1 **Seasonal Air Concentration Variability, Gas/Particle Partitioning, Precipitation**

2 **Scavenging, and Air-Water Equilibrium of Organophosphate Esters in Southern**

3 **Canada**

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18 **Abstract**

19 In response to increasing production and application volumes, organophosphate esters

20 (OPEs) have emerged as pervasively detected contaminants in various environmental media,

21 with concentrations often exceeding those of traditional organic contaminants. Despite the

22 recognition of the atmosphere's important role in dispersing OPEs and a substantial number

23 of studies quantifying OPEs in air, investigations into atmospheric phase distribution

24 processes are rare. Using measurements of OPEs in the atmospheric gas and particle phase,

25 in precipitation and in surface water collected in Southern Canada, we explored the seasonal

26 concentration variability, gas/particle partitioning behaviour, precipitation scavenging, and

27 air-water equilibrium status of OPEs. Whereas consistent seasonal trends were not observed

28 for OPEs concentrations in precipitation or atmospheric particles, gas phase concentrations

29 of several OPEs were elevated during the summer in suburban Toronto and at two remote

30 sites on Canada's east and west coast. Apparent enthalpies of air-surface exchange fell

31 mainly within or slightly above the range of air/water and air/octanol enthalpies of exchange,

32 indicating the influence of local air-surface exchange processes and/or seasonally variable

33 source strength. While many OPEs were present in notable fraction in both gas and particle

34 phase, no clear relationship with compound volatility was apparent, although there was a

35 tendency for higher particle-bound fractions at lower temperature. High precipitation

36 scavenging ratios for OPEs measured at the two coastal sites are consistent with low air-

37 water partitioning ratios and the association with particles. Although beset by large

38 uncertainties, air-water equilibrium calculations suggest net deposition of gaseous OPEs

39 from the atmosphere to the Salish Sea and the St. Lawrence River and Estuary. The

40 measured seasonal concentration variability is likely less a reflection of temperature driven

41 air-surface exchange and instead indicates that more OPE enter, or are formed in, the

42 atmosphere in summer. More research is needed to better understand the atmospheric gas-

43 particle partitioning behaviour of the OPEs and how it may be influenced by transformation

44 reactions.

45 **Key words:**

46 OPEs, air, precipitation, water, partitioning, air-water exchange, relative abundance

1. INTRODUCTION

Organophosphate esters (OPEs) are synthetic organophosphorus compounds consisting of a central phosphate molecule substituted with non-halogenated, halogenated alkyl, or aryl groups. Widely used as flame retardants, plasticizers, stabilizers, and defoaming agents in various industries and consumer products (Environment and Climate Change Canada, 2023abcd; Salamova et al., 2016; van der Veen and de Boer, 2012), OPEs are typically physically incorporated into materials rather than chemically bonded (Wang et al., 2020b; Wong et al., 2018), facilitating their release into the environment. Following restrictions on many brominated flame retardants, e.g. through listing in the Stockholm Convention, OPEs use has increased, reaching 620 kilotons globally in 2013, accounting for 30% of total flame retardant usage (Sühring et al., 2016; Xie et al., 2022). The extensive application of OPEs, coupled with their potential for long-range atmospheric transport (Na et al., 2020; Sühring et al., 2016) and persistence (Möller et al., 2012; Salamova et al., 2014), has resulted in their ubiquitous presence in the environment (Han et al., 2020; Li et al., 2019a, b; Lu et al., 2017; Mi et al., 2023; Regnery and Püttmann, 2009; Stackelberg et al., 2007), often at concentrations exceeding those of traditional flame retardants and plasticizers (Salamova et al., 2014; Shoeib et al., 2014; Zhao et al., 2021b). Given their potential toxicity (Gu et al., 2019; Li et al., 2020; Rosenmai et al., 2021; Wang et al., 2022; Yan and Hales, 2019, 2020), understanding the fate, occurrence, and distribution of OPEs in the environment is critical for assessing their ecological and human health impacts.

The atmosphere plays a key role in the dispersion and transport of OPEs, with concentrations and spatial and temporal variability in air being influenced by emission sources, atmospheric transport, chemical transformation (Liu et al., 2023; Liu and Mabury, 2019) and deposition processes. The distribution of OPEs between different atmospheric phases (gas phase, particles, precipitation) affects these processes and is influenced by their partition properties. Most studies on OPEs in the atmosphere report concentrations in the particle phase, whereas studies on the presence in the gas phase are far more limited, which may be related to the relatively short half-lives of gas phase OPEs (Shi et al., 2024; Zhang et al., 2016). However, gaseous OPEs can constitute 15% to 65% of atmospheric OPEs (Möller et al., 2011), and diffusive air-water gas exchange of OPEs can be 2-3 orders of magnitude higher than dry particle deposition (Castro-Jiménez et al., 2016; Ma et al., 2021), highlighting the need for more research on OPE vapours.

Precipitation acts as a major pathway for the removal and redistribution of OPEs from the

80   atmosphere to aquatic and terrestrial environments (Shi et al., 2024). It can scavenge and

81   deposit both gas-phase and particle-bound OPEs. Depending on regional emissions,

82   temperature, precipitation type, and the physicochemical properties of the OPEs (Lei and

83   Wania, 2004), the wet deposition flux of OPEs can be significantly larger than the dry

84   deposition flux (Kim and Kannan, 2018). Despite its importance, fewer than ten studies have

85   reported OPE concentrations in precipitation (Bacaloni et al., 2008; Casas et al., 2021; Fries

86   and Püttmann, 2003; Kim and Kannan, 2018; Marklund et al., 2005b; Mihajlović and Fries,

87   2012; Regnery and Püttmann, 2009; Zhang et al., 2020), and only one study has reported

88   precipitation scavenging ratios for atmospheric OPEs (Casas et al., 2021).

