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Occurrence of Legacy and New Persistent Organic Pollutants in Avian Tissues from King George Island, Antarctica

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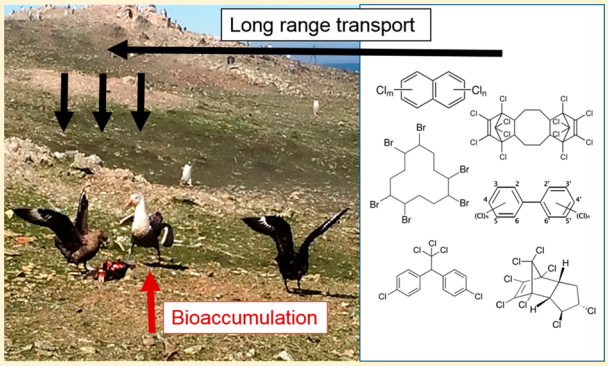
Supporting Information

ABSTRACT: Legacy and new persistent organic pollutants (POPs), including polychlorinated naphthalenes (PCNs), Dechlorane Plus (DPs) and related compounds (Dechloranes), hexabromocyclododecanes (HBCDs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs), were analyzed in avian tissue samples from King George Island, Antarctica. The avian species consisted of the Gentoo penguin (*Pygoscelis papua*), the Adelie penguin (*Pygoscelis adeliae*), the South polar skua (*Stercorarius maccormicki*), and the Brown skua (*Stercorarius antarcticus*). HBCDs were detected in all samples and ranged from 1.67−713 pg/g-lipid. In the penguin samples, the concentrations of PCNs ranged from 0.69−2.07 ng/g-lipid, whereas those in the skua samples ranged from 7.41−175 ng/g-lipid. The levels of Dechloranes ranged from 0.60−1.30 ng/g-lipid in the penguin samples and from 6.57−47.4 ng/g-lipid in the skua samples. The concentrations and congener distributions of OCPs and PCBs were similar to the results of previous reports. The three new POPs were detected in all samples, and this study was one of the first reports on the occurrence of these pollutants in the Antarctic biota. Because Antarctica is one of the most pristine places on Earth, the detection of new POPs in the Antarctic birds, especially penguins, is direct evidence of the long-range transport of pollutants. Furthermore, the concentration ratios of the penguin to the skua samples ($BMF_{s\text{-}p}$) were greater than 1 in most legacy and new POPs, and the $BMF_{s\text{-}p}$ values of the new POPs were comparable to those of some OCPs, suggesting a possibility of biomagnification. Despite the small sample size, the results of this study identified POP contamination of the Antarctic avian species and long-range transport and biomagnification of HBCDs, Dechloranes, and PCNs.



1. INTRODUCTION

In 2001, the United Nations Environmental Programme (UNEP) ratified the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention) to phase out 12 groups of toxic, persistent, long-range transporting, and bioaccumulative chemicals, which were named persistent organic pollutants (POPs).[1] Since then, the Stockholm Convention POP review committee has assessed properties of the chemicals to update the list; 23 chemical groups in total have been registered in the Stockholm Convention thus far.[1] The chemicals on the list include polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), perfluorinated chemicals (PFCs), and polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), which were used as pesticides, insulating oils, flame retardants, and waterproofing, or were produced as unintentional by-products. Since the ban on POP production and usage, alternative chemicals, which were modified to reduce toxicity, stability, and bioaccumulation, have been developed and used to replace the legacy POPs.

Because of their similar structures to the legacy POPs, however, the alternatives still have the possibility of exhibiting POP-like properties. Therefore, it is important to evaluate whether the alternatives fulfill the POP criteria of the Stockholm Convention Annex D. In screening for POP criteria, Antarctica is an advantageous research region; because it is one of the most untouched places on Earth. First, the detection of an anthropogenic chemical in this region confirms the long-range transport of the chemical because Antarctica itself has few chemical sources. In addition, the Antarctic ecosystem is relatively isolated from most other ecosystems, and the gradation of chemical levels in the food chain there clearly reflects the bioaccumulation of chemicals through the transfer from prey to predators.

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Another crucial need for the monitoring of new POPs in Antarctica arises from the potential toxicity of the chemicals. The toxic effects of POP exposure on wildlife have been well reported during the past few decades. For example, DDT and DDE induce the weakening of eggshells, which was reported by Rachel Carson in her work "Silent Spring"[2] and has also been reported by other early researchers.[3−7] Various toxic effects of POP exposure on the polar ecosystem, including immunological, developmental, reproductive, and behavioral disorders, have been reported by previous studies, as summarized by Letcher et al.[8] and Sonne.[9] Furthermore, recent studies noted that even lower levels of POP exposure can induce various toxic effects such as DNA methylation[10] and hormonal dysfunctions.[11]

Despite the importance of POP monitoring in Antarctica, previous studies have mainly focused on the monitoring of legacy POPs; hence, the Antarctic monitoring of the new POPs has been minimal. For example, polychlorinated naphthalenes (PCNs), which were proposed for inclusion in the Stockholm Convention list, were detected in Antarctica by Corsolini et al.,[12] but a follow-up study on PCNs in Antarctica has not been conducted. Recent studies by Möller et al.[13,14] reported the occurrence of the alternative flame retardants Dechlorane Plus (DPs) and its related compounds (Dechloranes) in the Antarctic atmosphere. However, the detection of Dechloranes in the other Antarctic matrices has never been reported. In addition, even the detection of hexabromocyclododecanes (HBCDs) in the Antarctic environment, although they were listed in the Stockholm Convention in 2013, has not been reported. These chemicals have been reported as having adverse ecotoxic effects: PCNs cause aryl hydrocarbon receptor (AhR)-related toxicity,[16] and HBCDs alter eggshell thickness, reproductivity, and parental behavior in birds.[17−20]

As Dechloranes and HBCDs were widely used as alternative flame retardants, the detection of these compounds in Antarctica would be helpful to reduce pollution and their harmful effects on the Antarctic ecosystem. In addition, because it has been controversial whether PCNs and Dechloranes have POPs-like properties, investigation on their long-range transport and bioaccumulation could give valuable evidence to update the Stockholm Convention POPs list.

