Are ingested plastics a vector of PCB contamination in northern fulmars from coastal Newfoundland and Labrador?

J.F. Provencher¹,⁎, S. Avery-Gomm², M. Liboiron³, B.M. Braune⁴, J.B. Macaulay⁵, M.L. Mallory⁶, R.J. Letcher⁷

¹ Biology Department, Acadia University, 15 University Drive, Wolfville, Nova Scotia, Canada B4P 2R6
² Centre of Excellence for Environmental Decisions, University of Queensland, St. Lucia, Brisbane, Queensland 4103, Australia
³ Department of Geography, Memorial University of Newfoundland, St. John’s, Newfoundland, Canada A1B 3X9
⁴ Environment and Climate Change Canada, National Wildlife Research Centre, Carleton University, Ottawa, ON, Canada K1A 0H3
⁵ Research and Productivity Council, Fredericton, NB, Canada E3B 6Z9

ABSTRACT

While marine animals are exposed to environmental contaminants via their prey, because plastic pollution in the aquatic environment can concentrate some chemicals, ingested plastics are thought to increase the exposure of biota to contaminants. Currently, in the literature there are contradictory results relating to how higher levels of ingested plastics by birds may lead to higher levels of polychlorinated biphenyl (PCBs). To date none of these have incorporated known Toxic Equivalency Factors (TEFs) for non-ortho and mono-ortho congeners of PCB which is critical to assessing the potential effects from PCBs. We examined northern fulmars (Fulmarus glacialis) from the Labrador Sea region Canada, and the ingested plastics from these same birds for comparative PCB concentrations. We found no significant correlations between the PCB concentrations in the birds and the mass or number of retained ingested plastic pieces in the stomach, this held true when PCBs were considered by a number of different ways, including ΣPCB, ΣPCB, lower-chlorinated, high-chlorinated, non-ortho PCB, and mono-ortho congeners. PCB concentrations were lower in plastics as compared with livers. We found significant differences in congener profiles between the ingested plastics and seabird livers suggesting that while plastics do not contribute to the PCB concentrations, there may be some interactions between plastics and the chemicals that the birds are exposed to via ingested plastics.

1. Introduction

Plastic and pollution is recognized as a major pollutant in marine ecosystems (STAP, 2011; UNEP, 2014). While plastic pollution has been identified as a problem from an economic perspective (loss of product, clean-up costs), a large body of research has also demonstrated that plastic pollution can be harmful to aquatic biota (Kühn et al., 2015; Provencher et al., 2017; Vegter et al., 2014). In particular, plastic pollution has been identified as a problem to biota due to both entanglement and ingestion (Kühn et al., 2015). A recent review demonstrated how biota may be affected by ingested plastic pollution across the range of biological organization, from cellular impacts at the genetic level to population level impacts (Galloway et al., 2017). It has been estimated that marine plastic pollution will continue to be a problem for aquatic ecosystems for decades to come due to current lack of international agreements (Borrelle et al., 2017). Thus, a better understanding of the impacts of plastic pollution on biota is critical.

Over 200 seabird species have been found to ingest plastic and other debris items since this phenomenon was first reported in the 1960s (Kühn et al., 2015; Provencher et al., 2017). Research investigating the potential negative impacts from plastic ingestion in seabirds has often focused around the physical impacts of ingested plastic pollution. There is a growing recognition that ingested plastics can also affect seabirds by altering the exposure levels and patterns of a number of environmental contaminants (Koelmans et al., 2016; Teuten et al., 2009; Ziccardi et al., 2016). Plastic pollution may have high concentrations of a range of hydrophobic environmental contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) as compared to the surrounding seawater, suggesting that plastics can act as an sorptive platform for contaminants (Endo et al., 2005; Mendoza and Jones, 2015; Zhang et al., 2015). In turn, enhanced desorption of persistent organic pollutants (POPs) has been shown to

⁎ Corresponding author.
E-mail address: jennifer.provencher@acadiau.ca (J.F. Provencher).

https://doi.org/10.1016/j.envres.2018.07.025
Received 5 June 2018; Received in revised form 6 July 2018; Accepted 14 July 2018
Available online 17 July 2018
0013-9351/ Crown Copyright © 2018 Published by Elsevier Inc. All rights reserved.
occur under simulated digestive conditions in laboratory settings (Bakir et al., 2014; Tanaka et al., 2015), and experiments have shown that plastic-associated environmental contaminants can be taken up by aquatic biota when exposed to plastics including invertebrates, birds and fish (Chua et al., 2014; Hamlin et al., 2015; Tanaka et al., 2013). Studies examining wild birds have also found that ingested plastic burdens are associated with higher levels of contaminants in seabirds (Lavers and Bond, 2016; Ryan et al., 1988).

