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Individual Prey Specialization Drives PCBs in Icelandic Killer Whales

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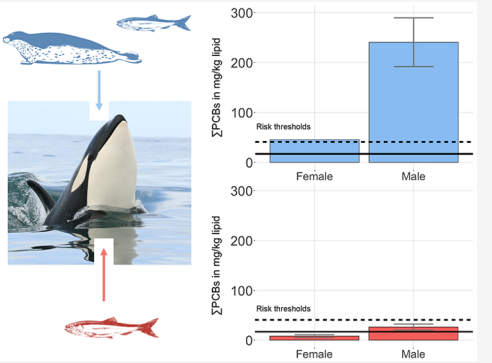
ABSTRACT: Interindividual variation in prey specialization is an essential yet overlooked aspect of wildlife feeding ecology, especially as it relates to intrapopulation variation in exposure to toxic contaminants. Here, we assessed blubber concentrations of an extensive suite of persistent organic pollutants in Icelandic killer whales (*Orcinus orca*). Polychlorinated biphenyl (PCB) concentrations in blubber were >300-fold higher in the most contaminated individual relative to the least contaminated, ranging from 1.3 to 428.6 mg·kg^{-1} lw. Mean PCB concentrations were 6-to-9-fold greater in individuals with a mixed diet including marine mammals than in fish specialist individuals, whereas males showed PCB concentrations 4-fold higher than females. Given PCBs have been identified as potentially impacting killer whale population growth, and levels in mixed feeders specifically exceeded known thresholds, the ecology of individuals must be recognized to accurately forecast how contaminants may threaten the long-term persistence of the world's ultimate marine predator.



KEYWORDS: *POPs, stable isotopes, diet, intrapopulation prey specialization, trophic position, contaminants, risk assessment*

INTRODUCTION

Environmental contaminants of toxicological concern such as persistent organic pollutants (POPs), and polychlorinated biphenyls (PCBs) in particular, biomagnify within food webs, making feeding ecology an important aspect of understanding contaminant accumulation in wildlife.[1] Yet, most feeding ecology and wildlife contaminant assessments have focused on populations mean diets or contaminant concentrations, with limited consideration of individual variation in foraging behavior, also referred to as individual specialization.[2,3] Although individual specialization may, in part, be explained by biological factors such as age and sex, it may also be driven by factors that go beyond demographic variation, including interindividual and population variations in patterns of resource competition, predation, and ecological opportunities.[2] Studies examining variation in diet among individuals demonstrated the importance of individual traits in describing feeding ecology and associated individual specialization with better overall fitness and survival in marine mammal populations.[2,4,5] With dietary absorption as a main route for contaminant accumulation, individuality in diet is expected to lead to variations in pollutant exposure and associated health risks, both within and among populations.[1,6]

As a generalist apex predator with a tendency to adopt prey specializations at the individual or population level, killer whales (*Orcinus orca*) may provide critical insights into how feeding ecology may influence/drive contaminant accumulation.[7−10] In well-studied regions, such as the eastern North Pacific, substantial differences in feeding ecology among killer whale populations have led to their classification into different ecotypes based largely on prey specialization (i.e., fish feeders vs marine mammal feeders).[8,10] However, far less is known about the foraging habits of killer whales in the North Atlantic.[11] In the North Atlantic, killer whales have been tentatively identified as generalist and specialist feeding ecotypes.[12] The supporting evidence suggests that Greenlandic and Canadian whales seem to rely mainly on marine mammals.[13−15] In contrast, whales in Norway and Iceland seem to vary in their intake of fish and marine mammals, between a diet composed predominantly of fish on one hand to a diet including marine mammal prey to an unknown extent on the other hand.[16] Nevertheless, new stable isotope analyses pointed to the possibility of individual specialization within the Icelandic and Norwegian populations.[17,18]

Killer whales are among the most contaminated animals on the planet, and their exposure to high levels of contaminants like POPs has been thought to contribute to reduced reproductive success and population growth.[3,19,20] For marine mammals specifically, POP levels have been linked to altered immune function, reduced reproductive success, endocrine

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disruption, and carcinogenicity.[19,21] Modeling studies have suggested that PCB contamination alone could contribute to reduced population growth in highly exposed populations of killer whales worldwide[3,22,23] (but see ref 24). While the relationship between killer whale POP levels and diets is not well-known across the North Atlantic, Greenlandic killer whales evaluated in recent years showed high POP concentrations that aligned with fatty acid signatures supportive of marine mammals as dietary components.[3,14,15,19] A recent study highlighting the role of intrapopulation variation in diets on contaminant accumulation and PCB patterns in Norway showed that seal-feeding killer whales were four times more contaminated than fish-feeding killer whales with PCB profiles dominated by higher chlorinated compounds.[6,18] This study demonstrated the need to account for intrapopulation fine-scale variations in feeding habits when quantifying contaminant accumulation in North Atlantic killer whale populations.

