thus, polar marine predators usually bear high burdens of contaminants (Bustnes et al., 2003; Bargagli, 2008), with exposure being governed by various factors such as foraging habitat and trophic position (Fisk et al., 2001; Carravieri et al., 2013). Seabirds are often considered to be ideal models to biomonitor contaminants in the marine environment, since they forage over large geographic areas and feed at different trophic levels (Furness and Camphuysen, 1997). In contrast to Arctic species (e.g., Braune et al., 2005; Dietz et al., 2009), contaminant exposure of Southern Ocean seabirds has received little attention, although pioneer studies have reported a wide diversity of compounds in their tissues (Bocher et al., 2003; Tao et al., 2006; Anderson et al., 2010).

Several tissues have been used to evaluate seabird contamination, particularly feathers (e.g., Bustnes et al., 2002; Seco Pon et al., 2011), blood (e.g., González-Solís et al., 2002; Bustnes et al., 2007) and soft tissues such as liver (e.g., Colabuono et al., 2012; Jerez et al., 2013). The interpretation of contaminant burdens in these tissues depends on the understanding of contaminant dynamics within the whole organism. For instance, blood has a transport role for contaminants, and circulating concentrations are believed to reflect short-term dietary exposure (Burger and Gochfeld, 1997). On the other hand, the liver and kidney are specifically involved in contaminant detoxification and/or storage, while muscles could function as a temporary storage tissue (Lewis and Furness, 1991). Finally, feathers are known to sequester both metallic and organic contaminants during their synthesis (Burger, 1993; García-Fernández et al., 2013). Overall, however, these mechanisms are still poorly known for the large majority of environmental contaminants. Namely, there have been only few comprehensive studies that have simultaneously quantified trace elements and POPs in a suite of seabird tissues, and that have investigated between-contaminant and between-tissue relationships (Eagles-Smith et al., 2008; Colabuono et al., 2012). Data are particularly lacking for low trophic level seabirds, because they usually bear lighter burdens of contaminants than top predators, with residues being more difficult to detect.

The present study describes the concentrations of 14 trace elements and 30 POPs (seven polychlorinated biphenyls, PCBs; 12 organochlorine pesticides, OCPs; and 11 polybrominated diphenyl ethers, PBDEs) in several internal tissues and in feathers of 10 Antarctic prions (*Pachyptila desolata*) from Kerguelen Islands, a remote subantarctic archipelago in the southern Indian Ocean. The Antarctic prion breeds in Antarctic and subantarctic islands, with important populations at South Georgia (southern Atlantic Ocean), Auckland (southern Pacific Ocean) and Kerguelen Islands (Weimerskirch et al., 1989; Marchant and Higgins, 1990). At the latter locality, breeding Antarctic prions forage in cold waters where they prey primarily on swarming crustaceans (pelagic amphipods) to feed their chicks (Weimerskirch et al., 1999; Cherel et al., 2002). The composition of stomach oil indicates that adults also prey on mid-water fish when they feed for themselves (Connan et al., 2007). During the inter-breeding season, birds shift north to the warmer subtropical waters where they moult (Quillfeldt et al., 2015).

Our main goal was to investigate the contaminant distribution pattern, and inter-tissue and inter-contaminant relationships, in order to depict co-exposure and/or similar bioaccumulation and detoxification patterns among contaminants. Furthermore, correlations of soft tissue burdens with blood and/or feather concentrations is necessary to validate the use of these tissues as appropriate proxies of internal contamination, which has surprisingly received little attention in polar seabirds (Henriksen et al., 1998; Bustnes et al., 2003). Based on previous knowledge (Bocher et al., 2003), we expected the liver to bear high contaminant burdens when compared to other organs, and feathers to present high Hg concentrations, considering their excretory role (Braune and Gaskin, 1987). Given the relatively low trophic level, and thus potentially low contaminant exposure of Antarctic prions, we expected overall low contaminant concentrations in this species when compared to higher trophic level seabirds from the same environments.

2. Materials and methods

2.1. Sample collection and preparation

Ten freshly dead Antarctic prions trapped in the vegetation (*Acaena adscendens*) were opportunistically collected on January 26th, 2012, on the Kerguelen archipelago (49°21′S, 70°18′E), southern Indian Ocean. Only intact specimens were collected and then stored at −20 °C until dissection. Age and breeding status of birds were not known. However, because in Kerguelen Islands Antarctic prions' eggs are laid in December (incubation of the single white egg takes 44–46 days) and chicks fledge at 45–55 days old (Weimerskirch et al., 1989) these birds cannot be newly fledged chicks.

During necropsies, internal tissues (liver, kidneys and pectoral muscle) were sampled, weighed and wrapped individually in plastic bags and in aluminium foils for trace element and POP analyses, respectively. The stomachs were also dissected in order to check their contents. Plastic debris were found in five individuals. Clotted blood was collected from heart auricles and stored in microtubes at −20 °C. Four body feathers were pulled out from the lower back and stored dry in plastic bags. Birds were first sexed during necropsies by visual gonad examination. Sex was then confirmed using the molecular method described by Fridolfsson and Ellegren (1999). Prior to chemical analyses, internal tissues and blood were freeze-dried, ground to powder and then stored in plastic and glass tubes for trace element and POP analyses, respectively. Feathers were washed to remove surface dirt and adsorbed contaminants in a chloroform-methanol solution and then oven dried as described by Carravieri et al. (2013). For each individual, the four body feathers were pooled to limit potential inter-feather differences in trace element concentrations (Carravieri et al., 2014a); feathers were homogenised by cutting them with scissors into small fragments (1–2 mm). Samples were weighed before and after freeze-drying to calculate water content (moisture, see Table S1, Supplementary material).

2.2. Analyses of trace elements

Trace elements were determined in blood, liver, kidney, muscle and feathers. Total Hg analysis was carried out with an advanced mercury analyser (ALTEC AMA 254) on dried tissue aliquots (2–4 mg) following Blévin et al. (2013). All analyses were repeated 2–3 times until having a relative standard deviation <10%. Accuracy was checked using TORT-2 Lobster Hepatopancreas (NRC, Canada) as certified reference material (CRM) with a certified Hg concentration of 0.27 ± 0.06 μg g^{-1} dry weight (dw). Our measured values were 0.267 ± 0.006 μg g^{-1} dw ($n = 18$). Thirteen other elements (silver, Ag; arsenic, As; cadmium, Cd; cobalt, Co; chromium, Cr; copper, Cu; iron, Fe; manganese, Mn; nickel, Ni; lead, Pb; selenium, Se; vanadium, V; and zinc, Zn) were analysed using a Varian Vista-Pro ICP-OES and a Thermo Fisher Scientific X Series 2 ICP-MS (following Métian et al., 2008). Aliquots of the biological samples (30–300 mg) were digested with 6 ml 67–70% HNO_3 and 2 ml 34–37% HCl (Fisher Scientific, trace element grade quality), except for feathers (1.8 ml HNO_3 and 0.6 ml HCl).

