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# Climatic Influence on Temporal Trends of Polychlorinated Biphenyls and Organochlorine Pesticides in Landlocked Char from Lakes in the Canadian High Arctic

Ana Cabrerizo,*[,†] Derek C. G. Muir,*[,†] Günter Köck,[‡] Deborah Iqaluk,[§] and Xiaowa Wang[†]

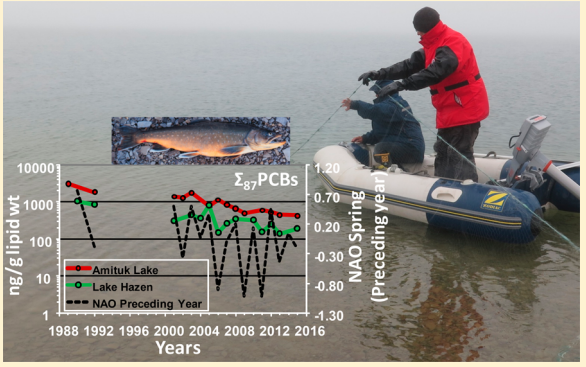
[†]Water Science and Technology Directorate, Environment and Climate Change Canada, Burlington, Ontario L7S 1A1, Canada

[‡]Institute for Interdisciplinary Mountain Research, A-6020 Innsbruck, Austria

[§]Resolute Bay, Nunavut XOA OVO, Canada

Supporting Information

**ABSTRACT:** Temporal trends and climate related parameters affecting the fate of legacy persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were examined in landlocked Arctic char from four lakes in the Canadian Arctic. Among biological parameters, lipid content was a key factor explaining the concentration of most POPs in Arctic char. Legacy PCBs and OCPs generally showed declining trends of concentrations in Arctic char, consistent with past restriction on uses and emissions of POPs. However, increases in lake primary productivity (measured as chlorophyll a) exerted a dilution effect on POPs concentrations in Arctic char. Concentrations of POPs in char from the last two decades were positively correlated with interannual variations of the North Atlantic Oscillation (NAO). Higher concentrations of POPs in Arctic char were observed in 3 of the 4 lakes during positive NAO phases. This, together with increasing local Arctic temperatures, could lead to increases on POPs concentrations in char from remote Arctic Lakes in future decades. Also, if there are nearby secondary sources as may be the case for Resolute Lake, located near an airport where increasing levels were found for hexachlorobenzene and toxaphene, probably due to the mobilization from secondary sources in soils.




## INTRODUCTION

Although the Arctic is one of the most pristine areas of the world, the presence of persistent organic pollutants (POPs) has been well documented over the past 30 years.[1−4] Legacy POPs such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDTs), and hexachlorocyclohexane (HCHs), and toxaphene have been detected in various biota samples from the High Arctic.[2,3,5] While much information on POPs is available on Arctic marine food webs,[6−9] less information is available on High Arctic lakes and their food webs. High Arctic lakes have simple food webs making them valuable for studies of bioaccumulation pathways and processes. Non-anadromous or landlocked Arctic char (*Salvelinus alpinus*) are usually the only fish species in lakes which are isolated from the ocean.[10] Due to its circumpolar distribution, Arctic char has been used as a sentinel species, which has allowed large scale spatial and temporal comparisons, mainly for mercury.[11−14] The few available published data on POPs in Arctic char are from lakes in Norway,[15] Sweden,[16] and Greenland,[17−19] although a recent POPs assessment from the Canadian Arctic includes a summary of trends in Arctic char.[20] These studies generally show significantly declining trends of PCBs, DDTs, toxaphene, and HCHs. Several factors have been proposed to account for accumulation of POPs in Arctic char and other northern freshwater fishes including food chain structure,[21] feeding strategy,[22] growth rate,[23] age, and lipid content,[22] as well as the trophic status of the lake.[15] However, it is still unclear how these factors, or their combination with other anthropogenic perturbations such as global warming, may affect the body burdens of POPs in Arctic char. Modeling efforts,[24,25] reviews,[26−29] limited atmospheric measurements in the Arctic,[30] and field studies in Antarctica[31] suggest that, as the Polar Areas warm, contaminants once trapped in ice/sediments and permafrost may revolatilize, leading to increasing concentrations. One way to study the influence of climate on POPs in food webs, is to examine the correlations between climate indicators and long temporal series.[32] Rigét and co-workers[33] first attempted this in landlocked char from a lake in Western Greenland based on 5 sampling years over the

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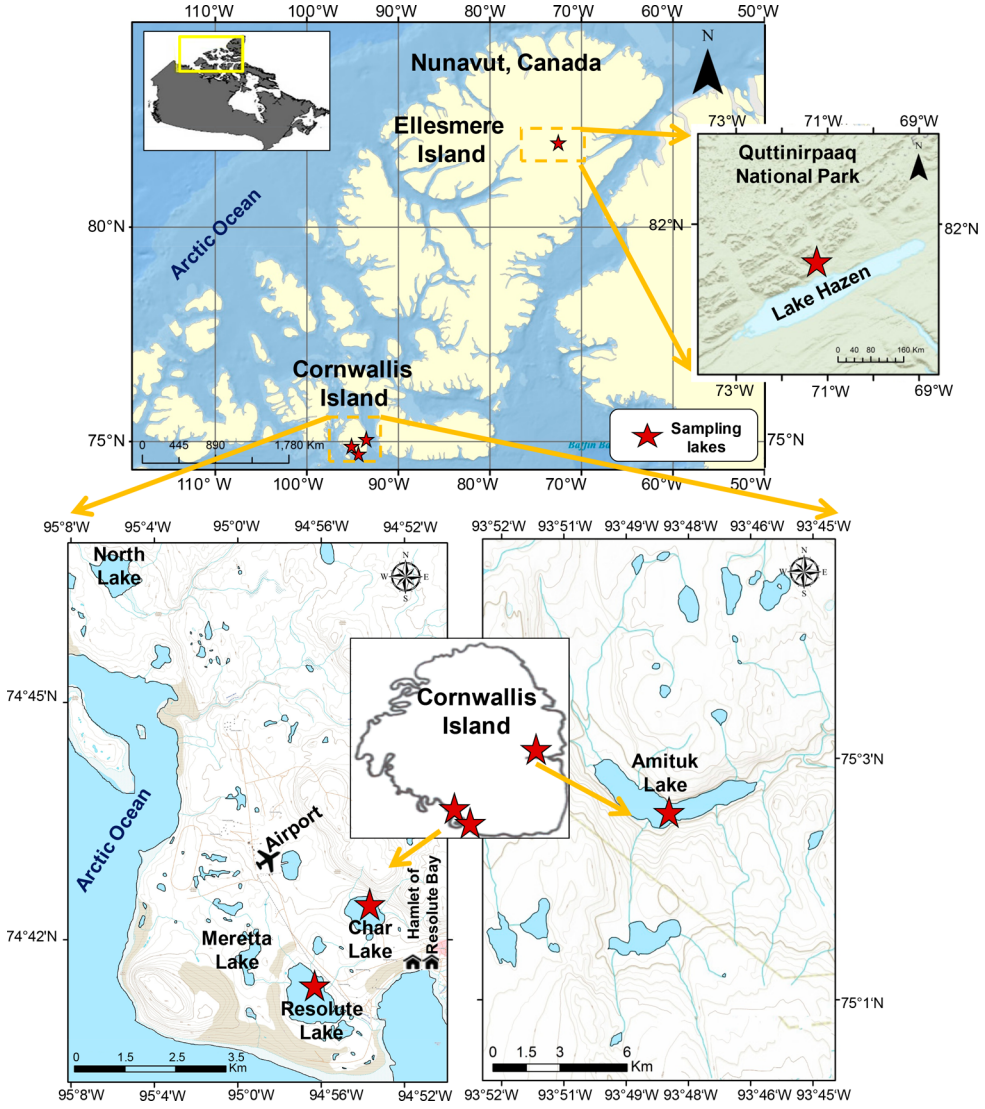


**Figure 1.** Sampling sites on Cornwallis Island (Resolute, Char, and Amituk Lakes) and on Ellesmere Island (Lake Hazen).

period 1994−2008 but did not find a correlation of PCBs and monthly mean summer temperature, which suggested that longer temporal trends would be needed. Therefore, the main objectives of this study were (i) to examine the trends of legacy POPs such as PCBs, OCPs (DDTs, HCHs, and HCB), and toxaphene in Arctic char, collected at four lakes in the Canadian Arctic, over a long time period (1989 and early/mid 1990s to 2015), (ii) to study which parameters are affecting the occurrence of POPs in Arctic char, and (iii) to investigate whether or not climatic parameters and climatic oscillation indices may be linked to the temporal trends of POPs in Arctic char.

