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

2 **Precipitation Scavenging, and Air-Water Equilibrium of**

3 **Organophosphate Esters in Southern 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

113   in the atmospheric gas phase and in water in the two coastal regions. The passive air

114   sampling data have been presented previously (Li et al., submitted). This unique data set

115   allowed us to estimate the gas-particle distribution in the atmosphere, precipitation

116   scavenging ratios, and the state of air-surface water equilibrium, often in their seasonal

117   dependence or their variability between urban, rural and remote locales. Finally, we used

118   this dataset to explore the relative abundance of OPEs in the different types of samples.

119   **2. MATERIALS AND METHODS**

120   **2.1 Active Air Sampling and Precipitation Collection.** 24-hour air samples were collected

121   monthly for one year using a high-volume active air sampler (AAS); twelve at a location on

122   Saturna Island, British Columbia (BC) (48.7753N, -123.1283W), and twelve in the vicinity

123   of Tadoussac, Quebec (QC) (48.1415N, -69.6991W). Forty-eight consecutive week-long

124   AASs were taken with a mid-volume pump in the Eastern suburbs of Toronto (43.78371 N,

125   −79.19027 W) (Li et al., 2023a, b, 2024). At all three sites, polyurethane foam

126   (PUF)/XAD/PUF sandwiches and glass-fiber filters (GFFs) were used to collect OPEs in

127   the gas and particle phase, respectively. Precipitation samples (PCPNs) were collected at the

128   AAS sampling locations in BC and QC during the same months as the air samples and the

129   sampling length was ~ 30 days (Oh et al., 2023; Zhan et al., 2023).

130   **2.2 Passive Air and Water Sampling.** In QC, 86 passive air samplers (PASs) were

131   deployed at 71 unique sampling sites on either shore of the St. Lawrence River and Estuary,

132   including in Montreal and Quebec City between 2019 and 2022. In BC, 83 PASs were

133   deployed at 47 sites in the lower mainland around Vancouver and on the Canadian shore of

134   the Salish Sea during different time periods between 2020 and 2022. More details are given

135   in Table S5 in the Supporting Information (SI) of Li et al. (submitted) and in previous

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

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

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

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

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

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

142   **2.3 Sample Analysis.** Prior to extraction all samples were spiked with seven isotopically

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

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

145 PCPN and PWS samples were extracted using liquid-liquid extraction with dichloromethane
146 and soaking in hexane, respectively. Extracts were concentrated to 0.5 mL using a rotary
147 evaporator and nitrogen blow-down. Triamyl phosphate was added into the concentrated
148 extracts as an injection standard. Gas chromatography-tandem mass spectrometry (GC-
149 MS/MS) was used to detect and quantify 16 OPEs (Tables S1 and S2).

150 **2.4 Quality Assurance and Quality Control.** All extraction and concentration procedures
151 were carried out in a trace analytical laboratory. The glassware was cleaned using a machine
152 with detergents, then rinsed with deionized water, and finally baked with GFFs at 450 °C in
153 a muffle furnace for 24 hours. Experimental materials that came into contact with samples
154 or extracts were thoroughly cleaned and rinsed three times with solvents (acetone and
155 hexane, or dichloromethane) before use. Field blanks, procedure blanks, and solvent blanks
156 were prepared with each batch of extractions and analyses (Oh et al., 2023; Zhan et al., 2023).
157 OPEs were not found in procedure or solvent blanks. Only a few analytes were present in
158 the field blanks, and for these, the average detected amount was subtracted from the amounts
159 of target chemicals in the field samples. Method detection limits (MDLs) were calculated as
160 three times the standard deviations of levels in field blanks when analytes were detected
161 (signal-to-noise ratio (S/N) > 3); otherwise, MDLs were based on concentrations at which
162 S/N is 3 (Desimoni and Brunetti, 2015). MDLs are provided in the Supplementary
163 Information (Tables S5, S8, S10, S11, and S13). The average recoveries of five surrogates
164 in AASs, PCPNs, and PWSs ranged from 78% to 232% (Table S3). The concentrations
165 reported have been corrected for recovery.

166 **2.5 Data Analysis.** Water concentration of OPEs were calculated from the amounts
167 quantified in PWS extracts following the method by Booij and Smedes (Booij et al., 2003;
168 Booij and Smedes, 2010), with details provided by Oh et al. (2023).