Therefore, in this study, we analyzed several new POPs, including HBCDs, PCNs, and Dechloranes, as well as legacy POPs, including OCPs and PCBs, in avian tissue samples from King George Island, Antarctica. The avian species included Gentoo and Adelie penguins, and Brown and South polar skuas, which are the abundant species in the Antarctic ecosystem. From the results of this analysis, we assessed the long-range transport of the pollutants and calculated the biomagnification factors between penguins and skuas to identify the possibilities of the biomagnification of each pollutant.

2. METHODS AND MATERIALS

2.1. Sampling and Sample Preparation. All samples were collected in the Barton peninsula of King George Island, Antarctica from December 2008 to February 2009 and were taken from animals that were already dead; thus, no animal was euthanized for this study. The pectoralis tissues were separated from the carcasses of two Gentoo penguins (*Pygoscelis papua*), two Adelie penguins (*Pygoscelis adeliae*), one South polar skua (*Stercorarius maccormicki*), and four Brown skuas (*Stercorarius antarcticus*). The tissues were stored in polypropylene conical tubes and frozen at −40 °C until their analysis. Before pretreatment, the samples were left at room temperature for 12 hours to defrost, and the thawed samples were ground and divided into three equivalent samples for the analysis of PCNs and PCBs, OCPs and Dechloranes, and HBCDs, respectively.

The OCP compounds analyzed in this study included pentachlorobenzene (PCBz), hexachlorobenzene (HCBz), hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH, and δ-HCH), chlordanes and the other chlorinated cyclodienes (*trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, oxychlordane, mirex), and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and its metabolites (*o,p*-DDT, *o,p*-DDE, *o,p*-DDD, *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD). Among the homologues of PCBs and PCNs, tri- to hepta-CBs, and tetra- to octa-CNs were analyzed along with Dechloranes, including *syn*- and *anti*-DPs, and Dechlorane 602−604 (Dec 602, Dec 603, Dec 604). Only the α-, β-, and γ-HBCDs of the 16 HBCD diastereomers were analyzed in this study.

The sample preparation procedures followed those described Park et al.[21] for PCBs and PCNs, Kang et al.[22] for OCPs and Dechloranes, and Vorkamp et al.[23] for HBCDs, with small modifications. Briefly, the samples were spiked with an internal standard (ECN-5102, ES-5465, CLM-8588-1.2, and CLM-8569-1.2 from Cambridge Isotope Laboratories, Inc., USA, and $^{13}C_{12}$-labeled α-, β-, and γ-HBCD, and P48-M-ES from Wellington Laboratories Inc., Canada) and then extracted by ultrasonication 3 times for 30 min each. For cleanup of the extract, a multisilica column and an alumina column were employed for PCN and PCB analysis, and a florisil-silica column was employed for detecting OCPs and Dechloranes. A multisilica−alumina column was used for pretreatment for the HBCD analysis. The final eluates were concentrated and were spiked with nonane and recovery standards (ED-910 and EC-5350 from Cambridge Isotope Laboratories, Inc., USA, and P48-M-RS from Wellington Laboratories Inc., Canada).

2.2. Instrumental Analysis. For the instrumental analysis of PCNs, PCNs, Dechloranes, and OCPs, a gas chromatograph (GC) (HP 6890, Avondale, PA) equipped with a high-resolution mass spectrometer (HRMS) (800D, JEOL, Japan) was employed. The PCN, PCB, and OCP samples were injected in the splitless mode at 260 °C and separated with a DB-5UI column (Agilent Technologies Inc., Santa Clara, CA), which had a 60-m length, a 0.25-mm inner diameter (I.D.), and a 0.25-μm film thickness. For Dechloranes analysis, a DB-5HT column with a 15-m length, 0.25-mm I.D., and 0.10-μm film thickness (Agilent) was used. The interface and ion source were kept at 280 °C, and the ionization was performed using 38 eV in EI mode.

HBCD analysis was performed using an HPLC-MS/MS system composed of an Agilent 1100 series HPLC binary pump and an Agilent ZORBAX Eclipse XDB-C18 (4.6 × 75 mm I.D., 3.5-μm particle size) coupled with a Sciex API 2000 triple quadrupole mass spectrometer. The mobile phase consisted of 50% methanol/50% acetonitrile (A) and 75% water/25% methanol (B) at a flow rate of 320 μL min^{-1}. An initial mobile phase composition of 20% A and 80% B was linearly increased over 4 min to reach a final composition of 100% A, and it was held for 10 min before returning to the initial mobile phase composition. An MS/MS detector operated with an electrospray source (ESI) in negative-ion mode with multiple reaction monitoring (MRM) was used for the quantitative determination of native and $^{13}C_{12}$-HBCD isomers based on the $[M - H]^- \rightarrow [Br]^-$ transition at m/z 640.6 → 79, 640.6 → 81 and m/z 652.6 → 79, 652.6 → 81, respectively.