## EXPERIMENTAL SECTION

**Study Site and Sample Collection.** Three lakes (Amituk, Resolute, and Char Lakes) located on Cornwallis Island (75°04′60.00″ N, 95°00′0.00″ W) and one lake (Lake Hazen) located on Ellesmere Island (80°45′1.40″ N, 72°39′54.69″ W) (see Figure 1 for sampling site location) were selected for this study. Contaminant trends in Arctic char from these lakes have been extensively studied but mainly for mercury and other metals.[11,34] Adult char (>200 g) were collected in late July from almost every year from 2001 to 2015 and less frequently in the 1990s in Amituk, Resolute, and Hazen Lakes, by gill netting or by jigging through the ice at a rate of 7−25 adult fish per lake and year, with the exception of Char Lake, where the collection was in the range of 3−10 fish per year. All fish were length measured (cm), weighted (g), and dissected in situ within 1 to 4 h after collection. Subsamples of muscle+skin and otoliths were kept frozen for transport and storage (−30 °C). In total, $n$ = 474 samples from Arctic char (muscle+skin) were collected and analyzed for POPs in this study.

Water samples, collected annually at the same time as fish sampling, were analyzed for chlorophyll a (CHLa) as described in the Supporting Information and elsewhere.[35] One surface soil sample from the catchment areas of Amituk, Resolute, and North Lakes was also collected in 2016. Each soil sample consisted of a pool of several soil samples located within 2 $m^2$ of the selected sampling site. Soil samples were collected in clean certified jars and kept at −30 °C until the analysis.

*Analytical Methods.* Char muscle+skin samples were analyzed for PCBs, organochlorine pesticides, and other chlorinated organics by ALS Global Laboratories (Burlington, ON) (2011−2015) and by Environment Canada (National Laboratory for Environmental Testing (NLET)) for others from 1992 to 2010. Both laboratories are accredited by the


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Canadian Association for Laboratory Accreditation and ISO 17025 certified. Samples from 1989 to 1992 from Amituk Lake and 1990 from Hazen Lake were analyzed at the Freshwater Institute (Fisheries and Oceans, Winnipeg).[36] Extraction and isolation steps in all three laboratories generally followed US EPA Method 1699[37] and have been previously described.[38,39] Further details regarding extraction, isolation steps, and methodology used for the analysis of each pollutant are given in Annex I of the Supporting Information. PCBs (87 congeners from mono- to decachloro PCBs) and OCPs (HCHs, including $\alpha$-HCH, $\beta$-HCH, and $\gamma$-HCH; DDTs including o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT, p,p′-DDT, and HCB) were analyzed, together with toxaphene, quantified using a technical toxaphene standard.[40] Individual toxaphene congeners (P26, P50, P62) were also determined in a subset of samples from all four lakes (2012–2015). The reference to the sum of homologue groups or the total sum of PCB (ΣPCBs), HCHs (ΣHCHs), and DDTs (ΣDDTs) considers the congeners and isomers mentioned above and in Annex I of the Supporting Information.

For the soils, wet subsamples (35 g) were homogenized, weighed, and mixed with equal parts of clean Hydromatrix (diatomaceous earth; Dionex); then, the mixture was spiked with $^{13}$C-labeled PCBs and extracted in an accelerated solvent extractor (ASE 300; Dionex). PCBs (70 congeners from mono- to decachloro PCBs) together with HCB were analyzed. Further details on soil extraction and analysis are described in Annex I of the Supporting Information.

*Quality Assurance/Quality Control.* All samples were homogenized and extracted in dedicated clean laboratories with positively pressured and HEPA filtered air. Batches of char samples were extracted with method blanks and standard reference materials (SRM1946 or SRM1947 lake trout, National Institute of Standards and Technology, Gaithersburg, MD, USA) at a rate of 1 every 9 samples processed. Method detection limits (MDLs) of analytes were determined as 3 times the standard deviation (SD) of method blank concentrations and are reported in Table S1. Laboratory blanks were also included in every set of soil sample extractions (1 blank every 5 samples). Low levels of PCBs were found in the blanks, indicating minimal contamination during processing. Further information is shown in Annex I of the Supporting Information and Table S2.

Stable carbon ($\delta^{13}$C) and nitrogen ($\delta^{15}$N) isotope ratios were determined on all fish muscle at the Environmental Isotope Laboratory (University of Waterloo, Waterloo, ON, Canada). The age of the fish was determined from the otoliths using the break and burn method or thin-section method reported elsewhere.[34,35] Climatic parameters such as North Atlantic Oscillation (NAO), Arctic Oscillation (AO), and Pacific North American Pattern (PNA) for all the relevant years were obtained from the Web site of the U.S. National Weather Service, Climate Prediction Centre (http://www.cpc.ncep.noaa.gov/), while local climatic parameters such as temperature ($T$), precipitation, snow cover, and ice thickness were obtained from the weather stations in Resolute and Eureka (http://climate.weather.gc.ca/).

All statistical analyses were conducted using SPSS 20. Non-detected concentrations were replaced with half of the detection limit for calculation of arithmetic and geometric means and standard deviations. Results for all POPs were $\log_{10}$ transformed in order to reduce coefficients of skewness and kurtosis. Statistically significant results were assessed against a type-1 error rate of probability <0.05. Temporal trends were examined using the PIA software package[41] that has been utilized for studies of trends and statistical power of Arctic data sets.[1,42]

## RESULTS AND DISCUSSION

**Fish Biology.** The individual Arctic char ranged from 8 to 37 years in age, from 21 to 82 cm in body length, and from 200 to 3148 g of weight (Table S3). A close coupling correlation ($r^2$ = 0.69, $p$ < 0.001) was observed between length and weight over the data set (Figure S1). Analyses of $\delta^{15}$N and $\delta^{13}$C for the four lakes are shown in Figures S2 and S3. Although Arctic char from the different lakes are at the same trophic level, the $\delta^{15}$N isotopic signature varied significantly. The wide range of stable isotope signature has been previously observed in Arctic char collected within these lakes[34,43] and may reflect the fact that there are different morphotypes of char present[34] and therefore different feeding behaviors among individual char. Additionally, nitrogen (N) deposition caused by recent anthropogenic N may have influenced $\delta^{15}$N, but little is known about the variability of atmospheric N inputs to the Arctic.[34] Some studies[44] based on ice corer records have pointed out slight increases of N deposition in the Arctic caused by recent anthropogenic N enrichment of the atmosphere, although data for profundal sediments in Lake Hazen showed no significant trends despite the increase of nitrogen inputs from glacial rivers.[45] Mean $\delta^{13}$C showed marked significant differences between the lakes (Figure S3). Arctic char $\delta^{13}$C values were generally more negative (i.e., more pelagic carbon) in Char, Resolute, and Amituk Lakes than in Lake Hazen (Figure S4). Although fluctuations on $\delta^{13}$C were found within the years, a significant decline of $\delta^{13}$C (arithmetic means vs years) was observed only in Amituk Lake ($r^2$ = 0.81, $p$ < 0.001) and Lake Hazen ($r^2$ = 0.57, $p$ < 0.05) which may suggest a change in the carbon sources, while no decline or increasing trends were observed in Resolute and Char Lakes. Fish condition factor (CF),[46] which is a measure of the overall health for the fish (CF: [body weight (g)/body length (cm)$^3$] × 100), ranged from 0.44 to 1.07.

**Occurrence of Legacy POPs in Arctic Char.** Among the selected POPs measured in Arctic char, toxaphene and PCBs always showed the highest concentrations followed by ΣDDT > ΣHCH ≥ HCB (Table S4). Geometric mean concentrations ranged from 1.6 to 172 ng/g ww (wet weight) for toxaphene, from 4.8 to 127 ng/g ww for total PCBs ($\Sigma_{87}$PCB; sum of 87 PCB congeners and coeluters), from 0.54 to 61 ng/g ww for ΣDDT, from 0.03 to 4.24 ng/g ww for ΣHCHs, and from 0.48 to 4.37 ng/g ww for HCB (Table S4). Concentrations of individual toxaphene congeners such as P26, P50, and P62 determined in a subset of samples from 2005 to 2015 ranged from 0.32 to 7.86, 0.20 to 9.33, and 0.02 to 3.37 ng/g ww, respectively (Table S5). The predominance of PCBs and toxaphene in freshwater fish from lakes and rivers in northern Canada was first noted in samples collected in the 1980s[47] and confirmed in more recent studies.[20,48] Overall, PCB homologue profiles were not statistically different among years and lakes, with those congeners having 5 and 6 chlorine atoms contributing up to ∼70% of $\Sigma_{87}$PCB in Arctic char (Figure S5), illustrating the higher bioaccumulation and persistence of these PCB congeners. Although the concentration of PCBs and other POPs has fluctuated over the years as discussed further below, the concentrations reported here are of similar magnitude to those previously reported in the peer reviewed


