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# Improved sampling efficiency of volatile halomethoxybenzenes and persistent organic pollutants reveals increasing concentrations in Canadian air†

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Two long-term air monitoring programs for persistent organic pollutants (POPs) have been established in the Great Lakes Basin (GLB), Ontario, and Alert, Nunavut, Canada since the 1980s for evaluating regional and long-range transport (LRT) dynamics. With growing attention towards Chemicals of Emerging Arctic Concern (CEACs), including volatile halomethoxybenzenes (HMBs) and POPs, these programs have been expanded to monitor CEACs, which can experience significant sampling breakthrough due to their high volatility. To improve collection efficiency, a high-volume air sampler utilizing a polyurethane foam-XAD2 resin sandwich was implemented for concentration characterization at the Alert and GLB sites. At Alert, the air concentrations of hexachlorobutadiene (HCBd), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), 2,4-dibromoanisole (DBA), 2,4,6-tribromoanisole (TBA), and drosophilin A methyl ether (DAME) have increased from 2009 to 2020, with the rising levels of HCBd, HCB, and PeCB potentially linked to unintentional byproducts from industrial processes. Atmospheric concentrations of HMBs and POPs at Alert are primarily governed by LRT, whereas local surface–air exchange exerts a secondary influence on DBA and TBA. In contrast, at GLB sites, local surface–air exchange is the predominant driver of HMB and POP concentrations, regardless of emission origins, with the exception of TBA at Evansville, where additional influencing factors may be involved (*i.e.* LRT).

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## Environmental significance

Persistent organic pollutants (POPs) are toxic organic chemicals known for their environmental persistence, bioaccumulation, long-range transport (LRT) potential, and adverse toxicological effects. Similarly, Chemicals of Emerging Arctic Concern (CEACs) possess these properties, necessitating long-term monitoring to evaluate concentration trends and provide early warnings. This study utilized an improved sampling system, which revealed increasing concentrations of halomethoxybenzenes (HMBs) and POPs, particularly hexachlorobutadiene (HCBd) in the Canadian High Arctic air. The rising levels of these pollutants pose a threat to the Arctic environment and underscore the need for continued monitoring and regulatory action. Considering the potential for LRT and regional deposition, targeted interventions are essential to prevent further contamination and safeguard Arctic ecosystems from the effects of persistent and emerging organic pollutants.

## 1 Introduction

Persistent organic pollutants (POPs), regulated under the Stockholm Convention, are recognized for their environmental persistence, bioaccumulative nature, capability for long-range transport (LRT), and toxicological impacts. As new chemicals are introduced into the global market annually, a growing number of substances exhibit similar properties to POPs, raising concerns about their potential to be transported to and accumulate in remote regions such as the Arctic. Moreover, advancements in analytical techniques now allow for the detection of previously unrecognized substances in these

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environments. These newly introduced or recently detected compounds, collectively termed “Chemicals of Emerging Arctic Concern” (CEACs),<sup>1–6</sup> represent a significant challenge for environmental monitoring and regulation.<sup>6</sup>

In Canada, long-term air monitoring of POPs was initiated in the 1980s at background sites in the Great Lakes Basin (GLB), including Point Petre on Lake Ontario and Burnt Island/Evansville on Lake Huron in support of the Canada/US Great Lakes Water Quality Agreement, and at a remote Arctic site at Alert, Nunavut, in 1992 under the Northern Contaminants Program (NCP). Monitoring at these sites is to assess regional and LRT of pollutants that may deposit to the Great Lakes and Arctic environment, impacting wildlife and people. Recent attention has expanded to CEACs<sup>1–6</sup> including volatile halomethoxybenzenes (HMBs) and POPs (*e.g.*, hexachlorobutadiene (HCBd)). HMBs, including anisoles and veratroles, exhibit POP-like properties and originate from both natural and anthropogenic sources.<sup>7–14</sup> Bromoanisoles (BAs), such as 2,4-dibromoanisole (DBA) and 2,4,6-tribromoanisole (TBA), are found in terrestrial and marine environments.<sup>14</sup> They are also produced through the O-methylation of 2,4-dibromophenol and 2,4,6-tribromophenol, which are widely used in the manufacture of flame retardant productions and pesticide,<sup>15</sup> as well as from disinfection byproducts of wastewater chlorination, and various industrial activities.<sup>14,16</sup> A chlorinated dimethoxybenzene drosophilin A methyl ether (DAME) may originate from terrestrial wood-rotting fungi.<sup>16,17</sup> In contrast, chloroanisoles and veratroles are predominantly anthropogenic, *e.g.*, 1,2,3,4-tetrachloro-5,6-dimethoxybenzene (TeCV, tetrachloroveratrole), and pentachloroanisole (PeCA).<sup>16,17</sup>

Traditionally, routine air monitoring of POPs at these sites has been conducted using high-volume air samplers (hi-vol) equipped with a glass fiber filter (GFF) and one or two polyurethane foam plugs (PUFs) to capture particle-bound and gas phase chemicals, respectively.<sup>18,19</sup> Due to their volatility and polarity, CEACs might not be effectively captured by PUFs alone as they tend to breakthrough the PUF.<sup>20–23</sup> To address the breakthrough issue, starting in 2009 at Alert and in 2018/19 at the GLB sites, styrene-divinylbenzene copolymeric resin (XAD) was introduced into the hi-vol sampling train. The new setup employed a hi-vol sample cartridge with one GFF followed by a PUF-XAD2-PUF sandwich. XAD is a high-capacity sorbent which can effectively capture these more volatile or polar CEACs.

This study characterizes the concentrations of CEACs, including volatile HMBs and POPs measured at the Alert site from 2009 to 2020, allowing for an assessment of multi-year temporal trends. Additionally, comparative measurements were conducted at two GLB stations from 2018 to 2022. These findings address prior uncertainties in measurements at these sites attributed to sampling artifacts. To our knowledge, these three stations are the only long-term air monitoring stations worldwide that have employed active air samplers with the PUF-XAD2-PUF configuration to minimize the breakthrough issue and are capable of reporting multi-year measured results of this particular suite of CEACs, namely volatile HMBs and POPs (*i.e.*, HCBd) during this specific period.

