Seasonal Air Concentration Variability, Gas/Particle Partitioning, Precipitation Scavenging, and Air-Water Equilibrium of Organophosphate Esters in Southern Canada

Yuening Li,[1] Faqiang Zhan,[1] Chubashini Shunthirasingham,[2] Ying Duan Lei,[1] Jenny Oh,[1,3] Amina Ben Chaaben,[4] Zhe Lu,[4] Kelsey Lee,[5] Frank A. P. C. Gobas,[5] Hayley Hung,[2] Frank Wania[1, 3*]

[1] *Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4*

[2] *Environment and Climate Change Canada, Downsview, 4905 Dufferin St, North York, Ontario, Canada M3H 5T4*

[3] *Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4*

[4] *Institut des Sciences de la Mer de Rimouski, Université du Quebec à Rimouski, 300 allée des Ursulines, Rimouski, Québec, Canada G5L 3A1*

[5] *School of Resource and Environmental Management, Simon Fraser University, 8888 University Dr, Burnaby, British Columbia, Canada V5A 1S6*

*Corresponding author: frank.wania@utoronto.ca

Abstract

In response to increasing production and application volumes, organophosphate esters (OPEs) have emerged as pervasively detected contaminants in various environmental media, with concentrations often exceeding those of traditional organic contaminants. Despite the recognition of the atmosphere's important role in dispersing OPEs and a substantial number of studies quantifying OPEs in air, investigations into atmospheric phase distribution processes are rare. Using measurements of OPEs in the atmospheric gas and particle phase, in precipitation and in surface water collected in Southern Canada, we explored the seasonal concentration variability, gas/particle partitioning behaviour, precipitation scavenging, and air-water equilibrium status of OPEs. Whereas consistent seasonal trends were not observed for OPEs concentrations in precipitation or atmospheric particles, gas phase concentrations of several OPEs were elevated during the summer in suburban Toronto and at two remote sites on Canada's east and west coast. Apparent enthalpies of air-surface exchange fell mainly within or slightly above the range of air/water and air/octanol enthalpies of exchange, indicating the influence of local air-surface exchange processes and/or seasonally variable source strength. While many OPEs were present in notable fraction in both gas and particle phase, no clear relationship with compound volatility was apparent, although there was a tendency for higher particle-bound fractions at lower temperature. High precipitation scavenging ratios for OPEs measured at the two coastal sites are consistent with low air-water partitioning ratios and the association with particles. Although beset by large uncertainties, air-water equilibrium calculations suggest net deposition of gaseous OPEs from the atmosphere to the Salish Sea and the St. Lawrence River and Estuary. The measured seasonal concentration variability is likely less a reflection of temperature driven air-surface exchange and instead indicates that more OPE enter, or are formed in, the atmosphere in summer. More research is needed to better understand the atmospheric gas-particle partitioning behaviour of the OPEs and how it may be influenced by transformation reactions.

Key words:

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 atmosphere to aquatic and terrestrial environments (Shi et al., 2024). It can scavenge and deposit both gas-phase and particle-bound OPEs. Depending on regional emissions, temperature, precipitation type, and the physicochemical properties of the OPEs (Lei and Wania, 2004), the wet deposition flux of OPEs can be significantly larger than the dry deposition flux (Kim and Kannan, 2018). Despite its importance, fewer than ten studies have reported OPE concentrations in precipitation (Bacaloni et al., 2008; Casas et al., 2021; Fries and Püttmann, 2003; Kim and Kannan, 2018; Marklund et al., 2005b; Mihajlović and Fries, 2012; Regnery and Püttmann, 2009; Zhang et al., 2020), and only one study has reported precipitation scavenging ratios for atmospheric OPEs (Casas et al., 2021).

