Factors Influencing Legacy Pollutant Accumulation in Alpine Osprey: Biology, Topography, Or Melting Glaciers?

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Ⓢ *Supporting Information*

ABSTRACT: Persistent organic pollutants (POPs) can be transported long distances and deposited into alpine environments via cold trapping and snow scavenging processes. Here we examined biotic and abiotic factors determining contaminant variability of wildlife in alpine ecosystems. We measured POPs in eggs and plasma of an apex predator, the osprey (*Pandion haliaetus*) breeding in 15 mountainous watersheds across a broad latitudinal, longitudinal and altitudinal range in western Canada. After accounting for proximate biotic factors such as trophic level ($\delta^{15}N$) and carbon source ($\delta^{13}C$), variability in contaminant concentrations, including ΣDDT (sum of trichlorodiphenylethane-related compounds), toxaphene, hexachlorobenzene (HCB), total chlordane, and ΣPCBs (polychlorinated biphenyls) in osprey tissues was explained by interactions among relative size of watersheds, water bodies, elevation, and glacial input. ΣDDT in nestling plasma, for example, decreased with lake elevation, probably as a result of local past inputs from agricultural or public health usage at lower altitude sites. In contrast, toxaphene, never used as an insecticide in western Canada, increased with elevation and year-round snow and ice cover in both plasma and eggs, indicating long-range atmospheric sources as dominant for toxaphene. Lower chlorinated PCBs in plasma tended to decrease with elevation and ice cover consistent with published data and model outcomes. Temporal trends of POPs in osprey eggs are coincident with some modeled predictions of release from melting glaciers due to climate change. Currently we suggest that contaminants largely are released through annual snowpack melt and deposited in large lower elevation lakes, or some smaller lakes with poor drainage. Our study highlights the importance of understanding how biological processes integrate physical when studying the environmental chemistry of wildlife.

INTRODUCTION

Deposition of atmospherically transported volatile contaminants by trapping in cold environments, as a result of either increased latitude[1] or altitude[2] is well documented. That process, when coupled with the efficient scavenging of these chemicals through adsorption to snow crystals[3] can result in accumulation of persistent organic pollutants (POPs) in arctic and alpine environments.[4,5] Recent global warming trends have caused the contraction of many of the world's large ice masses.[6,7] Assessment and modeling of the impact of global warming trends and melting of polar and glacial ice on accumulation of contaminants have yielded varying predictions as to the degree and direction of patterns and trends.[8−10] However, recent studies in alpine environments indicate stored POPs are released into receiving waters from glacial melting.[11−17]

Concentrations of specific compounds in fish tissue, such as more volatile PCBs (polychlorinated biphenyls) and hexachlorocyclohexane (HCH), increase with latitude across Canada.[18,19] Other chemicals, particularly DDT (trichlorodiphenylethane), total PCBs and toxaphene in fish samples from alpine and remote northern lakes exceed consumption guidelines for humans and wildlife.[20,21] However, in contrast to the Arctic, where numerous studies have examined uptake and transfer of contaminants to fish-eating top predators,[4,22] there are no such studies from alpine regions.

Western Canada affords an interesting opportunity to examine the influence of topography and ecological variation on contaminant accumulation in the alpine. The region is dissected by a number of mountain ranges up to 4000 m altitude running north to south, and is the first landfall for pollutants transported atmospherically from the increasingly industrialized economies of Asia.[23] The osprey (*Pandion*

haliaetus) is an obligate piscivore and a common breeding species on lakes and rivers across much of the globe. Ospreys integrate exposure from the entire food chain, and were selected here and elsewhere as effective sentinels of environmental contamination.[24−27] As top predators, they are among the more highly exposed wildlife in most systems; DDE (dichlorodiphenylethylene), PCBs and PBDEs (polybrominated diphenyl ethers) have all been associated with biological effects in ospreys.[26,28−31] Although ospreys are long distance migrants and winter in Latin American countries that continued to use organochlorine pesticides after they were banned in North America, contaminant levels in satellite-tracked osprey eggs have been related to breeding and not to winter exposure for many of the same nests as the present study.[25]

To examine topographical and ecological influences on contaminants in osprey, from 1999 to 2003 we measured organochlorine pesticides and PCBs in egg and plasma samples. Because POPs and other contaminants biomagnify within food chains and disperse more uniformly in aquatic compared with terrestrial ecosystems, we measured $\delta^{15}N$ as a measure of trophic level and $\delta^{13}C$ as indication of carbon input which has been effectively applied in other aquatic and marine birds.[32−35]

We employed an information theoretic approach to examine the importance of biotic factors: trophic level, carbon source, and topographic abiotic factors: altitude, lake area, water basin size, water body type (river, reservoir or natural lake), percent of glacier in watersheds and ratio of lake size to watershed size along with physical-chemical parameters in determining contaminant levels. We hypothesized that contamination would be greater for birds feeding at higher trophic levels, and in drainage basins at increased elevation and with more coverage in permanent snow and ice.

