

Perfluorinated Chemicals in Meromictic Lakes on the Northern Coast of Ellesmere Island, High Arctic Canada

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ABSTRACT. Perfluorinated chemicals (PFCs) have been recorded in many types of marine and freshwater ecosystems. The aim of the present study was to examine meromictic lakes and their catchments on the far northern coast of Ellesmere Island, Nunavut, Canada, and to evaluate the results in the context of climate change. Our analyses revealed the presence of several PFCs in catchment snowpack, inflowing streams, lake water, and the aquatic food web of Lake A (83°00'N, 75°30'W), showing that dispersal of these contaminants reaches the northern limit of the terrestrial High Arctic. However, the concentrations were low (total PFCs: 27–754 pg L⁻¹ for water, 134–848 pg L⁻¹ for melted snow, 5–2149 pg g⁻¹ wet weight for fish; PFOS: 66 pg g⁻¹ dry weight in surficial sediments) and at or below values reported to date in the literature for other remote lakes. PFHpA, PFOA, and PFNA were the main compounds detected in water and melted snow, while PFNA, PFDA, and PFUnA were the predominant compounds in the aquatic biota, indicating their bioaccumulative potential. Salinity-temperature-depth profiles suggested that most of the present contaminant load enters the lake via streams and flows directly under the lake ice to the ocean. The onset of summer open water in this perennially ice-covered lake in response to climate warming, and the increased duration of open water in recent years, have implications for the distribution, transport, and retention of PFCs in Arctic lakes.

Key words: perfluorinated chemicals, lake, transport pathways, climate change, snow, water, sediments, arctic char, zooplankton, meromictic

RÉSUMÉ. Les composés perfluorés ont été retrouvés dans plusieurs types d'écosystèmes marins et d'eau douce. L'objectif de cette étude était d'étendre ces mesures à des lacs méromictiques situés sur la côte nord de l'île d'Ellesmere au Nunavut, et d'évaluer les résultats dans le contexte des changements climatiques. Nos analyses ont révélé la présence de plusieurs composés perfluorés dans la neige du bassin versant, les affluents, l'effluent, l'eau de lac, et le réseau alimentaire d'un de ces lacs, le lac A (83°00'N, 75°30'O). Ces résultats soulignent que la distribution de ces contaminants atteint la limite nordique de l'Arctique terrestre. Cependant, les concentrations mesurées étaient très faibles (au total : 27–754 pg L⁻¹ pour l'eau, 134–848 pg L⁻¹ pour la neige fondue, 5–2149 pg g⁻¹ pour les poissons et PFOS : 66 pg g⁻¹ dans les sédiments de surface) et en-dessous des valeurs publiées pour d'autres lacs de régions éloignées. PFHpA, PFOA et PFNA étaient les principaux composés détectés dans l'eau et la neige fondue alors que PFNA, PFDA et PFUnA étaient les composés prédominants pour le biote aquatique, indiquant leur potentiel de bioaccumulation. Des profils de salinité et de température ont suggéré que la majorité des contaminants entre dans le lac via les affluents et s'écoule directement sous le couvert de glace jusqu'à l'océan. Les conditions d'eau libre observées pendant l'été dans ce lac auparavant couvert de glace en permanence, et la durée accrue des conditions d'eau libre des dernières années ont des implications pour la distribution, le transport et la rétention des composés perfluorés dans les lacs arctiques.

Mots clés : composés perfluorés, lac, transport, changement climatique, neige, eau, sédiments, omble chevalier, zooplancton, méromictique

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INTRODUCTION

The Arctic is currently experiencing an amplitude of climate warming much greater than the global average, a trend that is predicted to accelerate over the next several decades

(Anisimov et al., 2007). An additional stress imposed on northern polar ecosystems is the widespread presence of contaminants, as these enter and move through Arctic food webs (Wrona et al., 2006). Lakes are a major feature of the Arctic terrestrial landscape, and their food webs

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already exhibit contamination by a variety of bioaccumulative chemicals, in contrast to Arctic land-based food webs, which are among the least contaminated in the world (AMAP, 2004; Gamberg et al., 2005). Arctic lakes may therefore be prone to the potential interactions between climate change and the presence of contaminants.

Most High Arctic lakes lie in relatively pristine catchments, and their contaminant burdens are likely to be derived from long-range transport and deposition. Catchment basins act as receptors through snow, rain, and dry deposition during winter, and as conveyors of snow and ice melt during the intense two- to three-week runoff period (freshet) in late spring to early summer (Macdonald et al., 2000). Meltwater enters Arctic lakes as stream inputs mostly in spring, while the lakes are inversely thermally stratified beneath an ice cover (Bergmann and Welch, 1985; Macdonald et al., 2000; Helm et al., 2002; Semkin et al., 2005). Much of this meltwater could potentially exit at the outflow with little mixing of its contaminant burden into the deeper water column (Semkin et al., 2005). As a result of this short surface-water residence time, ice-capped Arctic lakes may be less efficient at capturing inflowing contaminants, thereby minimizing the exposure of their aquatic biota.

Current trends in contaminant burden in the Arctic environment vary among different classes of compounds. There was a general decline in the concentrations of persistent organochlorines in the 1990s as a result of their reduced usage (e.g., PCBs, DDT; AMAP, 2004); however, there is little evidence that mercury levels have begun to show a similar trend (Muir et al., 2009a). Attention is now turning to less studied contaminants such as perfluorinated chemicals (PFCs), which are used as surfactants and in industrial processes, and which are also produced in the atmosphere as degradation products of volatile precursors (Ellis et al., 2004). Over the last decade, PFCs have been detected in humans, wildlife, water, sediment, and air at many locations, including sites in remote polar and alpine regions (Martin et al., 2004a; Stock et al., 2007; Wei et al., 2007; Loewen et al., 2008). PFCs are of high priority to regulators given their long-range transport, persistence in the environment, potential bioaccumulation through food webs, and toxicity to humans and wildlife (UNEP, 2006; de Silva et al., 2009). Water is expected to be the primary environmental compartment in which PFCs accumulate given their high water solubility, low sorption to organic matter, and low volatility of the anions (Arp et al., 2006; Higgins and Luthy, 2006). PFCs found in the environment include perfluorosulfonamido alcohols (PFSOHs) and fluorotelomer alcohols (FTOHs) ([online] Appendix A1: Table S1).

