Sub-Indicator: Toxic Chemicals in the Atmosphere

Overall Assessment

Status: Fair

Trends:

10-Year Trend (2013 – 2022): Improving

Long-term Trend (1990s – 2022): Improving

Rationale: The large surface area of the Great Lakes provides an opportunity for substantial atmospheric inputs of toxic chemicals. While atmospheric concentrations of some toxic chemicals are very low at rural sites, they are much higher in urban areas. Lake Michigan, Lake Erie, and Lake Ontario have greater atmospheric contaminant inputs from urban areas. Of the rural sampling locations, the Lake Erie site (Sturgeon Point) tends to show higher contaminant concentrations than at other remote sites, most likely since it is located closer to an urban area (ex. Buffalo, NY), and may also receive some chemical input from the East Coast of the U.S. where there are a greater number of emission sources.

The overall assessment is based on Chemicals of Mutual Concern (CMCs). The overall status and trend for CMCs in the atmosphere is Fair and Improving, which is consistent with the overall assessment for the 2022, 2019, 2017 and 2011 Toxic Chemicals in the Atmosphere reports (previously known as Atmospheric Deposition of Toxic Chemicals prior to 2019). Note: not all chemicals have been monitored over the full period noted. Six CMCs were used in the evaluation, with two not having enough data to establish a status or trend (see the listing of CMCs in the Ecological Condition section).

Lake-by-Lake Assessment

Each lake was not specifically categorized for status and trend because of limited sample stations for each lake basin to allow for a lake-by-lake assessment. Site specific trends for many chemicals (not all are CMCs) are available (Salamova et al. 2015; Shunthirasingham et al., 2016). There has been no new loadings analysis since the last report.

Status Assessment Definitions

Good: The metrics show that the CMC concentrations and/or loadings are meeting the ecosystem objectives, or they are otherwise in an acceptable condition.

Fair: The metrics show that the CMC concentrations and/or loadings are not meeting the ecosystem objectives, but they are exhibiting minimally acceptable conditions.

Poor: The metrics show that the CMC concentrations and/or loadings are not displaying minimally acceptable conditions and are severely impacted.

Undetermined: Data are not available or are insufficient to assess status of CMC concentrations at this time, or the different groups of CMC chemicals are assessed in Good and Poor rankings and an expert opinion of the overall

status cannot be agreed on.

Trend Assessment Definitions

Improving: Decrease in concentrations or frequency of detection of CMCs.

Unchanging: No change in the concentration or frequency of detection of CMCs.

No Trend: Data are available for a 10-year or longer period, but the trend is not statistically significant due to high variability in the data.

Deteriorating: Increased concentration or frequency of detection of CMCs.

Undetermined: Data are not available or are insufficient to assess the trends or frequency of detection of CMC concentrations at this time, or the different groups of CMCs are not trending in the same direction and an expert opinion of the overall direction of the trend cannot be agreed on.

The magnitudes of the trends are expressed as a "halving time", or time to which the concentration of the chemical is decreased by a factor of two. The halving time ($t_{1/2}$) was estimated by dividing *ln* 2 with the negative value of the linear regression slope of the trend line between the natural log of air concentrations, *C* (pg m^{-3}), and time, *t* (year, y). Positive halving time ($t_{1/2} > 0$) indicate a decreasing trend. Negative halving time (i.e. $t_{1/2} < 0$) (doubling time) indicates an increasing trend. Halving times are only used to compare the relative rates of decline between stations. Readers are advised to use the absolute values of these halving times with caution.

Time trends were developed using the Digital Filtration (DF) technique or linear regression. For the DF technique, an approximate long-term time trend and an average seasonal cycle were iteratively fitted to the measurement data using a smoothing Reinsch-type cubic spline and Fourier components, respectively. Outlier data points more than 3 standard errors away from the fitted curve were rejected after each iterative fit. When the fitted curves become unchangeable, digital filters are applied to extract the long- and short-term variations to refine the trend and seasonal cycle which are statistically significant with 95 % confidence. Details are described in Hung et al. (2005). For the linear regression, the log transformed concentrations (either as individual data points or annual medians) were regressed against time. Trends were considered significant at a 95% confidence level.

Endpoints and/or Targets

The target or endpoint for this sub-indicator will have been met when the Waters of the Great Lakes are free from pollutants in quantities or concentrations that could be harmful to human health, wildlife or aquatic organisms, and/or through direct exposure or indirect exposure through the food chain. The CMC status and trends will be determined on a case-by-case basis taking a weight-of-evidence approach in making an expert assessment. Progress will be determined based on whether trends of the CMCs are positive (i.e. increasing) or negative (decreasing), the rate of change in the concentrations, and by the number of chemicals which are doing so.

Sub-Indicator Purpose

- The purpose of this sub-indicator is to assess CMCs in the atmosphere and in precipitation in the Great Lakes region.

- The sub-indicator will infer potential impacts of CMCs from atmospheric deposition on the Great Lakes aquatic ecosystem and progress toward virtual elimination of anthropogenic CMCs.
- The sub-indicator will also inform the risk assessment of potentially harmful chemicals and the development of risk management strategies for toxic substances other than CMCs, including persistent organic pollutants (POPs) and other harmful substances.

Ecosystem Objective

This sub-indicator is relevant to the General Objective #4 of the 2012 Great Lakes Water Quality Agreement (GLWQA) that the waters of the Great Lakes "be free from pollutants in quantities or concentrations that could be harmful to human health, wildlife, or aquatic organisms, through direct exposure or indirect exposure through the food chain." This sub-indicator is also relevant to Annex 3-Chemicals of Mutual Concern of the GLWQA, the purpose of which is to "reduce the anthropogenic release of chemicals of mutual concern, recognizing: (i) that chemicals of mutual concern released into the air, water, land, sediment, and biota should not result in impairment to the quality of the Waters of the Great Lakes; and (ii) the need to manage chemicals of mutual concern including, as appropriate, by implementing measures to achieve virtual elimination and zero discharge of these chemicals."

The Annex 3 further calls for the Parties to (i) monitor and evaluate the progress and effectiveness of pollution prevention and control measures; (ii) exchange, on a regular basis, information on monitoring, surveillance...; (iii) identify and assess the occurrence, sources, transport, and impact of chemicals of mutual concern, including spatial and temporal trends in the atmosphere...; (iv) identify and assess loadings ... from the atmosphere; and (v) coordinating research, monitoring, and surveillance activities as a means to provide early warning for chemicals that could become chemicals of mutual concern.

Methods

This sub-indicator measures the concentrations of CMCs in the atmosphere and in precipitation of the Great Lakes region. This sub-indicator tracks whether concentrations are decreasing, staying the same, or increasing over time where data are available. The sub-indicator also assesses whether the spatial trends in concentrations are changing or staying the same. The monitoring data was used by the Parties to the GLWQA to inform the selection of CMCs for Annex 3 of the GLWQA in 2016. Monitoring data are used to inform the continued selection of CMCs as well as monitor to assess the progress and effectiveness of pollution prevention and control measures for those compounds.

The sub-indicator primarily reports using data from the Canada-US binational efforts in monitoring toxic substances in air and in precipitation in the Great Lakes region, including the Integrated Atmospheric Deposition Network (IADN), Great Lakes Basin (GLB) Monitoring and Surveillance Network under Canada's Chemicals Management Plan (CMP) and the National Atmospheric Deposition Program's Mercury Deposition Network (NADP MDN). These monitoring efforts follow well-established international monitoring protocols for sampling frequency, site selection, and sampling and analytical methods, with stations in the Great Lakes region. The sub-indicator also considers the most recent atmospheric loadings as estimated by IADN and GLB (see data limitations section).

CMCs that are relevant to this sub-indicator include PCBs, mercury, LC-PFCAs (C9-C20), PFOA, PFOS, PBDEs, HBCDD and SCCPs. Air concentrations, atmospheric deposition and loading information are reported in this sub-indicator report. For CMCs that do not have sufficient information to base a determination, air and atmospheric deposition information are gathered and presented in this sub-indicator but will not contribute to the Status and

Trend Assessments. Air and atmospheric deposition data for Persistent Organic Pollutants (POPs) that are included under the United Nations Environment Programme (UNEP) Stockholm Convention on POPs and other chemicals that may be of concern in the future are also presented in this sub-indicator as additional information but only data on the CMCs are used for the status and trend assessments.

Precipitation samples are integrated over each month. Annual average concentrations are calculated and reported using these measurements. Spatial and temporal trend analyses are performed on the IADN and GLB data using a variety of statistical tools (Venier et al., 2012; Venier and Hites, 2010a; Venier and Hites, 2010b).

Weekly composite precipitation samples are collected and analyzed for mercury across the Great Lakes basin at MDN stations, using the same strict sampling and analytical protocols established under the network. Annual mercury concentrations, precipitation depths, and wet deposition are calculated and reported using this data. Spatial and temporal trend analyses are performed on the MDN data using a variety of statistical tools (Olson et al., 2020; Weiss et al., 2016; Risch et al., 2012; Prestbo and Gay, 2009).

Discussion

Air concentrations respond rapidly to changes in emissions, ("environmental hysteresis") (Hites et al, 2021). This makes atmospheric measurements a very useful tool for tracking progress as a result of chemical control efforts. Since air has a short response time to changes in atmospheric emissions and is a relatively well-mixed environmental medium, this sub-indicator is also suitable in providing early warning for chemicals that could become CMCs. The occurrence of additional potentially harmful substances in Great Lakes air and precipitation are presented in this report but are not included in the Status and Trend Assessments.

The United States' Integrated Atmospheric Deposition Network (IADN) and Canada's Monitoring and Surveillance in the Great Lakes Basin (GLB) are the primary source of data for this sub-indicator report. IADN and GLB form a collaborative binational monitoring network that has been in operation since 1990, with five master monitoring stations, one near each of the Great Lakes, and several satellite stations (Figure 1). The Burnt Island Master station was closed in March 2013 and is replaced by the nearby Evansville Station for both air (started January 2014) and precipitation (started July 2013) measurements. A flow-through sampler was used to measure air concentrations at this site from January 2014 to mid-2019. Subsequently, the flow-through sampler was replaced with a high-volume (HiVol) air sampler in May 2019. In this report, air concentrations measured using the HiVol sampler are presented. Concentrations of CMCs and other contaminants that are persistent, bioaccumulative and toxic are measured in the atmospheric gas and particle phases (reported in pg/m^3) and precipitation (reported in ng/L). Spatial and temporal trends of these concentrations and atmospheric loadings to the Great Lakes can be examined using these data. CMC data from other networks and surveillance studies are used here to supplement the IADN and GLB data, particularly for mercury and SCCPs. In this assessment, only CMC data are used to assess this sub-indicator while in earlier assessments (prior to 2019), other contaminants (non-CMCs) were also considered in assessing the status and trend. Despite the difference in chemicals used for the 2025, 2022 and 2019 assessments as compared to that for 2017, the overall status and trends remain the same. However, some of the CMCs, e.g. HBCDD/HBCD and SCCPs, do not have sufficient data to assess their status and trends under this sub-indicator. Although the 2025 assessment focuses on CMCs, trends of non-CMCs are also included in this report for reference.

Status of Chemicals of Mutual Concern (CMCs)

The Parties to the GLWQA designated the first set of Chemicals of Mutual Concern in May 2016. For State of the Great Lakes reporting in 2019 and moving forward, the toxic chemical sub-indicators will support reporting on Chemicals of Mutual Concern (CMCs) in a more consistent and transparent way, based on available data. Information

on additional chemicals of interest for the Great Lakes (non-CMCs) is valuable for inclusion in the report and will be included in a separate section below, as appropriate.

The following chemicals were identified as the first set of CMCs:

- Polychlorinated Biphenyls (PCBs)
- Polybrominated Diphenyl Ethers (PBDEs)
- Perfluorooctane sulfonate (PFOS)
- Perfluorooctanoic acid (PFOA)
- Long-Chain Perfluorinated carboxylic acids (LC-PFCAs)
- Mercury (Hg)
- Hexabromocyclododecane (HBCDD/HBCD)
- Short-Chain Chlorinated Paraffins (SCCPs)

Polychlorinated Biphenyls (PCBs)

Canadian data have been updated up to 2022. Burnt Island (100 km north of Toronto on Georgian Bay off of Lake Huron, Figure 1) and Egbert (~70 km north of Toronto, between Lake Huron and Lake Ontario) ceased operation since 2013 and 2006 respectively, hence there is no new data for these two sites (Shunthirasingham et al., 2016; Hung et al. 2021). The Burnt Island station has been replaced by the nearby Evansville Station, and air sampling of PCBs commenced in May 2019. No trends for PCBs at this site have been established due to insufficient data (only 4 years are available at this location). However, the annual average of the total gaseous concentrations of the 26 congeners (Σ_{26}PCBs) ranged from 2.9-13 pg/m^3 and an annual median of 2.9-6.7 pg/m^3. US data has been updated to 2022. The half-lives of individual PCBs in the Canadian air are given in Table 1. The atmospheric concentrations of ΣPCBs (sum of 26 congeners on the Canadian side and 62 congeners on the US side) continue to decline on both sides of the lakes with halving times of about 11 to 14 years on the US side and 17-59 on the Canadian side (Figures 2 and 3). There is no change in the halving times of PCBs in Point Petre (180 km east of Toronto on the shore of Lake Ontario, Figure 1) when compared to data in the last report. The rather long half-lives (especially at Burnt Island, Point Petre and Egbert) imply the tendency towards equilibrium with surrounding environmental surfaces (land, vegetation and aquatic surfaces). The 10-year trend at the Point Petre site from 2013 to 2022 indicates decreasing concentrations of PCB congeners such as PCB18, PCB28/31, PCB52 and PCB101, with halving times ranging from 6 to 24 years, consistent with the overall trend. However, the concentrations of certain PCB congeners, including PCB153, and PCB180, show an increasing trend, with doubling time of 4 years. This is likely attributed to changes in air sampling and quantification methods implemented in 2018. The 10-year trend at the US sites (i.e. 2013-2022) shows that PCB concentrations are generally decreasing, with halving times in the range of 8 to 10 years. The only exception is Chicago, for which the halving time is not significant. The decline is faster for US sites compared to the Canadian sites.

Although PCB production was banned in the early 1970s in North America, the slow decline in air concentrations can be attributed to volatilization from the lakes themselves (Khairy et al. 2015), building sealants (Robson et al., 2010; Shanahan et al. 2015), drying sewage sludge (Shanahan et al. 2015), and paints (Hu and Hornbuckle, 2010). In addition, there are continued emissions from older electrical and hydraulic equipment still in use and in the waste stream (Diamond et al., 2010). Urban areas are believed to be the main sources of PCBs to rural regions (Buehler et al. 2001; Hafner and Hites 2003; Cleverly et al. 2007; Melymuk et al., 2012; Shunthirasingham et al. 2016).

There is no new data about the loading of PCBs since the last report. Based on the last report, volatilization of PCBs

from the lakes is shown by atmospheric loadings analysis (Shunthirasingham et al. 2016; Guo et al., 2018). The output flows of PCB-52, 101, and 118 due to volatilization from the lakes to the air are increasing exponentially with time. In these three cases, the flows are doubling every 4–9 years. On the other hand, the input flows of the PCBs into lake water are generally small compared to the output flows. In addition, PCBs are likely being released from the sediment into the water column from which they could volatilize into the atmosphere. Once in the atmosphere, PCBs could be degraded by reactions with hydroxyl radicals (Anderson and Hites, 1996). Clearly, the lakes are slowly releasing PCBs to the atmosphere, but it is not yet clear how long until PCB releases will cease from surface water.

3,3'-Dichlorobiphenyl (PCB-11) is thought to be a byproduct of the production of yellow pigments, and thus, it has sources to the environment that differ both in type and magnitude compared to the PCBs that made up the, now banned, Aroclor commercial products. The atmospheric concentrations of the Aroclor-PCBs are decreasing with halving times of about 10 years, but the atmospheric concentrations of PCB-11 have not changed significantly over this time period. The halving times are significant only at Eagle Harbor (4.2 ± 2.7) and at Sturgeon Point (8.7 ± 5.2). These results suggest that PCB-11 is being released into the environment, while at the same time sources of Aroclor-PCBs are decreasing.