OPEs can enter water bodies through air-water gas exchange (Castro-Jiménez et al., 2016; Ma et al., 2021), wet and dry deposition (Castro-Jiménez et al., 2016; Kim and Kannan, 2018; Ma et al., 2021), wastewater effluent (Marklund et al., 2005a), industrial and municipal discharges (Bacaloni et al., 2008; Fries and Püttmann, 2003), and surface runoff (Awonaike et al., 2021; Regnery and Püttmann, 2010). Some OPEs, including tris(1-chloro-2-propyl) phosphate (TCPP) and tris (phenyl) phosphate (TPhP), have been detected in fish (Ma et al., 2013; Sundkvist et al., 2010). A comprehensive understanding of the environmental fate and occurrence of OPEs, and in particular a better understanding of the contribution that the atmosphere makes for the delivery of OPEs to aquatic ecosystems, would benefit from investigations that quantify OPE concentrations in multiple environmental media sampled in the same area and at the same time. Despite the substantial number of studies on OPEs in the environment, those examining OPEs across three or more phases are very rare (He et al., 2019; Li et al., 2019b; Mi et al., 2023) and most studies focus on just one or two media, usually gas and/or particle phases (Li et al., 2018; Ma et al., 2022; Sühring et al., 2016; Zhao et al., 2021b) or the water phase (Choo and Oh, 2020; Ding et al., 2015; McDonough et al., 2018; Shi et al., 2020). No previous study has investigated OPEs in atmospheric gas and particle phases, precipitation, and surface water simultaneously.

To address this research gap and gather information on the contribution that the atmosphere makes to OPEs in coastal waters of Southern Canada, we aimed to characterize the occurrence, behavior, and fate of OPEs in different atmospheric phases. We measured OPEs in precipitation and atmospheric gas and particle phase for one year at two remote sites on Canada's East and West coast, respectively, and complemented this dataset with the results of a year-long measurement campaign of OPEs in the gas and particle phase in Toronto. We 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. 24-hour air samples were collected monthly for one year using a high-volume active air sampler (AAS); twelve at a location on Saturna Island, British Columbia (BC) (48.7753N, -123.1283W), and twelve in the vicinity of Tadoussac, Quebec (QC) (48.1415N, -69.6991W). Forty-eight consecutive week-long AASs were taken with a mid-volume pump in the Eastern suburbs of Toronto (43.78371 N, −79.19027 W) (Li et al., 2023a, b, 2024). At all three sites, polyurethane foam (PUF)/XAD/PUF sandwiches and glass-fiber filters (GFFs) were used to collect OPEs in the gas and particle phase, respectively. 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).

Forty-eight low-density polyethylene (LDPE) based passive water samplers (PWSs) were spiked with performance reference compounds (PRCs), deployed at 10 sites in BC and 10 sites in QC, and collected after deployment lasting 20-35 days in BC and 27-70 days in QC. Detailed information on the PWS sampling is provided in the SI (Table S13) and previous publications (Oh et al., 2023; Zhan et al., 2023).

2.3 Sample Analysis. Prior to extraction all samples were spiked with seven isotopically labeled OPEs (Table S1) as surrogates. XAD from the PASs, the PUF/XAD sandwiches and GFFs from the AASs were extracted using a Dionex Accelerated Solvent Extractor 350. The

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

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

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

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

Measured scavenging ratios (SRs) were calculated as the ratios between the concentrations of an OPE in precipitation and air (sum of gas and particle phase). We also estimated SRs by assuming equilibrium of OPE between the atmospheric gas phase and water droplets (Oh et al., 2023), and that all OPEs are sorbed to the same particles, which are scavenged with a scavenging ratio W_P of 200,000 (Kim et al., 2006). An estimated SR thus is $(1-\Phi)K_{WA} + \Phi W_P$, where K_{WA} is the temperature-adjusted partition ratio between water and air ($K_{WA} = K_{AW}^{-1}$, Table S4).

The fugacities of OPEs in water f_W, at average sea surface temperature T_w in K, were 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 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 water and air, respectively, and R is the gas constant.

