Environ. Sci. Technol. **2005**, *39,* 8090−8098

Identifying Sources and Biomagnification of Persistent Organic Contaminants in Biota from Mountain Streams of Southwestern British Columbia, Canada

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We assessed whether biota occupying mountain streams accumulate and biomagnify remotely derived organic pollutants originating from atmospheric inputs to snowpack and glacial runoff and from marine sources introduced by migrating anadromous salmon. Several persistent organic pollutants including polychlorinated biphenyls (PCBs), *p,p*′-dichloro-diphenyl-dichloroethylene, hexachlorobenzene, and *trans*-nonachlor were commonly detected in benthic invertebrates, salmon fry (*Oncorhynchus* spp.), and eggs of an aquatic passerine, the American dipper (*Cinclus mexicanus*) from the Chilliwack River watershed, British Columbia, Canada. Total PCBs and several organochlorines (OCs) biomagnified from benthic invertebrate composites to salmon fry to dipper eggs. Invertebrate samples generally did not differ significantly in contaminant burdens between the river main stem where salmon are more abundant and higher-elevation tributaries where the salmon density is lower. Concentrations of total OCs and total PCBs in dipper eggs were positively related to drainage basin area and collection year but not to elevation. No differences in PCB congener patterns existed between dipper egg samples from the Chilliwack watershed and other watersheds in southwestern British Columbia. However, principal component analysis revealed significant spatial differences in egg PCB congener patterns between the main Chilliwack River and the higher-elevation tributaries. This difference was primarily due to a greater occurrence of lower chlorinated PCB congeners (66 and 105) in dipper eggs collected from the tributaries and higher loadings of the more stable and persistent congeners (153, 138, 130, and 128) in eggs from the river main stem. The results suggest that atmospheric sources are the main contributor of contaminants detected in biota from the region and that biomagnification is a common pathway for accumulation in lotic predators such as the American dipper.

Introduction

Persistent and toxic substances produced from agricultural, urban, and industrial processes are major sources of pollutants to remote regions worldwide. Many persistent semivolatile compounds, such as organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs), have frequently been detected in remote northern latitudes, often exceeding levels found in more industrialized regions (*1*). Deposition of pollutants to distant regions is largely a result of atmospheric transport, precipitation, and cold condensation—a process of volatilization in warmer low latitude regions and subsequent condensation in colder high latitudes (*2*). High elevation mountain ranges are similar to northern arctic environments in their low average temperatures and precipitation in the form of snow, thus promoting atmospheric deposition from cold condensation (*3*). Davidson et al. (*4*) reported terrestrial vegetation in alpine ecosystems accumulating OCs and PCBs to the same degree as that observed in polar regions.

Atmospherically deposited organic pollutants have contaminated freshwater ecosystems across North America (*5*−*8*). High rates of snow deposition in mountains can lead to a large release of contaminants to watersheds especially during peak snowmelt (*9*). In western Canada, rivers and lakes receiving annual snowmelt and glacial melt from surrounding mountains have been found to contain elevated levels of persistent organic pollutants originating from local and long-range sources (*7*, *10*). As a result of their persistence and bioaccumulation potential, many chlorinated hydrocarbon compounds are rapidly assimilated in biological tissues and biomagnified in food chains to levels sometimes approaching or in excess of human consumption guidelines (*11*). In Canada and Europe, OC concentrations in fish were reported to increase with lake elevation, leading researchers to propose that sources were primarily atmospheric in origin (*12*, *13*). Although many previous studies have identified atmospheric deposition as a major contributor to food chain contamination in arctic environments (*14*−*16*) and remote lake ecosystems (*5*, *6*, *17*), the phenomenon has rarely been studied in lotic mountain systems where deposition would similarly be expected (*9*, *18*, *19*).

Biological transport represents another potential source of contaminants to watersheds. In the Pacific Northwest, spawning salmon were identified as potentially important sources of persistent chlorinated hydrocarbons to rivers and lakes (*20*−*22*). The migrating salmon, which acquire marine-derived nutrients in addition to organic contaminants during their time at sea, have the potential to elevate loads of chlorinated hydrocarbons to streams and lakes directly through deposition of salmon roe and decaying carcasses (*22*). Since a considerable proportion of the mass of salmon in streams enters the aquatic and terrestrial food chains through direct consumption of flesh and eggs, transfer of contaminants by this pathway is likely more efficient than through processes of atmospheric deposition (*23*).

In southwestern British Columbia, Canada, prevailing oceanic westerly winds move a combination of urban, suburban, marine, and agricultural emissions of pollutants originating from the city of Vancouver up the Fraser River Valley (Figure 1). The Chilliwack River watershed, located in the central Fraser Valley, was hypothesized to receive inputs of persistent organic pollutants through wet and dry deposition processes. Additional inputs of marine-derived nutrients and organic contaminants are also likely introduced through the large natural and hatchery-enhanced salmon runs that occur in this watershed. Our main objective in this study was to characterize the degree of contaminant contributions to a lotic food chain from atmospheric deposition and biological transport. Given the lack of knowledge about the significance

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10.1021/es050431n CCC: $30.25

