Legacy and Emerging Persistent Organic Pollutants (POPs) in Terrestrial Compartments in the High Arctic: Sorption and Secondary Sources

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S Supporting Information

ABSTRACT: Legacy persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and emerging perfluoroalkyl substances (PFASs) were measured in vegetation and soil samples collected at remote lakes in the Canadian High Arctic. Field studies were carried out in 2015 and 2016 to assess concentrations of POPs, study the relevant sorbing phases, and determine whether Arctic soils were sinks or sources of legacy POPs to the atmosphere and to neighboring lakes. The patterns of legacy POPs in vegetation and soils were dominated by low molecular weight PCB congeners along with OCPs, confirming the importance of long-range atmospheric transport. Lipid and non-lipid organic matter was a key determinant of legacy POPs in Arctic vegetation. Soil organic matter was the main descriptor of hydrophobic PCBs and OCPs in soils, while soil inorganic carbon content, was an important driver of the sorption of PFASs in soils. While contaminant concentrations were low in soil and vegetation, higher PCBs and PFOS organic and inorganic carbon-normalized concentrations were found at Resolute Lake indicating the presence of local sources of contamination. Comparison of fugacities of PCBs in soil and air from Resolute Lake indicated soils as net sources of PCBs to the atmosphere.
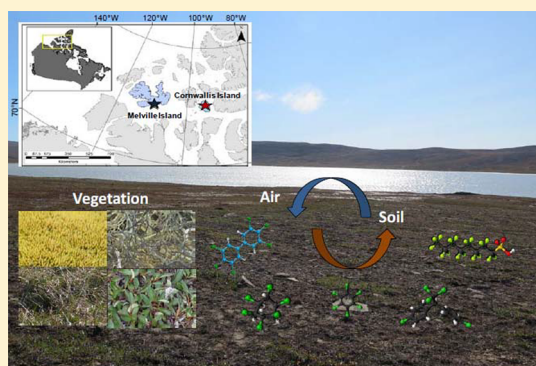
INTRODUCTION

Emission of persistent organic pollutants (POPs) in urban, agricultural, and industrial regions of the world has resulted in a substantial influx of pollutants to the Canadian Arctic. Legacy POPs such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), e.g., hexachlorocyclohexane (HCHs), dichlorodiphenyltrichloroethane (DDTs), and hexachlorobenzene (HCB), have been well documented in the Arctic over the past 30 years, especially in the Arctic atmosphere[1] and marine food webs.[2−5] Emerging POPs such as perfluoroalkyl substances (PFASs) were first identified in Arctic wildlife in the early 2000s and since then have been monitored in sentinel marine species including ringed seals, seabirds, and polar bears.[6−10] However, there have been far fewer studies of legacy and emerging POPs in terrestrial Arctic environments and the scarce studies are mainly focused on freshwater[11,12] and terrestrial food webs.[13−17] Little information is available on the presence of POPs in terrestrial compartments such as soils and vegetation across the circumpolar Arctic despite their importance as major ecosystem features. Since vegetation and especially soils are important pools of organic carbon[18] and therefore potentially large reservoirs of POPs, analyses are warranted to better discern the sorption of contaminants in these terrestrial

compartments. Lichen and vegetation such as mosses have been the main focus of the limited terrestrial food web studies in the Arctic[13−16] given their importance as dietary items for herbivores such as caribou and muskoxen. Scarce information is available on legacy POPs in vascular plants (e.g., grass, graminoids, shrubs),[19,20] which are also important sources of food for herbivores, especially during spring and summer.[21] A limited number of studies in the 1990s and early 2000s examined contamination of vegetation and soils by airborne PCBs from local sources such as military bases.[22,23] Soils play an important role in the global cycling of contaminants and are critical links between global atmospheric and hydrologic processes. Any alteration on soils due to warming or other perturbations will likely provide large inputs of stored pollutants to the atmosphere and to adjacent lakes affecting water quality and Arctic terrestrial and aquatic food webs. However, Arctic terrestrial food web studies have omitted the soil compartment on their studies despite its importance, and the analysis of POPs in soils conducted in the 1990s were
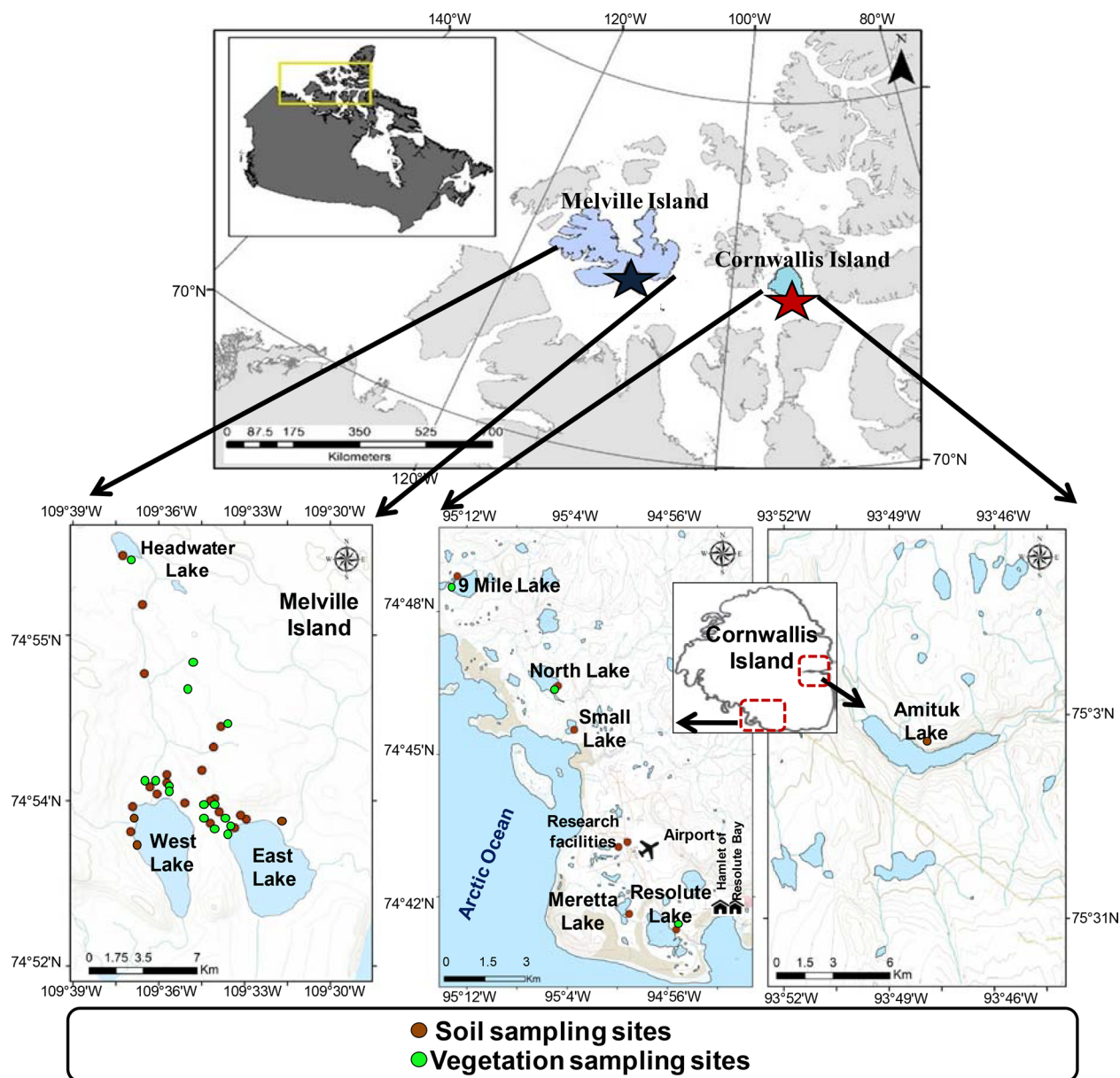
Figure 1. Sampling locations on Melville and Cornwallis Islands in the High Arctic.