The two most widely studied and detected PFCs worldwide are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Both PFOS and PFOA have an eight-carbon backbone and are the final degradation products of precursor volatile alcohols (PFSOHs and FTOHs). PFSOHs and FTOHs have been detected in air samples at latitudes up to 75° N (Shoeib et al., 2006; Stock et al., 2007),

indicating the efficient long-range atmospheric transport of these chemicals from the south. However, the PFOS and PFOA precursors reaching the northern Ellesmere Island region are likely emitted in Eurasia, while locations south of 75° N are influenced by mid-latitude North American sources (Goto-Azuma and Koerner, 2001; AMAP/UNEP, 2008). PFCs are also transported via the ocean (Wei et al., 2007; Yamashita et al., 2008; Armitage et al., 2009).

The most northerly lakes that have been sampled and analyzed for PFCs to date are in the latitudinal range 73°–75° N, and sampling consisted of one-time measurements in water, sediment, and air (Stock et al., 2007). PFSOHs and FTOHs have been reported in air from the Canadian Arctic (Shoeib et al., 2006; Stock et al., 2007), and PFCs have been measured in High Arctic ice caps (75°–80° N; Young et al., 2007). In the present study, we extended these observations 1000 km farther north to ice-capped lakes along the northern coastline of Ellesmere Island (latitude 83° N). These lakes, among the most northerly lakes in the world, are meromictic (permanently stratified as a result of strong salinity gradients). They lie in pristine catchments (described in Vincent et al., 2011) and may be especially vulnerable to ongoing climate change because until recently they were perennially ice-covered (Mueller et al., 2009). The objective of this study was to determine the presence and concentrations of PFCs in the different compartments of Lake A, the deepest of these far northern meromictic lakes (Vincent et al., 2011). We analyzed samples of the lake water, sediments, food web constituents (zooplankton and arctic char, *Salvelinus alpinus*), catchment snowpack, and inflowing and outflowing water in order to quantify the PFC burden in each component. Comparative measurements of arctic char, the only fish species present in these ecosystems, were also made in another meromictic lake, Lake C2 (unofficial name), which lies in a separate catchment 40 km to the west of Lake A. We made fine-structure profiles (cm depth resolution) of temperature and salinity to help us understand the hydrodynamic processes influencing the PFC distribution in these far northern ecosystems.

METHODS

Study Area

Lake A (unofficial name; 83°00' N, 75°30' W) and Lake C2 (unofficial name; 82°50' N, 75°05' W) are two of a series of meromictic lakes located on the northwestern coast of Ellesmere Island, Nunavut, Canada (Fig. 1; Hattersley-Smith et al., 1970). These lakes were formed by isostatic rebound, which caused their isolation from the Arctic Ocean several thousand years ago (Jeffries et al., 1984; Ludlam, 1996). A similar process also formed meromictic lakes found in the Antarctic (Gibson, 1999). Lake A, located at an elevation of ~ 4 m above sea level, has a surface area of 4.9 km², a water volume of 98.1 × 10⁶ m³, a maximum known

depth of 128 m, and a catchment of 37 km² that contains no glaciers (Fig. 1; Van Hove et al., 2006). Its catchment rises to 600 m (Van Hove et al., 2006) and is composed of frost-shattered rock with sparse herbaceous tundra vegetation and willows. The main inflow of Lake A is located at the delta on the eastern side of the lake. It also has an inflow from Lake B and several other streams and an outflow (30–40 cm deep) at its northern end that passes directly to the Arctic Ocean (Veillette et al., 2010). Observations of the inflows to Lake A indicated that they begin flowing at the onset of the melt season (June); their discharge peaks at freshet (end of June–early July) and stops when the melt is completed (August), except for the inflow draining Lake B, which flows throughout the open water season (Fig. 1). Outflow from Lake A follows the onset of inflowing water, as the outflow can be blocked by an ice dam that prevents the exit of the initial meltwater from the lake. Lake C2, 40 km to the west of Lake A, is one of three lakes located along the coast of Taconite Inlet (Ludlam, 1996). This lake, which lies 1.5 m above sea level, has a surface area of 1.8 km², a maximum known depth of 84 m, and a catchment basin of 23.3 km² with glaciers, rising to 1200 m (Bradley et al., 1996). Lake C2's main outflow is at a delta on its southeastern shore, and it drains to Taconite Inlet.

Lake A was highly stratified, with a halocline at 10 m at all times when sampled, consistent with earlier observations (Fig. 2; Mueller et al., 2009). Profiles above the halocline, however, indicated considerable variation according to ice and mixing conditions at the time of sampling. Before the onset of snowmelt (e.g., May 2008), the profile showed inverse temperature stratification and uniform salinity down to just above the halocline. During the melt period (e.g., July 2007 and 2009), the uppermost 2 m showed a discrete layer of lower salinity and low-temperature water immediately under the ice. This layer was likely composed of meltwater from the catchment basin, as indicated by salinity and temperature data of the inflow at the delta (conductivity: 25.3 $\mu\text{S cm}^{-1}$; temperature: 0.36°C; 1.8 m³ s⁻¹) in July 2009. During ice-off conditions (e.g., August 2008), which have rarely occurred in the past (Mueller et al., 2009), the profiles showed homogenous temperature and salinity in the epilimnion, indicative of complete mixing to the halocline.

Climate data from Lake A were recorded by a 3 m automated weather station that has been in operation since August 2003 as part of the SILA (*climate* in Inuktitut) climate network of the Centre d'études nordiques (CEN; Centre for Northern Studies). The mean annual temperature during 2005–08 was -18.3°C, and the mean summer (June–July–August) temperature was 0.4°C. Summer air temperatures were typically between -7° and 9°C, but a maximum temperature of 20.5°C was recorded on 2 August 2008. Temperatures at Lake C2 are typically slightly lower (< 1.0°C) than those at Lake A (Mueller et al., 2009). Temperatures on the northern coastline of Ellesmere Island have increased significantly over the last six decades at a rate of up to 0.48°C per decade (Mueller et al., 2009). This region

is classified as a polar desert with a total annual precipitation at Alert of 154 mm water equivalent, composed of 173 cm snowfall and 16 mm rain (www.climate.weather-office.ec.gc.ca). The measured snow thickness on Lake A at the end of May 2008 was 49 cm.