A population of North Atlantic killer whales regularly frequents Icelandic coastal waters where they seasonally congregate at wintering and spawning grounds of their assumed primary prey, Atlantic herring (*Clupea harengus*).[17,25] This population has been reported to prey on fish, cephalopods, seabirds, and marine mammals.[26] Long-distance photographic matches have also noted several individuals traveling to Scotland to feed on high trophic prey, including seals.[17,27] Here, we analyzed blubber samples from 50 Icelandic killer whales to quantify within-population variation in blubber concentrations of major POP groups, identify how POPs vary with individual foraging specialization, and assess how associated risks of health effects may vary with individual foraging specializations.

MATERIAL AND METHODS

Sampling. Sixty-four biopsies were collected opportunistically from 50 killer whales (35 males, 13 females, and 2 juveniles) in 2014 (n = 45 individuals) and 2016 (n = 5 individuals) in western and southern Iceland waters, where they are frequently seen feeding on herring (Table S2).[17,25] Biopsies comprising skin and blubber were collected using an ARTS pneumatic darting system (LKARTS-Norway, Norway) and stainless steel 25 × 7 mm (CetaDart, Denmark) biopsy tips. Biopsy tips were sterilized before use and stored in clean plastic bags. Samples were generally collected from the body's midlateral region, below the dorsal fin, and stored frozen in the field at −20 °C in aluminum foil. Once back at the lab, samples were stored at −80 °C until analysis. The shipment was conducted in Styrofoam boxes with dry ice until arrival in the lab at Carlton University, Ottawa. All sampled killer whales were photographically identified[28] to minimize the risk of resampling the same individuals within a single field season. Sampled individuals were sexed based on genetic analysis for whales sampled in 2014. Because genetic analyses were not completed for the 2016 samples, sex was assigned based on morphological characteristics and sighting history, which were further relevant to determine individuals' age class.[29,30] Age class was defined based on morphological characteristics and divided into three categories (per ref 29) as follows: (1) adults were defined differently for males and females; adult males were considered individuals that have reached sexual maturity and presented a distinguishably taller dorsal fin, including individuals whose dorsal fin has started its growth spurt but is not fully grown yet; in the case of females, these were defined as mature-sized individuals, with a relatively smaller dorsal fin than adult males, seen consistently with a calf in echelon position, or without developing dorsal fin for at least three years. (2) Large juveniles—unknown sex or known males (genetically sexed) which have dorsal fins of the same apparent size as adult females but whose dorsal fin does not appear to have started its growth spurt. (3) Juveniles, smaller sized individuals that have not reached mature size for which sex is unknown. No calves or young juveniles (≤3 years age) were sampled.

Contaminant Analyses. Analytes monitored were as follows: 62 individually eluting or coeluting PCB congeners; 20 individual organochlorines (OCs); 25 individual or coeluting polybrominated diphenyl ethers (PBDEs); and 23 other non-PBDE flame retardants (FRs) (Full list of analyzed contaminants in the Supporting Information). Extraction and analysis of PCBs/OCs/PBDEs/non-PBDE FRs were based on methods previously described.[31,32] Briefly, blubber biopsies were cut lengthwise into two equal depth segments: one slice (excluding skin) for analysis of POP concentrations and the other preserved for future studies. The blubber subsample for POP analysis (mean weight: 0.04 g, range: 0.01 to 0.18 g) was then accurately weighed into a mortar and homogenized with precleaned diatomaceous earth (DE). An aliquot was used to determine lipid content gravimetrically. After spiking with a mixture of 13C-labeled and nonlabeled C/PCB/FR surrogates as internal standards, extraction was performed by accelerated solvent extraction; then, extracts were subjected to cleanup by gel permeation chromatography and solid phase extraction. The final extract was separately analyzed for PCBs and OCs, by gas chromatography−mass spectrometry (GC-MS) with electron ionization (EI), and then for PBDE/non-PBDE FRs, by GC-MS with electron capture negative ionization (ECNI). Identification and quantification were performed using MassHunter Quantitative Analysis software (Version B.07.01, Agilent Technologies). Each batch included ten samples, a blank, and standard reference material, the National Institute of Standards and Technology pilot whale (*Globicephala melas*) blubber homogenate (NIST-1945).

QA/QC Results. The standard reference material SRM (NIST 1945 pilot whale blubber) was run eight times and checked for precision and accuracy. The overall POP recovery was 102% (96−109%) for ∑OCs (14 compounds), 105% (99−111%) for ∑PCBs (thirty-three congeners), and 112% (91−135%) for ∑PBDEs (five congeners). Internal standard recoveries were 85% (68−95%) for PCBs (six ^{13}C-labeled congeners), 70% (47−106%) for OCs (18 ^{13}C-labeled compounds), and 150% (89−214%) for FRs (five ^{13}C-labeled compounds). Method limits of detection (MLODs) and quantification (MLOQs) were defined as the minimum amount of analyte which produced a peak with a signal-to-noise ratio of 3 and 10, respectively.[33] A blank was run with each batch. No contamination was present in any of the blanks.

