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DISSOLVED ORGANOPHOSPHATE ESTERS AND POLYBROMINATED DIPHENYL ETHERS IN REMOTE MARINE ENVIRONMENTS: ARCTIC SURFACE WATER DISTRIBUTIONS AND NET TRANSPORT THROUGH FRAM STRAIT

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ABSTRACT

Organophosphate esters (OPEs) have been found in remote environments at unexpectedly high concentrations, but very few measurements of OPE concentrations in seawater are available, and none are available in subsurface seawater. In this study, passive polyethylene samplers (PEs) deployed on deep-water moorings in the Fram Strait and in surface waters of Canadian Arctic lakes and coastal sites were analyzed for a suite of common OPEs. Total OPEs (Σ_{11}OPE) at deep-water sites ranged from 6.3-440 pg/L and were similar in eastern and western Fram Strait. Chlorinated OPEs were present at the greatest concentrations in surface waters (mean concentration ranged from < DL to 4400 pg/L), while non-halogenated alkyl/aryl-substituted OPEs remained low (1.3-55pg/L), possibly due to the greater long-range transport potential of chlorinated OPEs. In comparison, polybrominated diphenyl ethers (PBDEs) were found at much lower concentrations than OPEs (< DL-14pg/L). Surface-water concentrations of tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were similar for both active and passive sampling approaches. Several OPEs were estimated to be undergoing net transport out of the Arctic, ranging from 17 kg/yr for ethylhexyldiphenylphosphate (EHDPP) to 3400 kg/yr for tris (2-chloroisopropyl) phosphate (TCIPP). This study highlights the importance of OPEs as poorly understood contaminants present at unexpectedly high concentrations in remote marine environments.

INTRODUCTION

Organophosphate esters (OPEs) are a group of synthetic organic contaminants expected to have a low potential for long-range transport based on traditional models.[1] However, they have recently been measured in Arctic air at unexpectedly high concentrations (10^1-10^3 pg/m^3).[2,3] This suggests that OPEs are capable of long-range transport to remote regions, though the transport mechanisms and ultimate fates of these compounds remain poorly understood. Very few measurements of seawater concentrations are available for OPEs, and none are currently available in subsurface seawater. As OPEs have been identified as the fastest growing sector of flame-retardant products,[4] more information on their concentrations in fresh and marine waters is urgently needed to better understand the transport and fate of these emerging contaminants in the marine environment.

In this study, passive polyethylene samplers (PEs) were used to derive the first estimates of dissolved OPE concentrations from deep-water moorings in Fram Strait, the passage between the North Atlantic and Arctic Ocean. Fram Strait is the only deep-water passage between the North Atlantic and central Arctic Ocean. Meridional transport in the upper water column brings warm Atlantic Ocean water north to the Arctic Ocean along the eastern side of Fram Strait via the West Spitsbergen Current while cold, fresh Polar Water from the Arctic Ocean is brought south along the western side of Fram Strait via the East Greenland Current.[5] Fram Strait deep water results from mixing of end members including Greenland Sea Deep Water and Eurasian Basin Deep Water from the Arctic Ocean, though the degree of mixing changes considerably depending on the location considered within the strait, and other water masses may also be involved.[6]

Passive sampling is a low-cost approach to obtain time-weighted average concentrations of dissolved organic contaminants in water. Because passive samplers do not require any power supply and can be left out for a long time to obtain integrated measurements at multiple remote locations, they are gaining attention as tools for measuring deep-water distributions of organic contaminants. Booij et al. used semi-permeable membrane devices (SPMDs) to measure time-integrated vertical distributions of various persistent organic pollutants (POPs) in the North Atlantic and Indian Oceans.[7] Sun et al. also deployed PEs on a deep-water mooring at a similar location to this study from 2012 to 2013 to investigate depth profiles of several POPs.[8]

In this study, extracts from PEs deployed at two mooring stations in eastern and western Fram Strait were analyzed for OPEs to construct the first depth profiles for these compounds in marine waters. PEs deployed in surface waters at three lakes and three coastal marine sites in the Canadian Arctic were also analyzed for OPEs to compare composition and concentrations of dissolved OPEs in these two remote environments. Concentrations of OPEs from surface-water passive samplers were compared with concentrations from active sampling during the same time period to determine whether passive-derived concentrations agreed with those collected via more traditional sampling techniques. Concentrations of OPEs were also compared to those of legacy organic flame retardants (i.e., polybrominated diphenyl ethers; PBDEs).

METHODS

Passive Sampler Preparation. PE sheets of 50-µm thickness were cut into 10 x 30 cm strips weighing about 2 g and precleaned by incubation in methylene chloride and hexane for 24 h each. Seven performance reference compounds (PRCs; dibromobiphenyl (PBB 9), tetrabromobiphenyl (PBB 52), pentabromobiphenyl (PBB 103), octachloronaphthalene (OCN), fluorene-d_{10}, pyrene-d_{10}, and benzo(a)pyrene-d_{12}) were loaded into the PEs for estimation of *in situ* sampling rates. PRC loading was done via a 1-month incubation in an 80:20 methanol:water solution containing the PRCs. PEs for field deployments were shipped out for deployment along with field blanks, which were shipped to field deployment sites, handled, and returned. Additional PEs were stored in the freezer for use as laboratory blanks. After deployments, all PEs were shipped cold to URI (University of Rhode Island) and stored in the freezer until extraction.

Deep-Water PE Deployments. Deep-water PEs were deployed for about one year (June, 2014 to July, 2015) at two sites maintained by the HAUSGARTEN long-term ecological research observatory in Fram Strait.[9] PEs were deployed at 4 depths (221 m, 446 m, 1151 m, and 2513 m) in eastern Fram Strait (79.010 N, 4.328 E) from June 23, 2014 to July 27, 2015, and at 5 depths (341 m, 504 m, 1184 m, 1690 m, 2439 m) in western Fram Strait (78.528 N, 2.764 W) from June 20, 2014 to July 31, 2015 (yellow triangles in Figure 1). Depths of PE deployments were determined based on the mooring design. PEs were strung on stainless steel wire and installed within stainless steel cages, with one PE at each depth. Hydrographic parameters (temperature, current speed and direction, and salinity) were recorded during the deployment by current meters (Aanderaa RCM9/11®) and self-recording CTDs (SeabirdSBE37®). Data are available in the PANGEA database.[10,11] Data were binned and averaged for depths relevant to each PE. Deployment dates and meteorological data are summarized in Table S1.

