Historical analysis of salmon-derived polychlorinated biphenyls (PCBs) in lake sediments

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ABSTRACT

Several recent studies have highlighted the importance of salmon as a means to deliver biomagnifying contaminants to nursery lakes. There is a lack of studies, however, which demonstrate empirically how this source has varied through time. This is of great significance because past salmon-derived contaminant loading was potentially greater than it is today. By analyzing radiometrically dated sediment cores collected from ten lakes in Alaska and British Columbia (B.C.), we relate historical numbers of sockeye salmon spawners to $\Sigma$PCB concentrations and $\delta^{15}N$ values (a paleolimnological proxy for past salmon-derived nitrogen) in the sediments. The results confirm that sockeye salmon have provided an important route for PCBs to enter the lakes in the past, a finding that is especially evident when the data of all lakes are pooled. Significant relationships between sockeye salmon numbers and $\Sigma$PCBs and $\delta^{15}N$ in sediments, were also found. However, it is difficult to establish relationships between salmon numbers, $\Sigma$PCBs and $\delta^{15}N$ in individual lakes. This may be due to a number of factors which may influence contaminant loadings to the lakes. The factors include: a) changing salmon contaminant loads over time resulting from a lag in the upper ocean reservoir and/or changing salmon feeding locations; b) greater importance of atmospheric transport in lakes with relatively low salmon returns; and c) increased PCB scavenging due to higher algae productivity in the lakes in recent years.

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1. Introduction

Persistent organic pollutants (POPs), which have been distributed widely into the environment in megatonne quantities during the past 50 years (Macdonald et al., 2000), pose risks to high trophic level animals where they bioaccumulate. Environmental concentrating mechanisms that lead to high concentrations of POPs in aquatic predatory animals are becoming well understood (Macdonald et al., 2002). However, it has only recently been recognized that mass transport and focusing of contaminants within the life cycles of some animals provides another mechanism by which enhanced
exposure can occur at critical locations (reviewed in Blais et al., 2007). Spawning sockeye salmon are now known to dominate the transport of POPs into some nursery lakes in B.C. and Alaska (Ewald et al., 1998; Krümmel et al., 2003, 2005). The efficacy of this mechanism depends on the complex life-cycle of Pacific salmon, especially sockeye salmon (*Oncorhynchus nerka*). Sockeye salmon spawn in gravel beds associated with lakes and their tributary streams. The juveniles rear in these nursery lakes for 1 to 3 years, before they migrate to the ocean (Burgner, 1991). The maturing salmon then spend 1 to 4 years in the ocean, where they feed on zooplankton, small fish, and squid, and accumulate up to 99% of their total body weight (Burgner, 1991; Mathisen et al., 1988). Upon returning to their freshwater nursery streams, sockeye salmon stop feeding and begin a process of metabolizing their stored fat. After spawning, they die. A large increase in the abundance of dissolved nutrients follows the massive die-off of spawned-out Pacific salmon (Brickell and Goering, 1970; Richey et al., 1975; Sugai and Burrell, 1984) and it has been suggested that this source of nutrients can be significant in the nursery lakes, which tend to be oligotrophic (Krohkin, 1975; Koenings and Burkett, 1987; Naiman et al., 2002; Moore et al., 2007).

Several studies have examined the nutrient input to freshwater systems by Pacific salmon using stable isotopes, especially $^{15}$N. Marine-derived nitrogen is enriched in $^{15}$N relative to terrestrial and freshwater nitrogen sources (Kline et al., 1990). $^{15}$N is also higher in organisms that feed at higher trophic levels (DeNiro and Epstein, 1981; Peterson and Fry, 1987; Cabana and Rasmussen, 1994). By measuring the enrichment of $^{15}$N, it has been shown that salmon play a major role in the nitrogen dynamics of some nursery lakes (Mathisen et al., 1988) and in the associated ecosystem: salmon-derived nutrients have been found in riparian vegetation, soil, and insects, as well as top predators such as bears (e.g., Hocking and Reimchen, 2002; Mathewson et al., 2003; Reimchen et al., 2003; Hilderbrand et al., 1996). Unfortunately, the salmon transport pathway is also very effective in moving contaminants to that same ecosystem (e.g. Gregory-Eaves et al., 2007; Christensen et al., 2005; Krümmel et al., 2003).

Clearly, the salmon biovector transport pathway has been operating since the time biomagnifying contaminants first entered the ocean, although historical tissue samples that would permit an assessment of its past importance are lacking. It therefore remains unclear whether salmon spawners delivered higher amounts of the now largely banned contaminants in the past during their peak usage, or whether this pathway had not yet achieved its maximum due to a delay in loading intervening reservoirs such as the upper ocean and its foodweb. Similarly lacking are long-term historical measurements of atmospheric loadings which would not only allow for the determination of global trends, but would also help to understand how global change may have altered contaminant pathways (Macdonald et al., 2005).

Traditionally, lake sediment cores have provided a window into historical contaminant loadings (Smol, 2008). For example, paleolimnological approaches have been used to evaluate the significance of atmospheric transport and distillation of PCBs headed for the Arctic (Muir et al., 1995, 1996), processes leading to deposition of POPs at remote locations (Doskey and Talbot, 2000; Rawn et al., 2001) and local sources of POPs to coastal BC environments (Macdonald et al., 1998). Sediment cores have also been applied convincingly to reconstruct historical sockeye salmon population dynamics using proxy indicators which show either direct evidence of marine sources (e.g., $^{15}$N), or indirect evidence of lake enrichment (diatoms); both of which provide clear salmon ‘fingerprints’ in the sediment record (Schindler et al., 2005; Gregory-Eaves et al., 2003; Finney et al., 2000, 2002). Given the affinity of many POPs for particles, it is likely that salmon-derived contaminants can be traced in down-core profiles and linked to past sockeye salmon spawner abundance, at least qualitatively if not quantitatively. Similar approaches have been used to study biotransport of contaminants by seabirds (reviewed in Blais et al., 2007). Here we use dated sediment cores collected in lakes distributed from Alaska to southern British Columbia to investigate historical relationships between sockeye salmon spawners and PCBs by comparing historical counts of sockeye salmon spawners with sediment records of $^{15}$N and PCBs.