Published on Web 09/21/2005

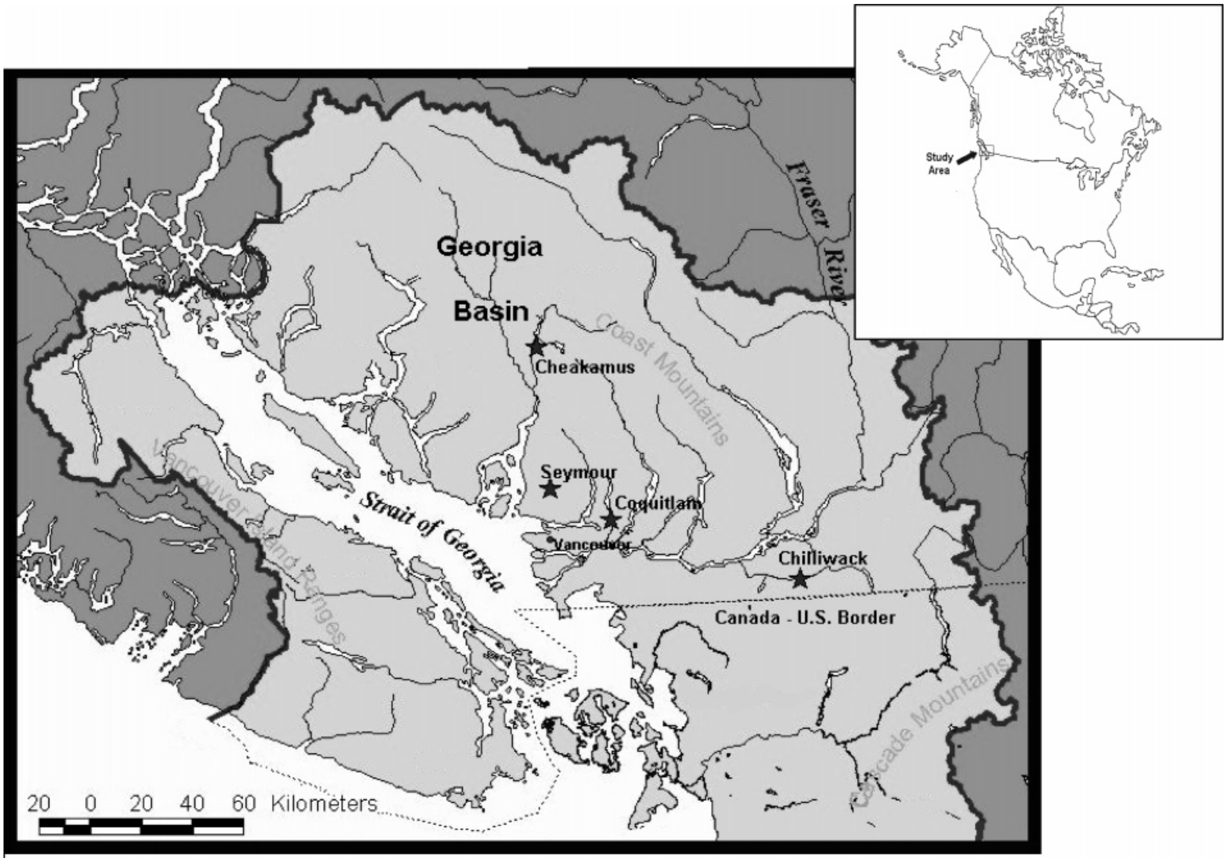

FIGURE 1. Map of the Georgia Basin region of southwestern British Columbia, Canada. The Chilliwack River is shown relative to the city of Vancouver in addition to other American dipper egg collection sites: the Cheakamus, Seymour, and Coquitlam Rivers.

of remotely derived sources of organic contaminants bioaccumulating in aquatic food chains, we also attempted to estimate the degree to which they were able to biomagnify using three distinct trophic levels including larval freshwater invertebrates, juvenile salmon, and aquatic passerines (American dippers, *Cinclus mexicanus*). To our knowledge, this study is the first in North America to identify the patterns of OC and PCB deposition and biomagnification in mountain streams using the eggs and prey of an aquatic passerine, the American dipper.

Experimental Section

Study Area. The Chilliwack River watershed (49°10′ N, 121°04′ W) is located within the Georgia Basin, British Columbia, Canada (Figure 1). The watershed drains an area of 1274 km^2 with elevation ranges from near sea level to over 2000 m at several mountain peaks. Tributaries are typically first- through third-order streams, and the river is dominantly a fourth- or fifth-order stream, partially sourced by a glacial-fed lake at its upper end. Annual precipitation to the Chilliwack area averages 1850.5 mm with mean daily temperatures of 10.4 °C (data from 1879 to 1990).

The Chilliwack River supports substantial breeding populations of Pacific chum, coho, pink, and chinook salmon (*Oncorhynchus keta*, *O. kisutch*, *O. gorbuscha*, *O. tshawytscha*) as well as cutthroat trout (*O. clarki*), steelhead trout (*O. mykiss*), and Dolly Varden (*Salvelinus malma*) (BC Fisheries data, http://www.fishwizard.com). Annual breeding runs of anadromous salmon and steelhead spawn from late summer through winter within the watershed, but peak runs occur along the main stem of the river and at the hatchery in autumn. Juvenile salmonids are most abundant in spring and summer, feeding on a variety of benthic aquatic invertebrate larvae present throughout the watershed.

Study Species. The effectiveness of birds as pollution monitors in a variety of ecosystems is widely established (*24*). However, few avian species occupy mountain streams year-round or feed exclusively in lotic environments, thus reducing their value in identifying the specific sources of contaminants to watersheds. The American dipper is a year-round resident in mountain streams and has an exclusively aquatic diet of benthic invertebrates and small fish. Dippers are also territorial and typically make only short distance altitudinal movements within a watershed (*25*). Although the European dipper (*Cinclus cinclus*) has been extensively used as a monitor of organochlorines, PCBs, and mercury pollution in watersheds (*26*–*28*), the North American species has not been studied for this purpose until recently (*29*).

Collection of Aquatic Invertebrates and Fish. In April 2002, prior to the spring freshet, composite samples of benthic invertebrates were collected at eight different sites along the main stem of the Chilliwack River and from seven different tributaries in the watershed. Aquatic larval invertebrates (~4 g wet weight) were collected either by "kick-sampling" in the stream (disturbing the rocks directly upstream of a Surber sampler) or by turning over rocks by hand. The sample represented a mixture of insect taxa that dippers would naturally prey upon, including approximately equal proportions of Ephemeropteran, Plecopteran, and Tricopteran larvae in addition to a much smaller fraction by mass of Coleopteran and Dipteran larvae. During invertebrate collections, eight additional composite samples consisting of 10 individual wild salmon fry (*Oncorhynchus* spp.) (age-0) that each weighed 100–200 mg fresh weight were captured live from the same eight sites along the main river using a dip net. Each collection represented a pooled sample of predominantly coho and chum salmon fry (~80%), but pink and chinook salmon (~20%) were also included at some sites.

All samples were subsequently washed three times with distilled deionized water to remove any surface contamination or streamwater and stored frozen in acetone/hexane-washed glass vials until preparation for contaminant residue analysis.

Egg Collection and Contaminant Residue Analysis. We collected a single egg from a clutch of four or five eggs at 32 American dipper nests throughout the Chilliwack watershed during spring 1999, 2000, and 2001. In addition, a single dipper egg was collected at random from nests in three other reference watersheds in the Georgia Basin of British Columbia in 2000: the Coquitlam River, Seymour River, and Cheakamus River (Figure 1). Both fresh and failed eggs were used for the contaminant analysis. There were no differences in contaminant burdens between fresh (viable) and failed eggs (total PCBs, $t_{30} = -0.13$, $p = 0.9$; total OCs, $t_{30} = -1.6$, $p = 0.1$), permitting the sample to be pooled for statistical analyses. Similarly, no differences in moisture or lipid content existed between fresh and failed eggs ($p > 0.05$); however, arithmetic corrections (reported contaminant residues multiplied by a correction factor) were applied to wet weight residues of any desiccated samples that deviated by more than 5% from the mean moisture content (79%) of freshly collected, undeveloped eggs. Whole eggs were stored refrigerated for up to 4 weeks. Egg contents were then transferred into an acetone/hexane-rinsed glass jar to be frozen at −25 °C until analysis.

Chemical analyses included determination of chlorobenzenes (tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzes), hexachlorocyclohexanes (α-, β-, and γ-HCH), chlordane-related compounds (oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, and heptachlor epoxide), *p,p′*-dichloro-diphenyl-trichloroethane (DDT) and metabolites (*p,p′*-dichloro-diphenyl-dichloroethylene (DDE) and *p,p′*-dichloro-diphenyl-dichloroethane (DDD), mirex and photomirex, dieldrin, and PCBs (National Wildlife Research Centre, Hull, Quebec). Total PCBs were calculated by summing the peaks of 59 individual congeners identified as CB 16/32, 17, 18, 22, 28, 31, 33/20, 49, 47/48, 44, 42, 52, 56/60, 64, 66, 70/76, 74, 85, 87, 92, 95, 97, 99, 101/90, 105, 110, 118, 128, 130, 137, 138, 141, 146, 149, 151, 153, 156, 157, 158, 170/190, 171, 172, 174, 176, 177, 178, 179, 180, 183, 187, 194, 195, 196/203, 200, 201, 202, 208, 206, and 207. Samples were quantitatively analyzed by capillary gas chromatography coupled with a mass-selective detector operated in selected ion monitoring mode according to CWS Method No. MET-CHEM-OC-04B (*30*). As part of the quality control, blanks and CWS reference material (1989 Lake Ontario Herring Gull QA) were run concurrently with the samples. The method detection limit for all compounds was 0.1 ng/g wet weight. Residues were not corrected for internal standard recoveries, which were typically between 80% and 110%. All egg values are reported on a wet weight basis (*31*) and converted to lipid basis for comparison with prey samples.