■ MATERIALS AND METHODS

Calculation of Geographic Features. The Spatial Analyst toolbox and Hydrology toolset in ARCGIS 9.2 were used to measure the size (area) of 24 watershed drainage basins and of local osprey foraging lakes and rivers within the Canadian Cordillera (ESRI, www.esri.com). Elevation (m) of osprey nest location and watershed area (km^2) were calculated using the digital elevation model and glacier data archived at NRC Geomatics Canada.[36,37] Glacial areas (km^2) were calculated using current glacier extents. All data was reprojected into the same coordinate system UTM Zone 11N, NAD83 to ensure area conformity. Postprocessing of data with the Hydrology toolset required sink-filling using the sink tool (see ref 38 for the algorithm) and the calculation of slope, aspect, flow direction and accumulation of water, and stream networks using flow direction and accumulation, watershed and stream network algorithms.[39−41] Once watersheds were developed, areas of both watersheds and glaciers were calculated using the script within ARCGIS 9.2.

Sample Collection. From 1999 to 2003, we collected 88 eggs (one per nest) from incubating ospreys, plasma and feather samples from 70 nestling ospreys from 59 nests, and 11 plasma samples from adult ospreys nesting in 15 watersheds of the Canadian Cordillera in British Columbia and the Yukon (Figure 1). The sampled watersheds varied from small, 1170 km^2 of the Pitt to very large of the Williston, 66,623 km^2 (Table 1). Lake area varied over several orders in magnitude from the 6 km^2 of Athabasca Lake to 1660 km^2 of the Williston reservoir. Elevation ranged from sea level at Pitt Lake to 1210 m at Athabasca Lake. The glaciated area of the studied watersheds
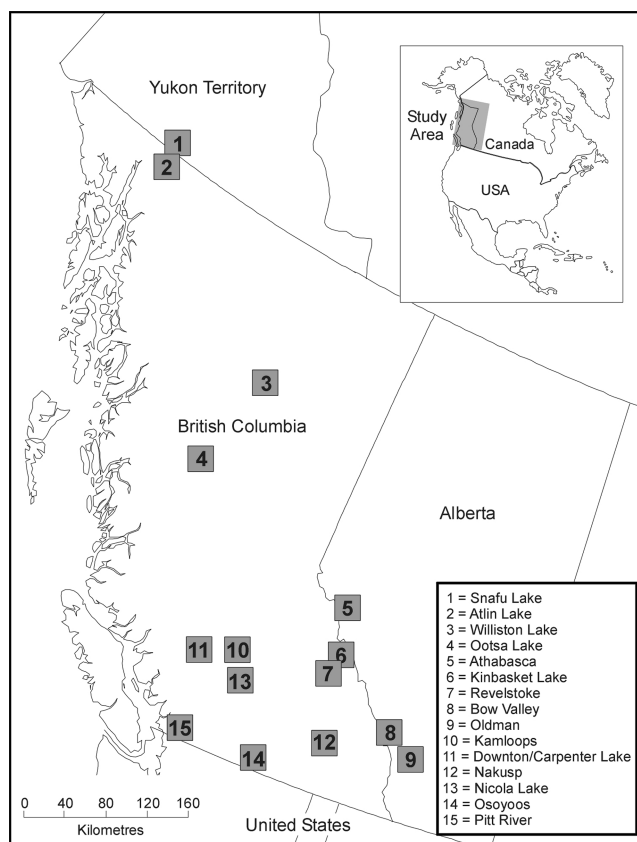

Figure 1. Locations where osprey eggs and plasma samples were collected, 1999−2003, in British Columbia, Alberta, and the Yukon Canada.

was somewhat polarized, eight sites having only zero to one percent glaciated and five watersheds with 9 to12%.

We captured adult ospreys using a domed noose carpet (balchatri) placed over the active nest or modified dho-ghaza mist nets with a tethered Great Horned Owl, *Bubo virginianus*, as a lure bird and attached a satellite transmitter to their back.[24] Each bird was weighed, measured, and banded with a U.S. Fish and Wildlife Service band on one leg and a red alphanumeric band on the other leg. Eggs and chicks were sampled by climbing into the nest platform. At some nests, it was possible to safely remove an egg but not a chick for blood sampling, thus sample sizes are fewer for chicks. Further details on nest access, nestling and adult sampling, and transmitter attachment procedures were described previously.[23,24]

Contaminant Analysis. (See Supporting Information for more detailed methods). Organochlorine pesticides and PCBs in eggs and plasma were analyzed at the National Wildlife Research Center (Ottawa, ON, Canada) using gas chromatography with an electron capture detector (GC-ECD) as described previously.[27] Briefly, lipid and moisture concentration was determined gravimetrically, samples were cleaned and analyzed along with blanks and reference samples in a Hewlett-Packard model 5890 Series II Plus gas chromatograph with 63Ni-ECD detector, HP-3396 integrator, HP-7673A autosampler (Hewlett-Packard, Palo Alto, CA).

