



Occurrence, distribution, and bioaccumulation of new and legacy persistent organic pollutants in an ecosystem on King George Island, maritime Antarctica

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ABSTRACT

The occurrence and bioaccumulation of new and legacy persistent organic pollutants (POPs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexabromocyclododecanes (HBCDs), and Dechlorane Plus (DPs) and their related compounds (Dechloranes) in an ecosystem on King George Island, Antarctica are investigated. The new and legacy POPs were widely detected in the animal samples collected from Antarctica, which included Limpet, Antarctic cod, Amphipods, Antarctic icefish, Gentoo and Chinstrap penguins, Kelp gull, and South polar skua. The trophic magnification factors indicated that the levels of PCNs and HBCDs, as well as the legacy POPs, were magnified through the food web, whereas DPs might be diluted through the trophic levels contradicting the classification of Dechloranes as POPs. This is one of the first extensive surveys on PCNs, HBCDs, and Dechloranes, which provides unique information on the distribution and trophic biomagnification potential of the new and legacy POPs in the Antarctic region.

1. Introduction

Even though there is no industrial production and little human activity in Antarctica, some chemicals, such as persistent organic pollutants (POPs), have been detected in the Antarctic environment (Scheringer, 2009; Choi et al., 2008). The detected POP concentrations are lower than those in the Arctic, and in mid- and low-latitude regions, but the exposure of the Antarctic environment to POPs poses a higher critical risk. This is because the POPs are released into the environment during spring and summer when biota of the Antarctic ecosystem are most vulnerable due to reproduction and growth (Meyer and Wania, 2008; Wania et al., 1998). To assess the risk to the Antarctic ecosystem, the legacy POPs have been continuously monitored in the Antarctic environmental matrices, including air (Choi et al., 2008), snow (Galbán-Malagón et al., 2013), soil (Klánová et al., 2008; Wang et al., 2012), vegetation (Cabrerizo et al., 2012; Wang et al., 2012), fish (Weber and Goerke, 2003), and birds (Corsolini et al., 2011). Moreover, because of very few chemical sources and an almost isolated ecosystem in

Antarctica, the monitoring of new POPs provides additional academic and political benefits, which include screening of POP criteria, long-range transport (LRT) and bioaccumulation (UNEP, 2001).

Among the new POPs reported in recent studies on the Antarctic ecosystem, polychlorinated naphthalenes (PCNs), hexabromocyclododecanes (HBCDs), and Dechlorane plus (DP) and related compounds (Dechloranes) have been of particular concern. PCNs have been detected in the Antarctic atmosphere and ecosystem, indicating LRT (Corsolini et al., 2002; Krasnobaev et al., 2018). Because of their dioxin-like physicochemical toxicity, PCNs were listed on the POP list presented at the 7th meeting of the Conference of the Parties to the Stockholm Convention in 2015 (UNEP, 2015). To date, the levels of PCNs in the Antarctic ecosystem have only been reported from the Ross Sea (Corsolini et al., 2002; Grotti et al., 2016) and their trophodynamics have only been studied in northern mid-latitudes (Bohai Sea) (Cui et al., 2018). Hexabromocyclododecanes, alternative brominated flame retardants of the polybrominated diphenyl ether (PBDEs), were added to Annex B of the Stockholm Convention in 2013 (UNEP, 2013) because of

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their toxicity and persistence. Their possible source and spatial distribution in the Antarctic ecosystem have been reported in only a few previous studies (Chen et al., 2015; Kim et al., 2015, 2018) while their trophodynamics have not been investigated yet.

Of all new POPs, the listing of Dechloranes under the Stockholm Convention has been debated recently (UNEP, 2019). Dechloranes have been detected in the Antarctic atmosphere (Möller et al., 2012, 2010) and have a long enough environmental half-life to have a high potential for LRT and persistence. The toxicity of DPs was found in a few animal studies, including transcriptomic and metabolic alteration (Crump et al., 2011; Wu et al., 2012; Yang et al., 2016; Zhang et al., 2014) and developmental disorder (Chen et al., 2019; Li et al., 2020), but that of other Dechloranes is still unclear. Bioaccumulation of Dechloranes is even more controversial. For example, no trophic magnification or dilution of *anti*-DP were found in an E-waste cycling region in China (Zhang et al., 2011), whereas significant trophic magnifications of *syn*- and *anti*-DPs were found in the freshwater ecosystem of a chemical production region (Wang et al., 2015) and a different E-waste cycling region (Wu et al., 2010) in China. In a study on the Liaodong Bay in China, no significant DPs but significant Dec 602 magnification was reported. As for Antarctica, a recent study by Na et al. (2017) found trophic magnification of *syn*- and *anti*-DPs in the Fildes Peninsula. This inconsistency can be ascribed to multiple pollution sources, different characteristics of ecosystems, and complicated food web structures. Therefore, a systematic study designed to investigate the distribution and trophodynamics in an isolated ecosystem is needed to resolve the inconsistencies.

In this study, the distribution and trophodynamics of PCNs, HBCDs, and Dechloranes in an ecosystem on King George Island, Antarctica, were investigated and compared with those of the legacy POPs polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). Animal tissue samples were collected from a maritime ecosystem on King George Island. The levels of new and legacy POPs, and stable carbon and nitrogen isotopic ratios in the samples were determined. Trophic magnification factors (TMFs) were estimated based on the trophic levels and POP concentrations.

2. Materials and methods

2.1. Samples

Table 1 presents detailed sample information. Animal samples were collected from the Barton Peninsula and Maxwell Bay, King George Island, Antarctica (62°13'S, 88°47'W) from December 2013 to January 2014. The samples were collected during summer, after the melting of seasonal snow and ice and during the breeding period of many seabird species, such as the Chinstrap and Gentoo penguins, Kelp gulls, Antarctic terns, and Brown and South polar Skuas.

The Limpets were collected from 15 points in intertidal zones along the coast of the Barton Peninsula and Maxwell Bay (Fig. S1, Supplementary Material). The Amphipods were collected from the intertidal zone of the coast (Amphipods 1, *Gondogeneia antarctica*) and using a baited trap (Amphipods 2, *Cheirimedon femoratu*). The Amphipods were

roughly identified based on previous reports of the species and distribution in the Marian Cove (Kim et al., 2014). The Antarctic cods were caught using a fishing rod, and an Antarctic icefish carcass was found in the intertidal zone. The carcasses of Gentoo penguins, Chinstrap penguins, a South polar skua, and a Kelp gull were collected from Narębski Point, Antarctic Specially Protected Area (ASPA) no. 171 (62°14'S, 58°46'W), where 3,000 pairs of Chinstrap Penguins (*Pygoscelis antarcticus*), 2,300 Gentoo Penguins (*Pygoscelis papua*), and 16 other bird species were breeding during this season (Secretariat of the Antarctic Treaty, 2014). All the penguins were chicks that had frozen or starved to death.

Because the Limpets and the Amphipods are too small to be used as a single sample, more than ten Limpets and fifty Amphipods were collected in a 50 mL conical tube and samples from each tube were pooled. Only the soft part of the Limpets was collected in the conical tubes, i.e. all shells were removed. For the birds and fish, only muscle tissue was used for isotopic and POP analysis because the turnover rate of muscle is lower than that of the liver and, therefore, reflects the feeding habit over a longer period (Borgå et al., 2012). The samples were stored in polypropylene conical tubes and kept frozen at -20 °C. After transport to the laboratory, the frozen samples were freeze-dried and ground with pestle and mortar.

2.2. POP analysis

In this study tri- to hepta-CBs, and tetra- to octa-CNns were analyzed among the PCB and PCN homologues. The OCPs included 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, and 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, and *p,p'*-DDD). The Dechloranes analyzed in this study were DPs, including *syn*- and *anti*-DPs, and Dechlorane 602–604 (Dec 602, Dec 603, and Dec 604). Among the 16 HBCD diastereomers, Only the α -, β -, and γ -HBCDs were analyzed in this study.