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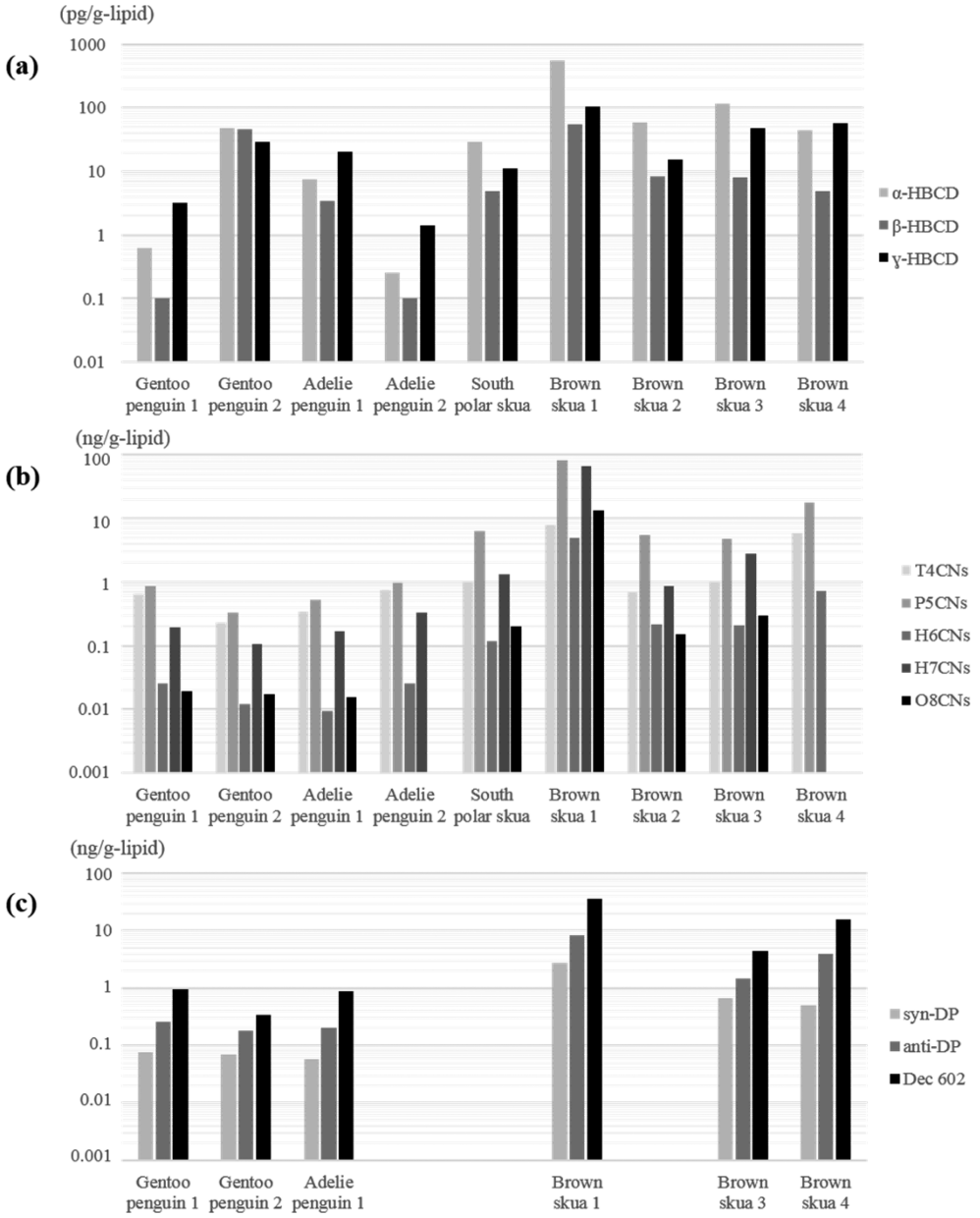

Figure 1. Concentrations of (a) HBCDs, (b) PCNs, and (c) Dechloranes in avian tissues.

2.3. QA/QC. The isotope dilution method was used for quantification, and the recoveries of the internal standards were within 50−120%. The concentrations with recoveries less than 50% were assigned as "not available (NA)". A laboratory method blank was included in every sample batch, and the background contamination was less than 5% for all compounds.

The resolution of HRMS was over 10 000 in all SIM ranges, and the PFK difference in the mass calibration was less than 5 ppm. The error in the isotopic ratio between two selected ions was within 15%. The r^2 values of the linear relative response factor (RRF) were greater than 0.99 for the calibration compounds, and the relative standard deviations of the RRF were less than 15%. The limit of detection (LOD) for the analytes was calculated as 3 times the instrumental signal-to-noise ratio (S/N), and the concentrations below the LOD were treated as LOD/2. The detailed concentrations of all compounds analyzed in this study are presented in tables in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Levels of HBCDs. Concentrations of HBCDs listed on the Stockholm Convention in 2013 have been reported in various environmental and biotic samples, as summarized by Law et al.,[24] Marvin et al.,[25] and Covaci et al.[26] In Antarctica, however, the detection of HBCD had not yet been reported. Thus, this is the first study to report the detection of HBCDs in Antarctica. Figure 1a presents the HBCD levels in the Antarctic avian tissue samples. The total concentrations of HBCDs ranged from 1.67 to 713 pg/g-lipid, and the levels in the skua samples were on average 1 order of magnitude higher than those in the penguin samples.

The levels of HBCDs in the penguin tissues were much lower than those reported in the previous studies, which are as follows: 2000 ng/g-lipid in Chinese pond heron tissue, 73.4 ng/g-lipid in white-breasted water hen tissue, 52 ng/g-lipid in common snipe tissue, 73.6 ng/g-lipid in spotted dove tissue, 112 ng/g-lipid in Chinese francolin tissue from the Chinese E-

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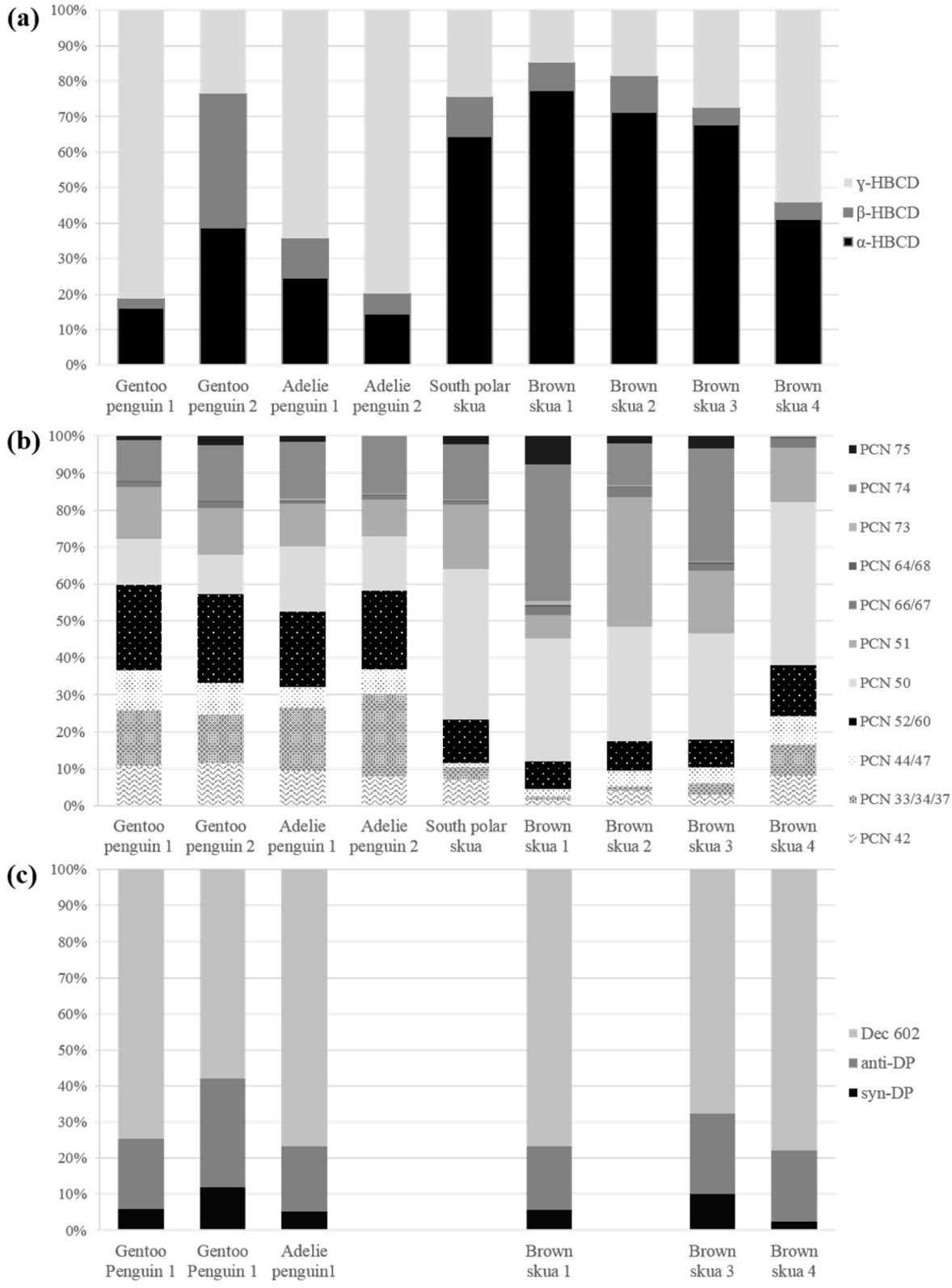