## 2 Methods and materials

### 2.1. Sampling sites

Air sampling was conducted at the Canadian High Arctic station at Alert, Nunavut, Canada, from 2009 to January 2021, using a Tisch PS-1 hi-vol (Tisch Environmental, Cleves, OH). Additional samples were collected at Point Petre, Ontario from October 2018 to December 2022, and Evansville, Ontario from May 2019 to November 2022 in the GLB for comparison. The coordinates of sites are listed in Table 1 and the map of sampling sites is displayed in Fig. SI 1.† The difference in sampling periods for Alert and GLB is due to delays in sample shipment from the Arctic during the pandemic.

### 2.2. Sampling

At the Alert site, the sampling duration was 7 days (approximately 2000 m<sup>3</sup> of air) due to the low concentration of the target chemicals. Seasonal adjustments were applied to the sampling frequency: one sample was collected monthly from October to February due to harsh dark winter conditions making field operation more difficult, while biweekly sampling occurred from March to September to improve temporal resolution for summer events, such as revolatilization. At the GLB sites (Point Petre and Evansville), samples were collected every 36 days over a 24 hour period (approximately 350 m<sup>3</sup> of air), with collection days varying to avoid repeatedly sampling on the same day of the week, thereby minimizing the chance of day-specific bias.

Each sample at the Alert site includes a sampling head with a GFF (TE-G653, Tisch Environmental Inc.) and a PUF-XAD2-PUF sandwich consisting of two PUFs (5.08 cm length ×

Table 1 Sampling site

| Site              | Alert   | Great Lakes Basin (GLB)                                     |                                       |
|-------------------|---|---|---------------------------------------|
|                   |   | Point Petre   | Evansville                            |
| Coordinates       | 82°27'03"N<br>62°30'26"W  | 43°50'34"N<br>77°09'13"W                                    | 45°49'07"N<br>82°39'06"W              |
| Monitoring period | 2009–2021   | 2018–2022   | 2019–2022                             |
| Site description  | Global background site for long range transport in the Canadian high Arctic | Regional background site on the north shore of Lake Ontario | Rural site on the shore of Lake Huron |



6.35 cm diameter and 2.54 cm length  $\times$  6.35 cm diameter, Tisch Environmental Inc.) and 5 g of XAD2 (SupelpakIS™-2, 20-6-mesh, pre-cleaned, Sigma Aldrich). At the GLB sites, the PUF-XAD2-PUF sandwich included 15 g of XAD2 to increase the sampling capacity for gas phase chemicals at these temperate locations as higher temperatures increase chemical volatility.

### 2.3. Sample analysis

In brief, the collected samples were extracted using either Soxhlet extraction with hexane or Dionex ASE350 with a hexane and acetone mixture (6 : 1; v/v), followed by analysis using gas chromatography coupled to tandem mass spectrometry. The chemicals analyzed in this study are volatile HMBs including DBA, TBA, TeCV, DAME and PeCA, and volatile POPs including HCB, hexachlorocyclohexane (HCHs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) (Table 2).  $\beta$ -HCH and  $\delta$ -HCH concentrations were below the method detection limits (MDLs) and thus excluded in this study. Details on sample extraction, and analysis are described in ESI SI 1† and have been previously described in Hung *et al.*<sup>24</sup> and Wong *et al.*<sup>25</sup>

### 2.4. Quality assurance (QA)/quality control (QC)

All concentrations in this study were recovery and blank corrected. The average blank values and the instrument detection limits (IDLs) are listed in Table SI 1.†

Although the sampling and analytical procedures differ between the Alert and GLB monitoring programs, the laboratory responsible for Alert and GLB sample analysis consistently adhere to well-established QA/QC protocols to ensure high-quality, comparable results. For instance, all laboratories under AMAP that analyze Alert air samples across participating countries actively participate in relevant laboratory QA/QC initiatives. Specifically, all laboratories took part in the annual NCP/Arctic Monitoring Assessment Programme (AMAP) QA/QC Interlaboratory Comparison Study, which evaluates their performance through the analysis of injection-ready standards and air extracts. This study covers a wide array of POPs and CEACs, including organochlorine pesticides (OCPs).<sup>26–30</sup>

Moreover, the laboratory participates in other significant international inter-laboratory studies, such as the International

Polar Year multinational inter-laboratory comparison study,<sup>31</sup> the AMAP/EMEP/NCP air monitoring inter-laboratory study,<sup>32</sup> the Quality Assurance of Information in Marine Environmental Monitoring in Europe laboratory performance testing program (<http://www.quasimeme.org>), the U.S. National Oceanic and Atmospheric Administration/National Institute of Standards and Technology QA/QC program, and the United Nations Environment Programme's Biennial Global Interlaboratory Assessment on POPs.<sup>33</sup>

### 2.5. Data analysis

**2.5.1. Trend analysis.** Only chemical concentrations with a detection frequency (DF) exceeding 75%<sup>34</sup> (concentrations above the MDLs) were incorporated in the long-term trend analysis. To facilitate long-term trend analysis, air concentrations below the MDLs were considered and substituted with 2/3 of the IDLs<sup>35,36</sup> for the corresponding compound. Temporal trend analysis was conducted on samples from the Alert site, whereas analysis on samples from Point Petre and Evansville was not performed due to the insufficient length of the 4 year dataset for meaningful temporal trend analysis. The trend analysis was executed using the digital filtration method, a statistical approach that employs a Reinsch-type cubic spline for temporal trends and Fourier components for seasonal cycles.<sup>18,37</sup>

The apparent first order half-life ( $t_{1/2}$ ) or doubling time ( $t_2$ ) (eqn (1)) is applied to characterize the decreasing or increasing trend of chemicals of interest with the assumption that the concentrations increase, or decrease is independent from the chemical properties. The relationship is expressed as:

$$\ln C = a \times t + b \quad (1)$$

where:  $C$  is the concentration ( $\text{pg m}^{-3}$ ),  $t$  is the time (years),  $a$  and  $b$  are the slope and the intercept, respectively.

If  $a < 0$  ( $p < 0.05$ ), this indicates a decreasing trend,  $t_{1/2} = \ln 2/a$ .