Dietary Indicators. A Stable Isotope Bayesian Ellipses analysis (SIBER) was performed, per ref 17, on already published δ^{13}C and δ^{15}N data from the 45 whales sampled in 2014 to determine diet types.[34] On the basis of this analysis, a δ^{15}N cutoff was established to delineate a diet-type, which was further validated using observational or photographic evidence of movement patterns and feeding habits based on predation events for these same whales, whenever available. Five whales sampled in 2016 were not assigned to a diet-type because the samples were not analyzed yet for δ^{15}N values. *Diet-type* was

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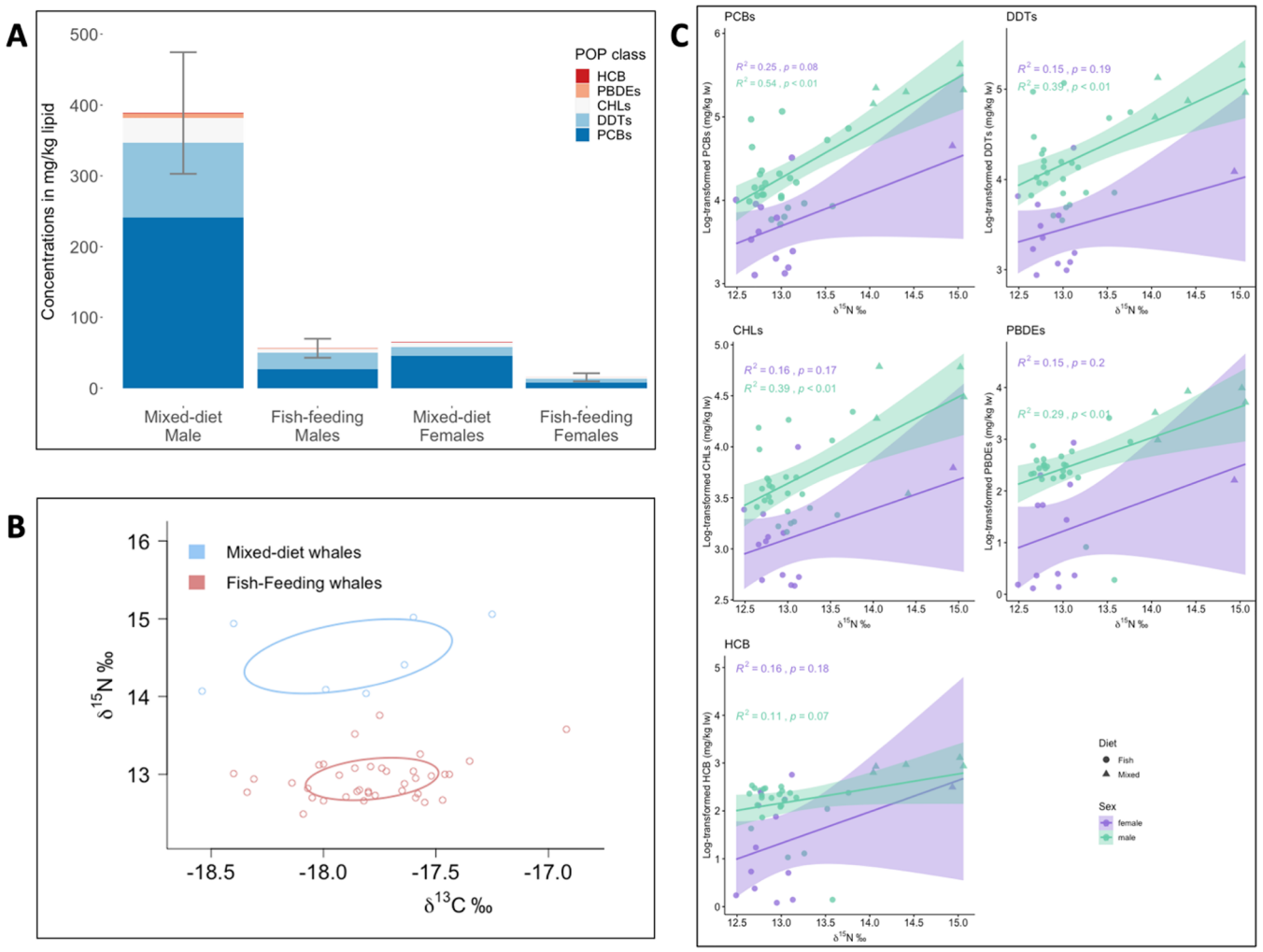

