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Distinctive patterns and low concentrations of persistent organic pollutants in Northwestern Pacific killer whales (*Orcinus orca*)

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ABSTRACT

Persistent organic pollutants (POPs) in killer whale (*Orcinus orca*) populations in the Northwestern Pacific Ocean are much less studied compared to the Northeastern Pacific and North Atlantic populations. The objective of this study was to address that knowledge gap by analysis of biopsy samples obtained as part of studies of killer whale feeding and habitat use in coastal waters of the Russian Far East. Skin/blubber biopsies collected from 26 killer whales at five locations in coastal waters of the Kamchatka Peninsula (Avacha Gulf), North Kuril Islands, Western and Northern Sea of Okhotsk, and further north in Chukotka, between 2012 and 2016, were analysed for a suite of organochlorine pesticides and byproducts (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). DDT related compounds and PCBs were the most prominent POPs in the biopsy samples with geometric mean concentrations in the 5 regions ranging 34.4 to 161 ng/g (wet weight, ww) for total DDT and 8.10 to 58.5 ng/g ww for total PCBs. Principal components analysis using the data for OCPs showed that key contributors to the geographic differences were DDT isomers as well as the more volatile OCPs, hexachlorobutadiene and pentachlorobenzene. The concentrations of individual OCPs and PCBs agreed with previous reports for female killer whales sampled in the Northwestern Pacific region in 2002–2004 but were up to 180-fold lower than reported in transient males. Overall concentrations of POPs in killer whales in this region are among the lowest for killer whale populations in the northern hemisphere.

1. Introduction

As apex predators, killer whales (*Orcinus orca*) have among the highest concentrations of persistent organic pollutants (POPs) of all marine mammals (Desforges et al., 2018; Jepson et al., 2016; Mongillo et al., 2016; Remili et al., 2023). Desforges et al. (2018) concluded that elevated PCB exposure posed significant risk to growth of most killer whale populations in the North Atlantic and Northeastern Pacific Oceans due to effects on reproduction and immune function. Reduced metabolic ability of odontocetes to metabolize and eliminate PCBs and other POPs makes them particularly vulnerable to adverse effects of these contaminants (Sonne et al., 2018). Recently published studies have documented the concentrations of POPs in blubber and skin biopsies of killer whales in the northern North Atlantic collected over the period 2012–2021, including populations from Iceland (Remili et al., 2021), Baffin Island (Desforges et al., 2024), southeast Greenland (Pedro et al., 2017), and northern Norway (Andvik et al., 2020; Dietz et al., 2020). There are also data for POPs in killer whales of the Northern Pacific, however, to our knowledge, the most recent samples analysed for POPs were collected in the period 1996–2005 (Atkinson et al., 2019; Kajiwara et al., 2006; Krahn et al., 2007; Lawson et al., 2020); newer data are lacking. Differences in concentrations of POPs in killer whale tissue have been shown to reflect dietary composition typically between resident (fish-eating) and transient (marine mammal-eating) ecotypes in the North

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Pacific populations (Krahn et al., 2007; Lawson et al., 2020) although sex/maturity of individual animals has also been shown to be influential as well (Remili et al., 2021; Ross et al., 2000). The distinction between fish- and marine mammal-eaters and transient and resident populations is apparent from nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) stable isotope ratios, with values for the transients indicative of higher trophic level feeding compared with residents (Krahn et al., 2007). Remili et al. (2023) reached similar conclusions regarding the influence of diet on the wide range of concentrations of POPs in a large study of killer whale populations in northern North Atlantic, based on analyses of fatty acids as dietary tracers.

Levels and patterns of individual POPs such as PCB congeners have been shown to be useful tracers that help to differentiate cetacean stocks (Hobbs et al., 2003; Innes et al., 2002; Krahn et al., 1999). Metabolic capacity for biotransformation may be similar among populations giving rise to similar PCB congener profiles while exposure varies due to differences in dietary contamination (Desforges et al., 2013). Ratios of different classes of POPs (e.g. ΣDDT/ΣPCB, p,p′-DDE/ΣDDT) have also been used to discern regional foraging patterns, differentiating killer whales that fed in California waters from those that fed off Alaska, and documenting further spatial structure within Alaskan whales, attributed to a west-to-east gradient in the influence of DDT sources across the northern Pacific Ocean (Krahn et al., 2007; Lawson et al., 2020).

The ecology of killer whale populations in coastal Kamchatka peninsula, the Sea of Okhotsk, and Chukotka has been studied extensively (Filatova et al., 2023; Filatova et al., 2019; Volkova et al., 2019). Fish eating ecotypes prevailed in the coastal waters of eastern Kamchatka, and Kuril Islands and in the central Sea of Okhotsk, while mammal eaters dominated coastal waters off Chukotka and in the western and northern coastal Okhotsk Sea (Filatova et al., 2019). The fish-eating killer whales in Kamchatka peninsula, Commander Islands, and Kuril Islands are thought to belong to one population (genetically in terms of gene flow), but are partially segregated (Shabalina et al., 2015). Less is known about the status of mammal eating killer whales in this region, however, they are considered endangered and have been listed in the Russian Red Book (Russianorca, 2020). Surveys have recorded about 800 individuals in the Kamchatkan region and >1000 in the Commander Islands area. Stable isotope analyses of killer whale skin samples and major prey species in the region have provided insights into diets of these populations, showing, for example, that $\delta^{15}N$ values of fish eaters were consistent with feeding on a mix of large salmon species, mackerel and Pacific cod, while seals were surmised to comprise the largest portion of the diet of mammal eaters (Borisova et al., 2020).

Compared to the northeast Pacific and the Aleutian Islands, only a limited number of killer whale biopsy and blubber samples from the Northwest Pacific have been analysed for POPs. Concentrations of major POPs in studies of killer whales from this region as well as from Aleutian Islands and the northern North Atlantic are summarized in Table S1. Kajiwara et al. (2006) analysed blubber samples from five stranded/ice entrapped animals in northern Hokkaido Island (Japan) and reported ΣDDTs was the predominant contaminant (28 to 220 μg/g lipid weight (lw)) followed by ΣPCBs (18–64 μg/g lw). Lawson et al. (2020) included biopsy samples collected in 2002 from five resident killer whales from southeastern Kamchatka Peninsula to the northern Kuril Islands (Russia) and also found generally higher ΣDDTs (15 to 94 μg/g lw) compared to ΣPCBs (12–64 μg/g lw). The most extensive study of POPs in the Northwest Pacific killer whales, by Atkinson et al. (2019) analysed 25 samples from the Kamchatka Peninsula and the Kuril Islands collected in 2002–2003. Resident female killer whales (n = 6) had mean concentrations of ΣDDTs (0.33 μg/g lw) and ΣPCBs (1.2 μg/g lw) while male residents (n = 8) had means (ΣDDTs (25 μg/g lw) and ΣPCBs (18 μg/g lw) comparable to those reported by Lawson et al. and Kajiwara et al. The concentrations of ΣDDTs, ΣPCBs, and other major POPs in resident females in the study by Atkinson et al. are the lowest reported for any northern hemisphere killer whale population, male or female, resident or transient (Table S1). Further study of POPs in killer whales from this region is of interest to understand how the females could achieve such low exposure. Dietary differences along with sex/maturity must play a role but the previous Northwest Pacific studies did not include dietary indicators such as carbon and nitrogen stable isotopes in their assessment of POPs.