Acidic digestion was carried out overnight at room temperature and then in a Milestone microwave (30 min with constantly increasing temperature up to 120 °C, and finally 15 min at this maximal temperature). Each sample was completed to 50 ml (15 ml for feathers) with milli-Q water. Three control samples (two CRM, and one blank) treated and analysed in the same way as the samples were included in each analytical batch. CRMs were DOLT-4 dogfish liver (NRC, Canada) and TORT-2 (NRC, Canada). The results were in good agreement with CRMs, with a mean recovery rate of 87–104% for DOLT-4 and 88–102% for TORT-2. The limits of detection (LoD) are given in Table S2, Supplementary material. Trace element concentrations are expressed in μg g^{-1} dw.

2.3. Analyses of persistent organic pollutants (POPs)

POPs were analysed in liver, kidney and muscle. Seven indicators PCBs (CBs 28 + 50, 52, 101, 118, 138, 153, and 180) were targeted. These compounds are predominantly present in biotic and abiotic matrices and were thus recognised as compounds representative of the whole group of PCBs by the Agency for Toxic Substances and Disease Registry (ATSDR, 2000). Additionally, 12 OCPs (HCB, γ-HCH, heptachlor, cis-chlordane, trans-nonachlor, 2,4′-DDE, 4,4′-DDE, 2,4′-DDD, 4,4′-DDD, 2,4′-DDT, 4,4′-DDT and mirex) and 11 PBDEs (BDEs 17, 28, 47, 49 + 71, 66, 99, 100, 153, 154, 183 and 209) were also assayed. PCB and OCP standard solutions were provided by NIST (via LGC Standards, Molsheim, France, see Table S3, Supplementary material) while PBDE standards were provided by Wellington Laboratories (via BCP Instruments, Irigny, France). Analytes were extracted using microwave assisted extraction (Milestone Start-E) with 10 ml of dichloromethane on homogenised freeze-dried samples (0.2–1.0 g) spiked with internal standards: CBs 30, 103, 155 and 198, F-BDE-47 (Chiron, via BCP Instruments), DDTd8 (supplied by Dr. Ehrenstorfer), BDE-181 (Wellington Laboratories) and BB-209 (LGC Standards, Molsheim, France) (5–8 ng each) (Müller et al., 2001; Tapie et al., 2008). Extracts were reconcentrated into 300 μl of isooctane, using a RapidVap vacuum evaporation system from Labconco (Kansas City, MO, USA) and a nitrogen flow, prior to purification on acid silica gel column. PCBs, OCPs and PBDEs were eluted with 3 x 5 ml of pentane/dichloromethane (90/10; *v*/*v*), and final extracts were concentrated and transferred into isooctane as solvent keeper. Octachloronaphthalene (1 ng) was added as performance standard to quantify internal standards. Lipids were determined by gravimetry after filtration and evaporation of an aliquot of the DCM extract. PCBs and OCPs analyses were carried out on an HP 5890 series II gas chromatograph from Hewlett-Packard (Avondale, CA, USA) coupled to a ^{63}Ni electron capture detector (ECD). A capillary column HP5-MS (Agilent Technologies, Massy, France) was used (30 m × 0.25 mm × 0.25 μm). Helium (He, 5.6 quality, Linde Gas, Toulouse, France) was used as carrier gas at a flow rate of 1 ml min^{-1} and nitrogen (N_2, 5.0 quality, Linde Gas, Toulouse, France) was used as make up gas (60 ml min^{-1}). The injector temperature was 280 °C and detector temperature was 320 °C (Tapie et al., 2011).

PBDEs were analysed by gas chromatography coupled with mass spectrometry operated in negative chemical ionisation (GC–NCI-MS). Analyses were carried out using an Agilent 6890N GC coupled to a Quattro Micro GC (Waters Micromass). The system was fitted with J&W HP-5MS analytical column (15 m, 0.25 mm ID × 0.25 μm film thickness; Agilent Technologies, Massy, France) and operated in pulsed splitless injection mode (1.7 bar, 3 min) with an injector temperature of 280 °C. The helium carrier gas flow rate was 1.8 ml min^{-1} and temperature programme was as follows: 90 °C (0.1 min), 185 °C (25 °C min^{-1}), 275 °C (15 °C min^{-1}), and 305 °C (35 °C min^{-1}, held for 2 min). The transfer line temperature and the source temperature were set at 300 °C and 250 °C, respectively. Ions were monitored in SIM mode using a single acquisition window, with a dwell time set at 50 ms. $[Br]^-$ (m/z 79 and 81) was monitored for all PBDEs while m/z 402 and 404 were monitored for OCN.

PCBs, OCPs and PBDEs compounds were quantified relative to internal standards. CBs 30, 103, 155 and 198 were used to quantify PCBs, and DDTd8 was used to quantify OCPs, whereas F-BDE-47, BDE-181 and BB-209 were used to quantify PBDEs. A syringe standard (octachloronaphthalene) was used to quantify internal standards and verify recoveries for each sample. Quality control consisted of the analysis of solvent procedural blanks, reproducibility and repeatability tests, injection of standard solutions as unknowns, and CRM analysis (SRM 1947, National Institute of Standards and Technology, USA) for PCBs, OCPs (except for γ-HCH, heptachlor and cis-chlordane), and PBDEs (except for BDEs 17, 18, 49, 71, 183 and 209). Procedure details are given in Tapie et al. (2008). As described by Labadie et al. (2010), POP concentrations were blank corrected and the LoD was derived from the blank value variability. For analytes that were not detected in blanks, LoD was determined as the concentration with a signal to noise ratio of three. Regardless of the approach used for LoD calculation, the LoQ was set at three times the LoD for all analytes. LoD and LoQ values are reported in Table S4, Supplementary material.

2.4. Statistical analyses

Tissue contaminants with concentrations >LoQ in <70% individuals were included in summary statistics but excluded from subsequent statistical analyses (Borgå et al., 2006; Anderson et al., 2010). Therefore, contaminants included in statistical analyses were 10 trace elements (As except in feathers, Cd, Cr except in blood, Cu, Fe, Hg, Mn, Ni except in blood and feathers, Se and Zn), 4 PCBs (CBs 118, 138, 153 and 180), 9 OCPs (HCB, γ-HCH and 2,4′-DDE except in kidney, cis-chlordane, trans-nonachlor, 4,4′-DDE, 4,4′-DDD and 4,4′-DDT only in muscle, and mirex), and only 2 PBDEs (BDE-28 except in kidney, and BDE-183 only in muscle). For these contaminants, concentrations <LoQ and the detection limit (LoD) were replaced by LoQ * 0.5 and LoD * 0.5, respectively, and considered for statistical analyses (Anderson et al., 2010). Statistical analyses were performed using R 2.15.1 (R Core Team, 2012) mainly following Crawley (2007). All data were first checked for normality and homogeneity of variances by means of Shapiro–Wilk and Bartlett tests, respectively. In general, these assumptions were not achieved, non-parametric analysis of variance was thus applied to assess differences in contaminant concentrations between tissues or gender (Wilcoxon tests). Relationships between contaminant concentrations within and between tissues were tested using Spearman correlation rank tests. For these latter tests, the sum (Σ) of different POP categories was also considered (i.e., Σ_7PCBs, Σ_{12}OCPs, Σ_{11}PBDEs and Σ_{30}POPs). Statistical significance of correlation coefficients was evaluated by using a bootstrap estimation method (Hall, 1992), with details being presented in Tables S5, S6, S7 and S8 of the Supplementary material. Concentrations are presented as mean ± standard deviation (SD) in μg g^{-1} or ng g^{-1} dw.