169 The fraction of an OPE in the particle phase (Φ, %) was obtained by dividing the particle-
170 phase concentration by the sum of concentrations in the gas and particle phase. Gas-particle
171 partition ratios K_{PA} (m^3 air g^{-1} aerosol) were derived by dividing the measured concentrations
172 of an OPE in the particle phase (pg m^{-3}) by the product of the concentrations of particles less
173 than 2.5 µm in diameter (PM$_{2.5}$, g m^{-3}) obtained from nearby national air pollution
174 surveillance program (NAPS) stations (Table S8) and the measured concentrations of this
175 OPE in the gas phase (pg m^{-3}). More detail is given in previous publications (Li et al., 2023a;
176 Oh et al., 2023; Zhan et al., 2023).

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

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

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

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

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

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

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

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

185   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

186   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

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

188   **3. RESULTS**

189   **3.1 OPEs in the Atmospheric Gas Phase.** The gas phase concentrations obtained during

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

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

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

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

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

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

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

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

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

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

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

201   Toronto. We are no comparing here the gas phase concentrations recorded in our study with

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

222   2023).

223   **3.2 OPEs in Atmospheric Particle Phase.** The concentrations of five OPEs (TBP, TCEP,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

238   2016). TCPP in Tadoussac, 3 pg m^{-3}, is comparable to its level in Antarctica (6 pg m^{-3})

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

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

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

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

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

244   ^{3}), and one order of magnitude lower than levels in Toronto (12 pg m^{-3}) and those in Quebec

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

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

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

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

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

250   concentrations.

251   **3.3 OPEs in Precipitation.** Eight OPEs, i.e., TEP, TBP, TCEP, TCPP, TDCPP, TPhP,

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

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

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

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

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

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

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

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

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

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

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

263   (Regnery and Püttmann, 2009).

264   **3.4 OPEs in Water.** The OPEs concentrations in water, obtained with PWSs deployed in

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

266   1, S1, and S2. In BC, OPEs had elevated levels in the interior of Burrard Inlet close to Port

267   Moody (V1 and V2), at the southern mouth of the Fraser River (V5), and at some sites

268   around populated areas in Victoria, BC (V6-V8). TBP, TCPP, and TDCPP had higher

269   concentrations close to an industrial area near Esquimalt (V10). In QC, highest OPE water

270   concentrations were usually detected at site W5, in the Saint Lawrence River close to an

271   industrial area in Sorel-Tracy, rather than at sites in Montreal (W1 and W2) or Québec City

272   (W8 and W9). W4 also had elevated concentrations for some OPEs such as TBP. Water

273   concentrations at the one sampling site in the Saint Lawrence Estuary were much lower than

274   in the river. Overall the spatial patterns suggest that the water concentrations of OPEs were

275 related to both industrial activities and human populations in BC, whereas industrial

276 activities might have relatively higher impact on water concentrations of OPEs in QC. It

277 should be noted that the dispersion plume of the Montreal waste water treatment plant enters

278 the river at 45 40' N, 73 28' W and stays on the north side of the river (Marcogliese et al.,

279 2015), therefore, the OPEs in the dispersion plume might not be sampled at W3 and W4.
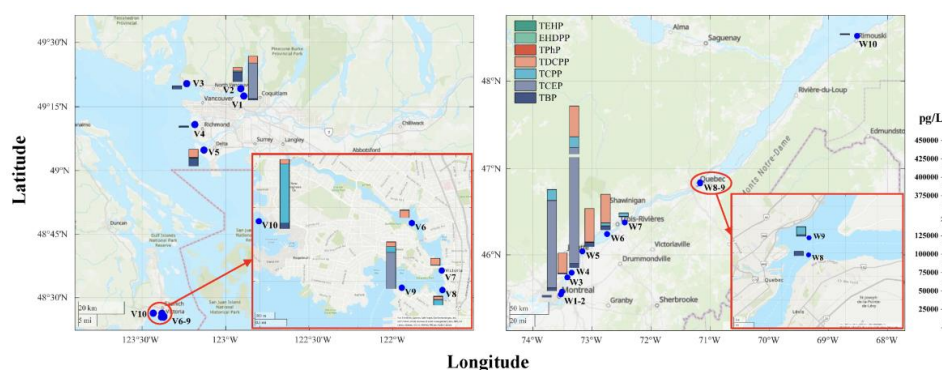
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281 **Figure 1**   Spatial patterns of OPEs in the water in British Columbia (left panel) and Quebec (right