The goals of this study were to determine concentrations of a broad suite of POPs in killer whale biopsy samples from the Northwestern Pacific region and to compare with results for other regions. Based on previous studies on killer whales in the region (Borisova et al., 2020; Filatova et al., 2019) we hypothesized that there would be distinctive differences in the profile and concentrations of individual PCB congeners, legacy organochlorine pesticides and byproducts, due to ecotype and regional sources of contaminants.

2. Methods

2.1. Sample collection

Biopsy samples were collected between 2012 and 2016 as part of a long term study of killer whales in the coastal waters of the Kamchatka Peninsula (Avacha Gulf), Chukotka, North Kuril Islands, Western and Northern Sea of Okhotsk (Borisova et al., 2020) (Table 1). Samples were obtained using a hollow-tipped biopsy dart fired by a crossbow, which provided the epidermis layer and a portion of the blubber layer (approximately 2 cm long and 0.5 cm in diameter). The age class of each individual was identified in the field and sex was determined through genetic analysis. Values of $\delta^{13}C$ and $\delta^{15}N$ were determined in skin samples and the ecotype (fish eating (R-type) or mammal eating (T-type)) of each individual was identified; see details in Borisova et al. (2020). Skin and blubber were separated and stored in 95 % ethanol during the field work and held at 4 °C. Subsamples of the blubber were sent to University of Windsor for contaminant analysis and held at −20 °C until submitted to the analytical lab.

2.2. Persistent organic pollutant analysis

Twenty-six blubber samples (0.032 to 0.152 g subsample from the biopsied tissue) were analysed for organochlorine pesticides and related byproducts (OCPs) following US EPA Method 1699 (US EPA, 2007) by ALS Global Laboratories (Burlington ON). In brief, blubber was thoroughly homogenized with pre-cleaned anhydrous Na_2SO_4 and Soxhlet extracted with dichloromethane (DCM). Prior to extraction a suite of 15 ^{13}C-OCP-related compounds were added as recovery surrogates. Lipids were removed by gel permeation chromatography (GPC) with n-hexane: DCM (1:1) as the eluent. The GPC eluate was split into OCP and PCB/PBDE fractions. Percent lipid was determined gravimetrically on a separate blubber biopsy subsample using DCM as the extraction solvent. The OCP fraction was cleaned up on 2 % deactivated silica gel then reduced to 0.05 mL for analysis by gas chromatography-high resolution mass spectrometry (GC-HRMS) with individual peaks characterized at 10,000 mass resolution. The PCB/PBDE fractions of 21 samples were analysed by the Organic Analytical and Nutrient Laboratory (OANL) at the Great Lakes Institute for Environmental Research (GLIER); 5 samples were lost during transport to GLIER. PCB34 and PBDE 71 were added to the extracts as recovery standards. The extracts were cleaned up on a Florisil^{R} column and then reduced to 1 mL for gas chromatography-low resolution mass spectrometry (GC-LRMS) analysis of 38 PCB congeners and 24 PBDE congeners. PCBs were analysed by GC-EI-LRMS equipped with a 60 m DB-5 column and individual peaks identified by retention time and by major ion under selective ion monitoring mode. PBDEs were analysed in negative ionization mode using a 30 m RTX 1614 column to characterize and quantify tri-heptabromo-congeners followed by reinjected of extracts on the same system re-fitted with a 10 m RTX-1614 column to characterize octa-, nona- and deca-BDEs and quantified by isotope dilution using the ^{13}C-surrogates (US EPA, 2007).

Table 1
Concentrations of major organochlorine pesticides/byproducts, PCBs and PBDEs in killer whale skin/blubber biopsy samples from the Western North Pacific Ocean (ng/g wet weight and lipid weight).[1]

Region[2]	Sample #	Eco-type	Sex	$\delta^{13}C$	$\delta^{15}N$	% Lipid	ΣDDT	ΣCHL	ΣCBz	ΣPCB	ΣPBDE	ΣDDT/ΣPCB
AG	50	R	M	−18.0	14.0	29	200	13.5	25.1	79.6	22.1	2.41
AG	51	R	M	−18.1	14.1	26	164	24.8	27.9	42.0	42.2	3.91
AG	61	R	M	−16.6	14.9	30	325	86.2	23.7	57.6	20.0	5.64
AG	65	R	M	−17.6	14.7	24[3]	34.3	3.0	17.8	18.4	6.5	1.93
AG	66	R	M	−18.0	13.6	23	158	14.6	13.7	42.6	5.0	3.70
AG	72	T	F	−16.3	16.3	11	170	69.1	27.7	187	92.8	0.98
AG Geomean, wet wt				−17.4	14.6	23 %	146	21.1	22.0	55.2	19.6	3.09
Lipid wt							646	93.2	97.1	244	91.9	
WO	86	T	M	−16.8	17.2	27[3]	37.4	16.2	19.9	12.1	14.3	2.61
WO	97	T	F	−17.2	15.9	27[3]	73.5	12.9	15.8	–[4]	–[4]	
WO	99	T	F	−17.2	16.3	27[3]	11.5	2.17	7.8	1.39	14.8	10.50
WO	139	T	F	−17.0	17.8	27[3]	23.1	1.7	30.3	31.7	13.4	0.56
WO	146	T	F	−17.1	17.4	27[3]	66.2	10.0	11.2	–	–	
WO	333	T	F	−16.9	18.1	9	71.1	30.7	16.1	9.12	3.0	7.73
WO Geomean, wet wt				−17.0	17.1	22 %	38.9	7.8	15.4	8.4	9.6	4.56
Lipid wt						35.2	69.1	41.0	48.3	174	35.2	
NO	102	T	F	−17.4	16.3	27[3]	68.2	21.4	25.5	46.8	9.1	1.23
NO	103	T	F	−17.4	15.9	27[3]	968	479	12.0	825	45.6	1.17
NO	131	T	M	−16.3	16.9	27[3]	142	17.7	17.9	33.3	77.1	4.27
NO Geomean, wet wt				−17.0	16.4	27 %	211	56.6	17.6	109	31.8	3.60
Lipid wt							791	212	66.1	407	119	
CO	1101	R	M	−17.5	13.7	24	34.4	13.7	12.7	–	–	–
Lipid wt							146	58.1	54.1	–	–	–
NK	1401	R	M	−19.0	13.2	24[3]	96.4	5.60	17.0	47.3	47.5	2.07
NK	1402	R	M	−18.9	12.8	15	45.3	3.60	13.6	10.4	7.2	3.69
NK	1405	R	M	−18.6	13.5	31	21.4	3.71	18.5	9.63	10.3	2.21
NK Geomean, wet wt				−18.8	13.2	22 %	45.4	4.2	16.2	16.8	15.2	2.66
Lipid wt							206	19.1	73.6	76.2	69.1	
CH	1701	T	M	−17.2	18.4	13	105	30.8	14.7	25.8	23.2	4.06
CH	1702	T	M	−17.0	17.9	28	115	33.1	21.7	–	–	
CH	1703	T	F	−17.0	17.6	27[3]	74.6	26.6	12.6	18.9	36.5	3.90
CH	1704	T	M	−16.9	17.3	27[3]	35.9	8.72	15.0	–	–	
CH	1705	T	M	−17.4	16.7	37	117	9.1	23.2	27.7	18.2	4.23
CH	1706	T	F	−17.2	16.6	53	81.8	14.1	25.5	86.7	8.2	0.98
CH	1707	T	M	−16.7	17.1	38	62.7	20.1	12.3	5.99	10.0	10.67
CH Geomean, wet wt				−17.1	17.3	29 %	79.2	18.0	17.2	23.4	16.6	4.77
Lipid wt							271	61.5	58.8	77.7	56.5	