focused on remediation studies on military bases or from local sources.[24] The significant impact of climate warming, demonstrated in Arctic terrestrial and freshwater ecosystems, has been shown to potentially increase legacy and emerging POPs through permafrost degradation, erosion, and summer rainfall.[25,26] This could alter the budget of POPs in the terrestrial Arctic compartments. Therefore, the main objectives of this work were to (i) provide a comprehensive data set on current concentrations of legacy pollutants (PCBs and OCPs) in remote Arctic soils and vegetation, (ii) assess for the first time the presence of PFASs in Arctic soils, and (iii) discern whether Arctic soils remain sinks of legacy POPs.

■ EXPERIMENTAL SECTION

Study Sites. Collection of soil and vegetation samples was performed around catchment areas of lakes sited in the Cape Bounty Arctic Watershed Observatory (CBAWO) on southern Melville Island (West, East, and Headwater lakes) and on Cornwallis Island (Resolute, North, Small, Meretta, 9 Mile and

Amituk lakes) in the Canadian Arctic Archipelago during summer 2015 and 2016 (late July-early August) (Figure 1). CBAWO is a remote and uninhabited location, 400 km from the nearest community of Resolute, Nunavut (Figure 1) and represents an environment largely unimpacted by direct human activity. The study site is considered as a High Arctic polar desert, and the climate of the region is among the coldest in North America[25] with prostrate shrub tundra vegetation. Permafrost in this High Arctic site is continuous[27] and likely exceeds 500 m thickness[28] and the active layer reaches a depth of approximately 50−70 cm in the summer season. Access to the site is available by short takeoff and landing aircraft only during the period of May−August when the field camp is open. Lakes in Cornwallis Island are located near the Inuit community of Resolute Bay (∼200 inhabitants), within the catchments of Resolute, Meretta, and Small lakes (Figure 1). North, 9 Mile, and Amituk lakes are located in more remote areas (7, 15, and 40 km, respectively from Resolute Bay). This community has a military and civilian airport in the Resolute

Lake catchment, operational since 1949 which discharged its wastewaters into the upper area of the catchment until 1997. The discharge greatly impacted the water chemistry of Meretta Lake[29,30] and water borne contaminants may have moved downstream into Resolute Lake. Three old solid waste landfills located 1.5 to 2 km west of the airport and used until the mid-1990s, have been studied for possible emissions of contaminants, including PCBs, to the ocean and the Meretta/Resolute Lake catchment.[31] Additionally, the logistics operations for Arctic research and military training use facilities are also located close to the airport. These activities (e.g., road dust from vehicle use, fire fighting, construction/demolition) may have introduced airborne contaminants into nearby catchment soils.

Soil, Lichen, and Vegetation Sampling. Soil samples (n = 34) from top 1 cm (Figure S1 to S4 of Supporting Information (SI) for details), and vegetation samples (including mosses, lichens, and vascular plants) (n = 18) (Figures S2 and S3) were collected within the lakes catchment areas. Additionally, two soil samples within the perimeter (5−10 m from the buildings) of the Arctic logistics operations at Resolute were also collected (Figure S4). Each soil and vegetation sample was pooled from several soil and vegetation samples located within the 2 m² to the sampling selected site. Surface soil samples were collected with clean stainless steel spoons, while clean stainless steel scissors and glove changed between samples were used for vegetation collection. All samples were stored in certified clean jars and kept at −30 °C until the analysis.

Fugacity Sampling. The fugacity sampler described elsewhere[32] and previously used to study the exchange of POPs in temperate[33,34] and polar regions[35], was used to assess whether Arctic soils are sinks or sources of legacy POPs to the atmosphere. A soil fugacity sampler coupled to an ambient air sampler was deployed during five consecutive days on the soil near Resolute Lake during summer 2016 (Figure S5 and Table S1 for details). The air passed through a quartz fiber filter (47 mm diameter) to remove dust particles and compounds in the gas phase were retained on polyurethane foam plugs (PUF; 10 cm × 2 cm). The main advantage of this sampler was that it allowed for accurately determining the POPs surface fugacity by sampling the air with sufficient time to reach equilibrium with the soil. In parallel, another sampler, operating in the same way, was deployed at 1.5 m above the ground surface, the typical height of conventional high volume air samplers. The sampling strategy performed in this study followed initial measurements reported in Antarctica,[35] although the sampler was slightly modified to use 12 V batteries because direct electric power was not available. A total air volume sampled were over 40 m³ and flow rate between 6 to 9 L/min. A paired sample of simultaneous air and soil fugacity measurements were taken for this study.