3. Results

3.1. Influence of sex on trace element and POP concentrations

No consistent gender differences were found in tissue concentrations of trace elements and POPs. Hence, female (n = 5) and male (n = 5) data were pooled for subsequent statistical analyses. Only five out of 101 comparisons were significantly different, namely (i) higher As and Cd concentrations in blood (respectively Wilcoxon test, W = 1, p = 0.019; W = 1.5, p = 0.027), and (ii) lower Hg concentrations in blood (W = 25, p = 0.012), kidney (W = 24, p = 0.016) and muscle (W = 22.5, p = 0.046) and slightly lower in liver (W = 21, p = 0.094) of females than males.

3.2. Tissue distribution of trace elements

Of all the targeted 14 trace elements, only Ag, Pb and V had concentrations below the LoD in all or almost all tissues (Table 1). Kidney and feathers presented the highest concentrations of the non-essential elements Cd and Hg, respectively (Wilcoxon test, $0 < W < 100$, $0.002 < p < 0.0002$) (Fig. 1). Liver presented the highest concentrations of the essential elements As, Fe, Mn and Zn (Wilcoxon or t tests, $81 < W < 100$ or $6.48 < t < 15.7$, all $p < 0.0001$), muscle had the highest amount of Cu ($95 < W < 100$, all $p < 0.0001$) and blood showed the highest amount of Se ($1.18 < t < 8.99$, $0.0001 < p < 0.015$).

3.3. Between-tissue and between-trace element relationships

Between-tissue relationships were investigated for each trace element. Only 11 correlations were significant out of 140, of which 8 were between blood and soft tissues. Significant positive relationships were found for Hg between blood and all soft tissues (Spearman test, $0.694 < rho < 0.776$, $0.008 < p < 0.026$) (Fig. 2), and between muscle and liver and kidney ($rho = 0.661$ and 0.646, $p = 0.038$ and 0.043, respectively). Significant positive correlations were also found for As between blood and kidney ($rho = 0.778$, $p = 0.009$). Between-element relationships were investigated within each tissue. Concerning non-essential trace elements, there were only significant relationships between Cd and Hg in liver ($rho = 0.693$, $p = 0.026$). Among essential elements, correlations were particularly strong between Cr and Ni in liver, kidney and muscle ($0.889 < rho < 0.957$, $0.0001 < p < 0.0006$). Other significant relationships involved Cu, Fe, Mn and Zn in blood ($0.711 < rho < 0.862$, $0.004 < p < 0.018$), liver ($0.713 < 0.764$, $0.013 < p < 0.041$) and muscle ($0.841 < rho < 0.934$, $0.0003 < p < 0.004$). Cd was involved in the majority of relationships between essential and non-essential elements in all tissues (for example in blood: As–Cd, Cd–Cu, Cd–Fe, Cd–Mn and Cd–Zn; and in muscle: Cd–Cu, Cd–Fe, Cd–Mn and Cd–Zn).

3.4. Tissue distribution of POPs

Of the 30 targeted POPs, only the following were below the LoD in all samples: 2,4′-DDD, BDE-17, BDE-49 + 71, BDE-66, and BDE-100 (Table 2). In all tissues, the PCB pattern was dominated by CB-153 > CB-138 > CB-118, which together accounted for more than 75% of the PCB burden. The prevalent OCPs were 4,4′-DDE > mirex > HCB, totalling more than 90% of the OCP burden. Among PBDEs, the highest concentrations were reported for BDE-209, but only three individuals had quantifiable levels. In contrast to PCBs and PBDEs, OCP concentrations varied among tissues (Fig. 3). Namely, γ-HCH, 2,4′-DDE, cis-chlordane and trans-nonachlor concentrations were higher in liver and muscle than in kidney (Wilcoxon test, $22 < W < 83$, $0.015 < p < 0.045$), and HCB concentrations were higher in liver and kidney than in muscle ($7 < W < 18$, $0.0005 < p < 0.015$).

3.5. Between-tissue and between-POP relationships

All between-tissue correlations were significant for Σ_{30}POPs and Σ_{12}OCPs (Spearman test, $rho > 0.7$, $p < 0.045$). Several individual PCB and OCP compounds were also significantly correlated between tissues, in particular between liver and kidney (4,4′-DDE, mirex, HCB, CB-138, CB-153 and CB-180, Fig. 4). Relationships between POPs within each tissue were also determined. Σ_7PCBs and Σ_{12}OCPs were significantly correlated in muscle, kidney and liver ($0.842 < rho < 0.879$, $0.002 < p < 0.004$). Significant relationships were found within two groups of compounds. The first group consisted of 4,4′-DDE, mirex, HCB, trans-nonachlor, CB-138, CB-153 and CB-180, which correlated in liver, kidney and muscle (Fig. 5). Additionally, 4,4′-DDD was strongly correlated to these compounds in muscle ($0.873 < rho < 0.932$, $0.001 < p < 0.004$). The second group consisted of γ-HCH, 2,4′-DDE, cis-chlordane, CB-118 and BDE-28, which correlated in liver

Table 1
Trace element concentrations (mean ± SD, μg g^{-1} dw; number of samples above the limit of detection (LoD) are given in brackets) in blood, liver, kidney, muscle and feathers of 10 Antarctic prions from Kerguelen Islands.