The all analytical procedure follows Kim et al. (2015). Briefly, 2 g of ground, dried samples were used for the analysis of PCBs and PCNs, another 2 g for OCPs and Dechloranes analysis, and the other 2 g of the samples for HBCDs analysis. Before pretreatment, isotopically labeled standard solutions were spiked (ECN-5102 for PCNs, ES-5465 for OCPs, CLM-8588, CLM-8569, and CLM-9282 for Dechloranes from Cambridge Isotope Laboratories, Inc., USA, and ¹³C12-labeled α -, β -, and γ -HBCD, and 68B-LCS for PCBs from Wellington Laboratories Inc., Canada). The spiked samples were then extracted 3 times for 30 min with hexane and dichloromethane (1:1 v:v) at 30 °C in an ultrasonic bath. The extracts were filtered and dried, resulting in pure lipid, and the lipids were weighted to calculate the lipid-normalized concentration. For PCB and PCN analysis, the dried lipids were cleaned up using a multi-layered silica column followed by an alumina column. The extracts for the OCP and Dechlorane analysis were cleaned up using a silica-florisil column, and those for the HBCD analysis with a multisilica–alumina column. The eluates were concentrated and spiked with recovery

Table 1
Sampling details.

Common name	Scientific name	Sample type	n	$\delta^{15}\text{N}$	$\delta^{13}\text{C}$	Trophic level
Limpet	<i>Nacella concinna</i>	Whole	15 (pooled)	6.11 ± 1.33	- 17.09 ± 1.38	2.00 ± 0.35
Antarctic cod	<i>Notothenia coriiceps</i> <i>Notothenia rossii</i>	Muscle	9	10.73 ± 0.39	- 20.50 ± 0.93	3.21 ± 0.11
Amphipod	1: <i>Gondogeneia antarctica</i>	Whole	2 (pooled)	8.47	- 19.53	2.62
	2: <i>Cheirimedon femoratu</i>			7.48	-	2.36
Antarctic icefish	<i>Chaenocephalus aceratus</i>	Muscle	1	13.26	- 22.26	3.88
Gentoo penguin	<i>Pygoscelis papua</i>	Muscle	21	7.08 ± 0.24	- 27.11 ± 0.96	2.69 ± 0.29
Chinstrap penguin	<i>Pygoscelis antarcticus</i>	Muscle	8	6.88 ± 0.13	- 27.58 ± 0.63	2.57 ± 0.03
Kelp gull	<i>Larus dominicanus austrinus</i>	Muscle	1	11.26	- 22.82	3.72
South polar skua	<i>Stercorarius maccormicki</i>	Muscle	1	8.71	- 23.47	3.05

standards (ED-910 and EC-5350 from Cambridge Isotope Laboratories, Inc., USA, and 68B-ISS from Wellington Laboratories Inc., Canada). The PCNs, PCBs, OCPs, and Dechloranes in the samples were analyzed using a gas chromatography high-resolution mass spectrometer (GC-HRMS, JMS-800D, JEOL Inc., Japan), while HBCDs were analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS, API 2000, Applied Biosystems/MDS Sciex, Canada).

2.3. QA/QC

For the qualitative and quantitative analyses of POPs, an isotope dilution method was employed. The recoveries of the clean-up standards were within 50–120%, and were used to correct the POP concentrations. The linearity (R^2) of the calibration curve was more than 0.99 and the relative standard deviations (RSD) of the relative response factor (RRF) was less than 15%. The resolution of the GC-HRMS was kept at more than 10,000 at 10% height over the entire selected selective ion monitoring (SIM) range. Two molecular ions were quantified for each compound, and the deviation of the two SIM ion ratios was below 15%.

The limit of detection (LOD) was determined as the higher value between the instrumental detection limit (IDL) and the limit of quantification of the blank samples (LOQ_{blank}). The IDL was calculated as 3 times the instrumental signal to noise ratio and the LOQ_{blank} as the mean plus 3.75 times the standard deviation of the field blank samples. The field blank samples ($n = 5$) were prepared as polypropylene conical tubes with small amounts of water. The values $< LOD$ were assigned as 0.0 for the calculation of the mean and median concentrations, and as $1/2 LOD$ for all further statistical tests. The IDL, recovery, field blank, and LOQ_{blank} values for PCBs, OCPs, PCNs, HBCDs, and Dechloranes are shown in [Table S1 in the Supplementary Material](#).

2.4. Analysis of $\delta^{13}C$ and $\delta^{15}N$

The stable isotope ratios of carbon and nitrogen, $^{13}C/^{12}C$ and $^{15}N/^{14}N$, were analyzed at the Korean Basic Science Institute (KBSI) using an elemental analyzer-isotope ratio mass spectrometer (EA-IR-MS) equipped with a graphite furnace (Isoprime, GV Instruments, Manchester, UK). Based on the measurements, the shifts of the isotopic ratios, $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰), were determined by comparison with a reference material (RM). The Vienna Pee Dee Belemnite standard and atmospheric N_2 were used as references for carbon and nitrogen, respectively. Prior to carbon isotope analysis, the lipid and inorganic carbon content were extracted from the ground samples using dichloromethane and hydrochloric acid ([Sweeting et al., 2006](#)). Each analysis was performed in either duplicate or triplicate. The standard deviations were less than 0.67 and 0.27‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively. The reproducibility evaluated using a lab RM was less than 0.02‰.

2.5. Trophic magnification factor (TMF)

As no study has determined an enrichment factor for $\delta^{15}N$ in the food web of King George Island, the enrichment factor was assumed as 3.4‰ as recommended in the literature ([Borgå et al., 2012](#); [Jardine et al., 2006](#)). The trophic levels (TLs) of the Limpets were the lowest among the analyzed species, as the major prey of Limpets from the intertidal zone in summer are epilithic microalgae and macroalgae ([Choy et al., 2011](#)). This implies that Limpets are the primary consumer in this food web, which is used as a baseline for trophic magnification. Therefore, Limpets are employed as the basal species in this study, with an assigned TL of 2.

The TLs for the samples were calculated using the following equation:

$$TL_{consumer} = 2 + \frac{(\delta^{15}N_{consumer} - \delta^{15}N_{Limpet})}{3.4} \quad (1)$$

For the birds, with $TL_{bird} = TL_{consumer} + 1$ and

$\delta^{15}N_{bird} = \delta^{15}N_{consumer} + 2.4$, the TL_{bird} was calculated as follows ([Fisk et al., 2001](#); [Jardine et al., 2006](#)):

$$TL_{bird} = 3 + \frac{(\delta^{15}N_{bird} - (\delta^{15}N_{limpet} + 2.4))}{3.4} \quad (2)$$

A simple linear regression analysis was used to establish the relationship between pollutant concentration and TL:

$$\log[POP] = a + b \cdot TL, \quad (3)$$

where a = intercept and b = slope of regression curve.

Finally, the TMF was calculated as:

$$TMF = 10^b. \quad (4)$$

The TMFs were derived for all compounds detected in more than 50% of the samples. Values below the IDL were regarded as $LOD/2$ for the TMF calculation. Values between the LOQ_{blank} and IDL were used unmodified in order to avoid systematic error, as recommended by [Borgå et al. \(2012\)](#).