Toxaphene measurements were conducted at the Canada Centre for Inland Waters (Burlington, ON, Canada). Gas chromatography−mass spectrometry was carried out using a Hewlett-Packard mass selective detector (HP5973 MSD) operated in negative ion mode.

Table 1. Summary Information on the Western Canadian Watersheds for Lakes and Rivers Included in the Study and Geometric Mean (Wet Weight) Concentrations of Contaminants in Eggs and Nestling Plasma of Ospreys, 1999-2002[a]

watershed	watershed area (km²)	lake area (km²)	% glac.	elev. (m)	$\delta^{15}N$	$\delta^{13}C$	N^b	ΣDDTs (ng/g) egg	ΣDDTs (ng/g) plas	toxaphene (ng/g) egg	toxaphene (ng/g) plas	Σchlordanes (ng/g) egg	Σchlordanes (ng/g) plas	HCB (ng/g) egg	HCB (ng/g) plas	ΣPCBs (ng/g) egg	ΣPCBs (ng/g) plas
Athabasca	2505	6	9	1210	9.3	−26.6	5,5	288	2.6	177	0.0	5.1	0.9	0.9	0.1	307	7.7
Atlin	8820	586	9	675	9.6	−24.3	6,4	716	6.7	22.1	0.3	3.9	0.5	0.8	0.3	178	2.5
Bow	2596	8	0.3	1546	11.4	−27.3	7,5	905	7.6	62.0	1.2	7.2	0.4	1.2	0.1	436	11.4
Columbia	16330	24	1.3	808	8.8	−26.6	7,6	575	5.5	NA[c]	2.6	1.4	0.4	0.4	0.2	109	5.5
Downton -Carpenter	2014	45	5	676	9.7	−27.0	6,3	924	5.1	NA	5.8	2.5	0.4	0.7	0.3	672	20.7
Kinbasket	14773	402	11.4	745	NS[d]	N.S.	6,0	747	NS	NA	NS	3.3	1.0	1.0	NS[d]	182	NS
Nicola	4296	24	0	645	NS	N.S.	6,3	775	7.8	238	0.0	19.6	0.3	2.5	0.5	1420	12.6
Oldman	8808	6	0	1264	13.1	−28.2	4,3	714	5.1	23.5	0.0	22.4	0.3	1.4	0.1	826	7.7
Ootsa	13225	365	1	852	10.6	−29.2	7,6	979	8.7	12.1	0.3	1.2	0.4	0.2	0.3	38.2	1.7
Osoyoos[e]	8203	369	0	305	13.9	−26.3	4,5	2660	104	NA	1.7	5.0	0.3	0.6	0.2	487	11.1
Pitt	1170	70	12	10	10.0	−25.7	5,2	760	4.1	NA	3.2	1.1	0.7	0.7	0.4	485	11.1
Revelstoke	5253	66	11	594	N.S.	N.S.	4,0	493	NS	11.9	NS	9.6	0.8	1.3	NS	250	NS
Snafu	1508	9	0	793	10.4	−26.9	1,1	1790	29.2	42.0	0.0	2.7	0.3	0.5	0.1	23.0	4.5
Upper Arrow	7643	228	4	431	8.1	−27.3	5,1	347	3.1	NA	0.9	0.6	0.4	0.5	0.2	120	28.2
Williston	66623	1660	0	690	N.S.	N.S.	7,0	42	NS	17.2	NS	1.3	0.3	0.6	NS	82.6	NS

[a]Stable isotope values ($\delta15N$ and $\delta13C$) are averages for nestling plasma. [b]Number of nests (number of eggs, number of chicks). [c]NA, not analyzed. [d]NS, not sampled. [e]For calculation of lake and watershed area, we used the whole Okanagan Lake system, given the past area of orchards and pesticide use throughout that lake system, and Osoyoos' location near the bottom of that drainage.

Results are presented on a wet weight basis throughout.

Stable Isotope Analysis. Egg and plasma samples were dried, 1 ± 0.2 mg encapsulated in tin, and sent to University of California (Davis, CA) stable isotope facility. Lipids were not removed from plasma and egg samples due to expected low lipid levels. Samples were first loaded into tin cups and combusted in a Robo-Prep elemental analyzer (Europa Scientific) at 1200 °C. The resultant CO_2 and N_2 gases were separated and analyzed using an interfaced Europa 20:20 continuous-flow isotope ratio mass spectrometer (Europa Scientific) Results were reported in delta notation in parts per thousand (‰) relative to air ($\delta^{15}N$) and Vienna Pee Dee Belemnite ($\delta^{13}C$).

We did not extract lipids as variance in carbon isotopes due to lipid fractionation (∼0.4−0.5‰, greater variance for piscivorous birds; reviewed in [43]) is much lower than spatial variation within our study population (chick SD = 2.04‰; egg SD = 1.96‰). We only considered correlations between contaminants and $\delta^{13}C$, not the absolute value of $\delta^{13}C$, so consistent depletion of ^{13}C in yolk would make no difference in the strength of correlations. We did not use C:N ratios or lipid content to account for variation in $\delta^{13}C$ because there was no correlation between $\delta^{13}C$ and C:N or percent lipids across the data set of within each lake ($p > 0.3$). Furthermore, the correlation coefficient between the lipid-corrected $\delta^{13}C$ values[44] and the nonlipid-corrected $\delta^{13}C$ values was 0.96, and using the lipid-corrected values did not change any of our selected models.