Research has demonstrated that plastic pieces can absorb PCBs in relatively high concentrations (Endo et al., 2005; Rochman et al., 2013; Taniguchi et al., 2016; Zhang et al., 2015). PCBs are of particular concern in wildlife as they are known to cause a number of negative health impacts in wildlife including alterations in endocrine functions (Murvoll et al., 2007; Rozemeijer et al., 1995; Tartu et al., 2015). While it is clear that wildlife that have ingested plastics are likely exposed to PCBs absorbed from the marine environment, it is not well understood if, and how, this increased exposure contributes to significantly higher concentrations of PCBs, and perhaps some PCB congeners, in biota (Ziccardi et al., 2016). Some studies show that seabirds have increased concentrations of contaminants in relation to higher levels of ingested plastic pollution. For example, Ryan et al. (1988) found a positive correlation between the mass of ingested plastics in Great Shearwaters (Ardenna gravis) and 27 congeners (ΣPCBs). Similarly, the mass of accumulated plastics in Northern Fulmars (Ardeida tenuirostris) was significantly, positively correlated with the concentrations of lower-chlorinated PCB congeners (Yamashita et al., 2011). However, these patterns did not hold for higher-chlorinated PCB congeners, nor with total PCB concentrations, suggesting that there may be congener-specific attributes that are important to consider when examining the relationship between ingested plastic and PCBs (Yamashita et al., 2011). In contrast to both of these studies, Trevail et al. (2014) found no association between plastic burdens and ΣPCB concentrations in Northern Fulmar (Fulmarus glacialis) hepatic tissue. Similarly, Herzke et al. (2015) found that plastics were not likely a significant route of ΣPCBs in Northern Fulmars. While the above studies examine PCB concentrations in relation to plastic ingestion in several different ways, the toxicity of PCBs to wildlife is complex and none consider the full implications of how the most toxic PCB congener concentrations may be influenced by plastic ingestion. For example, Toxic Equivalency Factors (TEFs) for individual (dioxin-like) PCB congeners have not been considered in plastic ingestion studies (Van den Berg et al., 1998). Therefore, while there can be a link between PCBs and ingested plastics in seabirds, what has not been determined to date is whether there are congener specific relationships, and how this may relate to the known negative effects of PCBs on biota.

The Northern Fulmar is a surface feeding seabird that spends most of its life at sea, and only returns to land to breed each summer (Mallory et al., 2012). The Northern Fulmar feeds on zooplankton and fish (Mallory et al., 2010, 2012), and is known to retain higher levels of plastic pollution than other seabirds feeding in the Canadian Arctic and sub-Arctic regions where plastic ingestion have been examined across a range of species (Bond et al., 2013; Poon et al., 2017; Provencher et al., 2014). In this study, we use the Northern Fulmar as a model species to examine how ingested plastic pollution may act as a vector for contaminants. We focused on PCB concentrations as these chemicals are known to associate with plastics (Endo et al., 2005), and studies from Pacific and southern waters have suggested a correlation between PCBs and ingested plastics in at least some seabird species (Ryan et al., 1988; Yamashita et al., 2011). The overall objective of this paper is to explore PCB congener concentrations in plastics and seabird livers to inform how PCB profiles in seabird livers may be related to accumulated plastics, including the use of TEFs, which has not been done to date. Additionally we also 1) characterize the PCB concentrations in female Northern Fulmars from the Labrador Sea; 2) characterize the PCB concentrations in ingested plastic pieces; 3) compare individual plastic ingestion metrics (the frequency of occurrence, number of plastic pieces and mass of plastic pieces) with individual hepatic PCB concentrations.