89   OPEs can enter water bodies through air-water gas exchange (Castro-Jiménez et al., 2016;

90   Ma et al., 2021), wet and dry deposition (Castro-Jiménez et al., 2016; Kim and Kannan,

91   2018; Ma et al., 2021), wastewater effluent (Marklund et al., 2005a), industrial and

92   municipal discharges (Bacaloni et al., 2008; Fries and Püttmann, 2003), and surface runoff

93   (Awonaike et al., 2021; Regnery and Püttmann, 2010). Some OPEs, including tris(1-chloro-

94   2-propyl) phosphate (TCPP) and tris (phenyl) phosphate (TPhP), have been detected in fish

95   (Ma et al., 2013; Sundkvist et al., 2010). A comprehensive understanding of the

96   environmental fate and occurrence of OPEs, and in particular a better understanding of the

97   contribution that the atmosphere makes for the delivery of OPEs to aquatic ecosystems,

98   would benefit from investigations that quantify OPE concentrations in multiple

99   environmental media sampled in the same area and at the same time. Despite the substantial

100 number of studies on OPEs in the environment, those examining OPEs across three or more

101 phases are very rare (He et al., 2019; Li et al., 2019b; Mi et al., 2023) and most studies focus

102 on just one or two media, usually gas and/or particle phases (Li et al., 2018; Ma et al., 2022;

103 Sühring et al., 2016; Zhao et al., 2021b) or the water phase (Choo and Oh, 2020; Ding et al.,

104 2015; McDonough et al., 2018; Shi et al., 2020). No previous study has investigated OPEs

105 in atmospheric gas and particle phases, precipitation, and surface water simultaneously.

106 To address this research gap and gather information on the contribution that the atmosphere

107 makes to OPEs in coastal waters of Southern Canada, we aimed to characterize the

108 occurrence, behavior, and fate of OPEs in different atmospheric phases. We measured OPEs

109 in precipitation and atmospheric gas and particle phase for one year at two remote sites on

110 Canada's East and West coast, respectively, and complemented this dataset with the results

111 of a year-long measurement campaign of OPEs in the gas and particle phase in Toronto. We

112 further used passive samplers to gather data on the spatial variability of OPE concentrations

in the atmospheric gas phase and in water in the two coastal regions. The passive air sampling data have been presented previously (Li et al., submitted). This unique data set allowed us to estimate the gas-particle distribution in the atmosphere, precipitation scavenging ratios, and the state of air-surface water equilibrium, often in their seasonal dependence or their variability between urban, rural and remote locales. Finally, we used this dataset to explore the relative abundance of OPEs in the different types of samples.

2. MATERIALS AND METHODS

2.1 Active Air Sampling and Precipitation Collection. Twelve 24-hour air samples were collected monthly at a location on Saturna Island, British Columbia (BC) (48.7753N, -123.1283W) between December 2019 and November 2020 and in the vicinity of Tadoussac, Quebec (QC) (48.1415N, -69.6991W) between December 2020 and November 2021 using high-volume active air samplers (AASs) consisting of a Tisch sampling head (TE-1002-non Teflon with a glass cartridge TE-1009 and a silicone gasket TE-1008-5-Special, Pacwill Environmental, Ontario, Canada) and a high-volume pump (Gast regenerative blower R1102, Cole-Parmer, Illinois, USA). Forty-eight consecutive week-long AASs were taken with the same sampling head assembly and a mid-volume pump (Ametek centrifugal blower DFS 116643-03, RS, Texas, USA) in the Eastern suburbs of Toronto (43.78371 N, −79.19027 W) (Li et al., 2023a, b, 2024) between June 2020 and May 2021. At all three sites, polyurethane foam (PUF)/XAD/PUF sandwiches and glass-fiber filters (GFFs, CA28150-214, A/E, 102 mm diameter from VWR) were used to collect OPEs in the gas and particle phase, respectively. The XAD-2 was Supelpak™-2 polymeric adsorbent (21130-U, MilliPoreSigma) and the PUF was a 3-inch TE-1010 (Pacwill Environmental, cut into a 1-inch top PUF and a 2-inch bottom PUF). Using the sampler described by Chan and Perkins (1989), precipitation samples (PCPNs) were collected at the AAS sampling locations in BC and QC during the same months as the air samples and the sampling length was ~ 30 days (Oh et al., 2023; Zhan et al., 2023).

2.2 Passive Air and Water Sampling. In QC, 86 passive air samplers (PASs) were deployed at 71 unique sampling sites on either shore of the St. Lawrence River and Estuary, including in Montreal and Quebec City between 2019 and 2022. In BC, 83 PASs were deployed at 47 sites in the lower mainland around Vancouver and on the Canadian shore of the Salish Sea during different time periods between 2020 and 2022. More details are given in Table S5 in the Supporting Information (SI) of Li et al. (submitted) and in previous publications (Oh et al., 2023; Zhan et al., 2023).

146 Forty-eight low-density polyethylene (LDPE) based passive water samplers (PWSs) were

147 spiked with performance reference compounds (PRCs), deployed at 10 sites in BC and 10

148 sites in QC, and collected after deployment lasting 20-35 days in BC and 27-70 days in QC.

149 Detailed information on the PWS sampling is provided in the SI (Table S13) and previous

150 publications (Oh et al., 2023; Zhan et al., 2023).

151 **2.3 Sample Analysis.** Prior to extraction all samples were spiked with seven isotopically

152 labeled OPEs (Table S1) as surrogates. XAD from the PASs, the PUF/XAD sandwiches and

153 GFFs from the AASs were extracted using a Dionex Accelerated Solvent Extractor 350. The

154 PCPN and PWS samples were extracted using liquid-liquid extraction with dichloromethane

155 and soaking in hexane, respectively. Extracts were concentrated to 0.5 mL using a rotary

156 evaporator and nitrogen blow-down. Triamyl phosphate was added into the concentrated

157 extracts as an injection standard. Gas chromatography-tandem mass spectrometry (GC-

158 MS/MS) was used to detect and quantify 16 OPEs (Tables S1 and S2). Molecular structures

159 of these 16 targeted OPEs are provided in Figure S1.

160 **2.4 Quality Assurance and Quality Control.** All extraction and concentration procedures

161 were carried out in a trace analytical laboratory. The glassware was cleaned using a machine

162 with detergents, then rinsed with deionized water, and finally baked with GFFs at 450 °C in

163 a muffle furnace for 24 hours. Experimental materials that came into contact with samples

164 or extracts were thoroughly cleaned and rinsed three times with solvents (acetone and

165 hexane, or dichloromethane) before use. Field blanks, procedure blanks, and solvent blanks

166 were prepared with each batch of extractions and analyses (Oh et al., 2023; Zhan et al., 2023).

167 OPEs were not found in procedure or solvent blanks. Only a few analytes were present in

168 the field blanks, and for these, the average detected amount was subtracted from the amounts

169 of target chemicals in the field samples. Method detection limits (MDLs) were calculated as

170 three times the standard deviations of levels in field blanks when analytes were detected

171 (signal-to-noise ratio (S/N) > 3); otherwise, MDLs were based on concentrations at which

172 S/N is 3 (Desimoni and Brunetti, 2015). MDLs are provided in the Supplementary

173 Information (Tables S5, S8, S10, S11, and S13). The average recoveries of five surrogates

174 in AASs, PCPNs, and PWSs ranged from 78% to 232% (Table S3). The concentrations

175 reported have been corrected for recovery.