We did not measure baseline levels of $\delta^{15}N$ at each water body. Variation in baseline levels measured from two snail species within mountain lakes in western Canada (SD = 0.77‰ and 0.80‰; range = 1.64‰ and 1.88‰; S. Lord, Pers. comm.) were about one-third the variation within our osprey population (SD = 1.83 (feathers), 1.61 (egg); range = 6.8 (chick), 6.6 (egg)), suggesting that most variation was due to

factors other than interlake baselines. Furthermore, provided the baselines were not correlated with levels of the various POPs, variation due to baselines would insert random noise that would increase variance without changing the direction of the relationship.

Statistical Analysis. We used Akaike Information Criterion (AIC) in statistical package SAS version 9.2 (Proc GLM) to examine models that included lipid content, isotopic (δN^{15}, δC^{13}) abundance, Henry's law constant and log K_{ow} (see next paragraph) and all geographic (watershed area, water body type and area, of glaciers within a watershed and elevation) as explanatory variables and DDE, PCB, HCB (hexachlorobenzene), chlordane, and toxaphene variables as response variables.[45] We completed separate analyses for eggs, nestling plasma and adult plasma. We log-transformed all contaminant values and all values below the detection limit were assumed to be equal to half the detection limit.

To examine whether variation in the chemical properties of the PCB and OC (organochlorine) congeners was reflected in the geographic distribution of the different congeners, we conducted a redundancy analysis (RDA) in SYNTAX 2000 (Scientia, Budapest, Hungary) to describe patterns in OCs and PCBs among eggs and chicks. RDA is a constrained form of multivariate multiple regression. It is positioned between principal components analysis (PCA) and individual multiple regressions of the dependent variables. RDA is a constrained version as the underlying dimensions in the dependent variables are forced to be multiple linear regressions of the independent variables.[46] Monte Carlo permutations are run in a stepwise procedure to select predictor variables which best explain variance in the response variables. An ordination diagram is produced where dependent variables are indicated by points, and independent variables as vectors, both of which represent different gradients in the data. The importance of variables in the data set is described by the vector's length or

Table 2. Results from General Linear Models Examining Variation in Concentrations of Five Contaminant Groups in Nestling Plasma of Ospreys from Western Canada[a]

contaminant	nestling plasma	nestling plasma	egg	egg
	model variables	ΔcAIC (null in brackets)	model variables	ΔAIC_c (null in brackets)
ΣDDT[b]	elevation + lipid + $\delta^{15}N$ + $\delta^{13}C$	0.00 (34.1)	glacial area + lake size + watershed size + $\delta^{13}C$	0.00 (15.3)
$\Sigma PCBs$[b]	lake size + $\delta^{15}N$ + $\delta^{13}C$	0.00 (15.8)	elevation + lake area + lipid + $\delta^{13}C$	0.00 (17.3)
HCB	lipid + watershed + glacial area + lake size + $\delta^{15}N$	0.00 (14.5)	watershed area + lipid + $\delta^{13}C$	0.00 (24.9)
Σchlordanes[b]	watershed size	0.00 (8.52)	watershed area + lipid + dN	0.00 (11.1)
toxaphene	glacial area × watershed size	0.00 (0.87)	elevation + lake area + lipid + $\delta^{13}C$	0.00 (18.2)

[a]ΔAIC_c values for the null and most parsimonious model are shown. Other models can be found in the SI.

distance from the origin for points. Variables are positively correlated if points and vectors are in the same direction. If at right angles, there is zero effective relationship. Pointing in opposite directions indicates negative correlations. To avoid variation below the detection level confounding our results, we included only those PCBs and OCs that had >70% of the data points greater than the detection level. We calculated RDA axes one to five by using $\delta^{15}N$, $\delta^{13}C$, percent lipids and the topographic features as the "environmental variables" to constrain the RDA and each PCB or OC as the dependent variables. We then correlated each of the axes with three measures of chemical properties: Henry's law constant (H), volatility (ν) and Log K_{ow}.[47,48]

Essential geographic variables, stable isotopes in plasma, and contaminant levels in eggs and plasma are summarized in Table 1.

Isotopic Composition. Trophic level, $\delta^{15}N$, and carbon source, $\delta^{13}C$, were factors in all of the best models ($\Delta AIC <$ 1.0, Table 2, Supporting Information (SI) Tables S1 and S2) for most contaminants in both plasma and egg samples, indicating the importance of variation in prey sources. Based on plasma samples, individual ospreys feeding at higher trophic levels accumulated greater concentrations of measured contaminants. ΣDDT, for example, correlated positively with $\delta^{15}N$, and adults had contaminant concentrations of about an order of magnitude higher at a given trophic level than their chicks (Figure 2). In eggs, only toxaphene was positively correlated with $\delta^{13}C$ (SI Figure S2)..