[1] ΣDDT = sum of 4,4′-DDE, 4,4′-DDD, 2,4′-DDT, and 4,4′-DDT; ΣCHL = sum of heptachlor epoxide B, oxychlordane and trans-nonachlor; ΣCBz = sum of 1,2,4,5-TeCBz, 1,2,3,4-TeCBz, PeCBz, and HCB; ΣPCB = sum of 33 PCB congeners with results >MDL; ΣPBDE = sum of 23 PBDE congeners with results >MDL.
[2] AG = Avacha Gulf, CH = Chukotka, CO = Commander Islands, NK = Northern Kuril Islands, NO = Northern Okhotsk Sea, WO = Western Okhotsk Sea.
[3] Estimated % lipid based on arithmetic means for animals identified as R or T ecotypes.
[4] Sample not analysed for PCBs or PBDEs.

2.3. Quality assurance (QA) and quality control (QC) procedures

Certified reference material (SRM 1946 fish tissue; National Institute of Standards and Technology [NIST]) and laboratory blanks were analysed with the samples. Average recoveries of 27 PCB congeners 15 OCPs and 9 PBDEs relative to the certified values for the NIST fish tissue were 97 ± 12 %, 96 ± 32 %, and 80 ± 27 %, respectively (full dataset in Table S2). Recoveries of PCB 34 and PBDE-71 at the Florisil cleanup stage averaged 85 ± 10 % and 93 ± 16 %, respectively (Table S3). Recoveries of ^{13}C-OCPs added at the extraction step averaged 63 ± 12 % (Table S3). OCP results were corrected for recovery following the isotope dilution methodology in USEPA Method 1699. Low concentrations of PBDEs and PCB congeners were detected in method blanks and results were subtracted by the average blank value.

Non-detect results were replaced with random numbers between the instrumental MDL and zero for statistical analysis for analytes with >15 % detection frequency. This substitution procedure was compared with Regression on Order Substitution used in the NADA R package (Helsel, 2011) for seven analytes ranging in detection frequency (DF) from 15 to 81 % (Table S4). There was good agreement between arithmetic means for 5 of the 7 analytes (deviation ranging from −2 to 12 %), with only dieldrin and endrin, which had a low detection frequency (15–19 %) having poor agreement (25–40 %). Larger deviations were seen for median and geometric means between the two substitution methods. Nevertheless we concluded that random number substitution was a practical method given the large suite of analytes, and was unlikely to bias our conclusions.

2.4. Statistical analysis

Wet weight concentrations of major POPs groups and individual OCPs, PCBs and PBDEs were log transformed. Coefficients of skewness and kurtosis of logged data were <2 for almost all analytes from each sampling location (Table S5A), confirming normal distributions. Use of wet weight (ww) concentrations was justified because % lipid was only available from 13 of 26 samples due to limited sample mass, and the measured % lipid was not correlated with concentrations of most major individual OCPs, PCBs and PBDEs (Table S6). Ratios of total (Σ)DDT and total (Σ)PCBs (ΣDDT/ΣPCB and 4,4′-DDE/ΣDDT), as well as pentachlorobenzene (PeCBz) to hexachlorobenzene (HCB) (PeCBz/HCB) were separately tested. However, given that the above ratios were not normally distributed, differences by region/ecotype and sex were tested by nonparametric Kruskal-Wallis Test. For all tests, significant probabilities were set at $p \leq 0.05$.

Principal components analysis (PCA) was used to identify groups of POPs influencing significant differences among regions and ecotypes. PCA was conducted with log wet weight concentrations of 14 OCPs for 26 samples and separately with 32 analytes (14 OCPs, 16 PCBs and 6 PBDEs) for 21 samples, using SigmaStat 4.0 (Grafiti LLC) with the correlation matrix option and standardization to unit variance. PCA was also conducted by combining the OCP and PCB data from the present study with results for the same analytes in individual samples published by Desforges et al. (2024), and Andvik et al. (2020). Separately, PCA was conducted with mean concentrations of OCPs and PCBs in northern North Atlantic killer whales reported in Remili et al. (2023) with means for each sampling location in the present study. To compare the results with those previous studies the OCPs and PCBs results were converted to lipid weight. Missing % lipid were replaced by average lipid for R- and T-type samples. For comparison with these other studies concentrations were normalized as a fraction of total analytes.

PCA scores were normally distributed (Shapiro-Wilk test, $P > 0.1$) and *t*-tests were used to examine the effects of ecotype on significant PCA components. Differences among sampling regions were examined using linear models with significant PCA components as dependent variable, and $\delta^{15}N$ or $\delta^{13}C$ as descriptor of ecotypes as independent variables and region as a categorical variable (using Systat Ver 13; Grafiti LLC). Model selection to balance parsimony was conducted by comparing Akaike's information criterion (AIC). Tukey's Honestly-Significant-Difference Test was used to identify significant differences among least square mean concentrations of the regions estimated by the best linear model.