176 **2.5 Data Analysis.** Water concentration of OPEs were calculated from the amounts

177 quantified in PWS extracts following the method by Booij and Smedes (Booij et al., 2003;

178 Booij and Smedes, 2010), with details provided by Oh et al. (2023).

179   The fraction of an OPE in the particle phase (Φ, %) was obtained by dividing the particle-

180   phase concentration by the sum of concentrations in the gas and particle phase. Gas-particle

181   partition ratios K_{PA} (m^3 air g^{-1} aerosol) were derived by dividing the measured concentrations

182   of an OPE in the particle phase (pg m^{-3}) by the product of the concentrations of particles less

183   than 2.5 µm in diameter (PM$_{2.5}$, g m^{-3}) obtained from nearby national air pollution

184   surveillance program (NAPS) stations (Table S8) and the measured concentrations of this

185   OPE in the gas phase (pg m^{-3}). More detail is given in previous publications (Li et al., 2023a;

186   Oh et al., 2023; Zhan et al., 2023).

187   Measured scavenging ratios (SRs) were calculated as the ratios between the concentrations

188   of an OPE in precipitation and air (sum of gas and particle phase). We also estimated SRs

189   by assuming equilibrium of OPE between the atmospheric gas phase and water droplets (Oh

190   et al., 2023), and that all OPEs are sorbed to the same particles, which are scavenged with a

191   scavenging ratio W_P of 200,000 (Kim et al., 2006). An estimated SR thus is $(1-\Phi)K_{WA} +$

192   ΦW_P, where K_{WA} is the temperature-adjusted partition ratio between water and air ($K_{WA} =$

193   K_{AW}^{-1}, Table S4).

194   The fugacities of OPEs in water f_W, at average sea surface temperature T_W in K, were

195   calculated using $C_W \cdot K_{AW}(T_W) \cdot R \cdot T_W$, and those in air ($f_A$), at average air temperature T_A in

196   K, were derived with $C_A \cdot R \cdot T_A$, where C_W and C_A are the OPE concentrations (mol m^{-3}) in

197   water and air, respectively, and R is the gas constant.

198   **3. RESULTS**

199   **3.1 OPEs in the Atmospheric Gas Phase.** The gas phase concentrations obtained during

200   the three one-year AAS campaigns in Tadoussac, on Saturna Island, and in Toronto are given

201   in Table S5. The gas phase concentrations obtained by passive air sampling in QC and BC

202   have been previously reported (Li et al., submitted) with tri-n-butyl phosphate (TBP),

203   tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris

204   (phenyl) phosphate (TPhP) being reliably and ubiquitously detected. Due to the higher

205   sampling volumes of the AAS (~520 m^3) compared to the PAS (less than 200 m^3), more

206   OPEs could be detected above the MDL in the AAS. At all three locations, TBP, TCEP,

207   TCPP, TPhP, and 2-ethylhexyl-diphenyl phosphate (EHDPP) were present above the MDL.

208   Additionally, triethyl phosphate (TEP) was detected on Saturna Island, TEP,

209   tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and tris (2-butoxyethyl) phosphate (TBEP)

210   were detected in Tadoussac, and tri-propyl phosphate (TPrP) and TDCPP were detected in

211   Toronto. We are not comparing here the gas phase concentrations recorded in our study with

212   those reported previously, because that had already been done in Li et al. (submitted).

213   For the four most frequently detected OPEs, it is possible to compare the levels obtained

214   with the AASs on Saturna Island and in Tadoussac and by PASs at the nearby sites L43 and

215   S57. On Saturna Island, the PAS deployment at site L43 overlapped with the timeframe of

216   the AASs (between May and October 2020) (Table S8). In Tadoussac, the deployment

217   period of the PAS at S57 (November 2019 – August 2020) preceded the AASs sampling by

218   about one year (December 2020 – September 2021). Except for TBP and TPhP on Saturna

219   Island, PAS levels generally trended lower than AAS levels at both locations, albeit within

220   a factor of 5. One contributing factor to this difference could be the episodic 24-hour active

221   air sampling's inability to represent long-term concentration levels compared to PAS. For

222   instance, AAS-measured concentrations of TBP in Tadoussac ranged from below detection

223   to approximately 200 pg m^{-3}. Another factor could be the spatial distribution variability of

224   atmospheric OPEs. Despite our efforts to use PAS data from sites closest to AAS locations

225   for comparison, the PAS and AAS sampling sites were not identical. To support the

226   hypothesis that spatial and temporal variability in OPE concentrations contributes to the

227   discrepancy, we also compared AAS and PAS results for hexachlorobutadiene (HCBD) and

228   hexachlorobenzene (HCB), which exhibit uniform spatial distribution and consistent

229   concentrations over time, using the same samples as for the OPEs. PAS levels for these two

230   compounds closely aligned with AAS levels within a factor of 1.5. Similarly,

231   halomethoxybenzene levels from PASs and AASs were within a factor of 3 (Zhan et al.,

232   2023).

233   **3.2 OPEs in Atmospheric Particle Phase.** The concentrations of five OPEs (TBP, TCEP,

234   TCPP, TPhP, EHDPP) in the atmospheric particles from the three AAS sampling locations

235   are compiled in Tables S9. Except for TPhP and EHDPP which were not detected in particles

236   from Saturna Island, all five OPEs most frequently detected in the gas phase could also be

237   quantified in particle samples. Again, TCPP is the most abundant OPE at all three sites.

238   Concentration levels on Saturna Island and in suburban Toronto are similar and almost one

239   order of magnitude higher than those in Tadoussac. The averaged TBP levels of 7 pg m^{-3}, 3

240   pg m^{-3}, and 9 pg m^{-3} on Saturna Island, in Tadoussac, and in Toronto are lower than those

241   in Antarctica (23 pg m^{-3}) (Wang et al., 2020a) and two order of magnitude lower than those

242   detected in cities in the Great Lakes area (130 pg m^{-3}) in 2012 (Salamova et al., 2013).