Analytical Methods. *Samples for Legacy POPs.* Homogenized soil (35 g), vegetation (10 g) and soil/ambient air fugacity samples were mixed with equal parts of cleaned Hydromatrix (diatomaceous earth; Dionex) (in the case of soil samples) or sodium sulfate (for vegetation samples) and spiked with $^{13}C_{12}$-labeled PCBs (PCB-28, PCB-52, PCB-101, PCB-153, PCB-138, PCB-180, and PCB-209). Soil and soil/ambient air fugacity samples were extracted by pressurized liquid extraction as described in Table S2 (Accelerated Solvent Extraction system (ASE), ThermoFisher/Dionex Instruments). Vegetation samples were Soxhlet extracted for 24 h in

dichloromethane (DCM) by ALS Global Laboratories (Burlington ON). ALS Global Laboratories (Burlington ON) is accredited by the Canadian Association for Laboratory Accreditation and ISO 17025 certified. A portion (75%) of the vegetation extracts was chromatographed on a gel permeation chromatography column (GPC) and shipped to Environment and Climate Change Canada for further processing. The remaining extract was used for gravimetric lipid determination. Extracts from soil and vegetation matrices were concentrated to 200 μL and subjected to further clean up using 5 g of activated silica (60−200 mesh silica gel) as described elsewhere.[11] Soil and ambient air fugacity samples were cleaned up and fractionated as reported in previous studies.[33−35]

PCBs (70 congeners from mono to decachloro PCBs (Wellington Laboratories)) and OCPs (HCB, HCHs, including α-HCH, β-HCH, and γ-HCH; DDTs including o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD o,p′-DDT, p,p′-DDT) were analyzed by gas chromatography (Agilent 7890B) coupled to tandem mass spectrometry (Agilent 7000C) (GC-MS/MS) operating in Multiple Reaction Monitoring (MRM) mode. The complete list of PCB congeners is presented in Table S3. Reference to the sum of homologue groups or the total sum of PCB (Σ_{70}PCBs), HCHs (ΣHCHs) considers the congeners and isomers mentioned above and in the SI.

Samples for PFASs. PFASs included in this study were perfluoroalkylcarboxylates (PFCAs) and perfluoroalkylsulfonates (PFSAs). PFCAs ranging from 4 to 13 carbons were included: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoDA, and PFTrA and summed together as ΣPFCAs. Total PFSA (ΣPFSAs) was comprised of PFOS, PFBS, PFHxS, PFHpS, PFDS, and PFECHS. Full names are provided in Table S4. Soil samples for PFCAs/PFSAs were extracted following a method reported previously for biota samples[12] with modifications to reduce matrix interferences (see Supporting Information for method details). PFASs were analyzed using an Acquity I-Class ultra performance liquid chromatograph coupled with a Xevo TQ-S tandem mass spectrometer system (UPLC-MS/MS, Waters, Mississauga, ON, Canada) operating in negative electrospray ionization mode with multiple reaction monitoring. Target analytes were quantified by relative response to the corresponding internal standard using a 15-point calibration curve.

Ancillary Parameters. Water content in soils and vegetation was also determined by freeze-drying until a constant weight was achieved. Total organic and inorganic carbon and total nitrogen in both soil and vegetation samples were determined by standard protocols at the National Laboratory for Environmental Testing (NLET, Environment and Climate Change Canada, Burlington, ON, Canada).

Quality Assurance/Quality Control. In order to minimize potential contamination, all samples were homogenized and processed in dedicated cleanroom laboratories (in Environment and Climate Change Canada). All analytical procedures were monitored using strict quality assurance and control measures.

For legacy POPs, batches of soil, vegetation, and soil/ambient air fugacity samples were extracted with method blanks at a rate of 1 every 5 samples processed. Only a few PCBs were detected in method blanks (PCB 49, 52, 87, 95, 149), and their contributions were in the range from 3% to 7% of levels found in the samples. Method detection limits
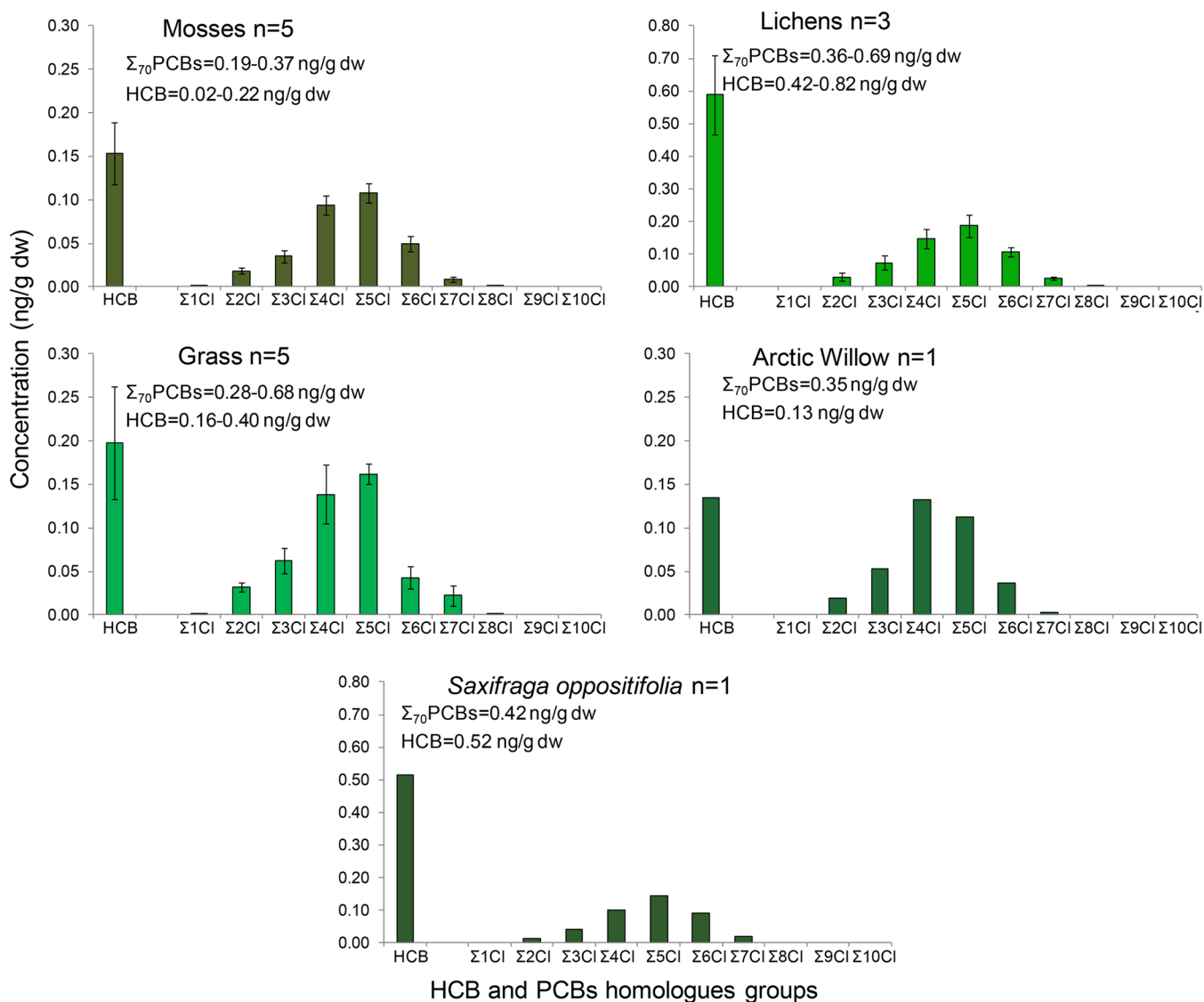
Figure 2. Profile distribution of PCBs and HCB in different types of vegetation and lichen from Melville Island.