3. RESULTS

3.1 OPEs in the Atmospheric Gas Phase. The gas phase concentrations obtained during the three one-year AAS campaigns in Tadoussac, on Saturna Island, and in Toronto are given in Table S5. The gas phase concentrations obtained by passive air sampling in QC and BC have been previously reported (Li et al., submitted) with tri-n-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris (phenyl) phosphate (TPhP) being reliably and ubiquitously detected. Due to the higher sampling volumes of the AAS (~520 m^3) compared to the PAS (less than 200 m^3), more OPEs could be detected above the MDL in the AAS. At all three locations, TBP, TCEP, TCPP, TPhP, and 2-ethylhexyl-diphenyl phosphate (EHDPP) were present above the MDL. Additionally, triethyl phosphate (TEP) was detected on Saturna Island, TEP, tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and tris (2-butoxyethyl) phosphate (TBEP) were detected in Tadoussac, and tri-propyl phosphate (TPrP) and TDCPP were detected in Toronto. We are not comparing here the gas phase concentrations recorded in our study with those reported previously, because that had already been done in Li et al. (submitted).

For the four most frequently detected OPEs, it is possible to compare the levels obtained with the AASs on Saturna Island and in Tadoussac and by PASs at the nearby sites L43 and S57. On Saturna Island, the PAS deployment at site L43 overlapped with the timeframe of the AASs (between May and October 2020) (Table S8). In Tadoussac, the deployment period of the PAS at S57 (November 2019 – August 2020) preceded the AASs sampling by about one year (December 2020 – September 2021). Except for TBP and TPhP on Saturna

Island, PAS levels generally trended lower than AAS levels at both locations, albeit within a factor of 5. One contributing factor to this difference could be the episodic 24-hour active air sampling's inability to represent long-term concentration levels compared to PAS. For instance, AAS-measured concentrations of TBP in Tadoussac ranged from below detection to approximately 200 pg m^{-3}. Another factor could be the spatial distribution variability of atmospheric OPEs. Despite our efforts to use PAS data from sites closest to AAS locations for comparison, the PAS and AAS sampling sites were not identical. To support the hypothesis that spatial and temporal variability in OPE concentrations contributes to the discrepancy, we also compared AAS and PAS results for hexachlorobutadiene (HCBD) and hexachlorobenzene (HCB), which exhibit uniform spatial distribution and consistent concentrations over time, using the same samples as for the OPEs. PAS levels for these two compounds closely aligned with AAS levels within a factor of 1.5. Similarly, halomethoxybenzene levels from PASs and AASs were within a factor of 3 (Zhan et al., 2023).

3.2 OPEs in Atmospheric Particle Phase. The concentrations of five OPEs (TBP, TCEP, TCPP, TPhP, EHDPP) in the atmospheric particles from the three AAS sampling locations are compiled in Tables S9. Except for TPhP and EHDPP which were not detected in particles from Saturna Island, all five OPEs most frequently detected in the gas phase could also be quantified in particle samples. Again, TCPP is the most abundant OPE at all three sites.

Concentration levels on Saturna Island and in suburban Toronto are similar and almost one order of magnitude higher than those in Tadoussac. The averaged TBP levels of 7 pg m^{-3}, 3 pg m^{-3}, and 9 pg m^{-3} on Saturna Island, in Tadoussac, and in Toronto are lower than those in Antarctica (23 pg m^{-3}) (Wang et al., 2020a) and two order of magnitude lower than those detected in cities in the Great Lakes area (130 pg m^{-3}) in 2012 (Salamova et al., 2013). Except in Tadoussac (1 pg m^{-3}), the TCEP levels of 50 pg m^{-3} and 17 pg m^{-3} on Saturna Island and in Toronto are higher than those in Antarctica (5 pg m^{-3}) (Wang et al., 2020a) and ca. 2~4 times lower than those detected in cities in the Great Lakes region (89 pg m^{-3}) (Salamova et al., 2013), and two orders of magnitude lower than the reported median concentration in Quebec City and near the St Lawrence River (1903 pg m^{-3}) (Sühring et al., 2016). TCPP in Tadoussac, 3 pg m^{-3}, is comparable to its level in Antarctica (6 pg m^{-3}) (Wang et al., 2020a), and TCPP on Saturna Island (122 pg m^{-3}) and in Toronto (90 pg m^{-3}) are three and four times lower than those detected in cities in Great Lakes area (321 pg m^{-3}) (Salamova et al., 2013), and one order of magnitude lower than the detected level in Quebec

