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

4

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21

22

23 **ABSTRACT**

24 Organophosphate esters (OPEs) have been found in remote environments at
25 unexpectedly high concentrations, but very few measurements of OPE concentrations in
26 seawater are available, and none are available in subsurface seawater. In this study,
27 passive polyethylene samplers (PEs) deployed on deep-water moorings in the Fram Strait
28 and in surface waters of Canadian Arctic lakes and coastal sites were analyzed for a suite
29 of common OPEs. Total OPEs ($\Sigma_{11}\text{OPE}$) at deep-water sites ranged from 6.3-440 pg/L
30 and were similar in eastern and western Fram Strait. Chlorinated OPEs were present at
31 the greatest concentrations in surface waters (mean concentration ranged from < DL to
32 4400 pg/L), while non-halogenated alkyl/aryl-substituted OPEs remained low (1.3-
33 55pg/L), possibly due to the greater long-range transport potential of chlorinated OPEs.
34 In comparison, polybrominated diphenyl ethers (PBDEs) were found at much lower
35 concentrations than OPEs (< DL-14pg/L). Surface-water concentrations of tris(2-
36 chloroethyl) phosphate (TCEP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were
37 similar for both active and passive sampling approaches. Several OPEs were estimated to
38 be undergoing net transport out of the Arctic, ranging from 17 kg/yr for
39 ethylhexyldiphenylphosphate (EHDPP) to 3400 kg/yr for tris (2-chloroisopropyl)
40 phosphate (TCIPP). This study highlights the importance of OPEs as poorly understood
41 contaminants present at unexpectedly high concentrations in remote marine
42 environments.

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46 INTRODUCTION

47 Organophosphate esters (OPEs) are a group of synthetic organic contaminants
48 expected to have a low potential for long-range transport based on traditional models.¹
49 However, they have recently been measured in Arctic air at unexpectedly high
50 concentrations (10^1 - 10^3 pg/m³).^{2,3} This suggests that OPEs are capable of long-range
51 transport to remote regions, though the transport mechanisms and ultimate fates of these
52 compounds remain poorly understood. Very few measurements of seawater
53 concentrations are available for OPEs, and none are currently available in subsurface
54 seawater. As OPEs have been identified as the fastest growing sector of flame-retardant
55 products,⁴ more information on their concentrations in fresh and marine waters is
56 urgently needed to better understand the transport and fate of these emerging
57 contaminants in the marine environment.

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

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

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

88

89 **METHODS**

90 **Passive Sampler Preparation.** PE sheets of 50- μ m thickness were cut into 10 x 30 cm
91 strips weighing about 2 g and precleaned by incubation in methylene chloride and hexane

92 for 24 h each. Seven performance reference compounds (PRCs; dibromobiphenyl (PBB
93 9), tetrabromobiphenyl (PBB 52), pentabromobiphenyl (PBB 103),
94 octachloronaphthalene (OCN), fluorene-d₁₀, pyrene-d₁₀, and benzo(a)pyrene-d₁₂) were
95 loaded into the PEs for estimation of *in situ* sampling rates. PRC loading was done via a
96 1-month incubation in an 80:20 methanol:water solution containing the PRCs. PEs for
97 field deployments were shipped out for deployment along with field blanks, which were
98 shipped to field deployment sites, handled, and returned. Additional PEs were stored in
99 the freezer for use as laboratory blanks. After deployments, all PEs were shipped cold to
100 URI (University of Rhode Island) and stored in the freezer until extraction.

101 **Deep-Water PE Deployments.** Deep-water PEs were deployed for about one year (June,
102 2014 to July, 2015) at two sites maintained by the HAUSGARTEN long-term ecological
103 research observatory in Fram Strait.⁹ PEs were deployed at 4 depths (221 m, 446 m, 1151
104 m, and 2513 m) in eastern Fram Strait (79.010 N, 4.328 E) from June 23, 2014 to July 27,
105 2015, and at 5 depths (341 m, 504 m, 1184 m, 1690 m, 2439 m) in western Fram Strait
106 (78.528 N, 2.764 W) from June 20, 2014 to July 31, 2015 (yellow triangles in Figure 1).
107 Depths of PE deployments were determined based on the mooring design. PEs were
108 strung on stainless steel wire and installed within stainless steel cages, with one PE at
109 each depth. Hydrographic parameters (temperature, current speed and direction, and
110 salinity) were recorded during the deployment by current meters (Aanderaa RCM9/11[®])
111 and self-recording CTDs (SeabirdSBE37[®]). Data are available in the PANGEA
112 database.^{10,11} Data were binned and averaged for depths relevant to each PE. Deployment
113 dates and meteorological data are summarized in Table S1.