282   panel). The inserted maps at the bottom right of each panel show the sampling sites

283   located within Victoria (left panel) and Quebec City (right panel). Concentrations in

284   duplicate samples were averaged. The stacked bars indicate the total concentrations

285   levels of all detected OPEs and individual OPE. Various colors are used for different

286   OPEs. The concentration scale is shown to the right of the maps, which were created

287   using the basemap of MATLAB, copyrighted to Esri, TomTom, Garmin, SafeGraph,

288   GeoTechnologies, Inc, METI/NASA, USGS, Bureau of Land Management, EPA, NPS,

289   US Census Bureau, USDA, USFWS, NRCan, and Parks Canada.

4. DISCUSSION

291 **4.1 Seasonality and Temperature Dependence.** Clear and consistent seasonal trends were

292 not observed for particle-bound OPEs at any location during the one year of sampling

293 (Tables S9). However, OPE gas phase concentrations at all three AAS sampling sites clearly

294 varied seasonally, allowing us to investigate the influence of temperature on those

295 concentrations (Figure 2). Except for EHDPP and TDCPP, concentrations of frequently

296 detected OPEs increased with increasing ambient temperature. The logarithm of the partial

297 pressures of OPEs (ln p) were linearly regressed against the reciprocal of absolute

298 temperatures ($1/T$) (Clausius-Clapeyron (CC) relationship), with the slopes, R^2 values, and

299 p values summarized in Table S7. Regressions for TBP were significant at the three AAS

300 sites ($p < 0.05$), whereas EHDPP did not show significant relationships at any site. The CC

301 relationships for other OPEs were only significant (p <0.05) at some locations, i.e., TCEP

302 and TCPP on Saturna Island, TEP and TPhP in Tadoussac, and TPrP, TCPP, TCEP, and

303 TDCPP in Toronto. In cases with R^2 >0.10, the trends indicate higher partial pressures at

304 higher temperatures.

305 Apparent enthalpies of air-surface exchange (ΔH_{AS-app}) were obtained from the slopes of the

306 CC relationships with R^2 >0.30 and p <0.05, and compared with enthalpies of exchange

307 between air and water (ΔH_{AW}) and between air and octanol (ΔH_{AO}), estimated using poly-

308 parameter linear free energy relationships (UFZ-LSER database v 3.2.1 [Internet], 2024)

309 (Table S7). Values of ΔH_{AS-app} that are similar to ΔH_{AW} and ΔH_{AO} have been interpreted as

310 being indicative of a dominant contribution of temperature-driven local air-surface

311 exchanges on the air concentration at a site (Bidleman et al., 2023; Wania et al., 1998; Zhan

312 et al., 2023). If ΔH_{AS-app} is much lower than ΔH_{AW} and ΔH_{AO}, advection from elsewhere is

313 presumed to play a more important role. ΔH_{AS-app} values of OPEs at the three sampling sites

314 were mostly within the uncertainty range of ΔH_{AW} and ΔH_{AO}. In several instances the

315 temperature dependence of air concentrations was even larger than might be expected from

316 air-surface equilibrium, i.e. ΔH_{AS-app} was larger than ΔH_{AW} and ΔH_{AO}. Examples are the

317 ΔH_{AS-app} values of TCPP on Saturna Island and in Toronto, as well as those of TBP and

318 TPhP in Tadoussac, and, to a smaller extent also TCEP on Saturna Island and in Toronto,

319 and TEP in Tadoussac.

320 This may simply be a result of high uncertainty, considering the relatively small number of

321 samples available for deriving the CC relationships for Saturna Island and Tadoussac. It

322 could also suggest that temperature influences not only the exchange between air and surface

323 but also the OPE source strength to the atmosphere. This source strength could be correlated

324 with temperature, e.g., because of enhanced release of OPEs from materials at higher

325 temperatures or higher indoor-outdoor exchange rates in summer. Furthermore, the

326 formation of TCPP, TCEP, and TPhP from precursor compounds (i.e., tris(2-

327 chloroisopropyl) phosphite (TCPPi), tris(2-chloroethyl) phosphite (TCEPi), and triphenyl

328 phosphite (TPhPi) by reaction with ozone could be higher in summer (Liu et al., 2023; Liu

329 and Mabury, 2019; Turygin et al., 2018; Zhang et al., 2021), when photooxidant

330 concentrations tend to be higher. Even though TCPP is widely used in large quantities, the

331 spatial distribution and usage of its precursor TCPPi has not been reported. The high ΔH_{AS-}

332 $_{app}$ of TEP and TBP in Tadoussac may also be related to the conversion of their

333 corresponding phosphite esters.