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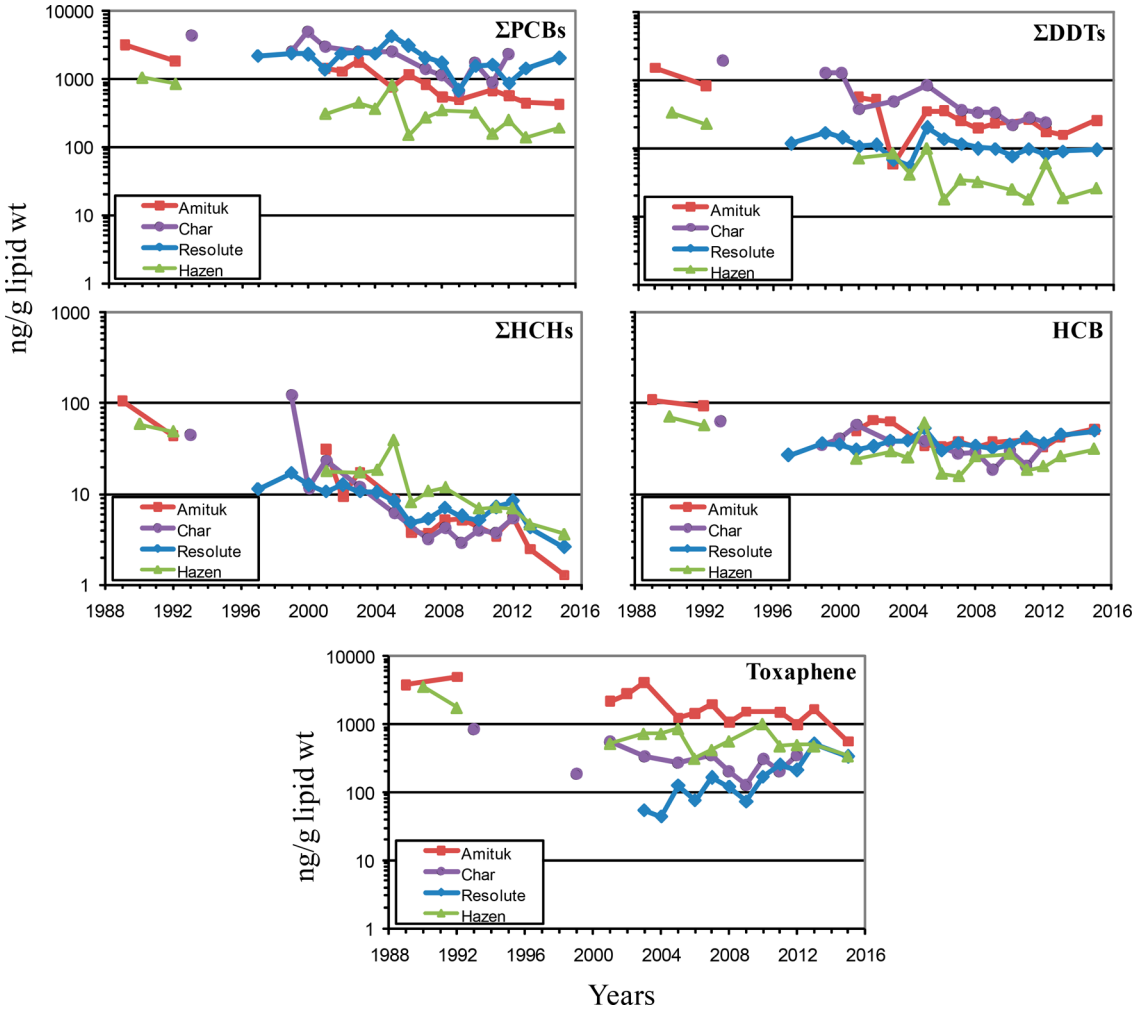


**Figure 2.** Trends in concentrations of ΣPCBs, ΣDDTs, ΣHCHs, HCB, and toxaphene (ng/g lipid wt) in Arctic char muscle from Amituk, Char, Resolute, and Hazen Lakes from 1989 to 2015.

literature (Table S6) for remote Arctic lakes in Nunavut (Canada)[2,3] and in a time series from 1994 to 2008 in Southwest Greenland.[33] Relatively higher $\Sigma_7$PCBs (sum of 7 congeners) concentrations have been reported in Arctic char collected from lakes on the island of Bjørnøya (Norway) averaging 695 ng/g ww for fish from Lake Ellasjøen and 49 ng/g ww for fish from Lake Øyangen. However, Ellasjøen is impacted by seabird guano which provides an additional source of POPs.[15]

Along with toxaphene, the $\alpha$- and $\gamma$-HCH isomers together with HCB and p,p′-DDE were the most common individual OCPs found in Arctic char from the four Canadian Arctic lakes. Mean concentrations of ΣDDTs, HCB, and ΣHCHs detected in Arctic char muscle of Greenland (Table S6) over the time series 1994−2008[33] were in the range from 0.74 to 7.51 ng/g ww for ΣDDTs, 0.25 to 0.73 ng/g ww for HCB, and 0.05 to 0.25 ng/g ww for ΣHCH, which are in a similar range as those reported in this study (Tables S4 and S6). Overall the highest concentrations of ΣPCBs and OCPs regardless of the sampling year occurred in Resolute and Char Lakes which may be attributed to reemissions from secondary sources (e.g., soils) in the area due to their proximity to the Resolute airport and hamlet of Resolute Bay (population of 200 inhabitants) (see Figure 1). In fact, higher concentrations of $\Sigma_{70}$PCBs (2.83 ng/g dry weight (dw)) and HCB (0.134 ng/g dw) were measured in soil collected in the Resolute Lake catchment, in comparison to those soils collected near Amituk Lake, a remote site 40 km north of Resolute Bay ($\Sigma_{70}$PCBs and HCB of 0.061 ng/g dw and 0.013 ng/g dw, respectively), or 5 km west of the airport near North Lake ($\Sigma_{70}$PCBs: 0.089 ng/g dw; HCB: 0.029 ng/g dw) (Table S7 and Figure 1). A military and civilian airport has operated in the Resolute Lake catchment since 1949, and its wastewaters were discharged into the upper area of the catchment until 1997. The discharge greatly impacted the water chemistry of Meretta Lake,[49,50] and waterborne contaminants could have moved downstream into Resolute Lake (Figure 1). PCB contamination of land surrounding military radar facilities in the Canadian Arctic has been relatively well documented.[51] However, to our knowledge, PCB contamination of soils within the Resolute Lake catchment has not been studied previously. Overall, lower concentrations of POPs were found in Arctic char from the most remote of the studied lakes (Lake Hazen).

The influence of lipids, which ranged from 1.54% to 7.96% (geometric means) on concentrations of POPs, was assessed by regression analysis. Figure S6 shows the significant dependence ($p$-level <0.05) of concentrations of $\Sigma_{87}$PCBs ($r^2$ = 0.13−0.20), ΣDDTs ($r^2$ = 0.13−0.28), ΣHCHs ($r^2$ = 0.19−0.45), HCB ($r^2$ = 0.24−0.64), and toxaphene ($r^2$ = 0.14−0.45) on lipid content, thus indicating that it is a key factor


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controlling POPs concentrations in Arctic char especially in Amituk, Resolute, and Char Lakes. On the other hand, lipid content was an important parameter explaining the concentration of ΣHCHs (Figure S7) only when insectivorous char from Lake Hazen ($\delta^{15}$N < 12‰) were considered. Previous studies showed that char in Lake Hazen were mainly insectivorous, feeding mostly on chironomids, which resulted in a lower $\delta^{15}$N signature, whereas some individuals may feed opportunistically on small char, which is reflected in the higher $\delta^{15}$N signature.[34] A positive statistically significant dependence of $\Sigma_{87}$PCBs and ΣDDTs on $\delta^{15}$N was observed in the four lakes (Figure S8) with $r^2$ in the range from 0.11 to 0.34. Concentrations of $\Sigma_{87}$PCBs, ΣDDT, ΣHCH, and HCB, but not toxaphene, were significantly correlated with each other (Table S8) across the whole set of char samples, which suggests common sources and pathways, as well as evidence of the common role of lipid content as a descriptor of the burden of hydrophobic pollutants. Due to the importance of lipid as a key parameter, lipid normalized concentrations (ng/g lipid weight (lw)) were regressed against covariates such as fish length, weight, age, CF, $\delta^{15}$N, and $\delta^{13}$C. However, no consistent statistically significant relationships were found. Further details are provided in Tables S9−S12. The modest influence of biological parameters, other than lipid content, to explain a small percentage of the variation in concentrations of POPs, and the year of sampling, suggests that other factors such as climate influences on the status of the lakes and their food webs or changes in the biogeochemical cycling of POPs may affect their bioaccumulation in Arctic char once primary sources have leveled off or disappeared.[52,53]