3. Results and discussion

3.1. Levels of OCPs, PCBs, $\delta^{13}C$, and $\delta^{15}N$ in the animal tissues

[Fig. 1](#) shows the distribution of $\delta^{15}N$, TL, and $\delta^{13}C$ in the analyzed samples. The $\delta^{13}C$ and $\delta^{15}N$ values in penguins, skuas, and Antarctic cods agree with previously published values from the study area ([Cipro et al., 2017](#)). Significant differences in $\delta^{13}C$ are found between aquatic poikilotherms, including Amphipods, Limpets, Antarctic icefish, and Antarctic cod, and terrestrial homeotherms, including Gentoo and Chinstrap penguins, Kelp gulls, and South polar skuas. These differences can be attributed to the difference in nutrient sources ([Cipro et al., 2011](#); [Gannes et al., 1998](#)) and the faster metabolic rate of homeotherms ([McCutchan et al., 2003](#)) or the seawater isotopic composition which is heavier in the deep sea and lighter at the coast of King George Island ([Fischer and Wiencke, 1992](#)). One of the strongest driving forces of isotopic fractionation is the carbon source of the primary producer which varies with distance from the shore and depth of the oceanic habitats ([Hill et al., 2006](#); [Nerot et al., 2012](#)). The penguins in this region forage up to 65 km away from the island and dive up to 180 m deep into the Southern Ocean. The $\delta^{13}C$ values of the penguin tissues are similar to the $\delta^{13}C$ values of the krill offshore of the Southern Ocean, which is 23–28‰ ([Polito et al., 2013](#)). Thus the ^{13}C -depleted krill and penguins can be ascribed to the ^{13}C depletion of offshore water and the deep sea ([Kokubun et al., 2015](#); [Lee et al., 2016, 2015](#)).

The measured concentrations of PCBs, HCHs, DDTs, and CHLs in the Antarctic animal samples are presented in [Fig. 2](#) and [Tables S3–S5 in the Supplementary Material](#). The levels of legacy POPs, such as OCPs and PCBs, in the Antarctic ecosystem have been reported by previous studies, and penguins in particular have been regarded as an indicator species of the Antarctic ecosystem ([Kim et al., 2015](#); [Roscales et al., 2016](#)). The levels of HCHs, DDTs, CHLs, and PCBs in this study range between 0.449 and 14.6, 5.71–2990, 2.49–940, and 0.382–526 ng/g lipid, respectively, in Gentoo penguins, and 9.05–124, 1.56–130, 2.31–22.1, and 9.05–124 ng/g lipid, respectively, in Chinstrap penguins. In general, the OCP and PCB levels in the penguins are comparable or slightly higher than those reported by [Kim et al. \(2015\)](#). Of the two species of penguins, Gentoo penguins return to the nest and breed their chicks earlier in this region ([Black, 2016](#)). Gentoo Penguins consume krill during the early stage, but a higher trophic diet, such as fish and squid, later on, while Chinstrap penguins feed on krill consistently ([Emslie et al., 2014](#)). In addition, Gentoo penguins forage in the in-shelf region, while Chinstrap penguins forage farther afield and even in the deeper sea ([Kokubun et al., 2010](#)). These differences can cause higher $\delta^{15}N$ and lower $\delta^{13}C$ values in the Gentoo penguins compared with the Chinstrap penguins. In this study, however, the differences are

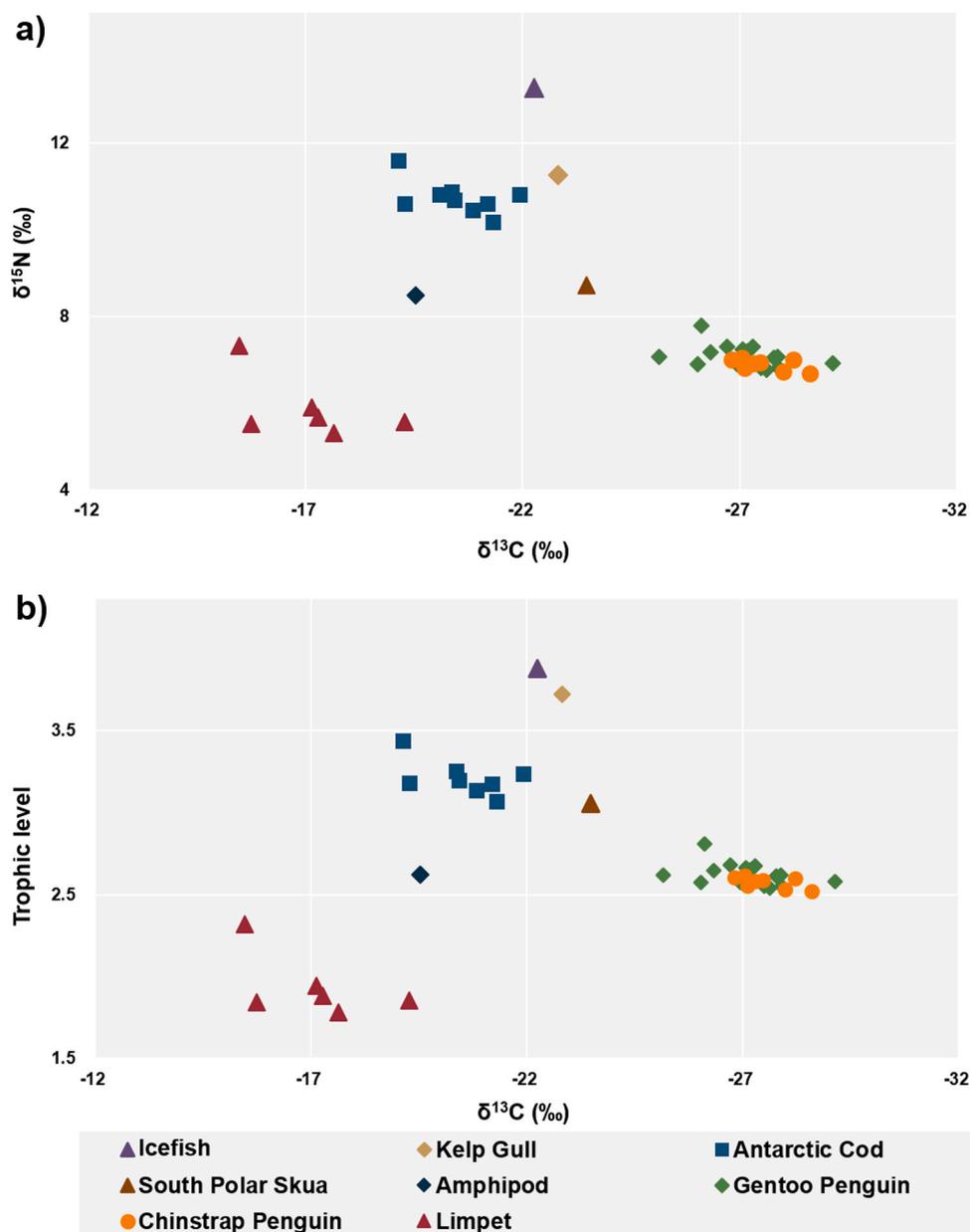


Fig. 1. Distribution of ^{13}C and ^{15}N stable isotopic ratios, and trophic levels of animal species from the Barton Peninsula and Maxwell Bay, King George Island. a) $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ and b) Trophic level and $\delta^{13}\text{C}$.

slight. Among the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and POP levels, only the tri-CB level is negatively correlated with body size, including bill depth, head length, and weight (Table S6 in the Supplementary Material). This may be due to a dilution of the POPs by the fast growth rate of the chicks, or a false positive in the statistical analysis.

In the South polar skua sample, the levels of HCHs, DDTs, CHLs, and PCBs are 46.3, 1620, 1340, and 9320 ng/g lipid, respectively, and those for the Kelp gull sample are 1.38, 199, 87.5, and 160 ng/g lipid, respectively. The OCP and PCB levels in the muscles of the South polar skua and Kelp gull collected from Adelaide Island in 2016/17 are slightly higher than those in this study (Krasnobaev et al., 2018), however, the results cannot be directly compared due to the small sample number of both studies. The high POP levels in the top predators, South polar skua and Kelp gull, can be attributed to bioaccumulation. In addition, these migratory birds can also accumulate POPs from the mid- and low-latitude overwintering regions, even though the influence of the overwintering region will be smaller than the influence of the breeding region (Leat et al., 2013).