3. Results

3.1. Concentrations and detection frequencies of major POPs

Concentrations of the five major groups of POPs (ΣDDT, ΣCHL, ΣCBz, ΣPCBs, ΣPBDEs) in the individual blubber biopsy samples along with stable isotope and % lipids are presented in Table 1 and geometric means in the five sampling regions are compared in Fig. 1. ΣDDT and ΣPCBs were the most prominent POPs in the killer whale biopsy samples with geometric mean concentrations in the 5 regions ranging from 34.4 to 161 ng/g ww and 8.10 to 58.5 ng/g ww, respectively (Fig. 1; Table S5A). Table S5B provides arithmetic mean concentrations of major POPs on a lipid basis for comparison with other studies (Table S1). Average ΣDDT/ΣPCBs ratios ranged from 2.7 to 4.8 (Table S5B) indicating the predominance of the DDT group. ΣDDT/ΣPCB ratios in samples from Avacha Gulf (AG) were significantly lower than in Western Sea of Okhotsk (WO) (Table S7).

Detection frequencies (DF) of the individual OCPs were low; from 4 to 17 out of 39 analytes had levels above MDLs. The most prominent (>46 % DF) were hexachlorobutadiene (HBCD), 1,2,3,4-tetrachlorobenzene (TeCBz), PeCBz, and HCB, trans-nonachlor, 4,4′-DDE, 2,4′-DDT, and 4,4′-DDT (Table S5A). Ratios of 4,4′-DDE/ΣDDT were significantly lower at NK compared to the four other sampling regions (Table S7)

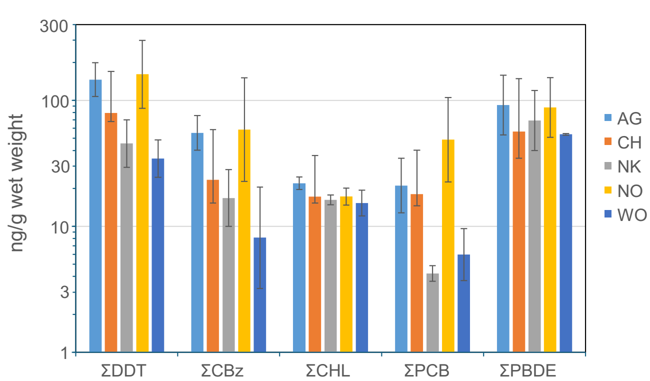

Fig. 1. Geometric mean concentrations (±SE; ng/g wet weight) of 5 major POPs groups in killer whale skin-blubber biopsy samples from five locations in the Russian coastal Northwestern Pacific. AG = Avacha Gulf (N = 6), CH = Chukoka (N = 7), NK = Northern Kuril Islands (N = 3), NO = Northern Okhotsk Sea (N = 4), WO = Western Okhotsk Sea (N = 5). Note that the vertical axis is a log scale.

implying different, possibly relatively recent, sources of DDT compounds.

Mean concentrations HCBD, PeCBz and HCB ranged from 4.6 to 14.9 ng/g ww with qualitatively little variation among sampling regions (Fig. 2A). PeCBz and HCB in water have been shown to approach equilibrium with atmospheric concentrations, and the PeCBz/HCB ratio has been suggested as a benchmark to assess contaminated and pristine marine waters (Allan et al., 2021). Mean PeCBz/HCB ratios ranged from 0.64 to 2.4 (Table S5A) and were significantly lower in samples from NK than the other 4 regions (Table S7). Ratios of CB52 and BDE28 with PeCBz and HCB showed good linearity with only three samples (a T adult male from WO (#86); a T adult female from AG (#72), and a T female (#103) from NO) deviating by ≥5-fold from the 1:1 line (Fig. S1). However, ratios of 4,4′-DDEs with PeCBz and HCB had a larger number of samples with greater deviation from the 1:1 line. A single sample from the Commander Islands (#1101) had high 4,4′-DDEs with PeCBz and HCB (Table S8A). While the ratios with PeCBz and HCB did not distinguish a specific region for unusual POPs exposure they did help to identify individual samples with unusual contaminant profiles. The use of the ratios of 4,4′-DDE, ΣDDT and ΣPCBs with other previously published killer whale datasets is discussed further below.

Among the 38 PCB congeners analysed in biopsy sample extract, highest DFs were found for trichloro (CB31/28; 76 %) and tetrachloro congeners (CB52, 49, 44; 76–95 %) (Table S5A). The dibromo BDE (BDE-7), tribromo (BDE-28), tetrabromo (BDE-47) and pentabromo (BDE-99, -100) had the highest DFs (57–100 %) among 24 PBDEs analysed (Table S5A). PCB congeners CB99, CB138, CB153_132, and CB180 were generally significantly correlated with the tri, tetra and penta BDE congeners (Table S7). Samples from NO had higher geometric mean concentrations of CB99, CB110, CB138, CB153 and CB180 than all other locations (Fig. 2B). However, these elevated mean concentrations were driven by a single individual sample, an adult female from NO (#103, Table S8B) that had ΣPCBs of 825 ng/g (ww), which was 25-fold higher than the median for all 21 samples analysed for PCBs.

No significant differences were observed between geometric mean lipid weight concentrations of OCPs, PCBs and PBDEs between T and R ecotypes or between males and females with the exception of PCB 153_132 (Table S9). Concentrations this hexachlorobiphenyl congener were significantly higher in T compared to R ecotypes and also significantly higher in females compared to males. However, the higher mean value for females was driven same high value for NO#103.

3.2. Principal components analysis

Principal components analysis based on 14 OCPs in 26 biopsy samples yielded 5 significant components that explained 73 % of the variance (Table S10A). PC1 had highest positive loadings for trans-nonachlor, heptachlor epoxide, dieldrin, 4,4′-DDE, and mirex, while PC2 was distinguished by negative loadings for 2,4′-DDT and 4,4′-DDT and positive loadings of HCBD, PeCBz, and endrin (Fig. S2). PC3 had high loadings of HCB and PeCBz (Table S10A; Fig. S2). PCA conducted with 32 analytes (21 samples with combined OCPs, PCB and PBDE results) yielded 5 significant components that explained 70 % of the variance (Table S10B). PC1 had highest positive loadings for 4,4′-DDE, CB99, CB138, CB180 and BDE66, while PC2 had positive loadings for PCBs and PBDEs (CB31, CB44, CB52, BDE7, and BDE99). PC3 was distinguished by positive loadings of OCPs only, including HCBD, 1234TeCBz, PeCBz, HCB, and 2,4′-DDT) (Fig. S3; Table S10B).