Surface-water PE Deployments. Surface-water PEs were deployed at 4-5 m depth at three lake sites and three marine sites in the Eastern Arctic during the summers (May to September) of 2015 and 2016. Lake and ocean sites are marked by green circles and orange pentagons, respectively, in Figure 1. At most sites, duplicate PEs were deployed, with the exception of North Lake. Only one PE was recovered from West Lake in 2016. Ambient concentrations derived from duplicate samplers were averaged to provide a single final concentration.

Atmospheric PE Deployments. PEs were deployed in air at one station on Cape Bounty (Melville Island, Fig 1) in between East Lake and West Lake. PEs were strung on stainless steel wire and deployed in duplicate within stainless steel cages on a stainless steel tripod at 1.5 m height (see Figure S1) to obtain measurements of gaseous OPEs for use in air-water exchange calculations.

Active Sampling of Canadian Arctic Surface Waters. Active sampling of surface water in Barrow Strait was conducted using Niskin samplers during ice covered (May) and open water (August) conditions. Duplicate 1 L samples were collected at depths between surface and 100 m, and transferred to precleaned amber glass bottles. Field blanks consisted of HPLC-grade water transported, exposed, and handled in the same manner as samples and compared to HPLC-grade water in the lab. The samples were shipped cold to Environment and Climate Change Canada and refrigerated until extraction.

Passive Sampler Extraction and Analysis. Preparation and analysis of passive samplers is described in the SI. Briefly, PEs were extracted overnight in hexane and concentrated to about 50 μL before analysis via gas chromatography coupled with mass spectrometry

(GC/MS) for 12 OPEs (tris(2-chloroethyl) phosphate (TCEP); tris(2-chloroisopropyl) phosphate (TCIPP); tris(1,3-dichloroisopropyl) phosphate (TDCIPP); tris(2,3-dibromopropyl) phosphate (TDBPP); tri-n-butyl phosphate (TNBP); triphenyl phosphate (TPHP); tris(2-butoxyethyl) phosphate (TBOEP); ethylhexyldiphenylphosphate (EHDPP); tris(2-ethylhexyl) phosphate (TEHP); tris(methylphenyl) phosphate (*ortho*, *para*, *meta*) (ToMPP; TmMPP; TpMPP)) and by GC coupled with triple quadrupole mass spectrometry (GC/MS/MS) for 12 PBDEs (BDE 2; BDE 8; BDE 15; BDE 30; BDE 28; BDE 49; BDE 47; BDE 100; BDE 99; BDE 154; BDE 153; BDE 183). Compounds are listed with CAS numbers in Table S2 and analytical parameters for passive sampler analysis are summarized in Table S3.

Method performance details are provided in the SI. Briefly, OPE spike recoveries were lowest for TDBPP (48-92%) and greatest for EHDPP (127-128%). Detection limits (DLs) were derived based on blank concentrations and are summarized in Table S4. DLs were greatest for TCIPP in deep-mooring samples (260 pg/L) and for TCEP in surface-water samples (1,600-15,000 pg/L). Relative percent difference (RPD) in ambient concentrations from duplicate surface-water samplers are summarized in Table S5.

Active Sampler Extraction and Analysis. 500 mL aliquots from active samples were extracted and analyzed by ultrahigh performance liquid chromatography with tandem mass spectrometry (UPLC-MS/MS) at Environment and Climate Change Canada as described further in the SI. Analytical parameters are summarized in Table S6. All OPE concentrations in active samples were corrected for internal standard recovery and blank-subtracted. Spike recoveries ranged from 33±6% for EHDPP to 101±9% for TPHP, and method detection limits were typically <600 pg/L (50 pg/L for ToMPP to 550 pg/L for

EHDPP) with the exception of TBOEP which was consistently observed in method blanks, resulting in a method detection limit of 5,900 pg/L (Table S7).

Passive Sampling Rate Determination. The rate of OPE absorptive uptake (k_o) into the PE was modeled as inversely proportional to the sum of the mass transfer resistance in the PE membrane and the water boundary layer, as shown below (Equation 1). This required estimating the molecular diffusivity of each target compound in polyethylene (D_{PE}) and in water (D_W), as well as the PE-water partitioning coefficient (K_{PEW}). The thickness of the PE boundary layer (δ_{PE}) was half the thickness of the PE sheet (25 μm) and the thickness of the water boundary layer (δ_{WBL}) was estimated by fitting PRC loss data to Equation 1 using the non-linear least squares regression function *nls* in R.[12] This approach is described in detail in previous studies.[13,14] More details on this approach and physicochemical properties used in calculations are provided in the SI.

$$\frac{1}{k_o} = \frac{\delta_{WBL}}{D_W} + \frac{\delta_{PE}}{D_{PE} \cdot K_{PEW}} \qquad \text{Eq 1}$$

Physicochemical Properties. One of the major challenges in understanding the transport and fate of OPEs is the paucity of empirical data on their physicochemical properties.[15] Here, PE-water partitioning coefficients (K_{PEW}) were estimated from subcooled liquid aqueous solubility (log $C_{w,sat}(L)$; mol/m^3) as in Lohmann 2012.[16] Lohmann reported that this regression exhibited a good fit (r^2=0.92; SE=0.35; N=100) for a wide variety of compounds with diverse properties, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), PBDEs, nonylphenols, and triclosan (log $C_{w,sat}(L)$ -5.2 to -0.01).