2. Methods

2.1. Collections and dissections of northern fulmars

A total of 31 fulmars were collected at sea by Inuit hunters on board a vessel in mid-July in 2015, off the coast of Newfoundland and Labrador (Avery-Gomm et al., 2018; OSM). For this study, a subset of 10 female northern fulmars were selected from this larger sample set for further analysis. A single sex was chosen to examine for patterns as sex differences in some contaminants have been detected in this species (Braune et al., 2010). We deliberately selected females that represented a wide spectrum of accumulated plastics from one individual that contained no plastic pieces, to the female that contained the highest levels of plastics in the larger sample. Detailed collection and dissection methods can be found in Avery-Gomm et al. (2018), and in Online Supplemental material (OSM). For each bird, the entire stomach (esophagus to cloaca) was removed upon dissection and refrozen. Individual gastro-intestinal tracts (GItS) were later examined for ingested plastic pieces and other debris at Environment and Climate Change Canada’s National Wildlife Research Institute in Ottawa (Avery-Gomm et al., 2018). Plastic ingestion metrics are summarized for the larger sample (n = 31) and more detail can be found in Avery-Gomm et al. (2018; Table 1). All plastic metrics are presented using the terminology recommended in Provencher et al. (2017), including frequency of occurrence (FO) with 95% confidence intervals, mean, median, and range reported.

During the dissection of each bird, the entire liver was removed and weighed. All complete livers were stored in chemically clean glass jars with foil-lined lids that had also been triple-rinsed with reverse osmosis filtered water, acetone and hexane. Whole livers were homogenized using a chemically cleaned blender, and a 3g aliquot of liver was analyzed for PCBs.

2.2. PCB analysis

Analysis for PCBs in plastics and livers was carried out by the Research and Productivity Council (RPC; Fredericton, NB, Canada). The analysis was for a total of all 209 PCB congeners (see Appendix A in the Supplemental material for a full list). Both liver tissue and plastics were analyzed for PCB concentrations. A subset of 50 debris pieces from the 676 found to be ingested by the northern fulmars were selected for PCB analysis. Liver tissue samples, a certified reference material (CRM) of ground whole carp tissue (CARP-2, Wellington Laboratories) and vegetable oil method blank (locally purchased canola oil) were spiked with 27 13C-isotopically-labelled PCB surrogate standards (Wellington Laboratories) and digested/extracted by adding 30% (w/w) concentrated sulphuric acid (H2SO4) adsorbed on silica gel (70 g), hexane (100 mL) and sonicking for one hour.

Fifty ingested plastic pieces were analyzed for PCBs as a part of this study. This included pieces that were visually sorted as industrial pellets, user fragments, fibers, foam, sheet, wax and rubber. Pieces were selected from the larger mass based on the minimum weight needed for the contaminant analysis, and to represent the range of ingested plastics. Plastic fragment samples and QC plastic samples (blanks and spikes; in-house purified nylon and low-density polyethylene (LDPE)) were spiked with twenty seven 13C-isotopically-labelled PCB surrogate standards. Thirty three native PCB congeners (Wellington Laboratories and Cambridge Isotope Laboratories) were added to QC spikes. Samples were extracted for 30 min by sonication in hexane (10 mL).

The extracts were concentrated by rotary-evaporation and purified by gravity column chromatography; top column: 21 mm i.d. × 280 mm packed (from bottom to top) with un-silanized glass wool plug, 10 mm silica gel, 3.0 g (± 0.1 g) 25% (w/w) 1 M sodium hydroxide (NaOH) adsorbed on silica gel, 5 mm silica gel, 8.0 g (± 0.1 g) 30% (w/w)
concentrated sulphuric acid adsorbed on silica gel, 10 mm silica gel; bottom column: 8 mm i.d. × 130 mm packed (from bottom to top) with un-silanized glass wool plug, 10 mm celite and 0.5 (± 0.01 g) hot activated 5% carbon adsorbed on silica gel and silanized glass wool plug. The dual column arrangement was eluted using 135 mL hexane. The top column was removed and the bottom column was further eluted using 3 mL 1:1 benzene:ethyl acetate followed by 3 mL 1:1 dichloromethane: cyclohexane. The column was inverted and further eluted using 30 mL toluene. The three fractions were combined. Note that the liver, CRM and vegetable oil extracts were subjected to additional purification; the initial 135 mL hexane fraction was concentrated by rotary-evaporation and further purified using a “Superclean sulfur-oxide” column (Sigma), eluting according to manufacturer’s instructions.