Sampling location and ecotype were examined with PC loadings plots (Fig. 3). The loadings for OCPs showed separation of most Chukotka and North Okhotsk Sea samples from Northern Kuril Islands (Fig. 3A) while the combined OCP/PCB/PBDE data distinguished most Chukotka samples from Avacha Gulf (Fig. 3B). However, neither of the two PCA loadings datasets clearly separated sampling locations from each other. Means of the scores for the PCs based on the OCP results did not show significant differences among ecotypes or sex (*t*-test, $P > 0.05$;

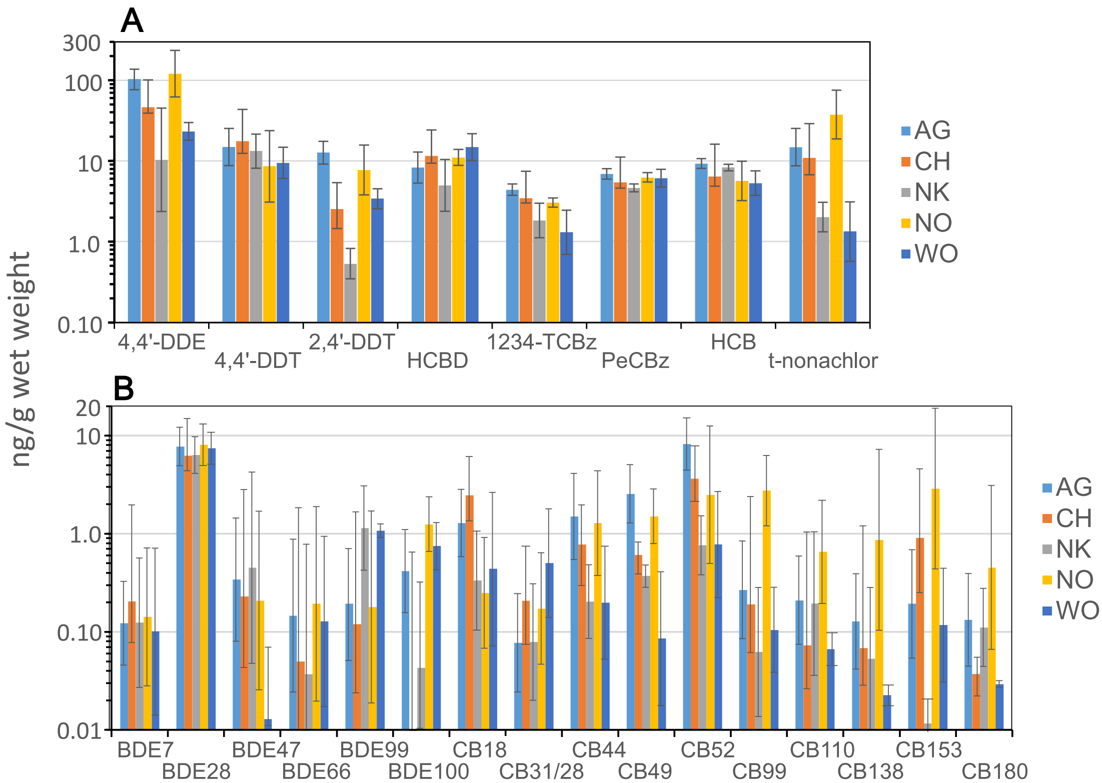

Fig. 2. A. Geometric mean concentrations (±SE; ng/g wet weight) of 8 individual OCPs and *B. major* individual PBDE and PCB congeners in killer whale blubber biopsy samples from five regions in the Russian coastal Northwestern Pacific. Note that the vertical axis is a log scale. Location abbreviations are in Fig. 1.

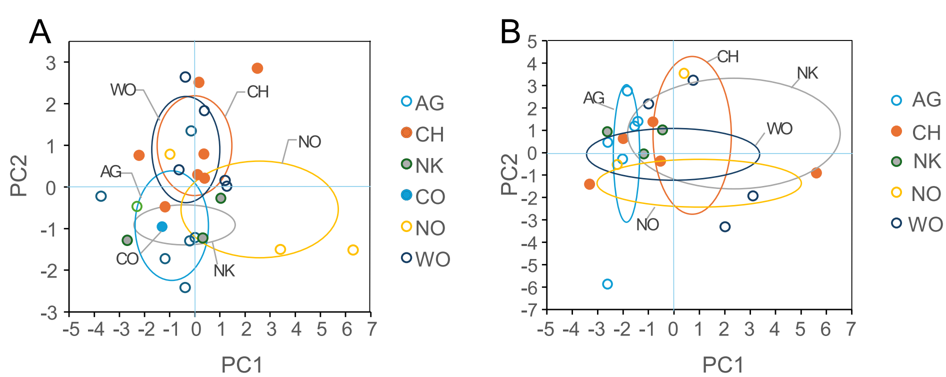

Fig. 3. Principal component scores based on (A) 26 individual killer whale biopsy samples from 6 sampling locations in the Northwestern Pacific using log-transformed results for 14 OCPs, and (B) based on 21 samples of OCPs, PCBs and PBDEs (32 analytes). Ellipses define mean scores (±SD) for each location.

Table S11). Similarly the loadings plots for PC1, PC2 and PC3 did not distinguish R-type vs T-type individuals (Figs. S2 and S3). Interestingly, samples from juvenile R-type animals (AG-51, AG-66, NK-1402) generally had similar loadings on PC1 and PC2 to T-type adults possibly reflecting transfer of POPs during lactation and in utero transfer.

3.3. Effect of ecotypes and region on PCA scores

Although differences between ecotypes were not found with PCA, given the significant differences in $\delta^{15}N$ and $\delta^{13}C$ (Table S7), ecotype might still be important to explain geographic differences between specific sampling regions/locations. To assess this question, linear models were developed with the available independent variables ($\delta^{15}N$, δ13C, region) and component scores for the PCA with 14 OCP analytes (Table S10A). The best models included PC1 and PC2 with Region + $\delta^{15}N$ or $\delta^{13}C$ + Region (r^2 ranging from 0.39 to 0.57) (Table S12). We did not combine $\delta^{13}C$ and $\delta^{15}N$ because they were significantly correlated (Table S6). The linear model with region only showed significant r^2 and low AIC for PC2 but not for PC1 (Table S12). Overall, the modelling indicated the influence of ecotype on the profile and concentrations of OCPs and may reflect differences in baseline organism isotope signatures among sampling regions.