243   Except in Tadoussac (1 pg m^{-3}), the TCEP levels of 50 pg m^{-3} and 17 pg m^{-3} on Saturna

244   Island and in Toronto are higher than those in Antarctica (5 pg m^{-3}) (Wang et al., 2020a) and

245   ca. 2~4 times lower than those detected in cities in the Great Lakes region (89 pg m^{-3})

246   (Salamova et al., 2013), and two orders of magnitude lower than the reported median

247   concentration in Quebec City and near the St Lawrence River (1903 pg m^{-3}) (Sühring et al.,

248   2016). TCPP in Tadoussac, 3 pg m^{-3}, is comparable to its level in Antarctica (6 pg m^{-3})

249   (Wang et al., 2020a), and TCPP on Saturna Island (122 pg m^{-3}) and in Toronto (90 pg m^{-3})

250   are three and four times lower than those detected in cities in Great Lakes area (321 pg m^{-3})

251   (Salamova et al., 2013), and one order of magnitude lower than the detected level in Quebec

252   City and near the St Lawrence River (1557 pg m^{-3}) (Sühring et al., 2016). TPhP and EHDPP

253   levels in Antarctica (1 pg m^{-3}) (Wang et al., 2020a) are close to those in Tadoussac (2 pg m^{-3})

254   , and one order of magnitude lower than levels in Toronto (12 pg m^{-3}) and those in Quebec

255   City and near the St Lawrence River (51 pg m^{-3}) (Sühring et al., 2016). The relatively higher

256   concentration levels of certain OPEs in Antarctica, such as TBP, may be due to preferential

257   partitioning of TBP to particles at low temperatures. Compared to the sites in the Great Lakes

258   region (Salamova et al., 2013) as well as Quebec City and near the St Lawrence River region

259   (Sühring et al., 2016), our sampling sites were more rural, which could explain lower OPE

260   concentrations.

261   **3.3 OPEs in Precipitation.** Eight OPEs, i.e., TEP, TBP, TCEP, TCPP, TDCPP, TPhP,

262   TBEP, and EHDPP, were reliably detected in the precipitation samples from Saturna Island

263   and Tadoussac (Table 1 & Table S11). Concentrations are generally higher on Saturna Island

264   than in Tadoussac. The OPE levels in Tadoussac were comparable to those in Antarctica

265   (Casas et al., 2021). TDCPP detected on Saturna Island and in Tadoussac are two times to

266   one order of magnitude higher than the levels in Antarctica (Casas et al., 2021), Nanjing

267   (Zhang et al., 2020), and New York (Kim and Kannan, 2018), and our measured EHDPP

268   levels were higher than those detected in Antarctica. Overall, except for TDCPP and EHDPP,

269   the average OPE concentrations detected in our study were comparable or one order of

270   magnitude lower than literature data (Table 1). Except for TBP in Tadoussac, OPE

271   concentrations varied greatly between months, whereby no distinct and consistent seasonal

272   trends were discernible (Table S11), which is consistent with previous observations

273   (Regnery and Püttmann, 2009).

274   **3.4 OPEs in Water.** The OPEs concentrations in water, obtained with PWSs deployed in

275   the summer 2021, are reported in Table S13. Their spatial patterns are displayed in Figures

276   1, S2, and S3. In BC, OPEs had elevated levels in the interior of Burrard Inlet close to Port

Moody (V1 and V2), at the southern mouth of the Fraser River (V5), and at some sites around populated areas in Victoria, BC (V6-V8). TBP, TCPP, and TDCPP had higher concentrations close to an industrial area near Esquimalt (V10). In QC, highest OPE water concentrations were usually detected at site W5, in the Saint Lawrence River close to an industrial area in Sorel-Tracy, rather than at sites in Montreal (W1 and W2) or Québec City (W8 and W9). W4 also had elevated concentrations for some OPEs such as TBP. Water concentrations at the one sampling site in the Saint Lawrence Estuary were much lower than in the river. Overall, the spatial patterns suggest that the water concentrations of OPEs were related to both industrial activities and human populations in BC, whereas industrial activities might have relatively higher impact on water concentrations of OPEs in QC.
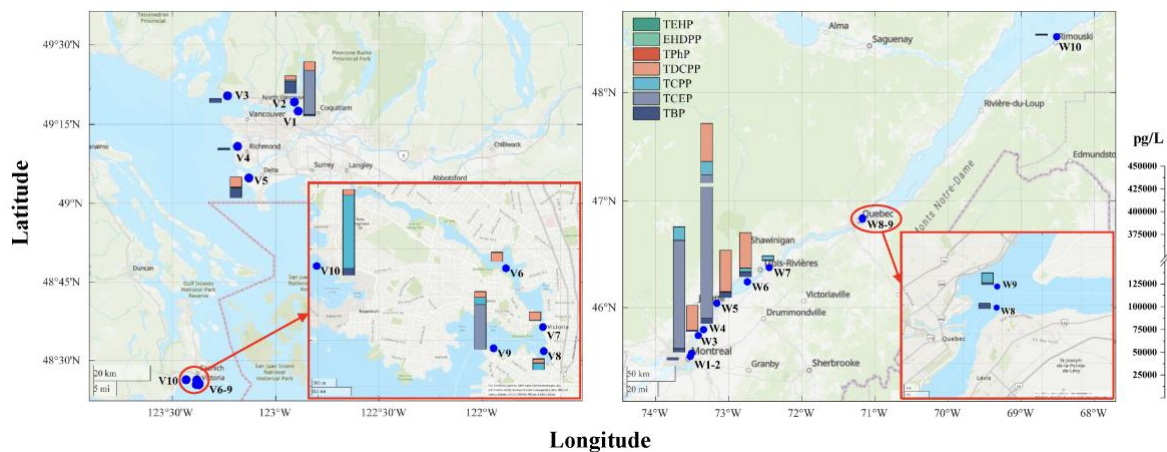
Figure 1   Spatial patterns of OPEs in the water in British Columbia (left panel) and Quebec (right panel). The inserted maps at the bottom right of each panel show the sampling sites located within Victoria (left panel) and Quebec City (right panel). Concentrations in duplicate samples were averaged. The stacked bars indicate the total concentrations levels of all detected OPEs and individual OPE. Various colors are used for different OPEs. The dispersion plume of the Montreal waste water treatment plant enters the river at 45 40' N, 73 28' W and stays on the north side of the river (Marcogliese et al., 2015), therefore, the OPEs in the dispersion plume might not be sampled at W3 and W4. The concentration scale is shown to the right of the maps, which were created using the basemap of MATLAB, copyrighted to Esri, TomTom, Garmin, SafeGraph, GeoTechnologies, Inc, METI/NASA, USGS, Bureau of Land Management, EPA, NPS, US Census Bureau, USDA, USFWS, NRCan, and Parks Canada.