If  $a > 0$  ( $p < 0.05$ ), this indicates an increasing trend,  $t_2 = \ln 2/a$ .

Half-lives presented here are only used for comparison of the relative increase and decline rates among the chemical species and other studies with the same methodology. It should be

Table 2 Volatile HMBs and POPs investigated in this study

| Chemical                                 | Abbreviation                 | Formula  |
|--|------------------------------|--|
| HMBs                                     |                              |  |
| 2,4-Dibromoanisole                       | DBA <sup>a</sup>             | C <sub>7</sub> H <sub>6</sub> Br <sub>2</sub> O              |
| 2,4,6-Tribromoanisole                    | TBA <sup>a</sup>             | C <sub>7</sub> H <sub>5</sub> Br <sub>3</sub> O              |
| 1,2,3,4-Tetrachloro-5,6-dimethoxybenzene | TeCV <sup>a</sup>            | C <sub>8</sub> H <sub>6</sub> Cl <sub>4</sub>                |
| 1,2,4,5-Tetrachloro-3,6-dimethoxybenzene | DAME <sup>a</sup>            | C <sub>8</sub> H <sub>6</sub> Cl <sub>4</sub> O <sub>2</sub> |
| Pentachloroanisole                       | PeCA <sup>a,d</sup>          | C <sub>7</sub> H <sub>3</sub> Cl <sub>5</sub> O              |
| POPs                                     |                              |  |
| Hexachlorobutadiene                      | HCB <sup>a,b,c</sup>         | C <sub>4</sub> Cl <sub>6</sub>                               |
| Alpha-hexachlorocyclohexane              | $\alpha$ -HCH <sup>b</sup>   | C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>                |
| Gamma-hexachlorocyclohexane              | $\gamma$ -HCH <sup>b,d</sup> | C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>                |
| Hexachlorobenzene                        | HCB <sup>b,c</sup>           | C <sub>6</sub> Cl <sub>6</sub>                               |
| Pentachlorobenzene                       | PeCB <sup>b,c</sup>          | C <sub>6</sub> HCl <sub>5</sub>                              |

<sup>a</sup> CEACs: chemicals of emerging Arctic concern. <sup>b</sup> Stockholm convention. Annex A (elimination). <sup>c</sup> Stockholm convention. Annex C (unintentional production). <sup>d</sup> PeCA and  $\gamma$ -HCH were previously reported by Wong *et al.*<sup>18</sup>



noted that the values of  $t_{1/2}$  or  $t_2$  should not be used as absolute values.

**2.5.2. Surface–air exchange process analysis.** The Clausius–Clapeyron (CC) relation (eqn (2)), a plot of the natural logarithm of the partial vapor pressure ( $\ln P$ ) as a function of the inverse temperature ( $1/T$ ), is applied to determine temperature dependence of chemicals of interest to investigate potential influences from the local surface–air exchange process.<sup>38</sup> The detailed calculation of the apparent enthalpy of surface–air exchange is described in ESI 2.†

$$\ln P = c \times (1000/T) + d \quad (2)$$

$$c \text{ (slope)} = -\Delta_{\text{SA}}H/R, d = \text{intercept}$$

where:  $P$  is the vapor pressure of a chemical in the gas-phase (Pa),  $T$  is the ambient temperature (K) (average temperature monitored during the sampling period),  $\Delta_{\text{SA}}H$  is the apparent enthalpy of surface–air exchange ( $\text{kJ mol}^{-1}$ ), and  $R$  is the ideal gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

## 3 Results and discussion

### 3.1. Volatile HMBs

Halomethoxybenzenes (HMBs) are aromatic compounds characterized by a benzene ring substituted with halogens and one or more methoxy groups. Some HMBs, *i.e.*, DBA, TBA and PeCA, originating from either natural, anthropogenic or both sources, exhibit properties similar to POPs, including bioaccumulation and LRT potential. These compounds, therefore, are listed as CEACs. In this study, the key HMBs of interest including DBA, TBA, DAME, TeCV, and PeCA are examined. Notably, sampling with the PUF-only configuration presented breakthrough issues for DBA and TBA.<sup>9</sup>

**3.1.1. Concentration comparison of Alert and GLB sites.** At Point Petre and Evansville, five HMBs were measured, while at the Alert station, four HMBs were reported here (PeCA was previously reported by Wong *et al.*<sup>18</sup>). At all three sites, median concentration levels followed the order: DAME ( $21.3\text{--}100 \text{ pg m}^{-3}$ ) > TBA ( $10.5\text{--}41.5 \text{ pg m}^{-3}$ ) > DBA ( $2.67\text{--}13.5 \text{ pg m}^{-3}$ ) > TeCV ( $1.21\text{--}2.16 \text{ pg m}^{-3}$ ) (Table SI 2†). Point Petre exhibited the highest concentrations for all four species among three sites (Fig. 1). Both TBA and DBA concentrations fell within the reported global measurements range.<sup>10,11,13,14,16,39</sup> The DFs were around 60% for TeCV and >80% for DBA, TBA and DAME. Median PeCA concentration (mean  $\pm$  standard deviation (SD)) were  $49.1 (81.9 \pm 104) \text{ pg m}^{-3}$  at Point Petre significantly higher than those,  $10.6 (15.1 \pm 16.5) \text{ pg m}^{-3}$ , at Evansville.