	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	V	Zn
Blood	<LoD	0.55 ± 0.20 (9)	1.2 ± 0.4 (10)	<LoD	0.10 (<LoD–0.10) (2)	2.5 ± 1.9 (10)	1620 ± 397 (10)	0.67 ± 0.11 (10)	0.65 ± 0.20 (10)	<LoD	<LoD	102 ± 33 (10)	<LoD	32 ± 10 (10)
Liver	<LoD	2.7 ± 0.8 (10)	36 ± 8 (10)	0.17 ± 0.05 (10)	2.7 ± 1.3 (10)	23 ± 6 (10)	2465 ± 863 (10)	1.8 ± 0.3 (10)	16 ± 4 (10)	1.1 ± 0.6 (10)	<LoD	73 ± 18 (10)	<LoD	249 ± 40 (10)
Kidney	<LoD	0.78 ± 0.25 (10)	105 ± 37 (10)	0.23 ± 0.04 (10)	3.1 ± 1.3 (10)	15 ± 3 (10)	568 ± 63 (10)	0.88 ± 0.16 (10)	6.9 ± 1.0 (10)	1.6 ± 0.7 (10)	<LoD	88 ± 17 (10)	<LoD	147 ± 18 (10)
Muscle	<LoD	0.93 ± 0.20 (10)	2.8 ± 0.8 (10)	0.10 ± 0.02 (10)	2.2 ± 1.1 (10)	37 ± 6 (10)	559 ± 108 (10)	0.28 ± 0.06 (10)	4.0 ± 0.6 (10)	0.83 ± 0.48 (9)	<LoD	34 ± 5 (10)	<LoD	92 ± 15 (10)
Feathers	<LoD	0.37 (<LoD–0.51) (2)	0.06 ± 0.03 (10)	<LoD	0.49 ± 1.05 (8)	6.1 ± 2.1 (10)	12.5 ± 5.4 (10)	2.8 ± 1.2 (10)	1.1 ± 0.7 (10)	0.71 (<LoD–1.34) (4)	0.15 ± 0.09 (10)	6.5 ± 2.5 (10)	<LoD	72 ± 19 (10)

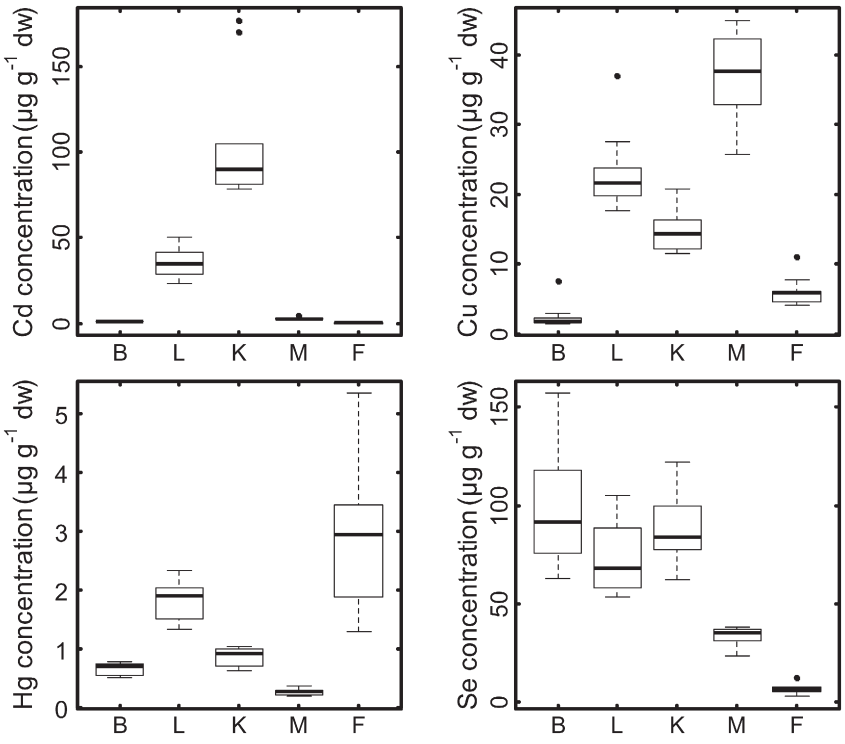

Fig. 1. Cd, Cu, Hg and Se concentrations (µg g^{-1} dw) in blood (B), liver (L), kidney (K), muscle (M) and feathers (F) of Antarctic prions from Kerguelen Islands (n = 10).

(0.951 < rho < 0.644, 0.001 < p < 0.004). In muscle, significant correlations were only found between γ-HCH and 2,4′-DDE (rho = 0.832, p = 0.001), 4,4′-DDT and 2,4′-DDE (rho = 0.673, p = 0.028), and between cis-chlordane and CB-118 (rho = 0.861, p = 0.002). The same correlations were highlighted using concentrations normalised by lipid content.

4. Discussion

Contaminant levels of procellariiform seabirds in the southern Indian Ocean have been previously investigated, focussing on trace elements (Hindell et al., 1999; Bocher et al., 2003; Blévin et al., 2013; Carravieri et al., 2013, 2014a, 2014b, 2014c) and POPs (Guruge et al., 2001a, 2001b; Tanabe et al., 2004; Carravieri et al., 2014b). However, to our knowledge, the present study is the first to consider such a large number of contaminants (n = 30), in particular PBDEs, measured on a significant number of tissues (n = 3 to 5) of the same individual birds (n = 10). The extent of metallic and organic contamination in the species is remarkable when considering both its small size and relatively low trophic position.

4.1. Tissue distribution of trace elements: comparison with other seabirds and other areas

Essential element concentrations (As, Co, Cu, Fe, Mn, Se and Zn) in internal tissues and feathers were in accordance with most previous studies on Southern Ocean Procellariiformes (Lock et al., 1992; Bocher et al., 2003; Seco Pon et al., 2011; Jerez et al., 2013). Surprisingly however, Cu and Fe concentrations in feathers were 30 and 100 times lower, respectively, than those observed in Antarctic prions from South Georgia (Anderson et al., 2010). In this last study, Cu and Fe concentrations were largely variable between individuals. Moreover, feathers were cleaned, but not washed prior to analysis, which may have introduced some errors into trace element results (Anderson et al., 2009), especially when considering that Antarctic prions nest in burrows or rock crevices. In contrast to soft tissues and feathers, essential element concentrations in blood were not in accordance with the literature (e.g., González-Solís et al., 2002; Anderson et al., 2010), with concentrations being higher than expected for Cu, Mn and Zn, and lower for Fe. This could be linked to the fact that blood was collected from heart auricles after death, instead of being sampled from living animals. The birds of the present study probably died of exhaustion, which could influence blood essential element concentrations. Previous research showed that body condition is one of the most important factors influencing essential element concentrations in blood, especially in the case of Cu, Fe and Zn (Debacker et al., 2000; Malinga et al., 2010). No major differences, except for blood, were found in essential element concentrations between Antarctic prions and seabirds feeding at higher trophic levels, such as albatrosses (e.g., Kim et al., 1998; Seco Pon et al., 2011). This is not surprising since essential elements are submitted to homeostatic control, with their absorption being regulated according to the nutritional requirements of the individual (Walsh, 1990). As expected, Fe, Mn and Zn were preferentially accumulated in the liver, where they appeared to be closely regulated (Elliott and Scheuhammer, 1997). In contrast and as previously observed by Bocher et al. (2003), Cu concentration was higher in muscle than in liver. This accumulation pattern has been reported in Barau's petrels (*Pterodroma baraui*) and Audubon's shearwaters (*Puffinus lherminieri bailloni*) from Réunion Island (Kojadinovic et al., 2007a). Se distribution in prion soft tissues is in agreement with previous works showing that this essential element is preferentially retained in kidney (e.g., Kim et al., 1998; Mendes et al., 2008). As already shown in Antarctic prions and other planktonophagous petrels at South Georgia (Anderson et al., 2010), blood Se concentrations were high, especially in comparison to wandering albatrosses from the southern Indian Ocean (Carravieri et al., 2014b). At the Kerguelen Islands, Antarctic prions feed largely on the pelagic amphipod *Themisto gaudichaudii* (Cherel et al., 2002), which bear large quantities of Se (Anderson et al., 2010). This suggests that the large Se burden in Antarctic prions' blood is diet-derived.