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

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

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

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

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

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

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

160 EHDPP) with the exception of TBOEP which was consistently observed in method
161 blanks, resulting in a method detection limit of 5,900 pg/L (Table S7).
162 **Passive Sampling Rate Determination.** The rate of OPE absorptive uptake (k_o) into the
163 PE was modeled as inversely proportional to the sum of the mass transfer resistance in
164 the PE membrane and the water boundary layer, as shown below (Equation 1). This
165 required estimating the molecular diffusivity of each target compound in polyethylene
166 (D_{PE}) and in water (D_W), as well as the PE-water partitioning coefficient (K_{PEW}). The
167 thickness of the PE boundary layer (δ_{PE}) was half the thickness of the PE sheet (25 μm)
168 and the thickness of the water boundary layer (δ_{WBL}) was estimated by fitting PRC loss
169 data to Equation 1 using the non-linear least squares regression function *nls* in R.¹² This
170 approach is described in detail in previous studies.^{13,14} More details on this approach and
171 physicochemical properties used in calculations are provided in the SI.

$$172 \quad \frac{1}{k_o} = \frac{\delta_{WBL}}{D_W} + \frac{\delta_{PE}}{D_{PE} \cdot K_{PEW}} \quad \text{Eq 1}$$

173 **Physicochemical Properties.** One of the major challenges in understanding the transport
174 and fate of OPEs is the paucity of empirical data on their physicochemical properties.¹⁵
175 Here, PE-water partitioning coefficients (K_{PEW}) were estimated from subcooled liquid
176 aqueous solubility ($\log C_{w,\text{sat}}(\text{L}); \text{mol}/\text{m}^3$) as in Lohmann 2012.¹⁶ Lohmann reported that
177 this regression exhibited a good fit ($r^2=0.92$; $\text{SE}=0.35$; $\text{N}=100$) for a wide variety of
178 compounds with diverse properties, including polycyclic aromatic hydrocarbons (PAHs),
179 polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), PBDEs,
180 nonylphenols, and triclosan ($\log C_{w,\text{sat}}(\text{L})$ -5.2 to -0.01).

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

183 $C_{w,sat}(L)$ used to estimate K_{PEW} for OPEs were taken from a collection of estimated
184 properties by Zhang et al.¹⁷ A range of calculated concentrations based on two different
185 sets of solubility values are presented in the SI, but concentrations calculated from EPI
186 Suite WSKOWWIN performed best in predicting $C_{w,sat}(L)$ values for a wide range of
187 compounds according to Zhang et al., and hence were applied in this study.¹⁷ However,
188 these values were often biased low, meaning that estimated ambient concentrations may
189 also be underestimated. To interpret results for PEs deployed in seawater, values of
190 $C_{w,sat}(L)$ were corrected for salinity, as described in the SI.¹⁸

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

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

200 **Fram Strait Net Transport Calculations.** Calculation of net transport through Fram
201 Strait is complicated by the hydrography in the region. While most studies concur that net
202 transport of water through Fram Strait is around 1-2 Sv southward, there are a wide range
203 of estimated volumes for transport in and out of the strait.^{5,19-22} Here, we estimated that
204 southward transport was 8.7 ± 2.5 Sv, as in de Steur et al.,²² and northward transport was

205 estimated as 6.6 ± 0.4 Sv, as in Beszczynska-Moller et al.⁵ These estimates were derived
206 from results of a long-term mooring array which is close to the PE mooring locations.

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

212

213 **RESULTS & DISCUSSION**

214 **Sampling Rates and Percent Equilibration.** PRC loss data is summarized in the SI for
215 deep-water (Table S9) and surface-water sites (Table S10). Percent equilibration
216 predicted for the OPEs at each site is presented in Table S11 for deep-water deployments
217 and Table S12 for surface-water deployments. At deep-water sites, where PEs were
218 deployed for about one year, the five smallest OPEs ($V_m < 300$ cm³/mol; $\log K_{PEW} < 5$)
219 were estimated to reach > 80% equilibrium during deployments (Table S11). Among the
220 non-equilibrated compounds, sampling rates calculated from best-fit δ_{WBL} ranged from
221 about 2-8 L/day, which is fairly reasonable considering that flow was limited by the
222 protective cages around each PE, and agrees well with estimated sampling rates for
223 eastern Fram Strait during 2012-2013 PE deployments (4-10 L/day), which were
224 calculated using an alternative PRC-based approach.⁸ Mean current velocity for all PEs at
225 all depths ranged from 7-13 cm/s. The greatest sampling rates and fastest current
226 velocities were observed for the shallowest PEs in Fram Strait. The lowest sampling rates
227 and slowest current velocities were found for the deepest PEs in eastern Fram Strait.