Figure 2. Distributions of (a) HBCD diastereomers, (b) PCN congeners, and (c) Dechlorane compounds in avian tissues.

waste region,[27] 38 ng/g-lipid in glaucous gull from East Greenland,[23] and 84−2360 ng/g-lipid in sparrowhawk tissues from the UK, Sweden, and The Netherlands.[28] Some studies revealed time trends of HBCD levels in the eggs of wild birds. The concentrations of HBCDs in the eggs of Swedish peregrine falcons[29] and German herring gulls[30] increased from the 1970s to the early 2000s, and then they have appeared to decrease ever since. Because the studies reflected only European HBCD contamination, a temporal trend in Antarctica still remains unknown.

The concentrations of HBCDs could reflect both the sampling location and the trophic level of the birds. For

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example, birds in China and European countries are expected to be more contaminated by HBCDs than birds in the Antarctica. However, the Antarctic skuas' HBCD levels and patterns seem to be more complicated due to the birds' migrating and predatory characteristics. In the case of penguins, they consume mostly fish and krill in the Antarctic Ocean, and their contamination levels should therefore be much less than those of skuas which are one of the top predators in the Antarctic ecosystem.

The diastereomeric distributions of HBCDs are presented in Figure 2a. Among α-, β-, and γ-HBCDs, γ-HBCD had the highest concentrations in the penguin tissues, whereas α-HBCD levels were highest in the skua tissues. γ-HBCD contributed to 75−89% of the total concentrations in the penguin samples, which had only a small proportion of α- and β-HBCDs. It is reported that the diastereomeric fraction of α-HBCD increases via weathering and bioaccumulation because of its physicochemical and biological stabilities.[25] Consequently, α-HBCD is the most dominant diastereomer in higher trophic animals. The diastereomeric composition in the skua tissues of this study corresponded with that of previous reports, but the diastereomeric fractionation was relatively unclear compared to that in bird samples from other regions.[26] It seemed that HBCD contaminations in the samples were affected by fresh HBCD contamination sources, possibly including human activity and melting glacier water, which might contribute higher amounts of β- and γ-HBCDs.

3.2. Levels of PCNs. The PCN levels in the Antarctic avian tissues are presented in Figure 1b. In the Gentoo and Adelie penguin tissues, total concentrations of PCNs were 0.69−2.07 ng/g-lipid, whereas those in the skua samples were 7.41−174 ng/g-lipid. The isomeric distributions of PCNs in each sample are presented in Figure 2b. Among the analyzed congeners, PCN 33/34/37, 52/60, 50, and 51 were dominant in the penguin samples, whereas PCN 50, 51, and 74 were highest in the skua samples.

Although PCNs have been proposed for inclusion on the Stockholm Convention list, their detection has rarely been reported in the Antarctic environment; however, long-range transport of PCNs to Antarctica has been suggested by indirect evidence. The atmospheric half-lives of PCNs, as estimated by a QSPR-based approach, were 2, 5, 10, 19, 39, 79, 163, and 343 days for mono- to octa-CNs, respectively,[31] which satisfyies the persistency criterion in Annex D of the Stockholm Convention. However, a Global Atmospheric Passive Sampling (GAPS) study from 2004 to 2005 reported that the PCN levels measured at the Antarctic Italian base were below the detection limit.[32] Because the atmospheric PCN concentrations in the Southern Hemisphere were much lower than in Europe and Asia in the GAPS study,[32] the Antarctic atmosphere seemed to be less affected by long-range transport from the low latitude regions.

Only a single study by Corsolini et al.[12] reported PCN concentrations in the Antarctic biota, such as Weddell seal, krill, icefish, sharp-spined notothen, silverfish, Adelie penguin egg, and South polar skua. In that study, the concentrations of tri- to octa-chlorinated homologues in the tissues of the South polar skua ranged from 6.07 and 5.71 ng/g-lipid, which were 10−100 times higher than in other samples. The concentrations in the South polar and Brown skua in the present study were much higher than those in the report by Corsolini et al., which could result from temporal and spatial differences because the samples in the previous report were collected from the Ross Sea in 1994−1995.[12] Although their commercial production officially ceased a decade ago, PCNs had already been used for many decades. Thus, the high PCN concentrations in the Antarctic animal likely show that PCNs have been spread to Antarctica via long-range transport.

The homologue distributions of PCNs, dominated by tetra- and penta-CNs, in the skua samples were similar to those of the South polar skua and other polar seabird tissue samples in previous studies.[12,33] However, the proportion of hepta-CNs in this study was considerable because of the high levels of PCN 74, which was unlike previous reports. Although the higher chlorinated PCN congeners have a stronger tendency to magnify with an increase of tropic levels, the low chlorinated congeners are easier to transport to remote regions due to their higher volatility. Therefore, the homologue patterns of PCNs in penguin tissues seemed to be affected by both biomagnification and the long-range transport capacity of each PCN congener.