Polybrominated Diphenyl Ethers (PBDEs)

The concentrations of halogenated flame retardants have been measured in IADN/GLB samples since January 2005. Capozzi et al. (2023) found that the atmospheric concentrations of polybrominated diphenyl ethers (PBDEs) were significantly higher in Chicago, Cleveland, and Sturgeon Point than at Sleeping Bear Dunes and Eagle Harbor. The temporal trends of individual PBDE levels are generally consistent with previous reports with significant decreases in atmospheric concentrations at urban, rural, and remote sites for BDE-47, BDE-99, and BDE-100 except for Eagle Harbor, where levels are unchanging. Significant declines are generally observed at the urban sites for most congeners, with a few exceptions. BDE-209 is slowly increasing in Chicago, which is consistent with our previous report (Liu, 2016); however, limiting the regression to years after the deca- BDE ban (e.g., 2014–2019) shows unchanging concentrations. In Chicago, the concentrations of BDE-47 and 99 decreased by a factor of two every 5.7 ± 2.2 and 8.1 ± 3.3 years, respectively, but the concentrations of BDE-209 doubled every 16 ± 10 years. In Cleveland, the concentrations of BDE-47 and 99 decreased by a factor of two every 4.9 ± 1.4 and 6.3 ± 2.2 years, respectively, and the concentrations of BDE-209 decreased by a factor of two every 11 ± 5 years. Use and emissions from products are gradually diminishing as products are removed from use, resulting in a slower declining trend than expected. Over the ten year trend period (2013-2022), the halving time is in the range of 6 to 10 years for BDE-47 but it was significant only for Cleveland and Sleeping Bear Dunes. BDE-99, -100, 163, and -183 are generally not changing significantly at most sites, with the exception of Sleeping Bear Dunes. The atmospheric levels of BDE-209 are still increasing with time, also for the 10 years trend, with doubling times of about 6 years.

PBDE concentrations have been steadily declining with time around the Great Lakes. This decline may be due to a general decrease in the use of these commercial mixtures and the progressive end of life of products containing tPBDEs, but this decline can also be due to degradation processes occurring in the environment. One natural degradation reactions is photolysis, either direct or indirect, that occurs in the atmosphere (Pan et al. 2016). To distinguish whether declining PBDE air concentrations were related to declining industrial uses or natural degradation reactions, a factor analysis was applied to the comprehensive IADN PBDE data set described above using positive matrix factorization (PMF). The PMF2 model resolved three factors whose fingerprints are presented in Figure 4.

At Point Petre, data was updated to 2022 (i. e. 2005-2022). There is no new data for Burnt Island and Egbert since the last report; hence the data reported here for these two sites are from 2005-2013. The Burnt Island station has

been replaced by the nearby Evansville Station, and air sampling of PBDEs commenced in May 2019. No trends for PBDEs at this site have been established due to insufficient data. However, the annual average of the total concentrations of the 15 PBDE congeners ((Σ_{15}PBDEs) ranged from 1.6-11 pg/m3 and an annual median of 1.4-10 pg/m3, with the highest average concentration observed for BDE47. Half-lives of PBDEs in the Canadian sites are given in Table 2. At Point Petre, BDE-47, BDE-99, and BDE-209 were the dominant PBDE congeners. At Point Petre, the annual average of the total concentrations of the 15 congeners (Σ_{15}PBDEs) ranged from 2.7-24 pg/m^3 and an annual median of 0.5-7.2 pg/m^3. At Burnt Island, the annual average of Σ_{15}PBDEs was 14-60 pg/m^3 and an annual median of 6.3-23 pg/m^3. At Egbert, the annual average of Σ_{15}PBDEs was 11-63 pg/m^3 and an annual median of 9.0–21 pg /m^3. Higher atmospheric concentrations of PBDEs were found at Egbert with a larger population (244, 446 within a 25 km radius of the site), while lower concentrations of PBDEs were detected at Point Petre, which is a remote site on Lake Ontario, with population of 15 966 within a 25 km radius) (Free map 2015). The time trends of BDE-28, -47, -99 and -209 in air at Point Petre were analyzed by the Digital Filtration method (Hung et al., 2016) and results are shown in Figure 5. The atmospheric PBDEs from 2005-2022 are decreasing, in which with half-lives of BDE-47, 99, 209 congeners are, respectively, 7, 7 and 7 years. BDE-28 is not changing with a very long half-life of 47 years and the trend is not significant. Examining the 10-year trend for Point Petre (2013-2022), the PBDEs display a similar pattern (decreasing trend) as observed in the overall trends. However, the 10-year trend is only statistically significant for BDE-209, with a calculated half-life of 1 year.

Perfluorooctane Sulfonate (PFOS)

Time trend of PFOS in GLB precipitation at Point Petre (Lake Ontario), Burnt Island/Evansville (Lake Huron) and Sibley (Lake Superior) between 2006 and 2018 was reported by Gewurtz et al. (2019). At the three sites, data was updated to 2022 (i.e. from 2006-2022). The median concentration of monthly-integrated precipitation for Point Petre was 1.3 ng/L, and Burnt Island/Evansville was 0.66 ng/L. PFOS in precipitation from Sibley was below detection limit, expect in a few samples (PFOS was only detected in ten samples). Time trend analysis was performed by the DF method showed that PFOA is declining at the 2 sites. The halving time derived by the DF method at Point Petre is 11 years, and Burnt Island is 7.7 years (Figure 6, right panel). As PFOS was only detected in a limited number of samples from Sibley, no trend analysis was conducted for this site. The overall decreasing trends were likely in response to North American phase-outs and regulatory actions for PFOS long-chained perfluoroalkyl carboxylates (PFCAs) and their precursors, ongoing since the early 2000s (Interstate Technology and Regulatory Council PFAS; Government of Canada, 2012). Concentrations of PFOS in Great Lakes precipitation are greater in the urbanized/industrialized Lake Ontario compared to the more remote locations of Lakes Huron and Superior, indicating the potential influence of local anthropogenic sources on atmospheric concentrations of PFOS.

In 2009, PFOS concentrations (geometric mean) measured using a high-volume air sampler were more than three times higher in Toronto (1.5 pg/m^3) (Ahrens et al., 2011) compared with Lake Superior air (0.43 pg/m^3) (Gewurtz et al., 2013). Air sampling of per-and polyfluoroalkyl substances (PFAS) in GLB has commenced in October 2018 at Point Petre (Lake Ontario) and in May 2019 at Evansville (Lake Huron). The detection frequency for PFOA was 79% at the Point Petre site and 42% at the Evansville site. Higher average concentrations were observed at the Point Petre site compared to the levels recorded at Evansville. Specifically, the average concentrations of PFOS at the Point Petre and Evansville sites were 10 pg/m³ and 0.38 pg/m³, respectively. This variation may be attributed to several factors, including the proximity to potential pollution sources, wind directions, and emission patterns. Point Petre is situated closer to urban areas that house industrial facilities, wastewater treatment plants, or other potential sources releasing PFAS into the environment. The presence of these local sources can significantly contribute to elevated PFAS concentrations in the atmosphere. The higher population density and increased urbanization around Point Petre may result in a greater use of PFAS in consumer products, leading to increased PFAS emissions into the air through usage, disposal, or runoff. The contamination of PFOS at the Point Petre site may potentially be linked to

specific areas in Pennsylvania, New Jersey, and Virginia in the United States, as well as in Ontario, Canada, serving as a source region.

PFAS precipitation samplers were installed at the US IADN sites in summer/fall 2020. No time trends can be calculated yet. The median ∑41PFAS concentration in precipitation for 2021-2022 across five sites was 3.1 ng/L, with a range of 2.4 – 4.5 ng/L, which was comparable to previous studies reported in the Great Lake region (Gewurtz, 2019). PFAS concentrations in precipitation were not significantly different across sites. The relative homogeneity of concentrations across sites indicates that PFAS, and in particular ionic PFAS, are ubiquitous. Median PFOS concentrations were in the range 0.19-0.33 ng/L and they were not significantly different among sites. Passive air samplers were also deployed at the US IADN sites. PFOS median concentrations in 2021 ranged from 2.5 to 6.1 pg/m^3 and they were not significantly different among sites. These values represent gas and particulate concentrations as passive samplers can't distinguish between the two phases.

Perfluorooctanoic Acid (PFOA)

PFOA is measured in precipitation under GLB at Point Petre (Lake Ontario), Burnt Island/Evansville (Lake Huron) and Sibley (Lake Superior) from 2006-2022. The median concentrations of monthly integrated precipitation samples at Point Petre = 0.54 ng/L, Burnt Island = 0.36 ng/L, Sibley = 0.34 ng/L. Time trend analysis by the DF method showed that PFOA is declining at the 3 sites. The halving times are respectively 11, 14 and 10 years for Point Petre, Burnt Island/Evansville and Sibley (Figure 6, left panel).

Air sampling for PFAS in the Great Lakes Basin began in October 2018 at Point Petre (Lake Ontario) and in May 2019 at Evansville (Lake Huron). PFOA was identified in 66% and 87% of samples gathered at the Point Petre and Evansville sites, respectively, with mean concentrations of 4.9 pg/m^3 at Point Petre and 2.0 pg/m^3 at Evansville. Higher concentrations of PFOA are typically observed during the summer months, attributed to elevated temperature. Elevated temperatures during summer can accelerate the degradation and transformation of PFAS precursors into more stable PFASs, for example from fluorotelomer alcohols (FTOHs) to PFOA under photochemical transformation (Ellis et al., 2003). The likely source regions of PFOA were identified as primarily originating from states such as Pennsylvania, New Jersey, and New York within the United States, as well as Ontario in Canada, using Potential Source Contribution Function (PSCF) modeling.

PFAS precipitation samplers have been established on the US side in summer/fall 2020. No time trends can be calculated yet. Median PFOA concentrations were in the range 0.25-0.33 ng/L and they were not significantly different among sites. Passive air samplers were also deployed at the US IADN sites. PFOA median concentrations in 2021 ranged from 1.8 to 3.1 and they were not significantly different among sites (Xia, 2024).

Long-chain Perfluorinated Carboxylic Acids (LC-PFCAs)

Under GLB, LC-PFCAs (C9-12) concentrations in precipitation are available at Point Petre, Burnt Island/Evansville and Sibley. At the three sites, data was updated to 2022 (i. e. 2006-2022). At the 3 sites, the medians of Σ_4LC-PFCA (C9-12) ranged from 0.67 to 0.75 ng/L. The concentrations of the sum of four long-chain PFCAs [Perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA)] exhibited a decline trend, with a half-time of 10-15 years determined by the DF technique. The concentrations of sum of the four long chain PFCAs did not monotonically decrease between 2006 and 2022. PFUnA and PFDoA have lower water solubility compared to PFNA, PFDA, and PFOA (Bhhatarai et al., 2011). The percent detection for these chemicals, including PFDA, in Great Lakes precipitation was relatively low, which may be the reason behind the observed trends (Gewurtz et al., 2019).

Air sampling for PFAS in the Great Lakes Basin began in October 2018 at Point Petre (Lake Ontario) and in May 2019 at Evansville (Lake Huron). LC-PFCAs, such as PFUnA, PFDoA, PFDA, and PFNA, were identified at both sites,

with detection frequencies ranging between 3% and 68%. Notably, the Point Petre site exhibited a higher detection frequency for PFNA and PFDA. The levels of these LC-PFCAs were found to be lower than those of PFOA and PFOS. At the Point Petre site, the mean concentrations of PFNA, PFDA, PFUnA, and PFDoA were 1.0, 0.79, 0.24, and 0.69 pg/m³, respectively. In comparison, at the Evansville site, the mean concentrations were 0.26, 2.9, 0.11, and 0.13 pg/m³ for PFNA, PFDA, PFUnA, and PFDoA, respectively.

PFAS precipitation samplers have been established on the US side in summer/fall 2020. No time trends can be calculated yet. Long chain PFCA such as PFNA, PFDA, and PFUdA were consistently detected at all sites at levels ranging from 0.1 for PFUdA to 0.2 for PFNA. The only spatial differences were observed for PFNA which was significantly higher at Cleveland than Sturgeon Point, with the other three sites being in between. Higher chain length PFAS compounds were seldom detected at the sites. Median concentrations of PFHxDA in precipitation ranged from 0.13 to 0.42 ng/L in precipitation. Detection frequencies of LC-PFCAs were even lower in air and they were proportional to the chain length. PFNA was detected in most of the samples with median concentrations ranging between 0.6 to 1.8 pg/m^3 (Xia, 2024).

Mercury

Atmospheric mercury has been measured in the Great Lakes Basin air shed in Ontario at three stations and one in Quebec, Canada. These stations include Egbert, Point Petre and Burnt Island. Atmospheric mercury measurements include different analytes such as total gaseous mercury (TGM) which includes elemental and inorganic reactive species, as well as gaseous elemental mercury (GEM) which only measures the elemental mercury species. Egbert has been collecting TGM since 1996 and continues today. Point Petre and Burnt Island measured TGM from 1996-2007 and 1998-2007, respectively. St. Anicet (located along the St Lawrence River, ~200 km east of eastern Lake Ontario) has been collecting mercury since 1994 and until 2021.

Total Gaseous Mercury (TGM) at Egbert had a mean concentration of 1.51 ± 0.31 ng/m^3 from December 1996 -2016. During this measurement period, the temporal trend decreased by -1.7 % per year (range of -1.9 to -1.5%) (GMA, 2018). Wet deposition measured at this site reported mean concentration of 8.0 ng/L between April 1998 and August 2007 (GMA, 2018). The annual trend for wet deposition was not found to be significant with a range of -1.2 % to +0.6 % per year (GMA, 2018). The annual GEM concentration from St. Anicet was 1.53 ± 0.35 ng/m^3 from August 1994 to December 2016. During this measurement period, the temporal trend decreased by 1.5% per year (range -1.6 to -1.3%). Wet deposition measured at this site reported a mean concentration of 8.1 ng/L between March 2000 and December 2015 where the annual trend decreased by 3.0 % per year (range -5.3 to -1.0%) (GMA, 2018).

In earlier years, the average TGM concentrations reported from Point Petre and Burnt Island were 1.75 ± 0.33 ng/m^3 and 1.55 ± 0.22 ng/m^3, respectively, with declining trends of -1.7 % per year (range of -2.2 to -1.2%) and -2.5% per year (-3.4 to -1.6%), respectively. Wet deposition of mercury was measured at both Point Petre (Nov 2001 – Mar 2003) and Burnt Island (Dec 2001 – Mar 2003) with reported mean concentrations of 8.4 and 10.1 ng/L, respectively (Cole et al., 2014). Atmospheric GEM concentrations were measured at Canada's Experimental Lakes Area (west of Lake Superior) from 2005 to 2013. The mean concentrations varied at this site and ranged between 1.21 and 1.62 ng/m^3 (±0.003). Trend analysis from this site showed a decrease of 2.2 ± 0.06 % per year during the same time period (St. Louis et al., 2019).

Wet deposition measurements of mercury from the National Atmospheric Deposition Network's (NADN) Mercury Deposition Network (MDN) have been made in many US states surrounding the Great Lakes since 1996. Figure 7 shows the annual concentration of mercury in precipitation and wet deposition of mercury for both 2003 (the first year of maps, top panel) and for 2022 (the most recent year for data available, bottom panel). Average concentrations in the Great Lakes have been generally lower than the rest of the contiguous U.S. and have decreased over time

(Prestbo and Gay, 2009; Zhang et al., 2016). However, an in-depth analysis of the wet deposition trends show that mercury concentrations have increased over short time intervals at some sites within or surrounding the Great Lakes region (Weiss et al., 2016). In general, the MDN trends follow these Canadian trends with fluxes decreasing about 1.6% per year since 1996. However, wet deposition trends may be increasing at monitoring stations in the Great Lakes region, potentially due to increase precipitation (Olson et al. 2020). All the NADP observations can be found online (http://nadp.slh.wisc.edu/MDN/). The NADP also makes GEM measurements in its Atmospheric Mercury Network (AMNet) but have few sites in the Great Lakes area.

Lepak et al. (2015, 2018) used stable isotope signatures to determine sources of mercury in Great Lakes sediment and predatory fish. It was found that atmospheric sources dominate offshore sediments of Lakes Huron, Superior, and Michigan, while watershed-derived and industrial sources dominate offshore and nearshore sediments in Lakes Erie and Ontario. However, isotope signatures in predatory fish, such as Δ^{200}Hg, which is a conservative tracer for Hg delivered via precipitation, showed that bioaccumulated mercury is more isotopically similar to atmospherically derived mercury than to lake sediment. This finding suggests that atmospherically derived mercury may be a more important source of methylmercury (methyl mercury is a more toxic form that is biomagnified in aquatic food webs) to higher trophic levels than sediments in offshore regions of the Great Lakes.

Hexabromocyclododecane (HBCDD/HBCD)

There is no new data about HBCDD/HBCD in air on the US side. In 2014, with the median HBCDD concentrations measured in atmospheric particles in Chicago = 2.0 pg/m^3, Cleveland = 2.1 pg/m^3, Sturgeon Point = 1.7 pg/m^3 and Sleeping Bear Dunes = 5.2 pg/m^3. Higher levels of HBCDD were observed at the remote site of Sleeping Bear Dunes with comparable levels at the remaining three sites. Higher levels at the remote site of Sleeping Bear Dunes suggest either an unknown source nearby or site-specific long-range atmospheric transport of HBCDD to this site. α-HBCDD and γ-HBCDD were the dominant isomers with an average contribution of about 40% and 50% to total HBCDD concentrations, respectively (Olukunle, et al., 2018).