Field Sampling

Field sampling and water-column profiling were undertaken at Lake A in 2002, 2007, 2008, and 2009, with complementary arctic char sampling in Lake C2 in 2006 ([online] Appendix 1: Tables S2 and S3). Water-column profiles were taken with an XR-420 or XR-620 CTD (conductivity-temperature-depth profiler; RBR Ltd., Ottawa, ON, Canada) slowly lowered through holes drilled in the lake ice or from a small, inflatable boat. Water samples for contaminant analyses from depths of 2 m (underneath the ice cover), 10 m (the bottom of the mixed layer), and 32 m (in the monimolimnion) were taken with a 6.2 L Kemmerer sampler (all-plastic construction) and transferred to two new 4 L polypropylene bottles rinsed three times with lake water. Snow from the catchment and water from the moat (i.e., the open water ringing the central pan of persistent lake ice), inflows, and outflow were each collected in duplicate with this same bottle type. Snow was collected with a stainless steel spatula that had been washed in lake water, and then further cleaned in the snow, prior to sampling. Three water field blanks were composed of 1 L SPE HPLC-cleaned water transported in new 4 L polypropylene bottles to the field and opened for 10 minutes at the sampling location (one for snow and two for water sampling).

The surface sediment core was collected at the same site as the water on 30 May 2008 (Fig. 1) at a water depth of 85 m with a 68 mm diameter gravity corer (Aquatic Research Instruments, Hope, ID, USA) in a tenite butyrate tube (United States Plastic Corp., Lima, OH, USA). The sediment core was dewatered and kept vertical during transport to the camp and then sectioned at 0.5 cm intervals. Although dating of Lake A sediment cores has been performed for cores from the northern portion of the lake (Tomkins et al., 2009), there is no chronological information for the location of the core used in the present study, which is from a more southerly, deeper location. As sedimentation rates are known to vary substantially within the lake basin, it is difficult to assign dates to our core sections, especially since ²¹⁰Pb activities are typically at or below detection limits at this latitude. All water, snow, and sediment samples were stored cold (~ 4°C) and in the dark until analyzed.

Zooplankton (composed mainly of calanoid copepods; Van Hove et al., 2001) was sampled between 1 and 10 m depth using a horizontal tow with a 3 m long conical net (mesh size 110 μm ; mouth diameter 1 m) (Filmar, Montreal, QC, Canada), and arctic char were captured by multi-mesh, nylon, multifilament gill nets (60 m gang of 10, 19, 33, 45, 55, and 60 mm bar-mesh) (Lundgrens Fiskredskapsfabrik AB, Stockholm, Sweden) and by angling (jigging). Special

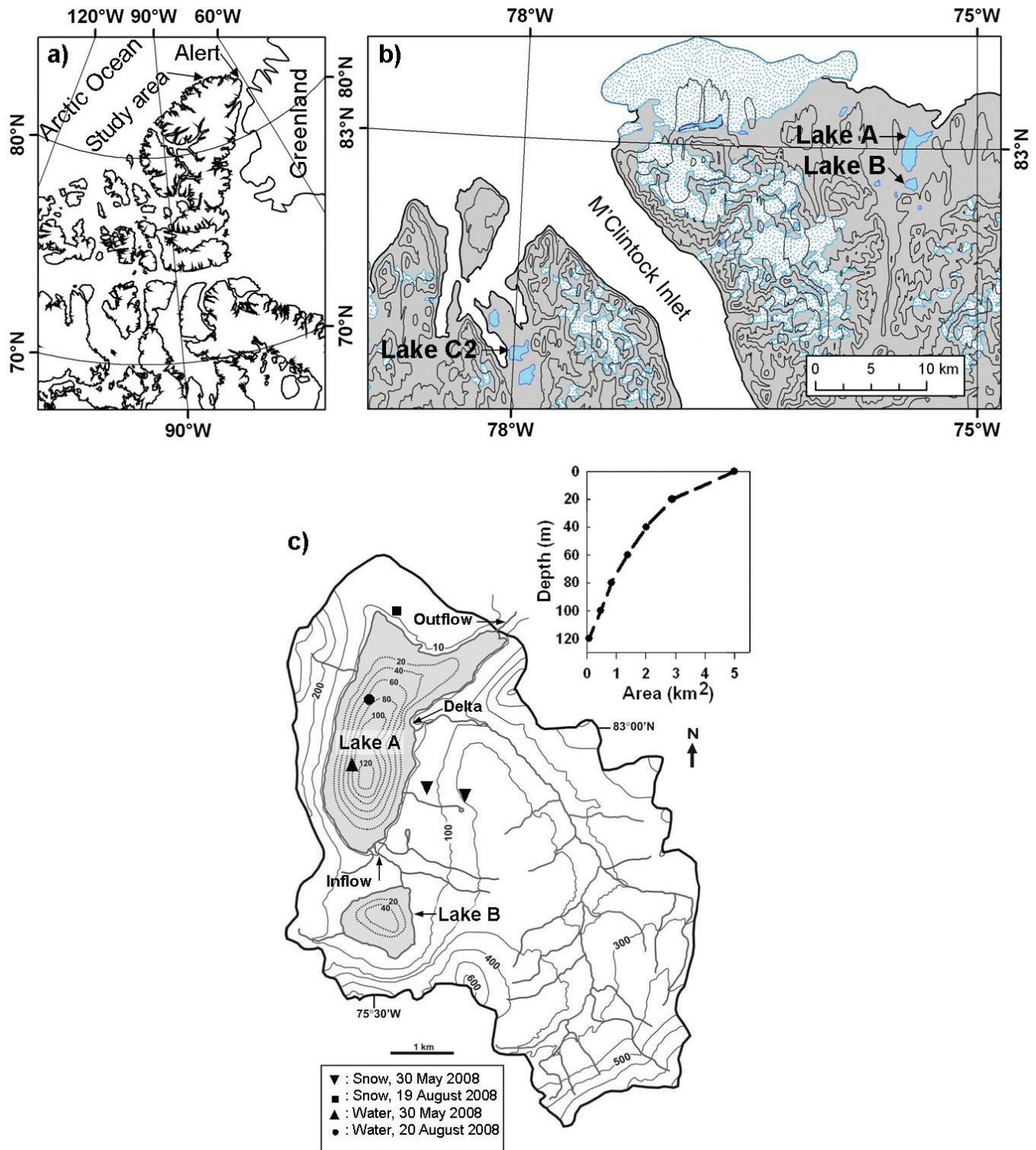


FIG. 1. a) Map of Ellesmere Island, Canada, indicating study area; b) study area showing locations of Lake A, Lake B, and Lake C2. Contour interval = 200 m, glaciers and ice rises are marked with stipples; c) Lake A catchment basin with sampling sites, and the hypsographic curve as the upper right inset. Lower inset (legend) indicates the locations and dates of sampling. The water sites correspond to the sites where water depth profiles were made.

precautions were taken to avoid contamination of the samples by wearing clothes free of PFCs and disposable gloves, by always sampling upwind and at least 100 m away from the helicopter used to arrive at sample sites, and by avoiding contact with Teflon™ throughout sampling and analysis.