334 **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
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

335
336 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 the average OPE concentrations in precipitation, we did not include these data in this table.

337
338 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 this table as well.
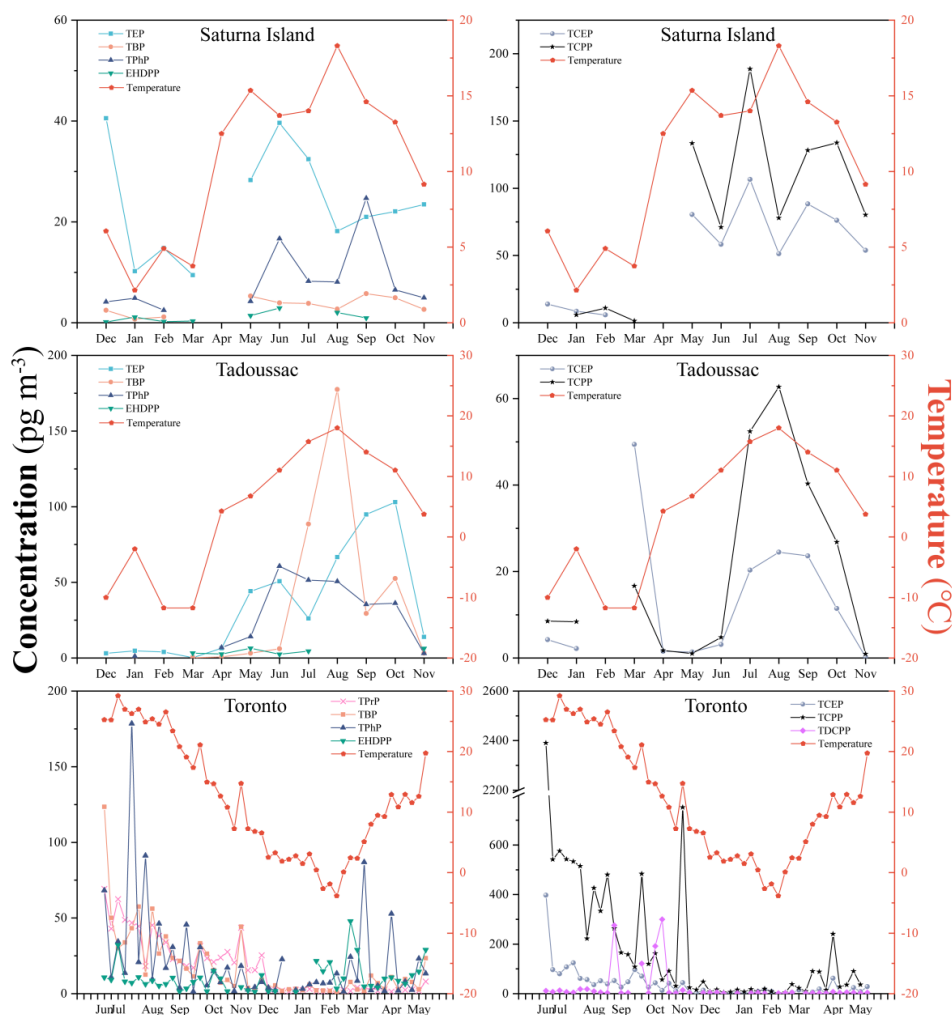
Figure 2 Seasonal variability in ambient temperature (right y axis) and gas phase concentrations of OPEs (left y axis) in the atmosphere of Saturna Island, BC (2019-2020, top), Tadoussac, QC (2020-2021, middle), and Toronto, Ontario (2020-2021, bottom). Only data for OPEs with detection frequency higher than 50% are shown.

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

13

350   uncertainties (Table S6) and were therefore not compared with theoretical values.

351   **4.2 Gas-Particle Partitioning.** The fraction of the OPEs in the particle phase (Φ, %) are

352   given in Table S9. As more than 50% of Φ values for TPhP and EHDPP in Tadoussac were

353   calculated using values < MDL, these data are not discussed further. Overall, Φ ranged

354   between 32% and 68 % and varied between OPEs and location. Among the five OPEs, the

355   Φ of TCEP is the smallest at almost all three AAS sites. The Φ values for TBP and TCPP

356   on Saturna Island (both ca. 66%) are 12 % higher than that for TCEP (54%). In Tadoussac,

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

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

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

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

361   (Wu et al., 2020).