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

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

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

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

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

259 Most deep-water samples were dominated by halogenated OPEs (TCEP, TCIPP,
260 and TDCIPP), which made up 34-100% of Σ_{11} OPE. Total alkyl/aryl-OPEs (Σ_7 Alkyl/Aryl-
261 OPE) ranged from 0.1 to 66 pg/L, and were present at lower concentrations than Σ_3 Cl-
262 OPE (6.2-430 pg/L). Previous studies of surface water, air, and sediment in the region
263 have also shown a predominance of chlorinated OPEs.^{3,23,29} This was expected, as
264 alkyl/aryl-OPEs are more readily degradable than Cl-OPEs by indirect photolysis and/or
265 hydrolysis.³⁰⁻³³ Additionally, Sühring et al. noted that Cl-OPEs may be more effectively
266 transported via ocean currents, while alkyl/aryl-OPEs are transported primarily through
267 the atmosphere.³ More effective waterborne transport of Cl-OPEs could also help explain
268 the predominance of Cl-OPEs in deep-water samples. TCIPP was the most abundant OPE
269 in the majority of samples, ranging from below detection limit (< DL) to 54 pg/L (0-93%
270 of Σ_{11} OPE). TCEP was the most abundant OPE in the two western Fram Strait samples
271 where it was above detection limits (350-390 pg/L), but was blank-censored in all other
272 cases.

273 In both eastern and western Fram Strait, little variation in dissolved OPE
274 concentrations was observed with depth. Trends with depth did not change appreciably
275 based on the set of estimated K_{PEW} values used to calculate ambient concentrations. Flat
276 depth profiles could be due to a high degree of vertical mixing, lateral advection, and/or
277 the release of particle-bound OPEs to the dissolved phase with depth.³⁴ Booij et al. also
278 observed little change in concentration for PCBs, PAHs, and OCPs over a depth range of
279 100-3,000 m in the Irminger Sea using SPMDs.⁷

280 **Dissolved PBDEs in Fram Strait Depth Profiles.** BDE 47 was the most frequently
281 detected PBDE in Fram Strait depth profiles (Figure 2). Concentrations of all PDBEs are
282 summarized in Table S15. Σ_{12} BDE was much lower than Σ_3 Cl-OPE levels (< 2 pg/L at all
283 sites), which was consistent with concentrations measured by Sun et al. in eastern Fram
284 Strait, as well as with active sampling-derived concentrations from Möller et al. in the
285 East Greenland Sea.^{8,35} Concentrations of OPEs were also much greater than surface-
286 water concentrations of Dechlorane Plus (< 1 pg/L) in the Fram Strait and several novel
287 brominated flame retardants (all < 2 pg/L) in the East Greenland Sea.^{35,36} This supports
288 findings from other recent studies showing that, though OPEs were originally expected to
289 have limited potential for long-range transport, they are being delivered to remote Arctic
290 regions in significant quantities.

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

296 Makarov Basins of the Arctic Ocean via active sampling of particle and dissolved
297 BDEs.³⁷
298 **Dissolved OPEs in Canadian Arctic Surface Waters.** Mean 2015-2016 surface-water
299 concentrations of OPEs are summarized in Table 1 and shown in Figure 3, along with
300 mean active-derived water concentrations from Barrow Strait collected at 1-5 m depth
301 from four different time points between May 2015 and August 2016. Concentrations of
302 all OPEs from all surface-water deployments are summarized in Table S14.

303 Surface-water $\Sigma_3\text{Cl-OPE}$ concentrations were much greater than in deep-water
304 sites in Fram Strait, with mean 2015-2016 passive-derived $\Sigma_3\text{Cl-OPE}$ ranging from < DL
305 in North Lake on Cornwallis Island to 4,400 pg/L at East Lake on Cape Bounty. $\Sigma_3\text{Cl-}$
306 OPE was greatest at lake sites in Cape Bounty and lowest at sites where TCEP was < DL
307 (North Lake and Barrow Strait). When detected, TCEP was the most abundant Cl-OPE,
308 making up 70-85% of $\Sigma_{11}\text{OPE}$. This is consistent with results from Ma et al. in Arctic
309 sediments and Sühling et al. in Canadian Arctic air, where TCEP was the dominant
310 OPE.^{3,29}