Physicochemical properties used to calculate ambient concentrations for OPEs and other target compounds are presented along with their sources in Table S8. Values of

$C_{w,sat}(L)$ used to estimate K_{PEW} for OPEs were taken from a collection of estimated properties by Zhang et al.[17] A range of calculated concentrations based on two different sets of solubility values are presented in the SI, but concentrations calculated from EPI Suite WSKOWWIN performed best in predicting $C_{w,sat}(L)$ values for a wide range of compounds according to Zhang et al., and hence were applied in this study.[17] However, these values were often biased low, meaning that estimated ambient concentrations may also be underestimated. To interpret results for PEs deployed in seawater, values of $C_{w,sat}(L)$ were corrected for salinity, as described in the SI.[18]

All K_{PEW}s were corrected for mean deployment temperature as previously described,[16] assuming an energy of solvation of 25 kJ/mol. As mentioned by Booij et al.,[7] there is most likely an effect of hydrostatic pressure on physicochemical properties of organic chemicals. Due to these pressure effects, Booij et al. observed increasing uncertainty in sampling rate estimation with increasing depth (0.2 log units in surface waters, increasing to 0.6 log units at 5 km depth).[7] This effect is not well characterized, so parameters used here were not adjusted for changes in pressure with depth.

Air-Water Exchange Calculations. The approach used to calculate air-water fugacity ratios for diffusive exchange at the air-sea interface is described in the SI.

Fram Strait Net Transport Calculations. Calculation of net transport through Fram Strait is complicated by the hydrography in the region. While most studies concur that net transport of water through Fram Strait is around 1-2 Sv southward, there are a wide range of estimated volumes for transport in and out of the strait.[5,19–22] Here, we estimated that southward transport was 8.7 ± 2.5 Sv, as in de Steur et al.,[22] and northward transport was estimated as 6.6 ± 0.4 Sv, as in Beszczynska-Moller et al.[5] These estimates were derived from results of a long-term mooring array which is close to the PE mooring locations.

Total masses of OPEs and BDEs entering and leaving the Arctic Ocean via the Fram Strait were roughly estimated by calculating depth-weighted average concentrations and scaling by the total transport volumes. In this estimation, concentrations < DL were replaced with 0 and OPE concentrations were calculated using WSKOWWIN-derived K_{PEW} values, yielding the lower of the two estimated concentrations in this study.

RESULTS & DISCUSSION

Sampling Rates and Percent Equilibration. PRC loss data is summarized in the SI for deep-water (Table S9) and surface-water sites (Table S10). Percent equilibration predicted for the OPEs at each site is presented in Table S11 for deep-water deployments and Table S12 for surface-water deployments. At deep-water sites, where PEs were deployed for about one year, the five smallest OPEs ($V_m < 300$ cm^3/mol; log $K_{PEW} < 5$) were estimated to reach > 80% equilibrium during deployments (Table S11). Among the non-equilibrated compounds, sampling rates calculated from best-fit δ_{WBL} ranged from about 2-8 L/day, which is fairly reasonable considering that flow was limited by the protective cages around each PE, and agrees well with estimated sampling rates for eastern Fram Strait during 2012-2013 PE deployments (4-10 L/day), which were calculated using an alternative PRC-based approach.[8] Mean current velocity for all PEs at all depths ranged from 7-13 cm/s. The greatest sampling rates and fastest current velocities were observed for the shallowest PEs in Fram Strait. The lowest sampling rates and slowest current velocities were found for the deepest PEs in eastern Fram Strait.

At surface-water sites, PEs were deployed for 20-70 days, and only two chlorinated OPEs (TCEP and TCIPP) were predicted to approach equilibrium. For the remaining OPEs, sampling rates ranged from 0.74 L/day for TNBP at Barrow Strait to 29 L/day for TDBPP at Sachs Harbour.

Dissolved OPEs in Fram Strait Depth Profiles. Range, mean, and median concentration for all OPEs derived from passive and active samplers in the Fram Strait and Canadian Arctic regions for this study are summarized and compared to active-derived values from Li et al.[23] in Table 1. Concentrations of all OPEs and BDEs from deep-water PEs are shown in Table S13. OPE concentrations in Table S13 are presented as a range of concentrations derived using two different K_{PEW}s based on different aqueous solubility values (WSKOWWIN- and WATERNT-derived, as in Zhang et al.[17]). Values presented in the text and figures are calculated from WSKOWWIN-derived K_{PEW}s, which are the lower of the two sets of OPE concentrations in Table S13.

Depth profiles of frequently detected dissolved OPEs (TDCIPP, TCIPP, TPHP, EHDPP, and TEHP) and BDEs (BDE 47) are shown in Figure 2. Current dynamics in the Fram Strait region are driven by complex bottom topography; lateral advection as well as downward transport are known to be important transport mechanisms in the deeper water column, and highly variable currents make source identification difficult.[24] Based on what is known about the hydrography of Fram Strait, samples from the upper water column in the eastern parts of the strait represent Atlantic Ocean water entering the Arctic, while samples from the upper column of the western strait are more representative of cold, low-salinity water leaving the Arctic Ocean, and deep waters (> 2000 m) are generally representative of Eurasian Basin Deep Water and Greenland Sea Deep Water.[5]

However, this picture is complicated by seasonal recirculation within the strait,[25] and the average current direction in the upper water column at both sites was moving to the south during passive deployments (Table S1).

Total OPEs (Σ_{11}OPE) at deep-water sites ranged from 6.3 to 440 pg/L, and concentrations of frequently-detected OPEs were similar at the eastern and western sites. Previous studies measuring OPEs via active sampling methods in coastal, estuarine, and lacustrine environments generally reported concentrations at least an order of magnitude greater than concentrations measured at deep-water sites in this study.[23,26–28]

Most deep-water samples were dominated by halogenated OPEs (TCEP, TCIPP, and TDCIPP), which made up 34-100% of Σ_{11}OPE. Total alkyl/aryl-OPEs (Σ_7Alkyl/Aryl-OPE) ranged from 0.1 to 66 pg/L, and were present at lower concentrations than Σ_3Cl-OPE (6.2-430 pg/L). Previous studies of surface water, air, and sediment in the region have also shown a predominance of chlorinated OPEs.[3,23,29] This was expected, as alkyl/aryl-OPEs are more readily degradable than Cl-OPEs by indirect photolysis and/or hydrolysis.[30–33] Additionally, Sühring et al. noted that Cl-OPEs may be more effectively transported via ocean currents, while alkyl/aryl-OPEs are transported primarily through the atmosphere.[3] More effective waterborne transport of Cl-OPEs could also help explain the predominance of Cl-OPEs in deep-water samples. TCIPP was the most abundant OPE in the majority of samples, ranging from below detection limit (< DL) to 54 pg/L (0-93% of Σ_{11}OPE). TCEP was the most abundant OPE in the two western Fram Strait samples where it was above detection limits (350-390 pg/L), but was blank-censored in all other cases.