Geographic Variation. Broad geographic factors explained much of the variation in contaminant profiles. Samples collected in Alberta, southern BC and northern BC clustered together within the RDA. For the nestling data set, the first axis represented 55% of the variation and the second axis represented 26% of the variation, with all other axes representing <8% of the variation (Figure 3a). Thus, we considered only the first two axes. Within the egg data set, the first axis represented 78% of the variation and the second axis represented 11% of the variation, with all other axes representing <5% of the variation, so again we considered only the first two axes (Figure 3b).

Both log K_{ow} and the Henry's law coefficient correlated strongly with RDA axes 1 and 2 for nestlings (SI Figure S3). In contrast, there was no relationship for eggs (all r^2 values <0.05 and $P > 0.6$ for all combinations of H, log K_{ow} and RDA axes 1−3) .

Limnologic and Topographic Factors. For nestling plasma data, water body type was included in the best models ($\Delta AIC < 1.0$) for the five main POPs (Table 2). Contaminant
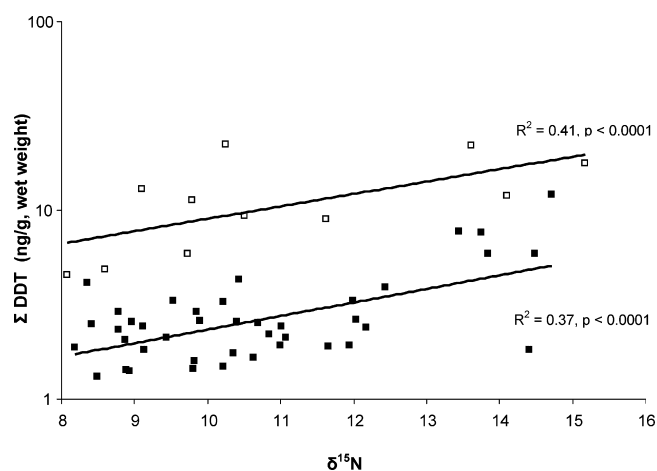

Figure 2. DDT plasma concentrations (ng/g, wet weight) increased with trophic level for both adult (open) and nestling (filled) osprey plasma from Western Canada ($p < 0.0001$ in both cases).

concentrations in plasma were lower in osprey samples from nests on rivers than lakes or reservoirs, and we removed river nests from analyses. For ΣDDT, the best single-factor model was trophic level, with elevation, carbon source, the proportion of glaciers within a watershed, percent lipids and the size of lakes relative to overall watershed size were all included in the most parsimonious models (SI Table S1; Figure S1a). The best model for PCBs included lake area, trophic level and aquatic input, while glacier and watershed area factored into the models with AIC < 1.0. Best models for other compounds are provided for nestling plasma in SI Table S1.

For nestlings, contaminant concentrations were positively related to elevation and glacial area; watershed area played a lesser role. Compounds with higher K_{ow}, such as PCB 187, tended to be negatively associated with lake area and positively associated with elevation. Compounds with lower K_{ow}, such as HCB and lower chlorinated PCBs tended to be more closely associated with large lakes, low elevation and high percent lipids. Notably, lower chlorinated PCBs such as CBs-28, -52, and -70, which have lower K_{ow}, also were negatively associated with elevation and glacial area.