## 2. Methods

### 2.1. Sample collection and chemical analysis

Sediment cores from 10 lakes in British Columbia (BC) and Alaska (Fig. 1) were collected in the years 2001–2003 (Table 1). Four lakes, sampled in 2002, are located on Kodiak Island, Alaska: Frazer, Karluk, Red and Upper Olga. The other lakes are located in BC: Fraser was cored in 2001, Bowron, Quesnel and Shuswap in 2002, and Kinaskan and Meziadin in 2003.

Sediments were collected using corers designed specifically for high-resolution paleolimnological work (Glew, 1989). Since lakes in Alaska were accessible only by float plane, whereas BC lakes were accessible by a small boat, different corers were used in the two regions. For the BC lakes, a gravity corer (built by Jan Slavicek, Winnipeg, Canada) with an acrylic tube (9.5 cm i.d.) was lowered slowly using an electric winch. The heavier weight of this corer allowed for retrieval of longer cores. In Alaska a smaller, hand-operated corer was used (inner diameter: 7.6 cm, built by John Glew, Kingston, Canada. See also Glew, 1989). Using bathymetric and topographical maps when available, cores were collected from deep sections of the lakes on flat surfaces and well away from river mouths or deltas. Cores were extruded and sectioned at fine intervals on site, the sediment slices were placed in WhirlPak® bags, sealed and frozen immediately.

Wet sediment samples were centrifuged at 2500 rpm to remove excess water and mixed with Hydromatrix® (Varian, Harbor City, CA, USA), which was pre-cleaned with petroleum ether. This mixture was spiked with surrogate recovery standards of PCB 30 and PCB 204, and extracted in an accelerated solvent extractor (ASE200, Dionex, Sunnyvale, CA, USA). The samples underwent two extractions at 2000 PSI and 100 °C each, first with acetone/hexane, followed by dichloromethane (DCM). The two extracts were then combined for liquid–liquid extraction, and dried over sodium sulphate (Fisher Scientific, 5421–3). The resulting volume of 150 mL was reduced to 1 mL in a TurboVap (at 14 psi using ultra high purity nitrogen gas, and 35 °C water bath temperature) and exchanged into isoctane. Cleanup and
fractionation was accomplished by passing the extracts through a chromatographic column (chromaflex column, Kontes, 420280–0213, dimensions: 200 ml reservoir, 11 mm internal diameter, 250 mm length) packed with 8 g of 100% activated silica gel (Davisil 635 Type 60A, Fisher Scientific, S735-1) and 1 g sodium sulphate. Both silica gel and sodium

Fig. 1—Map of the sampling locations in British Columbia and Alaska (Kodiak Island).

Table 1 – Coring location and lake information for the sites sampled

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Lat (N)</th>
<th>Long (W)</th>
<th>Coring year</th>
<th>Lake Area (km²)*</th>
<th>Lake depth max. (m)*</th>
<th>Watershed area (km²)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bowron B.C.</td>
<td>53°13′</td>
<td>121°22′</td>
<td>2002</td>
<td>10.2</td>
<td>63.4</td>
<td>3403</td>
<td></td>
</tr>
<tr>
<td>Fraser B.C.</td>
<td>54°05′</td>
<td>124°45′</td>
<td>2001</td>
<td>54</td>
<td>30.5</td>
<td>6268</td>
<td></td>
</tr>
<tr>
<td>Kinaskin B.C.</td>
<td>57°35′</td>
<td>130°08′</td>
<td>2003</td>
<td>28.7</td>
<td>N/D</td>
<td>1251</td>
<td></td>
</tr>
<tr>
<td>Meziadin B.C.</td>
<td>56°03′</td>
<td>129°16′</td>
<td>2003</td>
<td>34</td>
<td>133</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>Quesnel B.C.</td>
<td>52°30′</td>
<td>121°00′</td>
<td>2002</td>
<td>270</td>
<td>530</td>
<td>5930</td>
<td></td>
</tr>
<tr>
<td>Shuswap B.C.</td>
<td>51°00′</td>
<td>119°00′</td>
<td>2000</td>
<td>330</td>
<td>162</td>
<td>16221</td>
<td></td>
</tr>
<tr>
<td>Frazer</td>
<td>Kodiak Island</td>
<td>57°16′</td>
<td>154°08′</td>
<td>2002</td>
<td>16.6</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>Karluk</td>
<td>Kodiak Island</td>
<td>57°25′</td>
<td>154°05′</td>
<td>2002</td>
<td>39.4</td>
<td>282</td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td>Kodiak Island</td>
<td>57°15′</td>
<td>154°20′</td>
<td>2002</td>
<td>8.4</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Upper Olga</td>
<td>Kodiak Island</td>
<td>57°04′</td>
<td>154°10′</td>
<td>2002</td>
<td>7.9</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

* Information was taken from: Gilbert and Butler (2004), Honnold (1993), Kyle et al. (1990), Koenings and Burkett (1987), Kyle et al. (1988), Spafard and Edmundson (2000).
* There were no depth data available for this lake.
sulphate were previously muffled at 600°C for 6 h. The PCBs were eluted with 50 mL of hexane and evaporated to a final volume of 200 µL in iso-octane. A known concentration of Mirex was added as an internal standard. All solvents used were Omnisolv® high-purity grade from VWR (Mississauga, ON, Canada).