HBCDD is monitored in air samples collected at Point Petre and Burnt Island and is reported as the sum of the three isomers. There is no new data for HBCDD in the Great Lakes Basin since the last report. Annual mean concentrations were found to be 0.17-8.7 pg/m^3 at Point Petre from 2009-2017 (Shunthirasingham et al. 2018,.); and 0.054-0.38 pg/m^3 for Burnt Island from 2009-2013 respectively (Shunthirasingham et al. 2018). HBCDD tended to show an increasing trend with doubling time of 1.6 year but because it was only detected in 22% of all samples, this value is to be considered with caution as it may not be representative (Shunthirasingham et al. 2018) (Figure 8). Although HBCDD is a CMC, its time trend is not included in the assessment of this sub-indicator due to lack of data.

Short-Chain Chlorinated Paraffins (SCCPs)

At Point Petre, selected air samples collected in 2013 (n = 4) were analyzed for SCCPs. The mean concentrations was 410 pg/m^3 with range of 175 to 613 pg/m^3 (Hung et al., 2021). Under the Global Atmospheric Passive Sampling Program (GAPS), SCCPs have been measured in air using passive an air sampling method at the Toronto site. The concentrations found were 221.1 pg/m^3 in 2006, 5.5 pg/m^3 in 2009 Jan-Mar, 97.9 pg/m^3 in 2009 Oct-Dec and 77.7 pg/m^3 in 2011 (Harner et al., 2014; Jasmin Schuster, personal communication). The analysis was performed following the method of Tomy et al. (1997). Although SCCPs is a CMC, it is not included in the assessment of this indicator due to lack of data due to analytical difficulties.

Other Chemicals of Interest

Organochlorine Pesticides (OCPs)

Concentrations of banned or restricted OCPs

(https://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx) are generally declining in air in the Great Lakes Basin. There is no new OCP data for Burnt Island and Egbert of the Canadian sites. The Burnt Island station has been replaced by the nearby Evansville Station and air sampling for OCPs began in May 2019 at Evansville (Lake Huron). The annual average concentrations of the OCPs (Table 3) ranged from 0.1-43 pg/m^3 and an annual median of 0.1-46 pg/m^3, with the highest concentration recorded for HCB (hexachlorobenzene) and α-endosulfan. Data from the Canadian site of Point Petre are updated to 2022. Half-lives of OCPs in the Canadian sites are given in Table 3.

Halving times for dieldrin ranged from 11 years at Sturgeon Point to 23 years at Cleveland while those for heptachlorepoxide varied between 11 years at Pt. Petre and Sturgeon Point and 24 at Cleveland and those of oxychlordane were between 14 years at Chicago (1996-2021) and not significant at Cleveland (2003-2021) – (Hites, 2024). See Figure 9**.** Halving times in years for dieldrin, heptachlor epoxide, and oxychlordane at six sites on the shores of the Great Lakes. The error bars show the standard errors of the coefficients as determined from linear regressions. "NS" indicates that the time coefficient (a3) was not significant at $P < 0.05$.

Concentrations of α-HCH and γ-HCH (hexachlororcyclohexane) are decreasing rapidly in air, with halving times (by DF method) of approximately 5 years both at Point Petre and at the U.S. sites (Hites, 2023); see Figures 10 and 11a-b. At the Canadian sites, the 10-year time trend (2013-2022) of α-HCH has a half-life of 12 years, indicating a slower decline compared to the entire dataset (1992-2022). The 10-year time trend for US sites (2013-2022) for these compounds is similar to those of the overall time trend (1992-2022), albeit a bit larger, indicating a slower decline. For HCHs combined at US sites, the 10-year trend was significant at all sites except for Cleveland with halving times ranging from 5.3 at Sleeping Bear Dunes to 8.3 years at Chicago, averaging at about 7 years, which indicates a slower decline when compared to the whole dataset. These are the most rapid halving times observed for any compound measured as part of IADN/GLB.

Endosulfan is the last insecticide among the legacy pesticides to be removed from the market. Its phase-out began in 2010, when the Environmental Protection Agency (EPA) signed a Memorandum of Agreement with this compound's registrants. All allowed uses were progressively eliminated since then, with the last four terminated in 2016. Endosulfan exists in two isomeric forms, endo and exo, commonly known as I and II. Endosulfan sulfate is an oxidation product of endosulfan. Therefore, sometimes, in reporting, concentrations of endosulfan I, endosulfan II and endosulfan sulfate are summed together (e.g. Figure 12)**.** Their vapor phase atmospheric concentrations are decreasing with halving times respectively of 6.5 and 6.4 years from 1992-2022 at Point Petre and 4.4 to 6.1 years at US sites. Figure 10 and 12 show the time trends for endosulfans. The 10-year time trend for α-endosulfans at Point Petre showed a rapid decreasing trend with half-life of about 1.6 year for both isomers. The 10-year trend for vapor phase concentrations of endosulfans at the US sites showed a faster decline than for the whole dataset (i.e 1995-2022) with halving times between 2.4 and 3.1 years. Based on estimated use rates of endosulfan in the U.S. from 1997 to 2009, Salamova et al. (2015) estimated that endosulfan has an atmospheric chemical degradation rate of about 4 years, which suggests that endosulfan is less persistent in the environment than related compounds.

The atmospheric concentrations of DDTs (dichlorodiphenyltrichloroethane, reported as the sum of DDT, DDD and DDE congeners) continue to decline with halving times ranging from 10.0 ± 2.5 for Eagle Harbor to 15.9 ± 8.0 for Point Petre. The ten year trend for gas phase concentrations was significant only at Eagle Harbor, Sleeping Bear Dunes and Point Petre, with halving times of 5.6 ± 1.9, 6.5 ± 3.7, and 5.9 ± 3.7, respectively (Figure 13).

The geometric mean concentrations of HCB and octachlorostyrene (OCS) are ~60 and 0.7 pg/m^3, respectively, at all sites regardless of the local population, and these concentrations have not changed significantly over time. The concentrations of HCB measured here are similar to those reported by other studies (see Hites et al., 2022 for a list) of the northern troposphere and are ~3 times those reported in the southern troposphere, suggesting that HCB

sources are largely in the Northern Hemisphere. It is apparent that direct and recycled emissions of HCB and OCS into the northern troposphere are widespread in scope and, despite the elimination of HCB as a fungicide, have not changed in a meaningful way in the past 20–30 years. This situation is unlike the case for other legacy chemicals, for which global restrictions on their use have been more effective (Hites et al., 2022).

There is no update on the loadings of OCPs to the lakes since the last report. Loadings calculations up to 2010 suggest that the atmosphere is a source of endosulfan and *p,p'*-DDT to the lakes and that volatilization from the lakes are a source of *p,p'*-DDE to the atmosphere (Shunthirasingham et al. 2016).

The input and output flows to the lakes of both α- and γ-HCH are decreasing exponentially, and for both of these compounds the air and water concentrations are approaching equilibrium, and there will be no net transfer across the air-water interface (Guo et al., 2018). The changes over the 1992-2015 period for the other pesticides are variable, but with the exception of t-nonachlor (for which there is the least water data), the input and output flows are decreasing or not changing significantly. This seems to suggest that air-water transfer for these compounds is slowly approaching equilibrium. Incidentally, of these pesticides, only endosulfan was still on the market in North America during the study period of Guo et al. (2018), i.e. 2010-2015. Between 1992 and 2015, its use in the U.S. decreased (USGS, 2017), before being completely phased out in 2016 (U.S. EPA, 2010). Canada started to phase out the use of endosulfan in 2010, and all registrations of endosulfan-containing pesticide products expired on December 31, 2016 (ECCC, 2012).

Current Use Pesticides (CUPs)

In the United States, pesticide use has increased over the last few decades, and atrazine, chlorothalonil, pendimethalin, chlorpyrifos, and metolachlor are now among the most commonly used pesticides in agriculture, whereas permethrin and other pyrethroid insecticides are now among the most commonly used pesticides in homes and gardens.

There is no update on the levels and trends of CUPs since the last report. The concentrations of 15 CUPs, including nine pyrethroid insecticides, four herbicides, one organophosphate insecticide, and one fungicide, were measured in 24-hour air samples collected at IADN stations in 2017. Chlorothalonil, trifluralin, metolachlor, λ- cyhalothrin, cypermethrin, and chlorpyrifos were detected in more than 50% of the samples (Figure 1). Azoxystrobin, oxyfluorfen, atrazine, prometon, pendimethalin, bifenthrin, permethrin (both cis- and trans-), cyfluthrin, deltamethrin, esfenvalerate, and TCPy had detection frequencies of 20–45%. Median total CUP concentrations were 339, 238, 84, 33, 60, and 6.0 pg/m3 at Chicago, Cleveland, Sturgeon Point, Point Petre, Sleeping Bear Dunes, and Eagle Harbor, respectively. The concentrations of total CUPs and most individual CUPs were generally higher at urban sites of Chicago and Cleveland than at rural/remote sites of Sturgeon Point, Point Petre, Sleeping Bear Dunes, and Eagle Harbor. Chlorothalonil, trifluralin, bifenthrin, and chlorpyrifos were the most abundant individual CUPs among fungicides, herbicides, pyrethroid insecticides, and other insecticides, respectively. The spatio-seasonal variation suggests that fungicides at Sturgeon Point and Sleeping Bear Dunes, with the highest fraction of agricultural land use, were associated with agricultural activities while pyrethroid insecticides were generally driven by non-agricultural human activities. (Wang et al., 2021).

Non-BDE Flame Retardants

The concentrations of halogenated flame retardants (HFRs) have been measured in IADN/GLB samples since January 2005. Specifically, the atmospheric concentrations of eight non-PBDE halogenated flame retardants (HFRs) [pentabromoethyl benzene (PBEB), hexabromobenzene (HBBz), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), *bis*(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP), *syn*-Dechlorane Plus (*syn*-DDC-CO), *anti*-Dechlorane Plus (*anti*-DDC-CO), 1,2-*bis*(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenylethane (DBDPE)] were measured in each IADN samples. The levels of almost all of these flame retardants, except for PBEB, HBBz,

and DP, were significantly higher in Chicago, Cleveland, and Sturgeon Point. The concentrations of PBEB and HBBz continued to be relatively higher at Eagle Harbor and Sturgeon Point, respectively, than at the other sites for unknown reasons. The concentrations of anti-DP were relatively high at Cleveland, Point Petre, and Sturgeon Point, the sites closest to this compound's production site in Niagara Falls, New York, while when both isomers are combined (syn- and anti-) the concentrations follow the same trend as for the other compounds, being highest at Chicago (Capozzi, et al, 2023).

The concentrations of PBEB decreased at almost all sites except for Eagle Harbor, where the highest PBEB levels were observed. HBBz concentrations were generally not changing significantly except for Sturgeon Point, where HBBz levels were highest (2.5 ± 1.3 years). The reason for the relatively high levels of PBEB and HBBz at Eagle Harbor and Sturgeon Point are not clear. DP concentrations were increasing at Eagle Harbor with a doubling time of 4.9 ± 2.4 years and decreasing at Sturgeon Point – the site closest to the production site- with a halving time of 11 ± 7 year (Capozzi, et al, 2023). The ten year trend showed HBB decline at Sturgeon Point with a halving time of 1.3 ± 0.7, PBEB increase at Sleeping Bear Dunes with a doubling time of 3.3 ± 1.8 years and DP generally declining at most sites with halving times of about 5 years.

EH-TBB and BEH-TEBP are the two main components of FireMaster 550, which is a replacement for the penta-BDE commercial mixture. These two main components (EH-TBB and BEH-TEBP) were included in the analyses of IADN samples in 2008. Because EH-TBB and BEH-TEBP together are the major components of FireMaster 550, their concentrations were summed (notated here as EH-TBB and BEH-TEBP), and this sum was regressed as a function of time. The atmospheric concentrations of EH-TBB were significantly and rapidly increasing at Sturgeon Point and Eagle Harbor only, with doubling times of 8.2 and 2.4 years (i.e. 2005-2019) while those of BEH-TEBP were decreasing at Cleveland with a halving time of 4.2 years (Capozzi et al., 2023). The ten year range (2013-2022) doesn't show any significant trend for neither of these two compounds at any site.

Air samples collected at the Canadian sites are being analyzed for 13 non-PBDE HFRs [hexabromobenzene (HBBz), hexabromocyclododecane (HBCDD), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), allyl 2,4,6-tribromophenyl ether (TBP-AE), 2-bromoallyl-2,4,6-tribromophenyl ether (TBP-BAE), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), *anti*-dechlorane plus (*anti*-DDC-CO), *syn*-dechlorane plus (*syn*-DDC-CO), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), decabromodiphenylethane (DBDPE), and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE)]. There is no new data for Burnt Island and data for Point Petre is updated until 2022. The Burnt Island station has been replaced by the nearby Evansville Station and air sampling for non-BDE flame retardants began in May 2019 at Evansville (Lake Huron). The annual average of non-BDE flame retardants ranged from 0.08 to 33 pg/m^3 and an annual median of 0.08 to 7.1 pg/m^3. Figure 14 presents the updated for *anti*- and *syn*-DDC-CO, DBDPE, EH-TBB, HBB and PBT in air at Point Petre. The half-lives of HFRs for Point Petre and Burnt Island are presented in Table 4. *anti*-DDC-CO at Point Petre exhibited an overall declining trend with a half-life ($t_{1/2}$) of 3.0 years from 2008 to 2022. Its concentration decreased gradually from 2012 to 2016, followed by a rapid decline observed from 2016 to 2022. *anti*-DDC-CO in the atmosphere is decreasing, with $t_{1/2}$ = 3.4 years at Burnt Island. *syn*-DDC-CO at Point Petre also showed declining trend with $t_{1/2}$ = 4.0 years, but the levels are increasing at Burnt Island, with a doubling time of 7.6 years from 2008-2013. Another study, Liu et al. (2016), found that the concentrations of both compounds were decreasing in the air from the Great Lakes region from 2005 to 2014, which provides different results. The 10-year trend (2013-2022) indicates a significant decline specifically for anti-DDC-CO at the Point Petre site.

For other non-BDE flame retardants (FRs), DBDPE at Point Petre has shown an upward trend since 2018. This increasing pattern aligns with the hypothesis that DBDPE is a replacement for deca-BDE (Chen et al., 2023). The doubling time for DBDPE is 2.0 years. EH-TBB in the air at Point Petre has been decreasing with a half-life ($t_{1/2}$) of 3 years. Liu et al. (2016) reported an increase in EH-TBB+BEHTBP in the air at the Great Lakes region, suggesting that

these compounds are potential replacements for PBDEs. The air concentration of HBBz at Point Petre slowly increased from 2015 to 2019 and then stabilized, with an overall $t_{1/2}$ of 5 years. Pentabromotoluene concentrations are decreasing rapidly at Burnt Island and slowly at Point Petre, with half-lives of 2.1 years and 14 years, respectively. In a previous report, the doubling time of PBT at Point Petre was 13 years. The declining trend for PBT suggests a reduction in its usage. A declining trend is also observed for TBP-AE at Point Petre, with a half-life of 5 years. In general, the time trends of other non-BDE FRs in air at Point Petre were highly variable. There is no consistency in trends for the HFRs at Point Petre and there is no clear seasonal cycle. The highly variable air concentrations are likely an indication of continuous emission and episodic transport from either local or long-range sources.

Organophosphate esters (OPE) are industrial chemicals that are widely used as flame retardants, plasticizers, antifoaming agents, and as additives in hydraulic liquids, lacquers, and floor polishes. These chemicals have been in heavy use for decades. OPEs include tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate, and tris(1,3-dichloroisopropyl) phosphate, tri-*n*-butyl phosphate, triphenyl phosphate, and 2-ethylhexyl diphenyl phosphate (EHDP). Median total OPE concentrations (∑OPEs) ranged from 41.2 pg/m^3 at Eagle Harbor to 1320 pg/m^3 at Cleveland. Tris(1-chloro-2-propyl) phosphate (TCIPP) was the most abundant OPE measured in these samples and contributed 26% to ∑OPE concentrations. Samples collected in the summer had significantly higher levels of ∑OPEs than samples collected in the winter. The estimated dry deposition flow of ∑OPEs to the Great Lakes was 1.22 tons/year, exceeding the corresponding flows reported for polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCPs) (Wu et al., 2020).