The Limpet, *Nacella concinna*, is one of the most abundant species in the intertidal zone and has been used as an indicator of the extent of Antarctic contamination. In the Limpet samples, the levels of HCHs, DDTs, CHLs, and PCBs are 0.592–2.85, 0.192–29.6, 0.137–6.84, and 1.60–12.8 ng/g lipid, respectively. The legacy POP levels in the Limpets from the East Antarctic coast measured in 2009 (Ko et al., 2018) are similar to those in this study. The POP levels from King George Island in the summer of 2004/05 reported by Cipro et al. (2013) show a similar concentration range to the one reported in this study despite a 9-year time gap, while the levels of PCBs are 10–100 times higher than those observed in this study. This difference can be partly attributed to the decreasing trend of PCBs in coastal seawater, as established using *Trematomus bernacchii*, an Antarctic benthic fish as a bioindicator: PCB levels in the Antarctic seawater were the highest in the early 2000 s and then decreased sharply (Cincinelli et al., 2016).

The $\delta^{15}\text{N}$ and POP levels in Limpet samples from 15 different locations from the Barton Peninsula and Maxwell Bay indicate the influence of both human activity and secondary emission from penguin colonies

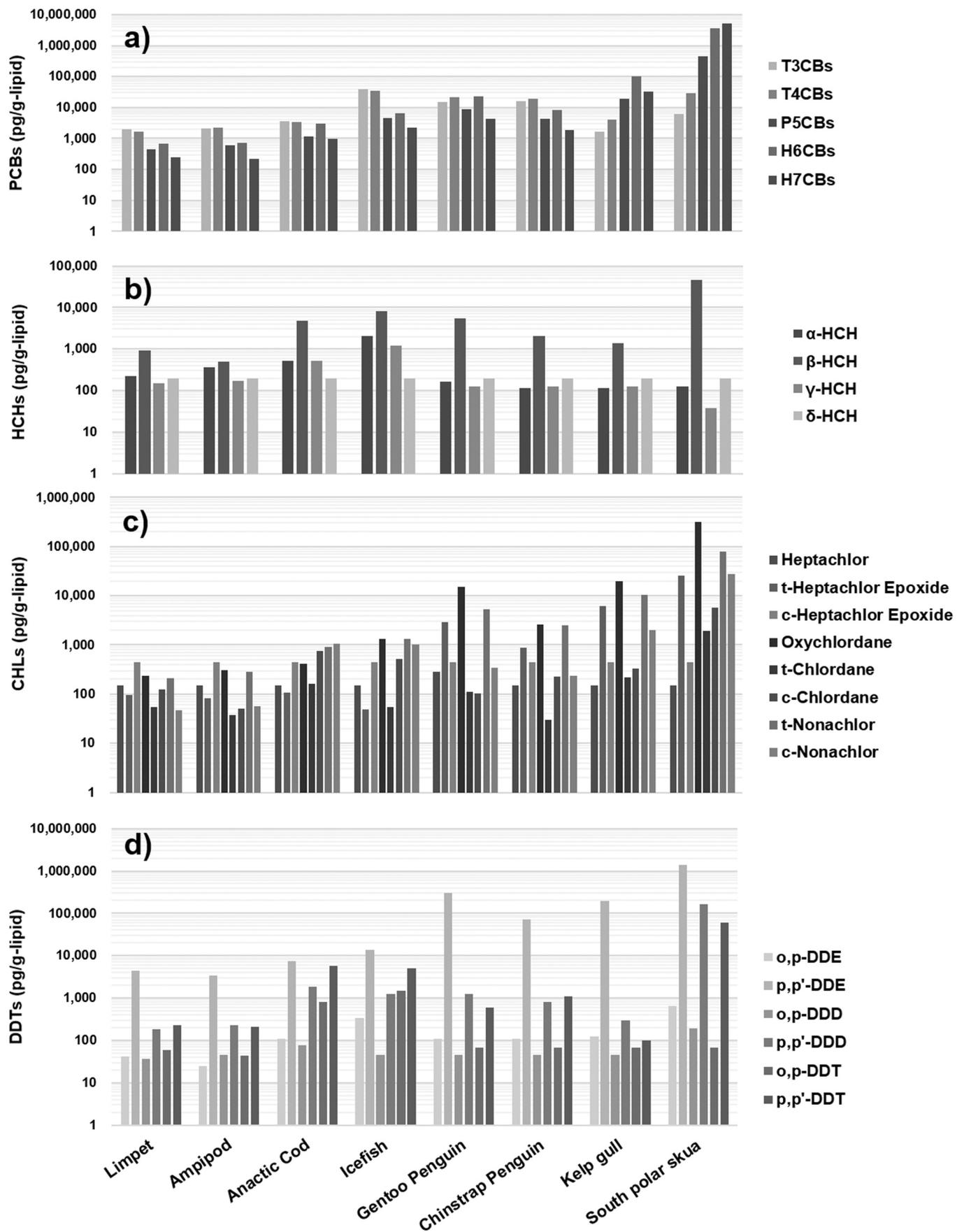


Fig. 2. Average concentrations of a) PCBs, b) HCHs, c) CHLs, and d) DDTs in the animal samples from the Barton Peninsula and Maxwell Bay, King George Island.

(Fig. S1). Therefore, we note that there are still emission sources other than LRT in the Antarctic ecosystem. Notably, the Antarctic cods were caught from the harbor in front of King Sejong Research Station, and therefore may be influenced by human activity, such as wastewater discharge.

The legacy POP levels in the Antarctic cod samples are 2.11–12.8, 10.4–35.3, 2.19–6.13, and 5.03–21.6 ng/g lipid for HCHs, DDTs, CHLs, and PCBs, respectively. The POP levels in Antarctic cods from King George Island in 2006/07 reported by Cipro et al. (2013) are 10 times higher than those in this study. Lana et al. (2017) also report CHL levels from King George Island in 2008–2011, that are similar to those reported in this study. In the Antarctic icefish, the HCH, DDT, CHL, and PCB levels are 11.5, 22.1, 7.43, and 87.9 ng/g lipid, respectively. These

values are 2–10 times higher than those from East Antarctica only 3–6 years back (Lana et al., 2017). These large spatial and temporal differences can be explained by the sampling locations, as the fish were caught at research stations and should be supplemented with further monitoring studies on samples from different locations. Among the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and POP levels, the CHL and DDT levels are significantly correlated with length and weight of the fish (Table S6).

In the Amphipod samples, the levels of HCHs, DDTs, CHLs, and PCBs are 0.910–1.04, 1.10–6.70, 0.698–2.47, and 4.13–7.39 ng/g lipid, respectively. Amphipod 1 (*Gondogeneia antarctica*), which was collected from the intertidal zone, and Amphipod 2 (*Cheirimonon femoratu*), which was collected with a baited trap, show the same magnitude of total OCP and PCB levels, but different congener profiles. In