PCBs were analyzed on a Hewlett-Packard 6890 series II gas chromatograph with a 63Ni micro electron-capture detector, using splitless injection with an inlet temperature of 250 °C. One microlitre of extract was separated on a 30 m x 0.25 mm (0.25 µm film) DB-5MS column (J&W Scientific, Agilent Technologies, Mississauga, ON, Canada) using helium carrier gas at 3.1 mL/min on constant flow. The oven ramping program is as follows: initial temperature of 80 °C held for 2 min, climbing to 110 °C at 10 °C/min, then to 280 °C at 3 °C/min and held for 5 min. The detector temperature was at 350 °C using constant column flow plus makeup nitrogen gas at 60 psi. The instrument was calibrated using a 5-point calibration curve, using standard concentrations ranging from 1.9 to 530 pg/µL with a correlation coefficient of ≥0.99. Chromatographic peaks were interpreted using HP Chemstation software (Rev. A.06.03, Hewlett-Packard, Palo Alto, CA). Compounds were identified by running sets of standards with known concentrations and comparing their retention times with those of the sample compounds. Concentrations of the sample compounds were calculated by taking the ratio of their peak areas and the peak area of the internal standard, Mirex. From the 209 PCB congeners in the standard mixture, usually about 100 peaks could be obtained, with small differences depending on GC maintenance. They appear in the following order (IUPAC number): 1, 3, 4–10, 7–9, 6–8, 5, 19, 30, 12–13, 18, 15–17, 24–27, 16–32, 54–29, 26, 25, 50–31–28, 33–20–53, 51, 22, 45, 46, 52, 49, 48–47, 44, 59–42, 40, 100, 63, 74, 70–76–98, 91–55, 56–60, 92, 84, 101, 99, 119, 83, 97, 87–81, 85, 136, 110, 82, 151, 135–144, 147–107, 149, 118, 133, 146, 153–132–105, 141–179, 137, 176, 138–163, 158, 129, 178, 175, 187–182, 183, 128, 167, 185, 174, 177, 202–171–156, 173, 157–200, 204, 172, 197, 180, 193, 191, 199, 170–190, 198, 201, 203–196, 189, 208–195, 207, 194, 205, 206, 209.

2.2. Quality assurance

Reference material (RF), consisting of the National Institute of Standards and Technology (NIST) 1944 River Sediment was run with each batch of sediment samples. A complete set of standards (recovery determinants, RDs), and method blanks were also routinely analyzed with every sample batch. RDs and surrogate recovery standards can be used to estimate the recoveries of the analyzed compounds. Method blanks represent the background contamination associated with the analytical process, which was then removed from the samples by subtracting the method blank from the sample value. The method blanks in our laboratory have low levels (<0.5 ng g⁻¹, typically 0.2 ng g⁻¹ of ∑PCBs, based on average sample weights). Method blanks were used to determine method detection limits (MDLs) by calculating the standard deviation of the averaged method blanks and multiplying it by two (which represents a 95% confidence level). Values for recoveries and MDLs can be found in Tables A.1 to A.4 (supporting material).

Our laboratory also participated in inter-laboratory studies (such as the QUASIMEME Laboratory Performance Studies) during the years 2003 and 2005 (when the study was carried out) to validate the quality of our contaminant analysis. The results were satisfactory with average Z-scores for the PCB analysis of 1.0 for 2003 and ~1.5 for 2005 (Z-scores between +2 and ~2 are deemed satisfactory).

2.3. Isotope analysis

For elemental and isotopic analysis of nitrogen and carbon, freeze dried sediments were weighed into small tin capsules and flash combusted at 1800 °C in an Elemental Analyser (Vario EL III, Elementar, Germany). The thereby produced gases of N₂, SO₂ and CO₂ were separated by “trap and purge” chemical traps for determination of total percentages of nitrogen, sulfur and carbon. The gases were then carried in the helium carrier gas stream to the Isotope-Ratio Mass Spectrometer (DeltaPlus Advantage, ThermoFinnigan, Bremen, Germany) via a Conflco interface and were analyzed for isotope ratios. Isotopic compositions are expressed as δ values, which are measured as parts per thousand differences from a standard (Peterson and Fry, 1987):

\[
\delta^{15}N = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 10^3,
\]

where R is the isotope ratio ¹⁵N/¹⁴N.

The standard for nitrogen is the nitrogen gas in air which, by convention, has a δ¹⁵N value of 0‰.

2.4. Dating of sediments

Sediment profiles were dated using standard ²¹⁰Pb dating procedures (Appleby, 2001). Briefly, sediments were freeze dried, ground to a fine powder, and placed in centrifuge tubes (8.4 cm high and 1.5 cm outer diameter) up to a height of ~2 cm (between 1–2 g). After the sediments had settled, the tubes were sealed with epoxy and allowed to equilibrate for three weeks before counting on a digital, high purity germanium spectrometer (DSpec, Ortec, Oak Ridge, TN, USA). The resulting spectrum files show ²¹⁰Pb activity with a peak at 46.5 keV, and ¹³⁷Cs at 662 keV. ²²⁶Ra activity was determined by γ-ray emissions of its daughter isotope ²¹⁴pb at 295 and 352 keV. The spectrum files were processed by a DOS-based software program developed and provided by Peter Appleby (University of Liverpool, U.K.), which included calculations for efficiency and corrections for self absorption (Appleby, 2001). All lakes were successfully dated using the constant rate of ²¹⁰Pb supply (CRS) model (Appleby, 2001). ¹³⁷Cs was measured to validate dates calculated with the model assuming an onset in 1954 and a peak in 1963 (Appleby, 2001; Blais et al., 1995).