4. DISCUSSION

4.1 Seasonality and Temperature Dependence. Clear and consistent seasonal trends were not observed for particle-bound OPEs at any location during the one year of sampling

303   (Tables S9). However, OPE gas phase concentrations at all three AAS sampling sites clearly
304   varied seasonally, allowing us to investigate the influence of temperature on those
305   concentrations (Figure 2). Except for EHDPP and TDCPP, concentrations of frequently
306   detected OPEs increased with increasing ambient temperature. The logarithm of the partial
307   pressures of OPEs (ln p) were linearly regressed against the reciprocal of absolute
308   temperatures ($1/T$) (Clausius-Clapeyron (CC) relationship), with the slopes, R^2 values, and
309   p values summarized in Table S7. Regressions for TBP were significant at the three AAS
310   sites ($p < 0.05$), whereas EHDPP did not show significant relationships at any site. The CC
311   relationships for other OPEs were only significant ($p < 0.05$) at some locations, i.e., TCEP
312   and TCPP on Saturna Island, TEP and TPhP in Tadoussac, and TPrP, TCPP, TCEP, and
313   TDCPP in Toronto. In cases with $R^2 > 0.10$, the trends indicate higher partial pressures at
314   higher temperatures.

315   Apparent enthalpies of air-surface exchange ($\Delta H_{\text{AS-app}}$) were obtained from the slopes of the
316   CC relationships with $R^2 > 0.30$ and $p < 0.05$, and compared with enthalpies of exchange
317   between air and water (ΔH_{AW}) and between air and octanol (ΔH_{AO}), estimated using poly-
318   parameter linear free energy relationships (UFZ-LSER database v 3.2.1 [Internet], 2024)
319   (Table S7). Values of $\Delta H_{\text{AS-app}}$ that are similar to ΔH_{AW} and ΔH_{AO} have been interpreted as
320   being indicative of a dominant contribution of temperature-driven local air-surface
321   exchanges on the air concentration at a site (Bidleman et al., 2023; Wania et al., 1998; Zhan
322   et al., 2023). If $\Delta H_{\text{AS-app}}$ is much lower than ΔH_{AW} and ΔH_{AO}, advection from elsewhere is
323   presumed to play a more important role. $\Delta H_{\text{AS-app}}$ values of OPEs at the three sampling sites
324   were mostly within the uncertainty range of ΔH_{AW} and ΔH_{AO}. In several instances the
325   temperature dependence of air concentrations was even larger than might be expected from
326   air-surface equilibrium, i.e. $\Delta H_{\text{AS-app}}$ was larger than ΔH_{AW} and ΔH_{AO}. Examples are the
327   $\Delta H_{\text{AS-app}}$ values of TCPP on Saturna Island and in Toronto, as well as those of TBP and
328   TPhP in Tadoussac, and, to a smaller extent also TCEP on Saturna Island and in Toronto,
329   and TEP in Tadoussac.

330   This may simply be a result of high uncertainty, considering the relatively small number of
331   samples available for deriving the CC relationships for Saturna Island and Tadoussac. It
332   could also suggest that temperature influences not only the exchange between air and surface
333   but also the OPE source strength to the atmosphere. This source strength could be correlated
334   with temperature, e.g., because of enhanced release of OPEs from materials at higher
335   temperatures or higher indoor-outdoor exchange rates in summer. Furthermore, the

formation of TCPP, TCEP, and TPhP from precursor compounds (i.e., tris(2-chloroisopropyl) phosphite (TCPPi), tris(2-chloroethyl) phosphite (TCEPi), and triphenyl phosphite (TPhPi) by reaction with ozone could be higher in summer (Liu et al., 2023; Liu and Mabury, 2019; Turygin et al., 2018; Zhang et al., 2021), when photooxidant concentrations tend to be higher. Even though TCPP is widely used in large quantities, the spatial distribution and usage of its precursor TCPPi has not been reported. The high $\Delta H_{\text{AS-app}}$ of TEP and TBP in Tadoussac may also be related to the conversion of their corresponding phosphite esters. The value of the measured $\Delta H_{\text{AS-app}}$ may potentially contain information on the contribution of the transformation of OPAs to OPEs in the atmosphere, i.e., the extent to which $\Delta H_{\text{AS-app}}$ exceeds ΔH_{AW} and ΔH_{AO} may indicate the extent of such transformation. However, this would be beset by high uncertainties considering the complex set of factors influencing the $\Delta H_{\text{AS-app}}$.

Incidentally, at 11 sites in BC, where PASs were deployed at least three times during different seasons with different average temperatures, higher OPEs concentrations were generally also observed during warmer deployments (Tables S6 and Table S5 in the SI of Li et al. submitted). 33 out of 55 CC relationships using these PAS data had $R^2 > 0.5$, and 27 of these 33 were negative (Table S6). Considering the limited number of data points (3~4) for PAS sites with multiple deployments in different seasons, $\Delta H_{\text{AS-app}}$ values may have high uncertainties (Table S6) and were therefore not compared with theoretical values.

356 **Table 1**   Summary of levels OPEs in precipitation reported in the literature and our study.

Region & locations	Years	TEP	TBP	TCEP	TCPP	TDCPP	TPhP	TBEP	EHDPP	References	Note
						Concentration, ng/L					
Literature data											
Livingston Island, Antarctic	2018	2.1	1.0	3.1	26.0	1.9			0.11	(Casas et al., 2021)	
Nanning, China	N/A		4.0	15	38	2.1	1.0			(Zhang et al., 2020)	Mean
Osnabrueck, Germany	2011			187	372	46				(Mihajlović and Fries, 2012)	Median
Bahnbrücke, Germany	2001		911	121				394		(Fries and Püttmann, 2003)	
Rome, Italy	2007	46	46	155	686	404		112		(Bacaloni et al., 2008)	Mean
Martignano, Italy	2007	12	11	19	28	108		38		(Bacaloni et al., 2008)	
New York, USA	2017	17.7	3.9	5.7	61.8	11.7	11.0			(Kim and Kannan, 2018)	Mean
Our study											
Saturna Island	2020	3.0	4.0	15.6	25.7	20.9	1.0	13.7	1.2	Our study	Mean
Tadoussac	2021	1.2	0.6	2.6	5.1	37.0	0.6	2.8	0.5	Our study	Mean

357 The concentrations of OPEs in snow and rain water samples from five locations in Germany during 2007-2008 were reported (Regnery and Püttmann, 2009). However, as we could not calculate
358 the average OPE concentrations in precipitation, we did not include these data in this table.