Additionally, a statistically significant correlation between DBA and TBA concentrations was observed at both the Point Petre site (Spearman coefficient,  $r = 0.507$ ,  $p < 0.05$ ; Table SI 3†) and the Alert site ( $r = 0.841$ ,  $p < 0.05$ ; Table SI 4†), suggesting that these compounds are likely influenced by similar sources or atmospheric processes at those locations. In contrast, no significant correlation was found at the Evansville site ( $r =$

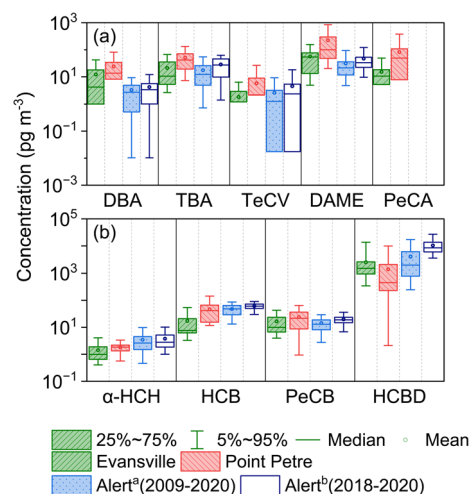


Fig. 1 Concentrations ( $\text{pg m}^{-3}$ ) of (a) five HMBs, including DBA, TBA, TeCV, DAME and PeCA; (b) four POPs including  $\alpha$ -HCH, HCB, PeCB and HCBd at the Alert and GLB sites (Point Petre and Evansville) (Alert<sup>a</sup> (2009–2020): data from 2009 to 2020 is used to characterize the concentration at the Alert site, while Alert<sup>b</sup> (2018–2020) data from 2018 to 2020 is to compare with GLB sites, where data was collected from 2018/2019 to 2022, as well as for temporal comparison).

$0.140$ ,  $p = 0.453$ ), indicating that distinct mechanisms may govern the presence of DBA and TBA there. This disparity may reflect differences in emission sources and atmospheric influences between Evansville and the other two sites. Overall, DBA and TBA are believed to originate from both natural and anthropogenic sources, and the degree of correlation may depend on the dominant sources and atmospheric processing at each site.

**3.1.2. Temporal trend.** The temporal trend analysis at the Alert site reveals a gradual but statistically significant increase in the concentrations of DBA, TBA, and DAME over the monitoring period (Fig. 2). The doubling times for these compounds were found to be 7.23 years for DBA, 5.58 years for TBA, and 10.7 years for DAME (all  $p < 0.05$ , Table SI 5†), suggesting that these chemicals are increasing in the Canadian Arctic atmosphere over time. These increases highlight the need to closely monitor CEACs, such as HMBs. A similar upward trend in DBA concentrations (weakly significant,  $p = 0.041$ ) was also observed at Pallas (situated in the interior of Arctic Finland) between 2002 and 2015.<sup>9</sup> However, with the inclusion of two additional years of data (2018 and 2019), the trend was no longer statistically significant, and no significant long-term trends were observed for either DBA or TBA at Pallas over the 2002–2019 period.<sup>13</sup> The underlying mechanisms driving these increases remain uncertain. Several plausible explanations have been proposed to account for the observed upward trends: (1) climate change:<sup>4,40</sup> in polar regions, climate change is accelerating the melting of sea ice, permafrost, and glaciers, which may release pollutants stored in ice and surface layers. The change in marine environment also affects the activities of marine organisms for BA production. The increased surface–air exchange during warmer seasons could mobilize volatile





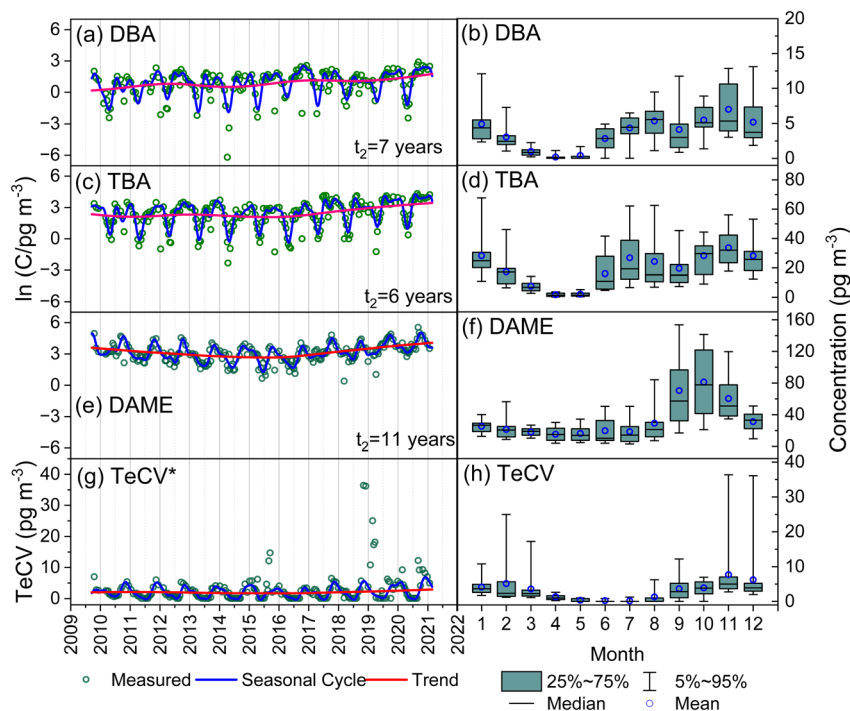


Fig. 2 Temporal trends and seasonal cycles (2009 to 2021) of concentrations for (a) DBA, (c) TBA, (e) DAME, and (g) TeCV, along with monthly variations for (b) DBA, (d) TBA, (f) DAME, and (h) TeCV at the Alert site (for TeCV with a detection frequency of less than 75%, the plot of concentration versus year is used to more accurately display the trend).

chemicals like DBA, TBA, and DAME, leading to higher atmospheric concentrations. Moreover, changes in precipitation patterns and storm intensities could facilitate the remobilization of these compounds from terrestrial and aquatic environments. (2) LRT: another possible explanation is an increase in the contribution of these chemicals *via* LRT, which brings contaminants from lower latitudes to the Arctic.<sup>10,41</sup> Chemicals with POP-like properties, including DBA, and TBA, can be transported over vast distances and deposited in remote regions like the Arctic. LRT plays a crucial role in the long-term presence of POPs and other CEACs contributing to their continuous deposition in polar environments.

**3.1.3. Seasonal trend.** Five HMBs, including DBA, TBA, DAME, TeCV and PeCA, exhibited a pronounced seasonal pattern characterized by elevated concentrations during the summer months at the GLB sites (Fig. SI 2†). Significant CC relations (Fig. SI 3 and Table SI 6†) were observed for HMBs with the significant correlation coefficients ranging from  $-0.834$  to  $-0.419$  at Point Petre and from  $-0.867$  to  $-0.619$  at Evansville (except TBA,  $r = -0.342$ ,  $p = 5.89 \times 10^{-2}$ ).