2.5. Escapement

Total numbers of escapement (the number of sockeye salmon that ‘escape’ predation including fisheries and return to their nursery lakes to spawn) were provided by authorities from the Department of Fisheries and Oceans (DFO) in British Columbia (B.C.) and the Alaska Department of Fish and Game (ADF&G). For most lakes (all the Alaskan lakes as well as Meziadin and
Fraser lakes in B.C.) precise counts are ensured due to the implementation of counting stations at fish ladders or fences (Table 2). For Shuswap and Quesnel lakes, the method of estimating escapement varies with spawner abundance: larger spawner numbers (>75,000) are enumerated using more precise techniques such as fence or mark-recapture, while lower spawner numbers (<75,000) are enumerated by aerial or ground viewing only (Keri Benner, DFO, pers. comm.). Since escapement to Bowron Lake is below 75,000 annually, spawner enumerations for this lake are based on viewing only. Unfortunately, no error estimates are available for the aerial or ground viewing versus fence counting techniques, but DFO error estimates for the mark-recapture techniques for Shuswap and Quesnel during the years of 2002 to 2005 varied between ±5–19% (Keri Benner, DFO, pers. comm.).

In many nursery systems, sockeye salmon returns exhibit a 4-year cycle; often a ‘dominant year’ with very high abundance can be observed, followed by intermediate abundance (‘subdominant year’), and two years with very low abundance (‘nondominant years’) (Hume et al., 1994). The presence of pronounced spawning abundance cycles can complicate the comparisons between the escapement time series and the sediment record, where the information from many years might be stored in only a few millimeters of sediment depth. To extract trends from escapement data, we found that it was typically sufficient to fit a 4-year running average to smooth the data (shown with the example of Red Lake, Fig. 1D supporting material). This was done for all lakes except Shuswap. In the case of Shuswap Lake, a second, 12 to 13-year escapement cycle emerged after the 4-year cycle was removed (Fig. 1A and B, supporting material). To extract the underlying trend from this additional cycle, the data were fitted with a sloped cosine function (\( p_1 + p_2(t−p_3) + p_3 \cdot \cos(2\pi(t−p_3)/p_4) \)), where \( p_1 \) to \( p_4 \) are fitting parameters, and \( t \) is time in years), and the residuals were then smoothed again by calculating a running average with a window size of 4 years. The resulting curve was used to represent the general trend of sockeye salmon abundance and to compare its pattern to that of the down-core profiles of Shuswap Lake.

### Table 2 - Escapement numbers (as total numbers and per lake area) and method of enumeration for the lakes studied

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean total escapement</th>
<th>Mean total escapement per lake area (km²)</th>
<th>Counting method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bowron</td>
<td>9718 ± 95%</td>
<td>953</td>
<td>Aerial and ground viewing</td>
</tr>
<tr>
<td>Fraser</td>
<td>96,038 ± 92%</td>
<td>1778</td>
<td>Fence/counting</td>
</tr>
<tr>
<td>Kinaskan</td>
<td>0</td>
<td>0</td>
<td>Fish ladder/counting</td>
</tr>
<tr>
<td>Meziadin</td>
<td>166,325 ± 61%</td>
<td>4892</td>
<td>Variable with year, stock</td>
</tr>
<tr>
<td>Quesnel</td>
<td>270,381 ± 241%</td>
<td>1001</td>
<td>Variable with year, stock</td>
</tr>
<tr>
<td>Shuswap</td>
<td>567,062 ± 157%</td>
<td>1718</td>
<td>Fish ladder/counting</td>
</tr>
<tr>
<td>Frazer</td>
<td>129,838 ± 98%</td>
<td>7822</td>
<td>Fence/counting</td>
</tr>
<tr>
<td>Karluk</td>
<td>670,143 ± 57%</td>
<td>17,009</td>
<td>Fence/counting</td>
</tr>
<tr>
<td>Red</td>
<td>271,776 ± 75%</td>
<td>32,354</td>
<td>Fence/counting</td>
</tr>
<tr>
<td>Upper Olga</td>
<td>263,632 ± 55%</td>
<td>33,371</td>
<td>Fence/counting</td>
</tr>
</tbody>
</table>

2.6. Statistical analysis

The significance of the regressions was evaluated using a bootstrap test (Efron and Tibshirani, 1986), because some of the data are likely to be autocorrelated. The bootstrap test was carried out in MATLAB, Version 7.0.4, with a user-written code. For the bootstrap, one variable was randomized, and the regression was repeated. This process was performed 1000 times, and the resulting \( R^2 \) values were plotted. If the \( R^2 \) of the original regression was found to lie above 97.5% of the bootstrap \( R^2 \) distribution, we concluded that this relationship is highly significant.

To compare the time-series profiles directly with one another, the data were mean centered and normalized to standard deviation (i.e., for each property the mean was subtracted, and the data were divided by their standard deviation). The significance of the relationship was then estimated using a bootstrap test, as described above.

3. Results and discussion

3.1. All lakes and years combined

It has been shown that across Alaskan and B.C. lakes, there are strong relationships between surface sediment ΣPCB concentrations and the contemporary number of salmon spawners relative to lake size (Krümmel et al., 2005, 2003). However, whether or not a similar relationship can be found within each lake in the down-core profiles depends on temporal variability and the signal to noise ratio, which is smaller within a lake than it is between lakes. To show the overall pattern of our data, we have plotted log [PCBs] versus log [Escapement] for all lakes (Fig. 2A). The data were log transformed to achieve a normal distribution. The normal distribution of the data was tested using the standard tests (e.g., normal quantile–quantile plots) provided by S-Plus (Version 6.0, Professional Release 1). Only data after 1960 were included in our analyses to ensure that the salmon pathway was an important source of PCBs to the lake systems. Although PCBs have been released to the environment since ca. 1930, the loading of environmental reservoirs has been delayed and peak atmospheric inputs did not occur until the late 1960s or early 1970s (see, e.g., Muir et al., 1996). Therefore, it seems likely that salmon would emerge as an important transport mechanism for PCBs during approximately the 1960s (e.g., see Hickie et al., 2007).