City and near the St Lawrence River (1557 pg m^{-3}) (Sühring et al., 2016). TPhP and EHDPP levels in Antarctica (1 pg m^{-3}) (Wang et al., 2020a) are close to those in Tadoussac (2 pg m^{-3}), and one order of magnitude lower than levels in Toronto (12 pg m^{-3}) and those in Quebec City and near the St Lawrence River (51 pg m^{-3}) (Sühring et al., 2016). The relatively higher concentration levels of certain OPEs in Antarctica, such as TBP, may be due to preferential partitioning of TBP to particles at low temperatures. Compared to the sites in the Great Lakes region (Salamova et al., 2013) as well as Quebec City and near the St Lawrence River region (Sühring et al., 2016), our sampling sites were more rural, which could explain lower OPE concentrations.

3.3 OPEs in Precipitation. Eight OPEs, i.e., TEP, TBP, TCEP, TCPP, TDCPP, TPhP, TBEP, and EHDPP, were reliably detected in the precipitation samples from Saturna Island and Tadoussac (Table 1 & Table S11). Concentrations are generally higher on Saturna Island than in Tadoussac. The OPE levels in Tadoussac were comparable to those in Antarctica (Casas et al., 2021). TDCPP detected on Saturna Island and in Tadoussac are two times to one order of magnitude higher than the levels in Antarctica (Casas et al., 2021), Nanjing (Zhang et al., 2020), and New York (Kim and Kannan, 2018), and our measured EHDPP levels were higher than those detected in Antarctica. Overall, except for TDCPP and EHDPP, the average OPE concentrations detected in our study were comparable or one order of magnitude lower than literature data (Table 1). Except for TBP in Tadoussac, OPE concentrations varied greatly between months, whereby no distinct and consistent seasonal trends were discernible (Table S11), which is consistent with previous observations (Regnery and Püttmann, 2009).

3.4 OPEs in Water. The OPEs concentrations in water, obtained with PWSs deployed in the summer 2021, are reported in Table S13. Their spatial patterns are displayed in Figures 1, S1, and S2. 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.