3.3. Levels of Dechloranes. The levels of Dechloranes in the avian tissues are shown in Figure 1c. Among the Dechlorane compounds, Dec 603 and 604 were not detected, whereas Dec 602 was detected in the highest concentrations in all samples, followed by *anti*-DP and *syn*-DP (Figure 2c). The DP concentrations were 0.250−0.329 ng/g-lipid in the penguin tissues and 2.12−11.1 ng/g-lipid in the skua tissues. The levels of Dec 602 were 0.345−0.966 and 4.46−36.3 ng/g-lipid in the penguin and skua tissues, respectively.

The occurrence of Dechloranes in the Antarctic seawater and atmosphere has been reported by Möller et al.,[13,14] suggesting atmospheric long-range transport of the pollutants. In the studies by Möller et al.,[13,14] the DP levels in the Antarctic atmosphere were comparable to those of the other brominated flame retardants, including PBDEs and polybrominated biphenyls (PBBs), even though they were lower than those in the Northern Hemisphere. Since Möller et al.[13,14] reported atmospheric levels of Dechloranes, however, no previous study has reported the occurrence of Dechloranes in the other Antarctic matrices. Therefore, this is the first study to report the occurrence of Dechloranes in the Antarctic biota.

The DP concentrations in the bird tissues of the present study were similar to those in the tissues of the Glaucous gull, ringed seal, polar bear from Greenland,[34] and the tissues of fishes and harbor seals, and the eggs of the double-crested cormorant from San Francisco Bay.[35] The DP levels in this study were generally much lower than those of wild bird tissues from E-waste recycling regions in southern China,[36,37] terrestrial raptors from northern China,[38] and the liver tissues of urban-breeding ring-billed gulls from Canada.[39] The concentrations of DP in the birds seemed to reflect the trophic levels of the species and the regional contamination.

There have been a few studies reporting concentrations of Dec 602 in bird samples from other regions. The levels of Dec 602 in gull tissues from Liadong Bay, China, including the black-headed gull and the black-tailed gull, were similar to those from the penguin tissues in this study.[40] The concentrations of Dec 602 in the skua tissues of the present study were similar to those in falcon, ciconiiforme, and charadriiforme eggs from Doñana, Spain. Additionally, concentrations in the penguin tissues of this study were similar to those of anseriforme eggs from the same region.[41] The peregrine falcon eggs showed regional differences: Dec 602 levels in the eggs from Canada were similar to those in the skua tissue samples in this study, whereas those from Spain were similar to those of the penguin tissue samples in the present study.

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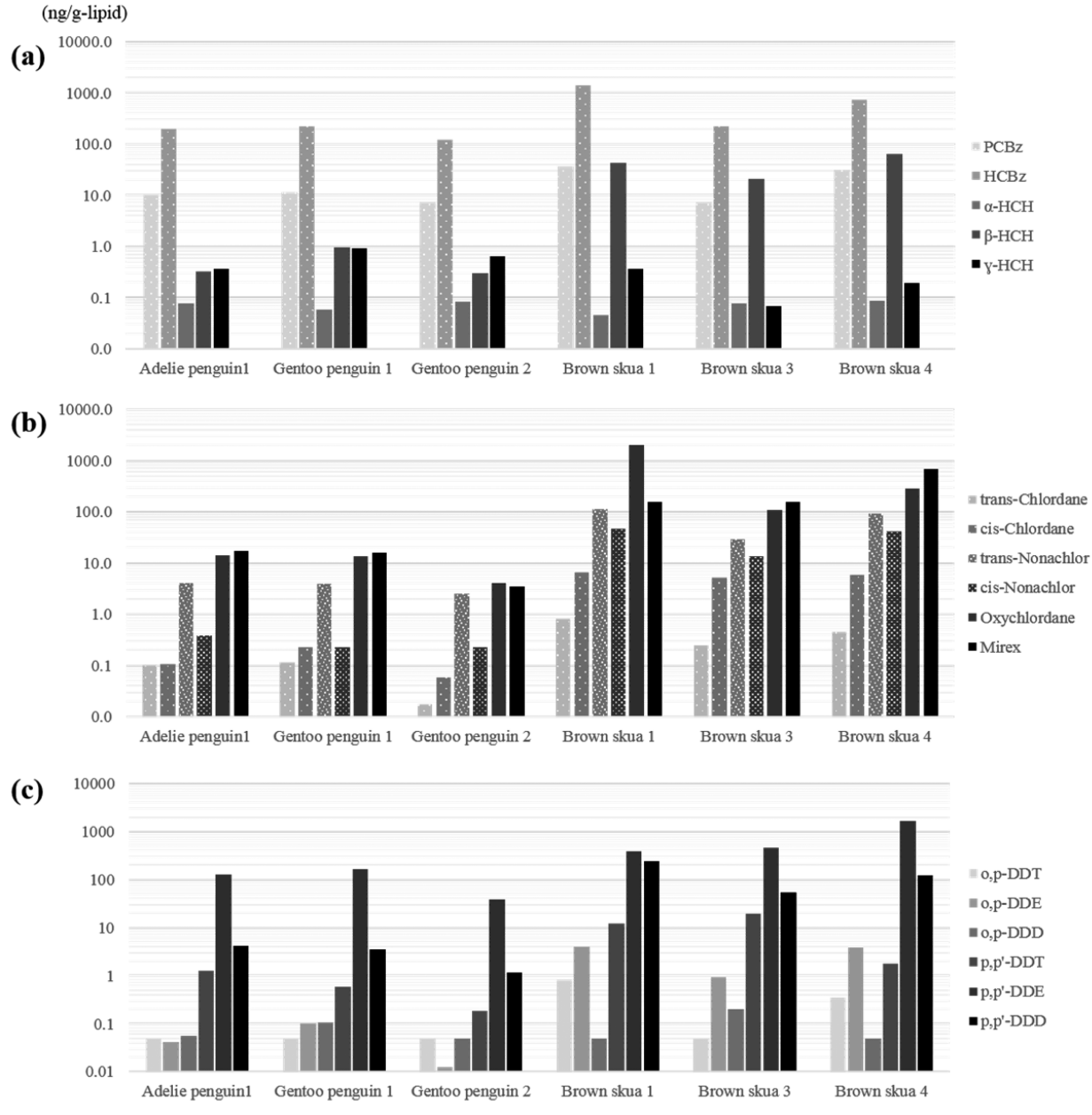

Figure 3. Concentrations of (a) chlorobenzenes and HCHs, (b) chlorinated cyclodienes, and (c) DDTs in avian tissues (ng/g-lipid).