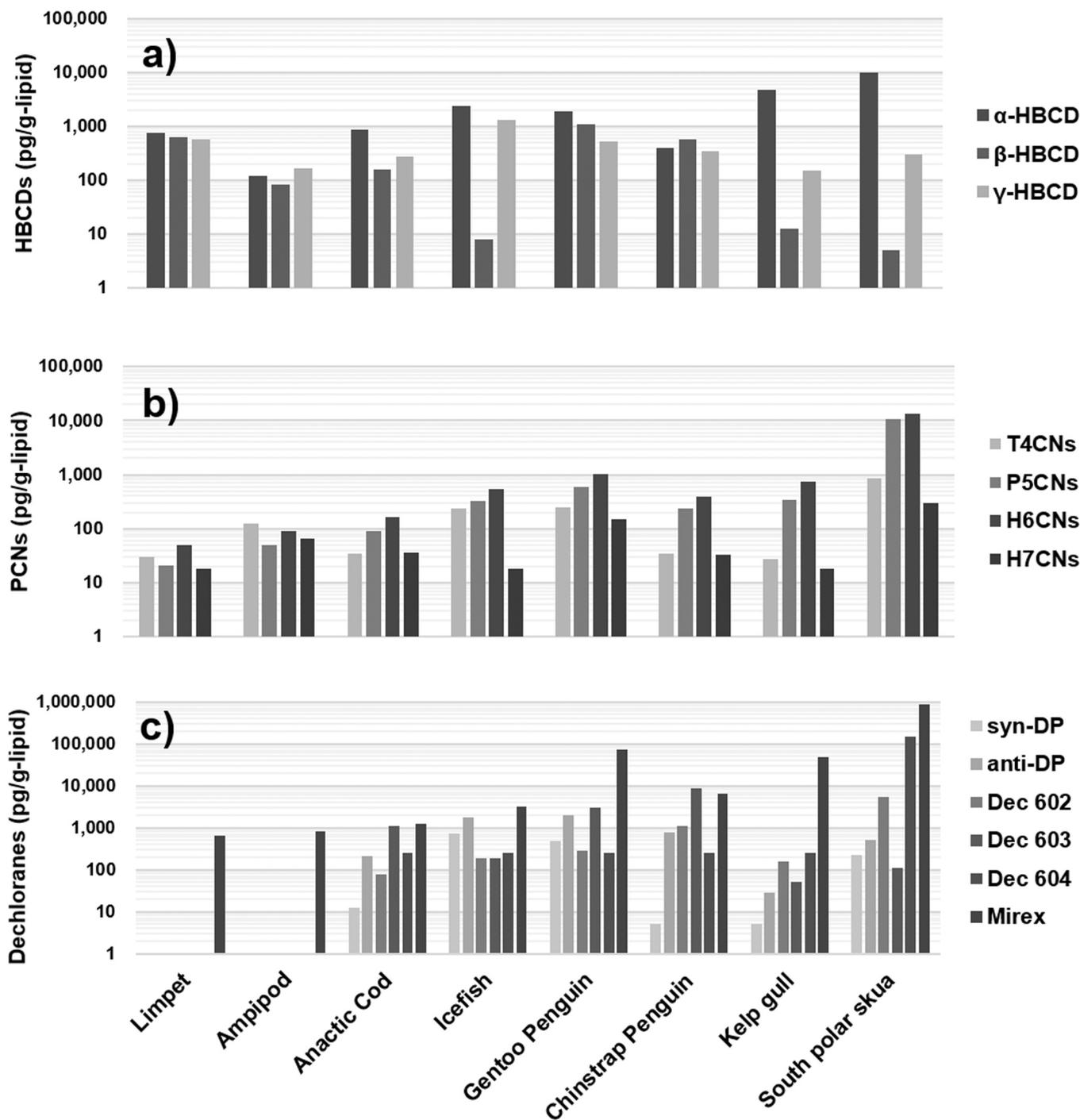


Fig. 3. Average concentrations of a) HBCDs b) PCNs, and c) Dechloranes in the animal samples from the Barton Peninsula and Maxwell Bay, King George Island.

Amphipod 2, heavier molecular PCBs are abundant and the DDE/DDT ratio is high, whereas Amphipod 1 accumulated predominantly lighter PCBs and shows a fresher DDT pattern. This seems to reflect the difference in dietary habits of coastal, herbivorous Amphipod 1 and benthic, carnivorous Amphipod 2. While little attention has been paid to the effect of pollution on Amphipods, a recent study warned that Amphipods, one of the key basal species in the Antarctic ecosystem, could be affected by organic contamination by direct exposure (Kang et al., 2015).

Collectively, the POP levels and isotopic compositions show significant differences among the animal species, but are still influenced by spatial variations of habitats, body size, foraging ecology, and overwintering areas. Even though it was not investigated in this study, the reproductive status, biotransformation efficiency, and omnivorous feeding can also affect the isotopic ratio and POP levels (Borgå et al., 2012). Recently, several studies reported that legacy POPs, such as OCPs, PCBs, and PBDEs, have been decreasing in Antarctic biota (Cincinelli et al., 2016; Markham et al., 2018), while some chemicals are maintained or increase slightly depending on the ecosystem and animal species (Ellis et al., 2018). Since the production of OCPs and PCBs has been restricted, emission from mid- to low-latitude regions as well as LRT to the Antarctic environment have decreased drastically. On-going climate change, triggering glacier melting and reducing the sea ice extent, may change transport and deposition patterns of POPs to Antarctica. Therefore, long-term trends of legacy POPs and their potential consequences should be investigated further.

3.2. Levels of PCNs, HBCDs, and dechloranes in Antarctic animal tissues

The levels of PCNs, HBCDs, and Dechloranes in the analyzed Antarctic animal samples are shown in Fig. 3, and concentrations are presented in Tables S3–S5. Few studies to date address the levels (Corsolini et al., 2002; Kim et al., 2015) and sources (Kim et al., 2018; Krasnobae et al., 2018) of PCNs, HBCDs, and Dechloranes in the Antarctic environment. However, the report on the fate and behavior, especially trophodynamics of the new POPs in the Antarctic environment has hardly been investigated.

The levels of PCNs measured in this study are 0.024–0.196 ng/g lipid in Limpets, 0.234–0.532 ng/g lipid in Antarctic cods, 0.222–0.603 ng/g lipid in Amphipods, 1.79 ng/g lipid in Antarctic Icefish, 0.012–25.6 ng/g lipid in Gentoo penguins, 0.158–1.53 ng/g lipid in Chinstrap penguins, 57.9 ng/g lipid in the South polar skua, and 2.00 ng/g lipid in the Kelp gull. Overall, PCN 73 and 74, followed by PCN 50 and 51, are the most abundant congeners across the food web, while PCN 74 and 51 are predominant in the Kelp gull and South polar skua. The concentrations and congener profile in this study corresponds well with our previous study on PCNs in the penguins and skua samples (Kim et al., 2015), despite a 5-year time lag. The results of this study are among the lowest for the species in similar niches in other ecosystems across mid-, low-latitude, and high northern latitudes (Kim et al., 2015).

HBCDs were detected in all samples and the levels are 0.15–20.7 ng/g lipid in Limpets, 0.423–2.59 ng/g lipid in Antarctic cods, 0.291–0.449 ng/g lipid in Amphipods, 3.73 ng/g lipid in Antarctic icefish, 0.008–19.4 ng/g lipid in Gentoo penguins, 0.619–3.38 ng/g lipid in Chinstrap penguins, 10.3 ng/g lipid in the South polar skua, and 4.81 ng/g lipid in the Kelp gull. Among the stereoisomers, α - and γ -HBCD are dominant in all samples, with the levels of α -HBCD being much higher than the γ -HBCD levels in the Limpet, Antarctic cod, Kelp gull, and South polar skua samples. The HBCD levels in the bird tissues are similar or slightly lower than those reported in our previous study conducted on King George Island (Kim et al., 2015). The levels in the cod, however, are much lower than those from the McMurdo and Scott stations, indicating the emissions vary from station to station (Chen et al., 2015). The proportions of α -HBCD and γ -HBCDs are 30–40% each in Limpets, Amphipods, and penguins, and the fraction of α -HBCD increases to 65% in the Antarctic icefish and Antarctic cods, and to 97% in

the Kelp gull and South polar skua samples. Compared with the percentage of γ -HBCD in the commercial mixture (75–89%) (Covaci et al., 2006), the proportion of α -HBCD is higher in the animal samples in this study. This diastereomeric fractionation might be attributed to the higher physicochemical and biological stability of α -HBCD, and the photochemical and biological transformation of γ -HBCD to α -HBCD during LRT and bioaccumulation (Marvin et al., 2011). It should be noted that there is no direct evidence of the long-range atmospheric transport (LRAT) of HBCDs. However, several previous studies indicate the possibility of the LRAT of HBCDs, such as the widespread detection of HBCDs in the South Shetland Islands (Kim et al., 2018), the occurrence of HBCDs in the other remote region (Zhu et al., 2013), and the detection of HBCDs in the Penguin chick tissues fed from the open Southern ocean (in this study).