Tissue concentrations of the non-essential elements Cd, Hg and Pb were in the same range of those found in small planktonophagous petrels at Kerguelen Islands (Bocher et al., 2003) and in other Procellariiformes worldwide (Kim et al., 1998; Kojadinovic et al., 2007a; Anderson et al., 2009, 2010; Bond and Lavers, 2011). Pb

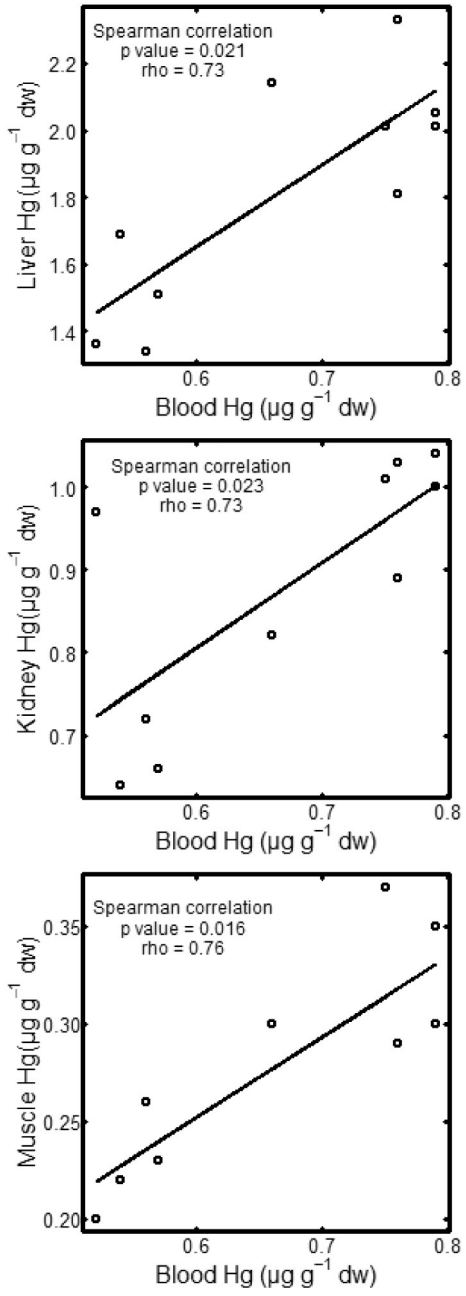

Fig. 2. Relationships between Hg concentrations (µg g^{-1} dw) in liver, kidney and muscle versus those in blood of Antarctic prions from Kerguelen Islands (n = 10).

concentrations were below the LoQ in all soft tissues but not in the feathers of Antarctic prions, as previously shown in seabirds (Jerez et al., 2013), likely because this non-essential element is preferentially accumulated in bone or feathers rather than in soft tissues (Scheuhammer, 1987). Antarctic prion Cd concentrations were higher than those found in fish-eating seabirds (Agusa et al., 2005; Mendes et al., 2008). Blood Cd concentrations were notably higher than those of the wandering albatross from the same subantarctic environments (Carravieri et al., 2014b). This is not surprising because Cd is not biomagnified through marine food webs, thus resulting in some cases in higher Cd concentrations in consumers with lower trophic positions (Sanchez-Hernandez, 2000). The high Cd burden of Antarctic prions could be explained by their significant consumption of *T. gaudichaudii* (Cherel et al., 2002), which shows high Cd concentrations in Kerguelen waters (Bocher et al., 2003). The preferential Cd accumulation in kidney,

Table 2
Persistent organic pollutant concentrations (mean ± SD, ng g^{-1} dw and, in *italics*, ng g^{-1} lipid weight (lw); number of samples above the limit of detection (LoD) are given in brackets) in liver, kidney and muscle of 10 Antarctic prions from Kerguelen Islands.

	CB-50 + 28	CB-52	CB-101	CB-118	CB-138	CB-153	CB-180	Σ_7PCBs
Liver	1.10 (<LoD–2.5)	2.8 (<LoD–6.2)	2.6 (<LoD–6.1)	5.7 ± 2.0	8.3 ± 3.5	14 ± 7	2.5 ± 1.4	37 ± 16
	7.9 (<LoD–21.4) (5)	*21.1 (<LoD–53.0)* (5)	*19.2 (<LoD–46.0)* (5)	*44.2 ± 16.6* (10)	*65.6 ± 31.4* (10)	*97.6 ± 61.3* (10)	*20.1 ± 11.6* (10)	*275 ± 146*
Kidney	0.24 (<LoD–1.63)	<LoQ	0.65 (<LoD–3.99)	3.6 ± 2.4	6.1 ± 3.4	10 ± 6	1.7 ± 1.3	23 ± 12
	1.4 (<LoD–8.5) (1)		*3.9 (<LoD–21)* (1)	*24 ± 17* (7)	*41 ± 25* (10)	*66 ± 47* (10)	*12 ± 9.4* (10)	*151 ± 95*
Muscle	1.5 (<LoD–7.5)	3.1 (<LoD–14.8)	2.4 (<LoD–12.4)	5.0 ± 2.8	6.8 ± 3.8	12 ± 7	2.2 ± 1.3	33 ± 18
	15 (<LoD–73) (6)	*28 (<LoD–144)* (5)	*22 (<LoD–121)* (5)	*53 ± 28* (10)	*74 ± 47* (10)	*131 ± 88* (10)	*24 ± 17* (10)	*347 ± 199*