Air sampling for OPEs in the Great Lakes Basin began in October 2018 at Point Petre (Lake Ontario) and in May 2019 at Evansville (Lake Huron). Air samples collected at the Canadian sites are being analyzed for 16 OPEs [triethyl phosphate (TEP), tripropyl phosphate (TPrP), tributyl phosphate (TBP), tri(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), triphenyl phosphate (TPhP), tris(2-butoxyethyl) phosphate (TBEP), 2-Ethylhexyl diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP), tri-o-tolyl phosphate (ToTP), tri-m-tolyl phosphate (TmTP), tri-p-tolyl phosphate (TpTP), tris(2-isopropylphenyl)phosphate (T2IPP), tris(3,5-dimethylphenyl)phosphate (T35DMPP), and tris(2,3-dibromopropyl) phosphate (TDBPP). The average concentrations of ∑OPEs from 2018 to 2022 at Point Petre and Evansville ranged from 0.09 pg/m³ to 530 pg/m³ and from non-detected levels to 440 pg/m³, respectively. The predominant OPEs detected at both sites include TBEP, TPhP, TCPP, and TCEP. TBEP exhibited the highest concentration, followed by TPhP and TCPP. Cl-OPEs (TCEP, TCPP, and TDCPP) showed higher levels at Point Petre compared to Evansville. TEP, along with two chlorinated OPEs (TCEP and TCPP) at Point Petre and TEP and TCEP at Evansville, displayed a distinct seasonal pattern, with elevated levels during the summer months and lower levels during winter. At both sites, numerous OPEs exhibited statistically significant correlations with each other, suggesting a common source, potentially linked to volatilization from commercial products.

Per- and polyfluoroalkyl substances (PFASs) (other than PFOS, PFOA and LC-PFCAs)

The time trends of short-chain PFASs in precipitation of GLB from 2006-2018 was reported by Gewurtz et al., (2019). In this report, time trends for short-chain PFASs were revised using data up to 2022. Figure 15 shows the time trends of PFBA and PFHxA in precipitation in Point Petre (Lake Ontario), Burnt Island/Evansville (Lake Huron) and Sibley (Lake Superior). PFBA, PFPeA, PFHxA, and PFHpA did not decrease monotonically at the three sites from 2006 to 2022. Furthermore, the DF trend line indicates that concentrations of PFBA and PFHxA appear to be increasing in the most recent years (~2010/2014 to 2022 at Point Petre and Burnt Island and ~2016 to 2022 at Sibley). These results may not be surprising considering that these short-chained PFCAs and their precursors have not been regulated in Canada (ECCC, 2018) or the US and are being used as replacement chemicals for PFOS, PFOA, and the longer-chain PFCAs (Wang et al., 2013).

Sampling for PFAS in the Great Lakes Basin commenced in October 2018 at Point Petre (Lake Ontario) and in May 2019 at Evansville (Lake Huron). Short-chain PFASs, including PFBA, PFPeA, PFHxA, and PFHpA, were detected at both sites, with detection frequencies ranging from 13% to 94%. Importantly, the Point Petre site exhibited a higher detection frequency for PFPeA, PFHxA, and PFHpA, whereas Evansville showed a higher detection frequency for PFBA. At the Point Petre site, the mean concentrations of PFBA, PFPeA, PFHxA, and PFHpA were 3.2, 0.63, 0.78, and 0.56 pg/m³, respectively. In comparison, at the Evansville site, the mean concentrations were 2.5, 0.45, 0.80, and 6.0 pg/m³ for PFBA, PFPeA, PFHxA, and PFHpA, respectively. Generally, higher average concentrations of PFASs were observed at Point Petre than Evansville since Point Petre is in closer proximity to potential sources in urban areas where more consumer products containing PFASs are used. At Toronto, levels of perfluorosulfonic acids (PFSAs, including PFOS) from an active air sampling campaign in 2010 of 0.38-3.1 pg/m^3 (Ahrens et al., 2012) were in line with levels measured using passive air samplers in 2009 (4.6 pg/m^3) and 2013 (0.29-4.7 pg/m^3) under GAPS, but lower than the levels seen in 2015 (8.1 pg/m^3).

PFAS precipitation samplers have been established on the US side in summer/fall 2020. No time trends can be calculated yet. PFAS concentrations were dominated by PFCAs (C4 – C16), accounting for 75 – 95% of total PFAS. Short-chain PFCAs (C4 – C6), i.e., PFBA, PFPeA, and PFHxA, were particularly abundant, accounting for 57 – 81% of total PFAS. Perfluoroalkyl sulfonic acids (PFSAs) (C4-C8) represented up to 6% of total PFAS. The most abundant PFAS in the air samples were FTOHs, accounting for 55 – 85% of total PFAS, while ionic PFAS represented 15 – 38% of the total PFAS. The median ∑41PFAS concentrations in air samples were significantly higher ($p < 0.05$) at the two urban sites (range 180 to 1147 pg/m3 at Chicago and Cleveland) compared to those at two remote sites (range 39 – 443 pg/m^3 (Xia, 2024). When combined, these results indicate that atmospheric deposition might be an important pathway delivering PFAS to the Great Lakes.

Polycyclic Aromatic Hydrocarbons (PAH)

IADN data for total PAH concentrations show some significant decreases over time, with halving times ranging from 10 to 16 years, confirming what we observed previously (Salamova et al., 2015). Trends at Eagle Harbor were marginally significant (p=0.06) with a halving time of 29 ± 20 years. When all sites are combined, the overall halving time increases to 28 ± 12 years. These declines can probably be attributed to emission reductions from the implementation of the Clean Air Act. PAH levels at Chicago were highest, followed by Cleveland, Sturgeon Point, Point Petre, Sleeping Bear Dunes, and Eagle Harbor.

A passive air and water sampling study in Lake Superior in 2011 showed that surface water and atmospheric PAH concentrations were greatest at urban sites (Ruge et al., 2015). Net air-to-water deposition of PAHs was observed near populated areas, but the net exchange is near equilibrium offshore (Ruge et al., 2015). A similar study conducted in the lower Great Lakes using polyethylene passive samplers in air and surface water demonstrated that gaseous PAH concentrations were strongly correlated with population density within 40 km of the sampling locations (McDonough et al., 2014). Source profiles differed for atmospheric and aqueous PAHs indicating that in addition to atmospheric deposition, runoff and sediment-water exchange contributed to dissolved concentrations.

No updates on atmospheric flows are available since the last report. Guo et al. (2018) assessed atmospheric flows to the Great Lakes for phenanthrene and benzo[a]pyrene as representative PAHs. These two compounds were selected because phenanthrene is relatively abundant and volatile and is used in several industries making dyes and explosives and because benzo[a]pyrene is a known human carcinogen. The overall region-wide input of phenanthrene to the five lakes has decreased slowly over the period 1992–2015. This is true despite the increasing inputs of phenanthrene into Lakes Superior, Michigan, Erie, and Huron. Presumably, some of these long-term decreases in PAH input flows are due to the wide-spread conversion from coal to cleaner fuels for energy production and due to the implementation of the Clean Air Act by the U.S. EPA (Liu et al., 2014) and of the U.S.-Canada Air

Quality Agreement (U.S. EPA, 1991).

There is no new data about the PAHs in air in the GLB since the last report**.** PAHs in air at Point Petre, Burnt Island and Egbert from 1997-2017 was reported (Li et al., 2021). The half-lives of the PAHs are presented in Figure 16. Li et al. (2021) reported that there were significant declining trends for most PAHs. For example, the concentrations of most of the higher mass PAHs, such as dibenz[a,c]anthracene (DacA) at the three sites, have decreased since 1997 with halving times of 4.1-5.4 years, which is much faster than the other PAHs. Other PAHs with halving times less than 10 years are anthracene at Burnt Island; benzo[g,h,i]fluoranthene (BghiF), chrysene (Chr), coronene (Coron), and retene (Ret) at Egbert; and benzo[e]pyrene (BeP), BghiF, dibenz[a,h]anthracene (DahA) at Point Petre, suggesting that these PAHs in the GLB atmosphere are decreasing rapidly. At Burnt Island, 6 PAHs are significantly decreasing, with the halving time in the range of 4.2-21 years. At Egbert, concentrations of 7 PAHs show significant decreasing trends from 1997 to 2006. At Point Petre, most of the PAHs in the atmosphere were significantly decreasing from 1997 to 2017, with half-lives in the ranges of 3.6-32 years. The declining trends are due to effective control of PAH emissions in the GLB. The main contributor of PAHs in the GLB is coal combustion. At the US sites, the concentrations of PAHs are decreasing with halving times of 15 to 20 years when the entire sampling period is considered. When only the last 10 years are included in the analysis, the trends are not significant.

Diagnostic ratios (DRs) and positive matrix factorization (PMF) models can help in characterizing source profiles of polycyclic aromatic hydrocarbons (PAHs). In general, pyrogenic sources, including coal combustion and vehicular emissions, were the most important contributors to atmospheric profiles, in particular at the urban sites. Diesel emissions accounted for a larger portion of the traffic-oriented PAHs than gasoline emissions at urban sites but this signature was less obvious at the remote sites. Temporal analyses for DRs revealed that the relative contribution of petrogenic sources and volatilization from surfaces has been increasing gradually, and that the gaps in PAH emissions between diesel- and gasoline-engines appeared to be further amplified in recent years. In the PMF model, coal combustion and non-pyrogenic emissions were the main PAH sources for winter and summer air, respectively, but none of the DRs responded to these changes accordingly. Only two DRs, i.e., I123P/(I123P+BGP) and BAP/(BAP+BGP), which are characteristic of pyrogenic sources and traffic related emissions respectively, were relatively consistent between vapor and particle phases. Although our analysis highlighted some limitations, DRs can provide useful information on spatial and temporal trends and source characterization. (Wu et al., 2020)

Metals

There is no new data about the metals in air in the GLB region since the last report. Li et al., (2020) reported 19 elements in PM_{10} samples that were collected at Point Petre. Burnt Island and Egbert from 1998-2017. The 19 measured elements included aluminum (Al), arsenic (As), barium (Ba), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Results showed a strong relationship between element concentrations and higher population densities, which suggested trace metal emissions were anthropogenically-related. The concentrations of most elements were significantly decreasing with halving times ranging from 10 to 48 years in response to national and international regulatory actions (Figure 17). The findings imply that metals in the GLB atmosphere were influenced by human settlement and industries not only from local emission but also through long-range atmospheric transport.

Dioxins and Furans (PCDD/Fs)

Areas with higher population generally showed higher annual mean air concentrations of PCDD/Fs in North America (CEC 2014; Venier et al. 2009; Cleverly et al. 2007). There are no new PCDD/F data since the last reporting period. Air concentration measurements under Canada's National Air Pollution Surveillance (NAPS) reported high toxic equivalency (TEQs) in air at the Walpole Island site (in Lake St. Clair) and the Windsor/University Ave. sites (Windsor,

ON), where profiles were characterized by a lower contribution of octachlorodibenzo-*p*-dioxin and an increased contribution of dibenzofurans. This profile might indicate the impact of a local emission source (CEC 2014). PCDD/F levels at rural, suburban, and urban NAPS sites (including sites in the Great Lakes Basin) declined after the early 1990s and in the early 2000s. This decline can be attributed to control measures taken in Canada with respect to PCDD/F emission sources. After the year 2005, a clear trend is not evident (CEC 2014).

Linkages

Atmospheric deposition is a significant route by which persistent, bioaccumulative and toxic chemicals (including CMCs), such as PCBs, currently enter the Great Lakes. Increases in the concentration and loadings of atmospheric chemicals of concern may result in increased contamination in sediment, toxic chemicals in offshore waters, and contaminants in whole fish and waterbirds. Bioaccumulation of these chemicals in fish may result in fish consumption advisories. This sub-indicator links directly to the other sub-indicators in the Toxic Chemicals category, particularly Toxic Chemicals in Water.

Atmospheric and hydrologic variabilities could affect contaminant exchange between air and water (Ma, Hung and Blanchard, 2004; Hung et al., 2022), for instance, increase in precipitation could result in greater wet/dry deposition of contaminants into the lakes. Conversely, decreased ice cover and increase in surface water temperatures would drive greater volatilization losses from the lakes. Further investigation would improve the understanding about how atmospheric exchange of contaminants in the lakes will change if precipitation, ice cover, and surface temperature conditions continue to change.

In addition, many CMCs and other chemicals of concern are related to anthropogenic activities and commercial products, future development of urban infrastructures, changes in land-use (e.g. remediation of contaminated sites, urbanization etc.) and growth/changes in populated areas will continue to impact the release and deposition of contaminants to the lakes. Continued monitoring of CMCs and other chemicals of concern is essential to assess the impacts of such developments.

Assessing Data Quality

Data Characteristics	Agree	Neutral or Unknown	Disagree	Not Applicable
Data are documented, validated, or quality-assured by a recognized agency or organization	X			
Data are from a known, reliable and respected generator of data and are traceable to original sources	X			
Geographic coverage and scale of data are appropriate to the Great Lakes Basin		X		
Data obtained from sources within the U.S. are comparable to those from Canada	X			

Uncertainty and variability in the data are documented and within acceptable limits for this sub-indicator report	X			
Data used in assessment are openly available and accessible	Yes	IADN dataset: Great Lakes Environmental Database – GLENDA | The Exchange Network About: IADN Data Vizualization: Indiana University (iu.edu) GLB dataset: Great Lakes Basin (GLB) Monitoring and Surveillance - Open Government Portal (canada.ca) NADP dataset: nadp.slh.wisc.edu/sites/mdn-ab08/		

Notes on Accessing Data

An account must be created to access the IADN GLENDA data.

Data Limitations

- Since air (gas and particle) measurements were conducted using active air sampling method consisting of 24-hour integrated samples collected once every 12 or 36 days, it is not possible to assess toxic chemical levels during the time between two samples.
- Since most sampling sites are remote, samples may not be able to return to the laboratory until 3-4 months after sampling. Also, the sample extraction and analytical process for organic chemicals are very time consuming. Over 180 different individual chemicals need to be analysed and quantified in each sample. All resulting data need to undergo strict QA/QC evaluation and flagging to ensure data quality due to the low levels found in air and precipitation samples. It is expected that data can only be reported in peer-reviewed publications 3-4 years after the samples were collected.
- Some of the estimation parameters of the loadings calculations are poorly known at present and calculations are based on assumptions that air, precipitation and water concentrations measured at a few specific locations on the lakes apply to the entire lake. Thus, uncertainties in such loadings calculations are high. The trends in the atmospheric concentrations of toxic chemicals, however, are better understood and track progress towards virtually eliminating anthropogenic sources. Errors in these trends should be clearly stated and tested against the null hypothesis (things are not changing).
- To understand the pollutant concentration trends related to atmospheric deposition, additional information is needed in interpreting pollutant load estimates. For example, information on the yearly variations in the rain rate (dry years versus wet years) is needed to understand the pollutant loadings associated with wet deposition. Also, since it is known that the pollutant loads associated with atmospheric deposition have seasonality for some components, time trends and seasonal trends should be determined separately using statistical methods.

Additional Information

Many remaining sources of PCBs are located in urban areas, which is reflected by the higher levels of PCBs measured in Chicago and Cleveland by IADN, and in Toronto by other researchers (Diamond et al., 2010; Robson et al., 2010, Melymuk et al, 2012, Csiszar et al., 2014) and in other areas (Wethington and Hornbuckle 2005; Totten et al. 2001). Research to investigate the significance of these remaining sources is underway (Shanahan et al. 2015). This is important because fish consumption advisories for PCBs exist for all five Great Lakes.

Among the CMCs, PCBs, PBDEs [tetrabromodiphenyl ether and pentabromodiphenyl ether, hexabromodiphenyl ether and heptabromodiphenyl ether, decabromodiphenyl ether (commercial mixture, c-decaBDE)], HBCDD, SCCP and perfluorooctanoic acid (PFOA), its salts and related compounds are listed under Annex A (Elimination) under the UNEP Stockholm Convention on POPs. PFOS, its salts and perfluorooctane sulfonyl fluoride are listed under Annex B (Restriction) of the Stockholm Convention. Canada is a party of the Stockholm Convention.

The Minamata Convention on Mercury is a UNEP led multilateral environmental agreement between 131 Parties (as of April 2021) including the U.S. and Canada. The convention came into effect in August 2017 and aims to protect human health and the environment from anthropogenic emissions and release of mercury and mercury compounds. The data collected through long term monitoring programs will provide critical information for effectiveness evaluation for the treaty. Canada is a net recipient of mercury where over 95% of the anthropogenic mercury deposited comes from outside of the country (Environment and Climate Change Canada, 2017). Regionally, many sources that emit mercury are reducing emissions. For instance, all coal-fired power plants in Ontario have ceased operation as of April 2014, being the first jurisdiction in North America to fully eliminate coal for producing electricity (Ontario Ministry of Energy, 2014). The United States has been demonstrated to have regional, national, and international Hg sources contributing to atmospheric concentrations (Tate et al. 2023) but has shown declines across matrices in response to domestic regulations (Lepak et al. 2019). Fish consumption advisories for mercury exist across the Great Lakes and their watersheds, hence it is important to mitigate mercury inputs and monitor expected changes in Canada and the United States due to international reduction efforts.