The calculated apparent enthalpies of surface-air exchange ( $\Delta_{SAH}$ ) for DBA were  $65.1 \pm 12.1$  kJ mol<sup>-1</sup> at Point Petre and  $64.3 \pm 10.3$  kJ mol<sup>-1</sup> at Evansville (Table SI 6†), surpassing values observed in Rão and Pallas.<sup>13</sup> The calculated apparent enthalpies of DBA were also close to the theoretical enthalpy of surface-air exchange, with air-water exchange ( $\Delta_{AWH} = 47.0$  kJ mol<sup>-1</sup>) and octanol-air exchange ( $\Delta_{OAH} = 61.6$  kJ mol<sup>-1</sup>)<sup>16</sup> implying that the local surface-air exchange process dominates the DBA concentrations at both locations.

Zhan *et al.*<sup>16</sup> estimated the apparent surface-air enthalpies of TBA, DAME, PeCA and TeCV concluding that the surface-air exchange process likely dominates the concentrations of these four HMBs in Toronto. Additionally, their analysis led to the conclusion that nearby Lake Ontario, next to Point Petre, serves as a potential source of HMBs. Comparing the apparent surface-air enthalpies at Point Petre and Evansville from this study with those in Toronto, it was found that the apparent enthalpy of surface-air exchange followed the order Point Petre > Toronto > Evansville for TBA, DAME, and TeCV, while the order was Toronto > Point Petre > Evansville for PeCA. Considering the higher enthalpy of surface-air exchange calculated in this study, it is likely that Point Petre might be closer to the emission sources (*i.e.*, Lake Ontario) of DAME, and TeCV, followed by Toronto and Evansville.<sup>38,42</sup> Conversely, the concentration of PeCA may be influenced by local sources in Toronto. PeCA is known to have anthropogenic sources as transformation product of pentachlorophenol which is used as a wood preservative in urban areas.<sup>16</sup> TBA at Evansville exhibits a shallow slope for CC relation (Fig. SI 3†), indicating a lower enthalpy of surface-air exchange compared to that at Point Petre. This suggests that surface-air exchange is not the primary mechanism driving TBA concentrations at Evansville.

In general, DAME is likely sourced from the terrestrial environment, while TeCV and PeCA are believed to originate from anthropogenic activities.<sup>13,14</sup> However, it becomes evident that the surface-air exchange process plays a crucial role in governing the concentrations of these HMBs in the GLB, regardless of initial emission sources.



At Alert, the monthly variations of DBA and TBA concentrations revealed a bimodal distribution, peaking in July/August and November (Fig. 2(b) and (d)), resembling the pattern observed in Southern Norway.<sup>43</sup> The first mode in July/August is typical for the chemical concentrations dominated by the surface–air exchange process which is similar to HMBs at the Point Petre site. For TBA, the concentration peak occurred in July (Fig. 2(d)), aligning with the highest annual temperatures as well as increased algal blooms during the summer months.<sup>44</sup> In contrast, the DBA concentration peak was delayed until August. This delay may be attributed to DBA's relatively faster photodegradation rate compared to TBA. Specifically, the estimated atmospheric half-life of DBA is 99 hours, significantly shorter than TBA's 205 hour half-life (estimated with Level III Fugacity Model, Estimation Programs Interface Suite™).<sup>45</sup> Both revolatilization emissions and photodegradation processes are temperature-dependent. When the emission rate surpasses the removal rate, peak concentrations coincide with peak temperatures, as observed for TBA. However, DBA's photodegradation rate may have been stronger than its revolatilization rate in July, suppressing the concentration peak. By August, the photodegradation rate likely declined relative to the revolatilization rate, resulting in the delayed peak concentration. The second peak in October showed a significant correlation between DBA and TBA concentrations ( $r = 0.841$ ,  $p < 0.05$ ; Table SI 4†), indicating that both compounds may be governed by similar environmental or atmospheric mechanisms during this period.

Conversely, DAME and TeCV showed low summer concentrations at Alert, with a sharp rise in September and peak in October (Fig. 2(f) and (h)). The half-life times in the air are DBA (99 h) < DAME (105 h) < TBA (205 h) < TeCV (450 h) (Estimation Programs Interface Suite™).<sup>45</sup> The low concentrations of TeCV with its long half-life time suggest no major sources of TeCV at the Alert site during the summer. The low DAME concentration, with a small peak in June and a shorter half-life time, indicates a potential minor emission source in the summer. The maximum monthly concentrations of DAME and TeCV in October align with the increasing peak observed for DBA and TBA. Significant relationships among four HMBs (Table SI 4†) suggest they might share the same source contributing to the maximum monthly concentrations in October, *i.e.*, LRT, due to the lack of local emission sources for four HMBs in October at the Alert site.

The distinct monthly variations of DBA, TBA, DAME, and TeCV at the Alert station and GLB sites suggest different controlling mechanisms. At the GLB sites, local surface–air exchange dominates HMB concentrations, except for TBA at Evansville, which is more influenced by other mechanisms. In contrast, at Alert, LRT is the primary mechanism for all four HMBs, with local surface–air exchange playing a secondary role for DBA and TBA in summer.

DBA, TBA, and DAME concentrations at Alert have been rising since 2009. Further investigation is recommended to explore the upward trend in DBA, TBA and DAME concentrations and the monthly variations of the four HMBs at the Alert site.

### 3.2. Volatile POPs

Legacy organochlorine substances such as HCHs, HCB, HCBd, and PeCB are listed for elimination under Annex A of the Stockholm Convention, with HCBd, HCB, and PeCB also regulated for unintentional production control under Annex C. These volatile POPs have previously shown breakthrough issues<sup>3,19,20,23,46</sup> using the PUF-only configuration, prompting the recommendation to switch to a PUF-XAD2 sandwich setup. This study presents monitoring results using this configuration in the following subsection.