311 $\Sigma_7\text{Alkyl/aryl-OPE}$ was also greater than at deep-water mooring sites, with mean
312 2015-2016 concentrations ranging from 1 pg/L in Sachs Harbour to 55 pg/L in North
313 Lake, though TNBP concentrations in surface waters were similar to those measured at
314 deep-water sites above 1000 m. TNBP was the most abundant alkyl/aryl-OPE in samples
315 where it was found above detection limits, with average concentrations ranging from <
316 DL to 48 pg/L at North Lake. TPHP was the only OPE detected > DL in all surface-water
317 samples, with average concentrations ranging from 1 pg/L at Sachs Harbour to 8 pg/L at
318 West Lake.

319 **Active- and Passive-Derived Surface-Water OPE Concentrations.** At Canadian Arctic
320 lake sites, the fraction of OPEs expected to be in the dissolved fraction (which is free to
321 diffuse into the PE membrane) was estimated based on dissolved organic carbon (DOC)
322 concentrations and DOC-partitioning coefficients (K_{DOC}). DOC was measured at each
323 lake once per sampling year during the summer months (June-August) and ranged from
324 0.7 mg/L in North Lake in July, 2015 to 2.5 mg/L in West Lake in June, 2016. K_{DOC} was
325 assumed to be one tenth of the octanol-water partitioning coefficient (K_{ow}) as in
326 Burkhard et al.³⁸ using K_{ow} values listed in Table S8. Based on these calculations, the
327 majority of frequently-detected OPEs (TNBP, TCEP, TCIPP, TDCIPP, TPHP, and
328 EHDPP) were expected to be > 90% in the dissolved phase, implying that differences
329 between active- and passive-derived concentrations are primarily the result of different
330 sampling periods and uncertainties in physicochemical properties, rather than differences
331 in selectivity between the two sampling methods.

332 Concentrations of TCEP were similar for active- and passive-derived samples,
333 with mean 2015-2016 passive-derived concentrations of 1,800-3,800 pg/L at Cape
334 Bounty freshwater sites, 1,300 pg/L at Sachs Harbour, 1,100 pg/L at Allen Bay, and 820-
335 2,000 pg/L from active sampling in Barrow Strait. Concentrations of TDCIPP were also
336 similar among passive samplers (< DL-400 pg/L) and active samplers (< DL- 960 pg/L).
337 However, active-derived concentrations of dissolved TCIPP were greater than passive-
338 derived concentrations (930-5,700 pg/L from active samplers, < DL to 570 pg/L in
339 passive samplers). This may be due to varying concentrations between active snapshot
340 sampling and time-weighted average passive sampling, coupled with uncertainties in
341 physicochemical properties used in calculating passive-derived concentrations.

342 Passive-derived dissolved Cl-OPE concentrations were similar to active-derived
343 total (particle + dissolved) concentrations in seawater measured by Li et al. in the North
344 Atlantic and Arctic Oceans (Table 1), where TCEP ranged from < DL to 2,400 pg/L,
345 TCIPP ranged from 300 to 5,800 pg/L, and TDCIPP ranged from < DL to 40 pg/L. Cl-
346 OPE concentrations measured in this study were comparable, but on the lower end, of
347 active-derived concentrations from other regions. Venier et al. measured Σ_3 Cl-OPEs in
348 the range 2,100-18,000 pg/L in the surface waters of the Great Lakes, with TCIPP most
349 abundant. In German Bight surface waters, Σ_3 Cl-OPEs ranged from about 1,000 to
350 10,000 pg/L, again with TCIPP most abundant.²⁷

351 Average passive-derived concentrations of Σ_7 Alkyl/Aryl-OPEs (1-55 pg/L) were
352 lower than active-derived concentrations from Barrow Strait, which ranged from (630-
353 1,800 pg/L). EHDPP and TPHP made more prominent contributions to active-derived
354 OPE profiles, where they made up 0-7% and 5-17% of total OPEs, respectively. This
355 could be due to active samplers collecting some amount of colloidal-bound OPEs in the
356 dissolved-phase fraction, as K_{DOC} estimates from DOC concentrations are somewhat
357 uncertain, and EHDPP and TPHP are expected to be more hydrophobic compounds that
358 would partition to a greater extent into the colloidal and particulate fraction (log K_{ow} of
359 4.7-5.7, as compared to 4.3 for TNBP).