Residential garbage burning (burn barrels) is now the largest current source of dioxins and furans (Environment Canada and U.S. Environmental Protection Agency, 2006). Basin and nationwide efforts are underway to eliminate emissions from burn barrels.

Continued long-term monitoring of the atmosphere is necessary in order to measure progress brought about by toxic chemical reduction efforts. Environment and Climate Change Canada and U.S. EPA continue to add new chemicals of concern to routine monitoring to the IADN and GLB programs. Screening and method development for additional non-PBDE flame retardants, per- and polyfluoroalkyl substances (PFASs) and SCCPs is currently under way. These efforts ensure the early detection of potential chemicals of concern and allow for the development of temporal trends in advance of the implementation of regulatory measures to enable future effectiveness evaluation of regulations. Sample and extract archiving practices in monitoring programs also provide the opportunity for the retrospective trend analysis of newly identified chemicals of concern. Results from these monitoring efforts on emerging chemicals of concern will contribute to the scientific information needed for the risk assessment and identification of additional chemicals of mutual concern.

Report Authors

This report was prepared on behalf of the IADN Steering Committee by Derek Ager, IADN Program Manager, U.S. Environmental Protection Agency, Great Lakes National Program Office; Hayley Hung and Chuba Shunthirasingham,

Air Monitoring in the Great Lakes Basin (GLB) Principal Investigator and Research Chemist, respectively, under the Chemicals Management Plan, Air Quality Processes Research Section, Environment and Climate Change Canada; Ron Hites and Marta Venier , Indiana University: and contributions from David Gay at the Mercury Deposition Network (MDN)

Report Contributors

Great Lakes Basin (GLB) Contacts

Hayley Hung, Air Monitoring in the Great Lakes Basin (GLB) Principal Investigator under the Chemicals Management Plan, Air Quality Processes Research Section, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, hayley.hung@ec.gc.ca, 416-739-5944.

GLB Data: https://open.canada.ca/data/en/dataset/5d8548c5-e284-4e85-aed4-c22536de615a, or contact Helena Dryfhout-Clark, GLB Data Manager, Air Quality Processes Research Section, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Helena.Dryfhout-Clark@ec.gc.ca, 613-995-9031.

IADN Contact

Derek Ager, IADN Program Manager, Great Lakes National Program Office, U.S. Environmental Protection Agency, 77 West Jackson Boulevard (G-17J), Chicago, IL, 60604, ager.derek@epa.gov. 312-353-9153.
IADN Data: Great Lakes Environmental Database – GLENDA | The Exchange Network and https://iadnviz.iu.edu/#/about/
Link to IADN websites: http://epa.gov/greatlakes/monitoring/air2/index.html

References

Ahrens, L., Shoeib, M., Harner, T., Lane, D. A., Guo, R., Reiner, E. J. (2011). Comparison of annular diffusion denuder and high volume air samplers for measuring per- and polyfluoroalkyl substances in the atmosphere. *Analytical Chemistry* 83: 9622-9628.

Ahrens, L., Harner, T., Shoeib, M., Lane, D.A., Murphy, J.G. (2012) Improved characterization of gas-particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. *Environmental Science and Technology* 46 : 7199-7206.

Ahrens, L., Harner, T., Shoeib, M., Koblizkova, M., Reiner, E.J. (2013) Characterization of two passive air samplers for per- and polyfluoroalkyl substances. *Environmental Science and Technology* 47: 14024-14033.

Anderson, P. N., Hites, R. A. (1996) OH radical reactions: The major removal pathway for poly-chlorinated biphenyls from the atmosphere. *Environmental Science and Technology*, 30: 1756–1763.

Bhhatarai, B., Gramatica, P. (2011). Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. *Environ. Sci. Technol.*, 45 (19), 8120–8128

Buehler, S.S., Basu, I., Hites, R. A. (2001). A comparison of PAH, PCB, and pesticide concentrations in air at two rural sites on Lake Superior. *Environmental Science and Technology* 35(12): 417–2422.

Capozzi, S.L., Lehman, D.C., Venier, M. Disentangling Source Profiles and Time Trends of Halogenated Flame Retardants in the Great Lakes. Environ Sci Tech. 2022, 57, 3, 1309-19.

Chen, A, Chen, C., Zhang, S., Li, L., Zhang, Z., Chen, J., Jing, Q., Liu, J. (2023) Emission and environmental distribution

of decabromodiphenyl ethane (DBDPE) in China from 2006 to 2026: Retrospection, forecasting, and implications for assessment and management. *Environmental Pollution*, 327: 121536.

Cleverly, D. H. et al. (2007). A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States. *Environmental Science and Technology* 41: 1537–1544.

Cole, A. S., Steffen, A., Eckley, C.S., Narayan, J., Pilote, M., Tordon, R., Graydon, J.A., St. Louis, V.L., Xu, X., and Branfireun, B.A. (2014) A survey of mercury in air and precipitation across Canada: Patterns and trends, *Atmosphere*, 5: 635-668. Doi:10.3390/atmos5030635, 2014.

Commission for Environmental Cooperation (CEC) (2014). Assessing Comparability of Atmospheric PCDD, PCDF and Coplanar PCB Data from North American Ambient Air Monitoring Networks. Montreal, Canada: Commission for Environmental Cooperation. 256 pp.

Csiszer, S. A., Diamond, M. L., Daggupaty, S. M. (2014) The Magnitude and Spatial Range of Current-Use Urban PCB and PBDE Emissions Estimated Using a Coupled Multimedia and Air Transport Model. *Environ. Sci. Technol.* 48 (2): 1075–1083.

Ellis, D. A., Martin, J. W., Mabury, S. A., Hurley, M. D., Sulbaek Andersen, M. P., Wallington, T. J. (2003) Atmospheric lifetime of fluorotelomer alcohols. *Environmental Science and Technology*, 37: 3816-3820.

Environment and Climate Change Canada (ECCC) (2012) Response to comments for amendment of schedule 3 (endosulfan) http://ec.gc.ca/lcpe-cepa/default.asp?lang=En&xml=5F1BC1BC-7DE3-45E1-9352-771A7056ACB1 (accessed 12/04/2017)

Environment and Climate Change Canada (2017) Canadian Mercury Science Assessment Report. Gatineau, Quebec, Canada, 793 p. ISBN: 978-0-660-04499-6 https://publications.gc.ca/collections/collection_2017/eccc/En84-130-3-2016-eng.pdfEnvironment Canada and U.S. Environmental Protection Agency, 2006. Great Lakes Binational Toxics Strategy 2005 Progress Report. En161-1/2005E/ 0-662-42910-9, 108 pp.

Environment and Climate Change Canada Canadian Environmental Protection Act, 1999 Federal Environmental Quality Guidelines: Perfluorooctane Sulfonate (PFOS); 2018; https://www.canada.ca/content/dam/eccc/documents/pdf/pded/feqg-pfos/20180620-PFOS-EN.pdf.

Federal Register, Endosulfan: Final product cancellation order. A notice by the Environmental Protection Agency on 11/10/2010. (2010) https://www.federalregister.gov/articles/2010/11/10/2010-28138/endosulfan-final-product-cancellation-order

Free map tools, 2015, Find population on map, http://www.freemaptools.com/2nd-population.htm.

Gewurtz, S. B., Backus, S. M., De Silva, A. O., Ahrens, L., Armellin, A., Evans, M., Fraser, S., Gledhill, M., Guerra, P., Harner, T., Helm, P. A., Hung, H., Khera, N., Kim, M. G., King, M., Lee, S. C., Letcher, R. J., Martin, P., Marvin, C., McGoldrick, D. J., Myers, A. L., Pelletier, M., Pomeroy, J., Reiner, E. J., Rondeau, M., Sauve, M.-C., Sekela, M., Shoeib, M., Smith, D. W., Smyth, S. A., Struger, J., Spry, D., Syrgiannis, J., Waltho, J. (2013) Perfluoroalkyl acids in the Canadian environment: Multi-media assessment of current status and trends, *Environment International*, 59: 183-200.

Gewurtz, S. B.; Bradley, L. E.; Backus, S.; Dove, A.; McGoldrick, D.; Hung, H.; Dryfhout-Clark, H. Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006-2018) Indicate Response to Phase-outs, Regulatory Action, and Variability in Fate and Transport Processes. Environ Sci Technol 2019, 53, (15), 8543-8552.

GMA 2018: AMAP, Environment U. (2019) *Technical Background Report to the Global Mercury Assessment 2018*. Oslo, Norway: 426pp.

Gouin, T., Harner, T., Blanchard, P., Mackay, D. (2005) Passive and active air samplers as complimentary methods for investigating persistent organic pollutants in the great lakes basin. Environmental Science and Technology, 39: 9115–9122.

Government of Canada Prohibition of Certain Toxic Substances Regulations, 2012 (Consolidation); 2018; https://laws-lois.justice.gc.ca/PDF/SOR-2012-285.pdf.

Guo, J., Romanak, K., Westenbroek, S., Hites, R. A., Li, A., Kreis, R., Venier, M., (2017) Up-dated polychlorinated biphenyl mass budget for Lake Michigan. *Environmental Science and Technology*, 51: 12455–12465

Guo, J., Salamova, A., Venier, M., Dryfhout-Clark, H., Alexandrou, N., Backus, S., Bradley, L., Hung, H., Hites, R. A. Atmospheric loadings of persistent organic pollutants to the Great Lakes estimated by the United States' Integrated Atmospheric Deposition and Canada's Great Lakes Basin Monitoring and Surveillance Networks. (2018) *Journal of Great Lakes Research*, 44(4): 670-681.

Hafner, W. D. and R. Hites. 2003. Potential sources of pesticides, PCBs, and PAHs, to the atmosphere of the Great Lakes. *Environmental Science and Technology* 37(17): 3764–3773.

Harner, T., Schuster, J, Sverko, E., Jantunen, L., Lee, S. C., Pozo, K. (2014) Surveillance of new priority chemicals in air under the Global Atmospheric Passive Sampling (GAPS) Network. *Organohalogen Compounds* 76:1309-1312

Hayley Hung, Air Quality Processes Research Section, Environment and Climate Change Canada, personal communication.

Health Canada Pest Management Regulatory Agency, Re-evaluation Note REV2011-01 Discontinuation of endosulfan (2011). Pest Management Regulatory Agency, Health Canada, Ottawa, Canada, 8pp. ISSN: 1925-0649

Hung, H., Alexandrou, N., Dryfhout-Clark, H., Wong, F. (2021) Environment and Climate Change Canada's Great Lakes Basin (GLB) Monitoring and Surveillance Program. In *Global Monitoring Plan for Persistent Organic Pollutants under the Stockholm Convention Article 16 on Effectiveness Evaluation – 3rd Regional Monitoring Report Western Europe and Others Group (WEOG) Region 2021; Annex 8.1a*, UNEP Stockholm Convention on POPs, p. 54-62.
http://chm.pops.int/implementation/globalmonitoringplan/monitoringreports/tabid/525/default.aspx.

Hung, H.; Blanchard, P.; Halsall, C.J.; Bidleman, T.F.; Stern, G.A.; Fellin, P.; Muir, D.C.G.; Barrie, L.A.; Jantunen, L.M.; Helm, P.A.; Ma, J.; Konoplev, A. (2005) Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: results from a decade of monitoring. *Sci. Tot. Environ.*, 342: 119-144.

Hung, H., Katsoyiannis, A., Brorström-Lund, E., Olafsdottir, K., Aas, W., Breivik, K., Bohlin-Nizzetto, P., Sigurdsson, A., Hakola, H., Bossi, R., Skov, H., Sverko, E., Barresi, E., Fellin, P., Wilson, S. (2016). Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.*, 217: 52-61.

Hites, R. A. (2018) Atmospheric concentrations of PCB-11 near the Great Lakes have not de-creased since 2004. *Environmental Science and Technology Letters*, 5: 131-135.

Hites RA, Lehman DC, Salamova A, Venier M. (2021) Temporal environmental hysteresis: A definition and implications for polybrominated diphenyl ethers. *Sci. Tot. Environ.* 753: 141849.

Hites, R.A., Bidleman, T.F. Venier, M. Atmospheric Concentrations of Hexachlorobenzene and Octachlorostyrene Are Uniform across the Great Lakes Region and Have Not Changed Much in 25 Years (2022) Environmental Science & Technology Letters, 9 (8), 660-665.

Hites, R.A., Venier, M. Good News: Some Insecticides Have Been Virtually Eliminated in Air near the Great Lakes 2023) Environmental Science & Technology 2023 57 (6), 2199-2204.

Hites, R.A., Capozzi, S. L., Venier, M. Spatial and temporal trends of chlorinated epoxides in the atmosphere near the North American Great Lakes (2024) Sci. Tot Environ, 907, 167921.

Hu, D., Hornbuckle, K. C. (2010). Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environmental Science and Technology,* 44(8): 2822-2827.

Hung, H., Halsall, C., Ball, H., Bidleman, T., Dachs, J., De Silva, A., Hermanson, M., Kallenborn, R., Muir, D., Sühring, R., Wang, X., Wilson, S. (2022) Climate change influence on the levels and trends of persistent organic pollutants (POPs) and chemicals of emerging Arctic concern (CEACs) in the Arctic physical environment – a review. Environmental Science: Processes & Impacts. 24: 1577.

Interstate Technology & Regulatory Council PFAS - Per- and polyfluoroalkyl substances: Regulations, guidance, and advisories; 2019; http://pfas-1.itrcweb.org/fact-sheets/.

Kwok, K. Y., Taniyasu, S., Yeung, L. W. Y., Murphy, M. B., Lam, P. K. S., Horii, Y., Kannan, K., Petrick, G., Sinha, R. K., Yamashita, N. (2010). Flux of perfluorinated chemicals through wet deposition in Japan, the United States, and Several Other Countries. *Environmental Science and Technology*, 44: 7043-7049.

Khairy, M., Muir, D., Teixeira, C., Lohmann, R. (2015). Spatial distribution, air–water fugacity ratios and source apportionment of polychlorinated biphenyls in the lower Great Lakes Basin. *Environmental Science and Technology*, 49(23): 13787-13797.

Lee, S. C., Sverko, E., Harner, T., Pozo, K., Barresi, E., Schachtschneider, J., Zaruk, D., DeJong, M., Narayan, J. (2016). Retrospective analysis of "new" flame retardants in the global atmosphere under the GAPS Network. *Environ. Pollut.,* 217: 62-69.

Lepak, R. F., Yin, R., Krabbenhoft, D. P., Ogorek, J. M., DeWild, J. F., Holsen, T. M., Hurley, J. P. (2015). Use of stable isotope signatures to determine mercury sources in the Great Lakes. *Environmental Science and Technology Letters*, 2: 335–341.

Lepak, R. F., Janssen, S. E., Yin, R., Krabbenhoft, D. P., Hurley, J. P. (2018). Factors Affecting Mercury Stable Isotopic Distribution in Piscivorous Fish of the Laurentian Great Lakes. *Environmental Science and Technology*, 52: 2768-2776.

Lepak, R. F., Hoffman, J. C., Janssen, S. E., Krabbenhoft, D. P., Ogorek, J. M., DeWild, J. F., Tate, M. T., Babiarz, C. L., Yin, R., Murphy, E. W., Engstrom, D. R., Hurley, J. P. (2019) Mercury source changes and food web shifts alter contamination signatures of predatory fish from Lake Michigan. *Proceedings of the National Academy of Sciences (PNAS)*, 116: 23600-23608.

Li, W.-L., Hung, H., Kasperkiewicz, A., Shunthirasingham, C., Chisamore, J., Rabu, M., Park, R., Huo, C.-Y., Lee, P., Dryfhout-Clark, H. Assessing the shifts in atmospheric per- and polyfluoroalkyl substances (PFAS) levels in the Great Lakes and implications for the environmental transport and fate. ES&T Air, under review.

Li, W., Dryfhout-Clark, H., Hung, H., (2020). PM10-bound trace elements in the Great Lakes Basin (1988–2017) indicates effectiveness of regulatory actions, variations in sources and reduction in human health risks. *Environ. Internat.*, 143: 106008.

Li, W., Park, R., Alexandrou, N., Dryfhout-Clark, H., Brice, K., Hung, H., (2021). Multi-year analyses reveal different trends, sources, and implications for source-related human health risks of atmospheric polycyclic aromatic hydrocarbons in the Canadian Great Lakes Basin. *Environ. Sci. Technol.*, 55:2254-2264.

Liu, L.-Y., Kukučka, P., Venier, M., Salamova, A., Klánova, J., Hites, R.A., (2014) Differences in spatiotemporal variations of atmospheric PAH levels between North America and Europe: Data from two air monitoring projects. *Environment International*, 64: 48–55.