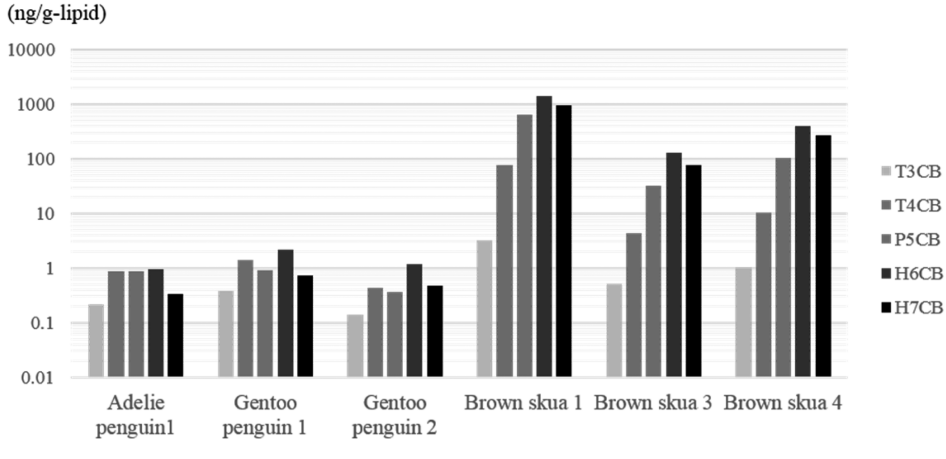

Figure 4. Concentrations of PCBs in avian tissues (ng/g-lipid).

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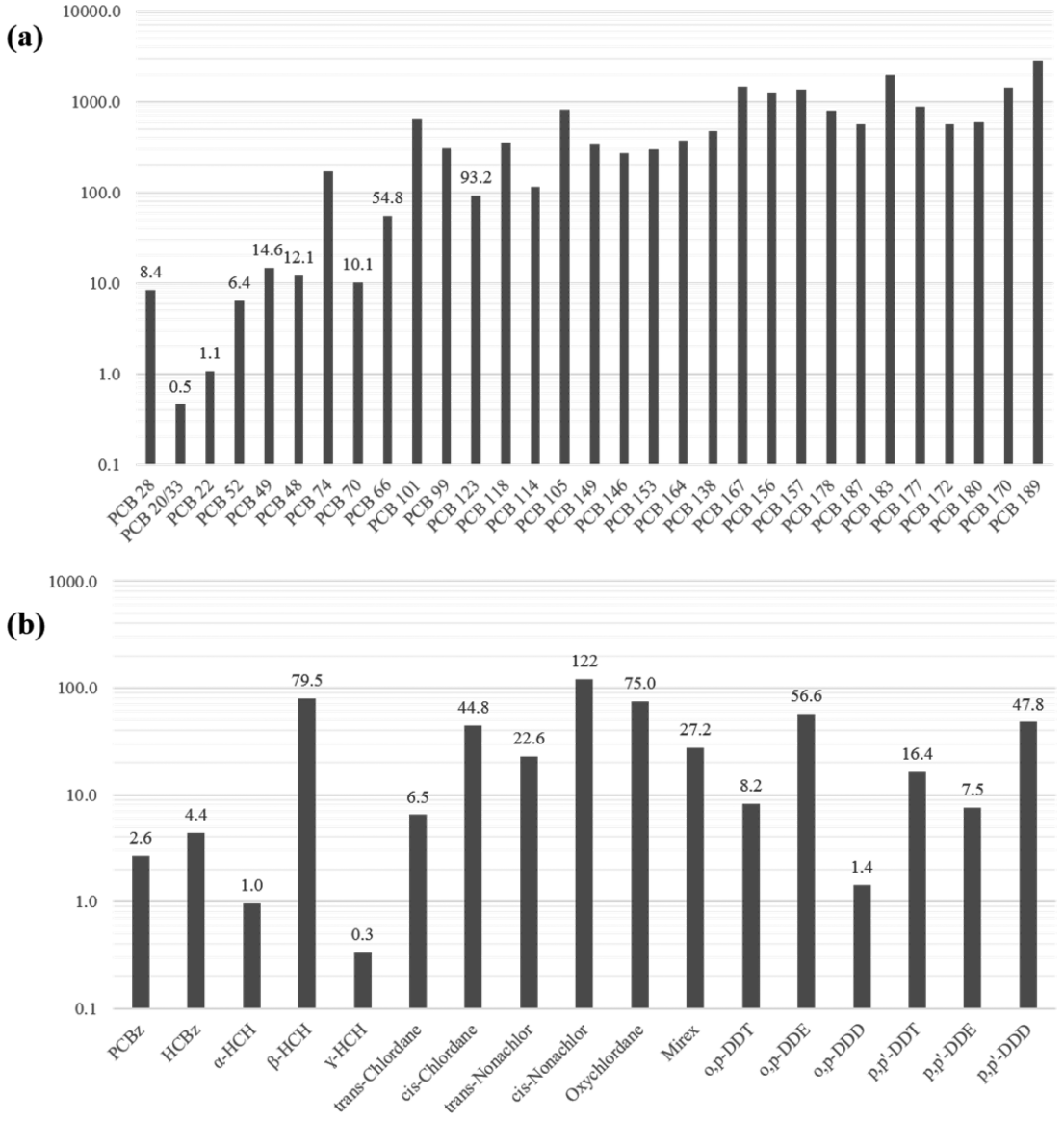

Figure 5. Biomagnification factors of (a) PCBs and (b) OCPs between penguin and skua tissues.

The isomeric ratio of *anti*- to *syn*-DPs, expressed as f_{anti} (fraction of anti-DP), has been reported as 0.65−0.75 in commercial mixtures and is lower in the atmosphere and seawater.[42] However, there have been inconsistencies in the previous reports on f_{anti} in biota samples,[42−44] implying a variety of influencing factors on the DP fractionation during bioaccumulation. In the present study, the f_{anti} values were 0.71−0.78 in the penguin samples and 0.69−0.89 in the skua samples without apparent trophic differences, and the values were slightly higher than those of commercial mixtures.