Data Analysis. Direct measurements of elevation (±1 m) for each egg collection site were taken using a calibrated digital altimeter (Suunto Escape 203, Finland). Environment Canada and U. S. Geological Survey hydrological databases provided digital watershed maps to calculate the drainage area for each breeding territory where eggs were collected. Raw chemical residue data (Supporting Information, Table 1S) were nonnormally distributed (KSL test) and subsequently log-transformed prior to statistical analyses. We report geometric mean values and data ranges. Where levels were below the detection limit for organochlorine compounds, a value equal to the minimum detection limit (0.1 ng/g wet weight) was applied. For PCBs, if no congeners were detectable, then the individual samples were also assigned a value equal to the minimum detection limit to permit data analysis, but if all of the samples were below detection (as in the case for benthic invertebrates), then the means were reported as nondetectable. The proportion (%) of each congener contribution to the total PCBs was calculated for each sample, and we report only those congeners that contributed an average of >0.5% to the total PCB burden in dipper eggs ($n = 28/59$ congeners and included >96% of total PCBs). The individual values were arcsine-transformed prior to statistical analysis testing for differences in PCB congener contribution (%) among the Chilliwack fish composites, Chilliwack dipper eggs, and other Georgia Basin dipper eggs.

Biomagnification factors (BMFs) were calculated on a lipid basis for only the most commonly detected compounds (DDE, hexachlorobenzene (HCB), *trans*-nonachlor, and total PCBs) by dividing the lipid-normalized geometric mean concentration in dipper eggs by the geometric mean concentration in the diet. This calculation assumed that the average dipper diet was comprised of 67% invertebrates and 33% fish as measured using stable isotope ratios of dipper blood collected from the Chilliwack River watershed (*29*). We tested whether the process of atmospheric deposition affected contaminant burdens among prey types (river invertebrates, tributary invertebrates, and salmon fry) from the main river and those from tributaries using a one-way analysis of variation (ANOVA). Similarly, a one-way ANOVA was used to test for differences in contaminant burdens among trophic levels (invertebrates, salmon fry, and dipper eggs). A two-sample *t*-test compared mean egg concentrations between the Chilliwack watershed and other Georgia Basin watersheds. Multiple regression models for predicting egg concentrations of total OCs and total PCBs included elevation, basin area, year of collection, lipid content, and significant interaction terms (elevation × basin area). PCB congener patterns in dipper eggs were identified by principal component analysis (PCA) using only selected congeners that contributed at least 0.5% to the total PCBs (Supporting Information, Figure 1S and Table 2S). Eggs were further grouped by breeding location (Georgia Basin, Chilliwack River, and Chilliwack tributaries) to determine if any differences in congener contributions were occurring. All statistical analyses were performed using JMP IN, version 4.0 (SAS Institute).

Results and Discussion

Identifying Sources of Contaminants to Watershed Biota. Eggs from American dippers in the Chilliwack watershed showed very similar contaminant patterns to their prey with respect to detection of common OCs (Table 1). DDE, PCBs, and HCB were detected in 100% of the egg samples and at the highest concentrations, while *trans*-nonachlor was detected in 75% of the samples and also represented a significant proportion of total OCs. Those compounds were also the only OCs routinely detected in benthic invertebrates and salmon fry collected from the watershed (Table 1). Dipper eggs from other watersheds in the Georgia Basin region also showed a similar composition of OC compounds as the Chilliwack samples (Table 2). Only HCB was significantly lower at other Georgia Basin sites relative to Chilliwack ($t_{33} = 2.6$, $p = 0.01$). The consistent presence and uniformity of three major OCs (DDE, HCB, and *trans*-nonachlor) and common PCB congeners in prey samples and dipper eggs collected from the Chilliwack River in addition to other watersheds suggest that sources of OCs and PCBs to the Georgia Basin region may have a common atmospheric origin. This is consistent with the study by Elliott et al. (*32*) who suggested that a similar composition of OC contaminants in seabird eggs were primarily from atmospheric sources that dominated a wide area of the British Columbia coast. Elliott et al. (*33*) also detected comparable OC and PCB profiles in bald eagle (*Haliaeetus leucocephalus*) eggs from the Georgia Basin region, with the dominant compounds

TABLE 1. Summary of Lipid-Normalized Geometric Mean Values (Range in ng/g) Lipid Weight for Commonly Detected Organic Contaminants in the Chilliwack Watershed Food Chain: Benthic Invertebrates (Tributary and River Locations), Salmon Fry, and American Dipper Eggs[a]

sample type	*N*	% moisture (± SE)	% lipid (± SE)	total PCBs	*p,p′* DDE	HCB	*trans*-nonachlor
tributary invertebrates	7	80.9 ± 1.0	2.6 ± 0.3	**ND**[b]	**40.5** (30.1−49.7)	**10.6** (3.6−19.2)	**3.9** (2.7−6.2)
river invertebrates	8	79.2 ± 0.5	3.6 ± 0.3	**ND**	**40.6** (28.4−58.3)	**7.1** (4.4−12.9)	**5.4** (2.4−24.1)
salmon fry	8	82.7 ± 0.5	2.4 ± 0.3	**27.8** (ND−1450)	**144** (36.0−933)	**15.6** (12.0−20.8)	**11.9** (6.0−41.7)
American dipper eggs	32	76.2 ± 1.2	6.4 ± 0.3	**842** (48.4−12000)	**935** (104−4810)	**50.8** (15.8−180)	**12.9** (1.2−123)
dipper diet (67% I/33% F)				**11.4**	**74.7**	**10.9**	**7.0**
BMF				**73.9 (30.3)**[c]	**12.5**	**4.7**	**1.8**

[a] Biomagnification factors (BMF) are calculated from dipper diet comprised of 67% invertebrates (I) and 33% salmon fry (F) to dipper eggs. [b] ND = not detected; sample detection limit for all compounds is 0.1 ng/g wet weight or approximately 3 ng/g lipid weight (invertebrates and salmon fry). [c] BMF value calculated from salmon fry only to dipper eggs.

TABLE 2. Concentrations of Organic Contaminants (ng/g wet weight) Detected in American Dipper Egg Samples from the Chilliwack River Watershed and from Three Other Reference Watersheds (Geometric Means) in the Georgia Basin, British Columbia

	Chilliwack River (*n* = 32)	Georgia Basin (*n* = 3)
% moisture (± SD)	76.2 ± 6.9	83.3 ± 4.1
% lipid (± SD)	6.4 ± 1.4	6.5 ± 2.1
total PCBs	52.4	71.5
p,p′ DDE	58.5	28.7
p,p′ DDT	0.2	0.2
p,p′ DDD	0.2	0.1
hexachlorobenzene	3.1	1.0
α-HCH	0.4	ND[a]
β-HCH	0.1	ND
heptachlor epoxide	0.1	0.1
oxychlordane	0.1	0.7
trans-nonachlor	0.9	1.8
cis-nonachlor	0.2	0.1

[a] ND = not detected in any samples; sample detection limit for all compounds is 0.1 ng/g wet weight.