	HCB	γ-HCH	Heptachlor	Cis-chlordane	Trans-nonachlor	2,4′-DDE	4,4′-DDE	2,4′-DDD	4,4′-DDD	2,4′-DDT	4,4′-DDT	Mirex	Σ_{12}OCPs
Liver	21 ± 8	0.58 ± 0.28	<LoD	1.9 ± 0.9	1.0 ± 0.5	0.96 ± 0.35	50 ± 51	<LoD	<LoQ	<LoQ	<LoQ	25 ± 17	103 ± 68
	163 ± 66 (10)	*4.4 ± 2.1* (9)		*14 ± 5.5* (10)	*8.1 ± 4.1* (10)	*7.5 ± 2.8* (10)	*402 ± 431* (10)					*197 ± 135* (10)	*797 ± 575*
Kidney	16 ± 6	0.27 (<LoD–0.78)	<LoD	1.0 ± 0.8	0.56 ± 0.40	0.43 (<LoD–1.07)	32 ± 41	<LoD	0.46 (<LoD–2.87)	<LoQ	<LoQ	23 ± 22	75 ± 60
	108 ± 52 (10)	*1.7 (<LoD–4.1)* (5)		*6.9 ± 4.9* (7)	*4.0 ± 3.0* (8)	*2.9 (<LoD–5.6)* (6)	*221 ± 283* (10)		*3.4 (<LoD–22)* (1)			*160 ± 174* (10)	*509 ± 442*
Muscle	9.8 ± 2.3	0.53 ± 0.58	<LoQ	1.3 ± 1.0	0.78 ± 0.28	0.80 ± 0.93	46 ± 53	<LoD	2.2 ± 1.4	<LoQ	0.27 ± 0.22	22 ± 11	85 ± 64
	107 ± 40 (10)	*5.1 ± 5.5* (9)		*13 ± 9.9* (10)	*8.5 ± 3.6* (10)	*7.9 ± 9.0* (9)	*509 ± 631* (10)		*24 ± 16* (8)		*2.6 ± 2.1* (8)	*242 ± 147* (10)	*920 ± 775*

	BDE-17	BDE-28	BDE-47	BDE-49 + 71	BDE-66	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ_{11}PBDEs
Liver	<LoD	0.22 ± 0.14	<LoQ	<LoD	<LoD	<LoD	<LoD	0.31 (<LoD–1.5)	0.04 (<LoD–0.26)	0.34 (<LoD–2.3)	115 (<LoD–1023)	118 ± 326
		1.7 ± 1.1 (10)						*2.4 (<LoD–12)* (2)	*0.37 (<LoD–2.2)* (1)	*2.7 (<LoD–19)* (2)	*957 (<LoD–8711)* (3)	*983 ± 2734*
Kidney	<LoD	<LoQ	0.06 (<LoQ–0.13)	<LoD	<LoD	<LoQ	<LoD	0.13 (<LoD–0.75)	0.03 (<LoD–0.18)	0.20 (<LoD–1.4)	36 (<LoD–321)	37 ± 101
			0.10 (<LoQ–0.16) (5)					*0.41 (<LoD–2.8)* (2)	*0.11 (<LoD–0.18)* (1)	*0.50 (<LoD–3.9)* (2)	*316 (<LoD–2659)* (4)	*290 ± 844*
Muscle	<LoD	0.23 ± 0.37	0.03 ± 0.02	<LoD	<LoD	0.02 (<LoD–0.04)	<LoD	0.27 (<LoQ–1.3)	0.06 (<LoD–0.30)	0.32 ± 0.62	4.1 (<LoD–25)	5.8 ± 10
		2.3 ± 3.6 (8)	*0.28 ± 0.22* (9)			*0.18 (<LoD–0.47)* (1)		*2.9 (<LoQ–15)* (4)	*0.69 (<LoD–3.6)* (2)	*3.5 ± 7.2* (7)	*41 (<LoD–244)* (5)	*59 ± 103*

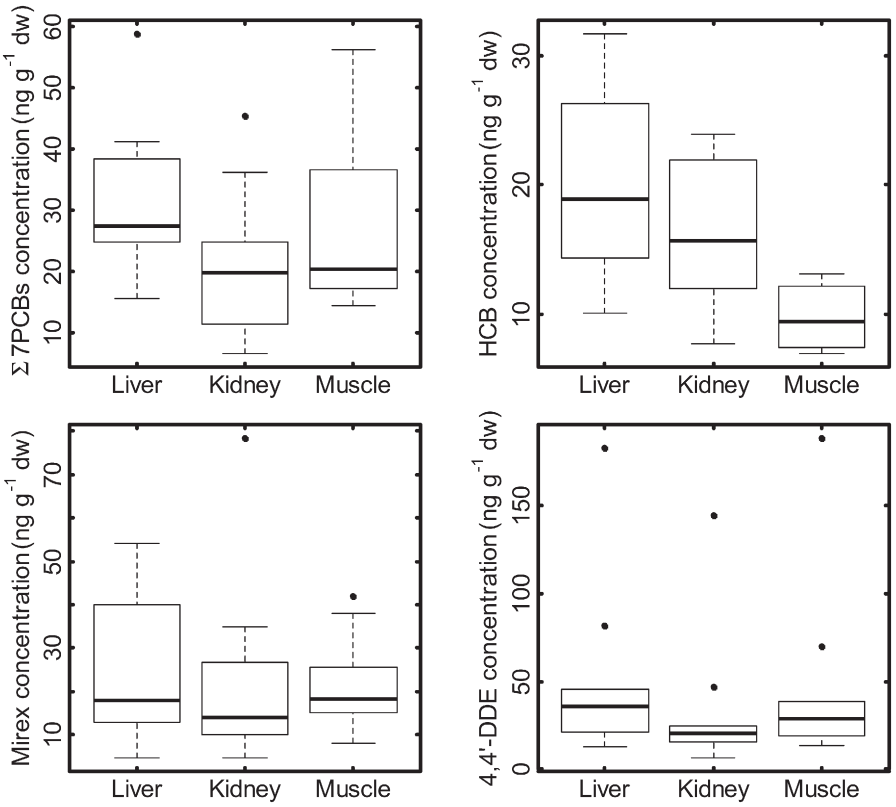

Fig. 3. Σ_7PCBs and selected OCPs (HCB, mirex and 4,4′-DDE) concentrations (ng g^{-1} dw) in liver, kidney and muscle of Antarctic prions from Kerguelen Islands (n = 10).

as shown here, is a usual trend in seabirds (Nam et al., 2005; Kojadinovic et al., 2007a; Mendes et al., 2008), and according to Scheuhammer (1987), a higher Cd concentration in kidney than in liver usually indicates chronic exposure to low Cd levels. Whatever the tissue type, Hg concentrations were lower in Antarctic prions than in fish- or squid-eating seabirds, such as albatrosses (Anderson et al., 2009; Carravieri et al., 2014b; Bustamante et al. 2016). This is consistent with Hg biomagnification within food webs, which leaves top predators at high risk of exposure through food intake (Furness and Camphuysen, 1997; Morel et al., 1998). As expected, the highest Hg concentration was found in feathers, since a large proportion of the Hg body burden can be excreted in the plumage during moult (up to 93%, Braune and Gaskin, 1987). Among soft tissues, liver presented the highest Hg concentrations, due to its important role in Hg detoxification and storage (Monteiro and Furness, 1995; Kim et al., 1998).