Because the sample size ($n = 11$) was small for adults, we never considered models with more than two variables. Elevation and trophic level were the most parsimonious variables for ΣDDT ($r^2 = 0.48$). Percent lipids and aquatic input were the most parsimonious variables for PCBs ($r^2 = 0.87$). Percent lipids and elevation were the most parsimonious variables for toxaphene ($r^2 = 0.44$) and chlordane ($r^2 = 0.66$).
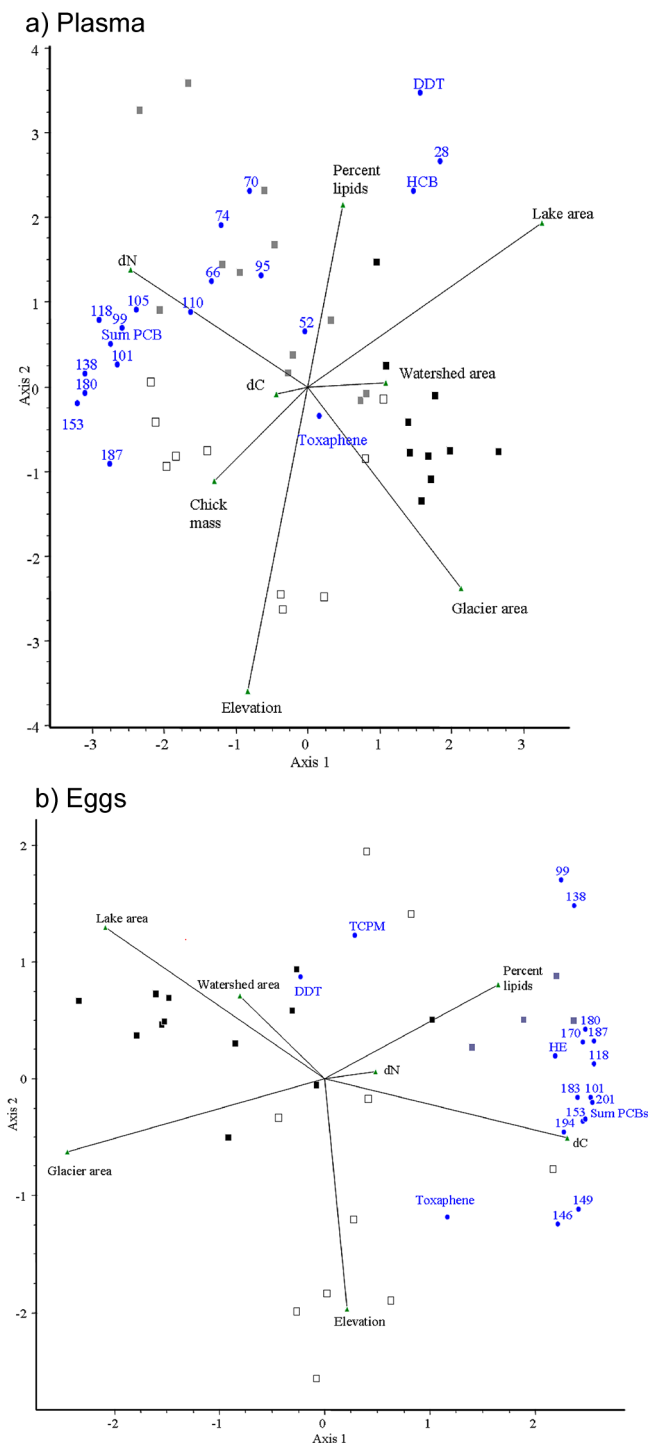
a) Plasma

b) Eggs

Figure 3. RDA (redundancy analysis) of POPs in (a) nestling plasma and (b) eggs relative to environmental variables. Open symbols are samples collected in Alberta, gray symbols are samples collected in southern BC and dark symbols are samples collected in northern BC.

and tended to decrease with glacial area and lake area (Table 2).

For egg samples, water body type also was included in the best models for all contaminants (SI Table S2). Lipid content of eggs was the best single-factor model for chlordane (r^2 = 0.17), toxaphene (r^2 = 0.33), and HCB (r^2 = 0.15), whereas the ratio of watershed size to lake size was the best single-factor model for r-DDT (r^2 = 0.04). Lake area was the best single

factor for PCB (r^2 = 0.13). The residuals of toxaphene on δ^{13}C decreased significantly with lake area (SI Figure S2).

Compounds with higher K_{ow}, such as PCB 146, PCB 149, and toxaphene, tended to be negatively associated with lake area and positively associated with elevation. Compounds with lower K_{ow}, including the less chlorinated PCBs, tended to be positively associated with larger lakes. In general, the hydrophobic and less volatile contaminants with lower K_{ow} were influenced by variation in lipid content, and were more common at large lakes at low elevations. All contaminants, with the exception of toxaphene, in eggs were negatively associated with glacial area.

◼ DISCUSSION

We began this investigation with the ambition to sample ospreys over a wide altitudinal gradient as had been done for abiotic variables and fish in both earlier[5,13,14,16,20,21] and more recent studies.[10−12,15] Ospreys and nests were reported for a number of higher altitude lakes across the region; subsequent surveys failed, however, to confirm active breeding at many sites. It was evident that at higher elevation lakes in western Canada, including some sampled for fish in previous studies,[13,14,49] the summer was too short to enable successful breeding by osprey or other avian top predators. Thus, we refocused efforts on lower altitude lakes and catchments with substantial portions of alpine and glaciated terrain.

Given the geographic and topographic expanse of this study, more than 1500 m in altitude, 2500 km in latitude, 1000 km of longitude and orders of magnitude variation in size of water bodies and drainage basins, we would expect ecologic and limnologic variability to be comparable. Anthropogenic factors such as impoundments and introduction of non-native game fishes[50] have further modified the food chains of these systems. Thus the prey available and taken by ospreys varied considerably. At a subset of six of the study sites, fish taken by osprey during the chick rearing period ranged from lower trophic level benthic feeding cyprinids to predatory pelagic feeding salmonids.[51] We know that osprey diet and foraging sites also may vary during the breeding season[24,25,28] and from our own detailed work on another alpine bird, the American dipper (*Cinclus mexicanus*),[48] which probably accounts for some of the variation in exposure between contaminants in eggs and nestling plasma. Nonetheless and despite those many and disparate sources of variability, measurement of δ^{15}N in particular and to a lesser extent δ^{13}C provided a quantitative integration of diet differentials and explained some of the patterns in contaminant exposure of osprey, as we had hypothesized previously.[24,25,28] We successfully applied this approach to a previous assessment of mercury in these same ospreys[27] and to studies of American dippers in alpine systems,[34,52] as have other researchers for studies of fish and invertebrates in some of our study sites.[15,49]