**Trends of Legacy POPs in Arctic Char.** Temporal trends of $\Sigma_{87}$PCBs, ΣDDTs, ΣHCHs, HCB, and toxaphene in Arctic char from the four lakes are shown in Figure 2, and the annual percent of change is in Table S13. Overall, most legacy POPs and OCPs showed declining trends which can be attributed to the past national and regional bans and restriction on uses and emissions of legacy POPs in circumpolar and neighboring countries. ΣPCBs and ΣDDTs declined in all lakes, at statistically significant rates from 6.7%/yr to 7.6%/yr for $\Sigma_{87}$PCBs and 7.1%/yr to 11%/yr for ΣDDTs, when considering the whole time series (between 12 and 17 years). The exception was Resolute Lake, where declines of 3.5%/yr for $\Sigma_{87}$PCBs and 2.3%/yr for ΣDDTs were not significant probably due to the presence of secondary sources of POPs in the catchment area as mentioned above. The p,p′-DDE/ΣDDTs ratio (Figure S9) in char has increased significantly during the last 15 years in all 4 lakes ($p$ < 0.05) indicating no ongoing or recent inputs of p,p′-DDT, consistent with previous studies on Arctic biota.[1,54] $\Sigma_{87}$PCBs and individual PCBs congeners (e.g., PCB153) have declined in the majority of time series studies for arctic marine and freshwater biota[1] including this study (Table S13). The mean annual decrease was 3.7% ($t_{1/2}$ = 18 yr) for $\Sigma_{10}$PCB, 3.8% ($t_{1/2}$ = 19 yr) for PCB153, and 4.2% ($t_{1/2}$ = 17 yr) for ΣDDT.[1] Thus, rates of decline reported here for char in Canadian Arctic lakes are actually more rapid than % declines for arctic biota as a whole.

α-HCH also declined significantly in all 4 lakes, with the overall greatest annual change (7.8%/yr to 14%/yr) of all POPs analyzed. Similar to ΣPCBs and ΣDDTs, Resolute Lake showed the lowest declines for α-HCH, about 40% slower than in nearby Char Lake. On the other hand, β-HCH did not show significant declines in Amituk, Resolute, and Char Lakes but increased significantly in Lake Hazen from 1990 to 2013 (6.1%/yr). The recent assessment of temporal trends of POPs in circumpolar arctic biota[1] found that β-HCH time series were quite different from those for α-HCH, with 64% of the time series starting before 2000 showing no significant trend. Air sampling at Alert showed increasing trends of β-HCH from 2003 to 2007 followed by a decline to 2012.[55] Re-emission of β-HCH from oceans due to sea ice retreat may sustain levels in Arctic air[53] and could be a factor, although it would be expected to influence lakes on Cornwallis Island as well. A unique aspect of Lake Hazen is the influence of glacier melting which increased in the period of 2003−2012 leading to increased fluxes of POPs to lake sediments.[45] Greater water solubility of β-HCH, resulting in its partitioning more strongly to water[56] (and greater recalcitrance due to its uniform equatorial chlorine substitution), may explain the differences between the trends of the two isomers.

HCB was found to have declined significantly in Amituk, Char, and Hazen Lakes at a rate of 4%/yr, while an increasing trend was observed in Resolute Lake (1.8%/yr). Most time series of HCB in biota across the North American and European Arctic have observed slowly decreasing trends of HCB at a rate of 2.6%/yr ($t_{1/2}$ = 18 yr).[1] HCB also showed a very slow decline in air at Alert ($t_{1/2}$ = 29 yr).[55] The limited decline compared to other POPs has been attributed to continuing primary and secondary emissions due to the presence of HCB as a byproduct, e.g., in some pesticides.[55] Increasing trends of HCB, since 2000, were also detected in black guillemot eggs[57] and adult polar bears[39] from eastern Greenland, suggesting that emissions and releases of HCB are still occurring in the environment.

Toxaphene was found to have only declined significantly in Amituk Lake (6.4%/yr) and Lake Hazen (7%/yr), which contrasts again with significant increases in Resolute Lake (19%/yr). Overall, declines in the concentration of toxaphene congeners, P26, P50, and P62, were also observed in Hazen and Amituk Lakes, while P62 showed an increasing trend in Resolute Lake, although trends were not statistically significant due to the limited number of years available (2012−2015) (Figure S10). The limited literature available on trends of toxaphene on freshwater fish shows variations with species and location. Declining toxaphene (sum of 6 congeners; 4.9%/yr from 2000 to 2012) was found in Arctic char from southwestern Greenland,[18] although the trend was not statistically significant, probably because average concentrations from 2010 to 2012 showed a slight increase. Decreasing trends were observed in lake trout from Lake Laberge (Yukon Territory) over the time period of 1993−2010.[48] A period of increasing toxaphene in burbot liver from the Mackenzie River was observed from 2001 to 2008[58] and was tentatively attributed to mobilization of old sources of toxaphene in the area.[20] Mobilization of old sources appears to be occurring as well in Resolute Lake and its catchment. Like DDT and possibly HCHs and toxaphene may have been brought into the airbase for insect control and subsequently deposited in the upper catchment from wastewater or sewage sludge. Remobilization of older atmospherically deposited sources within the catchment is less likely, given that no increases were observed in nearby Char Lake or at Amituk or Hazen Lakes.

Therefore, the declines of POPs observed in Arctic char seem consistent with the bans and phase outs of POPs during the 1970s and the following two decades,[2,3] declining trends of POPs in the Arctic atmosphere[1,59] and in freshwater and



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marine biota.[1,19,42] Differences in the decreasing/increasing trends of certain legacy POPs in the recent years, not explained by fish biological covariates, may be explained by (i) re-emissions from secondary sources, as suggested in other studies,[24,27,31,32] which may be enhanced by warming, (ii) changes in the atmospheric circulation patterns, which are responsible for the distribution of POPs around the globe, and on the lake biogeochemical cycles of POPs, or (iii) the combination of all these factors.

**Climatic Influence on the Biogeochemical Cycles of Legacy POPs in Arctic Char.** Annual air temperatures exhibited increasing trends on the study area over the time period of this study (1989−2015) with $r^2$ ranging from 0.29 to 0.64 (Figure S11). This warming has resulted in increasing summer glacier surface temperatures in the Canadian High Arctic Island over the period of 2005−2012,[60] together with a reduction of precipitation in the form of snow (Figure S12). Together these changes may have induced alterations in the lake productivity.[61] Our water chemistry results show that increases in primary productivity (indirectly measured as CHLa) have been observed since 2005 in Resolute and Amituk Lakes. Although analyses of CHLa were also carried out for the early years, CHLa was under the detection limit (0.1 $\mu$g/L) until 2005 and for some years after 2005. Therefore, only those CHLa measurements above the detection limit and in which POPs concentrations from char were available were included in the regression analysis. CHLa concentrations in Amituk and Resolute Lakes are significantly correlated with mean summer air temperatures (Figure S13). Several studies[62−65] have noted the important role that biomass (plankton) plays on lacustrine[62,63] and marine environments[64,65] in depleting dissolved-phase POPs concentration in aquatic environments, a process known as the biological pump. Figure 3 shows a statistically significant negative correlation between the concentration of PCBs (ng/g lw) in Arctic char and lake CHLa over the temporal series, when considering Resolute and Amituk Lakes together and in Figure S14 for the individual lakes. The declines of PCBs with increasing lake CHLa suggest that the declining trends of POPs in Arctic char observed over the temporal series may be not only due to the effect of the restrictions in the use of these chemicals in the past but also due to the effect of the biological pump. This is due to a coupling of air−water exchange and settling fluxes of particle-associated POPs, which may have led to the depletion of the hydrophobic compounds in the photic zone of the Arctic lakes, when the primary productivity (or plankton biomass) was higher and therefore exerting a biodilution effect on POPs concentrations in the lowest and therefore upper levels (such as Arctic char) of the food web. This suggests that the entrance of pollutants through the atmosphere may have not been fast enough to compensate the vertical losses of POPs with the exception of Resolute Lake, where the re-emission of pollutants from the catchment area may be influencing the temporal trends in char to a greater extent.