The purified extracts were concentrated under a stream of high purity nitrogen, using a TurboVap LV (Zymark) and spiked with five $^{13}$C isotopically labelled PCB recovery standards (Wentling Laboratories). One microliter aliquots were analyzed using an Agilent 6890 gas chromatograph (GC) equipped with an Autospec (M series) high resolution mass spectrometer detector (MasSpec Consulting), acquiring data by multi-group selected ion recording. The GC column was a Restek RTX-PCB (60 m × 0.18 mm × 0.18 µm). Quantification (MassLynx-TargetLynx software, v. 4.1, Waters Corp.) was by isotope dilution and internal standard methods with results corrected for recoveries of $^{13}$C-isotopically labelled PCB surrogate standards.

The vegetable oil blank $\Sigma$PCB concentration was 0.9 ng/g (whole lipid basis) whereas liver $\Sigma$PCB concentrations ranged from 84 to 998 ng/g (whole lipid basis). For liver samples, all $^{13}$C-labelled surrogate standard recoveries were within the range 40–135% (EPA Method 8290A) with the exception of $^{13}$C-PCB-77 in one sample, $^{13}$C-PCB-169 in three samples and $^{13}$C-PCB-209 in three samples. For the CRM, all PCB congener concentrations were within the upper/lower limits of certified or reference values.

In-house purified nylon and LDPE plastics were used for blanks and spikes with each batch of plastic samples. In all batches, the lowest $\Sigma$PCB concentration plastic sample exceeded the corresponding blank $\Sigma$PCB concentration. Blank $\Sigma$PCB concentrations were inversely proportional (approximately) to the weight used of purified plastic, suggesting that $\Sigma$PCB concentrations measured in the blanks could be attributed mostly to background PCB levels in the lab. For plastic samples, all $^{13}$C-labelled surrogate standard recoveries were within the range 40–135% with the exception of $^{13}$C-PCB-54 in six samples, $^{13}$C-PCB-189 in five samples, $^{13}$C-PCB-208 in one sample and $^{13}$C-PCB-209 in five samples. All native congener spike recoveries were within the range 65–135% with the exception of one congener (PCB-206) in one spike. Six of the plastic sample extracts were injected twice for GC/HRMS analysis. The relative percent difference (RPD) of the $\Sigma$PCB concentration results ranged from 2.5% to 12.3%.

The same PCB congeners were analyzed in the livers and the plastic pieces, but the total number of congeners that were quantifiable and contributed to the $\Sigma$PCB concentrations in the ingested plastics and livers did differ (plastic congeners = 163, liver congeners = 150), and thus reported values differ in the results we present.

The lipid contents of the liver samples were determined gravimetrically by the Organic Contaminants Research Laboratory at the National Wildlife Research Centre in Ottawa. Briefly, liver tissue homogenates were ground dried and homogenized with a pestle in a pre-cleaned diatomaceous earth mixture. The accelerated solvent extraction was performed using dichloromethane, after which the sample extract was evaporated using nitrogen evaporation, and the percent extractable lipid was determined in the sample. Blanks were included in the run to assess any lipid contamination. Lipid values are presented as percent mass of the total sample as a means for lipid correcting the PCB concentrations in the tissues.

2.3. Data treatment

The sum PCB and individual congener concentrations are presented for both northern fulmar liver and ingested plastic piece samples as arithmetic means with standard deviations, along with medians, maximum and minimum values (OSM). We compared liver concentrations of PCBs in northern fulmars sampled for this study to published PCB values for fulmars in nearby regions, (Foster et al., 2011; Herzke et al., 2015). We also compared PCB concentrations in plastic pollution to values from the published literature (Endo et al., 2005; Mendoza and Jones, 2015; Zhang et al., 2015).

For statistical analysis, we grouped PCB congeners and summed PCB values as outlined below. Summed PCB concentrations were log transformed as the data were right skewed. A General Linearized Model (GzLM) approach was employed in this study using R to complete all statistical analysis (R Development Core Team, 2017). The mass of ingested plastics and the number of ingested plastic pieces were both square-root transformed to achieve a more normal distribution in the data, and we used a quasi-Poisson distribution within the GzLM framework that accounted for the non-normal distributions within the data when we were not able to normalize distribution with transformations.