Dechloranes were also detected in all sampling species with *anti*-DP being the dominant phase. The levels of DPs in this study are 0.398–11.1 ng/g lipid in Limpets, 0.0–0.548 ng/g lipid in Antarctic cods, 0.227–8.71 ng/g lipid in Amphipods, 2.50 ng/g lipid in the Antarctic icefish, 0.009–11.8 ng/g lipid in Gentoo penguins, 0.0–3.00 ng/g lipid in Chinstrap penguins, 0.731 ng/g lipid in the South polar skua, and 0.028 ng/g lipid in the Kelp gull. The fraction of *anti*-DP (f_{anti}) of the Limpets and Antarctic cods are 0.68 ± 0.24 (mean \pm standard deviation) and 0.57 ± 0.11 , respectively. Gentoo and Chinstrap penguin samples show 0.74 ± 0.20 and 0.65 of f_{anti} , and the Antarctic icefish, the Kelp gull, and the South polar skua have 0.71, 0.10, and 0.79 of f_{anti} , respectively.

Compared with the results from King George Island in 2008/09 (Kim et al., 2015), the DP levels in the penguin samples have slightly increased, although the sample size of the previous study was small. As Dechloranes have replaced PBDEs as alternative flame retardants (Sverko et al., 2011; Wang et al., 2016), the DP levels were likely to increase between 2008/09 and 2013/14. The study of Na et al. (2017) in the same region one year previously shows similar DP concentrations in the Limpets, cods, penguins, and skuas. The f_{anti} in that study, however, ranges from 0.23 to 0.53, which is much lower compared to this study and another studies in Antarctica (Kim et al., 2015). The f_{anti} could have decreased because of diastereomerization during LRT (Wang et al., 2016), however, because of bioaccumulation, f_{anti} in biota samples, even in the remote regions, are expected to and are found to be similar or higher than those in commercial mixtures (Feo et al., 2012; Wang et al., 2016). The results of this study correspond with these previous reports, indicating the absence of confounding factors.

The levels of Dec 602 and 603 in this study are 0.0–0.207 and 0.0–0.838 ng/g lipid in Limpets, 0.0–0.155 and 0.0–5.17 ng/g lipid in Antarctic cods, 0.028–0.179 and 0.198–0.556 ng/g lipid in Amphipods, 0.184 and 0.189 ng/g lipid in the Antarctic icefish, 0.001–1.57 and 0.001–14.7 ng/g lipid in Gentoo penguins, 0.372–2.13 and 2.68–21.8 ng/g lipid in Chinstrap penguins, 5.54 and 0.112 ng/g lipid in the South polar skua, and 0.153 and 0.0 ng/g lipid in the Kelp gull, respectively. Dec 604 was only detected in the South polar skua and its concentration is 150 ng/g lipid. Dec 602 levels in the bird tissues are similar to those reported in our previous study (Kim et al., 2015), while Dec 603 and Dec 604 were detected for the first time in Antarctic biota, suggesting that these chemicals were also transported to this remote region.

In this study, PCNs, HBCDs, and Dechloranes were widely detected in animal samples from King Gorge Island, Antarctica, even though the concentrations of the new POPs are generally lower than those in other remote regions. It should be noted that human activity and penguin colonies significantly influence the distribution, as revealed by the analysis of Limpets (Fig. S1), mosses, and lichens (Kim et al., 2018). As there are many research stations and military bases, and tourism on the rise in the region, the use of chemicals and goods emitting chemicals should be further assessed and eventually regulated for the protection of this ecosystem. Moreover, input, accumulation, and temporal trends of the new POPs accumulation in Antarctica have barely been investigated

and should be studied.

3.3. TMFs of new and legacy POPs in the Antarctic ecosystem

To assess the trophic magnification of new and legacy POPs, we evaluated the TMFs in food web of the Antarctic ecosystem. It should be noted that the food web structure assumed in this study is not well constrained. The prey–predator relationships among the animal species in the adjacent area, Potter Cove, have been studied by the Alfred Wegener Institute (AWI) (Wiencke et al., 2008, 1998), and only a few strong prey–predator dependencies, such as krill-penguin chick-skua, krill-penguin-seal, and Limpet-Kelp gull, were found. Based on the studies, Marina et al., (2018) found that linkage density, connectance, omnivory percentage, and the clustering coefficient of the food web network of Potter Cove are low, that its path length is short compared to other ecosystems, and that there are multiple energy pathways across the food web. Therefore, even though this system is isolated and the samples include key species of this system, the food web model in this study had to be narrowly defined.

As the food web model is not well constrained, the TMFs of POPs were assessed in several different food web models. Firstly, we calculated the TMFs and compared the models with and without minor species including Amphipod, Antarctic icefish, Kelp Gull, and South polar skua. And then, as two different carbon sources are used in the food web, we tested the TMFs in sub-web models: (a) poikilotherms and (b) homeotherms. The TMF values in the whole food web excluding the minor species are presented in Table 2 and Fig. 4. And the TMFs in whole food web with all species, poikilotherms, and homeotherms are shown in Table S7 of Supplementary Material. The TMFs were significantly larger than 1 for most of PCBs and OCPs, and for α -HBCDs and PCNs. There were only a few differences between the models with and without the minor species. The finding that the legacy POPs of PCBs, HCHs, CHLs, and DDTs were significantly magnified through the trophic levels (TMF > 1) was consistent with previous studies (Fisk et al., 2001; Hop et al., 2002). In particular, the TMFs of PCB 153 and PCB 180, which are used to verify the feasibility of TMF evaluation models, were > 1 in all models. Therefore, the TMF evaluation models could be regarded to be appropriate for the food web study (Borgå et al., 2012; Fisk et al., 2001).

The TMFs of most POPs were significantly larger than 1 in poikilotherms, but only for some PCBs and CHLs in homeotherms (Table S7). It should be noted that the homeotherm models have some limitations: Firstly, there are too many penguins with similar TLs, with only two cases for the Kelp gull and the South polar skua. In addition, the metabolic turnover rate of penguin chicks is different from that of adults, and thus $\delta^{15}\text{N}$ and the TL of penguin chicks can vary depending on age and body condition. The much higher TMFs in homeotherm models compared to those of the poikilotherm models can be attributed to a higher turnover rate of the homeotherms (Borgå et al., 2012) and a too narrow TL range of the models. Therefore, particular care must be taken in the interpretation of the homeotherm models.

The TMFs of chemical compounds are known to depend mainly on two factors, lipophilicity (K_{OW}) and metabolic rate (k_m) (Walters et al., 2016, 2011). Lipophilicity facilitates the uptake and preservation in lipid compartments. When the lipophilicity of a chemical is too high, the absorption of the chemical is reduced, as the bioavailability decreases above $\log K_{OW} = 8$. The optimal range of $\log K_{OW}$ for TMFs has been reported as 6–8. Meanwhile, the chemicals with lower k_m are recalcitrant to the metabolism and excretion, and have a longer biological half-life, lower metabolic rate, and a greater tendency to be biomagnified. The legacy POPs with high TMFs in this study have $\log K_{OW}$ in the range of 6–8, and lower k_m .