Lake productivity and other local climatic events may also be linked to hemispheric scale trends. Interannual atmospheric climate fluctuations such as AO, PNA, and NAO have been shown to have an important impact on the global pollutant distribution and transport.[53,66,67] Of all of them, the NAO has been suggested to be one of the dominant patterns of large-scale climate variability in the Arctic with poleward transport from Europe, North America, and (though less pronounced) Asia being faster under NAO$^+$. This increases concentrations of

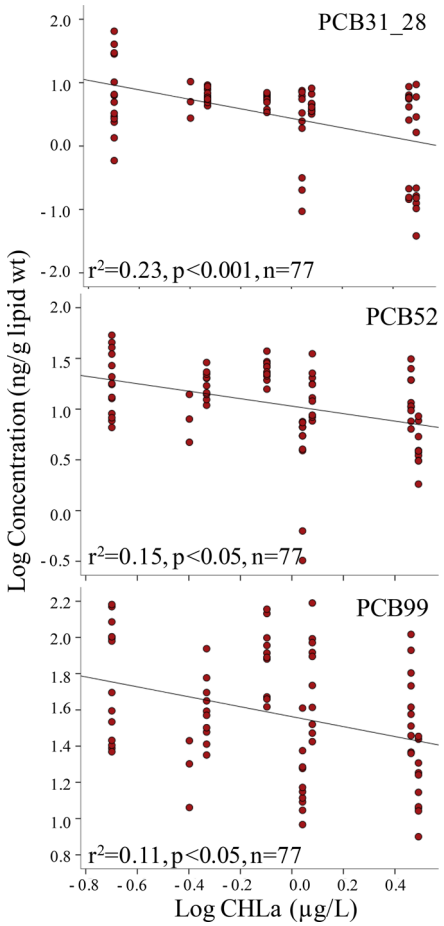


**Figure 3.** Influence of CHLa ($\mu$g/L) on the concentrations of selected PCBs (Log PCB31_28, PCB52, PCB99; ng/g lipid wt) on Arctic char in High Arctic lakes over the period of 2005−2015.

atmospheric pollutants in the Great Lakes and Arctic regions during spring and summer[67,68] and may influence the ice out of the lakes and food webs (e.g., insect emergence which supplies most carbon to the fish[35]). The influence of climate variability and temporal changes in POPs concentrations were assessed by a regression analysis considering the current spring and summer NAO. Also preceding spring and summer NAO were included in the analysis since concentrations of POPs found in Arctic char in a current year are likely to have been transported to the Arctic during the previous year.[26,69] Statistically significant correlations between preceding spring and summer NAO values and ΣPCBs, ΣDDTs, and ΣHCH concentrations were observed in Arctic char from the most northerly and remotest lake (Lake Hazen) (Figures 4 and S15) with $r^2$ between 0.16 and 0.33 ($p < 0.001$) while weaker (0.03−0.11 $p < 0.05$) or no statistically significant correlations were observed when using current spring and summer NAO (Figures 4 and S15). Overall, a similar pattern was observed in Char and Amituk Lakes (Figures S16 and S17). Although there was an overall negative trend in NAO, as of about year 2001, mean concentrations of POPs in Arctic char can be seen to follow NAO fluctuations in Lake Hazen (Figure 5). A few previous examples are available in the literature relating climatic indices and POPs in biota, but they have mainly focused on top predator mammals such as ringed seals,[70] terrestrial raptors,[71] and seabirds.[72] These studies also showed higher concentration of POPs following years with high air transport toward


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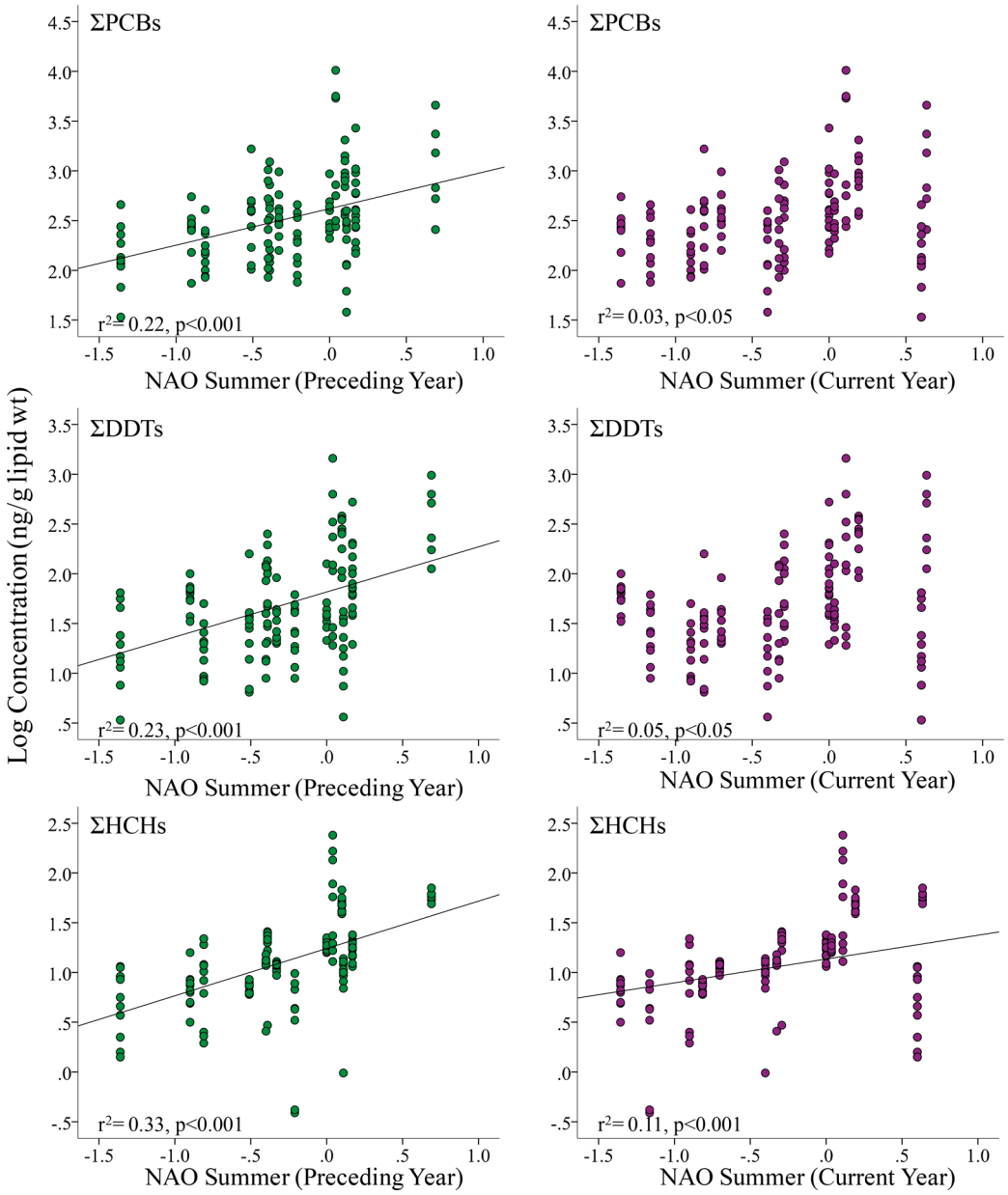


**Figure 4.** Relationships between the concentrations of Log ΣPCB, ΣDDTs, and ΣHCHs (in ng/g lipid wt) in char from Lake Hazen and the predictor: NAO in the preceding and current summers and springs (in Figure S15). Relationships for Amituk and Char Lakes are shown in Figures S16 and S17.

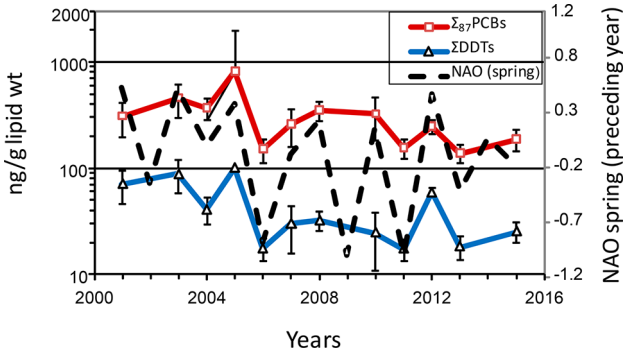


**Figure 5.** Temporal trends (2001 to 2015) of NAO index (preceding year spring NAO) and concentration of ΣPCBs and ΣDDTs (ng/g lipid wt) in Lake Hazen.

the Arctic during $AO^+$ or $NAO^+$ phases. To assess the influence of local and global climatic parameters on long temporal series of POPs in Arctic char, NAO and/or other local climatic parameters (e.g., *T*, precipitation, snow cover, ice thickness, CHLa, etc.) together with biological parameters such as body weight, length, CF, $\delta^{13}C$, or $\delta^{15}N$ were initially included in a multiple regression analysis. Although *T* is an important parameter affecting the fate and distribution of POPs not only in the Arctic but also at a global scale, it was not a statistically significant parameter ($p > 0.05$) when included in the multiple regression model. Different reasons may account for the lack of dependence: (i) local temperature variability may have not been registered by the selected weather stations, (ii) ambient air temperatures fluctuate considerably much more during the season than profundal lake water temperature where Arctic char live most of the time (unfortunately, no lake



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Environ. Sci. Technol. 2018, 52, 10380−10390

water $T$ was available in the study), or (iii) longer temporal series may be needed to see the effect on $T$.[33] Therefore, only the statistically significant and independent parameters were included in the final multiple regression model as [1].