In both eastern and western Fram Strait, little variation in dissolved OPE concentrations was observed with depth. Trends with depth did not change appreciably based on the set of estimated K_{PEW} values used to calculate ambient concentrations. Flat depth profiles could be due to a high degree of vertical mixing, lateral advection, and/or the release of particle-bound OPEs to the dissolved phase with depth.[34] Booij et al. also observed little change in concentration for PCBs, PAHs, and OCPs over a depth range of 100-3,000 m in the Irminger Sea using SPMDs.[7]

Dissolved PBDEs in Fram Strait Depth Profiles. BDE 47 was the most frequently detected PBDE in Fram Strait depth profiles (Figure 2). Concentrations of all PDBEs are summarized in Table S15. Σ_{12}BDE was much lower than Σ_3Cl-OPE levels (< 2 pg/L at all sites), which was consistent with concentrations measured by Sun et al. in eastern Fram Strait, as well as with active sampling-derived concentrations from Möller et al. in the East Greenland Sea.[8,35] Concentrations of OPEs were also much greater than surface-water concentrations of Dechlorane Plus (< 1 pg/L) in the Fram Strait and several novel brominated flame retardants (all < 2 pg/L) in the East Greenland Sea.[35,36] This supports findings from other recent studies showing that, though OPEs were originally expected to have limited potential for long-range transport, they are being delivered to remote Arctic regions in significant quantities.

As with OPEs, there was no clear BDE concentration gradient with depth at either mooring. Sun et al. also observed flat depth profiles for several persistent organic pollutants in eastern Fram Strait, including BDE 100 and several chlorinated pesticides.[8] Salvado et al. observed a significant increase with depth in concentrations of several lower-brominated BDE congeners, including BDE 47, in the Nansen, Amundsen, and

Makarov Basins of the Arctic Ocean via active sampling of particle and dissolved BDEs.[37]

Dissolved OPEs in Canadian Arctic Surface Waters. Mean 2015-2016 surface-water concentrations of OPEs are summarized in Table 1 and shown in Figure 3, along with mean active-derived water concentrations from Barrow Strait collected at 1-5 m depth from four different time points between May 2015 and August 2016. Concentrations of all OPEs from all surface-water deployments are summarized in Table S14.

Surface-water Σ_3Cl-OPE concentrations were much greater than in deep-water sites in Fram Strait, with mean 2015-2016 passive-derived Σ_3Cl-OPE ranging from < DL in North Lake on Cornwallis Island to 4,400 pg/L at East Lake on Cape Bounty. Σ_3Cl-OPE was greatest at lake sites in Cape Bounty and lowest at sites where TCEP was < DL (North Lake and Barrow Strait). When detected, TCEP was the most abundant Cl-OPE, making up 70-85% of Σ_{11}OPE. This is consistent with results from Ma et al. in Arctic sediments and Sühring et al. in Canadian Arctic air, where TCEP was the dominant OPE.[3,29]

Σ_7Alkyl/aryl-OPE was also greater than at deep-water mooring sites, with mean 2015-2016 concentrations ranging from 1 pg/L in Sachs Harbour to 55 pg/L in North Lake, though TNBP concentrations in surface waters were similar to those measured at deep-water sites above 1000 m. TNBP was the most abundant alkyl/aryl-OPE in samples where it was found above detection limits, with average concentrations ranging from < DL to 48 pg/L at North Lake. TPHP was the only OPE detected > DL in all surface-water samples, with average concentrations ranging from 1 pg/L at Sachs Harbour to 8 pg/L at West Lake.

Active- and Passive-Derived Surface-Water OPE Concentrations. At Canadian Arctic lake sites, the fraction of OPEs expected to be in the dissolved fraction (which is free to diffuse into the PE membrane) was estimated based on dissolved organic carbon (DOC) concentrations and DOC-partitioning coefficients (K_{DOC}). DOC was measured at each lake once per sampling year during the summer months (June-August) and ranged from 0.7 mg/L in North Lake in July, 2015 to 2.5 mg/L in West Lake in June, 2016. K_{DOC} was assumed to be one tenth of the octanol-water partitioning coefficient (K_{OW}) as in Burkhard et al. [38] using K_{OW} values listed in Table S8. Based on these calculations, the majority of frequently-detected OPEs (TNBP, TCEP, TCIPP, TDCIPP, TPHP, and EHDPP) were expected to be > 90% in the dissolved phase, implying that differences between active- and passive-derived concentrations are primarily the result of different sampling periods and uncertainties in physicochemical properties, rather than differences in selectivity between the two sampling methods.

Concentrations of TCEP were similar for active- and passive-derived samples, with mean 2015-2016 passive-derived concentrations of 1,800-3,800 pg/L at Cape Bounty freshwater sites, 1,300 pg/L at Sachs Harbour, 1,100 pg/L at Allen Bay, and 820-2,000 pg/L from active sampling in Barrow Strait. Concentrations of TDCIPP were also similar among passive samplers (< DL-400 pg/L) and active samplers (< DL- 960 pg/L). However, active-derived concentrations of dissolved TCIPP were greater than passive-derived concentrations (930-5,700 pg/L from active samplers, < DL to 570 pg/L in passive samplers). This may be due to varying concentrations between active snapshot sampling and time-weighted average passive sampling, coupled with uncertainties in physicochemical properties used in calculating passive-derived concentrations.