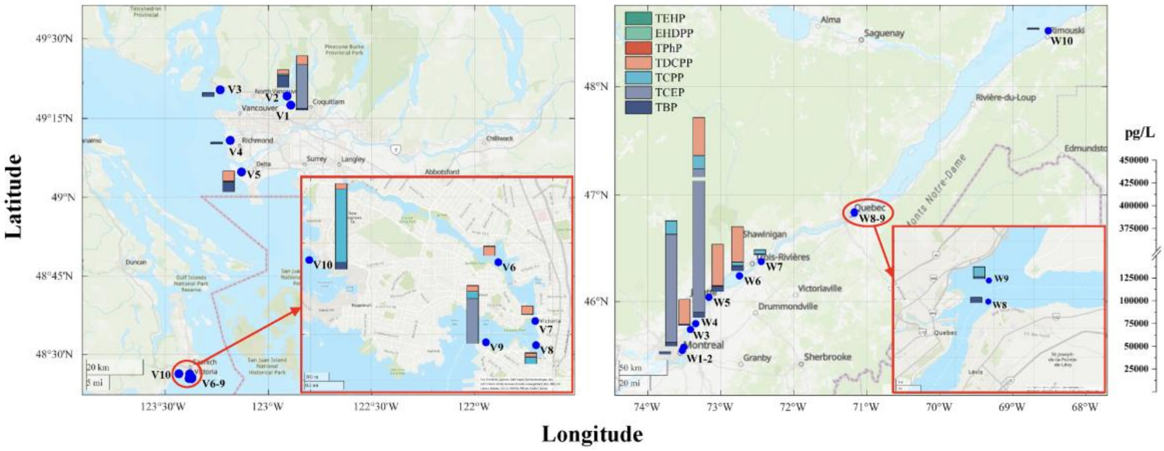

Figure 1 Spatial patterns of OPEs in the water in British Columbia (left panel) and Quebec (right panel). The inserted maps at the bottom right of each panel show the sampling sites located within Victoria (left panel) and Quebec City (right panel). Concentrations in duplicate samples were averaged. 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 (Tables S9). However, OPE gas phase concentrations at all three AAS sampling sites clearly varied seasonally, allowing us to investigate the influence of temperature on those concentrations (Figure 2). Except for EHDPP and TDCPP, concentrations of frequently detected OPEs increased with increasing ambient temperature. The logarithm of the partial pressures of OPEs (ln *p*) were linearly regressed against the reciprocal of absolute temperatures (1/*T*) (Clausius-Clapeyron (CC) relationship), with the slopes, R^2 values, and *p* values summarized in Table S7. Regressions for TBP were significant at the three AAS sites ($p < 0.05$), whereas EHDPP did not show significant relationships at any site. The CC relationships for other OPEs were only significant (p <0.05) at some locations, i.e., TCEP and TCPP on Saturna Island, TEP and TPhP in Tadoussac, and TPrP, TCPP, TCEP, and TDCPP in Toronto. In cases with R^2 >0.10, the trends indicate higher partial pressures at higher temperatures.

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

This may simply be a result of high uncertainty, considering the relatively small number of samples available for deriving the CC relationships for Saturna Island and Tadoussac. It could also suggest that temperature influences not only the exchange between air and surface but also the OPE source strength to the atmosphere. This source strength could be correlated with temperature, e.g., because of enhanced release of OPEs from materials at higher 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 $\Delta H_{AS\text{-}app}$ of TEP and TBP in Tadoussac may also be related to the conversion of their corresponding phosphite esters. The value of the measured $\Delta H_{AS\text{-}app}$ may potentially contain information on the contribution of the transformation of OPAs to OPEs in the atmosphere, i.e., the extent to which $\Delta H_{AS\text{-}app}$ 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 $\Delta H_{AS\text{-}app}$.

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, $\Delta H_{AS\text{-}app}$ values may have high uncertainties (Table S6) and were therefore not compared with theoretical values.

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

		Concentration, ng/L									
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

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.

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 either.