359 Marklund et al.(2005b) reported the concentrations of OPEs in combined dry and wet deposition samples, as there are no data for precipitation samples, therefore, these data were not included in
360 this table either.
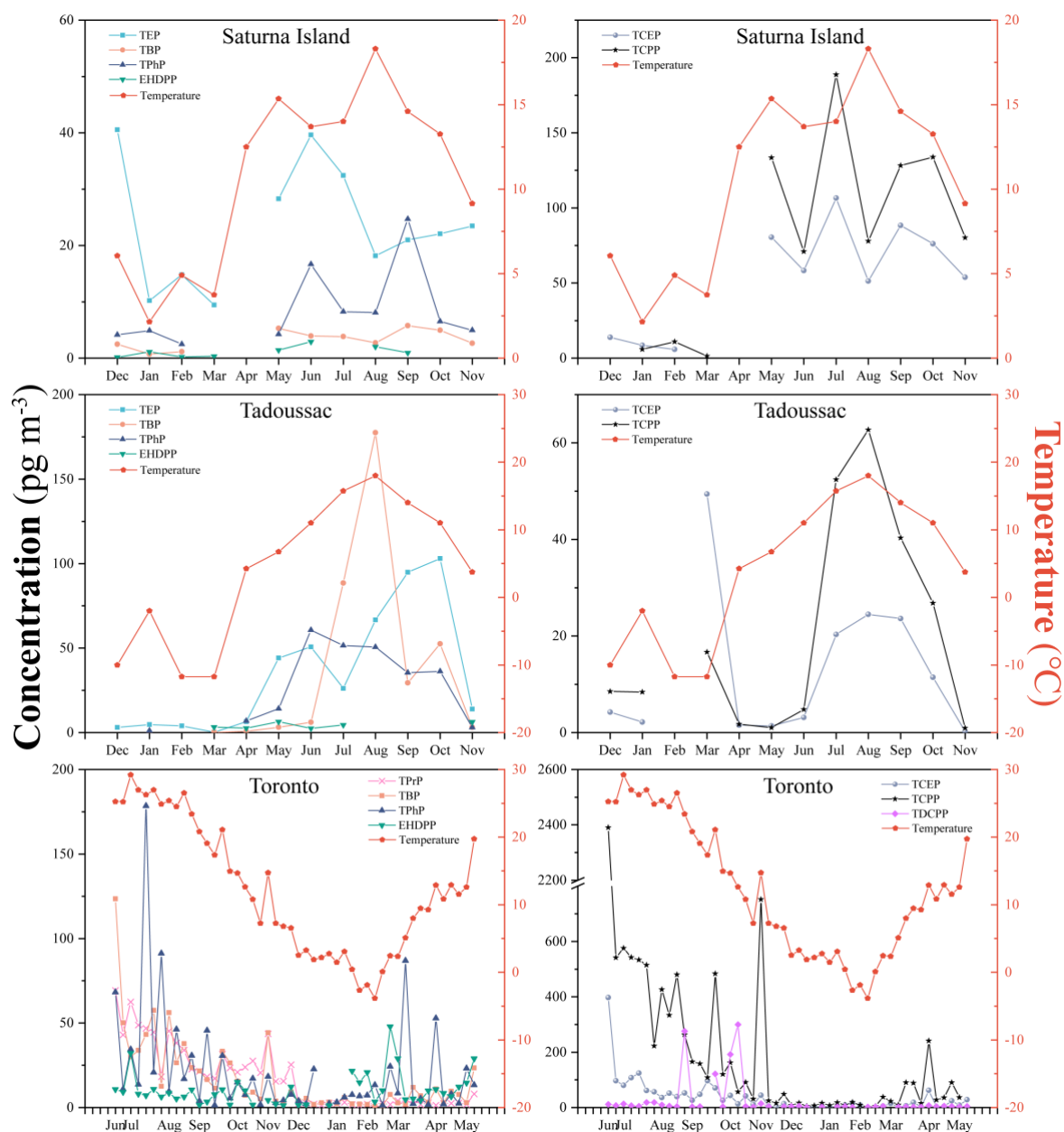
Figure 2   Seasonal variability in ambient temperature (right y axis) and gas phase concentrations of OPEs (left y axis) in the atmosphere of Saturna Island, BC (2019-2020, top), Tadoussac, QC (2020-2021, middle), and Toronto, Ontario (2020-2021, bottom). Only data for OPEs with detection frequency higher than 50% are shown.

4.2 Gas-Particle Partitioning. The fraction of the OPEs in the particle phase (Φ, %) are given in Table S9. As more than 50% of Φ values for TPhP and EHDPP in Tadoussac were calculated using values < MDL, these data are not discussed further. Overall, Φ ranged between 32% and 68 % and varied between OPEs and location. Among the five OPEs, the Φ of TCEP is the smallest at almost all three AAS sites. The Φ values for TBP and TCPP on Saturna Island (both ca. 66%) are 12 % higher than that for TCEP (54%). In Tadoussac,

372   the Φ for TCPP (38%) is comparable to that for TCEP (34%), whereas Φ for TBP (52%) is

373   the highest among three OPEs. In Toronto, the Φ values of the five major OPEs were in the

374   sequence of TCEP (50%) = TBP (50%) < TPhP (54%) < TCPP (56%) < EHDPP (68%).

375   This sequence is opposite to that found above the North Atlantic Ocean and in the Arctic

376   (Wu et al., 2020).

377   Theoretically, TCEP, TCPP, and TBP have very similar volatility with logarithmic

378   equilibrium partition ratios between octanol and air (log K_{OA}) around 9 and log (K_{PA} / m^3 g^{-1}

379   ^{1}) of ~1 at 15 °C estimated using the UFZ-LSER website (UFZ-LSER database v 3.2.1, 2024)

380   (Table S9). These three chemicals are expected to be largely in the gas phase at ambient

381   temperatures. TPhP and EHDPP have estimated log K_{OA} values > 12 and log (K_{PA} / m^3 g^{-1})

382   of ~5 at 15 °C which would indicate strong particle sorption in the atmosphere. However,

383   the unexpectedly low fraction observed in the particle phase may suggest that TPhP and

384   EHDPP are emitted at higher temperatures and are not in a state of equilibrium between gas

385   and particle phase (Zhao et al., 2021a). Alternatively, the fraction of TPhP and EHDPP in

386   the gas phase may have been overestimated if very fine and ultrafine particles containing

387   these OPEs passed through the glass fiber filters (Zhao et al., 2021b). While it has been

388   suggested that the composition of the particles (Li et al., 2017b), relative humidity (Li et al.,

389   2017b; Wu et al., 2020), and degradation of OPEs in gas and particle phases may also

390   influence the gas-particle partitioning of OPEs, we do not have the empirical data to explore

391   the influence of these factors on our measurements.