Passive-derived dissolved Cl-OPE concentrations were similar to active-derived total (particle + dissolved) concentrations in seawater measured by Li et al. in the North Atlantic and Arctic Oceans (Table 1), where TCEP ranged from < DL to 2,400 pg/L, TCIPP ranged from 300 to 5,800 pg/L, and TDCIPP ranged from < DL to 40 pg/L. Cl-OPE concentrations measured in this study were comparable, but on the lower end, of active-derived concentrations from other regions. Venier et al. measured Σ_3Cl-OPEs in the range 2,100-18,000 pg/L in the surface waters of the Great Lakes, with TCIPP most abundant. In German Bight surface waters, Σ_3Cl-OPEs ranged from about 1,000 to 10,000 pg/L, again with TCIPP most abundant.[27]

Average passive-derived concentrations of Σ_7Alkyl/Aryl-OPEs (1-55 pg/L) were lower than active-derived concentrations from Barrow Strait, which ranged from (630-1,800 pg/L). EHDPP and TPHP made more prominent contributions to active-derived OPE profiles, where they made up 0-7% and 5-17% of total OPEs, respectively. This could be due to active samplers collecting some amount of colloidal-bound OPEs in the dissolved-phase fraction, as K_{DOC} estimates from DOC concentrations are somewhat uncertain, and EHDPP and TPHP are expected to be more hydrophobic compounds that would partition to a greater extent into the colloidal and particulate fraction (log K_{ow} of 4.7-5.7, as compared to 4.3 for TNBP).

Concentrations of TNBP were similar to the mean concentration measured by Li et al. via active sampling in Northern Atlantic and Arctic Ocean seawater (120 pg/L; Table 1).[23] Other alkyl/aryl-OPEs were either < DL or found at very low concentrations in samples collected by Li et al. Previous studies of other regions have reported much greater concentrations of dissolved alkyl/aryl-OPEs than this study, again supporting the greater propensity of Cl-OPEs for long-range transport compared to alkyl/aryl-OPEs. Venier et al. measured Σ_3Alky/aryl-OPEs (TNBP, TPHP, and TBOEP) from 3,300-78,000 pg/L in the surface waters of the Great Lakes, with TBOEP most abundant.[28] In German Bight surface waters, Σ_3Alky/aryl-OPEs were only intermittently detected by Andresen et al. above detection limits at sites distant from shore, and ranged from < DL to 3,500 pg/L in the plume of the River Elbe.[27]

PBDEs in Canadian Arctic Surface Waters. Total average dissolved surface-water PBDE concentrations for each sampling year are shown along with OPE concentrations in Figure S2. Concentrations of all PBDEs in surface-water samples are summarized in Table S14. Σ_{12}BDE ranged from < DL at North Lake, Sachs Harbour, and Barrow Strait to 23 pg/L at East Lake in 2015.

As in deep-water samples, BDE 47 was the most frequently detected BDE, while other congeners were only detected intermittently. Previous work by Möller et al. found BDE 47 and 99 to be dominant in East Greenland Sea, with concentrations < 2 pg/L, which was similar to or lower than total BDEs measured at seawater sites in this study (1-6 pg/L, with elevated concentrations of 15 pg/L at Barrow Strait). Salvado et al. measured BDE 47 of < DL-1.5 pg/L in polar mixed layer samples from throughout the Arctic Ocean, and observed that BDEs were elevated in coastal shelf regions, which were more similar to sites monitored in this study.[37]

Potential Sources of OPEs and BDEs to Canadian Arctic Surface Waters. Total average OPE concentrations at each surface-water site in each sampling year (2015 and 2016) are shown in Figure S2.

Potential local sources of OPEs to both marine and lake sites appear to be fairly limited. For the Arctic lakes, sources of OPEs to water are limited to atmospheric deposition and catchment inputs from snowmelt and summer rains.[39,40] Among lake sites, North Lake was the least remote, within 4 km of a small airport and 6 km of a small village (approx. 125 inhabitants), while East and West Lake were located at the Arctic Watershed Observatory,[41] more than 500 km from any appreciable settlements. Marine sites at Allen Bay, Barrow Strait, and Sachs Harbour were 6-13 km from small towns and their airports (approx. 125-150 inhabitants).

Figure S2 shows that Cl-OPEs exhibited elevated concentrations at East Lake in 2016, while the opposite trend was seen for BDEs. Elevated Cl-OPE concentrations were due primarily to elevated TCEP and, to a lesser extent, TDCIPP. In comparison, dissolved alkyl/aryl-OPEs were greater in 2015 than 2016 at both lake sites. Similar to West Lake, concentrations of both alkyl/aryl-OPEs and Cl-OPEs were elevated in marine surface waters at Allen Bay in 2015 compared to 2016.

Differences in year-to-year dissolved OPE concentrations shown in Figure S2 may be due in part to the season in which passives were deployed, which offers some clues as to sources contributing to OPE concentrations in the Canadian Arctic. In 2015, passives were deployed in East and West Lake for the first three weeks of August, while in 2016, they were deployed from early June to late July. Typically, maximum snowmelt discharge into these river-fed lakes occurs in mid-June, with return to baseflow by early July.[40] This suggests that samples taken in 2016 may be more representative of the snowmelt influx, as well as ice-melt waters, as the primary period of ice-off for the lakes is generally mid-July to early August. If this is the case, it would appear that increased snowmelt in East Lake led to increased concentrations of Cl-OPEs, rather than causing a dilution effect, though the same trend is not seen in West Lake. Li et al. measured TCEP and TCIPP in snow collected from Arctic sea ice at mean concentrations of 2,400 and 6,300 pg/L, respectively, suggesting that this reservoir could act as a source of Cl-OPEs.[23] Cl-OPEs were all < DL in North Lake, where PEs were deployed later in the season (late July to early October), and pulses from snowmelt would not have been captured. Potential sources of OPEs that could be stored in snow are unknown, and further data from additional time periods would be needed to confirm whether seasonal fluctuations in riverine inputs and melting explain our observations.