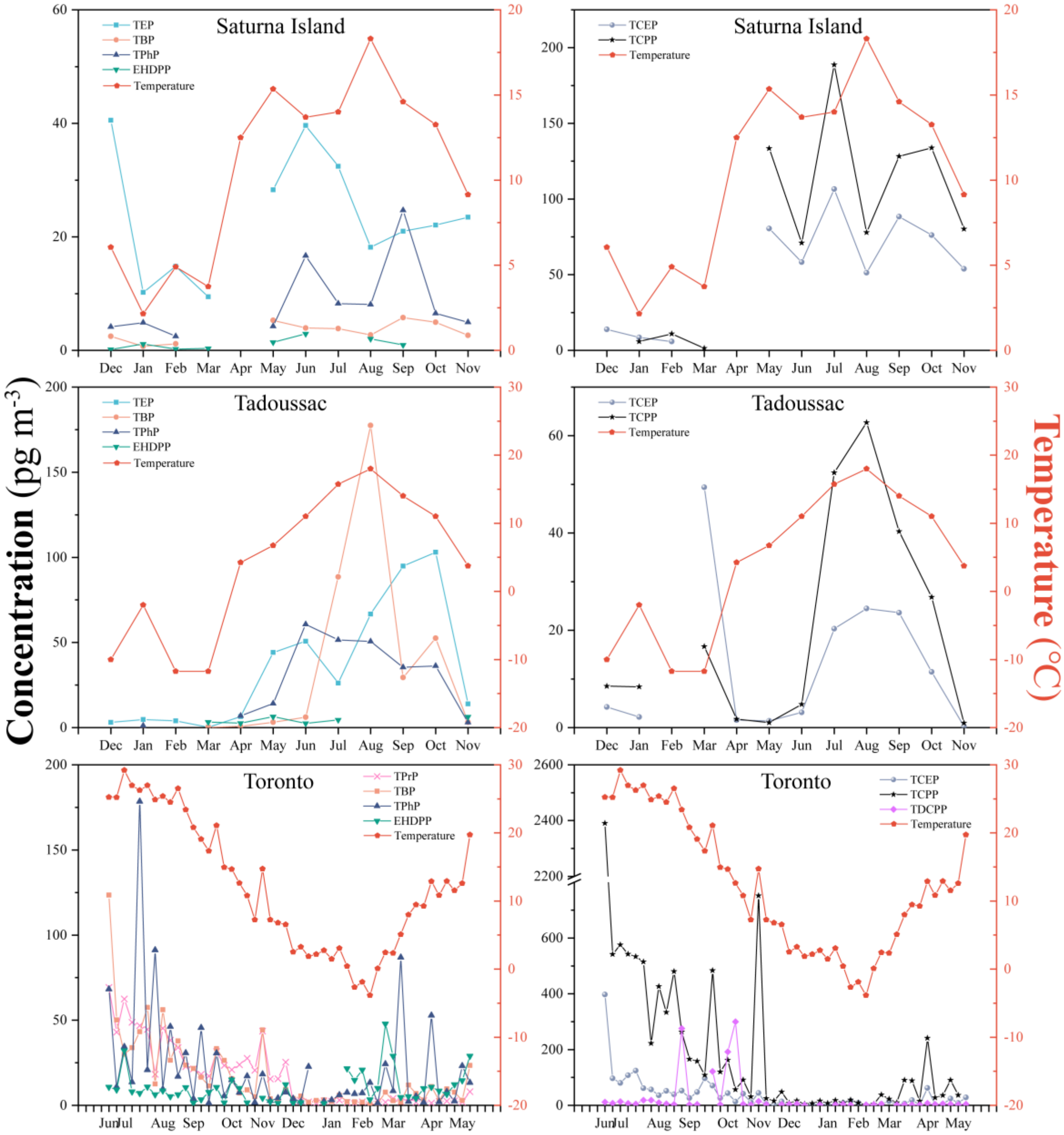

Figure 2 Seasonal variability in ambient temperature (right y axis) and gas phase concentrations of OPEs (left y axis) in the atmosphere of Saturna Island, BC (2019-2020, top), Tadoussac, QC (2020-2021, middle), and Toronto, Ontario (2020-2021, bottom). Only data for OPEs with detection frequency higher 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, the Φ for TCPP (38%) is comparable to that for TCEP (34%), whereas Φ for TBP (52%) is the highest among three OPEs. In Toronto, the Φ values of the five major OPEs were in the sequence of TCEP (50%) = TBP (50%) < TPhP (54%) < TCPP (56%) < EHDPP (68%). This sequence is opposite to that found above the North Atlantic Ocean and in the Arctic (Wu et al., 2020).

Theoretically, TCEP, TCPP, and TBP have very similar volatility with logarithmic equilibrium partition ratios between octanol and air (log K_{OA}) around 9 and log (K_{PA} / m^3 g^{-1}) of ~1 at 15 °C estimated using the UFZ-LSER website (UFZ-LSER database v 3.2.1, 2024) (Table S9). These three chemicals are expected to be largely in the gas phase at ambient temperatures. TPhP and EHDPP have estimated log K_{OA} values > 12 and log (K_{PA} / m^3 g^{-1}) of ~5 at 15 °C which would indicate strong particle sorption in the atmosphere. However, the unexpectedly low fraction observed in the particle phase may suggest that TPhP and EHDPP are emitted at higher temperatures and are not in a state of equilibrium between gas and particle phase (Zhao et al., 2021a). Alternatively, the fraction of TPhP and EHDPP in the gas phase may have been overestimated if very fine and ultrafine particles containing these OPEs passed through the glass fiber filters (Zhao et al., 2021b). While it has been suggested that the composition of the particles (Li et al., 2017b), relative humidity (Li et al., 2017b; Wu et al., 2020), and degradation of OPEs in gas and particle phases may also influence the gas-particle partitioning of OPEs, we do not have the empirical data to explore the influence of these factors on our measurements.