$$\text{Log [POPslw]} = a + b\ (Y) + c\ (\text{Log } W \text{ or Log } P) + d\ (\text{NAO\_preceding year}) \quad (1)$$

where $Y$ is the year of sampling, $W$ is the fish weight, $P$ is the total annual precipitation (rain + snow), and NAO is the preceding year spring or summer NAO. Table S14 shows the fitting parameters and $p$-values for each lake and POPs considered. Overall, the fitted eq 1 for each lake explained 18−41% of the variability of ΣPCBs ($r^2$ = 0.18−0.41, $p < 0.001$) for Hazen, Amituk, and Resolute Lakes. Inclusion of NAO_preceding year fluctuation in the regression model enhanced the explained variability of temporal trends of ΣPCB in the study lakes by 11−50%, in comparison to a regression model which did not include it (Tables S15 and S16). In the same way, the inclusion of climatic parameters on the regression model explained 11−55% of the variability of ΣDDTs ($r^2$ = 0.11−0.55, $p < 0.001$) in Arctic char from Hazen, Amituk, and Resolute Lakes which also accounted for an increase of 6−57% on the explained variability, although NAO had only a positive effect in the remotest lake. Greater variability ($r^2$ = 0.53−0.87) was explained by eq 1 for ΣHCHs, which suggests increases of 2−17% in comparison to a regression model where climatic parameters are not considered (Table S16). Concentration of ΣHCHs in Arctic char was positively correlated with annual precipitation (rain + snow) suggesting the importance of a wet deposition pathway delivering HCHs into the Arctic lakes. Climatic parameters (e.g., precipitation) and NAO were also able to explain the increasing trend of $\beta$-HCH (from 1990 to 2012) in Lake Hazen, the most northerly lake (Figure S18), with $r^2$ between measured and estimated of 0.21, $p < 0.05$. The fact that climatic parameters and climate indices are able to enhance the understanding of long temporal trends of POPs provides a potential tool for the estimation of environmental concentrations and the fate of POPs in Arctic char. Future simulations and more than half of multimodel analyses predict that a positive trend in the NAO[66,73−75] may be dominant in the following years as an effect of anthropogenic warming.[76] This fact together with increasing local Arctic temperatures could increase POPs concentrations in char from the High Arctic lakes in the following decades, particularly if there are nearby secondary sources as may be the case for Resolute Lake, where increasing levels have already been shown for HCB and toxaphene. However, this effect may be counteracted by the effect of the biological pump as suggested above. Whether this applies to other newer POPs such as perfluorinated alkyl acids and brominated flame retardants, which achieved maximum concentrations in char in the mid-2000s,[20] is still unknown and may require a longer time series.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01860.

Ancillary material and additional figures and tables: Analytical methods; fish biology; occurrence of legacy POPs in Arctic char; trends of legacy POPs in Arctic char; influence of climatic oscillations on the occurrence of legacy POPs in Arctic char (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail: derek.muir@canada.ca.
*E-mail: anacabrerizopastor@hotmail.com.

### ORCID

Ana Cabrerizo: 0000-0002-5933-1483


### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) AMAP. *AMAP Assessment 2015: Temporal Trends in Persistent Organic Pollutants in the Arctic*; Norway Arctic Monitoring and Assessment Programme: Oslo, 2016; vi+71 pp.

(2) De March, B. G. E.; De Wit, C.; Muir, D. C. G.; Braune, B. M.; Gregor, D. J.; Norstrom, R. J.; Olsson, M.; Skaare, J. U.; Stange, K. Persistent Organic Pollutants. In *AMAP Assessment Report: Arctic Pollution Issues, Chapter 6*; Arctic Monitoring and Assessment Programme: Oslo, Norway, 1998; pp 183−372.

(3) De Wit, C. A.; Fisk, A. T.; Hobbs, K. E.; Muir, D. C. G.; Gabrielsen, G. W.; Kallenborn, R.; Krahn, M. M.; Norstrom, R. J.; Skaare, J. U. *AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic*; Arctic Monitoring and Assessment Programme: Oslo, Norway, 2004; p xvi + 310.

(4) Muir, D. C. G.; de Wit, C. A. Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations. *Sci. Total Environ.* **2010**, *408*, 3044−3051.

(5) Villa, S.; Migliorati, S.; Monti, G. S.; Holoubek, I.; Vighi, M. Risk of POP mixtures on the Arctic food chain. *Environ. Toxicol. Chem.* **2017**, *36*, 1181−1192.

(6) Muir, D. C. G.; Braune, B.; de March, B.; Norstrom, R. J.; Wagemann, R.; Lockhart, L.; Hargrave, B.; Bright, D.; Addison, R.; Payne, J.; Reimer, K. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Sci. Total Environ.* **1999**, *230*, 83−144.

(7) Vorkamp, K.; Rigét, F. F.; Glasius, M.; Muir, D. C. G.; Dietz, R. Levels and trends of persistent organic pollutants in ringed seals (*Phoca hispida*) from Central West Greenland, with particular focus on polybrominated diphenyl ethers (PBDEs). *Environ. Int.* **2008**, *34* (4), 499−508.

(8) McKinney, M. A.; Pedro, S.; Dietz, R.; Sonne, C.; Fisk, A. T.; Roy, D.; Jenssen, B. M.; Letcher, R. J. A review of ecological impacts of global climate change on persistent organic pollutant and mercury pathways and exposures in arctic marine ecosystems. *Curr. Zool.* **2015**, *61* (4), 617−628.