Dominant PCN congeners, even though only four congeners were detected in more than 50% of whole food web models, were significantly magnified through the trophic levels. To our knowledge, this is the first study to identify TMFs of PCNs in the polar region and the second study of the global environment. Only one TMF study of PCNs from China (Cui et al., 2018) reported that penta- and hexa- PCNs are magnified through the aquatic food web, while other homologues have positive TMFs with higher p-values ($p > 0.05$), which corresponded with the results of this study. The trophic magnification of HBCDs was evaluated in Antarctica for the first time. The TMFs of α -HBCD are higher than 1 in all models and γ -HBCDs are magnified in the poikilotherm model. HBCDs have a bigger molecular size which may hinder cellular uptake as an alternative to PBDEs, but their $\log K_{OW}$ values range from 5.7 to 6.3 (EPA, 2014; Kuramochi et al., 2007), which is comparable with legacy POPs. In particular, the TMF for α -HBCD is found to be higher than those for the

Table 2

Trophic magnification factors of new and legacy POPs in the ecosystem of the Barton Peninsula and Maxwell Bay, King George Island^a.

	TMF	95% CI	p	DF		TMF	95% CI	p	DF
PCB 31/28	2.39	(0.93–6.09)	0.068	49	t-Hep. Epox.	1.01	(0.20–4.89)	0.987	25
PCB 21/20/33	1.96	(0.85–4.46)	0.108	49	Oxychlorodane	1.95	(0.33–11.5)	0.446	27
PCB 22	2.11	(0.94–4.74)	0.068	49	t-Chlordane	2.06	(0.79–5.35)	0.133	26
PCB 52	2.39	(0.95–6.02)	0.064	49	c-Chlordane	4.45	(1.81–10.8)	0.002	26
PCB 49	2.60	(1.02–6.57)	0.044	49	t-Nonachlor	2.88	(0.77–10.7)	0.111	28
PCB 48/47/75	3.27	(1.03–7.76)	0.008	49	c-Nonachlor	2.88	(0.85–9.68)	0.085	28
PCB 74	2.01	(0.82–4.90)	0.124	49	Mirex	2.15	(0.27–16.7)	0.451	28
PCB 70	2.45	(1.03–5.83)	0.042	49					
PCB 66/80	2.29	(0.96–5.42)	0.059	49	p,p'-DDE	4.51	(0.53–37.7)	0.158	27
PCB 101	2.04	(0.87–4.74)	0.096	49	p,p'-DDD	7.05	(2.47–20.0)	0.001	28
PCB 99	2.96	(1.75–4.98)	< 0.001	49	p,p'-DDT	9.95	(2.60–38.0)	0.002	28
PCB 118	6.85	(2.42–19.4)	0.001	49					
PCB 105	3.58	(1.38–9.20)	0.009	49	PCN 52/60	3.03	(1.18–7.72)	0.021	48
PCB 139/149	3.18	(1.36–7.37)	0.008	49	PCN 50	5.12	(2.16–12.0)	< 0.001	48
PCB 146	2.92	(1.10–7.74)	0.032	49	PCN 66/67	1.68	(0.62–4.50)	0.294	48
PCB 153/168	5.90	(1.99–17.4)	0.002	49	PCN 73	1.09	(0.59–3.22)	0.450	48
PCB 164/163	2.49	(1.09–5.68)	0.030	49					
PCB 138	5.93	(2.22–15.8)	0.001	49	α -HBCD	4.06	(1.81–9.09)	0.001	48
PCB 156	1.97	(0.82–4.70)	0.123	49	β -HBCD	3.44	(0.62–18.9)	0.153	48
PCB 187/182	2.88	(1.06–7.78)	0.038	49	γ -HBCD	1.74	(0.82–3.63)	0.139	48
PCB 183	3.03	(1.35–6.80)	0.008	49					
PCB 180/193	4.32	(1.32–13.9)	0.016	49	syn-DP	0.40	(0.22–0.69)	0.002	37
					anti-DP	0.31	(0.12–0.76)	0.013	37
α -HCH	1.40	(0.74–2.63)	0.281	28	Dec 602	1.12	(0.44–2.80)	0.806	37
β -HCH	2.02	(0.71–5.70)	0.177	28	Dec 603	1.10	(0.22–5.38)	0.901	37
γ -HCH	1.93	(1.12–3.30)	0.019	28					

^a except Amphipod, Antarctic icefish, Kelp gull, and South polar skua.

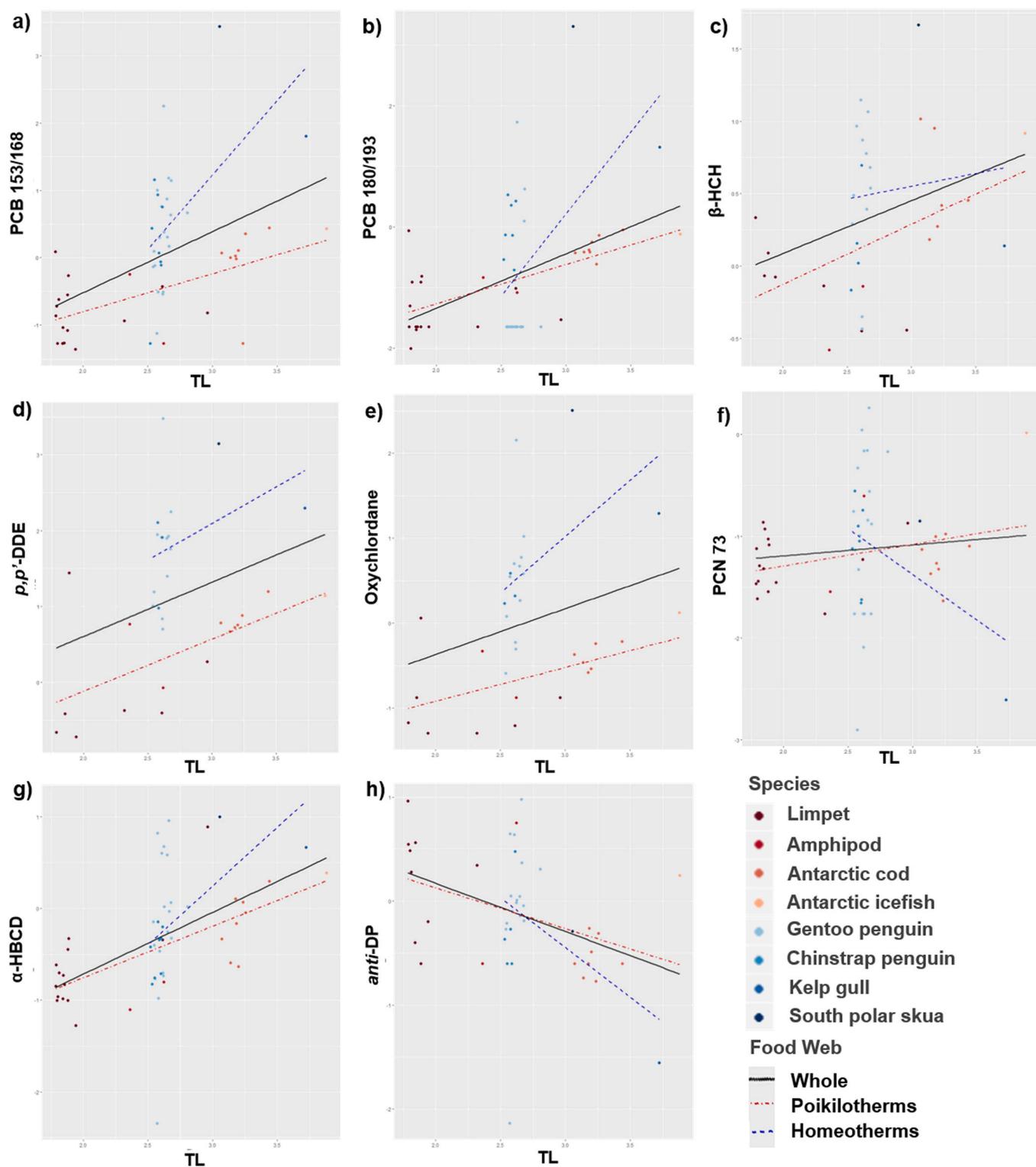


Fig. 4. Trophic magnification of major compounds; a) PCB 153/168, b) PCB 180/193, c) β -HCH, d) p,p' -DDE, e) Oxychlorane, f) PCN 73, g) α -HBCD, and h) $anti$ -DP. The y-axis is the logarithm of the concentration and the x-axis the trophic level. Homeotherms and poikilotherms are represented by red and blue dots, respectively, and the linear regression lines for each trophic magnification are represented as colored lines; red-dot-dashed line for poikilotherms, blue-dashed line for homeotherms, and black-solid line for whole food web with all samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

other diastereomers, indicating selective magnification and transformation of γ -HBCD into α -HBCD (Marvin et al., 2011).