PFC Analysis

Water, melted snow, sediment, zooplankton, and fish samples were analyzed for perfluorosulfonates (PFSAs), perfluorocarboxylates (PFCAs), perfluorosulfonamide

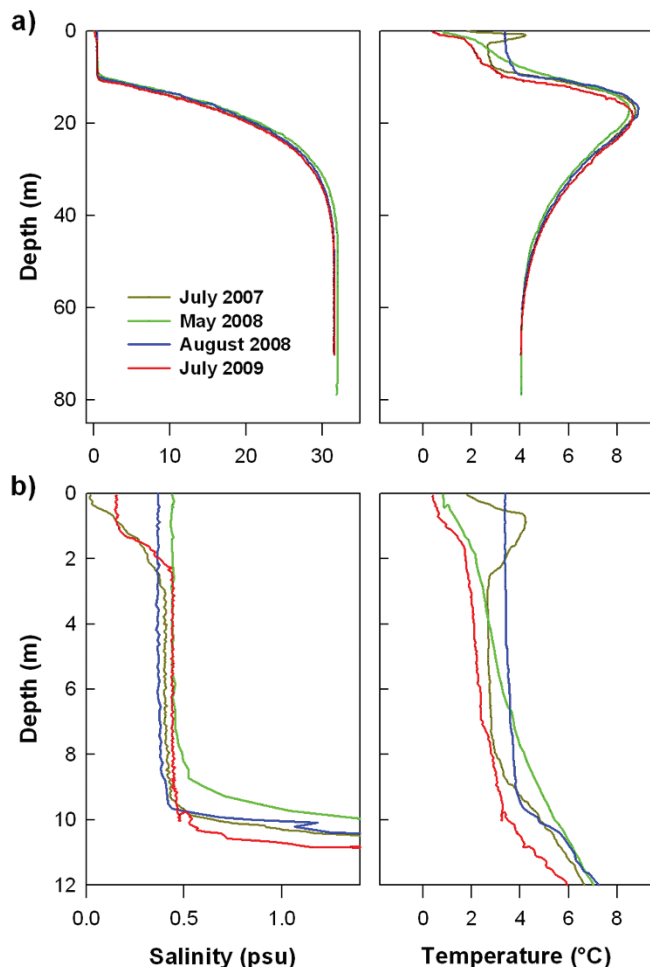


FIG. 2. Lake A 2007, 2008, and 2009 water-column profiles a) to 80 m depth and b) expanded scale to 12 m depth.

(PFOSA), and unsaturated fluorotelomer acids ([online] Appendix 1: Table S1) using liquid chromatography tandem mass spectrometry (API-4000, LC/MS/MS). Water and melted snow samples were extracted under clean room conditions (positively pressured HEPA and carbon-filtered air) following the method of Yamashita et al. (2004), with minor modifications. Duplicate subsamples (unless noted otherwise) of these waters, as well as a laboratory blank, consisting of the solvents and the cartridge, were all processed at the same time, and the subsample values were averaged. Each of the 1 L water samples was spiked with a recovery standard (mass-labelled PFCAs: PFOA, PFDA, PFUnA, PFDoA; PFOS, PFHxS, 6:2, 8:2, 10:2 PFUA; Wellington Laboratories, Guelph, ON, Canada) and extracted with conditioned (4 mL 0.1% ammonia hydroxide/methanol solution, 4 mL methanol and 4 mL SPE HPLC-cleaned water) Waters Oasis[®] cartridges (150 mg, Wax, 6 cc, 30 μ g) (Waters Corporation, Milford, MA, USA). The cartridges were then centrifuged and eluted with 6 mL methanol and 8 mL 0.1% ammonia hydroxide into pre-rinsed 15 mL polypropylene centrifuge tubes. The resultant extract was reduced to 0.25 mL before an instrument performance internal standard (mass-labelled C9; Wellington Laboratories, Guelph,

ON, Canada) and 0.25 mL SPE HPLC-cleaned water were added. The saline water sample (Lake A at 32 m) cartridges were washed with 200 mL SPE HPLC-cleaned water before elution. Laboratory blanks used the same solvents and cartridges as the samples. The SPE HPLC-cleaned water and 25% ammonia solution used were from EMD, and the methanol was from EMD Omnisolv (Gibbstown, NJ, USA).

Sediment samples (7–8 g wet weight) were spiked with an internal standard (mass-labelled PFCAs: PFOA, PFNA, PFDA, PFUnA, PFDoA; PFOS, 6:2, 8:2, 10:2 PFUA; Wellington Laboratories, Guelph, ON, Canada) before being extracted with methyl tert-butyl ether (MTBE) and the ion-pairing agent tetrabutylammonium hydrogen sulfate (TBAHS). Following two extractions, the MTBE aliquots were combined, brought to dryness under a gentle stream of high purity nitrogen, and reconstituted in 0.5 mL methanol and 0.5 mL SPE HPLC-cleaned water before being filtered through 0.2 μ m disposable syringes into polypropylene vials. One batch of six samples and three method blanks (consisting of sediments from depths greater than 5 cm) were processed.

An internal standard (mass-labelled PFCAs: PFOA, PFNA, PFDA, PFUnA, PFDoA; PFOS, 6:2, 8:2, 10:2 PFUA; Wellington Laboratories, Guelph, ON, Canada) was added to 0.2 g of zooplankton and fish samples (dorsal muscle or whole body homogenate) in a 15 mL polypropylene centrifuge tube. Three subsequent methanol extractions were made, and the resulting supernatants were evaporated under high-purity nitrogen gas (Tomy et al., 2006). These concentrates were filtered through 0.2 μ m disposable syringes into polypropylene vials and were processed as a batch of 11 samples and a laboratory blank of methanol.