3.4. Levels of OCPs and PCBs. Figure 3 shows the concentrations of OCPs, including (a) chlorobenzenes and HCHs, (b) DDTs, and (c) chlorinated cyclodiene pesticides. Among the compounds, the concentrations of DDTs were the highest, followed by HCBz, chlorinated cyclodienes, and HCHs. The levels of DDTs were 40−168 ng/g-lipid in the penguin tissues and 29−1770 ng/g-lipid in the skua tissues; *p,p′*-DDE was the most dominant in all of the samples, ranging from 12.6 to 100 ng/g-lipid and 3910 to 1680 ng/g-lipid in the penguin and the skua tissues, respectively. The level of HCBz was 122−1420 ng/g-lipid, and the level of PCBz was 7.3−31 ng/g-lipid in the samples. Among the chlorinated cyclodienes, the levels of mirex were the highest, with values of 3.5−17 ng/g-lipid in the penguin tissues and 155−1560 ng/g-lipid in the skua tissues, followed by oxychlordane and *trans*-nonachlor.

The concentrations of PCBs are presented in Figure 4. The total PCB concentrations ranged from 2.56 to 5.65 ng/g-lipid and from 242 to 3070 ng/g-lipid in the penguin and the skua samples, respectively. In the penguin tissue samples, the levels of tri- to hepta-CBs were 0.141−0.337, 0.431−0.865, 0.359−0.924, 0.946−2.207, and 0.329−0.735 ng/g-lipid, respectively, while those in the skua tissue samples were 0.509−3.182, 4.36−75.4, 32.3−633, 130−1402, and 75.2−959 ng/g-lipid, respectively. The concentration differences among the PCB homologues were not apparent in the penguin tissues. However, the contribution of highly chlorinated homologues apparently increased in the skua tissues; hexa-CBs were the highest in the skua samples, followed by hepta-, penta-, tetra-, and tri-CBs.

The concentrations of OCPs and PCBs in penguin and skua samples from Antarctica have been reported over the past decades, and have included the concentration changes during

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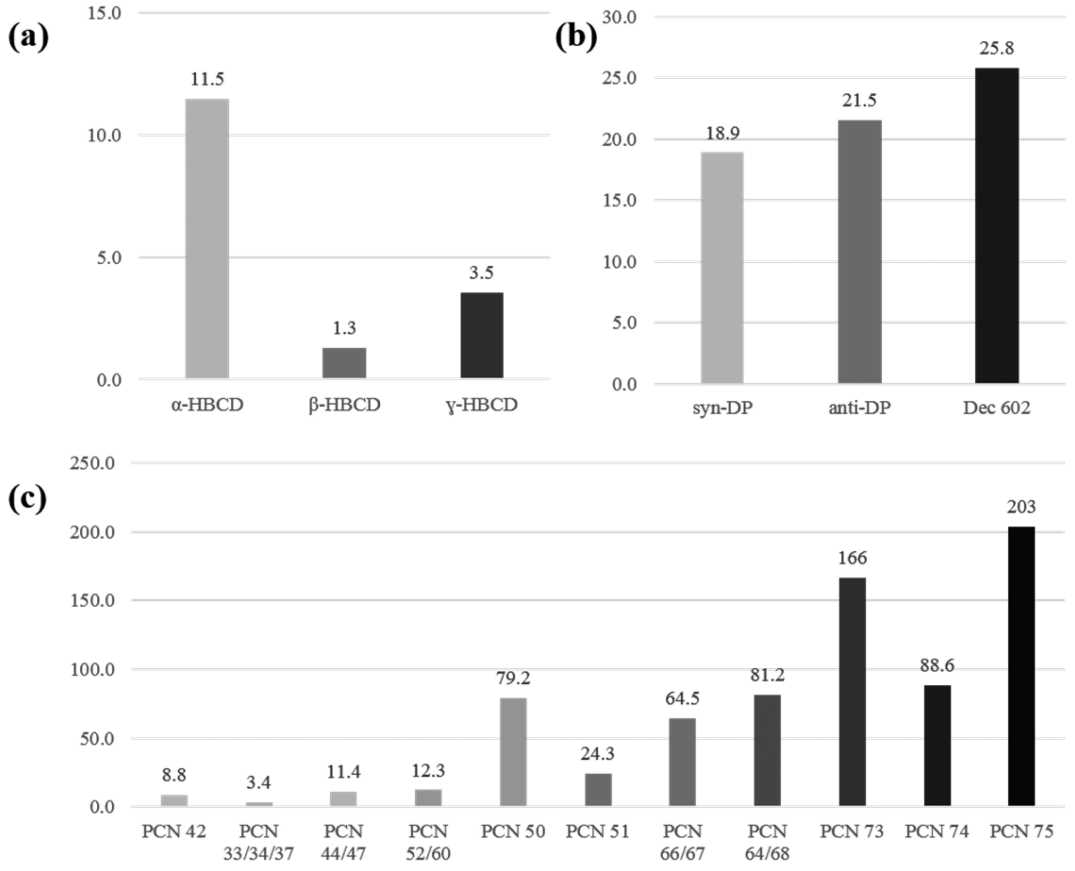

Figure 6. Biomagnification factors of (a) HBCDs, (b) PCNs, and (c) Dechloranes between penguin and skua tissues.

starvation and feeding periods,[45] biological half-lives,[46] and transfer rates from mother to egg.[47] Although a direct comparison was not possible due to the small sample size in the present study, the concentrations of the avian samples in this study were similar to those in previous studies from King George Island and the other regions in Antarctica.[48−53]

The trophic differences of congener patterns were also in agreement with previous studies,[48,53] which were influenced by weathering, long-range transport, and bioaccumulation. For example, the α- to γ-HCH ratios in our samples were much higher than those of low-latitude regions, reflecting the longer half-life of α-HCH in the environment and a remoteness from chemical sources.[54,55] The DDE/DDT ratio, fraction of β-HCH, and proportion of higher chlorinated CBs were higher in the skua tissues than those of penguin tissues, because the stable and lipophilic congeners or their metabolites were more easily biomagnified through trophic levels.[48,53,56]

3.5. Bioaccumulation of the New POPs. In the Antarctic terrestrial ecosystem, the skua is known as a predator of penguins.[57,58] On the basis of the prey−predator relationship, a biomagnification factor between skuas and penguins ($BMF_{s\text{-}p}$) was calculated by dividing the average concentration in the skua tissues by the average concentration in the penguin tissues.

$$BMF_{s-p} = \frac{\text{average concentration in skua tissue}}{\text{average concentration in penguin tissue}}$$

The $BMF_{s\text{-}p}$ values of each legacy and new POPs are presented in Figure 5 and Figure 6, respectively. The highest $BMF_{s\text{-}p}$ was found in PCBs, and most of the PCB congeners also had a high $BMF_{s\text{-}p}$, except for PCB 28/33. The $BMF_{s\text{-}p}$ of PCBs generally increased with the chlorination number of the congeners, which ranged from 0.5 to 5880. Although PCBz and HCBz are registered in the Stockholm Convention, the $BMF_{s\text{-}p}$ values were 2.6 and 4.4, respectively, which were relatively low values. The $BMF_{s\text{-}p}$ of *p,p′*-DDE was 7.5, which is comparatively low, even though it was the highest concentration of the samples; most of the major OCP compounds showed $BMF_{s\text{-}p}$ higher than 10.