DOI: 10.1021/acs.est.8b01860
*Environ. Sci. Technol.* 2018, 52, 10380−10390

(9) Vorkamp, K.; Muir, D. C. G. A circumarctic review of contaminants in ringed seals. In *From Pole to Pole. Implications and Consequences of Anthropogenic Pollution in Polar Environments*; Kallenborn, R. E., Ed.; Springer: Berlin Heidelberg, 2016; pp 229−25.
(10) Power, M.; Reist, J. D.; Dempson, J. B. Fish in high-latitude Arctic lakes. In *Polar Lakes and Rivers Limnology of Arctic and Antarctic Aquatic Ecosystems*; Vincent, W. F., Laybourn-Parry, J., Eds.; Oxford University Press: Oxford, UK, 2008; pp 249−268.
(11) Muir, D.; Wang, X.; Bright, D.; Lockhart, L.; Köck, G. Spatial and Temporal Trends of Mercury and other Metals in Landlocked Char from Lakes in the Canadian Arctic Archipelago. *Sci. Total Environ.* **2005**, *351−352*, 464−478.
(12) Gantner, N.; Muir, D. C.; Power, M.; Iqaluk, D.; Reist, J. D.; Babaluk, J. A.; Meili, M.; Borg, H.; Hammar, J.; Michaud, W.; Dempson, B.; Solomon, K. R. Mercury Concentrations in Landlocked Arctic char (*Salvelinus alpinus*) in the Canadian High Arctic: Part II. Influence of lake biotic and abiotic characteristics on geographic trends in 27 populations. *Environ. Toxicol. Chem.* **2010**, *29* (3), 633−643.
(13) Rigét, F.; Braune, B.; Bignert, A.; Wilson, S.; Aars, J.; Born, E.; Dam, M.; Dietz, R.; Evans, M.; Evans, T.; Gamberg, M.; Gantner, N.; Green, N.; Gunnlaugsdóttir, H.; Kannan, K.; Letcher, R.; Muir, D.; Roach, P.; Sonne, C.; Stern, G.; Wiig, O. Temporal trends of Hg in Arctic biota, an update. *Sci. Total Environ.* **2011**, *409* (18), 3520−3526.
(14) Chételat, J.; Amyot, M.; Arp, P.; Blais, J. M.; Depew, D.; Emmerton, C. A.; Evans, M.; Gamberg, M.; Gantner, N.; Girard, C.; Graydon, J.; Kirk, J.; Lean, D.; Lehnherr, I.; Muir, D.; Nasr, M.; Poulain, A. J.; Power, M.; Roach, P.; Stern, G.; Swanson, H.; van der Velden, S. Mercury in freshwater ecosystems of the Canadian Arctic: Recent advances on its cycling and fate. *Sci. Total Environ.* **2015**, *509−510*, 41−66.
(15) Evenset, A.; Christensen, G. N.; Skotvold, T.; Fjeld, E.; Schlabach, M.; Wartena, E.; Gregor, D. A comparison of organic contaminants in two high Arctic lake ecosystems, Bjørnøya (Bear Island), Norway. *Sci. Total Environ.* **2004**, *318*, 125−141.
(16) Nyberg, E.; Danielsson, S.; Eriksson, U.; Faxneld, S.; Miller, A.; Bignert, A. ″Spatio-temporal trends of PCBs in the Swedish freshwater environment 1981−2012.″. *Ambio* **2014**, *43* (1), 45−57.
(17) Cleemann, M.; Riget, F.; Paulsen, G. B.; de Boer, J.; Klungsoyr, J.; Aastrup, P. Organochlorines in Greenland lake sediments and landlocked Arctic char (*Salvelinus alpinus*). *Sci. Total Environ.* **2000**, *245* (1−3), 173−185.
(18) Vorkamp, K.; Rigét, F. F.; Dietz, R. ″Toxaphene in the aquatic environment of Greenland.″. *Environ. Pollut.* **2015**, *200*, 140−148.
(19) Rigét, F.; Vorkamp, K.; Bossi, R.; Sonne, C.; Letcher, R. J.; Dietz, R. Twenty years of monitoring of persistent organic pollutants in Greenland biota. A review. *Environ. Pollut.* **2016**, *217*, 114−123.
(20) Muir, D. C. G.; Kurt-Karakus, P.; Stow, J.; Blais, J.; Braune, B.; Choy, E.; Evans, M.; Kelly, B.; Larter, N.; Letcher, R.; McKinney, M.; Morris, A.; Stern, G.; Tomy, G. Occurrence and Trends in the Biological Environment. Chapter 4. In *Persistent Organic Pollutants in Canada' s North*; Muir, D. C. G., Kurt-Karakas, P., Stow, J. E., Eds.; Aboriginal Affairs and Northern Development Canada: Ottawa ON, 2013; pp 273−422.
(21) Kidd, K. A.; Hesslein, R. H.; Ross, B. J.; Koczanski, K.; Stephens, G. R.; Muir, D. C. G. Bioaccumulation of Organochlorines through a Remote Freshwater Food Web in the Canadian Arctic. *Environ. Pollut.* **1998**, *102*, 91−103.
(22) Kidd, K. A.; Schindler, D. W.; Hesslein, R. H.; Muir, D. C. G. Effects of trophic position and lipid on organochlorine concentrations in fishes from subarctic lakes in Yukon Territory. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 869−881.
(23) Hammar, J.; Larsson, P.; Klavins, M. Accumulation of persistent pollutants in normal and dwarfed Arctic char (*Salvelinus alpinus* sp. complex). *Can. J. Fish. Aquat. Sci.* **1993**, *50* (12), 2574−2580.
(24) Ma, J.; Hung, H.; Tian, C.; Kallenborn, R. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. *Nat. Clim. Change* **2011**, *1*, 255−260.
(25) Hansen, K. M.; Christensen, J. H.; Geels, C.; Silver, J. D.; Brandt, J. Modelling the impact of climate change on the atmospheric transport and the fate of persistent organic pollutants in the Arctic. *Atmos. Chem. Phys.* **2015**, *15*, 6549−6559.
(26) Macdonald, R. W.; Harner, T.; Fyfe, J. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342* (1−3), 5−86.
(27) Bogdal, C.; Scheringer, M. Environmental fate and long range transport of POPs. Chapter 3. In *Climate Change and POPs: Predicting the Impacts*; United Nations Environment Program (Secretariat of the Stockholm Convention) and Arctic Monitoring and Assessment Program: Geneva, Switzerland, 2011; pp 15−27.
(28) Cousins, I.; Kong, D.; Vestergren, R. Impact of climate change on exposure of POPs for wildlife and humans. Chapter 4. In *Climate Change and POPs: Predicting the Impacts*; United Nations Environment Program (Secretariat of the Stockholm Convention) and Arctic Monitoring and Assessment Program: Geneva, Switzerland, 2011; pp 21−28.
(29) Becker, S.; Halsall, C. J.; Tych, W.; Kallenborn, R.; Schlabach, M.; Manø, S. Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. *Atmos. Chem. Phys.* **2012**, *12* (9), 4033−4044.
(30) Kallenborn, R.; Halsall, C.; Dellong, M.; Carlsson, P. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. *J. Environ. Monit.* **2012**, *14* (11), 2854−2869.
(31) Cabrerizo, A.; Dachs, J.; Barceló, D.; Jones, K. C. Climatic and Biogeochemical Controls on the Remobilization and Reservoirs of Persistent Organic Pollutants in Antarctica. *Environ. Sci. Technol.* **2013**, *47* (9), 4299−4306.
(32) Ma, J.; Hung, H.; Macdonald, R. W. The influence of global climate change on the environmental fate of persistent organic pollutants: A review with emphasis on the Northern Hemisphere and the Arctic as a receptor. *Glob. Planet. Change* **2016**, *146*, 89−108.
(33) Rigét, F.; Vorkamp, K.; Muir, D. Temporal trends of contaminants in Arctic char (*Salvelinus alpinus*) from a small lake, southwest Greenland during a warming climate. *J. Environ. Monit.* **2010**, *12* (12), 2252−2258.
(34) Gantner, N.; Power, M.; Babaluk, J. A.; Reist, J. D.; Kock, G.; Lockhart, L. W.; Solomon, K. R.; Muir, D. C. Temporal trends of mercury, cesium, potassium, selenium, and thallium in Arctic char (Salvelinus alpinus) from Lake Hazen, Nunavut, Canada: effects of trophic position, size, and age. *Environ. Toxicol. Chem.* **2009**, *28* (2), 254−263.
(35) Lescord, G. L.; Kidd, K. A.; Kirk, J. L.; O'Driscoll, N. J.; Wang, X.; Muir, D. C. G. Factors affecting biotic mercury concentrations and biomagnification through lake food webs in the Canadian high Arctic. *Sci. Total Environ.* **2015**, *509−510*, 195−205.
(36) Muir, D.; Lockhart, W. L.; Grift, B.; Metner, D.; Billeck, B.; Lockhart, L.; Rosenberg, B.; Mohammed, S.; Wagemann, R.; Hunt, R. Contaminant trends in freshwater biota. In *Synopsis of research conducted under the 1992/93 northern contaminants program*; Murray, J. L., Shearer, R. G., Eds.; Aboriginal Affairs and Northern Development Canada: Gatineau, Quebec, 1993; pp 167−173.
(37) US EPA. *Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*; EPA-821-R-08-001; US Environmental Protection Agency, Office of Science and Technology: Washington DC, 2007; p 96.
(38) Hoekstra, P. F.; O'Hara, T. M.; Pallant, S. J.; Solomon, K. R.; Muir, D. C. G. Bioaccumulation of organochlorine contaminants in bowhead whales (Balaena mysticetus) from Barrow, Alaska. *Arch. Environ. Contam. Toxicol.* **2002**, *42* (4), 497−507.
(39) Muir, D. C. G.; Backus, S.; Derocher, A. E.; Dietz, R.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Norstrom, R. J.; Sonne, C.; Stirling, I.; Taylor, M. K.; Letcher, R. J. Brominated flame retardants in polar bears (*Ursus maritimus*) from Alaska, the Canadian Arctic, East Greenland, and Svalbard. *Environ. Sci. Technol.* **2006**, *40* (2), 449−455.