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

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

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

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

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

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

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

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

370   and particle phase (Zhao et al., 2021a). The composition of the particles, relative humidity

371   (Li et al., 2017; Wu et al., 2020), and degradation of OPEs in gas and particle phases may

372   also influence the gas-particle partitioning of OPEs.

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

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

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

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

377   **4.3 Scavenging Ratios.** Measured SRs could be calculated for eight OPEs and ranged

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

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

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

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

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

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

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

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

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

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

388 threshold of $\sim10^6$, the SR concept loses its usefulness, because the atmosphere will

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

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

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

392 surprising.

393 **4.4 Diffusive Air-Water Gas Exchange.** The water-air equilibrium status was evaluated

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

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

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

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

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

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

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

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

402 phase deposition in the Lower Great Lakes Region.

403 **4.5 Relative Abundance of OPEs in Different Environmental Media.** The frequent

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

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

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

407 TCEP) were dominant in all environmental media regardless sampling locations, which is

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

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

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

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

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

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

414 (59% in QC and 63% in BC) to rural sites (52% in QC and 53% in BC) with a concomitant

415 increase of two nonhalogenated OPEs (TBP and TPhP). This is consistent with previous
416 studies (Kurt-Karakus et al., 2018; Zhang et al., 2019), but contrasts with the predominance
417 of TCPP and TCEP reported for Antarctic air (Wang et al., 2020a). The higher abundance
418 of TPhP at rural sites would be consistent with a relatively higher long-range transport
419 potential (LRTP) estimated with the improved OECD Pov and LRTP Screening Tool
420 (OECD Tool) (Breivik et al., 2022) (Table S15). Even though the observed higher
421 abundance of TBP in remote areas is inconsistent with its relatively low estimated LRTP,
422 Sühring et al. (2020) indicated that non-chlorinated OPEs could be subject to LRTP.
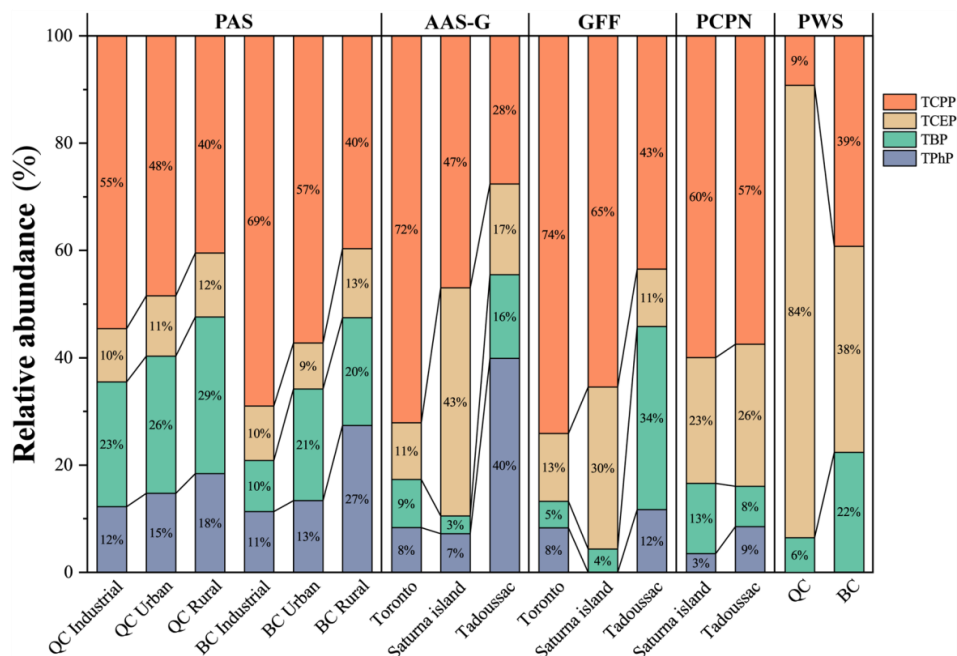
Figure 3 The relative abundance of four frequently detected OPEs in passive air samples (PAS),
gas phase active air samples (AAS-G), glass fiber filter samples (GFF), precipitation
samples (PCPN), and passive water samples (PWS) in QC and BC. Due to the large
concentration ranges, geomean was used for calculating the relative abundance for
PASs