(MDLs) of PCBs and OCPs were determined as 3 times the standard deviation (SD) of method blank concentrations. MDLs were derived from the lowest standard in the calibration curve for those PCBs with no signals in the blanks. MDLs were in the range from 0.1 to 13 pg/g dry weight (dw) for soil and vegetation and from 0.05 to 0.72 pg/m^3 for soil/ambient air fugacity measurements, respectively. Recoveries were routinely monitored in soil, vegetation and soil/ambient air fugacity samples using $^{13}C_{12}$-labeled PCBs and they ranged from 75 to 115%.

Spike and recovery tests were conducted for PFASs by spiking known concentrations of standards into samples ($n = 5$). In general, recoveries were >80%. Routine method blanks for PFASs were assessed in the same way as for legacy POPs. PFOA, PFDA, PFDoDA, and PFTriDa were detected in method blanks, but their contributions were less than 10% of levels found in samples, indicating minimal contamination during processing. MDLs determined, in the same way as for legacy POPs, were in the range from 0.1 to 18 pg/g dw. On the basis of good recoveries, concentrations reported herein were not corrected for recoveries but were corrected using average blanks.

All statistical analyses were conducted using IBM SPSS 20.0. Results for all POPs were $\log_{10}$ transformed in order to reduce coefficients of skewness and kurtosis, and Kolmogorov−Smirnov and Shapiro−Wilk tests were run to confirm normality. Statistically significant results were assessed against a type-1 error rate of probability <0.05.

RESULTS AND DISCUSSION

Occurrence of PCBs and OCPs in Arctic Vegetation. All the measured concentrations and Σ_{70}PCBs are listed in Tables S5−S7. Overall, low molecular weight PCB congeners groups (di- to hexa- PCBs homologues groups) dominated the vegetation profiles (Figures 2 and S6). Σ_{70}PCBs concentrations in vegetation from lakes on Melville Island were in the range of 0.36−0.69 ng/g dw in lichen; 0.19−0.37 ng/g dw in mosses; 0.28−0.68 ng/g dw in grass, and 0.35 ng/gdw and 0.42 ng/gdw in Arctic willow (*Salix arctica*) and *Saxifraga oppositifolia* respectively, while about 4-fold higher concentrations of PCBs (4.82 ng/g dw) were observed in mosses collected in the Resolute Lake catchment on Cornwallis Island (Figure S6). There are relatively few studies reporting data on pollutants in terrestrial Arctic vegetation. Mosses and lichens have been
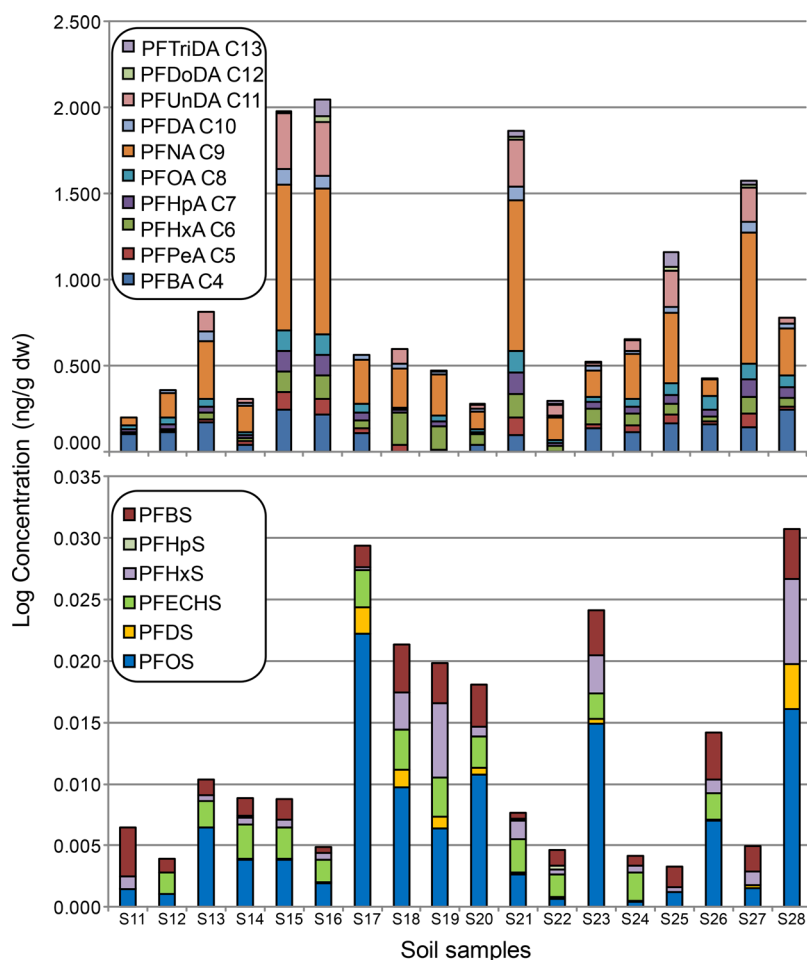
Figure 3. Profile distribution of PFASs in soils from Melville Island.