4.2. Tissue distribution and relative proportion of POPs: comparison with other seabirds and other areas

Overall, POP concentrations in Antarctic prions' tissues were low compared to the Southern Ocean Procellariiformes studied so far. Since POPs biomagnify in food webs, their accumulation in seabirds depends largely on their diet and trophic position (Borgå et al., 2001, 2005; Buckman et al., 2004). Accordingly, Σ_7PCBs concentrations in Antarctic prions were similar to those of Antarctic petrels (*Thalassoica antarctica*) and Cape petrels (*Daption capense*) (Van den Brink, 1997), which also feed mainly on crustaceans. Σ_7PCBs concentrations were lower than those of seabirds feeding at higher trophic levels, such as albatrosses and petrels (Guruge et al., 2001a, 2001b; Colabuono et al., 2012). Similarly, Σ_{12}OCPs concentrations in Antarctic prions were lower than those detected in albatrosses or skuas (Guruge et al., 2001a; Corsolini et al.,

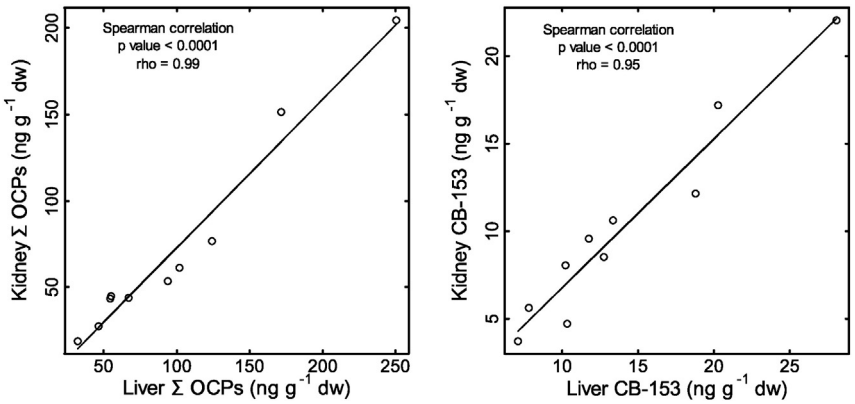

Fig. 4. Relationship between liver and kidney concentrations (ng g^{-1} dw) of Σ_{12}OCPs and CB-153 in Antarctic prions from Kerguelen Islands (n = 10).

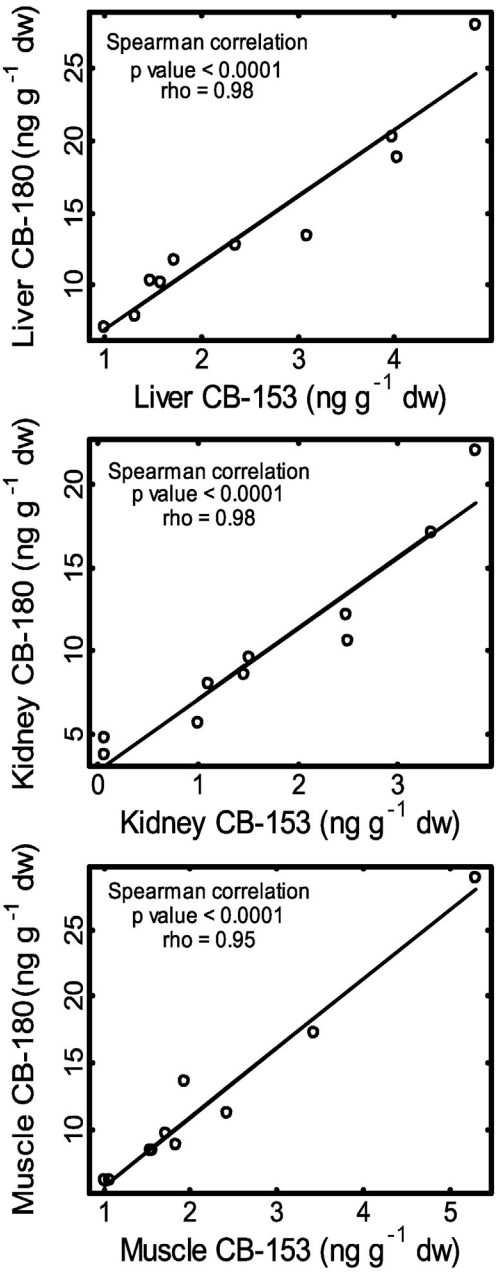

Fig. 5. Relationship between CB-153 and CB-180 concentrations (ng g^{-1} dw) in liver, kidney and muscle of Antarctic prions from Kerguelen Islands (n = 10).

2002), and similar to those in low trophic levels seabirds (Buckman et al., 2004; Mallory et al., 2004). Concentrations of OCPs and PCB congeners tended to be higher in liver (Table 2), which is consistent with its high metabolic activity and its role in lipophilic pollutant metabolism (Malcolm et al., 2003). Overall, the PCBs were largely less abundant than OCPs in all tissues (Fig. 6), as previously shown in the plasma of Crozet wandering albatrosses (Carravieri et al., 2014b). This pattern is probably linked to the large distance of these environments to industrialised zones and to the fact that PCBs were used in a less dispersive manner than OCPs. The high contribution of CBs 138, 153 and 180 to the PCB burden in Antarctic prions' tissues from Kerguelen Islands is similar to earlier data from various Southern Ocean seabirds (e.g., Court et al., 1997; Guruge et al., 2001a; Corsolini et al., 2011, Carravieri et al., 2014b) and Arctic regions (e.g., Henriksen et al., 1998, 2000; Buckman et al., 2004). Birds' capacity to metabolise PCBs decreases with increasing degree of PCB chlorination (Maervoet et al., 2004). Therefore, more chlorinated compounds like CBs 118, 138, 153 and 180 tend to be accumulated, while CBs 52 or 101 are more prone to be metabolised. The contribution of individual OCPs was also similar to earlier studies. 4,4′-DDE dominated the OCP pattern in Arctic and Antarctic seabirds, followed by HCB and mirex (Henriksen et al., 2000; Borgå et al., 2001; Goerke et al., 2004; Carravieri et al., 2014b). The particularly strong occurrence of 4,4′-DDE to OCPs in seabirds may be due to both dietary accumulation and DDT metabolism (Borgå et al., 2001). As shown by Sagerup et al. (2009), cis-chlordane, trans-nonachlor and γ-HCH presented lower liver concentrations than the most predominant OCPs, since these compounds seem to be more easily metabolised and excreted (Borgå et al., 2001). Typical PBDE patterns in wildlife, including seabirds, are dominated by BDE-47, followed by nearly equal contributions of BDEs 99, 100, 153 and 154 (Vorkamp et al., 2004; Fängström et al., 2005; Verreault et al., 2010). Surprisingly, BDE-183 and BDE-209 were detected in all tissues of some Antarctic prions, with BDE-209 concentrations being very high. The latter is the main component of decaBDE, a commercial mixture, which production and use is not regulated by the Stockholm Convention on POPs (www.pops.int). BDE-183 and BDE-209 have been recently documented in the tissues of some pelagic seabirds and marine mammals (Fängström et al., 2005; Jenssen et al., 2007; Tanaka et al., 2013). The presence of high brominated compounds in seabirds from these remote environments is puzzling, but exposure in northern wintering areas or along the migratory routes of some individual prions (Quillfeldt et al., 2015) is likely. Furthermore, BDE-183 and BDE-209 have a strong affinity to particles and have been detected in marine plastic debris, including at high concentrations (Hirai et al., 2001). Seabirds are prone to ingest plastic debris, mistaking them for prey (e.g., Ryan et al., 2009) and plastic-mediated exposure to BDE-183 and BDE-209 has already been hypothesised in short-tailed shearwaters (*Puffinus tenuirostris*) (Tanaka et al., 2013). Plastic pollution has been recently identified as a threat to subantarctic and Antarctic