Atmospheric OPE Concentrations and OPE Air-Water Exchange. The composition of gaseous OPEs derived from passive air samplers on Cape Bounty was dominated by Cl-OPEs. TCEP was most abundant, which was consistent with results from Li et al. in active-derived gaseous OPE concentrations from the Arctic Ocean, as well as Sühring et al. in atmospheric particulate samples from the Canadian Arctic.[3,23] Concentrations are fairly similar to those from Li et al., who used a high-volume active sampler with PUF/XAD-2 sorbent to collect gas-phase OPEs in the northeastern Atlantic and Arctic Oceans (Figure S3). Mean concentrations of TCEP (2.4 pg/m^3 in 2015 to 14 pg/m^3 in 2016) were somewhat lower than mean concentrations from Li et al. (23 pg/m^3),[23] and 1-2 orders of magnitude lower than those from Sühring et al. (170 ± 170 pg/m^3).[3]

The composition of alkyl/aryl-OPEs was similar to what was seen in the gaseous phase by Li et al., as well as in the particulate phase by Sühring et al. in Resolute Bay and Salamova et al. in Longyearbyen, Svalbard, with Σ_7Alky/aryl-OPEs dominated by TNBP when it was detected.[2,3,23] However, the particulate fraction measured in other studies contained more significant contributions of relatively hydrophobic OPEs such as EHDPP and TPHP than was observed in gas-phase samples from this study. Average concentrations of TNBP ranged from 9 pg/m^3 in 2015 to 18 pg/m^3 in 2016, which was greater than mean gaseous TNBP from Li et al. (2.2 pg/m^3), possibly because the majority of their sampling locations were further from land. Concentrations measured here were lower than particulate concentrations measured by Sühring et al. in Resolute via land-based sampling (mean TNBP 747 ± 876 pg/m^3) and by Salamova et al. in Longyearbyen, Svalbard (174 ± 46 pg/m^3).

Fugacity ratios calculated from average equilibrium-corrected PE concentrations in air and water at each site are shown in Figure S4. Generally, fugacity ratios were within the range of -0.5-1.5, which suggests that they are not significantly different from equilibrium, with the exception of some volatilization of TNBP observed at Cape Bounty lake sites in 2016 and of TDCIPP in Barrow Strait in 2015, and deposition of TPHP and/or TDCIPP seen in 7 out of 9 air-water sample pairs. All fugacity ratios were calculated using gaseous OPE concentrations from Cape Bounty, which increases the degree of uncertainty in calculations for sites other than East Lake and West Lake, as gaseous concentrations could have varied significantly from place to place, and between seasons.

Masses of OPEs and BDEs Transported via Fram Strait. The estimated transport of OPEs and BDEs are shown along with net exchange in Table 2. Only compounds detected at two or more depths per mooring are presented in the table. For the two most frequently detected BDEs (BDE 47 and BDE 8) net transport appeared to be northward into the Arctic Ocean (40±16 kg/yr and 21±12 kg/yr, respectively). For three of the OPEs

(TCIPP, TPHP, and EHDPP) net transport was southward into the North Atlantic Ocean, ranging from 17±19 kg annually for EHDPP to 3,400±3,200 kg annually for TCIPP. Among OPEs, only TDCIPP exhibited net transport into the Arctic Ocean (281±208 kg/yr northward). This implies that the Arctic Ocean has already been widely impacted by OPEs entering the region via the northward transport of water masses in the eastern Fram Strait, as well as numerous other sources, possibly including river inputs, which are a major source of freshwater to the Arctic Ocean previously identified as a possible source of OPEs by Sühring et al.,[3,42] and atmospheric deposition. While usage of OPEs has increased considerably in recent years due to the phase-out of many halogenated flame retardants, these compounds have been used to some extent for several decades,[43] so the timescales over which they have been delivered to deep-water masses are unknown.

Net export of several OPEs from the Arctic Ocean suggests that ocean currents are a significant pathway exporting OPEs from the Arctic. Along with their presence in Fram Strait deep-water samples, it also suggests that these compounds have reached the deep ocean and are already widespread and well-mixed in Arctic water masses. Little information is available on production volumes for OPEs, making it difficult to determine how mass transport derived in this study compares to total masses of these compounds that have been released. More measurements of OPE concentrations from throughout the region will be needed to constrain inventories for OPEs in deep-water masses.

ASSOCIATED CONTENT

Supporting Information. Detailed information on sampler deployments, site characteristics, and compound properties can be found along with calculated sampling rates, table of concentrations, and plots describing the results of principal component analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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Author Contributions. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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FIGURES AND TABLES

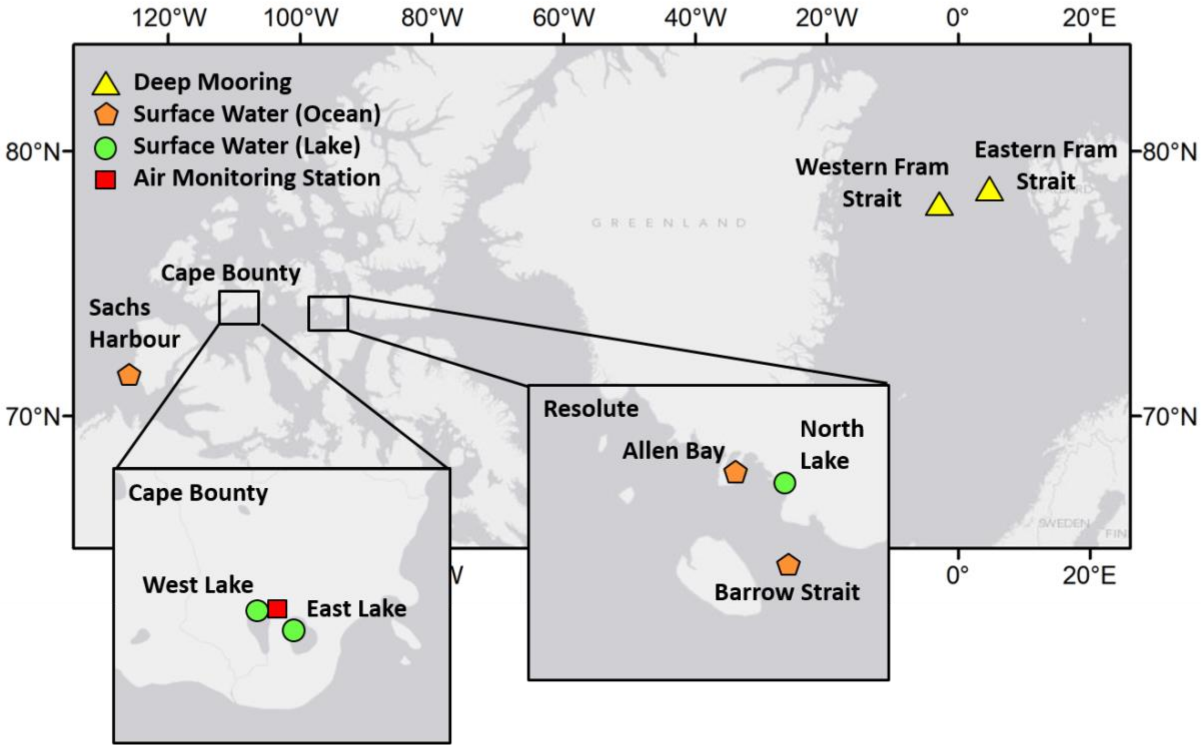


Figure 1. Locations of passive sampling deployments in lake surface waters (green circles) and marine surface waters (orange pentagons), air (red square), and on deep-water moorings (yellow triangles).