Liu. L. Y., Salamova, A., Venier, M., Hites, R. A. (2016). Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005-2013. *Environment International*, 92-93: 442-449.

Ma, J., Hung, H., Blanchard, P. (2004). How do climate fluctuations affect persistent organic pollutant distribution in North America? Evidence from a decade of air monitoring. Environmental Science and Technology, 38: 2538-2543.

McDonough, C.A., Khairy, M.A., Muir, D.C.G., Lohmann, R. (2014). Significance of Population Centers as Sources of Gaseous and Dissolved PAHs in the Lower Great Lakes. *Environmental Science and Technology*, 48(14): 7789-7797.

McGee, S.P., Konstantinov, A., Stapleton, H.M., Volz, D.C., 2013. Aryl phosphate esters within a major pentaBDE replacement product induce cardiotoxicity in developing zebrafish embryos: potential role of the aryl hydrocarbon receptor. Toxicol. Sci. 133, 144-156. https://doi.org/10.1093/toxsci/kft020.

Martin, J.W., D.C.G. Muir, C.A. Moody, D.A. Ellis, W.C. Kwan, K.R. Solomon and S.A. Mabury. 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. Anal. Chem. 74: 584–590.

Melymuk, L; Robson, M; Helm, P; Diamond, M. PCBs, PBDEs, and PAHs in Toronto air: spatial and seasonal trends and implications for contaminant transport. Sci. Total Environ., 2012, 429, 272-280

Miriam L. Diamond, Lisa Melymuk, Susan A. Csiszar, and Matthew Robson (2010). Estimation of PCB Stocks, Emissions, and Urban Fate: Will our Policies Reduce Concentrations and Exposure? Environmental Science & Technology 44 (8), 2777-2783. DOI: 10.1021/es9012036

Müller, C. E., Spiess, N., Gerecke, A. C., Scheringer, M., Hungerbühler, K. (2011). Quantifying diffuse and point inputs of perfluoroalkyl acids in a nonindustrial river catchment. *Environmental Science and Technology*, 45: 9901-9909.

Olson C., Fakhraei H., Driscoll C., Mercury Emissions, Atmospheric Concentrations, and Wet Deposition across the Conterminous United States: Changes over 20 Years of Monitoring. Environmental Science & Technology Letters 2020 7 (6), 376-381

Olukunle, O. I., Venier, M., Hites, R.A., Salamova, A. Atmospheric concentrations of hexabromocy-clododecane (HBCDD) in the Great Lakes region. Chemosphere, 2018, 200, 464-470.

Ontario Ministry of Energy. The end of coal. An Ontario primer on modernizing electricity supply (2014). ISBN 978-1-4606-6765-1 HTML. http://www.energy.gov.on.ca/en/files/2015/11/End-of-Coal-EN-web.pdf

Pan, Y., Tsang, D. C. W., Wang, Y., Li, Y., Yang, X. (2016) The photodegradation of polybrominated diphenyl ethers (PBDEs) in various environmental matrices: Kinetics and mechanisms. *Chemical Engineering Journal* 297: 74-96.

Prestbo, E.M., Gay, D.A. (2009) Wet deposition of mercury in the U.S. and Canada, 1996–2005: Results and analysis of the NADP mercury deposition network (MDN). *Atmospheric Environment* 43: 4223–4233.

Robson, M; Melymuk, L; Csiszar, SA; Giang, A; Diamond, ML; Helm PA. Continuing sources of PCBs: The

significance of building sealants. Environ. Internat., 2010, 36, 506-513.

Risch, M.R., Gay, D.A., Fowler, K.K., Keeler, G.J., Backus, S.M., Blanchard, P., Barres, J.A., Dvonch, J.T. (2012) Spatial patterns and temporal trends in mercury concentrations, precipitation depths, and mercury wet deposition

in the North American Great Lakes region, 2002–2008. *Environmental Pollution*, 161: 261–271.

Ruge, Z., Muir, D., Helm, P., Lohmann, R. (2015) Concentrations, trends, and air-water exchange of PAHs and PBDEs derived from passive samplers in Lake Superior in 2011. *Environmental Science and Technology*, 49(23):13777-86

Salamova, A., Hites, R. (2011) Discontinued and alternative brominated flame retardants in the atmosphere and precipitation from the great lakes basin. *Environmental Science and Technology*, 45, 8698–8706.

Salamova, A. Venier, M. Hites, R. A. (2015). Revised temporal trends of persistent organic pollutant concentrations in air around the Great Lakes. *Environmental Science and Technology Letters*, 2: 20-25.

Salamova, A., Peverly, A. A., Venier, M., Hites, R. A. (2016). Spatial and temporal trends of particle phase organophosphate ester concentrations in the atmosphere of the Great Lakes. *Environmental Science and Technology* 50: 13249-13255.

Sean Backus and Lisa Bradley, Water Science and Technology Branch, Environment and Climate Change Canada, personal communication.

Shanahan, C. E., Spak, S. N., Martinez, A., Hornbuckle, K. C. (2015) Inventory of PCBs in Chicago and opportunities for reduction in airborne emissions and human exposure. *Environmental Science and Technology* 49: 13878–13888.

Shunthirasingham, C., Alexandrou, N., Brice, K. A., Dryfhout-Clark, H., Su, K., Shin, C., Park, R., Pajda, A., Noronha, R. and Hung, H. (2018) Temporal trends of halogenated flame retardants in the atmosphere of the Canadian Great Lakes Basin (2005–2014). *Environmental Science: Processes and Impacts*, 20: 469-479.

Shunthirasingham, C., Gawor, A., Hung, H., Brice, K. A., Su, K., Alexandrou, N., Dryfhout-Clark, H., Backus, S., Sverko, E., Shin, C., Park, R., Noronha, R. (2016) Atmospheric Concentrations and Loadings of Organochlorine Pesticides and Polychlorinated Biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and Temporal Analysis (1992-2012). *Environmental Pollution*, 217: 124-133.

St. Louis, V. L., Graydon, J. A., Lehnherr, I., Amos, H. M., Sunderland, E. M., St. Pierre, K. A., Emmerton, C. A., Sandilands, K., Tate, M., Steffen, A., Humphreys, E. R. (2019) Atmospheric concentrations and wet/dry loadings of mercury at the remote experimental lakes area, northwestern ontario, Canada. *Environmental Science and Technology*, 53: 8017-8026.

Stapleton, H.M., Allen, J.G., Kelly, S.M., Konstantinov, A., Klosterhaus, S., Watkins, D., McClean, M.D., Webster, T.F., 2008. Alternate and new brominated flame retardants detected in U.S. house dust. Environ. Sci. Technol. 42, 6910-6916. https://doi.org/10.1021/es801070p.

Tate, M. T., Janssen, S. E., Lepak, R. F., Flucke, L., Krabbenhoft, D. P. (2023) National-scale assessment of total gaseous mercury isotopes across the United States. *Journal of Geophysical Research: PAtmospheres,* 128, e2022JD038276.

Tomy GT, Stern GA, Muir DCG, Fisk AT, Cymbalisty CD, Westmore JB. (1997) Quantifying C10–C13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Anal Chem*. 69:2762-71

Totten, L. A., Brunciak, P. A., Gigliotti, C. L., Dachs, J., Glenn, T. R. 4th, Nelson, E. D., Eisenreich, S. J. (2001). Dynamic air-water exchange of polychlorinated biphenyls in the New York-New Jersey Harbor Estuary. *Environmental Science & Technology*, 35(19): 3834-3840.

U.S. Environmental Protection Agency (USEPA) (2021). Great Lakes Integrated Atmospheric Deposition Network Program Technical Report. Publication No. EPA # 905-R-21-002.

USGS (2017) Estimated annual agricultural pesticide use https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2014&map=ENDOSULFAN&hilo=L&disp=Endosulfan (accessed 10/15/2018)

Venier, M, and Hites R. A. (2014). DDT and HCH, two discontinued organochlorine insecticides in the Great Lakes region: Isomer trends and sources, *Environment International* 69: 159–165

Venier, M., Hung, H., Tych, W., Hites, R. A. (2012) Temporal trends of persistent organic pollutants: A comparison of different time series models. Environ. Sci. Technol., 46(7): 3928-34.

Venier, M, Ferrario, J and Hites, R. A. (2009) Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Atmosphere Around the Great Lakes, *Environmental Science & Technology*, 43 (4), 1036–1041.

Venier, M., Hites, R. A. (2010a) Regression model of partial pressures of PCBs, PAHs, and organochlorine pesticides in the Great Lakes' atmosphere. *Environmental Science &Technology* 44 (2): 618–623.

Venier, M., Hites, R. A. (2010b) Time trend analysis of atmospheric POPs concentrations in the Great Lakes region since 1990. *Environmental Science and Technology* 44 (21): 8050–8055.

Venier, M., Salamova, A., Hites, R.A. (2015) Halogenated flame retardants in the Great Lakes environment. *Accounts Chem. Research*, 48: 1853-1861.

Venier, M., Salamova, A., Hites, R.A. (2016) Temporal trends of persistent organic pollutant concentrations in precipitation around the Great Lakes, *Environmental Pollution* 217: 143-148.

Wang, Z. Y.; Cousins, I. T.; Scheringer, M.; Hungerbuhler, K. (2013) Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environ. Int.* 60: 242–248.

Wang, Z., Xie, Z., Möller, A., Mi, W., Wolschke, H., Ebinghaus, R. (2014). Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast. *Atmospheric Environment*. 95: 207-213.

Wang S, Salamova A, Venier M. Occurrence, Spatial, and Seasonal Variations, and Gas–Particle Partitioning of Atmospheric Current-Use Pesticides (CUPs) in the Great Lakes Basin. Environmental Science & Technology 2021; 55: 3539-3548.

Weiss-Penzias P. S., Gay D. A., Brigham M. E., Parsons M. T., Gustin M. S., ter Schure A. 2016. Trends in mercury wet deposition and mercury air concentrations across the U.S. and Canada. *Science of the Total Environment*. 568: 546-556.

Wethington, D. M. 3rd, Hornbuckle, K. C. (2005). Milwaukee, WI, as a source of atmospheric PCBs to Lake Michigan. *Environmental Science & Technology*, 39 (1), 57-63.

Wu, Y., Venier., M., Salamova, A. Spatioseasonal Variations and Partitioning Behavior of Organophosphate Esters in the Great Lakes Atmosphere (2020) Environmental Science & Technology, 54 (9), 5400-5408.

Wu Y, Salamova A, Venier M. Using diagnostic ratios to characterize sources of polycyclic aromatic hydrocarbons in

the Great Lakes atmosphere. Sci Total Environ. 2021 Mar 20;761:143240.

Xia, C., Capozzi, S. L., Romanak, K.A., Lehman, D. C., Dove, A., Richardson, V., Greenberg, T., McGoldrick, D., Venier., M. (2024) The ins and outs of PFAS in the Great Lakes: the role of atmospheric deposition. Environmental Science & Technology, under review.

Zhang, Y., Jacob, D.J., Horowitz, H.M., Chen, L., Amos, H.M., Krabbenhoft, D.P., Slemr, F., St. Louis, V.L., Sunderland, E.M. (2016). Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions. *Proceedings of the National Academy of Sciences of the United States of America*, 113 (3): 526-531.

List of Tables

Table 1. Half-lives ($t_{1/2}$) of PCBs in air at Point Petre, Burnt Island and Egbert

Source: Hung et al., 2021

Table 2. Half-lives ($t_{1/2}$) of PBDE in air at Point Petre and Burnt Island (Wong et al., *in prep;* Shunthirasingham et al., 2018)

Source: Wong et al., *in prep;* Shunthirasingham et al., 2018

Table 3. Half-lives ($t_{1/2}$) of OCPs in air at Point Petre, Burnt Island and Egbert

Source: Hung et al., 2021

Table 4. Half-lives of non-PBDE HFRs in air at Point Petre and Burnt Island

Source: Shunthirasingham et al., 2018

List of Figures

Figure 1. Site map of Integrated Atmospheric Deposition Network (IADN) and Great Lakes Basin (GLB).

Source: Modified from USEPA 2021

Figure 2. Temporal trends of the annual median atmospheric concentrations (in pg/m^3) of total polychlorinated biphenyls (Σ2PCBs) in the vapor phase at IADN stations. In each plot, the red line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated, in years.

Source: USEPA

Figure 3. Time trends (pink line), seasonal cycles (black line) and measurements (blue cross) of sum of 26 PCBs in air at (a) Point Petre, (b) Burnt Island and (c) Egbert. Time trends and seasonal cycles are generated by the Digital Filtration method.

Source: Hung et al. 2021

Figure 4. Fingerprints of the three PBDE factors resolved from PMF modeling of total atmospheric PBDE concentrations collected at six IADN sampling stations between 2005 and 2019.

Source: Capozzi et al., 2022

Figure 5. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of BDE-28, -47, -99 and -209 in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method.

Source: Updated from Hung et al. 2021, data from Environment and Climate Change Canada

Figure 6. Time trends of PFOS (right) and PFOA (left) in precipitation collected from Point Petre, Burnt Island/Evansville, and Sibley. The lines showing seasonal cycles and trends were derived from application of the Digital Filtration model on the precipitation data.

Source: Hung et al. 2021, Li et al., under review

Figure 7. Total mercury concentration precipitation (left) and total mercury wet deposition (right) in the Great Lakes Area. Top panels for 2003 and bottom panels for 2022.

Source: NADP http://nadp.slh.wisc.edu/MDN/

Figure 8. Time trend (red line), seasonal cycle (black line) and measurements (blue cross) of HBCDD in air at Point Petre. The HBCDD are the sum of the γ-, β-, and γ-isomers. Time trends and seasonal cycles are generated by the Digital Filtration method.

Source: Environment and Climate Change Canada

Figure 9. Halving times in years for dieldrin, heptachlor epoxide, and oxychlordane at six sites on the shores of the Great Lakes. The error bars show the standard errors of the coefficients as determined from linear regressions. "NS" indicates that the time coefficient (a3) was not significant at $P < 0.05$.

Source: Hites et al., 2024

Figure 10. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of α-HCH, γ-HCH, *trans*-chlordane (TC), *cis*-chlordane (CC), α-endosulfan and p,p'-DDT in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method.

Source: Hung et al. 2021

Figure 11a. Temporal trends of the annual median atmospheric concentrations (in pg/m^3) of α- and λ-hexachlorocyclohexane (summed together) in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated.

Source: USEPA

Figure 11b. Annual geometric mean concentrations (in pg/m3) of ∑DDT, ∑Chlor, ∑Endo, lindane (γ-HCH), α-HCH, HCB, and OCS as a function of the six sampling sites on the shores of the North American Great Lakes and sampling year. The symbol color codes are red Chicago, pink Cleveland, cyan Sturgeon Point, yellow Sleeping Bear Dunes and Point Petre, and green Eagle Harbor. The black line shows, in each case, a regression of all the data for each compound(s) as a function of year. The halving times (t1/2) are given for each site except the –6.2 year value for ∑Endo is the doubling time in 1990.

Source : Hites and Venier, EST, 2023, DOI: doi=10.1021/acs.est.2c08318

Figure 12. Temporal trends of the annual median atmospheric concentration (in pg/m^3) of total endosulfans (sum of endosulfan I, endosulfan II and endosulfan sulfate) in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time is calculated.

Source: USEPA

Figure 13. Temporal trends of the annual median atmospheric concentration (in pg/m^3) of total DDTs in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated.

Source: USEPA

Figure 14. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of anti- and syn-DDC-CO, DBDPE, EHTBB, HBBz and PBT in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method.

Source: Environment and Climate Change Canada

Figure 15. Time trends of PFBA (left) and PFHxA (right) in precipitation collected from Point Petre, Burnt Island/Evansville, and Sibley. The lines showing seasonal cycles and trends were derived from application of the Digital Filtration method on the precipitation data.

Source: Environment and Climate Change Canada

Figure 16. Halving ($t_{1/2}$) and doubling (t_2) times of PAHs in air collected from Burnt Island (BNT), Egbert (EGB) and Point Petre (PPT). PPT-36d interval represents rates of change for PPT site using consistent 36-day interval for the pre-2012 data. Otherwise, 12-day interval sampling data was used for PPT.Only significant increasing or decreasing trends are presented. List of abbreviations: Acenaphthene (Ace), Anthanthrene (Anthan), Anthracene (Anthra), Benz[a]anthracene, (BaA),Benzo[a]pyrene (BaP),Benzo[b]fluoranthene (BbF), Benzo[e]pyrene (BeP),benzo[g,h,i]fluoranthene (BghiF), Benzo[g,h,i]perylene (BghiP),benzo[k]fluoranthene (BkF), Chrysene (Chr), Coronene (Coron), Dibenz[a,c]anthracene (DacA), Dibenz[a,h]anthracene (DahA), Fluorene (Fluor), Fluoranthene (Fluort), Indeno[1,2,3-c-d]pyrene (Ind), Phenanthrene (Phe), Pyrene (Pyr), Retene (Ret), Triphenylene (Trip).