First, we compared the $\Sigma_{150}$PCB congener concentrations to the mass and number of accumulated ingested plastics using a GzLM. To further explore PCBs congeners that were specifically found in high concentrations in the ingested plastics, we examined how different suites of PCB congeners related to plastic accumulation levels in the fulmar liver tissue. We next examined how $\Sigma$PCB concentrations of the dominant congeners (CB-153, -180, -138 and -118) related to the mass and number of accumulated ingested plastics as these represented on average 87% of the $\Sigma_{150}$PCB concentrations. A variety of techniques were used to investigate how the PCB congener/homolog profiles in the liver related to the accumulated plastics found in the same birds. First, the mass of plastics and the number of ingested plastics was compared with the different PCB homolog groups (mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-) using a GzLM (quasi-Poisson distribution) for each homolog group. A visual comparison was then carried out of the concentrations of homolog groups by individual bird in relation to the number and mass of accumulated plastics. The number of accumulated plastics and plastic mass was examined in relation to $\Sigma$PCB concentrations (CB-153, -180, 138 and -118), which are the most commonly reported congeners in this species (Braune et al., 2014; Braune and Simon, 2003). Using available Toxic Equivalency Factors (TEFs) for individual (dioxin-like) PCB congeners, concentrations were also expressed as Toxic Equivalent (TEQ) concentrations for the congeners that are known to elicit dioxin-like effects and toxicity in humans and wildlife and fish (Van den Berg et al., 1998). This included the non-ortho congeners CB-77,-81, -126 and -169, and mono-ortho congeners CB-105, -114, -118, -156, -157, -167 and -189 for $\Sigma_1$PCB value in the TEQ. These TEQ concentrations for the PCBs were then compared with the number of plastics and mass of plastics within the birds. The number and mass of accumulated plastics were also compared to the concentrations of the lower PCB congener group (di to tetra) and higher congener groups (penta- to deca-chloro; Yamashita et al., 2011).

3. Results

3.1. Ingested plastics

The fulmars examined included all adult birds. Importantly, examination of the reproductive organs indicate that none breed in the year of collection, therefore offloading of contaminants to eggs via lipid-rich egg formation is not likely to be a major contributing factor to our results. A detailed description of the ingested plastics in the larger sample of 31 northern fulmars used in this study (the n = 10 liver
sample subset) has already been reported in detail (Avery-Gomm et al., 2018). Therefore, we present just the ingested plastics in the 10 birds examined here for PCBs in order to allow comparisons with their contaminant concentrations. Of the 10 northern fulmars examined, 90% (95% Confidence Interval [CI]: 60–98%) contained at least one piece of plastic in their GIT, with only one single bird not containing any ingested plastics.

A total of 676 plastic pieces were found in the 31 northern fulmars examined in the study by Avery-Gomm et al. (2018). Of the plastic pieces recovered from the birds, 95% were classified as user plastics, and predominantly fragments were found to be ingested by the birds (55%). Of the 10 females examined in this study, fragments also dominated the samples by weight, with 67% of the accumulated debris mass in fulmars from fragments, with one individual having 97% of the plastic mass as fragments.

### 3.2. PCBs in plastics

A total of 163 PCB congeners could be quantified in the ingested plastics examined (Appendix A in the OSM; Fig. 1A). Congener-specific PCB concentrations in the plastics were dominated by CB-153, -180, -138 and -118, which were 17%, 8%, 8% and 7%, respectively, of the total PCB concentrations and collectively accounted for a total of 40% of the Σ150PCB (Supplemental Material). Penta-, hexa- and hepta-congeners accounted for 62% of the Σ163PCB concentration in the liver samples, with the ingested plastic samples showing a greater pattern diversity of PCB congeners as compared with the fulmar livers (Fig. 1).

### 3.3. PCBs in livers

A total of 150 PCB congeners were quantifiable in the livers of female northern fulmars from the Labrador Sea (Appendix A in the OSM; Fig. 1B). Similar to the plastic samples, congeners-specific PCB concentrations in the female fulmar livers were dominated by CB-153, -180, -138 and -118, which were 31%, 16%, 11% and 9% of the total PCB concentrations, respectively, which collectively accounted for over 67% of the Σ150PCB concentrations (OSM).