The $BMF_{s\text{-}p}$ values of α-, β-, and γ-HBCDs were 11.5, 1.1, and 3.5, respectively, implying that α-HBCD was preferentially magnified between penguins and skuas. The biomagnification of HBCDs was reported in previous studies,[25,26] which showed that the biomagnification and trophic level magnification factors (BMF and TMF) were larger than one. The diastereomer-specific biomagnification also matched that of previous studies, likely due to the physicochemical stability and the longer biological half-life of α-HBCD, as well as the biotransformation of γ-HBCD into α-HBCD.[25,26,59,60]

All of the analyzed PCN congeners had $BMF_{s\text{-}p}$ values larger than one with a dependence on the chlorine numbers, which is similar to the PCB congeners. Falandysz[15] suggested a congener-specific biomagnification of PCNs, indicating that biomagnification is relatively favorable in congeners without a vicinal carbon atom unsubstituted with chlorine (NVC-Cl PCNs). This includes PCN 42, 52, 58, 60, 61, 64, 66, 67, 68, 69, 71, 72, 73, 74, and 75 because these PCNs are relatively resistant to metabolism. In addition, the congeners with unsubstituted vicinal carbons in $\beta\beta$-positions, such as PCN 47, are more easily metabolized than those in $\alpha\beta$-positions.[15,33] However, the trend was unclear in the present study. The

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$BMF_{s\text{-}p}$ values were generally high, and tetra-CNs had comparatively lower values than the other congeners.

The $BMF_{s\text{-}p}$ values of DPs and Dec 602 were between 18.9 and 25.8, which were comparable to those of *trans*-nonachlor and *p,p′*-DDT. There have been inconsistent reports on the biomagnification of Dechloranes. Some previous studies reported that Dechloranes were biomagnified in the Chinese freshwater food webs[36,40] and for the rat−owl relationship in the Chinese terrestrial ecosystem.[61] However, some studies reported that Dechloranes did not biomagnify significantly, such as reports from the northern Chinese marine food web[62] and bird eggs from southwestern Spain.[41] In addition, Tomy et al.[63] reported higher TMF of *anti*-DP than *syn*-DP in the Lake Winnipeg food web, which corresponds to the results of this study. Some of the previous studies, however, reported that *syn*-DP was more bioaccumulative, possibly due to the higher lipophilicity of *syn*-DP.[36,40]

The inconstancies in the previous studies seemed to occur due to different conditions within the ecosystems. Tomy et al.[63] compared two samples from the Lake Winnipeg and the Lake Ontario food webs; the two ecosystems showed significant and nonsignificant bioaccumulation, respectively, suggesting that the bioaccumulation of Dechloranes might be dependent on different conditions of the ecosystems. In addition, the inconstancies might be attributed to a limitation of the BMF approach, which is the complicated behavior and prey−predator relationship of the birds.

Among the selected bird species, Gentoo and Adelie penguins are known to spend their whole lives in the Southern ocean and Antarctica.[64,65] However, South polar and Brown skuas are known as migratory species wintering over in low-latitude regions, such as the Atlantic, South America, and even the North Pacific.[57,58,66] Therefore, the POP levels of the skuas might reflect not only the Antarctic contamination but also the contamination in low-latitude regions. Consequently, the POP levels of the skuas and the $BMF_{s\text{-}p}$ values might be overestimated. In addition, although the prey−predator relationship between penguin and skua was identified in previous studies,[53,54] the prey of the Brown and South polar skuas includes not only penguins, but also other Antarctic birds, eggs of those birds, and different types of fish, varying with their habitats.[57,67−69]

In short, the bioaccumulation of the pollutants still have some uncertainties; therefore, further studies with bigger sample size obtained from more systematic sampling strategies are required to reduce the uncertainties. And, especially more progressive tools, such as the trophic magnification factor (TMF), may help to verify the results of this study.

In this study, we detected that new POPs, including HBCDs, Dechloranes, and PCNs, and the legacy POPs, such as OCPs and PCPs, were present in avian tissue samples of penguin and skua from King George Island, Antarctica. The pollutants were detected in all samples, showing the long-range transport of the pollutants. Among the possible chemical sources, including long-range atmospheric transport,[54,55] melting glacier and snow,[70,71] and migratory animals,[72−74] the LRAT might be the major source of POPs since the region has few chemical sources. However, we also should not neglect the effects of human activities in many research bases in the Antarctic continent,[54] especially for new POPs such as flame retardants and perfluorinated compounds. The $BMF_{s\text{-}p}$ values of the new POPs were comparable to those of some OCPs, which suggested biomagnification of the pollutants.

Although this study sought to determine the long-range transport and bioaccumulation of new POPs, there were some limitations. First, the sample size was relatively small to represent the general POP contamination of King George Island. Other limitations were related to the behavioral and ecological characteristics of the birds, which might lead to the overestimation of both levels and $BMF_{s\text{-}p}$, as discussed above.

Nevertheless, the results of this study still provide a significant contribution to the literature. First, this was the first study to detect Dechloranes and HBCDs in the Antarctic biota, and was the second study on the Antarctic PCNs. And the detection of the new POPs in the Antarctic animals, especially penguins, was a direct evidence of the long-range transport of the pollutants. Last, the concentration differences between the skua and the penguin samples suggested the possibility of POP biomagnification. This study determined the long-range transport and biomagnification of the pollutants, which are two of the four POP criteria in the Stockholm Convention Annex D.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03181.

Data Tables S1−S4, as noted in the text (PDF)

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Notes

The authors declare no competing financial interest.

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