The calculated Φ at the three AAS sites increases with decreasing ambient temperatures. This is consistent with lower temperatures favoring partitioning to particles (Table S9). This is also reflected in the positive linear relationships between the ln K_{PA} and reciprocal temperature (in K) in Tadoussac, Saturna Island, and Toronto (Table S10).

4.3 Scavenging Ratios. Measured SRs could be calculated for eight OPEs and ranged mainly from 10^4 to 10^7 (Table S12). These SRs are highly uncertain because of the uncertainty in the measured concentrations and because we combine a monthly precipitation sample with a 24-hour air sample taken during the same month. The estimated SRs are also uncertain due to the possibly high uncertainty in the estimated K_{WA} and the assumptions regarding equilibrium partitioning of OPE vapors between air and water droplets and the value and constancy of W_P. Despite these uncertainties, estimated SRs for TBP and EHDPP are generally around 10^5 and therefore comparable to the measured ones, which indicates that equilibrium between precipitation and these chemicals in the atmosphere was achieved.

The estimated SRs for other OPEs are mostly within the range of 2×10^6 to 10^9 and therefore orders of magnitude higher than the measured SRs. At very high values, exceeding a threshold of ~10^6, the SR concept loses its usefulness, because the atmosphere will essentially be cleansed of such compounds at the onset of a precipitation event and subsequent precipitation will simply dilute the concentrations (Lei and Wania, 2004). As such, measured SRs that are smaller than these very high estimated ones are not too surprising.

4.4 Diffusive Air-Water Gas Exchange. The water-air equilibrium status was evaluated using fugacity ratios (f_W/f_A), whereby f_W/f_A values lower (higher) than 1 indicate a tendency for net deposition (volatilization). The estimated fugacity ratios for five OPEs (TBP, TCEP, TCPP, TPhP, and EHDPP) are given in Table S14. This estimation of f_W/f_A incurs substantial uncertainty because of uncertainty in K_{AW} and the passive sampling rates, and because it involves combining air and water data obtained during different time periods (Oh et al., 2023; Zhan et al., 2023). Nevertheless, the f_W/f_A values in BC and QC were so far below unity, that one can confidently assert that all five OPEs were net deposited from atmosphere to water. Ma et al. (2021) also reported that almost all five OPEs, except TBP, underwent net gas phase deposition in the Lower Great Lakes Region.

4.5 Relative Abundance of OPEs in Different Environmental Media. The frequent detection of TCPP, TCEP, TBP, and TPhP in PASs, the gas and particle phase of the AAS, , PWSs, and PCPNs in QC and BC allows us to investigate the relative abundance of these OPEs in different environmental media (Figure 3). Chlorinated compounds (TCPP and TCEP) were dominant in all environmental media regardless of sampling locations, which is consistent with observations in gaseous and aqueous phases in the Great Lakes region (Ma et al., 2021). Specifically, TCPP was the most abundant of the four OPEs in all types of samples, except for the gas phase in Tadoussac and the PWS. By reporting the relative abundance of the OPEs in PASs separately for industrial, urban, and rural sites, we find a consistent pattern in both QC and BC, namely that the relative abundance of halogenated OPEs (TCPP and TCEP) decreased from industrial (65% in QC and 79% in BC) to urban (59% in QC and 63% in BC) to rural sites (52% in QC and 53% in BC) with a concomitant increase of two nonhalogenated OPEs (TBP and TPhP). This is consistent with previous studies (Kurt-Karakus et al., 2018; Zhang et al., 2019), but contrasts with the predominance of TCPP and TCEP reported for Antarctic air (Wang et al., 2020a). The higher abundance 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.