Tukey's HSD test on the means of PCA scores from the linear model with Region + $\delta^{15}N$ identified significant differences for PC1 between AG and NO and NK and NO, while means for PC2 did not differ significantly (Table S13). The model with Region + $\delta^{13}C$ also identified significant differences between AG and NO for PC1, and between AG and CH, for PC2. These differences are also evident qualitatively in Fig. 3A. Key contributors to the geographic differences are the DDT isomers (high positive loadings of 4,4′-DDE on PC1 and negative loadings for 2,4′-DDT and 4,4′-DDT on PC2) as well as the more volatile OCPs, HCBD and PeCBz, which had positive loadings on PC2.

4. Discussion

4.1. Comparison of concentrations with other regions

Lipid weight concentrations of OC0Ps, PCBs and PBDEs in all Northwestern Pacific killer whales (Table S5B) were generally lower than killer whales from the Northeastern Pacific and the North Atlantic (Table S1). However, average ΣDDT and ΣPCB concentrations were similar to concentrations for resident females collected from this region in 2002 and 2003 (Atkinson et al. (2019) (Table S1). No comparison was possible for PBDEs as we were not able to find any previous reports for killer whales from the Northwestern Pacific. More difficult to explain are the much lower OCP and PCB concentrations in "T"-type males (up to 180-fold) in the current study compared with previous reports for killer whales from the Kuril Islands and Kamchatka Peninsula (Atkinson et al., 2019) and even larger differences compared to samples from Northern Hokkaido (Kajiwara et al., 2006) (Tables S1 and S5B). The percent lipid in the biopsy samples in the current study ranged from 9 to 53 %, which was higher than reported for 5 samples from the Kamchatka Peninsula analysed by Lawson et al. (2020)(5.0–8.6 %) but similar to the range (5–43 %) for the 98 samples from the Aleutian Islands and Northeastern Pacific that were included in that study. Thus, adjusting the data to a lipid basis would not explain the generally low concentrations we have observed. The small sample size (0.032 to 0.152 g) available for analysis resulted in higher detection limits and thus lower detection frequencies, but accuracy was unlikely to have been affected given good agreement with certified reference materials (Table S2). The storage in 95 % ethanol following collection may also have contributed to the lower concentrations of some analytes. However, Lundin et al. (2016) found that concentrations of PCBs, PBDEs and DDT related compounds in killer whale scat samples were not affected by prior lyophilization and extraction with 70 % ethanol to recover hormones. Lundin et al. did not investigate recoveries of some less hydrophobic analytes such as HCH isomers, dieldrin, and oxychlordane. It is possible that the 95 % ethanol storage could have affected those analytes in the current study. Unfortunately, we did not have untreated blubber stored under the same conditions with which to make the comparison.

4.2. Biomagnification factors

Given that levels of POPs are strongly correlated with diet composition based on studies of fatty acid signature in the North Atlantic killer whales (Remili et al., 2023) it was of interest to compare with published data for likely major dietary species in the Northwestern Pacific and to estimate biomagnification factors (BMFs) where possible (Table 2). Salmon (*Oncorhynchus* sp.), are the main summer diet of fish-eating killer whales in the Sea of Okhotsk and Russian coastal waters of the Bering Sea (Volkova et al., 2019). Tsygankov et al. (2022) reported concentrations of ΣPCBs averaging 18.4 ng/g ww in muscle of sockeye salmon, 9.1 ng/g ww in chum salmon, and 86 ng/g ww for pink salmon in the Sea of Okhotsk and western Bering Sea. ΣPCB concentrations reported by Tsygankov et al. (2022) are very similar to those in adult salmon in the Salish Sea (Strait of Georgia (British Columbia, Canada) and Puget Sound (Washington)) region (Cullon et al., 2009; Mongillo et al., 2016). For example, Mongillo et al. (2016) found ΣPCBs in chinook salmon from the Salish Sea averaged 10 ng/g ww and 91 ng/g ww, respectively. Tsygankov et al. (2016) reported median concentrations of 4,4′-DDE in salmon muscle from Sea of Okhotsk ranging from 6.4 to 287 ng/g lipid or approximately 0.3 to 14 ng/g ww (assuming 5 % lipid). Seals and baleen whales constitute an important component of the diet

Table 2
Biomagnification factors for ΣDDT and ΣPCB in killer whales based on published data for dietary species in the Northwestern Pacific/Bering Sea, the Salish Sea, and the Eastern Canadian Arctic.*

1. Concentrations reported in dietary species (ng/g lw)

Analytes	NW Pacific	NW Pacific	Salish Sea	Salish Sea	E. Can Arctic	E. Can Arctic	E. Can Arctic
ng/g lw	Median Seals[1]	Median Salmon[2]	Median Seals[3]	Median Salmon[4]	Average Beluga[5]	Average Ringed seal[5]	Average Halibut[6]
ΣDDT	360	147	1890	88	1300	138	81
ΣPCB	460	368	2387	86	1020	126	60

2. Concentrations in killer whale blubber (ng/g lw)

Analytes	NW Pacific	NW Pacific	Salish Sea	E. Can Arctic
ng/g lw	Average "R" killer whale[7]	Average "T" killer whale[7]	Average Killer whale[8]	Average Killer whale[9]
ΣDDT	462	580	68,000	117,000
ΣPCB	149	455	39,000	94,100

3. Biomagnification factors

Analytes	NW Pacific	NW Pacific	NW Pacific	NW Pacific	Salish Sea	Salish Sea	E. Can Arctic	E. Can Arctic	E. Can Arctic
	"R"-KW/seals	"R"-KW/salmon	"T"-KW/seals	"T"-KW/salmon	KW/seals	KW/salmon	KW/beluga	KW/seals	KW/halibut
ΣDDT	1.3	3.2	1.6	4.0	36	770	90	850	1450
ΣPCB	0.3	0.4	1.0	1.2	16	450	92	749	1570

* Data sources.
1 Quakenbush et al. (2016) — median of published mean values for Bering & Chukchi Sea seals.
2 Tsygankov et al. (2022); Tsygankov et al. (2016) — median of published mean values for salmon.
3 Ross et al. (2013); Calambokidis et al. (1999) — median of published mean values for harbour seal pups.
4 Cullon et al. (2009); Mongillo et al. (2016) — median of published mean values for salmon.
5 Muir et al. (2013) — beluga (*Delphinapterus leucas*) and ringed seal (*Phoca hispida*) blubber, Cumberland Sound, Pangnirtung NU — average and geomean concentrations, respectively, for 2011.
6 Braune et al. (2005) — Greenland halibut (*Reinhardtius hippoglossoides*) Cumberland Sound, Eastern Canadian Arctic, 1999.
7 Present study (Tables S8 and S11) — using average concentrations.
8 Mongillo et al. (2016) — only average concentrations available for killer whales (2008–2013) — Strait of Georgia/Puget Sound.
9 Desforges et al. (2024) — average of combined results for Cumberland Sound and Eclipse Sound, Baffin Island, NU (2013–2021).