used for biomonitoring of heavy metals and rare earth elements in the Arctic.[36,37] Vascular plants were used to monitor PCBs in contaminated sites across the northern Canada, indicating concentrations spanning several orders of magnitude (0.11–49 000 ng/g dw) in samples collected near abandoned military sites.[38] In comparison, there is a paucity of information on background Arctic studies. Early studies (1989–1993) related to contamination from military sites, found PCB concentrations averaging 1.2 ng/g dw (Aroclor 1242 equiv; $n = 62$) at remote background sites.[22] Studies of PCBs and OCPs in lichens and willows in Bathurst Inlet and Cambridge Bay[13] (1997–1998), and in lichen along the coastline of eastern Hudson Bay[14] (1999–2002), reported levels of individual PCBs congeners in the same range as in this study (Tables S5–S7).[13,14] Concentrations of PCB congeners for mosses, lichens, and vascular plants in the present study were also similar to those reported for the Antarctic Peninsula.[39] The same ranges of concentrations have been reported in lichens (Σ_{18}PCB: 0.36 ng/g dw) and mosses (0.30 ng/g dw) in pristine areas of the Tibetan Plateau.[40] Higher concentrations of PCBs (in the range of 6.1 to 52 ng/g dw) were reported in mosses collected in remote areas of Norway,[41] but a potential contamination, due to contact with laboratory air, was suggested. Concentrations of HCB (0.02–0.82 ng/g dw), ΣHCHs (0.04–1.8 ng/g dw) and p,p′-DDE (0.006 and 0.22 ng/g dw) were similar among locations. Concentrations of HCB, ΣHCHs and p,p′-DDE reported in lichens collected from Bathurst Inlet and Cambridge Bay in 1997–1998, were

0.22–9.93 ng/g dw, 0.73–5.82 ng/g dw and 0.021–2.10 ng/g dw respectively,[13] which are in the same range or slightly higher than those reported here. Kelly et al[14] also reported a similar range of concentrations of HCB and ΣHCHs, but lower levels of p,p′-DDE (0.003–0.038 ng/g dw) in lichen from Eastern Hudson Bay. Similar ranges of OCPs have been previously reported in remote areas of the Antarctic Peninsula and Tibetan Plateau.[39,40] This is the first study to report legacy PCBs and OCPs in lichen and vegetation in the Arctic since 1999–2002, thus filling a data gap in terms of current concentrations of legacy POPs in Arctic terrestrial vegetation.

Occurrence of Legacy POPs in Soils. Soil concentrations of PCBs and soil physicochemical properties are listed in Tables S8–S11. Overall, Σ_{70}PCBs in soils collected in the catchment areas of lakes on Melville Island were in the range from 0.035 to 0.37 ng/g dw. The same ranges of concentrations were detected on Cornwallis Island, in those soils collected in catchment areas of Amituk Lake, a remote site 40 km northeast of Resolute Bay (Σ_{70}PCBs of 0.061 ng/g dw), as well as in sites 7 to 15 km west of the airport near North and 9 Mile lakes (Σ_{70}PCBs: 0.089 ng/g dw and 0.24 ng/g dw respectively). The same range of concentrations were found in soils on the Tibetan Plateau (0.057 ng/g dw (sum of 13 congeners)).[40] Slightly higher ranges of Σ_{70}PCBs concentrations (0.26–0.32 ng/g dw) were detected in soils collected within the perimeter (5–10 m of the buildings) of the Arctic logistics operations facilities and higher concentrations (2.83 ng/g dw), were detected in soil collected at

Resolute Lake,[11] which is in agreement with higher concentrations of PCBs detected in mosses collected at the same sampling site. The levels of PCBs reported here were comparable to other remote soils collected in Antarctica,[39,42,43] or slightly lower than previous reported concentrations in areas of the European Arctic, Ny-Ålesund and London Island (Svalbard) (0.57−2.52 ng/g dw).[44] Relatively higher concentrations (2.76−10.8 ng/g dw) were found in soils collected in areas close to the Chinese Yellow River Station (Svalbard),[45] or at 61 abandoned military and Coast Guard sites across the Canadian Arctic and Subarctic.[38] A profile dominated by more volatile, lower molecular weight PCBs homologue groups, such as Σtri to Σhexa-PCB was present in those soils collected on Melville Island and at remote lakes catchments soils on Cornwallis Island (Figure S7), which suggest long-range atmospheric transport (LRAT) as the main mechanism for PCBs delivery in those areas. A significantly different profile (Figure S7) with predominance of highly chlorinated PCBs up to octa and nona-PCB homologue group were found in soil collected at Resolute Lake and within the perimeter of the Arctic logistics operations facilities, suggesting a contribution of local PCBs sources (e.g., airport, older warehouse buildings, etc.) to the total burden of PCBs. The non-Aroclor congener PCB-11 (3,3′-dichlorobiphenyl) was also detected in the soil samples, but its contribution to the total burden of PCBs found in soils was quite low (<2%). No statistically significant differences between sampling locations and PCB-11 were observed. The extent of PCB-11 contamination in the Arctic is still unknown.[46] PCB-11 has been also detected in deep ice core and snow samples collected in Svalbard,[47] representing 0.9−4.5% of ΣPCBs. PCB-11 has also been reported in soil samples from the South Shetland Islands (Antarctica),[48] suggesting an ubiquitous global background distribution.