### 3.4. Relationships between plastics and avian liver PCB concentrations

We found that the proportions of the mono- to tetra-chlorinated congeners were generally higher in the plastics than in the livers and the livers generally had higher levels of hexa-, hepta- and octa-chlorinated congeners (Fig. 1). There were no significant differences in the concentrations of the mono-, di- and tri-chlorinated congeners (GzLM; all p > 0.05) between the liver and the plastic pieces, but there were significant differences for the other PCB homolog groups. Livers had significantly higher concentrations of hexa- (GzLM; t58 -7.52, p > 0.0001), hepta- (GzLM; t58 -8.30, p > 0.0001), and octa- (GzLM; t58 -7.06, p > 0.0001) chlorinated congeners, and the ingested plastic pieces had higher concentrations of tetra- (GzLM; t58 -8.08, p > 0.0001), penta- (GzLM; t58 -7.39, p > 0.0001), nona- (GzLM; t58 -6.49, p > 0.0001), and deca- (GzLM; t58 -5.35, p > 0.0001) chlorinated congeners (Fig. 1).

In the livers of northern fulmars from the Labrador Sea, the Σ150PCB concentration did not vary significantly with total mass of ingested debris (GzLM; t58 = -0.75, p = 0.47), nor with the total number of ingested debris pieces found in each bird (GzLM; t58 = 0.19, p = 0.85). There was also no significant relationship between Σ150PCB concentration with total mass of ingested debris (GzLM; t58 = -0.73, p = 0.48) or the number of pieces of debris (GzLM; t58 = 0.26, p = 0.80). No significant differences were found between PCB homolog group concentrations in relation to number of neither ingested plastics, nor mass of ingested plastics (GzLM; all p > 0.37).

PCB concentrations by homolog group for individual birds were compared to the number and mass of the plastics, although there were no obvious trends. In fact, the bird with no accumulated plastics in the gut had the second highest concentrations of Σ150PCBs and as well as many of the PCB homolog groups. To further examine how PCB congeners that were specific to plastics may influence the overall PCB congener profile, the 10 most concentrated congeners (after the top 4 congeners which are also the top 4 in the bird livers; -153, -180, -138, -118) were examined on how they varied with plastic number and mass. The 5–16 top PCB congeners (those that co-eluted are counted as one here) in the plastics were CB-11, -99, -170, -28, -18, -31, -8, -105, -196/203 and -20/21/33. No distinct patterns in these PCB congeners were found in relatively high concentrations in the plastics and relative to the levels of accumulated plastic pieces and mass in the birds (Fig. 2; OSM).

With respect to dioxin-like equivalent concentrations for applicable PCB congeners, there was no correlation between the total TEQ concentrations for Σ150PCBs and the number of pieces of accumulated plastics (GzLM; t58 = 0.63, p = 0.83) nor with the mass of accumulated plastics and the total TEQ concentration for Σ150PCBs (GzLM; t58 = -0.23, p = 0.49). Lastly, when compared to the number and mass of accumulated plastics in the birds and the lower-chlorinated congeners (di, tri, and tetra) and the higher-chlorinated congeners (penta-, hexa-, hepta-, octa-, nona- and deca-) (Yamashita et al., 2011), no significant correlations were found (GzLM, all p > 0.40).

### 4. Discussion

Overall, the birds examined in this study from the Labrador Sea, Canada (a sub-Arctic location) had higher PCB concentrations as compared to previous studies for northern fulmars from the Canadian High Arctic (Prince Leopold Island), and slightly higher levels as compared with a mid-Arctic colony (the Minarets) sampled in the last 15 years.
The PCBs that were quantified in the liver samples, again these results are similar to what other studies have reported in this species (Braune et al., 2014).

We found that the PCB congener concentrations detected in the plastics examined were lower than those detected in the northern fulmar livers. PCB concentrations in plastics in the present study were higher than plastics sampled from the North Pacific reported in Mendoza and Jones (2015), but similar to plastic PCB concentrations in Japan, Mexico, China and Portugal (Frias et al., 2010; Mato et al., 2001; Rios et al., 2007; Zhang et al., 2015). This suggests that plastics in the North Atlantic and Labrador Sea region have moderate levels of associated contaminants as compared to other regions that have been examined for PCB-plastic associations.