DOI: 10.1021/acs.est.8b01860
*Environ. Sci. Technol.* 2018, 52, 10380−10390

(40) Glassmeyer, S. T.; Shanks, K. E.; Hites, R. A. Automated toxaphene quantitation by GC-MS. *Anal. Chem.* **1999**, *71*, 1448−1453.
(41) Bignert, A. *PIA statistical application developed for use by the Arctic Monitoring and Assessment Programme*; Arctic Monitoring and Assessment Programme: Oslo, Norway, 2007; p 13 (available from www.amap.no).
(42) Rigét, F.; Bignert, A.; Braune, B.; Stow, J.; Wilson, S. Temporal trends of legacy POPs in Arctic biota, an update. *Sci. Total Environ.* **2010**, *408*, 2874−2884.
(43) Gantner, N.; Power, M.; Lawson, G.; Iqaluk, D.; Meili, M.; Köck, G.; Borg, H.; Sundbom, M.; Solomon, K. R.; Muir, D. C. G. Mercury Concentrations in Landlocked Arctic char (*Salvelinus alpinus*) in the Canadian High Arctic: Part I - insights from trophic relationships in 18 lakes. *Environ. Toxicol. Chem.* **2010**, *29* (3), 621−632.
(44) Goto-Azuma, K.; Koerner, R. M. Ice core studies of anthropogenic sulfate and nitrate trends in the Arctic. *J. Geophys Res.* **2001**, *106*, 4959−4969.
(45) Lehnherr, I.; St. Louis, V. L.; Sharp, M.; Gardner, A.; Smol, J. P.; Schiff, S. L.; Muir, D. C. G.; Mortimer, C. A.; Michelutti, N.; Tarnocai, C.; St. Pierre, K. A.; Emmerton, C. A.; Wiklund, J.; Köck, G.; Lamoureux, S.; Talbot, C. H. The High Arctic's only "Great lake" succumbs to climate warming. *Nat. Commun.* **2018**, *9*, 1290.
(46) Blackwell, B. G.; Brown, M. L.; Willis, D. W. Relative weight (Wr) status and current use in fisheries assessment and management. *Rev. Fish. Sci.* **2000**, *8*, 1−44.
(47) Muir, D. C. G.; Ford, C. A.; Grift, N. P.; Metner, D. A.; Lockhart, W. L. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 530−542.
(48) Ryan, M. J.; Stern, G. A.; Kidd, K. A.; Croft, M. V.; Gewurtz, S.; Diamond, M.; Kinnear, L.; Roach, P. Biotic interactions in temporal trends (1992−2010) of organochlorine contaminants in the aquatic food web of Lake Laberge, Yukon Territory. *Sci. Total Environ.* **2013**, *443* (0), 80−92.
(49) Schindler, D. W.; Kalff, J.; Welch, H. E.; Brunskill, G. J.; Kling, H.; Kritsch, N. Eutrophication in the high arctic - Meretta Lake, Cornwallis Island (75 N lat.). *J. Fish. Res. Board Can.* **1974**, *31*, 647−662.
(50) Douglas, M. S. V.; Smol, J. P. Eutrophication and recovery in the High Arctic: Meretta lake (Cornwallis Island, Nunavut, Canada) revisited. *Hydrobiologia* **2000**, *431* (2−3), 193−204.
(51) Stow, J. P.; Sova, J.; Reimer, K. J. The relative influence of distant and local (DEW-line) PCB sources in the Canadian Arctic. *Sci. Total Environ.* **2005**, *342*, 107−118.
(52) Nizzetto, L.; MacLeod, M.; Borgå, K.; Cabrerizo, A.; Dachs, J.; Guardo, A. D.; Ghirardello, D.; Hansen, K. M.; Jarvis, A.; Lindroth, A.; Ludwig, B.; Monteith, D.; Perlinger, J. A.; Scheringer, M.; Schwendenmann, L.; Semple, K. T.; Wick, L. Y.; Zhang, G.; Jones, K. C. Past, present, and future controls on levels of persistent organic pollutants in the global environment. *Environ. Sci. Technol.* **2010**, *44* (17), 6526−6531.
(53) Wöhrnschimmel, H.; Macleod, M.; Hungerbuhler, K. Emissions, fate and transport of persistent organic pollutants to the arctic in a changing global climate. *Environ. Sci. Technol.* **2013**, *47* (5), 2323−2330.
(54) Sturludottir, E.; Gunnlaugsdottir, H.; Jorundsdottir, H. O.; Magnusdottir, E. V.; Olafsdottir, K.; Stefansson, G. Temporal trends of contaminants in cod from Icelandic waters. *Sci. Total Environ.* **2014**, *476*−*477*, 181−188.
(55) Hung, H.; Katsoyiannis, A. A.; Brorström-Lundén, E.; Olafsdottir, K.; Aas, W.; Breivik, K.; Bohlin-Nizzetto, P.; Sigurdsson, A.; Hakola, H.; Bossi, R.; Skov, H.; Sverko, E.; Barresi, E.; Fellin, P.; Wilson, S. Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.* **2016**, *217*, 52−61.
(56) Li, Y. F.; Macdonald, R. W. "Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review. *Sci. Total Environ.* **2005**, *342* (1−3), 87−106.
(57) Vorkamp, K.; Christensen, J. H.; Glasius, M.; Riget, F. F. Persistent halogenated compounds in black guillemots (Cepphus grylle) from Greenland: Levels, compound patterns and spatial trends. *Mar. Pollut. Bull.* **2004**, *48* (1−2), 111−121.
(58) Stern, G. A.; Carrie, J.; Burt, A. Temporal Trend Studies of Trace Metals and Halogenated Organic Contaminants (HOCs), Including New and Emerging Persistent Compounds, In Mackenzie River Burbot, Fort Good Hope, NWT. In *Synopsis of research conducted under the 2013−2014 Northern Contaminants Program*; Aboriginal Affairs and Northern Development Canada: Ottawa, ON, 2014; pp 271−280.
(59) Hung, H.; Kallenborn, R.; Breivik, K.; Su, Y.; Brorström-Lundén, E.; Olafsdottir, K.; Thorlacius, J. M.; Leppänen, S.; Bossi, R.; Skov, H.; Manø, S.; Patton, G. W.; Stern, G.; Sverko, E.; Fellin, P. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993−2006. *Sci. Total Environ.* **2010**, *408* (15), 2854−2873.
(60) Mortimer, C. A.; Sharp, M.; Wouters, B. Glacier surface temperatures in the Canadian High Arctic, 2000−15. *J. Glaciol.* **2016**, *62* (235), 963−975.
(61) Wrona, F. J.; Johansson, M.; Culp, J. M.; Jenkins, A.; Mård, J.; Myers-Smith, I. H.; Prowse, T. D.; Vincent, W. F.; Wookey, P. A. Transitions in Arctic ecosystems: Ecological implications of a changing hydrological regime. *J. Geophys. Res.: Biogeosci.* **2016**, *121* (3), 650−674.
(62) Taylor, W. D.; Carey, J. H.; Lean, D. R. S.; McQueen, D. J. Organochlorine concentrations in the plankton of lakes in southern Ontario and their relationship to plankton biomass. *Can. J. Fish. Aquat. Sci.* **1991**, *48* (10), 1960−1966.
(63) Berglund, O.; Larsson, P.; Ewald, G.; Okla, L. Influence of trophic status on PCB distribution in lake sediments and biota. *Environ. Pollut.* **2001**, *113* (2), 199−210.
(64) Frouin, H.; Dangerfield, N.; Macdonald, R. W.; Galbraith, M.; Crewe, N.; Shaw, P.; Mackas, D.; Ross, P. S. Partitioning and bioaccumulation of PCBs and PBDEs in marine plankton from the Strait of Georgia, British Columbia. *Prog. Oceanogr.* **2013**, *115*, 65−75.
(65) Galbán-Malagón, C.; Berrojalbiz, N.; Ojeda, M.-J.; Dachs, J. The oceanic biological pump modulates the atmospheric transport of persistent organic pollutants to the Arctic. *Nat. Commun.* **2012**, *3*, 862.
(66) Octaviani, M.; Stemmler, I.; Lammel, G.; Graf, H. F. Atmospheric transport of persistent organic pollutants to and from the arctic under present-day and future climate. *Environ. Sci. Technol.* **2015**, *49* (6), 3593−3602.
(67) Eckhardt, S.; Stohl, A.; Beirle, S.; Spichtinger, N.; James, P.; Forster, C.; Junker, C.; Wagner, T.; Platt, U.; Jennings, S. G. The North Atlantic oscillation controls air pollution transport to the Arctic. *Atmos. Chem. Phys.* **2003**, *3* (5), 1769−1778.
(68) Ma, J.; Hung, H.; Blanchard, P. How Do Climate Fluctuations Affect Persistent Organic Pollutant Distribution in North America? Evidence from a Decade of Air Monitoring. *Environ. Sci. Technol.* **2004**, *38*, 2538−2543.
(69) Wania, F.; Mackay, D. Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.* **1996**, *30* (9), 390A−396A.
(70) Rigét, F.; Vorkamp, K.; Hobson, K. A.; Muir, D. C. G.; Dietz, R. Temporal trends of selected POPs and the potential influence of climate variability in a Greenland ringed seal population. *Environ. Sci. Process. Impact.* **2013**, *15* (9), 1706−1716.
(71) Bustnes, J. O.; Yoccoz, N. G.; Bangjord, G.; Herzke, D.; Ahrens, L.; Skaare, J. U. Impacts of climate and feeding conditions on the annual accumulation (1986−2009) of persistent organic pollutants in a terrestrial raptor. *Environ. Sci. Technol.* **2011**, *45* (17), 7542−7547.
(72) Bustnes, J. O.; Gabrielsen, G. W.; Verreault, J. Climate Variability and Temporal Trends of Persistent Organic Pollutants in the Arctic: A Study of Glaucous Gulls. *Environ. Sci. Technol.* **2010**, *44* (8), 3155−3161.


DOI: 10.1021/acs.est.8b01860
*Environ. Sci. Technol.* 2018, 52, 10380−10390

(73) Osborn, T. J. Simulating the winter North Atlantic Oscillation: the roles of internal variability and greenhouse gas forcing. *Clim. Dyn* **2004**, *22* (6), 605−623.
(74) Yeager, S.; Karspeck, A.; Danabasoglu, G.; Tribbia, J.; Teng, H. A Decadal Prediction Case Study: Late Twentieth-Century North Atlantic Ocean Heat Content. *J. Clim.* **2012**, *25* (15), 5173−5189.
(75) Miller, R. L.; Schmidt, G. A.; Shindell, D. T. (2006), Forced annular variations in the 20th century Intergovernmental Panel on Climate Change Fourth Assessment Report models. *J. Geophys. Res.* **2006**, *111*, D18101.
(76) Hoerling, M. P.; Hurrell, J. W.; Xu, T. Tropical Origins for Recent North Atlantic Climate Change. *Science* **2001**, *292* (5514), 90−92.



DOI: 10.1021/acs.est.8b01860
*Environ. Sci. Technol.* 2018, 52, 10380−10390