360 Concentrations of TNBP were similar to the mean concentration measured by Li
361 et al. via active sampling in Northern Atlantic and Arctic Ocean seawater (120 pg/L;
362 Table 1).²³ Other alkyl/aryl-OPEs were either < DL or found at very low concentrations
363 in samples collected by Li et al. Previous studies of other regions have reported much
364 greater concentrations of dissolved alkyl/aryl-OPEs than this study, again supporting the

365 greater propensity of Cl-OPEs for long-range transport compared to alkyl/aryl-OPEs.
366 Venier et al. measured Σ_3 Alky/aryl-OPEs (TNBP, TPHP, and TBOEP) from 3,300-
367 78,000 pg/L in the surface waters of the Great Lakes, with TBOEP most abundant.²⁸ In
368 German Bight surface waters, Σ_3 Alky/aryl-OPEs were only intermittently detected by
369 Andresen et al. above detection limits at sites distant from shore, and ranged from < DL
370 to 3,500 pg/L in the plume of the River Elbe.²⁷

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

376 As in deep-water samples, BDE 47 was the most frequently detected BDE, while
377 other congeners were only detected intermittently. Previous work by Möller et al. found
378 BDE 47 and 99 to be dominant in East Greenland Sea, with concentrations < 2 pg/L,
379 which was similar to or lower than total BDEs measured at seawater sites in this study (1-
380 6 pg/L, with elevated concentrations of 15 pg/L at Barrow Strait). Salvado et al.
381 measured BDE 47 of < DL-1.5 pg/L in polar mixed layer samples from throughout the
382 Arctic Ocean, and observed that BDEs were elevated in coastal shelf regions, which were
383 more similar to sites monitored in this study.³⁷

384 **Potential Sources of OPEs and BDEs to Canadian Arctic Surface Waters.** Total
385 average OPE concentrations at each surface-water site in each sampling year (2015 and
386 2016) are shown in Figure S2.

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

395 Figure S2 shows that Cl-OPEs exhibited elevated concentrations at East Lake in
396 2016, while the opposite trend was seen for BDEs. Elevated Cl-OPE concentrations were
397 due primarily to elevated TCEP and, to a lesser extent, TDCIPP. In comparison,
398 dissolved alkyl/aryl-OPEs were greater in 2015 than 2016 at both lake sites. Similar to
399 West Lake, concentrations of both alkyl/aryl-OPEs and Cl-OPEs were elevated in marine
400 surface waters at Allen Bay in 2015 compared to 2016.

401 Differences in year-to-year dissolved OPE concentrations shown in Figure S2
402 may be due in part to the season in which passives were deployed, which offers some
403 clues as to sources contributing to OPE concentrations in the Canadian Arctic. In 2015,
404 passives were deployed in East and West Lake for the first three weeks of August, while
405 in 2016, they were deployed from early June to late July. Typically, maximum snowmelt
406 discharge into these river-fed lakes occurs in mid-June, with return to baseflow by early
407 July.⁴⁰ This suggests that samples taken in 2016 may be more representative of the
408 snowmelt influx, as well as ice-melt waters, as the primary period of ice-off for the lakes
409 is generally mid-July to early August. If this is the case, it would appear that increased

410 snowmelt in East Lake led to increased concentrations of Cl-OPEs, rather than causing a
411 dilution effect, though the same trend is not seen in West Lake. Li et al. measured TCEP
412 and TCIPP in snow collected from Arctic sea ice at mean concentrations of 2,400 and
413 6,300 pg/L, respectively, suggesting that this reservoir could act as a source of Cl-
414 OPEs.²³ Cl-OPEs were all < DL in North Lake, where PEs were deployed later in the
415 season (late July to early October), and pulses from snowmelt would not have been
416 captured. Potential sources of OPEs that could be stored in snow are unknown, and
417 further data from additional time periods would be needed to confirm whether seasonal
418 fluctuations in riverine inputs and melting explain our observations.

419 **Atmospheric OPE Concentrations and OPE Air-Water Exchange.** The composition
420 of gaseous OPEs derived from passive air samplers on Cape Bounty was dominated by
421 Cl-OPEs. TCEP was most abundant, which was consistent with results from Li et al. in
422 active-derived gaseous OPE concentrations from the Arctic Ocean, as well as Sührling et
423 al. in atmospheric particulate samples from the Canadian Arctic.^{3,23} Concentrations are
424 fairly similar to those from Li et al., who used a high-volume active sampler with
425 PUF/XAD-2 sorbent to collect gas-phase OPEs in the northeastern Atlantic and Arctic
426 Oceans (Figure S3). Mean concentrations of TCEP (2.4 pg/m³ in 2015 to 14 pg/m³ in
427 2016) were somewhat lower than mean concentrations from Li et al. (23 pg/m³),²³ and 1-
428 2 orders of magnitude lower than those from Sührling et al. (170 ± 170 pg/m³).³