Based on PCB distributions in lake surface sediments (Krümmel et al., 2005, 2003), we expected the salmon-derived PCBs to dominate lake input, overriding the atmospheric signal even during peak deposition years. In support of this hypothesis, a relationship between ΣPCB concentrations and the number of salmon spawners is evident in Fig. 2A and Table 3. Given that the non-bootstrapped \( R^2 \) of 0.19 was found to lie above 97.5% of the bootstrap \( R^2 \) distribution, we conclude that this relationship is highly significant.

The strength of the regression of the whole data set in Fig. 2A is weakened by the emergence of two distinct groups to the left where three lakes (Bowron, Shuswap and Quesnel) exhibit uniformly higher PCB concentrations. There are several reasons why these three lakes may show a separation...
from the main group. First, these lakes may have higher PCB inputs due to their close proximity to anthropogenic point sources (Fig. 1). Second, the escapement enumeration for the three central/southern B.C. lakes is often based on less precise aerial or ground viewing compared to the ladder/fence counting stations for the other lakes leading to higher variations in spawner estimates, especially at low spawner abundance. Finally, salmon spawners migrating to these lakes may carry a higher load of contaminants due to interactions between foraging range and contaminant distribution in the ocean.

A strong relationship was found between $\delta^{15}N$ and escapement for the whole data set (Fig. 2B and Table 3), as might be expected from previous paleolimnological studies where $\delta^{15}N$ has been shown to track historical salmon abundance (e.g. Finney et al., 2002, 2000). In Fig. 2B, Bowron, Quesnel and Shuswap lakes no longer group separately, implying that these lakes have a different PCB–escapement relationship than that observed for other lakes in the dataset. This hypothesis is further supported by the significant relationship between $\Sigma PCB$ concentration and $\delta^{15}N$ (Table 3).

Because Bowron, Quesnel and Shuswap lakes group separately from the others in Fig. 2A, we conducted analyses with both the whole data set, and screened data set (i.e. main group) where Bowron, Quesnel and Shuswap lakes were excluded (Table 3). The regression of $\Sigma PCB$s versus escapement for the main group exhibits a higher slope (0.96 compared to 0.43) and considerably higher $R^2$ than that of the whole data set (0.4 compared to 0.19 (Table 3). However, in the case of the relationship between $\delta^{15}N$ and escapement, the main data set exhibits a slight decrease in the $R^2$ value (from 0.54 for the whole data to 0.49 for the main group, Table 3), and the slope does not change. For the regression of $\Sigma PCB$s versus $\delta^{15}N$, an improvement of the relationship is again clearly

Fig. 2 – Regression of data for all lakes combined. For easier identification of the two groups, triangles were assigned to Bowron, Quesnel and Shuswap lakes (BQS group), whereas the remaining lakes (main group) are represented by circles. In (A) PCBs are plotted against number of spawners after year 1960. In (B) $\delta^{15}N$ is plotted against numbers of spawners for all years.
visible when the three B.C. lakes are removed from the data set ($R^2$ of 0.32 and 0.54 and slope of 1.55 and 2.4 for the whole data set and main group, respectively). Since the removal of the three B.C. lakes results in an improvement in the relationships between ΣPCBs and escapement or $\delta^{15}N$, but not between escapement and $\delta^{15}N$, we infer that a higher PCB load to the three lakes is the main reason for the group separation visible in Fig. 2A, rather than an underestimate of escapement.

### 3.2. Down-core analysis of individual lakes

#### 3.2.1. Kinaskan, Fraser and Quesnel lakes

Kinaskan Lake, a lake that does not receive any salmon, was used to evaluate the atmospheric input of contaminants to lakes in the area. For this lake, ΣPCBs are first detectable in sediments that accumulated in the mid-1950’s. A maximum ΣPCB concentration is observed at about 1973 and then declines toward the surface (Fig. 3). This pattern follows the general usage history of PCBs, which have been produced commercially since 1929, but peak production and usage in the U.S. occurred in 1970 (Oliver et al., 1989; Rapaport and Eisenreich, 1988). Although new uses of PCBs have been banned in most countries by 1980, old PCBs from contaminated sites continue to be recycled. Macdonald et al. (2000) estimate that a total of $-2 \times 10^8$ kg of PCBs remain in the environment, which is approximately 35% of the overall production. Eisenreich et al. (1989), Oliver et al. (1989) and Stern et al. (2005) all have reported similar trends based on sediment core analyses from Lake Ontario and the High Arctic. However, delays in peak deposition of contaminants are also reported depending on geographic location of the lake (e.g., Muir et al., 1996; Blais and Muir, 2001), supporting the theory that PCBs undergo multiple hops between ground and atmosphere as they advect away from major sources in temperate, industrial regions.

Fraser (BC) and Quesnel lakes will not be discussed in detail due to their very low sedimentation rates, which resulted in an extremely low resolution in the down-core profiles. It can be generally noted that escapement as well as PCB down-core profiles show an increasing trend toward recent years. These trends, however, are based on three and four data points for Fraser and Quesnel, respectively, and thus should be treated with some caution.

#### 3.2.2. Meziadin Lake

Meziadin Lake provides an ideal setting to examine the relationship between salmon spawner numbers and other proxies, because it displays a very distinct pattern of escapement since 1950 and it is the lake for which we have the greatest sample resolution between 1950 and today, thus allowing for robust comparisons to be drawn (Fig. 3). If sockeye salmon were an important source of contaminants and nutrients to Meziadin Lake in the past, down-core profiles should resemble the historical escapement. Indeed, we find such a resemblance between $\delta^{15}N$ (nutrient proxy) and ΣPCBs (Fig. 3); both exhibit a relatively steady period from the late 1950’s up until the early 1980’s, a pronounced peak around 1990 (skewed toward 2000 in the $\delta^{15}N$ profile), followed by a steep decline with a small rise in the most recent sediment slice.