Figure 1. (A) Concentrations of POP classes (mg·kg^{-1} lipid weight) in Icelandic killer whale blubber biopsies (results are expressed as arithmetic mean ± SE (except for the single mixed-diet female). (B) Isotopic biplot from the SIBER[34] stable isotope analysis conducted on δ^{13}C and δ^{15}N between the two diet types, modified from Figure S1 to include the two defined diet-types.[17] (C) Correlations of log-transformed concentrations of ∑PCB, ∑DDT and ∑CHL, ∑PBDEs, and HCB with δ^{15}N values for males and females.

classified as "mixed-diet" for whales that appear to feed on both fish and higher trophic level prey (including seals and small cetaceans) and "fish-feeder" for whales believed to predominantly prey on herring.

Data Analysis. The five main contaminant classes, i.e., ∑PCBs, dichlorodiphenyltrichloroethane (∑DDTs), chlordane (∑CHLs), ∑PBDEs, and hexachorobenzene (HCB) were quantified in >70% of all samples. Hexachlorocyclohexanes ∑HCHs and ∑non-PBDE FRs were only quantified in 10% and 17% of the samples, respectively, and most concentrations were <LOD. Thus, these compounds were reported in the results but were not included in further statistical analyses. HCB was the only chlorobenzene detected. We henceforth refer to HCB instead of ∑ClBz. Three individuals were sampled in both 2014 and 2016 (IS018, IS067, and IS046, all males). We used a Student's *t* test to determine if there were differences between years (Supporting Information). For the other whales sampled more than once within the same year (n = 9 resampled individuals), we used a Student's *t* test to determine if there were differences in contaminant classes between the samples. Because duplicate and triplicate biopsies from the same individual showed similar congener concentrations and profiles, their concentrations were averaged (Supporting Information).

All POP concentrations were lipid corrected and expressed in mg·kg^{-1} lipid weight (lw). As lipid content was missing for three individuals (IS243, IS229, and IS174), we estimated the values by interpolation from a regression of contaminant concentration with lipid content. We examined CB153, as it is one of the most recalcitrant PCBs in marine mammals, as well as ∑PCB.[35] The latter showed a stronger correlation with lipid content (R^2 = 0.42, p < 0.001 versus R^2 = 0.36, p = 0.004) and was thus used to approximate lipid content for the missing samples. Two outliers (IS069 and IS229) were removed from the contaminant data set due to their high standardized residual values (>3) (Table S2). Prior to statistical analysis, concentrations were log-transformed (log x+1) to approximate normal distribution, which was evaluated and confirmed with qqplots on residuals and/or Shapiro tests.

We used a generalized linear modeling approach (GLM) to explore contaminant variation. The effect of three independent variables, *sex* (male, female), *diet-type* (fish, mixed), and *sampling-season* (2014-winter, 2014-summer), were tested for the concentrations of significant contaminant classes: ∑PCB, ∑DDT, ∑CHL, ∑PBDE, and HCB. The whales sampled in

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Table 1. Summary Results from the Generalized Linear Modelling Approach That Tested the Effects of Three Independent Variables (*Sex*, *Diet-Type* and *Sampling-Season*) on the Log-Transformed Concentrations of ∑PCBs, ∑DDTs, ∑CHLs, HCB, and ∑PBDEs in the Blubber Biopsies of the Icelandic Killer Whales Sampled in 2014 and 2016[a]

Models	AIC_c	ΔAIC_c	AIC_c Wt	Variance Explained	Intercept	CI 95%	Predictor: Sex	CI (95%)	Predictor: Diet-type	CI 95%
∑PCBs ~ sex + diet-type	41.8	0	0.78	0.67	3.61	3.41−3.81	**0.61**	0.37−0.85	**1.11**	0.79−1.43
∑PCBs ~ sex + diet-type + sampling-season	44.4	2.54	0.22	0.67						
∑DDTs ~ sex + diet-type	46.2	0	0.78	0.61	3.39	3.18−3.60	**0.74**	0.49−1.00	**0.82**	0.48−1.15
∑DDTs ~ sex + diet-type + sampling-season	48.8	2.57	0.22	0.61						
∑CHLs ~ sex + diet-type	41.6	0	0.78	0.55	3.05	2.85−3.25	**0.57**	0.33−0.81	**0.76**	0.44−1.08
∑CHLs ~ sex + diet-type + sampling-season	44.2	2.56	0.22	0.55						
HCB ~ sex + diet-type	559.2	0	0.56	0.31	4.64	4.15−5.23	**0.8**	0.13−1.42	**1.33**	0.55−2.28
HCB ~ diet-type	561.2	2.03	0.20	0.23						
HCB ~ sex + diet-type + sampling-season	561.7	2.53	0.16	0.31						
HCB ~ diet-type + sampling-season	563.6	4.46	0.06	0.23						
HCB ~ sex	566.6	7.39	0.01	0.13						
HCB ~ sex + sampling-season	568.0	8.85	0.01	0.15						
∑PBDEs ~ sex + diet-type	99.0	0	0.76	0.54	1.14	0.75−1.53	**1.22**	0.76−1.70	**1.22**	0.60−1.84
∑PBDEs ~ sex + diet-type + sampling-season	101.3	2.36	0.24	0.54						