429 The composition of alkyl/aryl-OPEs was similar to what was seen in the gaseous
430 phase by Li et al., as well as in the particulate phase by Sührling et al. in Resolute Bay and
431 Salamova et al. in Longyearbyen, Svalbard, with Σ_7 Alky/aryl-OPEs dominated by TNBP
432 when it was detected.^{2,3,23} However, the particulate fraction measured in other studies

433 contained more significant contributions of relatively hydrophobic OPEs such as EHDPP
434 and TPHP than was observed in gas-phase samples from this study. Average
435 concentrations of TNBP ranged from 9 pg/m³ in 2015 to 18 pg/m³ in 2016, which was
436 greater than mean gaseous TNBP from Li et al. (2.2 pg/m³), possibly because the
437 majority of their sampling locations were further from land. Concentrations measured
438 here were lower than particulate concentrations measured by Sühling et al. in Resolute
439 via land-based sampling (mean TNBP 747 ± 876 pg/m³) and by Salamova et al. in
440 Longyearbyen, Svalbard (174 ± 46 pg/m³).

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

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

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

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

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478 **ASSOCIATED CONTENT**

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

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485 **AUTHOR INFORMATION**

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487 **Author Contributions.** The manuscript was written through contributions of all authors.

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489

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FIGURES AND TABLES

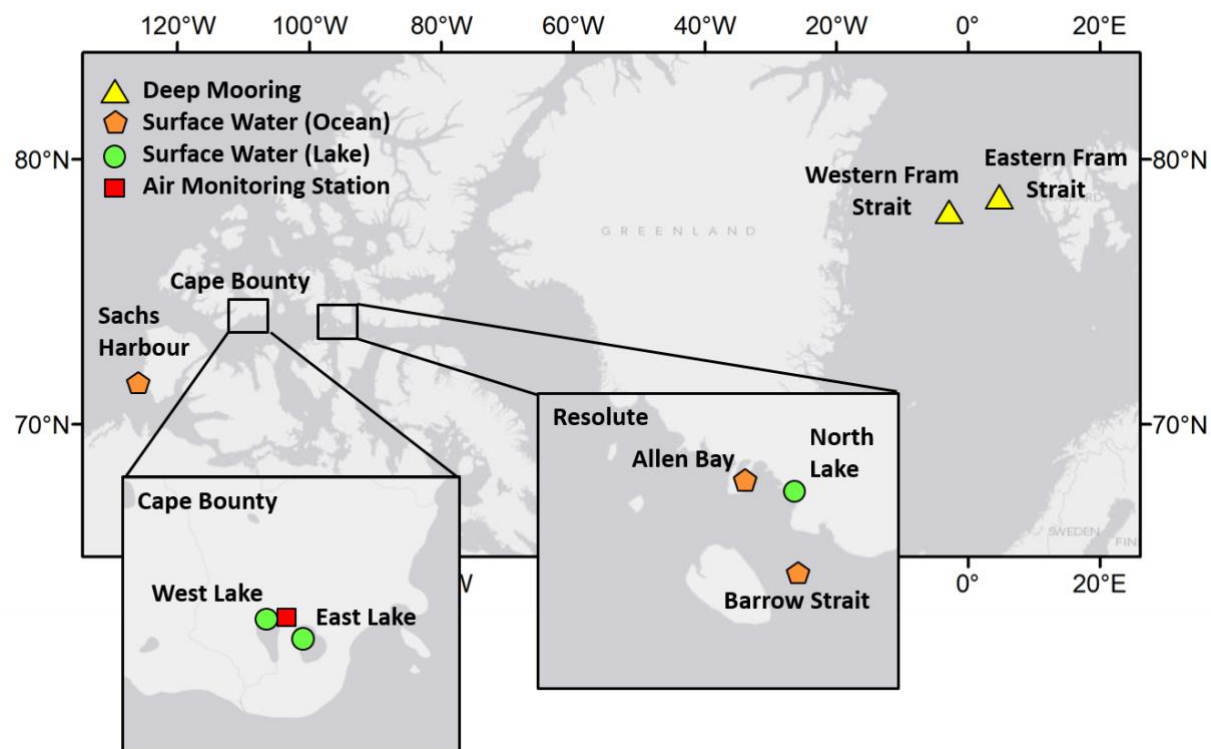


Figure 1. Locations of passive sampling deployments in lake surface waters (green circles) and marine surface waters (orange pentagons), air (red square), and on deep-water moorings (yellow triangles).