An eight-point calibration curve was used to quantify the PFCs, with an accuracy of the calibration curves between 70% and 130%. Instrument detection limits (IDLs) were defined as three times the signal-to-noise ratio for the lowest standard on the calibration curve divided by the volume or the mass of the sample analyzed. IDLs of the different compounds ranged from 1 to 11 pg g^{-1} for sediments and fish and from 0.1 to 0.9 pg L^{-1} for the water and melted snow samples ([online] Appendix 1: Table S4). Method detection limits (MDLs) were defined as three times the standard deviation of the mean blank divided by the volume or the mass of the sample analyzed. In the sediments, it was possible to calculate MDLs only for PFOS and PFOA (MDLs: $\sim 4 \text{ pg g}^{-1}$), since the other analytes were non-detectable (nd) in the method blanks. In the water samples, MDLs could be calculated for all compounds (MDLs: 0.3–16.3 pg L^{-1}) because the laboratory blanks had low levels of PFCs ([online] Appendix 1: Table S5). Laboratory blanks for fish analysis typically had non-detectable analyte concentrations; therefore, IDLs were used as the MDLs. Values lower than IDLs were reported as non-detectable (nd). All reported concentrations were blank-subtracted using the mean laboratory blank values. Since the PFC burden of field blanks was equal to or lower than that of laboratory blanks, we concluded that sampling did not contaminate the

samples. For the calculation of the means, nd values were treated as half IDLs. Mean recoveries were calculated using the recovery standard for water and melted snow samples and the internal standard for sediment, zooplankton, and fish samples ([online] Appendix 1: Table S6). Recoveries for major analytes (PFOS, PFOA, PFNA, PFDA, PFUnA) ranged from 50% to 67% for sediments, from 73% to 122% for zooplankton, from 71% to 122% for fish, from 54% to 123% for water, and from 28% to 119% for melted snow (Table S6). Except for PFDoA, mean recoveries of the different compounds were generally greater than 70%, which is considered an acceptable performance for organic contaminants in environmental samples (Keith, 1996; Pihlström, 2009). PFDoA was not detected in any samples and is not discussed further. In the case of PFHpA and PFBS, which were detectable, no extraction recovery standard was available, and thus caution must be used when comparing these concentrations with those found in other studies. In general, measurement uncertainty is not well characterized for PFCs (e.g., Van Leeuwen et al., 2006).

Statistical Analyses

Two-way ANOVA without interaction was used to test for differences in the horizontal and vertical distribution of total PFCs and each compound separately between the different sampling sites or depths and at the different sampling times, or at every sampling time. Since the sampling design was non-replicated (Milliken and Johnson, 1989), we used Tukey's non-additivity test to examine the interaction between the two factors (site or depth and time), but it was never significant. When the two-way ANOVA test result was significant, the Tukey a posteriori test was used to verify which samples differed from the others. Linear regression analysis was used to determine the relationship of total PFCs with fish age and length. A forward stepwise regression analysis was used to determine which variables (fish length, age, sex, anadromy or residency, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) influenced the fish total PFCs and each compound separately. SigmaStat 3.1 and SigmaPlot 9.0 were used for the statistical analyses.

RESULTS

PFCs in Lake A and Its Catchment

Surface water total PFC concentrations were in the same range in the lake (centre and littoral), the inflows, and the outflow, irrespective of the time of sampling (total PFCs = 243–754 pg L^{-1} ; Fig. 3 and [online] Appendix 1: Table S7). The compounds with the highest concentrations detected in surface water (above MDLs) were PFOA, PFNA, PFHpA, PFOS, PFBS, and PFDA. There was no significant difference between the three different sampling times in total PFCs, or in the different compounds analyzed separately, for either the centre or littoral lake surface water (see

details of statistical results in [online] Appendix 1: Table S9). When the catchment and lake sampling sites were grouped as inflow, outflow, lake, or snow (May 2008 only), neither total PFCs nor any individual compounds differed significantly between the four different groups of sampling sites or between the three sampling times. However, total PFCs and the compounds PFHpA, PFOA, and PFNA were detected in significantly higher concentrations in snow than in lake water in May 2008. The concentrations of PFCs in fresh snow collected in late summer (August 2008) were very low (total PFCs = 134 pg L^{-1}). In August 2008, PFC concentrations in the inflow from Lake B were significantly higher than those at the centre of Lake A (two-way ANOVA: $F = 3.99$, $p = 0.02$; Tukey: $q = 4.66$, $p = 0.01$).

PFCs in Lake A Water Column and Sediments

The vertical distribution of PFCs in Lake A did not differ significantly between 30 May and 20 August 2008 (two-way ANOVA; $F = 0.15$, $p = 0.74$; Fig. 4a and [online] Appendix 1: Table S8). The total PFC concentrations at depths of 2 and 10 m (both located within the mixed layer) did not differ significantly from one another, but both were significantly higher than the total PFC concentrations at 32 m, in the monimolimnion, which were close to our MDLs (two-way ANOVA: $F = 27.49$, $p = 0.04$). The relative abundance of PFC compounds (see above) was the same at the three depths.

PFOS was the only PFC detected in the sediments, with values above MDL in the topmost 2 cm (Fig. 4b). The concentration in the uppermost 0.5 cm was 66 pg g^{-1} dry weight.

PFC Burdens in Zooplankton and Fish

The total PFC burden in the zooplankton averaged 955 pg g^{-1} and was in the same range as in arctic char (Lake A: $n = 32$, mean = 203 pg g^{-1} and Lake C2: $n = 14$, mean = 481 pg g^{-1} ; Table 1). However, only PFNA and PFUnA were detected above MDLs in zooplankton, whereas PFNA, PFOS, PFOA, PFUnA, and PFDA were detected above MDLs in fish. The PFCs detected in fish were not detectable in every individual (Table 1). Total PFC concentrations were not significantly related to fish age or fork length for either lake ([online] Appendix 1: Table S10; Fig. 1).