[a]AIC_c: Akaike's Information Criterion corrected for small sample size. Only models with a ΔAIC_c below 10 are shown. AIC_c Wt represents the discrete probability of each model. Variance Explained was calculated for each model: 1-(Residual Deviance/Null Deviance).

more than one season (e.g., winter and summer) were randomly assigned to either winter or summer. Individuals only sampled in 2016 (n = 5) were excluded from the models due to the lack of $\delta^{15}N$ values. Age class was not included in the model due to low sample size (Table S2). The three large male juveniles from the mixed-diet type were pooled with adult males as they were close to adulthood. We ran each possible model combination of the three independent variables for each contaminant class. We used Akaike's information criterion corrected for small sample size (AIC_c) and considered smaller AIC_c values to be indicative of better models. We also used the variance explained (1-(residual deviance/null deviance)), also known as McFadden's pseudo R^2, to determine how well the different models explained variation in pollutant classes within the population. A *sex* × *diet-type* interaction could not be included in the models due to the low sample size for marine mixed-diet females (n = 1) (Table S2). However, to further investigate the relationship between diet-types and POP concentrations, Pearson correlation tests were performed on the log-transformed contaminant classes and nontransformed $\delta^{15}N$ values for males and females separately (data available only for 2014 samples;[17]). To assess how the individuals grouped in terms of contaminant concentration similarities, we performed a hierarchical agglomerative cluster analysis on log-transformed individual compound concentration when detected in more than 70% of the samples using the Euclidean distance, and Ward's D2 method, bootstrapped 1000 times (eclust function of the factoextra package in R).

The compounds detected in more than 70% of the samples were *cis*-chlordane, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, dieldrin, heptachlor epoxide, hexachlorobenzene, Mirex, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, and CBs 52, 74, 95, 99, 101, 105, 118, 128, 132, 138/163, 146, 149, 150, 153, 170, 174, 177, 179, 180, 183, 187, BDE 47, and 100 (Table S2). For these, any nondetects (N.D.) were assigned a random value between 0 and the MLOD of the compound before inferential statistical analysis. Compounds detected, but below the MLOQ, were assigned a random value between MLOD and MLOQ. Overall, 18% of the data set corresponded to values below MLOQ or MLOD. Finally, to further explore the intrapopulation variability in PCB patterns, we performed a PCA on arcsine-transformed CB congener percentages when they were detected in more than 70% of the samples.

RESULTS AND DISCUSSION

Concentrations of PCBs, which were the highest among all POP classes studied, showed a 300-fold difference among individuals within the population, ranging from 1.3 to 428.6 $mg{\cdot}kg^{-1}$ lw (Figure 1A). The next highest contaminant classes included DDTs and CHLs, which varied by up to 200- and 150-fold, respectively, among individuals (0.9 to 183.8 $mg{\cdot}kg^{-1}$ lw for ∑DDTs and 0.4 to 61.2 $mg{\cdot}kg^{-1}$ lw, for ∑CHLs) (Figure 1B). For comparison, a similar 300-fold difference in PCB concentrations was documented between different populations of fish vs mammal-specialists in the eastern North Pacific (range from 1.7 $mg{\cdot}kg^{-1}$ lw for the northern residents to 574 $mg{\cdot}kg^{-1}$ lw for the North Pacific transients).[10,36] This similar variation within Icelandic killer whales compared to distinct ecotypes in other areas is unexpected, given the killer whales in our study belong to the same population according to recent studies.[29,30] This suggests that the ecology of individuals plays a critical and previously overlooked role in population exposures to PCBs and other biomagnifying contaminants.

We tested the effects of *diet-type*, *sex*, and *sampling-season* for each major POP class. To do so, individuals were first assigned to a diet-type. We determined diet-types by reconducting a SIBER analysis on the published stable isotope data from Samarra et al. 2017c, using updated observed movement and feeding behavior data[17] (see SI for the full analysis). Fish-feeding killer whales were characterized by low $\delta^{15}N$ values (<14‰) and/or followed herring closely around Iceland