#### 3.2.1. Concentration comparison of Alert and GLB sites.

The four POP concentrations (median range) order follows HCBd ( $111\text{--}384\text{ pg m}^{-3}$ ) > HCB ( $7.61\text{--}47.9\text{ pg m}^{-3}$ ) > PeCB ( $7.61\text{--}13.0\text{ pg m}^{-3}$ ) >  $\alpha$ -HCH ( $0.993\text{--}2.61\text{ pg m}^{-3}$ ) at all three sites with the Alert station showing significantly higher levels for HCBd, HCB and  $\alpha$ -HCH (Fig. 1, and Table SI 2†). The mean ( $\pm$ SD) of  $\gamma$ -HCH were  $0.738 \pm 0.797$  and  $0.935 \pm 1.21\text{ pg m}^{-3}$  at Point Petre and Evansville, respectively. The elevated volatile POP concentrations at the Alert site over both the long-term (2009–2020) and short term (2018–2020) were unexpected compared to those at the GLB sites, given their anthropogenic origin. This trend contrasts with that of HMBs, which show higher concentrations at Point Petre and Evansville.

Wu *et al.*<sup>47</sup> performed col-located measurements for OCPs at the Point Petre site and identified a significant breakthrough of HCB, with a breakthrough rate of 97%, using two PUFs during the summer of 2004 when ambient temperatures ranged from 17.7 to 21.2 °C. Similarly, Shunthirasingham *et al.*<sup>49</sup> reported significant HCB breakthrough at the Point Petre site, along with a notable decline in HCH concentrations when using one or two PUFs. The concentrations of  $\alpha$ -HCH decreased from  $48 \pm 16\text{ pg m}^{-3}$  in 1992 to  $3.3 \pm 1.1\text{ pg m}^{-3}$  in 2012, and  $\gamma$ -HCH declined from  $12 \pm 12\text{ pg m}^{-3}$  to  $0.75 \pm 0.38\text{ pg m}^{-3}$  over the same period at the Point Petre site. In this study, from October 2018 to December 2022 at Point Petre, the concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH were  $1.78 \pm 0.816\text{ pg m}^{-3}$  and  $0.738 \pm 0.797\text{ pg m}^{-3}$ , respectively, comparable to the 2012 values reported. However, these comparisons should be interpreted with caution due to differences in sampling media.

Between 2014 and 2017, 18 measurements employing the PUF-XAD2 sandwich at the Alert site were co-located with measurements obtained using the two PUFs configuration by Wong *et al.*,<sup>18</sup> to evaluate the collection efficiency for volatile POPs. The results for HCBd, HCB, PeCB, and  $\alpha$ -HCH are shown in Fig. SI 4.† Both configurations displayed consistent seasonal patterns for HCBd, with higher concentrations in winter. The average HCBd concentrations were  $5.72\text{ pg m}^{-3}$  and  $355\text{ pg m}^{-3}$  for the 2 PUFs and PUF-XAD2 sandwich methods, respectively, indicating low collection efficiency (1.90%) and significant breakthrough for the 2 PUFs configuration.

Unlike at the Point Petre site, HCB concentrations at the Alert site were similar between the two methods, averaging  $41.1\text{ pg m}^{-3}$  for 2 PUFs and  $41.5\text{ pg m}^{-3}$  for the PUF-XAD2 sandwich. This consistency is likely due to the lower ambient temperatures at Alert, which minimized breakthrough.<sup>23</sup> Similarly,  $\alpha$ -HCH levels were comparable across the two methods. In contrast,



PeCB concentrations showed a noticeable discrepancy, averaging  $9.85 \text{ pg m}^{-3}$  for 2 PUFs and  $18.0 \text{ pg m}^{-3}$  for PUF-XAD2-PUF. The 2017 data highlight summer breakthrough issues, especially for PeCB (Fig. SI 4(d)†), where the PUF-XAD2-PUF method yielded higher concentrations, while the 2 PUF configuration exhibited an opposite trend, reinforcing the evidence of temperature-related breakthrough.

The lower ambient temperatures and larger sampling volumes ( $>700 \text{ m}^3$ )<sup>20</sup> at Alert likely mitigated breakthrough issues for HCB and  $\alpha$ -HCH, resulting in comparable measurements between the two methods. However, the adoption of the PUF-XAD2 sandwich method (or other high capacity sorbents) is essential for minimizing the breakthrough of more volatile organochlorines (*e.g.*, HCB and PeCB), particularly in warmer environments, thereby ensuring more accurate and reliable results.

**3.2.2. Temporal trend.** The HCB concentration at the Alert station, as illustrated in Fig. 3(a), has undergone a substantial increase since 2009 ( $t_2 = 2.60$  years,  $p < 0.05$ , Table SI 5†), characterized by two distinct stages: a gradual rise from 2009 to 2016 with an average growth rate of  $\sim 14\%$ , followed by a rapid escalation after 2017. For the GLB sites, sporadic elevated HCB concentrations were observed in 2019 and 2020 at Evansville (max:  $2150 \text{ pg m}^{-3}$ ) and Point Petre (max:  $1810 \text{ pg m}^{-3}$ ) (Fig. SI 5(a)†). PeCB concentrations also showed an increasing trend from 2009 to 2020, with  $t_2 = 6.42$  years (Fig. 3(c)). In contrast,  $\alpha$ -HCH and HCB concentrations demonstrated a decreasing trend from 2009 to 2015 and an

increasing trend after 2016 (Fig. 3(e) and (g)), similar to the pattern observed for DAME (Fig. 2(e)).