DISCUSSION

PFCs in Lake A and Its Catchment

The water concentrations of PFCs in the present study (27–754 pg L^{-1}) fall at or below the lower limit of values reported to date for lake ecosystems. Concentrations were similar among sampling sites and times of sampling probably because we sampled either before freshet events (May 2008) or after them (July 2007 and August 2008), but not during the freshet. Although Lake A was ice-covered on

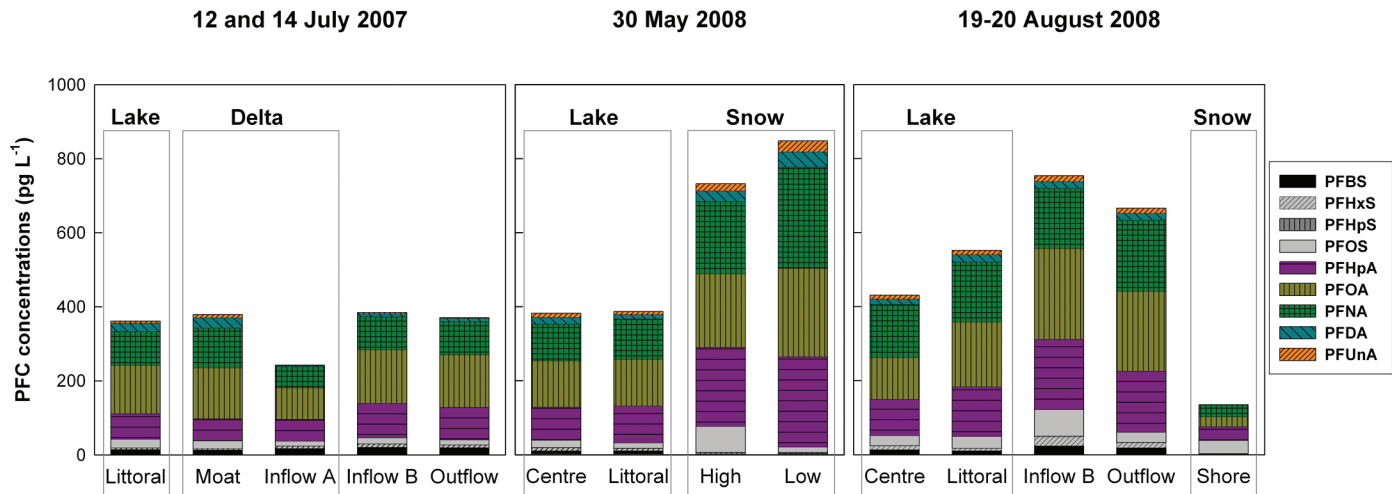


FIG. 3. The horizontal distribution of PFCs in surface water samples and snow of the lake catchment for all compounds that were above the method detection limits. Lake: sampling sites at the centre of the lake and in the littoral zone (30 m from the delta); delta: sampling sites at the moat around the delta and at the inflow of the delta (inflow A); inflow B: the inflow from Lake B; outflow: the outflow of Lake A to the Arctic Ocean. Snow sampled in May 2008 was collected from a higher and lower location in the catchment, while snow sampled in August 2008 was collected from the north shore within two days after snowfall.

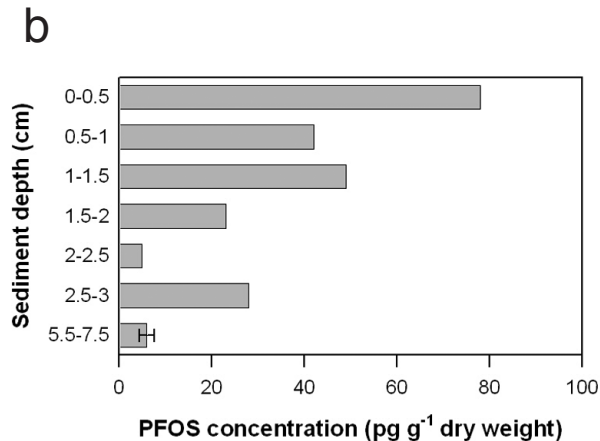
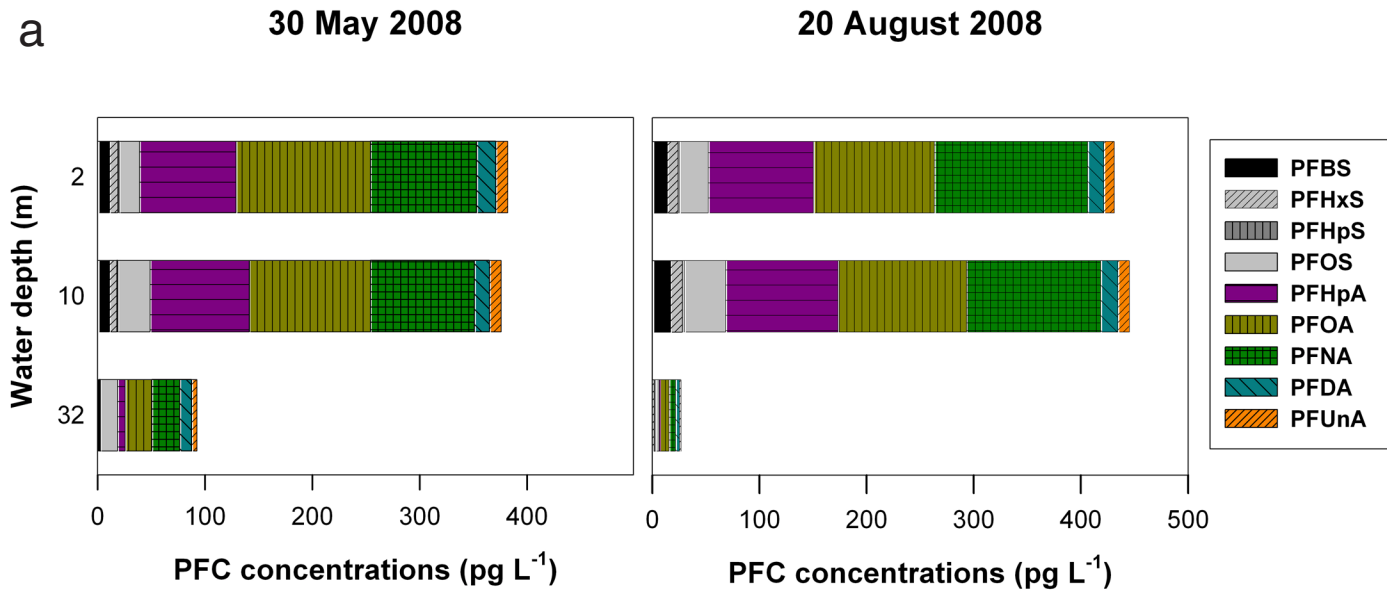


FIG. 4. Vertical distribution of PFCs in Lake A for all compounds with concentrations above the method detection limits. Depth profiles: a) in the water column; b) in the sediments. The error bars in b) indicate the 95% confidence interval of three subsamples from the 5.5–7.5 cm section.