PCBs, DDE, and *trans*-nonachlor present in the highest concentrations. Furthermore, OC pesticides including DDT were widely applied to crops in the Fraser Valley of the Georgia Basin, an intensively farmed region of British Columbia, prior to the mid 1970s. Volatilization of these persistent residues from Fraser Valley soils remains an important contributor of OC pesticides to the atmosphere decades after their ban (*34*, *35*).

We hypothesized that if atmospheric deposition were occurring, then concentrations of persistent organic pollutants would be related to elevation and drainage area. Snowpack samples and fish collected from alpine lakes have shown that higher-elevation samples have greater concentrations of OCs and PCBs, particularly the more volatile compounds (*3*, *7*, *13*). Larger drainage areas are thought to have greater retention of contaminants downstream because of increased nutrient loads (i.e., phosphorus) and changes in land use from agriculture and deforestation, resulting in higher contaminant concentrations in brown trout (*Salmo trutta*) (*18*). We compared the concentrations of contaminants in benthic invertebrates collected from the low-elevation, larger-drainage-area river sites to the higher-elevation, smaller-drainage-area tributaries (Table 1). Only *trans*-nonachlor was significantly elevated in river invertebrates compared to tributary sites ($F_{2,20} = 7.88$, $p = 0.003$). However, concentrations of total OCs ($\log_{10}$) found in American dipper eggs were significantly related to the size of the drainage area where the egg was collected ($p = 0.002$) and the year of collection ($p = 0.002$) (whole model, $F_{6,25} = 7.07$, $p = 0.0002$). Total PCBs ($\log_{10}$) in dipper eggs were significantly related to the size of the drainage area ($p = 0.007$), year of collection ($p = 0.001$), and lipid content ($p = 0.03$) (whole model, $F_{6,25} = 6.20$, $p = 0.0004$). A positive trend toward increasing contaminant concentrations with increasing drainage area was stronger for total OCs than total PCBs (Figures 2a and 2b). Although elevation and drainage area were negatively correlated ($r = -0.59$, $p = 0.0003$), increasing elevation did not have an additional influence on contaminant burdens in dipper eggs after correcting for drainage area effects. It is possible that our range of elevations where eggs were collected was not great enough to detect a difference (32−600 m). Alternatively, for lotic environments, elevation may not be a significant factor because volatilization, sorption, sedimentation, and dilution from other inputs are possibly important routes of loss to downstream sites in watersheds. Blais et al. (*10*) found that OC concentrations were 2−50 times higher in glacial outflows compared to alpine and valley streams because many compounds can be retained by the alpine and valley soils or volatilized in runoff. Although Berglund et al. (*18*) did not find a significant relationship between levels of contaminants in trout and watershed area, they did find a positive correlation of contaminants with total phosphorus. Increased nutrients (i.e., phosphorus) are thought to cause higher biomass and productivity of periphyton and benthic communities, ultimately increasing the contaminant uptake by stream biota (*18*, *19*). Greater retention and accumulation of more hydrophobic contaminants along with greater nutrient loads in larger drainage systems likely explain the observed relationship between egg residues and drainage area.

Year of collection was also an important factor in explaining variation in contaminant burdens to eggs. For both the total OC and the total PCB regression models, contaminant concentrations were significantly higher in 1999 than in the two subsequent collection years, 2000 and 2001 (total OCs, $p = 0.002$; total PCB, $p = 0.001$) (Figures 2a and 2b). Interannual variation in deposition patterns are expected to occur, especially if contaminants are originating from long-distance sources. Also, large increases in snowpack loadings of less volatile compounds have been found in mountainous areas with higher precipitation and snow depth (*3*). The winter of 1998−1999 had the highest snowpack recorded in 25 years throughout the southern region of the province (http://wlapwww.gov.bc.ca/rfc), which we speculate may have contributed to increased concentrations of contaminants in runoff for that year.

Congeners 153, 138, and 180 dominated the PCB signature in Chilliwack dipper eggs, which together contributed 53%

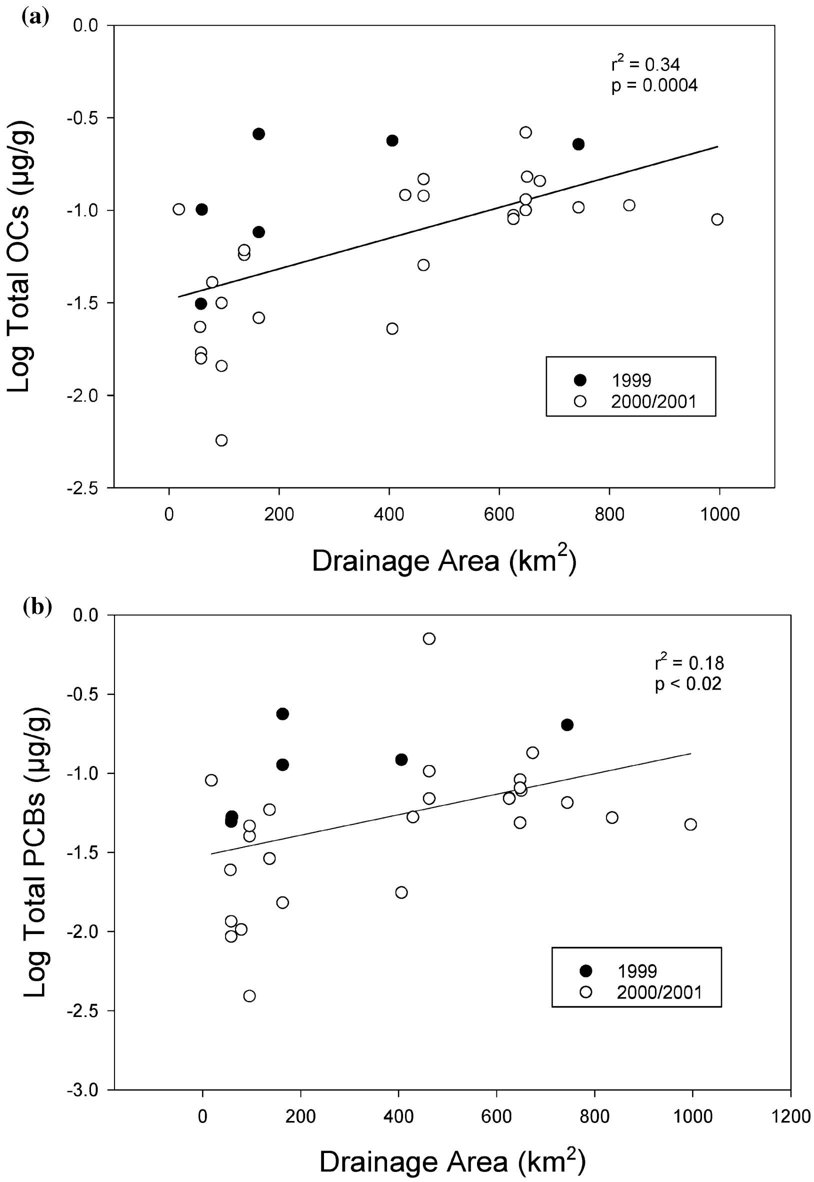

FIGURE 2. Relationship between the size of the drainage area and (a) total organochlorine or (b) total PCB concentrations in American dipper eggs collected from sites within the Chilliwack River watershed, British Columbia, for 1999 and 2000/2001. Linear regression lines represent the best fit for all years combined.