HCB, α-HCH, γ-HCH, and p,p′-DDE were the main OCPs detected in most of the soil samples, with concentrations ranging from 0.002 to 0.27 ng/g dw for HCB, MDL to 0.18 ng/g dw for α-HCH, MDL to 0.034 ng/g dw for γ-HCH and from MDL to 0.036 for p,p′-DDE in soils around catchment areas of selected lakes. The levels of OCPs reported here were comparable with previously reported values in soils in Arctic,[49] Antarctic regions[43] and the Tibetan Plateau.[40]

Occurrence of PFASs in Soils. Soil concentrations of individual perfluoroalkyl substances, ΣPFCAs and ΣPFSAs are listed in Tables S12−S15. ΣPFCAs (C4 to C13) concentrations in soils from Melville Island ranged from 0.20 to 2.05 ng/g dw. The most prominent PFCAs detected in soil samples were PFBA, PFOA, and PFNA contributing up to 60% of ΣPFCAs (Figure 3). PFBA, PFOA, and PFNA were also the dominant PFCAs in ice cores from a high altitude glacier in Eastern Alps[50] and in an ice core from the Devon Ice Cap on Devon Island in the Canadian Arctic archipelago.[51,52] PFBA, PFOA, and PFNA together with PFDA were also the most abundant PFCAs detected in ambient air samples at Alert.[53] In general, the levels of PFCAs in soil with odd-numbered carbon chain-length exceeded the levels of the corresponding one carbon shorter chain-length PFCAs (i.e., PFNA > PFOA, PFUnDA > PFDA and PFTrDA > PFDoDA), which agrees with the atmospheric transport and oxidation of PFCAs precursors (such as fluorotelomer alcohols)[51,54,55] as important sources of the observed PFCAs in the Arctic soils. This type of PFCAs profile has also been reported in terrestrial herbivores such as in caribou[15,56] and in moose[57] in northern Canada. Overall, correlations between carboxylate pairs (C5−C13)

were statistically significant (Table S16) with correlation coefficients ranging from 0.24 to 0.87. However, C4 PFBA, was only correlated with a few PFCAs suggesting that the presence of PFBA in Arctic soils may have different sources beside atmospheric transport and breakdown of PFCAs precursors. Recent studies have suggested that the occurrence of PFBA can be attributed to (i) direct emissions[50] or (ii) a shift in fluorotelomer production to short chain homologues[58] or (iii) atmospheric degradation of other C4 perfluorinated substances.[51] Direct emissions of PFBA are absent on Melville Island, which is uninhabited and very remote. The production shift to perfluorobutyl based chemistry does not account for the lack of correlation between PFBA and PFPeA. A more likely source of PFBA is chlorofluorocarbon replacement chemicals, which are known to yield PFBA.[51] These include hydrofluoroethers and hydrofluorocarbons which contain the C_4F_9 moiety.

Comparable ranges of ΣPFCAs (0.33−1.92 ng/g dw) were found in soils collected within the catchments of lakes on Cornwallis Island (Figure S8). The only available study[59] reporting PFCAs in remote soils from Antarctica (n = 1) (0.19 ng/g dw), South America (n = 3) (0.029−0.32 ng/g dw), Australia (n = 4) (0.079−1.2 ng/g dw), and Africa (n = 5) (0.012−1.49 ng/g dw) showed values in the same range as those reported in this study. In contrast, relatively higher concentration of ΣPFSAs, especially of PFOS, contributing up to 90% of total ΣPFSAs, were found in those soils collected within catchment areas of Meretta (7.60 ng/g dw), Resolute (0.28 ng/g dw) and Small lakes (0.47 ng/g dw), the lakes which are the closest to the local airport. Previous work[12] has shown that PFOS was the dominant PFASs reported in sediments of Meretta and Resolute lakes with concentration up to 57 and 64 ng/g dw, respectively, suggesting the strong influence of point source contamination by the local airport. However, soils located away from the airport, within the catchments areas of Amituk and North lakes, showed ΣPFSAs values of 0.001−0.024 ng/g dw, comparable with concentrations found in catchment soils of lakes in Melville Island (0.003−0.031 ng/g dw). The pathway of contamination of PFSAs to these distant lakes would have to be from airborne dust or releases of volatile precursors due to the activity at the airport. Concentrations reported here are similar than those levels reported in backgrounds soils in Lake Bonney (Antarctica) and Chile and Uruguay (South America).[59]

Sorbing Phases of POPs in Terrestrial Arctic. If long-range atmospheric transport is the main vector of POPs to the Arctic, then the uptake of POPs in Arctic vegetation and soils may be influenced by the occurrence of relevant sorbing phases, which for vegetation is given by the extractable lipid and non-lipid organic matter (NLOM).[13,14,16] Lipid content varies between species and within individual plants depending on different factors such as age,[60] growth rate, or structure.[61] Arctic mosses in this study showed lipid content <0.5% in all samples, at all locations. Lipid content of around 1% was detected in grass, Arctic willow (*Salix arctica*) and *Saxifraga oppositifolia*, while lichens showed slightly higher lipid content, in the range of 1.5 to 2.2%. The influence of lipid content, on PCBs and OCPs was assessed by regression analysis for those samples showing values above the detection limit (DL). Figures S9 and S10 show the significant dependence (p< 0.05) of OCPs (r^2 = 0.49−0.88) and individual PCBs (r^2 = 0.52− 0.85), on lipid content, especially on more hydrophobic PCB congeners (from 5Cl to 7Cl), while the correlation was not