TABLE 1. Mean PFC concentrations (wet weight) of compounds detected in zooplankton larger than 250 µm of Lake A (n = 3 subsamples of the same tow) and the arctic char populations of Lake A (n = 32, 27 from whole body homogenates and 5 from dorsal muscles) and Lake C2 (n = 14, dorsal muscles).

	Zooplankton–Lake A		Arctic char–Lake A			Arctic char–Lake C2		
	Mean (pg g ⁻¹)	Range	Mean (pg g ⁻¹)	Range	% detected	Mean (pg g ⁻¹)	Range	% detected
PFOS	< 6	< 6	21	< 6–161	41	105	< 6–286	93
PFOA	< 1.3	< 1.3	8	< 1.3–130	16	11	< 1.3–101	14
PFNA	809	700–882	129	< 1.2–748	53	248	< 1.2–1414	79
PFDA	< 1.4	< 1.4	21	< 1.4–228	31	44	< 1.4–193	79
PFUnA	146	61–285	24	< 1–307	31	74	< 1–256	64
ΣPFCs	955	826–1293	203	< 5–1340	59	481	< 5–2149	93

30 May 2008, similar concentrations at 2 and 10 m likely reflected the mixing that occurred at the end of the preceding summers. Previous research on mercury at Amituk Lake (75°03' N, 93°49' W; area 0.38 km², catchment 26.6 km²), also in the High Arctic but ~950 km to the south of Lake A, has shown that concentrations were highest during snowmelt in late spring and declined rapidly over the summer (Loseto et al., 2004).

Measurements from a single sampling expedition to Amituk Lake gave median PFOS and PFOA concentrations of 1200 and 2000 pg L⁻¹ (Stock et al., 2007), more than 15 times as high as those in the surface waters of Lake A. Surface water from Pingualuk Lake, an isolated crater lake in northern Québec, had PFOS and PFOA concentrations of 28 and 62 pg L⁻¹, respectively (Gantner et al., 2012), which are even lower than in Lake A. This implies that Arctic lakes vary greatly in their PFC contaminant burdens. Several features may account for the much lower concentrations in Lake A, compared to those on Cornwallis Island, including the greater distance of the lake from source regions, its smaller catchment area: lake area ratio (Amituk Lake: 70; Lake A: 8), and its perennial lake ice. Until recently, this ice cover on Lake A prevented direct transfer of contaminants from the atmosphere (whereas Amituk Lake is seasonally ice-free), although melted water from stream inputs could have percolated into the lake at the edge. Despite this large quantitative difference, the relative proportions of several PFCs were qualitatively similar between Amituk and Lake A. For example, PFOA/PFOS ratios were 3.4 in Amituk and 5.9 in Lake A. The major PFCAs, PFHpA, PFNA, PFDA, and PFUnA were prominent in both lakes. However, PFDA and PFUnA were relatively more prominent in Amituk than in Lake A.

The concentrations of PFCs in Lake A are well below those in temperate lakes that are close to industrial source regions. For example, PFOS and PFOA concentrations in the North American Great Lakes were one to two orders of magnitude higher than in Lake A (up to 8400 pg L⁻¹ for PFOS and up to 6700 pg L⁻¹ for PFOA; Furdui et al., 2008) and PFOA/PFOS ratios were less than 2.5 (de Silva et al., 2011), indicating greater predominance of PFOS sources.

PFC concentrations of Lake A catchment snow were similar to spring-summer concentrations in accumulated snow from the Devon Ice Cap (eight degrees of latitude south of Lake A) sampled in spring 2006 (Young et al.,

2007). The PFC burden difference in fresh snow deposited in late summer versus a snowbank that accumulated mainly over the fall is consistent with atmospheric accumulation of contaminants during winter, when the absence of sunlight inhibits the formation of PFCs from precursors, and subsequent deposition during spring as wet or dry fall (Goto-Azuma and Koerner, 2001). These winter contaminants would then be available for discharge to northern lakes during the spring freshet.

PFCs in the Lake A Sediments

PFOS was detected in the surface sediments of Lake A; the uppermost 0.5 cm stratum represented approximately the period 1985–2008 (Tomkins et al., 2009). PFOS concentrations decreased down the core, as expected, since the global production of PFOS-related compounds has been greatest during the last 20 years (Paul et al., 2009). The surface concentration (66 pg g⁻¹ dry weight) was similar to that detected in the topmost slice of Amituk Lake sediments (62 pg g⁻¹ dry weight, 0–1.5 cm, 1976–2003; Stock et al., 2007) although other PFCs were detected in this latter core and PFOS represented only 1% of total PFCs. PFOS concentrations in the surficial sediments of Resolute Lake (74°41' N, 94°55' W; 85 000 pg g⁻¹ dry weight, 0–1 cm, 1997–2003; Stock et al., 2007), Lake Ontario (28 000 pg g⁻¹ dry weight, 0–1 cm; Stock, 2007) and San Francisco Bay (nd–3760 pg g⁻¹ dry weight, 1–5 cm; Higgins et al., 2005) were several orders of magnitude greater than those detected in Lake A. PFNA is expected to have an affinity for organic matter similar to that of PFOS (Higgins and Luthy, 2006), yet this compound was not detected in the Lake A surficial sediments. We are unable to explain the apparent discrepancy implied by these results.

PFC Burdens in Zooplankton and Fish

Fish have been identified as a source of PFCs for Inuit in the Canadian Arctic (Dallaire et al., 2009; Ostertag et al., 2009). Although arctic char in northern Ellesmere Island lakes likely migrate to marine waters during the summer (T. Loewen, pers. comm. 2010), their levels of contamination in Lake A (203 pg g⁻¹) and Lake C2 (481 pg g⁻¹) were of similar magnitude to those in landlocked arctic char of Amituk Lake (n = 11; 890 pg g⁻¹) and Char Lake (n = 5; 1550