	North Atlantic Deep Moorings			Canadian Arctic Surface Waters			Active-Derived Barrow Strait Surface Waters			Active-Derived North Atlantic/Arctic Surface Waters (Li et al. 2017)		
	Min - Max	Mean	Median	Min - Max	Mean	Median	Min - Max	Mean	Median	Min - Max	Mean	Median
TNBP	<DL - 63	10	<DL	<DL - 48	25	26	170 - 630	430	450	<DL - 410	120	100
TCEP	<DL - 390	81	<DL	<DL - 5100	1600	1200	820 - 2000	1400	1300	<DL - 2400	700	610
TCIPP	<DL - 54	36	40	<DL - 570	190	170	930 - 5700	3100	2900	279 - 5800	1800	1600
TDCIPP	1.6 - 7.1	3.5	2.8	<DL - 530	160	110	<DL - 960	620	760	<DL - 43	7.0	4.0
TPHP	<DL - 1.2	0.60	0.70	0.99 - 8.2	4.8	5.1	410 - 790	570	540	<DL	<DL	<DL
EHDPP	0.06 - 0.33	0.21	0.24	<DL - 6.5	2.0	1.3	<DL - 630	290	280	NA	NA	NA
TEHP	<DL - 1.5	0.61	0.59	<DL	<DL	<DL	<DL - 47	23	22	<DL - 69	6.0	<DL
ToMPP	<DL	<DL	<DL	<DL	<DL	<DL	NA	NA	NA	NA	NA	NA
TmMPP	<DL - 0.03	0.003	<DL	<DL - 1.1	0.72	1.0	NA	NA	NA	NA	NA	NA
TpMPP	<DL	<DL	<DL	<DL - 0.28	0.08	<DL	NA	NA	NA	NA	NA	NA
TDBPP	<DL	<DL	<DL	<DL - 230	65	<DL	<DL - 110	45	36	NA	NA	NA

Table 1. Concentrations (pg/L) for OPEs in water samples (passive and active) from this study and from Li et al. 2017.

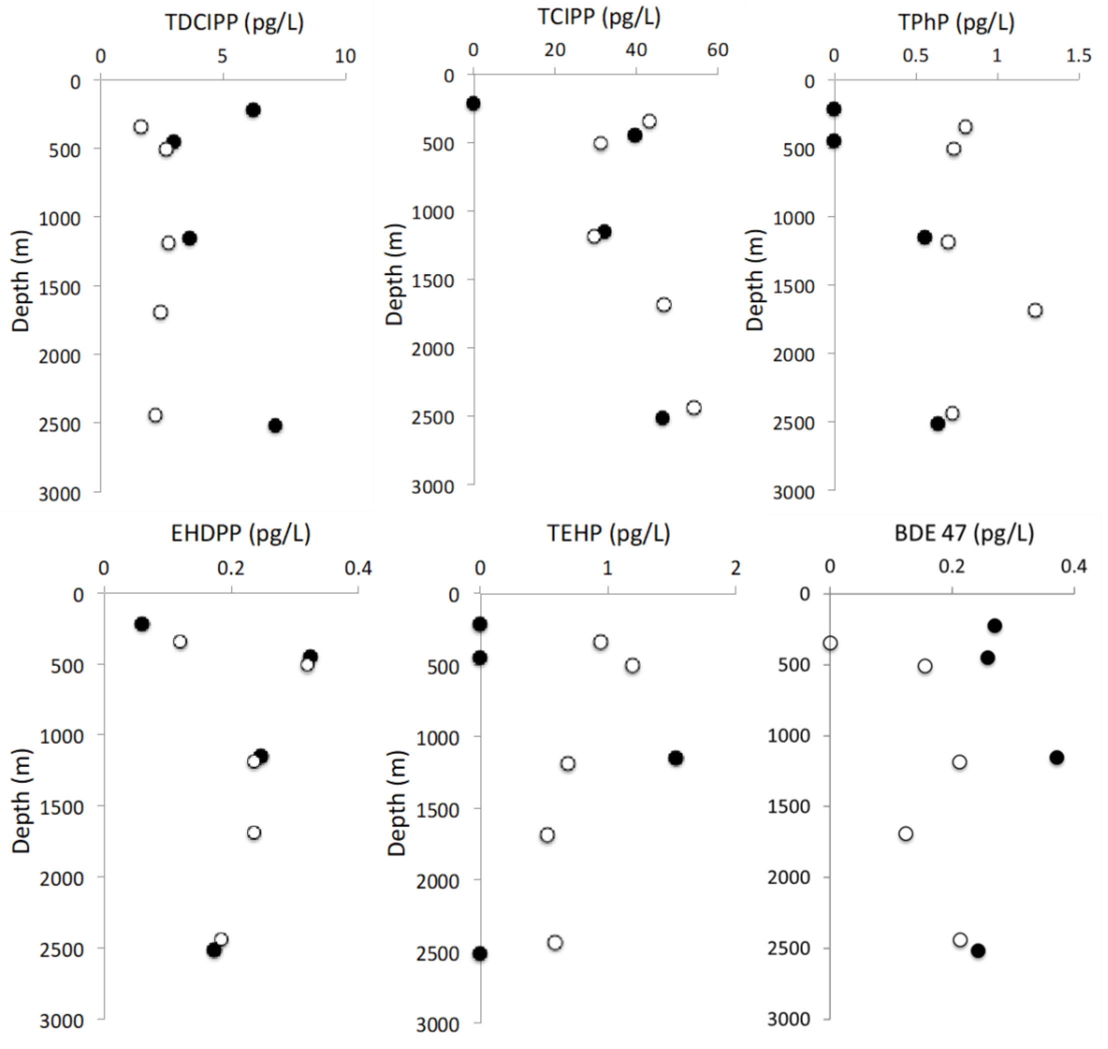


Figure 2. Depth profiles for frequently detected dissolved OPEs and BDE 47 for eastern (filled circles) and western (open circles) Fram Strait deep moorings.