to the total PCBs measured (Figure 3). Congener patterns were very similar to other Georgia Basin dipper eggs with no significant differences between the sites in the proportion of major congeners isolated (PCB 153, 138, 180, 99, and 170/190) ($p > 0.05$). PCB congeners detected in juvenile salmon from the Chilliwack watershed also appeared similar to those in the eggs of its dipper predator with major PCB congeners 153, 138, and 180 making up 61% of the total PCBs and congener 149 also contributing a further 12%. However, PCB 149 ($p < 0.0001$) and 138 ($p = 0.03$) made up a significantly larger proportion of the total PCBs in Chilliwack salmon fry compared to dipper eggs. In addition, PCB 99 ($p = 0.002$) comprised a significantly lower proportion of the total PCB burden in salmon fry than in dipper eggs. Elevated levels of PCBs 153, 138, and 180 have been associated with the presence of Aroclor 1260, a common constituent in transformer and capacitor oils, because of their high proportions in this mixture (*36*). Other avian species occupying different ecosystems throughout this region have been reported as having those congeners in higher concentrations within their eggs (*33*, *37*), indicating a widespread use of the mixture or persistence of those specific congeners surviving atmospheric transport processes. Alternatively, birds and salmon can likely efficiently metabolize many PCB congeners and bioaccumulate only the most recalcitrant congeners that are also commonly detected in Aroclor 1260 (e.g., PCB 153, 138, and 180) (*38*). PCB congeners with higher octanol−water partition coefficients (K_{ow}), as predominantly found in the Chilliwack River biota, have similarly been associated with greater trophic transfer and bioaccumulation in several other freshwater and marine food webs (*39*−*41*).

In the process of investigating the origin of organic contaminants, particularly PCBs, to watershed biota, we conducted a PCA analysis on the 28 PCB congeners that each contributed >0.5% to total PCBs (Supporting Information, Figure 1S and Table 2S). Two significant principal components explained 74% of the variation in Chilliwack dipper eggs. The first component (PC1) explained ∼64% of the variation, while the second component (PC2) explained ∼10%. Congener patterns were not significantly different between Chilliwack eggs and other Georgia Basin sites, likely indicating common atmospheric sources and pathways.

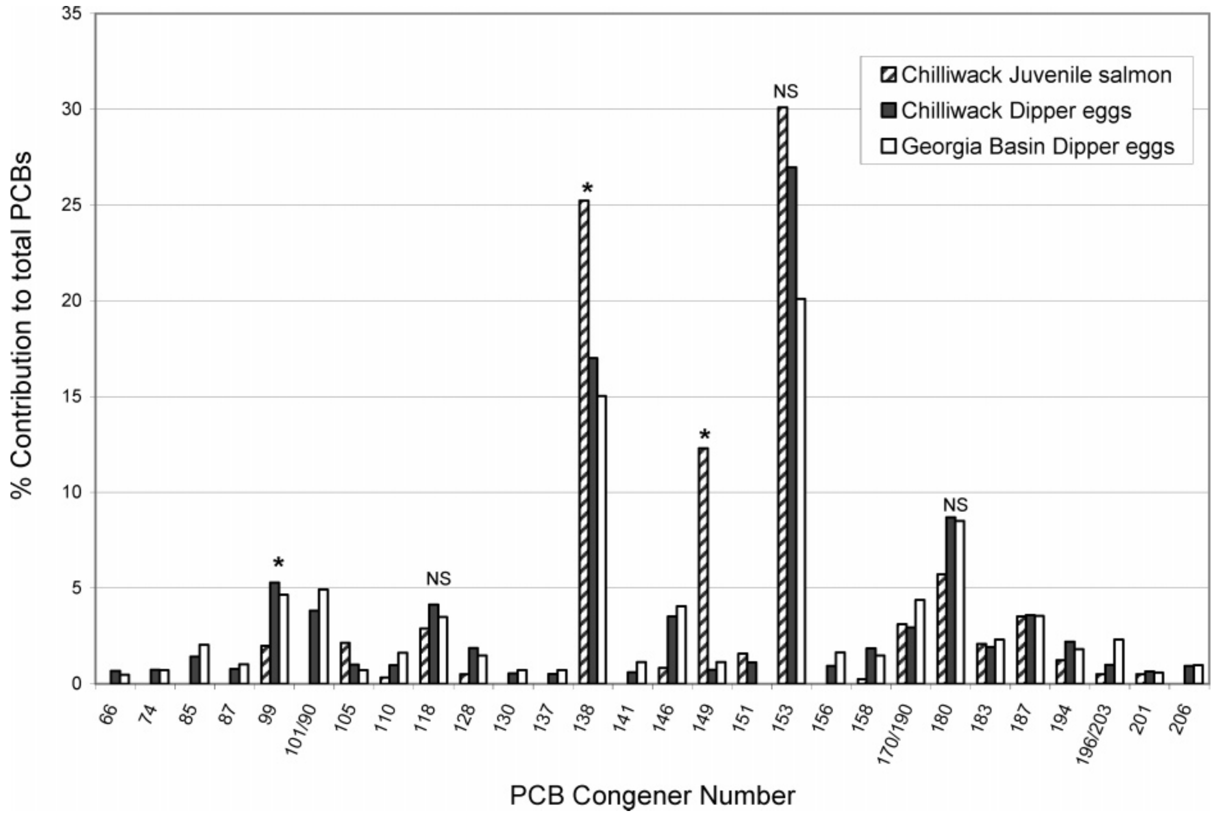

FIGURE 3. Proportion of PCB congener contributions to the total PCB burden of American dipper eggs ($n = 32$) and juvenile salmon prey ($n = 8$) from the Chilliwack River watershed, British Columbia, and from three other rivers in the Georgia Basin region of southwestern British Columbia, 1999–2002. Only the congeners (28/59) that contributed greater than 0.5% to the total PCB burden for dipper eggs are shown. Asterisks indicate significant differences ($p < 0.05$) between juvenile salmon and Chilliwack dipper eggs for the major PCB congeners detected.

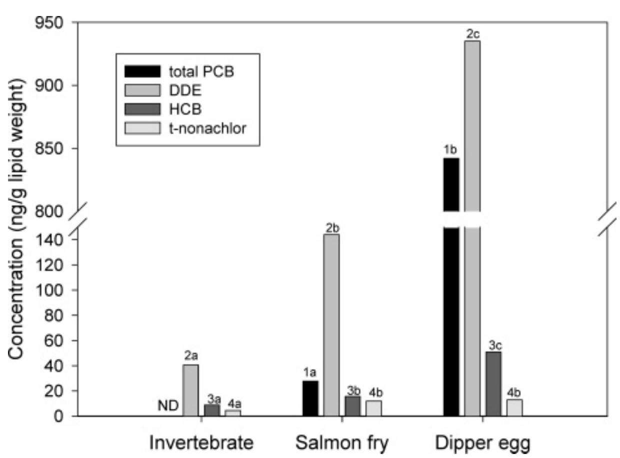

FIGURE 4. Relative concentrations (geometric means in ng/g lipid weight) showing biomagnification of commonly detected organic contaminants in benthic invertebrates, juvenile salmon, and American dipper eggs from the Chilliwack River watershed, British Columbia. Numbers/letters above bars represent groups of means that are significantly different.