Although the profiles in Fig. 3 have a very similar appearance, direct regression of the data yields only weak relations. When the resultant profiles are plotted together, it is clear that there is a small temporal offset with the PCB record in sediments pre-dating the escapement record by 1.5 years (Fig. 4A). Temporal offsets between down-core data and recorded time series may occur for several reasons. In Meziadin Lake, the offset is most likely due to uncertainty in sediment dating. Temporal offsets in the other direction can also occur due to the lag time between delivery of the contaminants to the lake and settling on particles at the bottom of the lake. It has been found that organic contaminants have a 2–3 times longer residence time in the Great Lakes compared to that of fine particles, which is estimated to be approximately one year (Eisenreich et al., 1989). Even after sedimentation, re-suspension can take place in the surface sediments, thus slowing down burial of contaminants and other particles. The deposition history can further be altered by mixing of the surface sediments, as well as by molecular diffusion and possible biotransformation (Eisenreich et al., 1989).

To account for temporal offsets between PCB and escapement, one of the curves was shifted in time relative to the other curve, until the best regression was achieved. The result of this process applied to the Meziadin Lake data is shown in Fig. 4B for escapement and ΣPCB concentration. Since more data-points were available for escapement, this curve was moved up (negative delay) and down (positive delay) with respect to the ΣPCB down-core profile. The resulting best fit achieved an $R^2$ of 0.8 after a delay of 1.5 years, which is within dating errors (Fig. 4A). This $R^2$ was found to lie above 97.5% of the bootstrap $R^2$ distribution, therefore indicating a highly significant relationship (Table 4).

Interestingly, the same time shift that produced the best fit between ΣPCBs and escapement did not also result in the best fit between $\delta^{15}N$ and escapement. We found that moving the escapement curve forward by 3 years produced the best correlation with $\delta^{15}N$. The resulting $R^2$, however, was only 0.25 (Table 4). The discrepancy between the two geochemical indicators may be explained by the sensitivity of these indicators to different mechanisms. Higher influxes of organic

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### Table 3 – Observed regressions of whole data set and the main group (Bowron, Shuswap and Quesnel lakes omitted)

<table>
<thead>
<tr>
<th>Regression</th>
<th>$R^2$</th>
<th>Bootstrap $R^2$ at 97.5%</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>log(ΣPCBs) vs log(escapement)</td>
<td>0.19</td>
<td>0.07</td>
<td>0.43±0.13</td>
</tr>
<tr>
<td>Main group</td>
<td>0.4</td>
<td>0.09</td>
<td>0.96±0.19</td>
</tr>
<tr>
<td>log($\delta^{15}N$) vs log(escapement)</td>
<td>0.54</td>
<td>0.04</td>
<td>0.61±0.07</td>
</tr>
<tr>
<td>Main group</td>
<td>0.49</td>
<td>0.07</td>
<td>0.68±0.1</td>
</tr>
<tr>
<td>log(ΣPCBs) vs log($\delta^{15}N$)</td>
<td>0.32</td>
<td>0.06</td>
<td>1.55±0.3</td>
</tr>
<tr>
<td>Main group</td>
<td>0.54</td>
<td>0.08</td>
<td>2.4±0.34</td>
</tr>
</tbody>
</table>

*a* Kinaskan was excluded because it has escapement of zero.

*b* One outlier removed: Frazer 1959.
matter and nutrients with a light isotopic composition, which did not influence contaminant profiles but caused the dip in $\delta^{15}N$ values around the year 1986, might explain the poor fit. Although the $\delta^{15}N$ value for this section of the core is very low, it is not likely a poor data point as it is accompanied by low values for $\delta^{13}C$ and percent carbonates and high values in

Fig. 3 - Down-core profiles for $\Sigma$PCBs and $\delta^{15}N$ for Kinaskan (no salmon spawners) and Meziadin (including spawners).

Fig. 4 - Shifting process of the down-core profiles of $\Sigma$PCBs and number of spawners (escapement) for Meziadin Lake. The data are standardized and dating errors are included with the PCB data in (A) to indicate a possible shift due to dating imprecision. (A) Overlaid curves without shifting. (B) Curves after a shift of the escapement of 1.5 years.
percent nitrogen, percent carbon, organic matter, sedimentation rate and C/N values (data not shown). This could have been caused by an incursion of land-based nutrients, due to a forest fire or intensive logging activity in the watershed.

Similarly, the relationship of $\delta^{15}$N with PCB concentration was positive, but not significant at 97.5% with an $R^2$ of 0.49 (Table 4).

### 3.2.3. Shuswap and Bowron

Comparisons between down-core patterns in the sediments and escapement for Shuswap Lake are impeded by the highly variable spawner abundance, as described earlier. Spawner abundance in Shuswap Lake fluctuates not only with a four-year cycle, but also with a decadal cycle (see Fig. I A, supporting material). Total spawner numbers reached a maximum in 2002 with more than 4.6 million spawners (~13,000 per km²), but the average spawning number is around 560,000 (~1600 per km²). Therefore, the translation of this signal into the sediments is difficult to reconstruct. Neither the $\delta^{15}$N nor PCB concentrations were correlated to salmon escapement, which suggests that the complex escapement record and/or the trend extracted from the escapement data is not well preserved in the sediments. The down-core profiles of $\delta^{15}$N and PCB concentration, however, are positively related ($R^2=0.69$ with a delay of $\delta^{15}$N of 1 year, Table 4). It is probable that these two signals do represent salmon abundance in the sediments of Shuswap Lake since both can be linked to salmon and are affected by similar settling processes in the lake. However, due to the absence of a relationship between sockeye salmon escapement and $\delta^{15}$N or PCB concentration, we cannot draw definitive conclusions at this time.