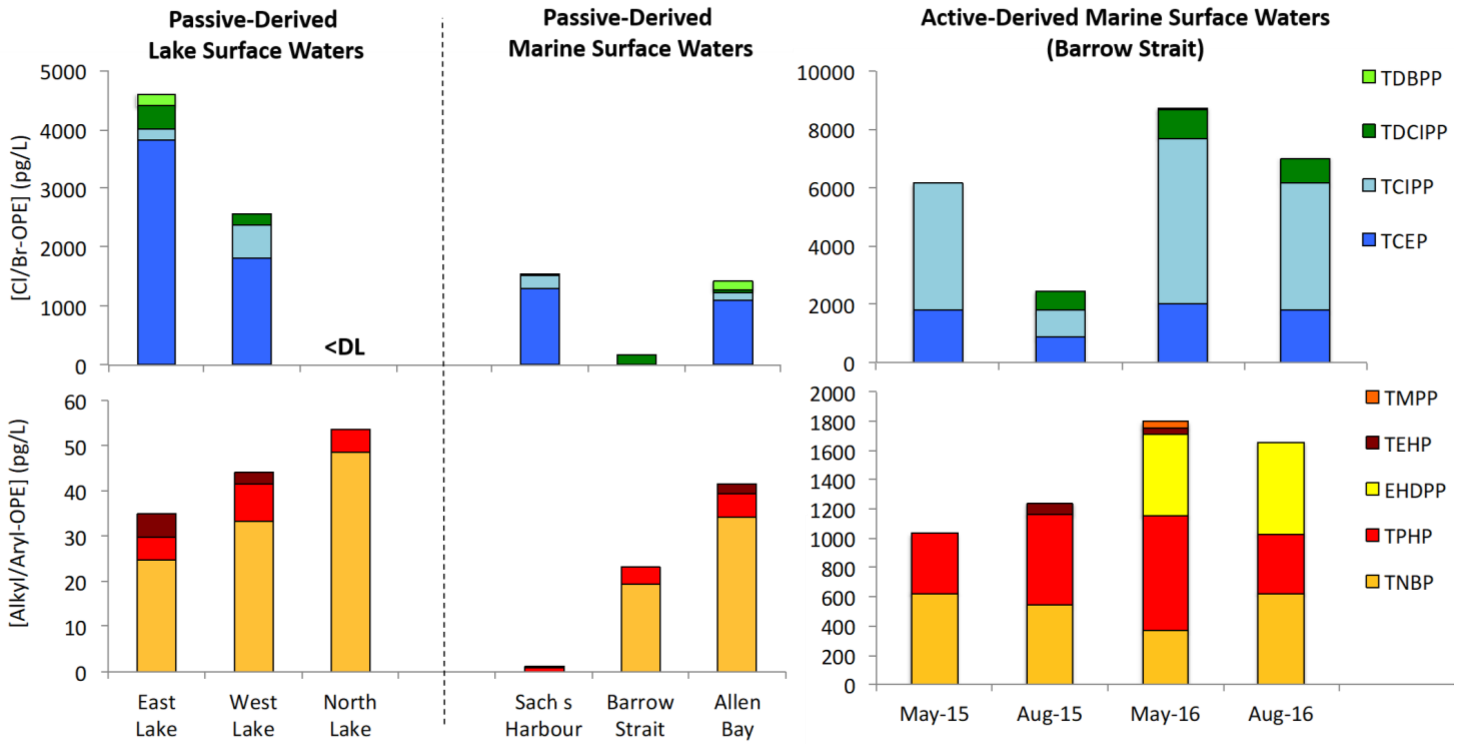


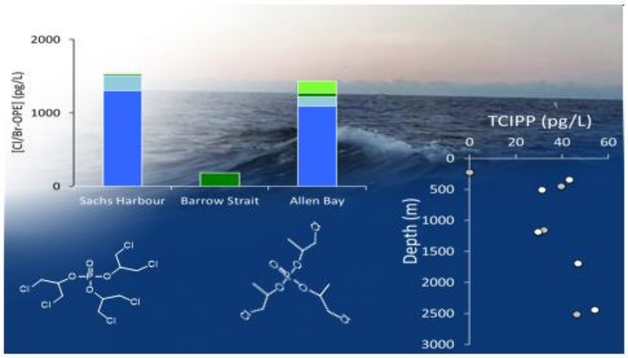
Figure 3. Mean (2015-2016) passive-derived dissolved concentrations of halogenated (top panel) and alkyl/aryl (bottom panel) OPEs in surface waters at Canadian Arctic lake and marine sites with mean active-derived concentrations in marine surface waters from four time points (Note different y-axis scales).

	Northward Transport (kg/yr)	Southward Transport (kg/yr)	Net Transport (kg/yr)
TCIPP	7500 ± 460	11000 ± 3100	-3400 ± 3200
TDCIPP	970 ± 59	690 ± 200	280 ± 210
TPHP	91 ± 5.5	240 ± 69	-150 ± 69
EHDPP	48 ± 2.9	66 ± 19	-17 ± 19
BDE 8	91 ± 5.5	51 ± 15	40 ± 16
BDE 47	59 ± 3.6	39 ± 11	21 ± 12

Table 2. Estimated total masses of dissolved OPEs and BDEs transported in and out of the Arctic Ocean via Fram Strait

Based on concentrations measured in depth profiles and estimated transport volumes. Net transport fluxes signify transport into (+) and out of (-) the Arctic Ocean. Uncertainty is calculated based on uncertainty in transport volumes from literature. Only compounds detected at two or more depths per mooring are presented in the table.

TOC ART


2000
1000
0
[Cl/Br-OPE] (pg/L)
Sachs Harbour
Barrow Strait
Allen Bay
TCIPP (pg/L)
0
20
40
60
0
500
1000
1500
2000
2500
3000
Depth (m)
Cl
Cl
Cl
Cl
Cl
Cl
O
P
O
O
O