Source: Li et al., 2021

Figure 17. Halving ($t_{1/2}$) and doubling (t_2) times of metals in Burnt Island (BNT), Egbert (EGB) and Point Petre (PPT). List of abbreviations: Aluminum (Al), arsenic (As), barium (Ba), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn).

Source: Li et al., 2020

Last Updated

State of the Great Lakes 2025 Report

Table 1. Half-lives ($t_{1/2}$) of PCBs in air at Point Petre, Burnt Island and Egbert (Source: Hung et al., 2021)

PCBs	**Period**	**$\sum_{26}$PCBs**		**18**		**28/31**		**52**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2022	17	0.91	9.4	0.94	22	0.74	15	0.84
Burnt Island (Lake Huron)	1992-2013	32	0.50	8.1	0.93	24	0.59	19	0.80
Egbert (Lake Huron)	1995-2006	54	0.09	9.4	0.48	22	0.21	22	0.32
		101		**118**		**153**		**180**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2022	14	0.82	38	0.15	61	0.06	94	0.02
Burnt Island (Lake Huron)	1992-2012	27	0.72	19	0.51	30	0.55	8.9	0.61
Egbert (Lake Huron)	1995-2006	-	-	12	0.54	19	0.42	21	0.52

Table 2. Half-lives ($t_{1/2}$) of PBDE in air at Point Petre and Burnt Island (Wong et al., *in prep;* Shunthirasingham et al., 2018)

	Point Petre (2005-2022)		**Burnt Island** (2005-2013)	
	$t_{1/2}$	**r^2**	**$t_{1/2}$**	**r^2**
BDE28	47	0.00	26	0.36
BDE47	7	0.13	-23	0.39
BDE99	7	0.13	13	0.44
BDE209	7	0.07	5.7	0.96

Table 3. Half-lives ($t_{1/2}$) of OCPs in air at Point Petre, Burnt Island and Egbert (Source: Hung et al., 2021)

OCPs	**Period**	**aldrin**		**α-HCH**		**γ-HCH**		***c*-chlordane**		***t*-chlordane**		***t*-nonachlor**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2022	5.7	0.35	4.9	0.85	4.7	0.64	12	0.17	10	0.23	13	0.12
Burnt Island (Lake Huron)	1992-2012	7.6	0.61	4.9	0.99	4.7	0.94	11	0.83	12	0.95	13	0.92
Egbert (Lake Huron)	1995-2006	7.1	0.81	4.2	0.98	4.7	0.87	34	0.25	31	0.26	52	0.16
OCPs	**Period**	**p,p'-DDT**		**p,p'-DDE**		**p,p'-DDD**		**o,p'-DDT**		**o,p'-DDE**		**Dieldrin**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2022	10	0.17	12	0.10					13	0.13	12	0.16
Burnt Island (Lake Huron)	1992-2012	7.4	0.94	9.6	0.94	9.5	0.86	9.3	0.88	7.2	0.98	10	0.94
Egbert (Lake Huron)	1995-2006	12	0.49	38	0.10	12	0.75	28	0.22	14	0.87	18	0.41

OCPs	**Period**	**α-endosulfan**		**β-endosulfan**		**endosulfan sulfate**		**heptachlor**		**heptachlor epoxide**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2022	6.5	0.15	6.4	0.14	6.3	0.09	5.8	0.44	7.3	0.33
Burnt Island (Lake Huron)	1992-2012	13	0.62	11	0.78	10	0.61	8.6	0.52	5.8	0.87
Egbert (Lake Huron)	1995-2006	38	0.1	28	0.10	4.5	0.96	8.3	0.33	12	0.82

OCPs	**Period**	**Oxychlordane**		**mirex**		**Photo-mirex**	
Station		**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**	**$t_{1/2}$**	**r^2**
Point Petre (Lake Ontario)	1992-2017	11	0.17	15	0.24	9.5	0.41
Burnt Island (Lake Huron)	1992-2012	12	0.90	28	0.16	6.1	0.76

Egbert (Lake Huron)	1995-2006	71	0.10	8.0	0.80	4.6	0.88

Table 4. Half-lives of non-PBDE HFRs in air at Point Petre and Burnt Island (Shunthirasingham et al., 2018)

	Point Petre (2005-2022)		**Burnt Island** (2005-2013)	
	$t_{1/2}$	**r^2**	**$t_{1/2}$**	**r^2**
TBP-AE	5	0.14	24	0.10
TBP-BAE	4	0.43		
PBT	14	0.04	21	0.99
TBP-DBPE	-6	0.17		
HBBz	5	0.17	27	0.11
PBEB	10	0.15		
DBDPE	-2	0.21		
EH-TBB	3	0.41		
HBCDD	-2	0.63		
anti-DCC-CO	3	0.21	3.4	0.36
syn-DCC-CO	4	0.18	-7.6	0.21

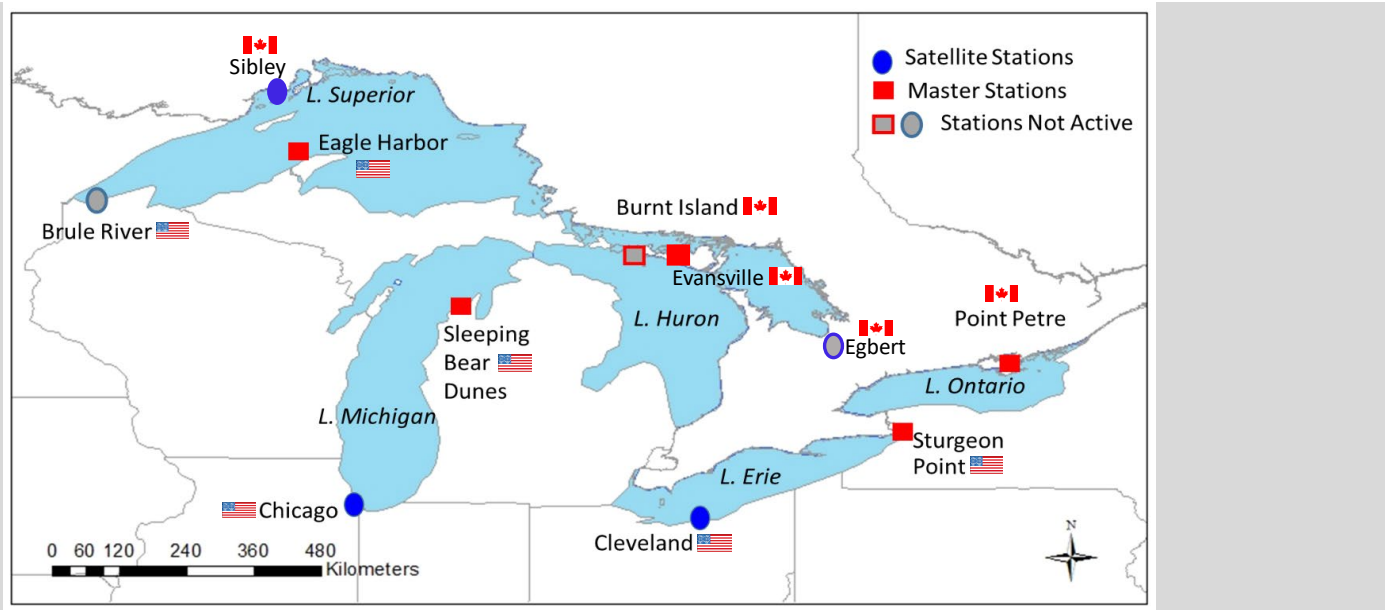

Figure 1. Site map of Integrated Atmospheric Deposition Network (IADN) and Great Lakes Basin (GLB). (Source: Modified from USEPA 2021)

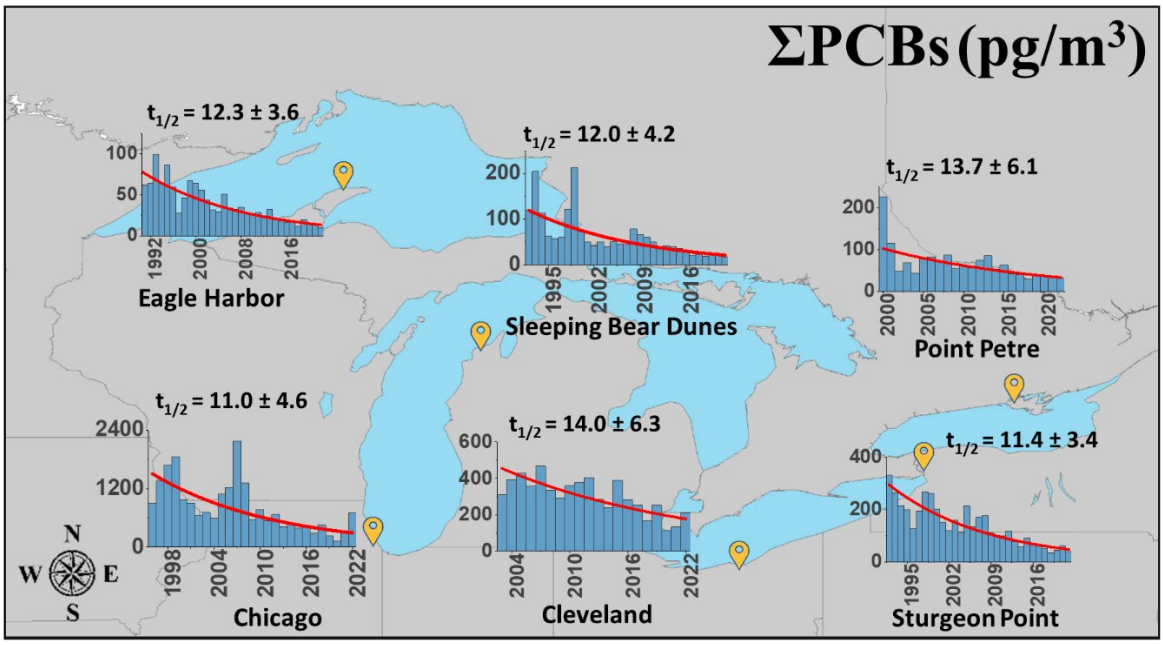

Figure 2. Temporal trends of the annual median atmospheric concentrations (in pg/m^3) of total polychlorinated biphenyls (Σ2PCBs) in the vapor phase at IADN stations. In each plot, the red line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated, in years. Source: USEPA.

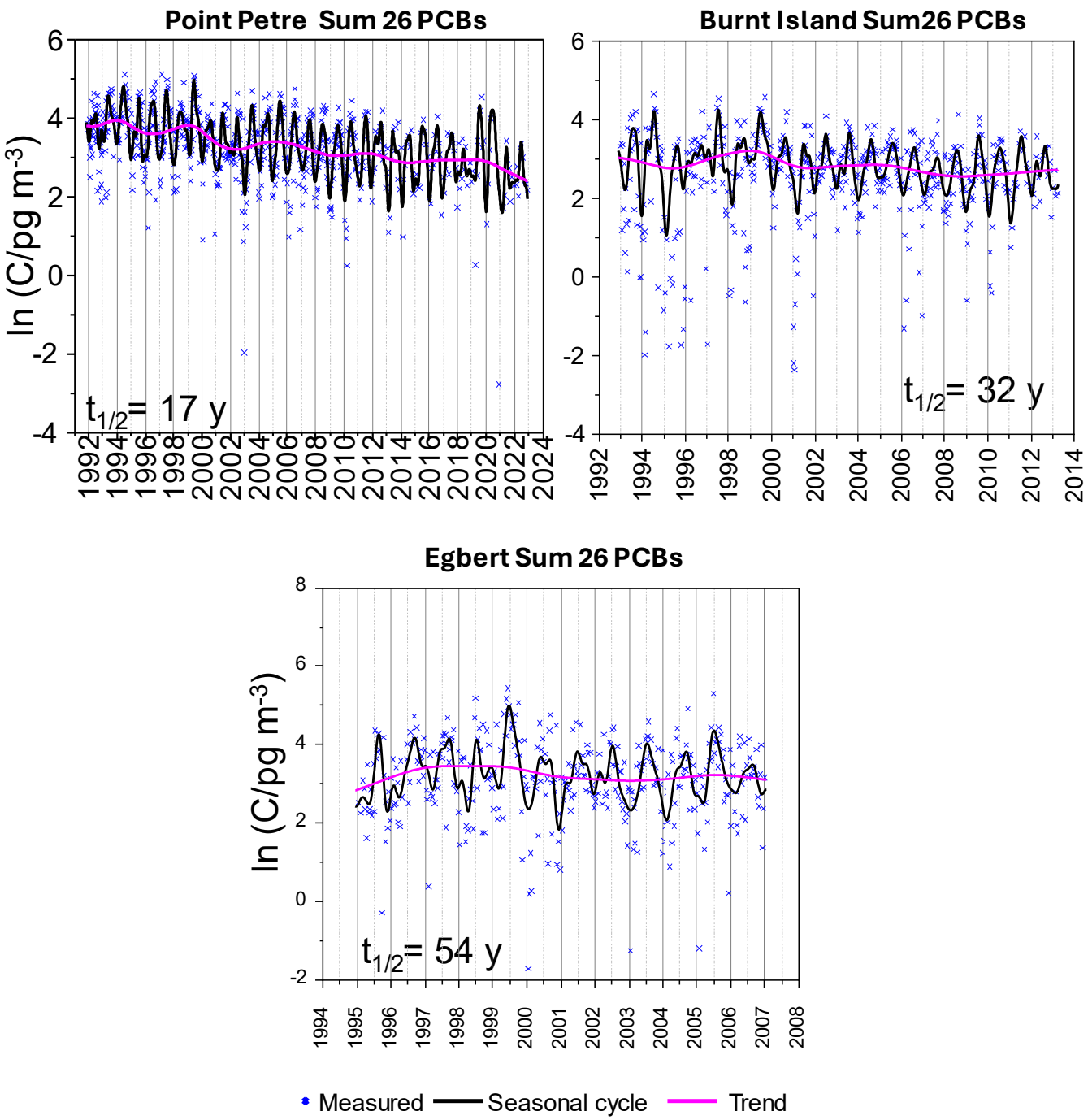

Figure 3. Time trends (pink line), seasonal cycles (black line) and measurements (blue cross) of sum of 26 PCBs in air at (a) Point Petre, (b) Burnt Island and (c) Egbert. Time trends and seasonal cycles are generated by the Digital Filtration method. Source: Hung et al. 2021.

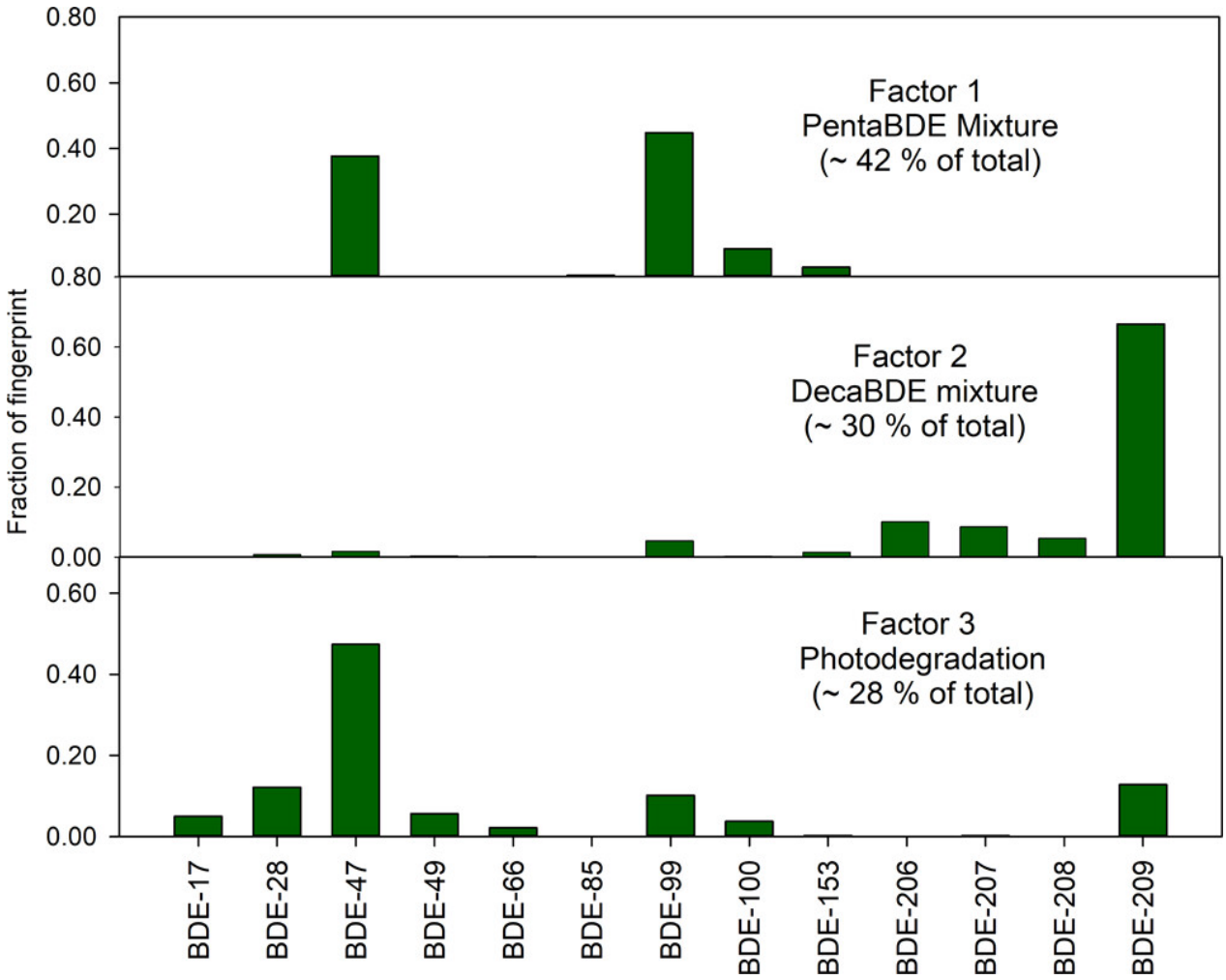

Figure 4. Fingerprints of the three PBDE factors resolved from PMF modeling of total atmospheric PBDE concentrations collected at six IADN sampling stations between 2005 and 2019. Source: Capozzi et al., 2022.