Comparisons between trends in down-core data and escapement for Bowron Lake are complicated by its relatively low sedimentation rate, which translates into a low resolution of the down-core profiles. The task is further obscured by the variable salmon abundance numbers (Fig. I C, supporting material), and uncertainty in how this variability might be recorded in sediments of such low resolution. Dominant spawner numbers that occurred in Bowron Lake between 1960 and 2000 are not well expressed in the averaged dataset because of the very low numbers in subdominant and nondominate years that followed each dominant year. Similar to what was found for Shuswap Lake, it is difficult to determine whether the down-core profiles of $\delta^{15}$N and PCBs capture past spawner numbers in the sediments (Fig. 5). Even though PCBs and $\delta^{15}$N are also positively related in Bowron Lake, none of the regressions were found to be significant (Table 4).

Generally, it can be expected that in lakes with overall low salmon escapements other sources of PCBs and nutrients (such as the atmosphere, watershed, etc.) will be of greater importance compared to lakes with high salmon escapements. Therefore, weak relationships in low spawner lakes between variables such as PCBs or $\delta^{15}$N and escapement should not be surprising.

### 3.2.4. Frazer, Karluk, Red, and Upper Olga lakes

Historically, sockeye salmon did not have access to Frazer Lake because a 10-m high waterfall in the outlet stream prevented them from entering the system (Gregory-Eaves et al., 2003). Beginning in 1951, however, sockeye salmon eggs were deposited in the lake, and fish ladders over the falls were constructed in 1962 and 1979. These measures allowed for a self-sustaining population of sockeye salmon to establish in Frazer Lake and their abundances peaked in the early 1980’s (Fig. 5). On a coarse level, the PCB down-core pattern follows a similar trajectory as to that apparent in the escapement time series. However, these two time series could not be successfully related quantitatively. (Table 4, Fig. 5). PCB down-core concentrations were positively, but not significantly, related to $\delta^{15}$N values ($R^2=0.266$, delay $=2$ years, bootstrap $R^2$ at $97.5%=0.31$, Table 4). The most likely reasons for the poor relationship are the steep increase of the $\delta^{15}$N and PCB values in recent years, which occurs at a time when recent salmon escapement to Frazer Lake is decreasing, as well as the missing PCB increase during peak escapement around 1980 (Fig. 5).

When comparing the smoothed historical escapement with the down-core profile of $\delta^{15}$N in this lake, the similarities become apparent (Fig. 5). A regression of the two time series is very significant after a delay of $\sim 3$ years (i.e. the escapement is moved upward), with an $R^2$ of 0.83 ($p=0.0018$, bootstrap $R^2$ at $97.5%=0.62$, Table 4). Frazer Lake has been fertilized during the late 1980’s and early 1990’s, and a small dip of the $\delta^{15}$N values

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**Table 4 – $R^2$ of regressions for down-core data of the individual lakes**

<table>
<thead>
<tr>
<th>Lake</th>
<th>$\delta^{15}$N vs escapement</th>
<th>PCBs vs escapement</th>
<th>PCBs vs $\delta^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$ $R^2$ bstp. delay (yrs)</td>
<td>$R^2$ bstp. delay (yrs) $R^2$ bstp. delay (yrs)</td>
<td></td>
</tr>
<tr>
<td>Bowron</td>
<td>0.08 0.01  -5  -5  0.32 0.64 -5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraser</td>
<td>0.25 0.11  -1  -3  0.59 0.39 1 6.09 0.37 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mezadin</td>
<td>0.32 0.13  -3  -3  0.27 0.35 3 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quesnel</td>
<td>0.38 0.11  -3  -3  0.59 0.39 1 6.09 0.37 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shuswap</td>
<td>0.01 0.09  -5  -4  0.05 0.40 4 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frazer</td>
<td>0.41 0.05  0 0.49 0.25 0.55 6 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Karluk</td>
<td>0.83 0.05  -3  -3  0.27 0.35 3 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red</td>
<td>0.01 0.09  -5  -4  0.05 0.40 4 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U. Olga</td>
<td>0.41 0.05  0 0.49 0.25 0.55 6 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For each regression, $R^2$ value, the bootstrap $R^2$ at 97.5% (significance at $p<0.05$), as well as the shift (delay) in years are given.

* Significant regression at 97.5% level.

* Only based on 5 values.
can be seen around 1990 in this core (Fig. 5). When sediments were analyzed at a higher resolution, a more prevalent decrease in $\delta^{15}N$ was noted (Gregory-Eaves et al., 2003). Since fertilizers usually have depleted $\delta^{15}N$ values, a diluting effect can be expected if significant amounts are being added to the system.

Similar to Frazer Lake, down-core concentrations of $\Sigma$PCBs in Karluk Lake are dominated by the pronounced increase in contaminant concentration in the surface sediments, and could not be related to escapement or $\delta^{15}N$ pattern (Fig. 5, Table 4). Karluk Lake was also fertilized from 1986 to 1990, but only modest amounts were applied compared to Frazer Lake (Gregory-Eaves et al., 2003). A large increase in sockeye salmon escapement occurred simultaneously with fertilization in Karluk Lake. Gregory-Eaves et al. (2003) interpreted the relatively static $\delta^{15}N$ during this time as the product of both the lake fertilization program and an increase in escapement.

In our analysis, we found that $\delta^{15}N$ in dated sediments closely matched historical salmon abundance, when a 5 year delay was included in the escapement time series ($R^2$ of 0.8 after a delay of −5 years, $p=0.001$, bootstrap $R^2$ at 97.5%=0.46, Table 4).