The increasing trend of HCB concentrations has also been observed in Japan<sup>48</sup> and globally.<sup>49</sup> Takasuga *et al.*<sup>48</sup> and UNEP<sup>1</sup> noted a significant increase in HCB concentration in Japan, reaching peak levels of  $20\,000$ – $23\,000 \text{ pg m}^{-3}$  in Spring 2017 and the HCB concentrations were  $330$ – $2900 \text{ pg m}^{-3}$  from 2009 to 2016 at a background site in Hedo, Okinawa, Japan (Table SI 7†). Back trajectory analysis revealed that the elevated HCB concentrations were resulting from the long-range transboundary transport. Since 2015, the Ministry of the Environment in Japan has conducted monitoring of HCB concentrations at 34–37 sites nationwide, gathering between 102 to 111 samples during each sampling event in the warm season (September/October). Fig. SI 6† illustrates the box plot of HCB concentrations at both the Alert site and across Japan, aiming to characterize the observed trends. From 2015 to 2016, median and geometric mean concentrations remained below  $1500 \text{ pg m}^{-3}$  in Japan. However, a notable increase occurred in 2017, with concentrations peaking around median of  $4000 \text{ pg m}^{-3}$ . Subsequently, since 2018, HCB concentrations have shown a gradual decline, though median and geometric mean values persist above pre-2017 levels. A similar pattern was observed at the Alert site with a sharp increase in 2018. The Global Atmospheric Passive Sampling (GAPS) network, employing XAD-resin based passive samplers for the measurement of POPs, revealed a global increasing trend for HCB, with levels rising by more than 10% annually from 2009 to 2016.<sup>49</sup>

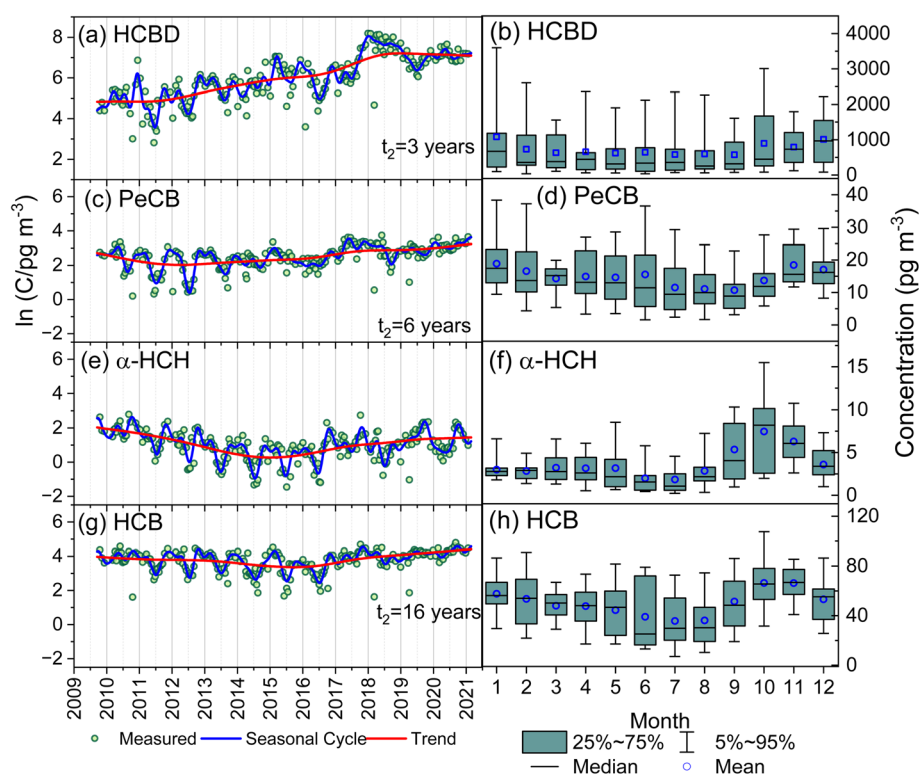


Fig. 3 Temporal trends and seasonal cycles (2009 to 2021) of concentrations for (a) HCB, (c) PeCB, (e)  $\alpha$ -HCH, and (g) HCB, along with monthly variations for (b) HCB, (d) PeCB, (f)  $\alpha$ -HCH, and (h) HCB at the Alert site.

Given the lack of natural and intentional production sources for HCBd, there is growing global concern about the unintentional production of HCBd.

Elevated concentrations of HCBd in ambient air and soil samples have been observed near various industrial sites and facilities involved in the production of trichloroethylene (TCE), and tetrachloroethylene (perchloroethylene, PCE) in China, and chlor-alkali plants in Spain.<sup>50–55</sup> Additionally, waste treatment facilities such as landfills, wastewater treatment plants, and waste incinerators have shown high levels of HCBd.<sup>50,54,56,57</sup> These concentrations have varied significantly, ranging from  $<20 \text{ pg m}^{-3}$  to  $5530 \text{ } \mu\text{g m}^{-3}$  from the recent literature (Table SI 7†). Tao *et al.*<sup>58</sup> investigated the sources and distribution characteristics of HCBd in the Yangtze River Delta, Beijing–Tianjin–Hebei, and Pearl River Delta using soil and water samples. They concluded that by-products of TCE and PCE manufacturing processes, along with wastewater treatment plants, were the primary sources of HCBd in these three regions.

A substantial emission of unintentionally produced HCBd in China has been reported in recent years.<sup>51–54,58,59</sup> Wang *et al.*<sup>60</sup> estimated that the unintentional production of HCBd in China increased from 60.8 MT per year in 1992 to 2871.5 MT per year in 2016 with an average growth rate of 17.4% closely aligning with the  $\sim 14\%$  increase in HCBd concentrations observed at the Alert site from 2009 to 2016. Their findings concluded that (1) the unintentional production of HCBd from chlorinated hydrocarbon production was the major emission source; (2) the emission was predicted to increase due to rapid development of the chlorinated hydrocarbon production in China.

To improve understanding of the global distribution and atmospheric transport of HCBd, the development of a comprehensive, spatially resolved global emission inventory is essential. While back-trajectory analyses<sup>48</sup> and available emission estimates<sup>60</sup> suggest that East Asia—particularly regions with established organochlorine production such as China—may be a significant source, additional observational data and modeling studies are needed to constrain and verify global source contributions. Additionally, the rise in PeCB and HCB levels may be linked to unintentional production in the organochlorine industry, where they occur as impurities or by-products in solvent production.<sup>51,61</sup> The  $\alpha$ -HCH concentrations reported by the GAPS network from 2005 to 2016 were consistent with the decreasing trend observed in this study and the trend noted in Arctic air from 1992 to 2016.<sup>18</sup> However, this study observed an unexpected increase in  $\alpha$ -HCH concentrations at the Alert site after 2016. Given that  $\alpha$ -HCH has not been in use or production for many years, the increase may result from secondary re-emissions driven by climate change and LRT to the Arctic. Conversely, HCB concentrations exhibited a different pattern. The XAD-derived data from the GAPS program showed a global decrease in HCB concentrations from 2005 to 2009, followed by an increase from 2009 to 2016. In this study, HCB concentrations decreased from 2009 to 2015, with  $t_{1/2} = 5.81$  years, as also observed by Wong *et al.*<sup>18</sup> and increased since 2016. Overall, three unintentional POPs including HCBd, HCB and PeCB have shown increasing trends at the Alert site from 2009 to 2020.