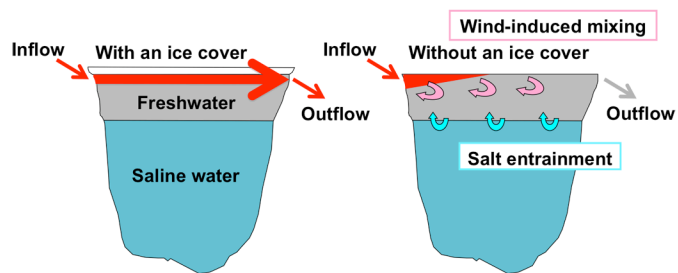


FIG. 5. Schematic diagram showing the implications of climate change during the freshet period with ice-free conditions. The left panel illustrates the short-circuit conduit (thick red arrow) that is likely present in Lake A during freshet under ice-covered conditions. The thin red arrows indicate the flow of water from the inflow towards the outflow of the lake. The right panel shows the disruption of the short-circuit conduit if the freshet occurs during ice-free conditions. Wind-induced mixing (pink arrows) would create turbulence and entrain saline water into the freshwater surface layer (green arrows).

pg g⁻¹) sampled in 2006 (Muir et al., 2009b). This similarity is surprising given the difference in anadromy, the large difference in the concentrations of PFCs in the water of the northern versus southern Arctic lakes, and the known variability in food web length between Arctic lakes (Gantner et al., 2010). The marine pelagic arctic cod (*Boreogadus saida*) of the western Canadian Arctic presented a greater level of contamination ($n = 10$; 5740 pg g⁻¹; Tomy et al., 2009). PFOS, PFNA, and PFDA were the main compounds detected in the arctic char of Amituk Lake and Char Lake, in agreement with the present study, and PFNA, PFDA, PFDoA and PFOSA were the main compounds in arctic cod (Tomy et al., 2009). PFC concentrations detected in the two lakes sampled here were several times lower than those found in lake trout (*Salvelinus namaycush*) from the Great Lakes (13 000–15 200 pg g⁻¹), where the main compounds detected were PFOS and longer chain PFCAs (PFOA, PFNA, PFDA, PFUnA, and PFTrA) (Furdui et al., 2007).

Only two compounds, PFNA and PFUnA, were detected in both arctic char and zooplankton. The extent of biomagnification of PFCs, which has been observed in several other studies of freshwater food webs (Martin et al., 2004b), is thus difficult to assess in Lake A. The contaminant burden in char may reflect other food sources, such as benthic invertebrates in the littoral zone or marine organisms consumed during periods spent at sea. The zooplankton of Lake A is composed mainly of calanoid copepods (*Limnocalanus macrurus* and *Drepanopus bungei*; Van Hove et al., 2001).

PFC Loss Processes

Surface lake concentrations of PFCs were similar to values in the inflows and in the outflow of Lake A, but the lake PFC concentrations were half the values found in spring snowpack in May 2008, which implies that contaminant loss or dilution processes are operating within the lake. Dilution would be mostly restricted to periods of wind-induced mixing during open water conditions, although high stream discharges could create turbulence and vertical

mixing under the ice cover (Bergmann and Welch, 1985). Loss via contaminant uptake by biotic particles or sedimentation seems unlikely since the short-chained PFCs detected in the present study have low sorption to sinking organic matter.

It is likely that the inflowing contaminants that enter during the freshet remain near the surface and exit via the outflow. The salinity-temperature-depth profiling data supported this hypothesis, in that the low conductivity and temperature values in the uppermost stratum of water under the ice were similar to those recorded at the inflow of the delta. This type of under-ice short-circuiting has been observed in Amituk Lake, where more than half of the total mercury input (Semkin et al., 2005) and about 70% of organochlorine chemicals were estimated to have exited directly through the lake outflow (Helm et al., 2002; Macdonald, 2005). In summers (such as 2008), with open water conditions following the freshet, the uppermost meltwater stratum under the ice and inflowing waters may mix into the topmost 10 m of the water column, carrying and diluting their PFC load. The residence time of PFCs within the lake and the exposure of aquatic organisms could therefore be increased with open water conditions. However, the primary sink for PFCs entering Lake A from its catchment is likely to be the Arctic Ocean, with eventual transport to the deep sea and sediments (Prevedouros et al., 2006).

Implications of Climate Change

Climate change will affect the stratification, mixing, and transport regimes of Lake A and other far northern lakes that were perennially ice-capped in the past. The short-circuit conduit now likely present in Lake A will be conserved with seasonal ice-cover loss, as long as the lake is still ice-covered during the critical freshet period, as was the case, for example, in Amituk Lake (Semkin et al., 2005). However, if the open water season were to begin earlier during the freshet, the short-circuit conduit would be disrupted, and the concentration and retention time of contaminants in the mixed layer would increase (Fig. 5).

Increased wind-induced turbulence under ice-free conditions will deepen the halocline and entrain saline water in the freshwater layer, thereby increasing its salinity, as observed in seasonally ice-free, meromictic Romulus Lake, farther to the south on Ellesmere Island (Van Hove et al., 2006). The formation of annual ice will in turn result in the formation of brine that would contain PFCs (as is the case for more complex molecules of higher molecular weight; Belzile et al., 2002), and these, along with the brine, may be transferred in density currents to the monimolimnion. This process would increase the contaminant burden in deeper waters, where primary production is maximal in Lake A because of anoxygenic bacterial phototrophs (Antoniades et al., 2009), and eventually, in the sediments. Moreover, year-to-year variability in atmospheric deposition, especially related to changes in emission strength over time, will remain a key determinant of absolute exposure levels.

Recent studies on the fate of PFCs during snowmelt in urban regions (Meyer et al., 2011; Plassmann et al., 2011) followed sampling campaigns that, if applied to High Arctic regions, would provide additional insights on the PFC transport pathways in Lake A. For instance, sampling continuously throughout the spring and summer (including the freshet) would give a better resolution of the transport dynamics. Long-term, multi-year sampling campaigns for contaminant burden and lake characteristics would also contribute to a better understanding of the Lake A ecosystem. It would also be possible to link climate parameters to contaminant burden in the ecosystem.

Additional effects of increased open water include colonization by aquatic birds, which were observed to arrive during the ice-out conditions of August 2008 (Vincent et al., 2009). Birds have been shown to be vectors of contaminants to Arctic ponds (Blais et al., 2005), and several studies have reported PFCs in Arctic bird populations (Tomy et al., 2004; Butt et al., 2007). The cascading effects of on-going climate change in these lakes (Mueller et al., 2009) may therefore include new transfer pathways as well as modified hydrodynamic processes, both favoring increased contaminant retention in these far northern, near-pristine ecosystems.

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APPENDIX

One figure and 10 tables of supporting information are available in the supplementary file attached to the online version of this article at <http://arctic.synergiesprairies.ca/arctic/index.php.arctic>.

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