While the PCB concentrations do not appear to correlate with northern fulmar liver PCB concentrations in relation to ingested plastics, the PCB congener profile between the ingested plastics and that of the bird livers do show differences. Of note is that some upper trophic bird species, such as northern fulmars are known to be able to metabolize or bio-transform contaminants including PCBs (Letcher et al., 2010). Lower trophic level biota, including prey of fish-eating birds have been reported to ingest plastics (Hipfner et al., 2018). Many PCB congeners are recalcitrant to biotransformation in fish as they generally lack the capacity to metabolize non-dioxin-like PCB congeners (James and Kleinow, 2014). As a result, relative to birds, fish may be more susceptible to the accumulation of plastic-associated PCBs, and subsequently could be biomagnified in fish-eating bird predators. We detected fewer PCB congeners in the fulmar livers as compared to their ingested plastics, which could mean that some congeners present in the plastics may have been metabolically depleted by the birds (to non-detectable levels). Biologically, this may mean that the formation of other byproducts, which may or may not have deleterious effects, or that the compounds are depleted and the effects from them are reduced. Additionally, we found that the livers generally had higher levels of hexa-, hepta- and octa-chlorinated congeners then in the ingested plastics. This may be an indication of congener-specific metabolism as lower chlorinated congeners and ones that are more likely to have adjacent non-chlorinated carbons (preferably meta-para chlorine unsubstituted), which tend to be the least recalcitrant and are more susceptible to enzyme-mediated metabolic depletion. Importantly, we did see a shift to more recalcitrant and higher chlorinated congeners in the bird liver as compared with the plastics. This suggests that those PCB congeners that are more stable persist much longer in the birds, but that other more unstable congeners may have been metabolized.

Importantly, it is the congeners that are the most toxic to birds that should be considered in analyses concerned with effects, and not just those that are more common, or most often reported. Among the 209 theoretical PCB congeners it is only the 11 non-ortho and mono-ortho chlorinated congeners where toxic equivalency factors (TEFs) have been generated and that are known to elicit dioxin-like effects and toxicity in humans and wildlife and fish (Van den Berg et al., 1998). This is relevant when considering how ingested plastics may contribute to dioxin-like toxic burdens within marine biota. While we detected all of the 11 non-ortho and mono-ortho chlorinated congeners with TEFs (Van den Berg et al., 1998), the detection frequency of these dioxin-like PCB congeners was lower in the plastic samples as compared with the fulmar livers. For example, CB-81 and -126 were detected in 100% of the liver samples, but CB-126 was detected in only 11 of the 50 plastic samples (21%), and CB-81 was not detected in any of the plastic samples.

Overall, these findings support previous studies that suggest that ingested plastics are not likely a major vector for PCB concentrations in northern fulmar livers, even when plastics are ingested at relatively high levels (Bakir et al., 2016; Herzke et al., 2015). Thus, prey are likely to most important vector for PCBs into seabird tissues (Herzke et al., 2015). Fish are also vulnerable to ingesting and retaining plastics in the marine environment (Brâte et al., 2016; Collard et al., 2015; Rochman et al., 2015), and so PCBs in seabirds could in part be from ingested plastics in fish, and then passed to seabirds, but much more work is needed to understand these potential trophic pathways related to plastics and its associated contaminants.

Additionally, our findings go further and suggest that even when congener specific patterns are considered and the dioxin-like toxicity of non-ortho and mono-ortho chlorinated congeners are considered,
Ingested plastics do not seem to be a significant source of this contaminant group. While PCB concentrations in at least some species may be correlated with plastic ingestion (Ryan et al., 1988; Yamashita et al., 2011), based on our findings this does not hold true for all species, and accumulated plastics do not appear to be a source of dioxin-like toxicity related to PCBs. Xenobiotic metabolism, including for PCB congeners, in some bird species such as northern fulmars would result in the more metabolically-stable congeners being more dominant as contaminant residues in the tissues of fulmars. Future research should focus on identifying which congeners may be transferred through the food web and are less vulnerable to metabolism by upper trophic predators. Conversely, organisms that are less capable of contaminant metabolism may be better models to examine how PCBS can enter the food web via plastic ingestion.