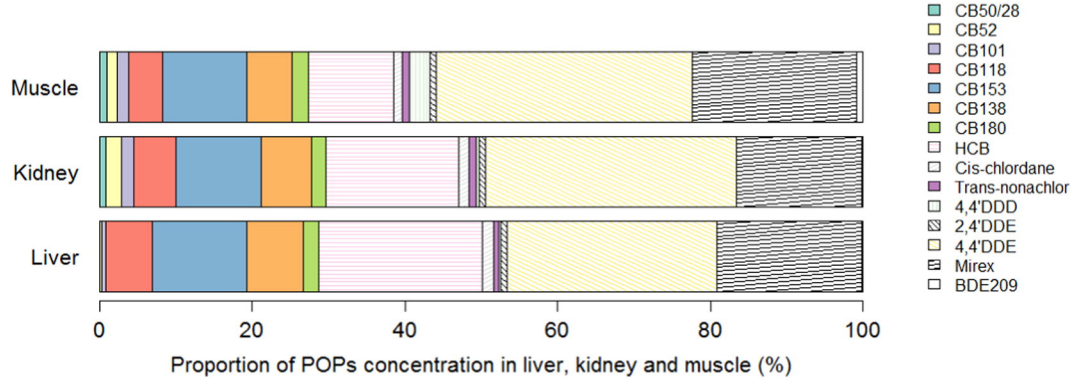

Fig. 6. POPs proportion in liver, kidney and muscle of Antarctic prions from Kerguelen Islands (n = 10). Values correspond to median concentrations. Compounds with a contribution <0.5% were not included (γ-HCH, heptachlor, 2,4′-DDD, 2,4′-DDT, 4,4′-DDT, and BDEs 28, 47, 99, 153, 154, 183, 206 and 207).

environments (Ivar do Sul et al., 2011). Plastic debris were found in five of our 10 individuals, confirming that this species is indeed prone to plastic ingestion. This result supports the hypothesis that the exposure to BDE-183 and BDE-209 in Antarctic prions from Kerguelen Islands could be plastic-mediated.

4.3. Relationships among tissues and between contaminants

In the present study, a large number of positive correlations were observed between trace elements in Antarctic prions' tissues, in broad agreement with the few previous investigations in seabirds (e.g., Nam et al., 2005; Mendes et al., 2008; Jerez et al., 2013). Concentrations of Cu, Fe, Mn and Zn presented positive relationships (Cu–Fe, Cu–Mn, Cu–Zn, Fe–Mn, Fe–Zn and Mn–Zn), especially in liver and muscle, which may indicate common sources of exposure, similar storage pathways, regulation and/or detoxification processes (e.g., Jerez et al., 2013). Additionally, these elements presented strong relationships with Cd that can be explained by Cd having similar regulatory mechanisms to Cu and Zn, such as detoxification by binding to metallothioneins and insolubilisation in mineral concretions (Ikemoto et al., 2004; Kojadinovic et al., 2007b; Lucia et al., 2009, 2012). Feathers and blood are the most targeted tissues to quantify trace element concentrations in birds mainly because they can be easily and non-destructively sampled on a large number of live individuals (e.g., Burger and Gochfeld, 2004). Importantly, the proportion of the body burden stored in the feathers is relatively constant for some elements, particularly Hg (Burger, 1993; Monteiro and Furness, 1995). Here, feather trace element concentrations, and particularly Hg, were not significantly correlated to the other tissues. The likely explanation of this discrepancy is a temporal mismatch between concentrations in metabolically active versus inactive tissues (soft tissues and feathers, respectively). Once the feather is formed, the blood supply atrophies, with no further element being deposited. Hence, feather Hg concentrations in Antarctic prions had not changed since their last moult, whereas Hg concentrations in the other tissues had progressively increased through dietary intake (bioaccumulation). Thus, feather Hg concentration reflects Hg levels of internal organs at the time of the previous moult, but not at the time of sampling. Cd and Pb are firmly bound to organic and inorganic compounds in kidney and bone, respectively, and thus only enter feathers in trace amounts (Walsh, 1990; Furness, 1993; Stewart et al., 1994). Therefore, it would be better to consider cautiously the use of feather concentrations to predict soft tissues burdens for these two non-essential elements (Nam et al., 2005). On the other hand, blood Hg concentration (Fig. 2), and to a lesser extent blood As concentration, appeared to be very good indicators of soft tissue concentrations.

Little information is available on POP inter-tissue and inter-compound relationships. In Antarctic prions, some PCBs (CBs 118, 138, 153 and 180) and OCPs (HCB, 4,4′-DDE and mirex) presented strong positive inter-tissue correlations. This pattern has been reported in seabirds including albatrosses and petrels (e.g., Henriksen et al., 1998; Colabuono et al., 2012). These compounds are highly persistent, highly lipophilic, and slowly metabolised (e.g., Borgå et al., 2001). Therefore, they partition among the various tissue lipid fractions relatively quickly to establish equilibrium (Norstrom, 2002). The most persistent POPs such as CB 153 and 180 were also highly correlated within each tissue (Fig. 5), likely indicating co-exposure. Interestingly, significant positive relationships were also reported between PCBs and OCPs in all tissues (e.g., between 4′-DDE, mirex, HCB, trans-nonachlor, CB-138, CB-153 and CB-180). Correlations between POPs of different chemical families have previously been documented in seabirds' plasma, and strongly suggest that contaminant exposure happens by feeding on prey containing similar relative amounts of both PCBs and DDTs (Bustnes et al., 2001; Mora et al., 1993; Finkelstein et al., 2006).

5. Conclusions

The present study shows that relatively low trophic level seabirds (zooplankton-eaters) breeding in the remote southern Indian Ocean are exposed to a wide range of environmental contaminants. This study corroborates previous results showing that an amphipod-rich diet is associated with a high Cd and Se intake, and low Hg exposure, in small petrels. Feeding at low trophic levels surprisingly implied the occurrence of a variety of OCPs and PBDEs in internal tissues, which merits complementary studies on the contamination of Antarctic prions' prey. Results of our work validate the use of blood as a good indicator of internal tissue concentrations of As and Hg in small petrels. The lack of correlations of Hg and other trace element concentration between feathers and soft tissues does not indicate that feathers are not good indicators of internal contamination, but rather that the temporal integration of contaminants into feathers must be carefully considered. Further studies investigating feather and internal contaminant concentrations during moult are highly needed to understand the mechanism of excretion, in particular for POPs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.11.114.

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