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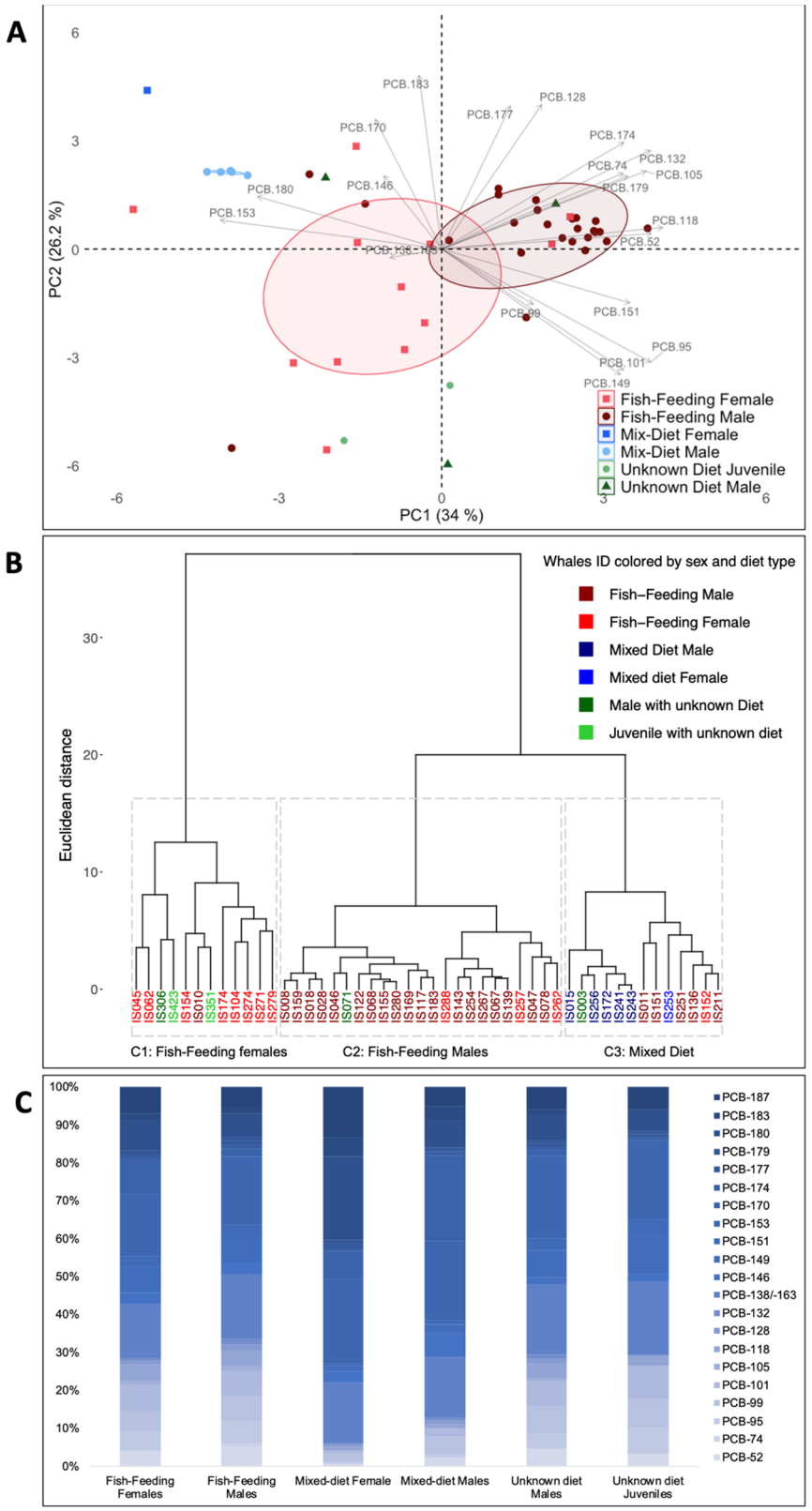

Figure 2. Pattern analysis of contaminants in Icelandic killer whales. (A) Principal component analysis on PCB congener composition among Icelandic killer whales. (B) Hierarchical agglomerative cluster analysis based on log-transformed individual POP concentrations showing three clusters: C1: Fish-feeding females, C2: Fish-feeding males and C3: Mixed-diet. (C) PCB congener composition among Icelandic killer whales. Each bar represents the percentage of each PCB congener in ∑PCBs.

(Figure 1B). Mixed-diet killer whales were frequently observed in herring grounds feeding on herring, but they had also been observed to prey on marine mammals (i.e., seals or small cetaceans), had elevated δ^{15}N values (>14‰), and/or traveled to Scotland where they target marine mammals (Figure 1B) (SI). Five individuals could not be assigned to a diet-type due