While marine birds often ingest a variety of polymer types in this region of the world (Avery-Gomm et al., 2016), information was not available on the polymer types for the plastics reported in this study. Importantly, chemical concentrations in plastic debris can vary with polymer type (O’Connor et al., 2016; Rochman et al., 2013). For example, Rochman et al. (2013) found that PCBs adsorbed to polyethylene (PE) and polypropylene (PP) more than other polyvinyl chloride (PVC) and polyethylene terephthalate (PET), suggesting that polymer type may influence the level PCBs leached into biota once ingested. Pascall et al. (2005) also found that PCB uptake occurred at the highest concentrations on PE as compared to PVC and polystyrene (PS). Thus, polymer type and contaminant pairings are important factors to consider in estimating plastics as a route for contaminants. Additionally, different PCB congeners may absorb to plastics differently. It is possible that different polymer types are carrying different PCB concentrations and congeners, and therefore, in order to fully understand how the transfer of chemicals may occur, polymer type needs to be considered when contaminants uptake by biota is examined. Future studies examining how plastics can act as a vector for contaminants in seabirds should employ a polymer characterization technique, such as Fourier transform infrared spectroscopy (FTIR) or Raman Spectroscopy to better estimate the chemical properties of ingested debris (Desforges et al., 2015; Lenz et al., 2015; Qiu et al., 2016).

While PCBS are an important contaminant group examined in ecotoxicological studies, there is a wide array of plastics-associated contaminants that should be examined to fully understand the relationships between plastics and contaminant uptake in biota. Recently, plastic-associated contaminants (perfluoroalkyl sulfonic and carboxylic acids) have been detected at relatively high levels in black-footed albatross (Phoebastria nigripes) (Chu et al., 2015), a species known to regularly ingest plastics (Gray et al., 2012). Also, lead (Pb) has been shown to be bio-accessible from ingested plastics (Turner and Lau, 2016), and is known to be correlated with high levels of ingested plastics (Lavers and Bond, 2016). Thus, studies examining the potential for plastics to act as a route for contaminants in wildlife should consider a wide range of plastic-associated contaminants. Additionally, plastic additives may be leached from ingested plastics to wildlife along with hydrophobic organic contaminants and trace metals (Hermabessiere et al., 2017). The effects of these cocktails of contaminants need to be better understood in order to assess the true impacts of ingested plastics in wildlife.

5. Conclusions

Ingested plastics and PCB concentrations were not correlated when ∑PCB, ∑PCB, lower-chlorinated, high-chlorinated, non-ortho, and mono-ortho congener combinations were considered. This suggests that ingested plastics do not significantly contribute to the PCB concentrations in northern fulmars even when Toxic Equivalency Factors (TEFs) are considered. PCB concentrations were lower in plastics as compared with livers, and there were significant differences in congener profiles between the ingested plastics and seabird livers. This may indicate there may be some interactions between plastics and the chemicals that the birds are exposed to via ingested plastics. Future research efforts should further explore how contaminants from plastics may be metabolized by biota upon ingestion.

Acknowledgements

Many thanks to the boat crew and Inuit hunters that helped collect the birds used for this research, including Captain Joey Angnatok, John Ross Angnatok, Amy-Lee Kouwenberg, Captain Lloyd Normore, Morely Normore, Marcel O’Brian, Benny Saimat, and Lee Shepard. Collections for this work were done in conjunction with a project funded by the Environmental Studies Research Fund (ESRF). We are very appreciative of the Environmental Technology Program (ETP) students at the Nunavut Arctic College (NAC) in Iqaluit, Nunavut for their assistance with bird dissections for this project. Funding for the contaminant portion of this work was provided by MEOPAR/TSI (project 2.11) under M. Liboiron. All dissections were completed during the annual Wildlife Contaminants Workshop which is funded by the Northern Contaminants Program under Indigenous and Northern Affairs Canada (INAC; 2017-18 M-21). JFP was funded by the Garfield Weston Foundation through a Post-doctoral Fellowship in Northern Research, which is administered by the Association for Canadian Universities for Northern Research (ACUNS), for this work.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envres.2018.07.025.

References