It is noteworthy that *syn*- and *anti*-DPs are significantly diluted through trophic levels in the entire food web and the poikilotherm models. As described in the introduction, the bioaccumulation potential

of Dechloranes is controversial. The result of this study is consistent with a study from an E-waste recycling region in southern China (Zhang et al., 2011), but contradicts previous studies of freshwater ecosystems in China (Wang et al., 2015; Wu et al., 2010). Notably, the results reported by Na et al. (2017), the first attempt to determine TMFs of Dechloranes

on King George Island, are also opposite to the results of this study. The study includes a wide range of trophic levels and evenly distributed numbers of sample species, but still only one skua sample was included in the food web model. In addition, abnormally low f_{anti} reported in that study also raises the question of the validity of the evaluated DP levels. The inconsistency of these two studies needs to be clarified. Eventually,

reassessment using an improved design with more evenly distributed species and large sample numbers should be carried out.

Fig. 5 shows the relationship between TMFs estimated in this study and K_{OW} . The K_{OW} values were evaluated using EPI Suite™ (USEPA, Washington, DC, 2012) and other sources (Chou et al., 1979; Kuromochi et al., 2010; Puzyn and Falandysz, 2005). The TMFs increase with K_{OW}

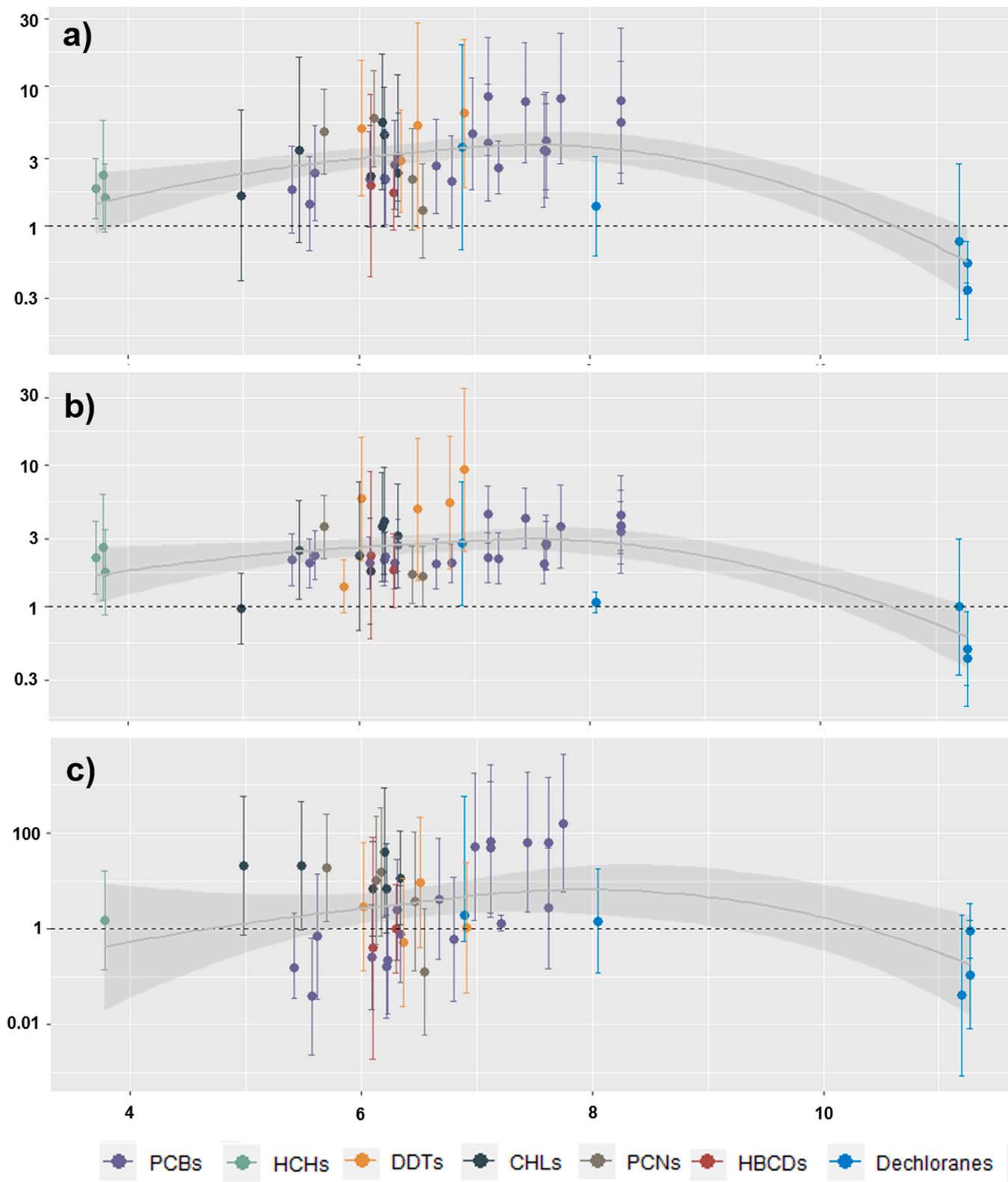


Fig. 5. Relationship between TMF and K_{OW} of the new and legacy POPs in a) the whole food web, b) homeotherms, and c) poikilotherms.

and then decrease in the range of $\log K_{OW} > 8$. DPs are the only compounds with high K_{OW} values to be magnified through the trophic levels. The $\log K_{OW}$ of DPs covers a wide range from 9.3 (Chou et al., 1979) - 11.3 (USEPA, Washington, DC, 2012). In addition, it is dependent on the estimation methods. In any case, the relationship between K_{OW} and TMF is consistent in this study. As shown in Fig. 5, the TMF is dependent on K_{OW} and reaches maximum values for $\log K_{OW} = 6-8$, consistent with the literature (Walters et al., 2016, 2011).

4. Conclusions

In this study, the levels of new and legacy POPs, including OCPs, PCBs, PCNs, HBCDs, and Dechloranes, in an Antarctic ecosystem and their trophic magnification and dilution was investigated. Due to the difficulty of sampling in the Antarctic, this study has an intrinsic limitations, including an unbalanced replication for individual species, ignorance of confounding factors, and reliance on an estimated enrichment factor. Nevertheless, this study successfully has identified widespread contamination and trophic distribution of PCNs, HBCDs, and Dechloranes in the Antarctic ecosystem. The results of this study provide the evidence of LRT and bioaccumulation of the new chemicals which are under consideration of adding to the Stockholm Convention POPs list.

CRedit authorship contribution statement

Jun-Tae Kim: Conceptualization, Formal analysis, Writing - original draft. **Yun-Jeong Choi:** Investigation. **Mandana Barghi:** Investigation. **Jeong-Hoon Kim:** Funding acquisition, Methodology. **Jin-Woo Jung:** Investigation, Methodology. **Kitae Kim:** Funding acquisition, Writing - review & editing. **Jung-Ho Kang:** Funding acquisition, Writing - review & editing. **Gerhard Lammel:** Writing - review & editing, Validation. **Yoon-Seok Chang:** Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2020.124141](https://doi.org/10.1016/j.jhazmat.2020.124141).

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