392   The calculated Φ at the three AAS sites increases with decreasing ambient temperatures.

393   This is consistent with lower temperatures favoring partitioning to particles (Table S9). This

394   is also reflected in the positive linear relationships between the ln K_{PA} and reciprocal

395   temperature (in K) in Tadoussac, Saturna Island, and Toronto (Table S10).

396   **4.3 Scavenging Ratios.** Measured SRs could be calculated for eight OPEs and ranged

397   mainly from 10^4 to 10^7 (Table S12). These SRs are highly uncertain because of the

398   uncertainty in the measured concentrations and because we combine a monthly precipitation

399   sample with a 24-hour air sample taken during the same month. The estimated SRs are also

400   uncertain due to the possibly high uncertainty in the estimated K_{WA} and the assumptions

401   regarding equilibrium partitioning of OPE vapors between air and water droplets and the

402   value and constancy of W_P. Despite these uncertainties, estimated SRs for TBP and EHDPP

403   are generally around 10^5 and therefore comparable to the measured ones, which indicates

404   that equilibrium between precipitation and these chemicals in the atmosphere was achieved.

405 The estimated SRs for other OPEs are mostly within the range of 2×10^6 to 10^9 and therefore

406 orders of magnitude higher than the measured SRs. At very high values, exceeding a

407 threshold of ~10^6, the SR concept loses its usefulness, because the atmosphere will

408 essentially be cleansed of such compounds at the onset of a precipitation event and

409 subsequent precipitation will simply dilute the concentrations (Lei and Wania, 2004). As

410 such, measured SRs that are smaller than these very high estimated ones are not too

411 surprising.

412 **4.4 Diffusive Air-Water Gas Exchange.** The water-air equilibrium status was evaluated

413 using fugacity ratios (f_W/f_A), whereby f_W/f_A values lower (higher) than 1 indicate a tendency

414 for net deposition (volatilization). The estimated fugacity ratios for five OPEs (TBP, TCEP,

415 TCPP, TPhP, and EHDPP) are given in Table S14. This estimation of f_W/f_A incurs substantial

416 uncertainty because of uncertainty in K_{AW} and the passive sampling rates, and because it

417 involves combining air and water data obtained during different time periods (Oh et al., 2023;

418 Zhan et al., 2023). Nevertheless, the f_W/f_A values in BC and QC were so far below unity, that

419 one can confidently assert that all five OPEs were net deposited from atmosphere to water.

420 Ma et al. (2021) also reported that almost all five OPEs, except TBP, underwent net gas

421 phase deposition in the Lower Great Lakes Region.

422 **4.5 Relative Abundance of OPEs in Different Environmental Media.** The frequent

423 detection of TCPP, TCEP, TBP, and TPhP in PASs, the gas and particle phase of the AAS, ,

424 PWSs, and PCPNs in QC and BC allows us to investigate the relative abundance of these

425 OPEs in different environmental media (Figure 3). Chlorinated compounds (TCPP and

426 TCEP) were dominant in all environmental media regardless of sampling locations, which

427 is consistent with observations in gaseous and aqueous phases in the Great Lakes region (Ma

428 et al., 2021). Specifically, TCPP was the most abundant of the four OPEs in all types of

429 samples, except for the gas phase in Tadoussac and the PWS. By reporting the relative

430 abundance of the OPEs in PASs separately for industrial, urban, and rural sites, we find a

431 consistent pattern in both QC and BC, namely that the relative abundance of halogenated

432 OPEs (TCPP and TCEP) decreased from industrial (65% in QC and 79% in BC) to urban

433 (59% in QC and 63% in BC) to rural sites (52% in QC and 53% in BC) with a concomitant

434 increase of two nonhalogenated OPEs (TBP and TPhP). This is consistent with previous

435 studies (Kurt-Karakus et al., 2018; Zhang et al., 2019), but contrasts with the predominance

436 of TCPP and TCEP reported for Antarctic air (Wang et al., 2020a). The higher abundance

437 of TPhP at rural sites would be consistent with a relatively higher long-range transport