	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.

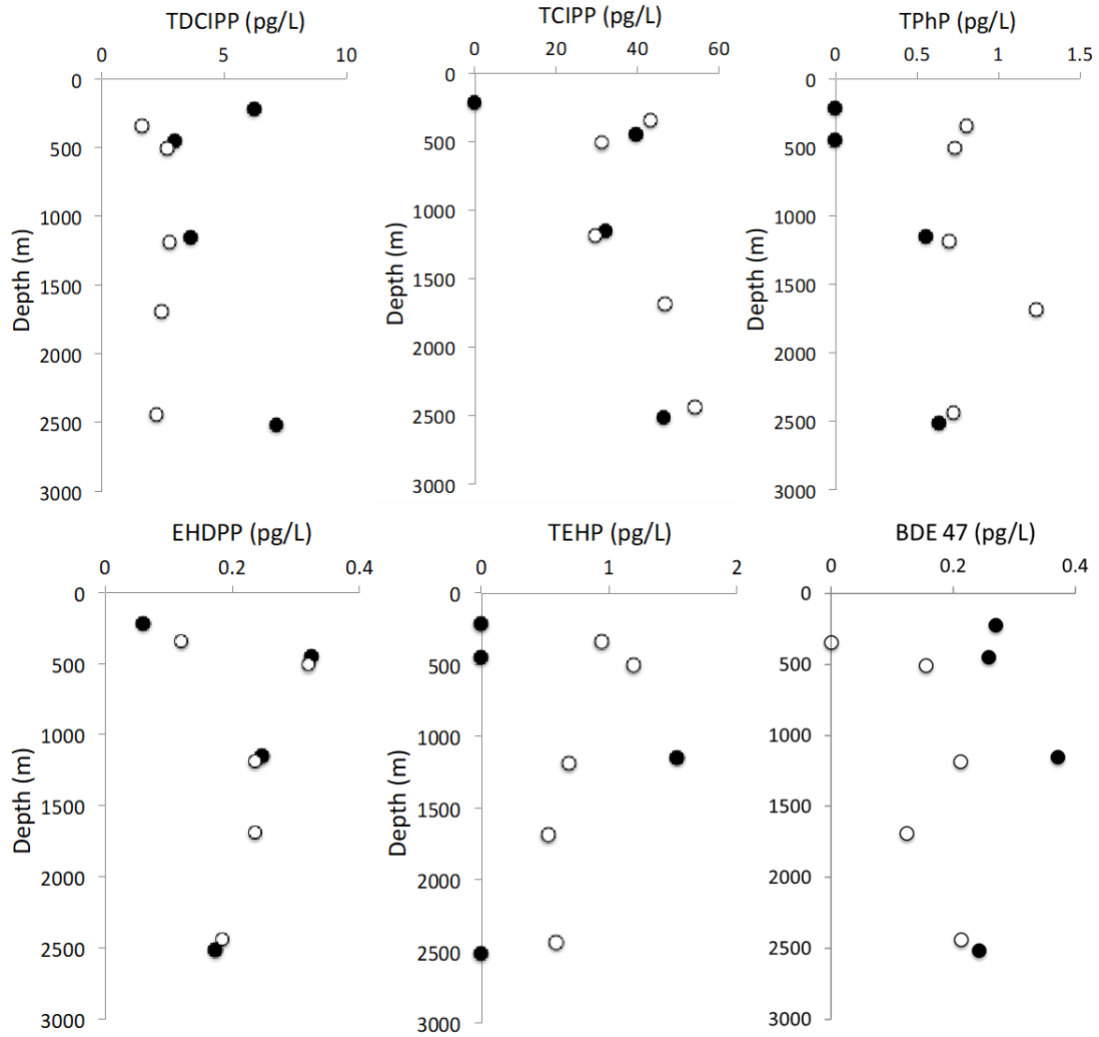


Figure 2. Depth profiles for frequently detected dissolved OPEs and BDE 47 for eastern (filled circles) and western (open circles) Fram Strait deep moorings.