Red Lake had the highest sockeye salmon escapements (on a per area basis) of all the lakes in this study, and historically was one of the highest sockeye salmon producing lakes on Kodiak Island. Unfortunately, there are no escapement data available for Red Lake between 1953 and 1963. Comparisons between historical escapement and the down-core profiles clearly show that $\delta^{15}N$ values do not track past salmon abundance in the sediments of Red Lake (Fig. 5, Table 4). The lack of a positive relationship between $\delta^{15}N$ in sediment cores and escapement has been observed previously, but reasons for this have not yet been resolved. It is unlikely that lower $\delta^{15}N$ values in sediments of remote lakes is caused by anthropogenic nitrogen deposition as reported by Wolfe et al. (2001) because of relative intensity of the salmon signal in these nursery lakes. A more likely explanation is related to the faster sedimentation rate of Red Lake, which is coupled to a relatively high total nitrogen content in the sediments. The total nitrogen content of Red Lake sediments is higher than in the other lakes, and increases towards the surface (data not shown). Under such conditions, diagenesis of the surface sediments may be less complete than in lower sediments,
resulting in a higher abundance of the lighter isotopes in the top few centimeters of the core relative to the older sediment.

Sockeye salmon escapement in Red Lake between 1960 and recent years has been relatively steady and without striking fluctuations that could be easily compared to contaminant down-core profiles (Fig. 5). In general, spawner numbers increased between 1960 and 1990, and declined thereafter. The down-core profile of \( \Sigma PCB \) concentrations also increased since the 1940’s but, similar to what was found in the other lakes, recent concentrations are not declining. Small peaks in spawner abundance during the 1980’s and early 1990’s may be reflected by the small peaks in the PCB down-core profile (Fig. 5). However, no significant regressions were found between \( \Sigma PCB \) concentrations and escapement or \( \delta ^{15}N \) (Table 4).

For Upper Olga Lake, no spawner numbers were available between 1958 and 1970, but the dip in \( \delta ^{15}N \) values around that time might suggest that spawner abundance in those years was in fact low (Fig. 5). A regression between escapement and the \( \delta ^{15}N \) down-core profile was positive (\( R^2 = 0.40 \)) after a shift of ~3.5 years (i.e., the escapement was shifted upward), but the regression is then based on only 5 values, which does not allow for reliable conclusions on its significance (Table 4). The \( \Sigma PCB \) down-core profile shows a maximum at the surface, a dip around 1990, and a relatively broad shaped peak between 1960 and 1980 (Fig. 5). A relationship between the \( \Sigma PCB \) down-core pattern and escapement or \( \delta ^{15}N \) was not detected (Table 4).

A common feature across all lakes studied was the rise in contaminant concentrations toward the surface sediments, which cannot generally be linked to sockeye salmon abundance. A recent study of a remote lake in the Canadian High Arctic likewise observed maximum concentrations of PCBs, endosulfan and other POPs at or near the sediment surface (Stern et al., 2005). These authors hypothesized that climate change producing a recent increase in algal productivity led to increased scavenging of contaminants from the water column (Stern et al., 2005). Similarly, a recent study of two lakes in the Canadian High Arctic found evidence of increased mercury scavenging due to increases in autochthonous primary productivity (Outridge et al., 2007). In our study, algal productivity was not investigated, but it is conceivable that similar mechanisms play a role in these sub-Arctic lakes, which also experience a prolonged winter with extensive ice cover.

Other possible reasons for an increase in PCB concentrations in surface sediments include higher loadings of PCBs in salmon, either due to a lag of PCB concentrations in the upper ocean reservoir relative to the atmosphere, or a shift of salmon feeding patterns in the ocean (e.g., salmon feeding in more contaminated areas). Since reliable measurements of contaminant concentrations in salmon over time are not available, it is difficult to verify this assumption. However, when salmon contaminant data derived from published studies in the same geographic area are compared (e.g., Gregory-Eaves et al., 2007; Hites et al., 2004; Ewald et al., 1998), it seems unlikely that contaminant concentrations in salmon increased over the last ~10 years.

4. Conclusions

We identified a historical relationship between PCB concentration and salmon spawner numbers for a sufficiently large dataset (as displayed in Fig. 2), where variation due to error and noise is small compared to the overall signal. In individual lakes, temporal relationships between salmon escapement, its proxy \( \delta ^{15}N \), and PCBs were complex. Only in Meziadin Lake could a PCB record be interpreted in the context of escapement intensity. For this site, the escapement density was moderately high and displayed a distinct pattern, and we had adequate sample resolution. In lakes with low salmon escapements a number of factors likely have a distorting influence on down-core profiles of the contaminants. In these lakes the relative importance of atmospheric input of POPs can result in higher contaminant concentrations in the sediments, which are not related to salmon abundance. Elevated contaminant inputs may also be observed due to events in the watershed, or nearby anthropogenic point sources. Recent increases in contaminants, which are not related to salmon numbers, may be related to higher algal productivity due to climate warming, with subsequent increased contaminant scavenging.

Furthermore, translation of the original signal (sockeye spawner numbers) into the lake sediment proxies (e.g., \( \delta ^{15}N \), PCBs) remains unclear especially where spawner abundance is highly variable (as seen with some lakes in B.C.). Extracting underlying trends from sediments in these circumstances is difficult. The problem is perhaps best illustrated in the Shuswap Lake data where a significant relationship between \( \delta ^{15}N \) and PCBs was detected in the sediment profile. This result suggests that PCB transport is mediated by the salmon in Shuswap Lake, even though escapement numbers could not be related to these profiles.

Overall, the data presented here show that very significant relationships between historical \( \Sigma PCB \) concentrations in lake sediments and sockeye salmon escapement, or its tracer in lake sediments, \( \delta ^{15}N \), may be found. However, the naturally high variability in the data from individual lakes resulted in an unfavorable signal to noise ratio. Even with data manipulation such as smoothing of escapement data and shifting of the time-series, significant regressions were rare in individual lakes. Data pooling was therefore necessary to develop sufficient power to overcome the noise.

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Appendix A. Supplementary data


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