potential (LRTP) estimated with the improved OECD Pov and LRTP Screening Tool (OECD Tool) (Breivik et al., 2022) (Table S15). Even though the observed higher abundance of TBP in remote areas is inconsistent with its relatively low estimated LRTP, Sühring et al. (2020) indicated that non-chlorinated OPEs could be subject to LRTP.
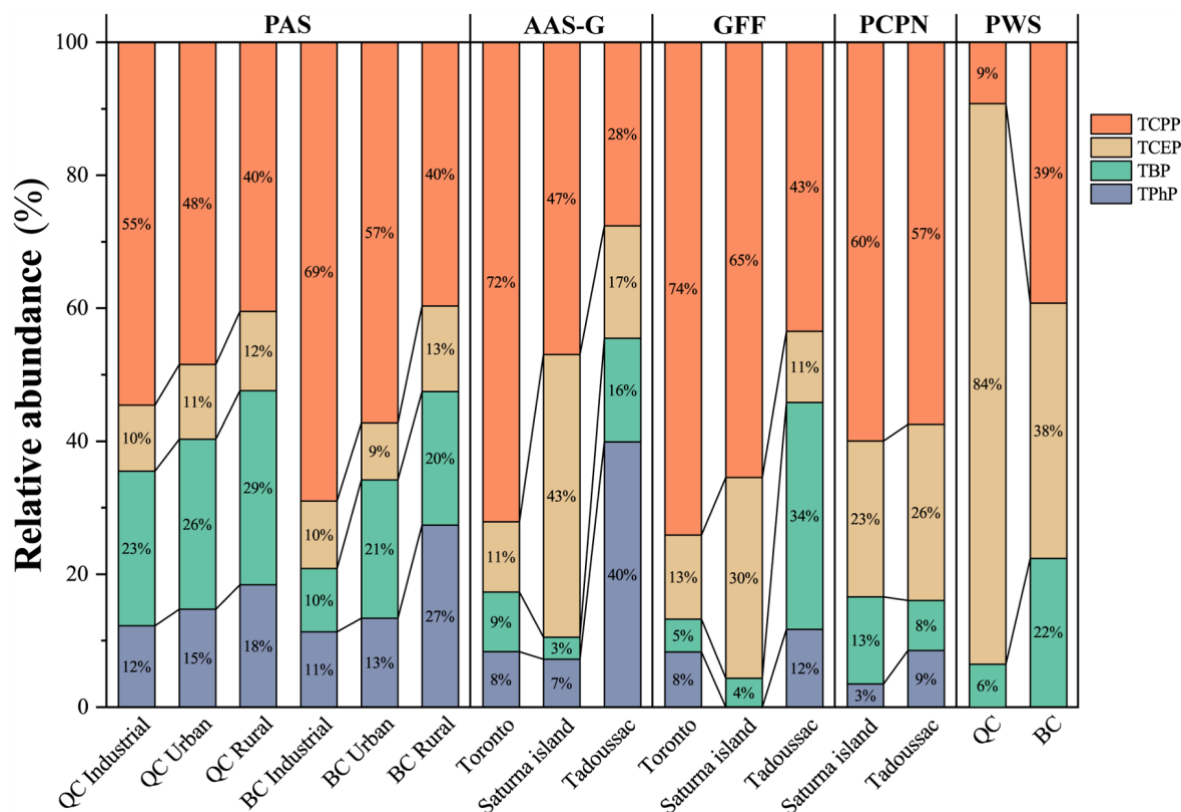
Figure 3   The relative abundance of four frequently detected OPEs in passive air samples (PAS), gas phase active air samples (AAS-G), glass fiber filter samples (GFF), precipitation samples (PCPN), and passive water samples (PWS) in QC and BC. Due to the large concentration ranges, geomean was used for calculating the relative abundance for PASs

The relative abundance of OPEs in the gas and particle phase at the three AAS sites was similar. Mirroring the observation in the PASs, the relative contribution of chlorinated OPEs was higher in urban and industrial Toronto than in rural Saturna and remote Tadoussac. Chen et al. (2019) and Salamova et al. (2013) reported a similar trend for OPEs in dust and atmospheric particles, respectively. Interestingly, in the atmospheric gas and particle phases, the higher abundance for TPhP in Tadoussac compared to Toronto suggests that long-range transport was dominant, despite Toronto being a highly populated city. This observation aligns with the above findings of a low ΔH_{AS-app}, the low median concentration level in Toronto compared to that in Tadoussac (Table S5), as well as the spatial patterns, cluster

457 analyses, and a weak linear relationship with population previously reported in Li et al.
458 (submitted). Collectively, these pieces of evidence indicate that TPhP is more closely related
459 to industrial activities and subject to long-range transport.

460 The abundance of chlorinated OPEs in PCPN and PWS was much greater than those of the
461 nonhalogenated OPEs, which is consistent with the dominance of TCPP and TCEP in the
462 dissolved phase of water sampled from urban and rural watersheds in Toronto (Awonaike et
463 al., 2021). Based on section 4.4, net diffusion from the atmosphere to water occurred in BC
464 and QC, therefore, the high abundance of chlorinated OPEs can be explained by their
465 relatively high K_{WA} (Tables S4 & S15).

466 **5. IMPLICATIONS**

467 Some observations made here are conforming with general expectations regarding the
468 environmental behaviour of semi-volatile organic chemicals, such as higher gas phase
469 concentrations and a decrease in the particle bound fraction at higher ambient temperatures.
470 Also, the measured precipitation scavenging ratios, while high, can be reconciled with
471 equilibrium partitioning ratios of gaseous OPEs that favour aqueous phases over the gas
472 phase. Other observations are more puzzling, such as the general lack of a clear relationship
473 between OPE volatility and the observed gas-particle partitioning behaviour. Furthermore,
474 the strong temperature dependence of OPE gas phase concentrations that indicates the
475 importance of temperature-driven local air-surface exchange processes is not entirely
476 consistent with the low air/water fugacity ratios which suggest that gaseous air-water
477 exchange is strongly depositional. One possible explanation is that the measured seasonal
478 concentration variability is less a reflection of temperature driven air-surface exchange and
479 instead indicates that more OPE enter, or are formed in, the atmosphere in summer. Potential
480 mechanisms are (i) an increased release of OPEs at higher temperatures from outdoor
481 materials to which they have been added (Kemmlein et al. 2003), (ii) a faster ventilation of
482 OPE emitted indoors (Stamp et al., 2022, Han et al., 2024), (iii) more active industrial
483 activities, such as construction, using products containing OPEs in the summer months, and
484 (iv) the atmospheric oxidation of organophosphite precursors (Liu et al., 2023).

485 Our data also highlight that the understanding of the atmospheric dispersion potential of
486 OPEs is still incomplete. While a relatively high long range transport potential for aryl-OPE
487 (TPhP) is consistent with the results from the OECD Tool (Kung et al., 2022; Sühring et al.,
488 2020), the higher or constant relative abundance for TBP at remote sites does not align with

489 predictions, which indicate a limited LRTP for TBP. This, too, may be related to the
490 unpredictable gas-particle partitioning behaviour of the OPEs and the role of gas and multi-
491 phase transformation processes, e.g. the possibility that TBP originates in part from the
492 transformation of precursors. More research is needed to better understand the atmospheric
493 gas-particle partitioning behaviour of the OPEs and to elucidate the role that transformation
494 reactions may play in this regard.

Code and data availability

496 All data generated for this project are contained in the Supplement.

Supplement

498 The supplement related to this article is available online at: xxxxx.

Author contributions

500 YL, FZ, and JO prepared and extracted the PASs and the Toronto AASs. YL and FZ also
501 took the Toronto AAS. YDL prepared standards. CS prepared, obtained, and extracted
502 samples from Saturna Island and Tadoussac as well as the PWSs and analyzed the particle
503 samples. KL and FAPCG deployed and retrieved PASs and PWSs in British Columbia. ABC,
504 ZL, HH, FZ, and FW deployed/retrieved PASs and PWSs in Quebec. YL compiled and
505 interpreted data. YL wrote the manuscript under the guidance of FW with input by the other
506 co-authors. HH coordinated the project. All authors reviewed the manuscript.

Competing interests

508 The contact author has declared that none of the authors has any competing interests.

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