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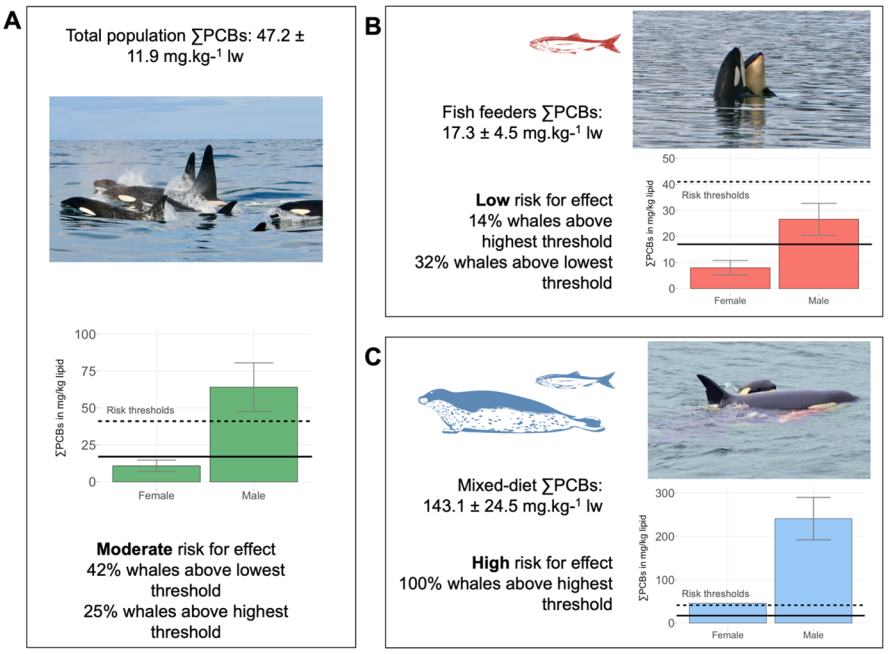

Figure 3. Risk assessment for Icelandic killer whales with respect to PCB exposure for (A) the population as a whole, (B) fish-feeding killer whales (25 males and 12 females) and (C) mixed-diet killer whales (5 males and 1 female).

to a lack of δ^{15}N values for these whales. The clear distinction between the isotopic niches of individuals strongly suggests intrapopulation variation in foraging behavior[17] (Figure 1B).

Diet-type and *sex* were the two factors that most strongly explained concentrations of POPs within the Icelandic killer whale population based on our GLM modeling approach. Best fit models (Table 1) including these two predictors explained >50% of the variance among individuals in concentrations of PCBs, DDTs, CHLs, HCB, and PBDEs. The second-best or third-best models for all POP classes included *sampling season*. However, sampling season and its 95% confidence intervals overlapped zero in all POP classes and thus was considered not significant in the POPs variation. *Diet-type* had a stronger effect than *sex* on contaminant variation for all POP classes, with estimates for *diet-type* predictors being on average 0.5 higher than estimates for *sex* predictors (Table 1). As a result, mixed-diet males and females had mean PCB concentrations 9.0- and 5.7-fold higher than fish-feeding males and females, respectively. Conversely, mean PCB concentrations for mixed-diet and fish-feeding males were just 5.3- and 3.3-fold higher than the mixed-diet and fish-feeding females, respectively (Table S1). PBDEs and hexabromocyclododecane (HBCDD) behaved similarly to legacy POPs, being detected more frequently and in higher concentrations in mixed-diet versus fish-feeding whales (Table S1). Furthermore, the effect of diet was evident from the positive linear association of POPs with trophic position (δ^{15}N) across males and females, based on Pearson correlation tests (Figure 1C). Indeed, a moderate positive correlation was found for ∑PCBs, weak positive correlations were found for ∑DDTs, ∑CHLs and ∑PBDEs, and a positive, but not significant, correlation was found for HCB, in males. For females, correlations were positive between the major POP classes and δ^{15}N, although none of these relationships were significant. This similar association between δ^{15}N values and POP concentrations suggests an absence of a *sex* x *diet-type* interaction. Moreover, the difference in POP concentrations in Icelandic killer whales was larger between fish-feeding and mixed-diet whales than what was reported for Norwegian killer whales, where mixed-diet whales had PCB concentrations four times higher than fish-feeding whales.[6] This difference is consistent with a more pronounced dietary segregation between feeding types in Iceland.

Icelandic whales appear to manifest a long-term individual specialization on different prey rather than a generalist feeding behavior. Fish-feeding killer whales in our study had lower overall contaminant concentrations and a contaminant composition characteristic of fish-eating mammals[6,8] (Figure 2A–C). Indeed, the C2 cluster "fish-feeding males" (Figure 2B) included most of the fish-feeding males, which were separated by low Euclidian distances, suggesting little differences in contaminant concentrations among them. Specifically, fish-feeding males were associated with less chlorinated and/or less persistent congeners in the PCA analysis (CBs 52, 95, 105, 101, 118). Limited variation in POP concentrations and patterns within males of this diet-type is consistent with reports of long-term dietary specialization on herring[17,25] (Figure 2A,B). Our cluster and PCA analyses revealed that POP profiles are similar among mixed-diet individuals but differed markedly from fish-feeding individuals (Figure 2A–C). All mixed-diet individuals were grouped in the C3 cluster "mixed-diet" and PCB congener profiles were characterized by a large proportion of highly chlorinated and persistent congeners (CBs 153, 180, 170, 177, and 183), a characteristic of a marine mammal-based diet[6,8] (Figure 2A,C).