of T-type killer whales in the Northwestern Pacific (Borisova et al., 2020), however, data on concentrations of POPs in marine mammals in the region are limited. Tsygankov et al. (2015) reported average ΣDDTs concentrations in gray whales (*Eschrichtius robustus*) harvested (2010−2011) in coastal waters of the Western Bering Sea of 360 ng/g lw in muscle. Mean concentrations of ΣPCBs in blubber of four species of seals sampled in the northern Bering and Chukchi seas in 2003–2007 ranged from means of 220 to 700 ng/g (ww) (Quakenbush et al., 2016). The BMFs for ΣDDT in Northwestern Pacific killer whales based on seals and salmon as prey species range from 1.3 to 3.7 and ΣPCBs from 0.3 to 1.2 (Table 2). These BMFs are 10 to >100-fold lower than those estimated using results for harbour seal (*Phoca vitulina*) pups, salmon, and killer whales (Mongillo et al., 2016) in the Salish Sea, or for three possible prey species and killer whales (Desforges et al., 2024) from Baffin Island in the Eastern Canadian Arctic (Table 2; see footnotes in the table for data sources). The BMFs for the Northwestern Pacific killer whales are highly uncertain given the limited data for concentrations in salmon and seals from the Sea of Okhotsk and coastal Kamchatka peninsula region. This is particularly the case for seals because concentrations reported by Quakenbush et al. (2016) are for samples collected in 2003–2007 and could have declined over time. For example, Houde et al. (2019) found declines of 2.5 to 3.0 %/yr for ΣDDT and 1.2 to 4.1 %/yr for ΣPCBs in ringed seal (*Phoca hispida*) blubber from two Canadian Arctic communities in the Eastern Beaufort Sea region (1980s to 2016). Assuming similar rates in the Western Bering Sea over the period 2003 to the sampling period of the current study (2012–2016) would only account for declines of 30 to 40 % and this would only change BMFs by <2-fold.

BMFs for ΣDDT and ΣPCBs were slightly higher for "T" compared with "R" ecotypes in the Northwestern Pacific killer whales but the differences were minor compared to differences with food webs in other regions (Table 2). Ecotype has previously been shown to be an important variable explaining the variation of POPs in killer whales from the North Pacific (Krahn et al., 2007; Lawson et al., 2020) and North Atlantic (Andvik et al., 2020; Remili et al., 2023). Remili et al. (2023) found, using PCA, that PCB153 distinguished baleen whale eating ecotypes from those with fish and seal diets in a study that included 162 skin-blubber samples from across the northern North Atlantic. However, our results for PCA with the combined OCP, PCBs and PBDEs did not distinguish ecotypes (Fig. S3A, B) although recalcitrant congeners (with 2,4,5-substitution on one or both rings; CB99, CB 138, CB153, CB180) had high loadings on PC1. The lack of distinctive differences among ecotypes for recalcitrant PCB congeners and OCPs such as 4,4′-DDE in the present study may simply be due to the limited sample sizes for each ecotype at each location. Only T-type samples were available for analysis from three geographically widely separated regions, CH, NO and WO, thus potentially confounding comparisons among sampling location. Overall, the available data for ΣDDT and PCBs in species that probably constitute a major component of the diet of the Northwestern Pacific killer whales, or for ecotype based on stable isotope analyses, do not explain the much lower concentrations in the skin biopsies. The killer whales appear to be feeding on fish and marine mammals that have much lower contaminant levels than reported for salmon or seals.

4.3. Geographical differences among killer whale populations

Geographical differences between the results in this study and other studies on killer whales from the North Pacific and North Atlantic were explored further with PCA by combining the results for mean concentrations of individual OCPs and PCBs published by Andvik et al. (2020), Remili et al. (2023) and Desforges et al. (2024) with the same analytes in the present study (Fig. 4). The data were normalized to total POPs and standardized to unit variance. The Northwestern Pacific sites were clearly distinguished from the North Atlantic driven by positive loadings on PC1 for chlorobenzenes, mirex, 4,4′-DDT and 4,4′-DDE and other OCPs, while the North Atlantic samples had negative loadings of penta-, hexa- and heptachloro-PCBs on PC1. Unfortunately PCA could not be conducted with other samples from the North Pacific (Lawson et al., 2020; Atkinson et al., 2019; Kajiwara et al., 2006) due to the limited number of analytes measured or reported. The predominance of ΣDDTs relative to ΣPCBs in this study and in other North Pacific killer whales (ΣDDT/ΣPCB > 1 for all locations) distinguishes them from most reports for the North Atlantic (Table S1 and Table S5B). However, it should be noted that apart from the current study, most previous killer whale biopsy samples from the Northwestern Pacific were collected in the late 1990s and early 2000s and ΣDDT/ΣPCB could have changed with the bans on use that started in North America and Japan in the 1970s in the case of DDT and in the 1980s for PCBs.

We examined the question of whether differences in collection dates or time periods might explain differences between the Northwestern Pacific and other regions using PCA with results for individual samples that were available in the supporting information of Andvik et al. (2021) for northern Norway, and Desforges et al. (2024) for the Eastern Canadian Arctic (Pond Inlet and Cumberland Sound) (Fig. S4). Sample