Accounting for dietary variation from isotopic composition, there were some general patterns in the data. HCB, chlordane, and ΣPCBs decreased with watershed size; toxaphene, ΣDDT and HCB decreased with watershed size divided by lake size. Thus, there were lower levels of contamination in relatively small lakes draining areas of large watersheds, contrary to our predictions that such lakes would be contaminant sinks for large watersheds. Perhaps water in lakes that are closer in size to their watersheds has longer residence time, and thus those lakes accumulate more contaminants than lakes that are smaller relative to their watershed, which may act as intermediates

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flowing into larger lakes. There are few similar data sets, certainly with avian species, with which to compare. Within a single watershed, concentrations of total OC pesticides and ΣPCBs increased significantly with drainage area in eggs of American dippers.[53] In contrast, previous examination of PCB loadings and bioaccumulation in predatory fish over a wide range of geographic and limnologic conditions found relationships to be complex and unpredictable. Paterson et al,[54] for example, found neither systematic associations between lake size and PCB concentrations or evidence of strong biomagnifications up the food chain in fish, nor among PCB concentrations in various matrices with other physical, chemical, or biotic conditions at the time of sampling. Similar complex patterns and few systemic relationships were reported in a survey of POPs in predatory fish from European alpine lakes.[55] Given that we are able to discern relations, even if correlations were not always that strong, perhaps attests to the value of using a terrestrial sentinel such as the osprey, where POPs exposure is determined almost totally by dietary intake, to examine trends in POPs loadings over broad spatial scales.

Our RDA analysis indicated a decrease in the proportion of lower chlorinated PCBs (CBs 28−99), HCB and DDT with elevation and glacial area, related to variation in K_{ow} and Henry's law constant, also evident from the RDA. Despite the potential for some confounding local inputs on hydro-electric reservoirs, that result was in reasonable accord with the prediction by Wania and Westgate.[2] Their determination was consistent with data for fish in some studies of European mountains of a relative increase in more chlorinated PCBs such as CBs-138 and 153 at higher elevations, the result of more efficient altitudinal cold trapping of those heavier compounds.[2,17,49]

ΣDDT decreased significantly in osprey tissues with elevation and with amount or proportion of glacial cover within the watershed, probably at least in part due to local contaminant inputs at lower elevations, an issue raised by Daly and Wania[56] for fish studies. Local contaminant sources, for example of DDT used in the fruit growing south Okanagan region, including exposure of osprey was discussed in more detail in previous papers.[24,25,28,42,51]

Toxaphene, which was never used as an insecticide in western Canada, was the one compound found at greater concentrations in osprey samples at higher elevation drainages with more coverage by permanent snow and ice. Toxaphene was used as a piscicide prior to stocking game fish at some lakes within the study areas. However, the distinctive 2-exo,3-endo,5-exo,6-endo,8,9,10-heptachlorobornane (B7−1001; Hp-Sed) congener pattern found in fish from treated lakes[57] was not evident in osprey samples which were dominated by congeners such as B8−1412 and Parlars 40−50, strongly indicative of atmospheric loadings. Elevated concentrations of toxaphene in osprey samples from higher elevation lakes from the Rocky Mountains were consistent with findings in fish.[57]

The potential for release of POPs stored in ice fields and glaciers to rivers and lakes has been examined by a number of researchers.[11−17] Glacial meltwater is routed rapidly to surface waters after being canalized on the glacial surface. Such runoff may be enriched with entrained POPs because the meltwater has minimal contact with catchment soils and sediments, creating little opportunity for POPs to dissipate through evaporation and binding to organic-poor glacial sediments.[11,13,14] For example, POPs increased with altitude in snow collected at high alpine lakes of the Canadian Rockies[5]

and POPs were about an order of magnitude higher in biota samples from glacially fed compared to nonglacially fed lakes in the Italian Alps.[11,12] Toxaphene, increased 1000-fold over a 1500 m change in altitude in the Canadian Rockies.[5,13,16,21]

However, our examination of spatial variability does not support a glacial input hypothesis for osprey, as we did not find greater contamination in lakes draining areas with larger proportions of glacial coverage and at higher elevations, as reported for abiotic components.[11,13,14] Data for fish and other biota are more complex than water or sediments with the influence of factors such as growth dilution[15] and food chain structure/resource partitioning,[49] although the studies of Italian lakes certainly support the role of glacial melting as an important source of POPs to biota.[11,12,58−61] We observed the reverse pattern; with the exception of toxaphene, we found generally lower POPs in higher elevation and more glaciated drainages.