However, dippers occupying the main stem of the Chilliwack River had a different congener pattern than dippers breeding on tributaries. Grouping of tributary dippers separate from river birds was primarily attributed to variability in factor loadings on PC2. Dipper eggs collected from tributary nests had significantly higher scores on PC2 ($t_{27} = 3.3$, $p = 0.003$), containing more of the less chlorinated and more volatile congeners (PCB 66, 105, and 110), whereas river eggs produced higher scores on the PC1 component ($t_{27} = -2.3$, $p = 0.03$) and contained the more highly chlorinated and stable PCB congeners (PCB 153, 130, and 138). Blais et al. (*3*) found that the more volatile, less chlorinated PCBs were prevalent in higher-elevation snowpack. Tributary eggs were collected from territories at higher average elevations (tributary, 328 ± 43 m vs river, 208 ± 25 m) with smaller drainage areas (tributary, 96 ± 12 km^2 vs river, 615 ± 40 km^2), possibly explaining the greater presence of less chlorinated congeners. Longitudinal patterns have been shown to exist in watersheds with respect to changes that occur in streamflow, water chemistry, nutrient levels, and contaminant loads from headwaters to downstream river sites (*42*). Therefore, PCB congener patterns provide further evidence that patterns of contaminant uptake and retention in lotic systems are not uniform and that biota occupying low-elevation larger drainage areas are exposed to higher levels of the more persistent stable compounds.

Atmospheric deposition appeared to be a major source of chlorinated hydrocarbons to the Chilliwack watershed; however, we explored whether other marine-derived sources may be amplifying the residue levels found in lotic biota. Large annual salmon and steelhead runs on the Chilliwack River contribute substantial organic matter to the lotic food chain via salmon roe and decaying carcasses (*43*). Decaying salmon could increase the organic contaminant loads in peak spawning areas, particularly along the main river channel (*22*). Contributions from salmon appear minor because we found few differences in contaminant concentrations in benthic invertebrates collected from the main river where salmon densities are high and the tributaries where salmon densities are lower (Table 1). This is despite the fact that stable nitrogen isotope signatures of invertebrates from the river main stem are known to be significantly higher ($\delta^{15}N = 5.4 \pm 0.3‰$) than those of invertebrates from the tributaries

($\delta^{15}N = 0.1 \pm 0.4‰$) in the Chilliwack watershed (*29*). However, data by Morrissey et al. (*29*) showed that river resident dippers ingest larger proportions of salmon fry than tributary migrants, so that differences in levels of OCs and PCB congener patterns may also be affected by differences in diets originating from marine salmon sources. Other sources of OCs and PCBs may have come from commercial salmon feed released from the local hatchery (*44*). Salmon feed is incorporated into the lotic food chain through ingestion by juvenile salmon or benthic invertebrates in and around hatchery waterways, which are routinely preyed upon by dippers. This was not supported by our contaminant data on benthic invertebrates and salmon fry taken directly from the hatchery waterways and surrounding areas, which were not elevated in either total PCBs or individual OCs as compared to other samples collected in the watershed (C. Morrissey, unpublished data). Future research investigating contaminant burdens in dippers occupying streams with and without anadromous fish and hatchery inputs would be valuable to compare levels of OCs and PCBs among lotic food chains.

Biomagnification. Various xenobiotics frequently increase with trophic level in aquatic biota, a process known as food chain biomagnification (*11*, *39*). However, research on the transfer of contaminants to organisms in lotic food chains, particularly to upper trophic levels through biomagnification, has rarely been explored (*18*, *19*). Stable isotope ratios ($\delta^{15}N$) of identical prey composites from Morrissey et al. (*29*) demonstrated that invertebrate samples (means 0.1−5.4‰) were at a lower trophic level than both salmon fry ($13.6 \pm 0.5‰$) and American dipper blood samples ($8.3 \pm 0.9‰$). Concentrations of total PCBs, DDE, HCB, and *trans*-nonachlor significantly increased with a species' trophic level from invertebrates to salmon fry to dippers, with dipper eggs having the highest concentrations of all contaminants measured (Figure 4, Table 1). This pattern remained consistent even after correcting for differences in lipid content among groups. The composition of organic contaminants was similar between prey types, but residues in salmon fry tended to exceed those of benthic invertebrates. For example, PCBs were detected in fish samples (mean = 27.8 ng/g lipid weight, $n = 8$), but no PCB congeners were found in any of the invertebrate samples (<3.0 ng/g lipid weight, $n = 15$) from the Chilliwack watershed, while DDE ($F_{2,20} = 9.02$, $p < 0.002$) and *trans*-nonachlor ($F_{2,20} = 7.88$, $p = 0.003$) were also significantly higher in fish over invertebrates. Therefore, dippers were likely receiving the majority of their OC and PCB burdens from ingestion of salmon fry.

Biomagnification factors (BMFs) offer the potential to estimate avian egg concentrations just from analyzing diet items, assuming those items are the predominant food eaten and differences in metabolism between avian species are small (*45*). BMFs from American dipper prey to eggs were highest for total PCBs and DDE (Table 1). The degree of biomagnification of many persistent organic pollutants in aquatic systems is known to be higher for substances with large K_{ow} values (*11*, *39*, *40*). Therefore, significant potential exists for those persistent and lipophilic contaminants to biomagnify within food chains of mountain streams, such that predators including the dipper would be expected to have higher concentrations in their tissues.

Most other studies that calculate BMFs for other avian species in freshwater or terrestrial habitats including American robins (*Turdus migratorius*) (*46*), herring gulls (*Larus argentatus*) (*47*), and osprey (*Pandion haliaetus*) (*48*) show similar BMF values as our data for American dippers. However, they report BMFs on a wet weight basis only, thus preventing direct comparisons. Our BMF values are calculated on a lipid-normalized basis to correct for differences in accumulation caused by differences in lipid content observed among trophic levels (Table 1). A discrepancy in BMF values between studies for various contaminants may be attributed to differences in calculating BMFs that do not control for lipid content. Alternatively, interspecific differences in accumulation, metabolism, and excretion or a large variability in individual prey and egg values by location may be important in determining BMF values. The BMFs calculated here represent an average diet of 67% invertebrates and 33% fish and do not reflect variability in lipid content or diet composition among individuals. Calculating BMFs is designed to predict contaminant burdens to wildlife consumers and to estimate the potential risk of exposure prior to analyzing eggs. In applying the BMF to a dipper biomonitoring program, we recommend that it be reported on a lipid basis due to observed differences in lipid content between birds, fish, and insects and across regions, especially where variation in the density of salmon is expected.