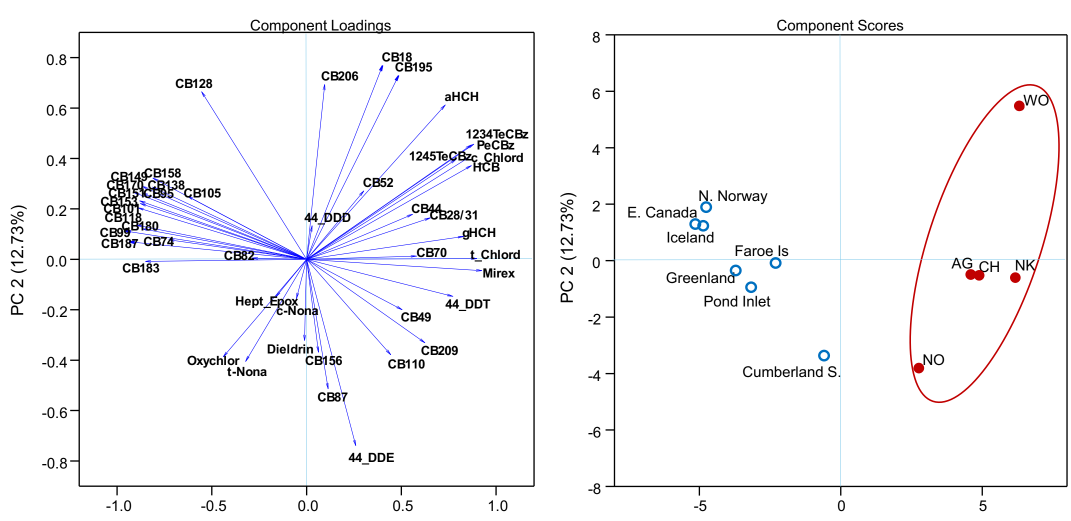

Fig. 4. Principal components analysis based on results for OCPs and PCBs in killer whale biopsies reported for Eastern Canada, Iceland, the Faroe Island and Greenland in Remili et al. (2023), and with means for the same analytes reported for Northern Norway (Andvik et al., 2021), the Eastern Canadian Arctic (Pond Inlet and Cumberland Sound) (Desforges et al., 2024) and from the Northwestern Pacific (present study; sites AG, CH, NK, NO and WO).

collection periods were similar for the Norway (2017–2019) and the Canadian Arctic (2013−2021) and overlapped with the present study (2012–2016). Positive loadings of penta-, hexa- and heptachloro-PCBs and negative loadings of HCB, 4,4′-DDT, 4,4′-DDD and CB 28 and CB52 on PC1 distinguished the samples from Norway and the Canadian Arctic from the five northern Northwestern Pacific sites. Thus, temporal trends are unlikely to be a factor in the different proportions of PCBs and DDT related compounds in the above studies.

PCA also showed that TeCBz, PeCBz and HCB along with DDT-related compounds distinguished the samples in the current study from the killer whales in the North Atlantic. Global air monitoring using passive samplers over the period 2005 to 2016 has shown that PeCBz and HCB are among the most prominent POPs in air globally with increasing concentrations (5–10 %/year) at most sites in the Arctic, Western Europe, North America, and southeast Asia (Shunthirasingham et al., 2024). HCB and PeCBz were prominent atmospheric POPs at two background monitoring sites in Japan over the period 2009–2018 with no decline (HCB) or slight increases (PeCBz) (UNEP, 2021). Emissions of HCB and PeCBz in the region, i.e., from China, the Republic of Korea, and Japan, are occurring due unintentional generation in thermal processes and as impurities in production of chlorinated chemicals (solvents, dyestuffs and pigments) (Liu et al., 2018). However, seawater monitoring during an oceanographic cruise along a transect in the northwest Pacific, did not show elevated HCB in ocean waters or in air in the Sea of Japan near the above source regions (Cai et al., 2012; Wu et al., 2014). Thus, the distinctive pattern of chlorobenzenes relative to other POPs in the Northwestern Pacific killer whales is probably best explained by lower contributions of PCBs and higher proportions of DDT in total POPs concentrations. China and Korea were not major producers or emitters of PCBs (Melymuk et al., 2022; Li et al., 2023) and while Japan and the former Soviet Union were major users, the overall quantities were much smaller than for the USA and Europe (Li et al., 2023). In the case of DDT, agricultural use continued in China until 1983 and until the late 1980s in the former Soviet Union. It was banned for agricultural use in Japan and South Korea as of 1971 and 1973, respectively (Japan MOE, 2005; UNEP, 2021). However, the Democratic Republic of Korea (North Korea) was still using DDT in agriculture and forestry as of the mid-2000s (van den Berg et al., 2017). An oceanographic cruise in the Northwest Pacific Ocean in 2008 found a declining trend of ΣDDT with latitude from Shanghai to the Bering Sea and 4,4′-DDE/ΣDDT ratios indicative relatively fresh DDT inputs (Wu et al., 2011). Average ratios of 4,4′-DDE/ΣDDT were lower at all five sampling sites (0.57–0.80) than in killer whales from the Eastern Pacific and the North Atlantic (Table S1) due to higher proportions of 4,4′-DDT and 2,4′-DDT confirming more recent DDT inputs to the Northwestern Pacific.

5. Conclusions

Concentrations of individual OCPs and PCBs in killer whale samples from the Northwestern Pacific are among the lowest reported for killer whales in the northern hemisphere. While Atkinson et al. (2019) found similar low concentrations in resident females from the Kamchatka Peninsula and the Kuril Islands regions, we found relatively low concentrations in R and T-type individuals, both male and females. The lower concentrations are not easily explained based on published data for POPs for salmon or seals, the assumed main diet items, from the same region. Declining levels of DDT-related compounds and PCBs due to national and global phase outs which were in place in Japan and Russia by the early 1990s, may explain some of the differences given that the samples in the present study were collected 10 to 15 years after those analysed by Atkinson et al. (2019) and Lawson et al. (2020). To our knowledge, there are currently no published temporal trend data for killer whales available for the North Atlantic or Eastern North Pacific populations, which could be used for comparison. However, declines of 10-fold or more for PCBs and major OCPs in a top predator over a 15 year period seem unlikely based on temporal trends for ringed seals and other marine predators in the Arctic (Houde et al., 2019; Rigét et al., 2019). A more likely explanation is that contamination the killer whales we sampled have other prey species with lower levels than salmon or seals and that the marine food web of the Russian Far East has much lower concentrations of POPs than the northern North Atlantic or Salish Sea region in the Eastern North Pacific as discussed by Tsygankov and Lukyanova (2019). Given the relatively low exposure to POPs, the Northwestern Pacific populations would be a good reference group for evaluating biological effects for example by metabolomic profiling or gene transcript profiles using skin samples (Noël et al., 2014; Simond et al., 2020).

CRediT authorship contribution statement

Derek C.G. Muir: Writing – original draft, Funding acquisition, Conceptualization. **Aaron T. Fisk:** Writing – review & editing, Funding acquisition, Conceptualization. **Olga A. Filatova:** Writing – review & editing, Data curation. **Ken Drouillard:** Writing – review & editing, Methodology, Data curation. **Nargis Ismail:** Methodology, Data curation. **Olga Shpak:** Methodology. **Ivan Fedutin:** Methodology, Data curation.

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. Supplementary data

Concentrations of major OCPs, PCB and PBDE congeners with detection frequency > 25 % in individual killer whale biopsy samples from the Northwestern Pacific (ng/g wet weight) are provided in the Supplementary Information file (Tables S8 and S11). Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2025.117927.

Data availability

Data will be made available on request.

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