429 The relative abundance of OPEs in the gas and particle phase at the three AAS sites was
430 similar. Mirroring the observation in the PASs, the relative contribution of chlorinated OPEs
431 was higher in urban and industrial Toronto than in rural Saturna and remote Tadoussac.
432 Chen et al. (2019) and Salamova et al. (2013) reported a similar trend for OPEs in dust and
433 atmospheric particles, respectively. Interestingly, in the atmospheric gas and particle phases,

16

434   the higher abundance for TPhP in Tadoussac compared to Toronto suggests that long-range

435   transport was dominant, despite Toronto being a highly populated city. This observation

436   aligns with the above findings of a low $\Delta H_{AS\text{-}app}$, the low median concentration level in

437   Toronto compared to that in Tadoussac (Table S5), as well as the spatial patterns, cluster

438   analyses, and a weak linear relationship with population previously reported in Li et al.

439   (submitted). Collectively, these pieces of evidence indicate that TPhP is more closely related

440   to industrial activities and subject to long-range transport.

441   The abundance of chlorinated OPEs in PCPN and PWS was much greater than those of the

442   nonhalogenated OPEs, which is consistent with the dominance of TCPP and TCEP in the

443   dissolved phase of water sampled from urban and rural watersheds in Toronto (Awonaike et

444   al., 2021). Based on section 4.4, net diffusion from the atmosphere to water occurred in BC

445   and QC, therefore, the high abundance of chlorinated OPEs can be explained by their

446   relatively high K_{WA} (Tables S4 & S15).

5. IMPLICATIONS

448   Some observations made here are conforming with general expectations regarding the

449   environmental behaviour of semi-volatile organic chemicals, such as higher gas phase

450   concentrations and a decrease in the particle bound fraction at higher ambient temperatures.

451   Also, the measured precipitation scavenging ratios, while high, can be reconciled with

452   equilibrium partitioning ratios of gaseous OPEs that favour aqueous phases over the gas

453   phase. Other observations are more puzzling, such as the general lack of a clear relationship

454   between OPE volatility and the observed gas-particle partitioning behaviour. Furthermore,

455   the strong temperature dependence of OPE gas phase concentrations that indicates the

456   importance of temperature-driven local air-surface exchange processes is not entirely

457   consistent with the low air/water fugacity ratios which suggest that gaseous air-water

458   exchange is strongly depositional. One possible explanation is that the measured seasonal

459   concentration variability is less a reflection of temperature driven air-surface exchange and

460   instead indicates that more OPE enter, or are formed in, the atmosphere in summer. Potential

461   mechanisms are (i) an increased release of OPEs at higher temperatures from outdoor

462   materials to which they have been added (Kemmlein et al. 2003), (ii) a faster ventilation of

463   OPE emitted indoors (Stamp et al., 2022, Han et al., 2024), and (iii) the atmospheric

464   oxidation of organophosphite precursors (Liu et al., 2023).

465   Our data also highlight that the understanding of the atmospheric dispersion potential of

466   OPEs is still incomplete. While a relatively high long range transport potential for aryl-OPE

467   (TPhP) is consistent with the results from the OECD Tool (Kung et al., 2022; Sühring et al.,

468   2020), the higher or constant relative abundance for TBP at remote sites does not align with

469   predictions, which indicate a limited LRTP for TBP. This, too, may be related to the

470   unpredictable gas-particle partitioning behaviour of the OPEs and the role of gas and multi-

471   phase transformation processes, e.g. the possibility that TBP originates in part from the

472   transformation of precursors. More research is needed to better understand the atmospheric

473   gas-particle partitioning behaviour of the OPEs and to elucidate the role that transformation

474   reactions may play in this regard.

Code and data availability

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

Supplement

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

Author contributions

480   YL, FZ, and JO prepared and extracted the PASs and the Toronto AASs. YL and FZ also

481   took the Toronto AAS. YDL prepared standards. CS prepared, obtained, and extracted

482   samples from Saturna Island and Tadoussac as well as the PWSs and analyzed the particle

483   samples. KL and FAPCG deployed and retrieved PASs and PWSs in British Columbia. ABC,

484   ZL, HH, FZ, and FW deployed/retrieved PASs and PWSs in Quebec. YL compiled and

485   interpreted data. YL wrote the manuscript under the guidance of FW with input by the other

486   co-authors. HH coordinated the project. All authors reviewed the manuscript.

Competing interests

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

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