Dipper eggs in this study had mean total PCB and DDE concentrations less than 0.1 μg/g, and all individual eggs were below 1 μg/g wet weight, which is within or below the range of previously reported concentrations in other passerine eggs from British Columbia (*49*) and in dipper eggs (*Cinclus cinclus*) from Europe (*26*, *27*). None of those species, including American robins that were more heavily contaminated by DDE, showed any measurable adverse effects on reproductive performance. Studies on dippers in Europe also found no strong evidence of reproductive effects or reduced postfledging survival, with OC and PCB concentrations equal to or in excess of those detected in this study (*26*, *27*). Subtle effects can occur as a result of in ovo exposure to concentrations much lower than those associated with overt reproductive effects (*45*). However, we have no evidence from published literature to suggest that the current loadings of organic contaminants to lotic biota and their biomagnification potential are putting American dipper populations at risk in Georgia Basin watersheds.

Acknowledgments

Major funding for this project was provided by Environment Canada under the Georgia Basin Ecosystem Initiative. We thank R. McKibbin, I. Pollet, H. Middleton, and J. Morrissey for their assistance in sample collections in the field. M. Mulvihill, H. Won, M. Simon, and B. Wakeford at the National Wildlife Research Centre performed or supervised the OC/PCB analysis. We also thank R. Butler, F. Cooke, R. Ydenberg, P. Shaw, and three anonymous reviewers for their advice and/or their assistance in reviewing the manuscript.

Supporting Information Available

Raw contaminant data, principle component scores, and summary of principle component analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Dewailly, E. A.; Nantel, J. P.; Weber, J. P.; Meyer, F. High levels of PCBs in breast milk of Inuit women from Arctic Quebec. *Bull. Environ. Contam. Toxicol.* **1989**, *43*, 641−646.

(2) Wania, F.; Mackay, D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* **1993**, *22*, 10−18.

(3) Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Kimpe, L. E.; Donald, D. B.; Rosenberg, B. Melting glaciers: A major source of persistent organochlorines to subalpine Bow Lake in Banff National Park, Canada. *Nature* **1998**, *395*, 685−688.

(4) Davidson, D. A.; Wilkinson, A. C.; Blais, J. M.; Kimpe, L. E.; McDonald, K. M.; Schindler, D. W. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of western Canada. *Environ. Sci. Technol.* **2003**, *37*, 209−215.

(5) Swackhamer, D. L.; Hites, R. A. Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior. *Environ. Sci. Technol.* **1988**, *20*, 879–883.

(6) Johnson, M. G.; Kelso, J. R. M.; George, S. E. Loadings of organochlorine contaminants and trace elements to two Ontario lake systems and their concentrations in fish. *Can. J. Fish. Aquat. Sci.* **1988**, *45* (Suppl. 1), 170–178.

(7) Donald, D. B.; Bailey, R.; Crosley, D.; Muir, D.; Syrgiannis, J. *Polychlorinated Biphenyls and Organochlorine Pesticides in the Aquatic Environment along the Continental Divide Region of Alberta and British Columbia: Technical Report*; Inland Waters Directorate: Regina, Saskatchewan, Canada, 1993.

(8) Datta, S.; McConnell, L. L.; Baker, J. E.; Lenoir, J.; Seiber, J. N. Evidence for atmospheric transport and deposition of polychlorinated biphenyls to the Lake Tahoe Basin, California–Nevada. *Environ. Sci. Technol.* **1998**, *32*, 1278–1385.

(9) Daly, G. L.; Wania, F. Organic contaminants in mountains. *Environ. Sci. Technol.* **2005**, *39*, 385–398.

(10) Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Sharp, M.; Donald, D.; Lafreniere, M.; Braekevelt, E.; Strachan, W. M. J. Melting glaciers: A major source of persistent organochlorines to subalpine Bow Lake in Banff National Park, Canada. *Ambio* **2001**, *30*, 410–415.

(11) Kidd, K. A.; Schindler, D. W.; Muir, D. C. G.; Lockhart, W. L.; Hesslein, R. H. High concentrations of toxaphene in fishes from a subarctic lake. *Science* **1995**, *269*, 240–242.

(12) Donald, D. B.; Stern, G. A.; Muir, D. C. G.; Fowler, B. R.; Miskimmin, B. M.; Bailey, R. Chloroboronanes in water, sediment, and fish from toxaphene treated and untreated lakes in western Canada. *Environ. Sci. Technol.* **1998**, *32*, 1391–1397.

(13) Grimalt, J. O.; Fernandez, P.; Berdie, L.; Vilanova, R. M.; Catalan, J.; Psenner, R.; Hofer, R.; Appleby, P. G.; Rossland, B. O.; Massabuau, J. C.; Battarbee, R. W. Selective trapping of organochlorine compounds in mountain lakes of temperate areas. *Environ. Sci. Technol.* **2001**, *35*, 2690–2697.

(14) Norstrom, R. J.; Muir, D. C. G. Chlorinated-hydrocarbon contaminants in arctic marine mammals. *Sci. Total Environ.* **1994**, *154*, 107–128.

(15) Bard, S. M. Global transport of anthropogenic contaminants and the consequences for the Arctic marine ecosystem. *Mar. Pollut Bull.* **1999**, *38*, 356–379.

(16) Wilson, R.; Allengil, S.; Griffin, D.; Landers, D. Organochlorine contaminants in fish from an arctic lake in Alaska, USA. *Sci. Total Environ.* **1995**, *161*, 511–519.

(17) Macdonald, C. R.; Metcalfe, C. D. Concentration and distribution of PCB congeners in isolated Ontario lakes contaminated by atmospheric deposition. *Can. J. Fish. Aquat. Sci.* **1991**, *48*, 371–381.

(18) Berglund, O.; Larsson, P.; Bronmark, C.; Greenberg, L.; Eklov, A.; Okla, L. Factors influencing organochlorine uptake in age-0 brown trout (*Salmo trutta*) in lotic environments. *Can. J. Fish. Aquat. Sci.* **1997**, *54*, 2767–2774.

(19) Berglund, O. Periphyton density influences organochlorine accumulation in rivers. *Limnol. Oceanogr.* **2003**, *48*, 2106–2116.

(20) Geisy, J. P.; Verbrugge, D. A.; Othout, R. A.; Bowerman, W. W.; Mora, M. A.; Jones, P. D.; Newsted, J. L.; Vandervoort, C.; Heaton, S. N.; Aulerich, R. J.; Bursian, S. J.; Ludwig, J. P.; Ludwig, M.; Dawson, G. A.; Kubiak, T. J.; Best, D. A.; Tillit, D. E. Contaminants in fishes from Great Lakes-influenced sections and above dams of three Michigan rivers. I: Concentrations of organochlorine insecticides, polychlorinated biphenyls, dioxin equivalents, and mercury. *Arch. Environ. Contam. Toxicol.* **1994**, *27*, 202–212.

(21) Ewald, G.; Larsson, P.; Linge, H.; Okla, L.; Szarzi, N. Biotransport of organic pollutants to an inland Alaska lake by migrating Sockeye salmon (*Oncorhynchus nerka*). *Arctic* **1998**, *51*, 40–47.

(22) Krummel, E. M.; Macdonald, R. W.; Kimpe, L. E.; Gregory-Eaves, I.; Demers, M. J.; Smol, J. P.; Finney, B.; Blais, J. M. Delivery of pollutants by spawning salmon. *Nature* **2003**, *425*, 255–256.