Longer term temporal trends in glacial extent may also be a factor. Globally, following more than a century of retreat, during the 1950s to early 1970s coinciding with the 'organochlorine (OC) era', there was a period of glacial expansion when on balance POPs and other contaminants were presumably accumulating in glacial ice and snow (SI Figure S4). Donald et al.[16] sampled ice strata deposited over the period 1959 to 1995 from a glacial ice mass on Snow Dome Mountain at 3300 m elevation in the Canadian Cordillera. They reported a 10 year delay in maximum flux to this high elevation ice mass relative to depositional trends in eastern North America, probably influenced by trans-Pacific POPs transport,[31] and concluded that glacial meltwater would continue to contribute significant quantities of organochlorine pesticides into alpine ecosystems for at least decades and perhaps centuries. In SI Figure S4, we combined temporal trends in global glacial mass with POPs use and deposition to the Canadian Rockies. Therefore, the material melting out of a typical glacier over our study period (1999−2003) would date from at least a century previous, well prior to the OC era. The POPs era, however, may have been extended even into the early 1990s by ongoing usage in Asia and elsewhere.[31]

We recognize that accounting by glacial input by a simple calculation of area covered by year-round snow and ice is a simplification. Glaciers have both a horizontal and vertical component constituting the mass of the glacier and the dynamics of melting and runoff are complex and variable,[62] and are only part of the overall hydrological mass balance of the watershed. Other factors, particularly deposition of black carbon, may also be accelerating glacial melt by reducing snow albedo,[63] and influencing POPs deposition, accumulation and availability.[64]

In contrast to our simple reconstruction of glacial melt, Bogdal et al.[10] modeled the dynamics of POPs release from a Swiss glacier. Their model predicted significant POPs increases during the early 1990s, and lower inputs later in that decade. Those predictions are coincident with the apparent temporal trends we see in ospreys, indicating that previous glacial melting may have been a factor influencing contaminant trends in western Canada. During the early 1990s, concentrations of DDE and chlordane were elevated in osprey eggs across British Columbia, including several of the present sites.[65] More than 25% of sampled eggs exceeded the toxicity threshold of 4.2 μg/g, and the spatial pattern was not explained by known local sources and partially prompted use of satellite telemetry to examine wintering sources.[24] The rapid melting of glacial ice

during the 1980s and 1990s combined with the decadal delay in POPs flux reported by Donald et al.[16] may have released substantial DDE and other POPs to osprey food chains. In the present data from 1999 to 2003, only one of 88 eggs exceeded 4.2 μg/g.

The decline in concentrations of ΣDDT and ΣPCBs in osprey eggs over the period 1991 to 2003 at one of our monitoring sites is shown in SI Figure S4. Kamloops is a river location which does integrate runoff from the surrounding alpine drainage basin. Henny et al.[66] also reported significant declines in DDE, other OC pesticides and PCBs, 1997−2004, in osprey eggs from the lower Columbia River. Such decreasing concentrations of DDTs, PCBs, and other chlorinated hydrocarbons in British Columbia ospreys would have been principally due to the regulatory restrictions on usage imposed during the 1970s and early 1980s in North America (ref 65, SI Figure S4). Previously, we documented significant decreases in egg burdens of chlorinated dioxin and furan compounds in osprey eggs downstream of pulp and paper mills, subsequent to voluntary and regulatory changes in pulp bleaching processes.[24] However, given the substantial area covered in permanent snow and ice in many of the drainages studied here, and the timing of documented recession of glacial area (refs 6,7,62, SI Figure S4), the possibility of further dilution of contaminants by input of large volumes of relatively clean meltwater during the 1980s to 1990s should not be discounted.

Bogdal et al.[10] predicted a further influx during the current decade of glacial bound contaminants to receiving waters, but we do not have samples to test that prediction for western Canada. Overall, the coincidence with the osprey data is interesting and would merit further sampling particularly at a site where features were similar to the Oberaar glacier. The influence of glacial meltwater on POPs contamination of alpine lakes also is likely more apparent at lower trophic levels and over smaller spatial scales, and could vary substantially among and within alpine regions, depending on variability in factors such as finer scale POPs deposition patterns and glacial melting trends. We plan to examine data on POPs in fish selected by osprey as prey and collected from a subset of the lakes in the present study.

Further regarding the toxicological implications of the exposure levels of the compounds measured in this study, not only have the DDE levels decreased over the decade of the previous study, but other chemicals also were below effect levels. Variation in reproductive success at six of the sites were examined in more detail and related to energetics as measured by rates of prey delivery to nests.[51]

In summary, relatively simple models involving watershed and lake size, elevation, and the percent of year-round snow and ice explained much of the variation in contaminant levels in ospreys. The effect of geography was most evident in the finding of lower contaminant levels in ospreys breeding along rivers, as contaminants do not accumulate readily in active fluvial systems. We suggest that similar GIS and environmental chemistry models could be used to predict contamination levels at continental or even global scales, provided they also factor in ecology and physiology of organisms.

ASSOCIATED CONTENT

Ⓢ Supporting Information

More details about the chemical analytical methods, water body and osprey summary data, and results of data analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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