The results from this study provide new insights into the complexity of feeding habits adopted by Icelandic killer whales. First, the whales categorized as mixed-diet were frequently sighted feeding on herring in Iceland[17] but exhibited contaminant profiles consistent with a diet that includes marine mammals. Second, our pattern analyses (Figure 2A–C) suggest that the diets of some nonmixed-diet whales may, in fact, contain some higher trophic level prey (IS003, IS251, and IS136). This suggestion is supported by the large variability of both PCB and δ^{15}N values across individuals (Figure 1C) and

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previous opportunistic observations of different prey events in Icelandic waters that involved mammals, birds, and other prey species.[26] Indeed, while contaminant loads reflect the whales' long-term feeding habits, at least for males, isotopic ratios only are indicative of feeding habits for the few weeks prior to sampling (based on studies performed on other cetacean species).[37,38] As a result, whales with lower δ^{15}N values could seasonally or occasionally prey on marine mammals and these events may only be detected in the whales' POP concentrations (Figure 1C). Some individuals in the population might thus be true generalists, occasionally preying on marine mammals, and show elevated POP concentrations. Higher-resolution dietary tracers like fatty acid signatures are needed to shed further light on individual-level prey composition.[15,39]

Sex was the second most important factor contributing to contaminant variation in the Icelandic killer whale population. PCB concentrations were ∼4-fold higher in males than in females for each diet-type, consistent with previous findings across reproducing killer whale (Tables S1, S2).[36,40] Fish-feeding females had the largest within-group variation in contaminant concentrations and profiles (Figures 2, 3). Indeed, most fish-feeding females grouped in the C1 cluster "fish-feeding females" showed a large interindividual variation in POP concentration and their ellipse was the largest in our PCA, reflecting different PCB profiles. Adult female cetaceans are known to transfer ∼10% and 60% of their body burdens to their offspring during gestation and lactation, respectively.[40−42] As the largest portion of these burdens are offloaded during the first pregnancy (and nursing), contaminant levels may also vary with the number of births and thus, age.[40,43] This could explain why three fish-feeding females clustered with the 25 fish-feeding males, and one clustered with the mixed-diet whales, possibly reflecting females that have not yet (successfully) reproduced (Figure 2C). An exception to the established gender effect for contaminant transfer occurs in populations where contaminant loads impair reproduction, eliminating the primary excretion route for these compounds in females, leading to elevated tissue concentrations.[20]

The striking differences in contaminant concentrations among Icelandic killer whales suggest that individual prey specialization and associated intrapopulation variation in POP loads should be considered in risk assessments going forward. A commonly used PCB concentration threshold for immunotoxic effects in marine mammals is 17.0 mg·kg^{-1} lw, while the highest PCB toxicity threshold for impaired reproduction calculated for marine mammals is 41.0 mg·kg^{-1} lw (Figure 3).[44,45] In the North-Atlantic, some mixed-diet killer whales from Norway were recently reported to have PCBs concentrations above thresholds for health effects.[6] In this study, out of the seven whales preying on seal to a certain extent, four had levels above the 41 mg·kg^{-1} lw threshold. In Greenland, mean PCB concentrations for mammal-feeding subadult and adult killer whales were also above the 41 mg·kg^{-1} lw.[14] A recent global killer whale modeling study predicted based on available blubber PCB data that the Icelandic killer whale population was not likely to face meaningful risk to population growth.[3] The model in this study used PCB concentrations based on five females (range: 14 to 41 mg·kg^{-1} lw) from Iceland, showing concentrations similar to the fish-feeding killer whales in our study. However, these concentrations did not account for intrapopulation variation in feeding ecology and higher contaminant concentrations in mixed-diet individuals, particularly the males, as found in this study. All Icelandic mixed-diet killer whales from our study had PCB concentrations above the highest toxicity threshold, suggesting that these whales face increased risks of adverse reproductive and immune effects from PCB exposure alone, with potential consequences on population growth. Thus, the ecology of individuals must be understood to accurately forecast how environmental contaminants of toxicological concern may threaten the long-term persistence of the world's ultimate marine predator.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c08563.

Materials and Methods and Additional Results (PDF)

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Author Contributions

R.J.L., M.A.M, R.D., and C.S. designed the study. F.I.P.S and G.V. collected the samples in Iceland. R.D. and C.S. ensured the transfer of the samples to Canada. A.R. and D.B. performed the lab experiment. A.R. and J.P.D. analyzed the data. A.R. wrote the manuscript. All authors discussed the results and implications and commented on the manuscript at all stages. Competing interests: Authors declare no competing interests.

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