In 2023, China added HCBd to its List of New Pollutants under Priority Control ([https://www.gov.cn/zhengce/2022-12/30/content\\_5734728.htm](https://www.gov.cn/zhengce/2022-12/30/content_5734728.htm)) and implemented stringent regulations, including: (1) prohibiting its production, use, and trade; (2) enforcing emission standards for the oil, gas, and chemical industries; (3) mandating hazardous waste management for HCBd-containing byproducts; and (4) mandating soil pollution risk assessments for relevant enterprises. These measures aim to reduce unintentional production and limit HCBd emissions into the environment. If effectively enforced, the regulations could lead to lower HCBd concentrations in the Arctic atmosphere.

**3.2.3 Seasonal trend.** The seasonal patterns of  $\alpha$ -HCH and HCB concentrations (Fig. 3(f) and (h)) at the Alert station, characterized by lower levels during summer months and peak monthly concentrations consistently occurring in October, align with the monthly variation of DAME and TeCV. In contrast, at the GLB stations, the concentrations of  $\alpha$ -HCH,  $\gamma$ -HCH, HCB, and PeCB are elevated during summer months with significant CC relations (Table SI 8†), suggesting potential surface–air exchange. The HCB seasonal variations from 2009 to 2016 with summer minimum at Alert were also observed in Norway (*i.e.*, Birkenes and Andoya) in 2019 by Bohlin-Nizzetto *et al.*<sup>62</sup> The authors proposed two potential explanations: higher emissions from combustion during colder months or breakthrough in the sampler during warmer months, leading to underestimations of summer concentrations.<sup>62</sup> In this study, the use of PUF-XAD2-PUF sampling medium effectively minimized potential breakthroughs, making breakthrough an unlikely reason for low concentrations of volatile HMBs and POPs during summer months at the Alert site.

The seasonal trends of HCBd, PeCB, HCB and  $\alpha$ -HCH at the Alert site were similar from 2009 to 2016, featuring elevated levels in winter months. However, the seasonal trend of HCBd, PeCB and HCB became unclear from 2017 to 2018 which may reflect increased primary emissions at source with minimal degradation during LRT to site. The good correlation between HCBd and PeCB ( $0.650, p < 0.05$ ) and HCB ( $0.452, p < 0.05$ ), as well as the correlation between HCB and  $\alpha$ -HCH ( $0.728, p < 0.05$ ) and PeCB ( $0.752, p < 0.05$ ) (Table SI 4†), further suggests the notion of shared sources followed by LRT reaching the Arctic. Interestingly, the strong correlations between HCBd and three POPs (including HCB, PeCB, and HCH) were also observed in Japan.<sup>48</sup>

The dramatic increase in HCBd concentrations after 2017 is a trend not mirrored by any other substances proportionally. HCBd, HCB and PeCB are related to unintentional emissions, *e.g.* incineration, combustion and industrial activities as discussed above. During LRT, physical and chemical processes, including deposition, and photodegradation, exhibit variations for each chemical. Consequently, the rates of increase for different chemicals may differ upon reaching the Alert site.

## 4 Conclusion

This study highlights the broader significance of using a high-capacity sorbent (*e.g.* XAD) in the sampling train for





advancing global monitoring of volatile organic compounds. Its demonstrated effectiveness supports the harmonization of sampling protocols across regions, facilitating improved data comparability and more accurate assessments of environmental trends. As international monitoring efforts progress under frameworks such as the Stockholm Convention, adoption of robust and consistent methods—like the one presented here—will be essential for informed decision-making and effective long-term chemical management.

This study found that HMB concentrations were higher at the GLB sites than at the Alert site, while POP concentrations showed the opposite trend—an unexpected result given their anthropogenic origins. Strong seasonal variability was observed for five HMBs and four POPs at the GLB sites, except for TBA in Evansville. This suggests that surface–air exchange plays a dominant role in regulating their concentrations, regardless of their source origins.

Long-term monitoring data from the Alert site (2009–2020), obtained using the PUF-XAD2-PUF setup, indicate increasing concentrations of DBA, TBA, DAME, HCB, and PeCB. The seasonal variability observed in HMBs (DBA, TBA, and DAME) suggests the influence of multiple factors beyond direct emissions. In contrast, the post-2017 rise in HCB, and PeCB concentrations appears to be more closely associated with direct anthropogenic sources *via* LRT. Notably, the pronounced rise in HCB levels underscores the necessity of a comprehensive global assessment of its emission sources. The implementation of targeted mitigation strategies will be essential for reducing HCB concentrations in Arctic air, thereby minimizing potential environmental and human health impacts in northern regions.

## Data availability

Raw data were generated at Environment and Climate Change Canada. Derived data supporting the findings of this study are available from the corresponding author H. H. on request.

## Author contributions

Y.-M. H. and F. W. contributed equally as the first authors of this article. Y.-M. H.: data curation, formal analysis, investigation, visualization, writing – original draft, writing – review & editing. F. W.: conceptualization, data curation, formal analysis, investigation, writing – original draft, writing – review & editing. H. H.: conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, writing – review & editing. C. Shunthirasingham: conceptualization, data curation, formal analysis, investigation, methodology, supervision, writing-review & editing. W. L.: formal analysis, investigation, writing-review & editing. N. A.: supervision, formal analysis, investigation, methodology, writing-review & editing. H. D.-C.: data curation, formal analysis, investigation, writing – review & editing. C. Shin: formal analysis, investigation. R. P.: formal analysis, investigation. J. C.: formal analysis, investigation. A. P.: formal analysis, investigation. R. N.: formal analysis,

investigation. E. B.: supervision, formal analysis, methodology. P. F.: supervision, investigation. H. L.: supervision, formal analysis, investigation, methodology.

## Conflicts of interest

There are no conflicts of interest to declare.

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