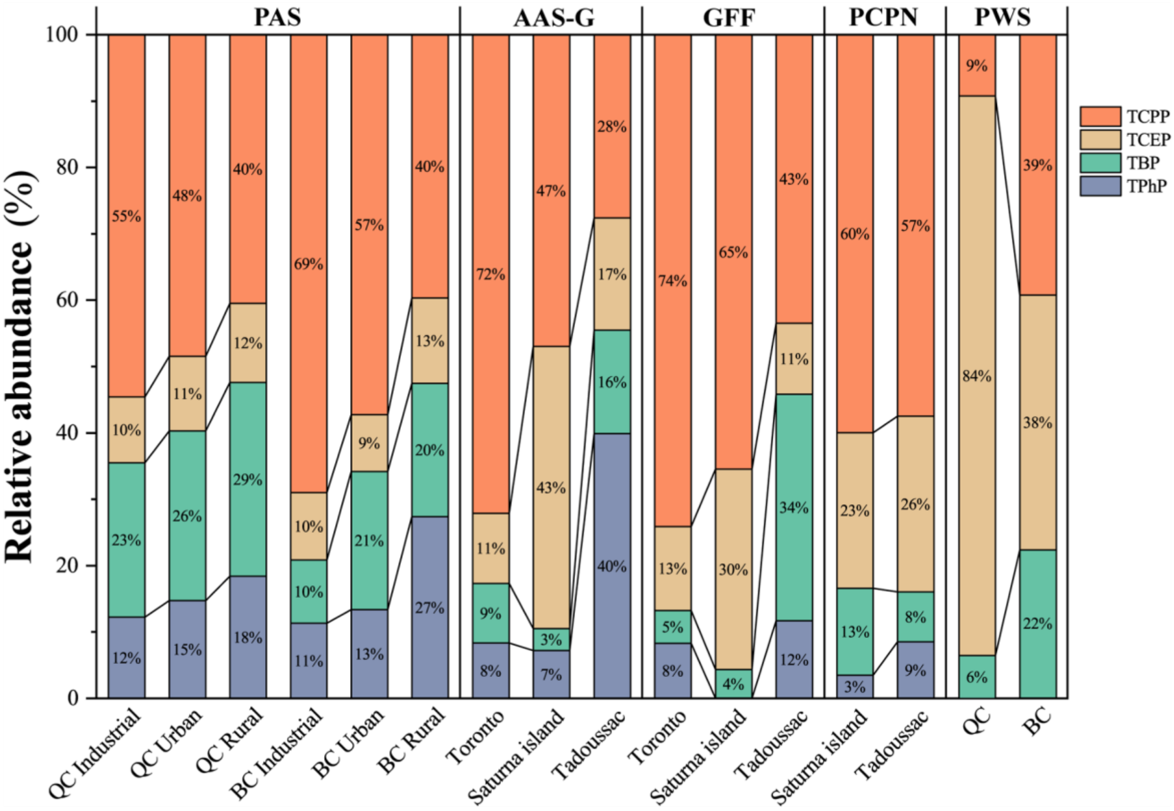

Figure 3 The relative abundance of four frequently detected OPEs in passive air samples (PAS), gas phase active air samples (AAS-G), glass fiber filter samples (GFF), precipitation samples (PCPN), and passive water samples (PWS) in QC and BC. Due to the large concentration ranges, geomean was used for 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 $\Delta H_{\text{AS-app}}$, the low median concentration level in Toronto compared to that in Tadoussac (Table S5), as well as the spatial patterns, cluster analyses, and a weak linear relationship with population previously reported in Li et al. (submitted). Collectively, these pieces of evidence indicate that TPhP is more closely related to industrial activities and subject to long-range transport.

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

5. IMPLICATIONS

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

Our data also highlight that the understanding of the atmospheric dispersion potential of OPEs is still incomplete. While a relatively high long range transport potential for aryl-OPE (TPhP) is consistent with the results from the OECD Tool (Kung et al., 2022; Sühring et al., 2020), the higher or constant relative abundance for TBP at remote sites does not align with predictions, which indicate a limited LRTP for TBP. This, too, may be related to the unpredictable gas-particle partitioning behaviour of the OPEs and the role of gas and multi-phase transformation processes, e.g. the possibility that TBP originates in part from the transformation of precursors. More research is needed to better understand the atmospheric gas-particle partitioning behaviour of the OPEs and to elucidate the role that transformation reactions may play in this regard.

Code and data availability

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

Supplement

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

Author contributions

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

Competing interests

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

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