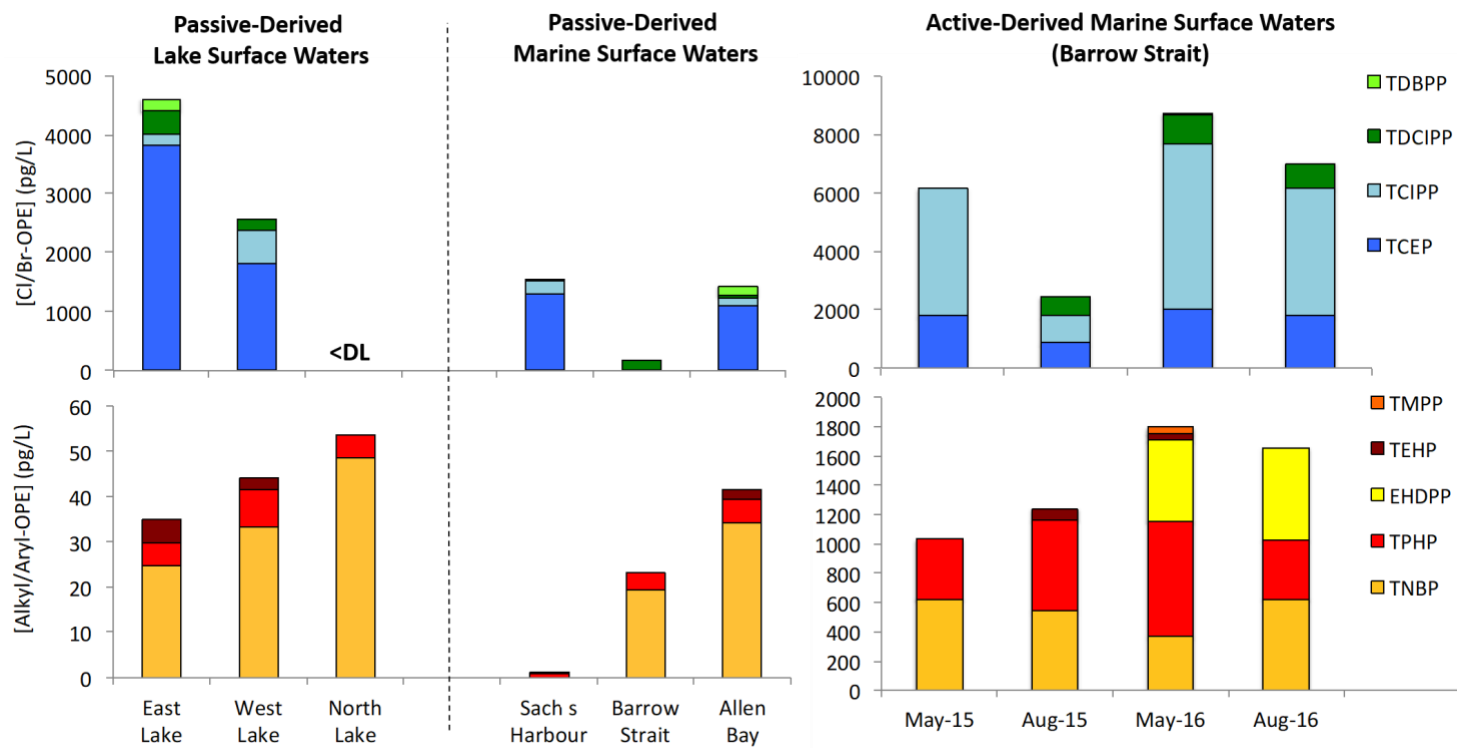


Figure 3. Mean (2015-2016) passive-derived dissolved concentrations of halogenated (top panel) and alkyl/aryl (bottom panel) OPEs in surface waters at Canadian Arctic lake and marine sites with mean active-derived concentrations in marine surface waters from four time points (Note different y-axis scales).

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	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

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

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Based on concentrations measured in depth profiles and estimated transport volumes.

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Net transport fluxes signify transport into (+) and out of (-) the Arctic Ocean.

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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.

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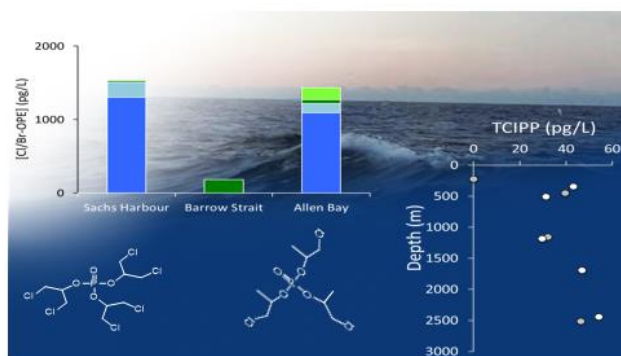
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