(23) Naiman, R. J.; Bilby, R. E.; Schindler, D. E.; Helfield, J. M. Pacific salmon, nutrients, and the dynamics of freshwater and riparian ecosystems. *Ecosystems* **2002**, *5*, 399–417.

(24) Furness, R. W. Birds as monitors of pollutants. In *Birds as Monitors of Environmental Change*; Furness, R. W., Greenwood, J. J. D., Eds.; Chapman & Hall, London, 1993; pp 86–143.

(25) Morrissey, C. A.; Bendell-Young, L. I.; Elliott, J. E. Seasonal trends in population density, distribution and movement of American dippers within a watershed of southwestern British Columbia, Canada. *Condor* **2004**, *106*, 815–825.

(26) Ormerod, S. J.; Tyler, S. J. Patterns of contamination by organochlorines and mercury in the eggs of two river passerines in Britain and Ireland with reference to individual PCB congeners. *Environ. Pollut.* **1992**, *76*, 233–243.

(27) Ormerod, S. J.; Tyler, S. J.; Jüttner, I. Effects of point-source PCB contamination on breeding performance and post-fledging survival in the dipper *Cinclus cinclus*. *Environ. Pollut.* **2000**, *109*, 505–513.

(28) O'Halloran, J.; Irwin, S.; Harrison, S.; Smiddy, P.; O'Mahony, B. Mercury and organochlorine content of Dipper *Cinclus cinclus* eggs in south-west Ireland: Trends during 1990–1999. *Environ. Pollut.* **2003**, *123*, 85–93.

(29) Morrissey, C. A.; Bendell-Young, L. I.; Elliott, J. E. Linking contaminant profiles to the diet and breeding location of American dippers using stable isotopes. *J. Appl. Ecol.* **2004**, *41*, 502–512.

(30) Won, H. T.; Mulvihill, M. J.; Wakeford, B. J. *Multi Residue Methods for the Determination of Chlorinated Pesticides and Polychlorinated Biphenyls (PCBs) in Wildlife Tissues by Gas Chromatography/Mass Spectrometry*; Technical Report Series No. 335; Canadian Wildlife Service, Environment Canada: Hull, Quebec, 2000.

(31) Peakall, D. B.; Gilman, A. P. Limitations of expressing organochlorine levels in eggs on a lipid-weight basis. *Bull. Environ. Contam. Toxicol.* **1979**, *23*, 287–290.

(32) Elliott, J. E.; Noble, D. G.; Norstrom, R. J.; Whitehead, P. E. Organochlorine contaminants in seabirds from the Pacific coast of Canada, 1971–1986. *Environ. Monit. Assess.* **1989**, *12*, 67–82.

(33) Elliott, J. E.; Norstrom, R. J.; Smith, G. E. J. Patterns, trends, toxicological significance of chlorinated hydrocarbon and mercury contamination in bald eagle eggs from the Pacific coast of Canada, 1990–1994. *Arch. Environ. Contam. Toxicol.* **1996**, *31*, 354–367.

(34) Szeto, S. Y.; Price, P. M. Persistence of pesticide residues in mineral and organic soils in the Fraser Valley of British Columbia. *J. Agric. Food Chem.* **1991**, *39*, 1679–1684.

(35) Finizio, A.; Bidleman, T. F.; Szeto, S. Y. Emission of chiral pesticides from an agricultural soil in the Fraser Valley, British Columbia. *Chemosphere* **1998**, *36*, 345–355.

(36) Jones, K. C. Determination of polychlorinated biphenyls in human foodstuffs and tissues: Suggestions for a selective congener analytical approach. *Sci. Total Environ.* **1988**, *68*, 141–159.

(37) Elliott, J. E.; Butler, R. W.; Norstrom, R. J.; Whitehead, P. E. Environmental contaminants and reproductive success of Great Blue herons *Ardea herodias* in British Columbia, 1986–87. *Environ. Pollut.* **1989**, *59*, 91–114.

(38) Drouillard, K. G.; Fernie, K. J.; Smits, J. E.; Bortolotti, G. R.; Bird, D. M.; Norstrom, R. J. Bioaccumulation and toxicokinetics of 42 PCB congeners in American kestrels (*Falco sparverius*). *Environ. Toxicol. Chem.* **2001**, *20*, 2514–2522.

(39) Oliver, B. G.; Niimi, A. J. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environ. Sci. Technol.* **1988**, *22*, 388–397.

(40) Catalan, J.; Ventura, M.; Vives, I.; Grimalt, J. O. The roles of food and water in the bioaccumulation of organochlorine compounds in high mountain lake fish. *Environ. Sci. Technol.* **2004**, *38*, 4269–4275.

(41) Fisk, A. T.; Hobson, K. A.; Norstrom, R. J. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants on Northwater Polynya marine food web. *Environ. Sci. Technol.* **2001** *35*, 732–738.

(42) Giller, P. S.; Malmqvist, B. *The Biology of Streams and Rivers*; Oxford University Press: New York, 2000.

(43) Kline, T. C., Jr.; Goering, J. J.; Mathisen, O. A.; Poe, P. H.; Parker, P. L.; Scalan, R. S. Recycling of elements transported upstream by runs of Pacific salmon: II. δ^{15}N and δ^{13}C evidence in the Kvichak River watershed, Bristol Bay, Southwestern Alaska. *Can. J. Fish. Aquat. Sci.* **1993**, *50*, 2350–2365.

(44) Easton, M. D. L.; Luszniak, D.; Von der Geest, E. Preliminary examination of contaminant loadings in farmed salmon, wild salmon and commercial salmon feed. *Chemosphere* **2002**, *46*, 1053–1074.

(45) Hoffman, D. J.; Rice, C. P.; Kubiak, T. J. PCBs and dioxins in birds. In *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*; Beyer, W. N., Heinz, G. H., Redmon-Norwood, A. W., Eds.; Setac Special Publication, CRC Press: Boca Raton, FL, 1996; pp 165–207.

(46) Harris, M. L.; Wilson, L. K.; Elliott, J. E.; Bishop, C. A.; Tomlin, A. D.; Henning, K. V. Transfer of DDT and metabolites from fruit orchard soils to American robins (*Turdus migratorius*) twenty years after agricultural use of DDT in Canada. *Arch. Environ. Contam. Toxicol.* **2000**, *39*, 205–220.

(47) Braune, B. M.; Norstrom, R. J. Dynamics of organochlorine compounds in herring gulls: III. *Environ. Toxicol. Chem.* **1989**, *8*, 957−968.
(48) Henny, C. J.; Kaiser, J. L.; Grove, R. A.; Raymond Bentley, V.; Elliott, J. E. Biomagnification factors (fish to osprey eggs from Willamette River, Oregon, U.S.A.) for PCDDs, PCDFs, PCBs and OC pesticides. *Environ. Monit. Assess.* **2003**, *84*, 275−315.
(49) Elliott, J. E.; Martin, P. A.; Arnold, T. W.; Sinclair, P. H. Organochlorines and reproductive success of birds in orchard and non-orchard areas of central British Columbia, Canada, 1990−91. *Arch. Environ. Contam. Toxicol.* **1994**, *26*, 435−443.

Received for review March 2, 2005. Revised manuscript received July 18, 2005. Accepted August 1, 2005.

ES050431N