statistically significant for the lighter PCBs. This suggests that despite the low values, lipid content is a key factor controlling highly chlorinated PCBs and OCPs in Arctic vegetation. The fact that mosses showed lipid content below the DL, together with the low values of lipids found in lichens and vascular plants, suggest that other biological constituents such as proteins and carbohydrates (the non-lipid organic matter) are likely relevant in the sorption capacity of POPs as suggested elsewhere.[13,14,16,62] The presence of adhering particles (dust, soil, etc.) may potentially be an artifact because vegetation samples were not washed prior to extraction. The lipid equivalent fraction (f_{Leq}) calculated as the sum of the lipid, protein and carbohydrate fractions[13,14,62] (see SI for further information on the calculation of the f_{Leq}) was 3.6% for mosses, 4.2% for lichens and between 5.5 and 6.4% for vascular plants and showed significant dependence ($p < 0.05$) on individual PCBs congeners ($r^2 = 0.23-0.53$), especially for less chlorinated PCBs, for which the influence of lipid content itself did not show a significant correlation (Figure S11). This suggests that non-lipid macronutrients such as proteins and carbohydrates appear to provide a substantial sorptive capacity of organic contaminants in Arctic vegetation especially for less chlorinated PCBs. As for vegetation, for soils, organic matter (measured as the fraction of organic carbon, f_{OC}) is generally considered as the main descriptor of the concentration of hydrophobic pollutants[63,64] at local, regional and global scales, especially for those having hydrophobic and lipophilic characteristics such as PCBs and OCPs. Soil f_{OC} in catchment soils from lakes at Melville and Cornwallis Islands ranged from the DL (<0.1%), detected in soils at the lake shoreline to 13.3% in soils with vegetation. These are relatively larger values than those found in remote soils from Antarctica.[39] A regression analysis showed significant dependence of PCBs homologue groups (Figure S12) and Σ_{70}PCBs (Figure S13) on the f_{OC} with r^2 of 0.18–0.58, $p < 0.05$. Less strong but statistically significant dependence ($p < 0.05$) was also observed for OCPs ($r^2 = 0.20-0.25$; Figure S13), which suggests the important role of f_{OC}, in the retention of legacy PCBs and OCPs in the terrestrial compartments in the High Arctic. The PFASs differ from legacy POPs in having both a perfluorocarbon chain which is both hydrophobic and lipophobic and an ionizable hydrophilic functional group, and thus their environmental behavior is more complex.[65] The relationship between f_{OC} and individual PFCAs and PFSAs concentrations in Arctic soils was studied, although only a significant dependence of PFSAs (PFOS, PFDS, PFHxS) on f_{OC} was observed (Figure S14) with r^2 in the range from 0.21 to 0.37, suggesting a modest influence of the organic carbon (OC) in the sorption of PFASs. Understanding the driving factors for sorption of PFASs in OC is only emerging. While some studies, mostly conducted in laboratory at fixed pH, have found strong relationships between sorption of the PFASs in sediments and f_{OC},[65–68] other studies have found only weak relationships[69] or a lack of correlation,[70] suggesting that other factors, such as the mineral content, water pH and temperature may be important in the sorption of these compounds. Given the importance of electrostatic interaction in the sorption of PFASs, it would be expected that the soil components that carry a surface charge enabling electrostatic interaction such as the mineral fraction, may be an important factor in the sorption process, although little is known about this sorption under field studies or in remote Arctic soils. The mineral composition of Arctic soil is varied, with feldspars, quartz and

clays being the most abundant soil mineral materials.[71] Although no direct measurements on those minerals were carried out, the determination of inorganic carbon (which may be a proxy of the soil mineral content) was performed. Soil inorganic carbon (SIC) in soils collected within lake catchment areas showed, overall, lower content than OC, in the range from DL = 0.1 to 3.45% and its influence on soil PFCAs and PFSAs concentrations was studied (Figure S15). Overall, a significant dependence of PFCAs (PFHxA, PFNA, PFDA) and PFSAs (PFOS, PFDS, PFHxS) on the SIC (reported as the inorganic carbon fraction, f_{IC}) was observed, with r^2 of 0.33–0.39 for PFCAs and of 0.34–0.48 for PFSAs, slightly higher r^2 coefficient than those correlations found with OC. The sorption of selected PFASs (PFHxA, PFOA, PFNA, and PFOS) from a water solution into a soil mineral such as alumina has recently observed in laboratory experiments,[72] confirming the important role of electrostatic interactions, which may explain the link found between the PFASs functional group (negative), and the inorganic carbon on the accumulation of PFCAs and PFSAs in remote Arctic soils.

Local Sources of Legacy and Emerging POPs in the High Arctic. Arctic soils were shown to have low to moderate content of f_{OC} (0.45–13.3%) and its presence was localized. Higher values of f_{OC} found in this study belong to soils covered by vegetation, in contrast to bare soils on shore of the lakes which showed f_{OC} values below 0.1%. Anthropogenic activities within the Arctic logistics operations facilities may have contributed significantly to increasing f_{OC} (11.4–12%). To elucidate potential sources of the compounds that showed the greatest differences between locations, Σ_{70}PCBs and PFOS, soil concentrations were normalized to organic and inorganic carbon content, respectively. Significantly higher OC-normalized PCB concentrations were observed in soil collected at Resolute Lake in comparison to other lakes in Cornwallis Island (e.g., North, Amituk, 9 Mile lakes) (Figure S16). OC-normalized PCBs concentrations in soils from most remote lakes on Cornwallis Island (e.g., North, Small, Amituk, 9 Mile) were comparable to those soils collected in lakes from Melville Island. PCB concentrations in soil collected at Resolute Lake, were higher even after OC-normalization, which may suggest a remobilization of old sinks of legacy POPs. Analogously, significantly higher inorganic carbon-normalized PFOS concentrations were observed in soils from Resolute and Meretta lakes, which further support the influence of the nearby local airport as a source of PFOS.[12] Σ_{70}PCBs and PFOS concentrations (OC- and IC-normalized, respectively) within soils at the Arctic logistics operation base area were small and similar to remote lake catchment soils (Figure S16) suggesting that this area was not a source to the broader local environment. Sampling at the base of three old solid waste landfills west of the airport, also found non-detectable concentrations of total PCBs in soils (less than the Canadian Environmental Quality guideline of 1.3 $\mu g/g$ dw) suggesting a general absence of PCB point sources in this region.[31]

Soil as Secondary Source and Soil-Air Exchange Controls on Atmospheric Concentrations of Legacy POPs. The role of Arctic soils as sinks and sources of PCBs to the atmosphere is germane,[73,74] although very few assessments are available in polar areas,[35,75] probably due to the logistical challenges and cost of performing sampling in remote places such as the Arctic. This is particularly relevant to areas close to neighboring lakes, rivers and the Arctic Ocean such as Resolute Lake, which have the highest PCBs loads and could affect

nearby lakes, rivers and marine waters, if acting as a source instead of a sink. Recent studies have suggested the importance of soils as secondary sources of PCBs to the polar atmosphere,[76] especially during summer seasons.[35,75] There is evidence from long-term temporal trends of PCBs in Arctic air (sampling stations at Alert, Pallas, and Zeppelin), that the rate of PCB decline in the Arctic atmosphere has slowed in recent years or even increased post- 2000, suggesting a mobilization of old sinks of pollutants.[1] The increasing temperatures may also have enhanced the re-emission of previously deposited PCBs from oceans, ice,[77] and neighboring soils, through processes such as soil−air exchange. These processes would be expected to result in increases in relatively lighter PCBs, consistent with observations of PCB-52 and PCB-101 in the Arctic atmosphere.[1] Arctic lakes, including those in this study, are mainly ice free during Arctic summer (July to August). In those months, lakes likely receive POPs inputs from snowmelt, river inflow, LRAT, and diffusive processes such as soil−air exchange. The soil−air exchange of POPs in the catchment soil of Resolute Lake was studied. Ambient air (f_A) and soil fugacities (f_S) were determined in situ in Resolute Lake (Figure S5) using a soil fugacity sampler[32] placed above soil with vegetation. PCB fugacity (expressed in Pascals) in soil (f_S) and ambient air (f_A) was determined directly under field conditions by:

$$f_A = 10^{-9} C_A RT / MW \qquad (1)$$

$$f_S = 10^{-9} C_{SA} RT / MW \qquad (2)$$

where C_A is the measured ambient air concentration at 1.5 m height (ng/m^3) (Table S17), R is the gas constant (8.314 Pa m^3 mol^{-1}K^{-1}), MW is the chemical molecular weight (g/mol), T is the respective air or soil temperatures, and C_{SA} (ng/m^3) is the gas phase concentration in equilibrium with the soil as measured using the soil fugacity sampler.[32] Σ_{70}PCBs in the atmosphere of Resolute Lake were 21 pg/m^3. Similar ranges of PCBs concentrations have been reported by the AMAP air monitoring stations in Alert, Pallas, Stórhöfdi, Zeppelin,[78,79] or on oceanic Arctic campaigns (Σ_{29}PCBs in the range from 3.3 to 130 pg/m^3[77] or Σ_{27}PCBs = 16−87 pg/m^3[80]). In this study, f_S was always higher than f_A for PCBs/OCPs, and the load of PCBs/OCPs found in the atmosphere was significantly correlated with the load of POPs escaping from the soil of Resolute Lake ($r^2 = 0.68$, $p < 0.05$, upper panel of Figure 4 and S17). This further supports the relevance of secondary emissions of PCBs and OCPs as drivers of the atmospheric concentrations in High Arctic environments. The comparison of fugacities in soil and ambient air allows determining the direction of soil−air exchanges. Soil-to-air fugacity ratios (f_S/f_A) ratios higher than 1 reflect a net volatilization of a chemical, while lower than 1 indicate net deposition. The effect of the uncertainty in the fugacities measurements has been previously quantified[33−35] to be less than 70%. Therefore, air-soil equilibrium is considered for Log f_S/f_A values between −0.52 and 0.23. Bottom panel of Figure 4, shows the soil-to-air fugacity ratios in log scale versus octanol-air partition coefficient (K_{OA}), for Resolute Lake. K_{OA} is widely used in the literature to predict the partitioning behavior of organic compounds between air and environmental matrices such as soil. Soil-to-air fugacity ratios in the catchment soil of Resolute Lake always showed close to equilibrium conditions to net volatilization (Figure 4) for PCBs with Log K_{OA} less than 7.5,
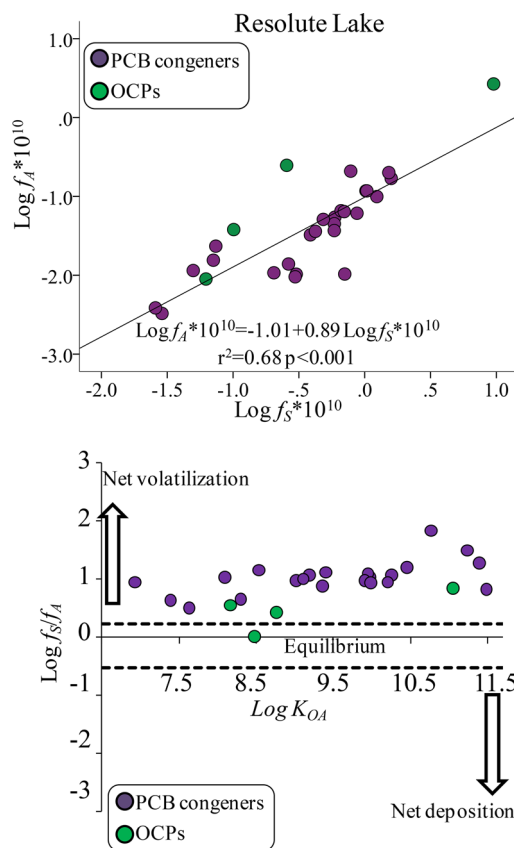

Figure 4. Fugacity in soil (f_S) versus fugacity in air (f_A), expressed on a log scale for individual PCB congeners and OCPs at soil from Resolute Lake (upper panel) and soil to air fugacity ratio (f_S/f_A) versus Log K_{OA} for individual PCBs and OCPs (bottom panel). Dashed lines indicate the equilibrium interval.

while a net volatilization was observed for the rest of PCBs. OCPs, especially α-HCH was in equilibrium, while a tendency to net volatilization from soil to the atmosphere was observed for HCB, γ-HCH and p,p′-DDE. This behavior suggests the importance of Arctic soils, especially during summer time, as significant sources of PCBs and OCPs to the atmosphere. The revolatilization of POPs from the soil reservoirs, especially during summer time has also been shown in remote soils at Svalbard[75] and in coastal soils of the Antarctic Peninsula.[35] The strength of POPs re-emission from soils may be also retarded in soils with vegetation in comparison to bare soils due to the differences in soil organic matter content.[35] The re-emission of POPs from soils at Resolute Lake, may be exerting a key influence on the temporal trends of Arctic char (*Salvelinus alpinus*), in the neighboring lake, since PCBs in Arctic char from Resolute Lake have not declined significantly since the mid 1990s.[11] Soil−air exchange may not be crucial in the mobilization of PFASs from catchment soils to neighboring lakes due to their physicochemical properties, particularly water solubility. However, climate modeling suggests a strong increase in Arctic precipitation over this century, attributed primarily to enhanced surface evaporation associated with sea-ice retreat.[81] It will not only affect Arctic hydrology (e.g., river discharge, permafrost thaw) but it may also affect terrestrial reservoirs of PFASs such as soils, enhancing their solubility and discharge. This would likely result in a decrease of PFASs stocks in Arctic soils and increased releases into Arctic rivers and lakes, as has already been reported during flooding

events.[82] This would alter current levels of PFASs in Arctic terrestrial and freshwater environments, affecting water quality and probably the temporal trends of aquatic food webs, although its magnitude is still unknown.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05011.

Ancillary material and additional figures and tables are included Annex I, II, and III (PDF)

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