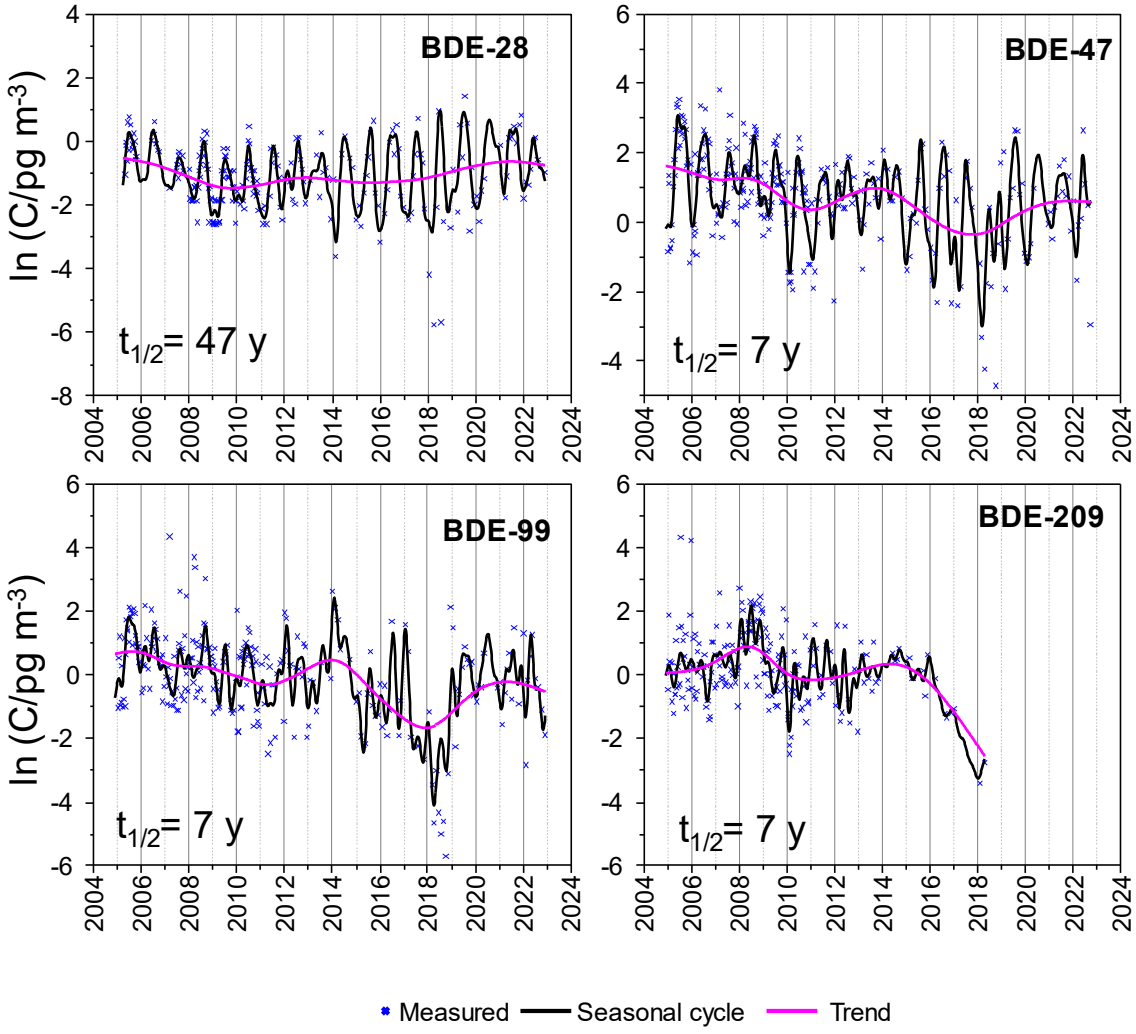

Figure 5. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of BDE-28, -47, -99 and -209 in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method (Source: Hung et al. 2021). Source: Updated from Hung et al. 2021, data from Environment and Climate Change Canada.

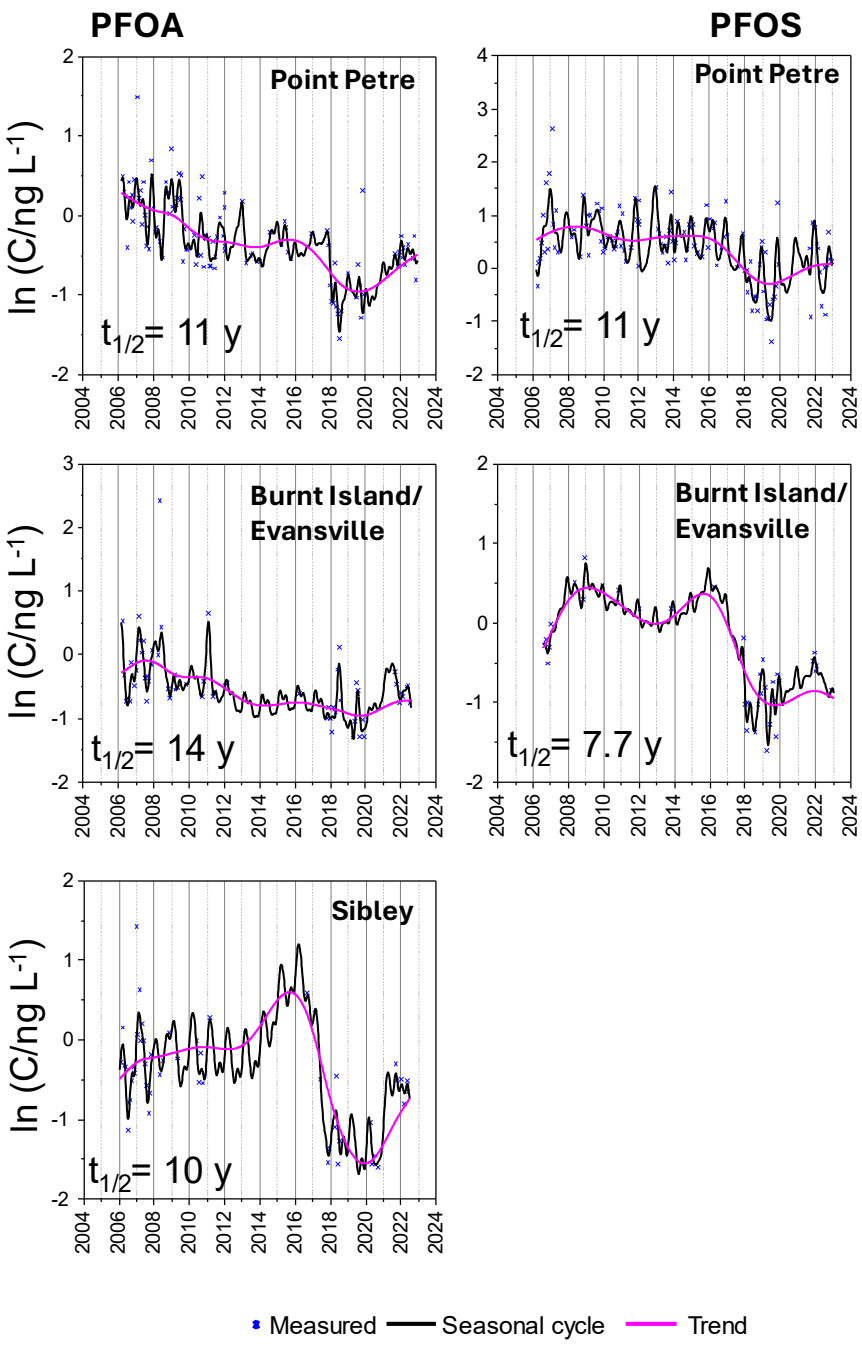

Figure 6. Time trends of PFOS (right) and PFOA (left) in precipitation collected from Point Petre, Burnt Island/Evansville, and Sibley. The lines showing seasonal cycles and trends were derived from application of the Digital Filtration model on the precipitation data. Source: Hung et al. 2021, Li et al., under review.

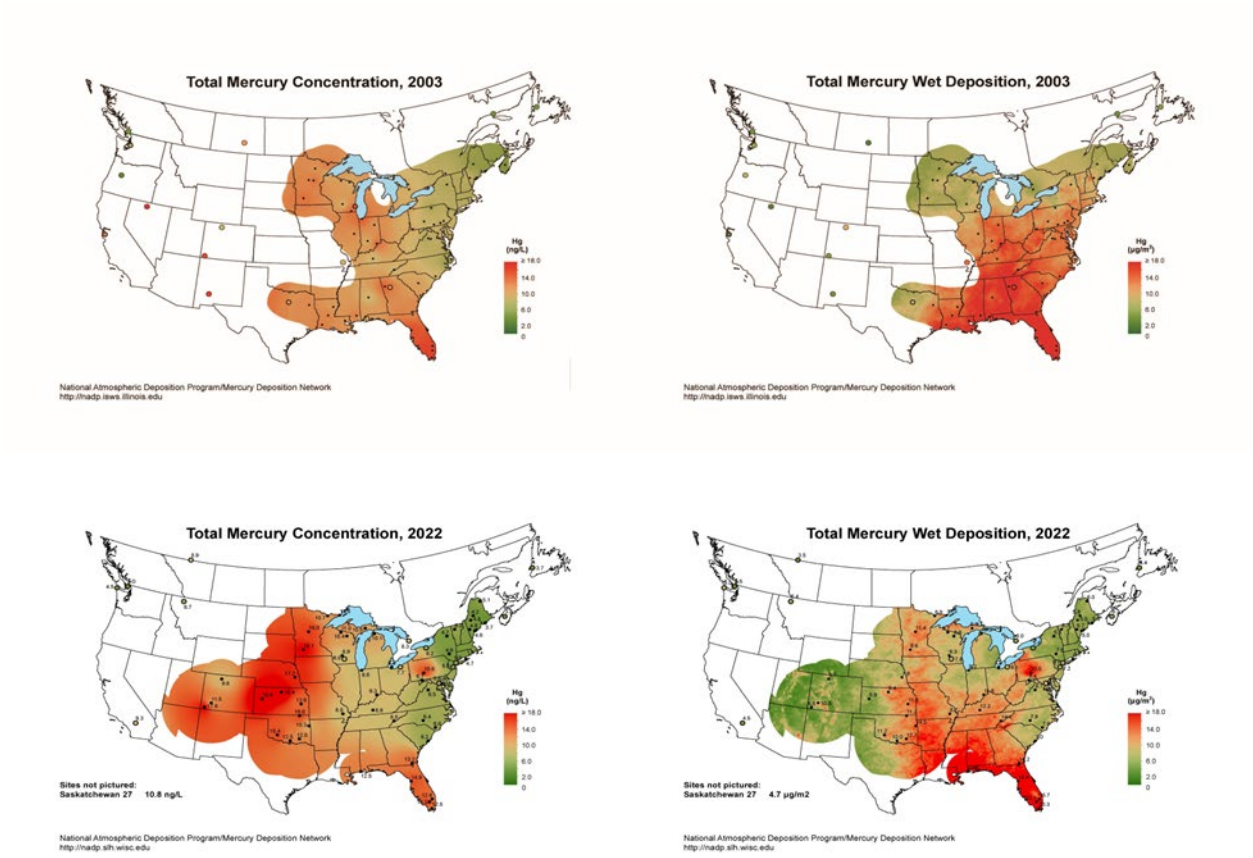

Figure 7. Total mercury concentration precipitation (left) and total mercury wet deposition (right) in the Great Lakes Area. Top panels for 2003 and bottom panels for 2022. Source: NADP http://nadp.slh.wisc.edu/MDN/.

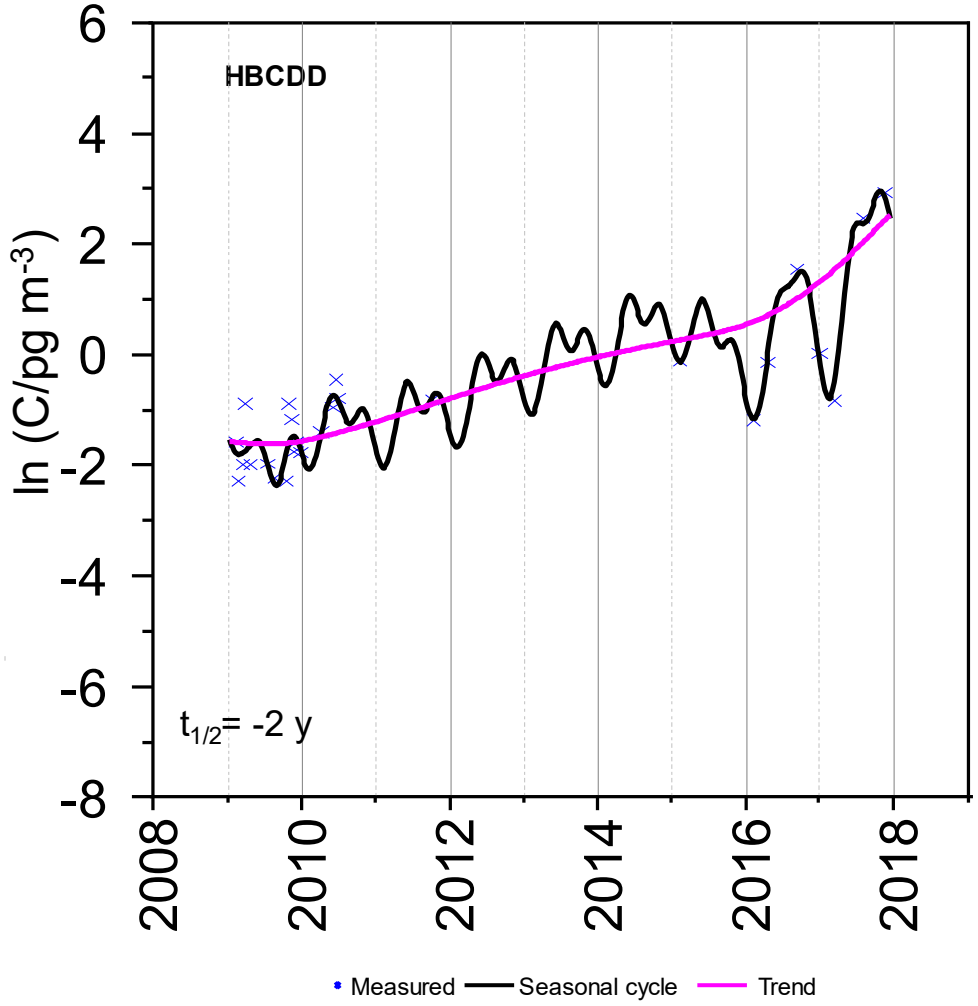

Figure 8. Time trend (red line), seasonal cycle (black line) and measurements (blue cross) of HBCDD in air at Point Petre. The HBCDD are the sum of the γ-, β-, and γ-isomers. Time trends and seasonal cycles are generated by the Digital Filtration method. Source: Environment and Climate Change Canada.

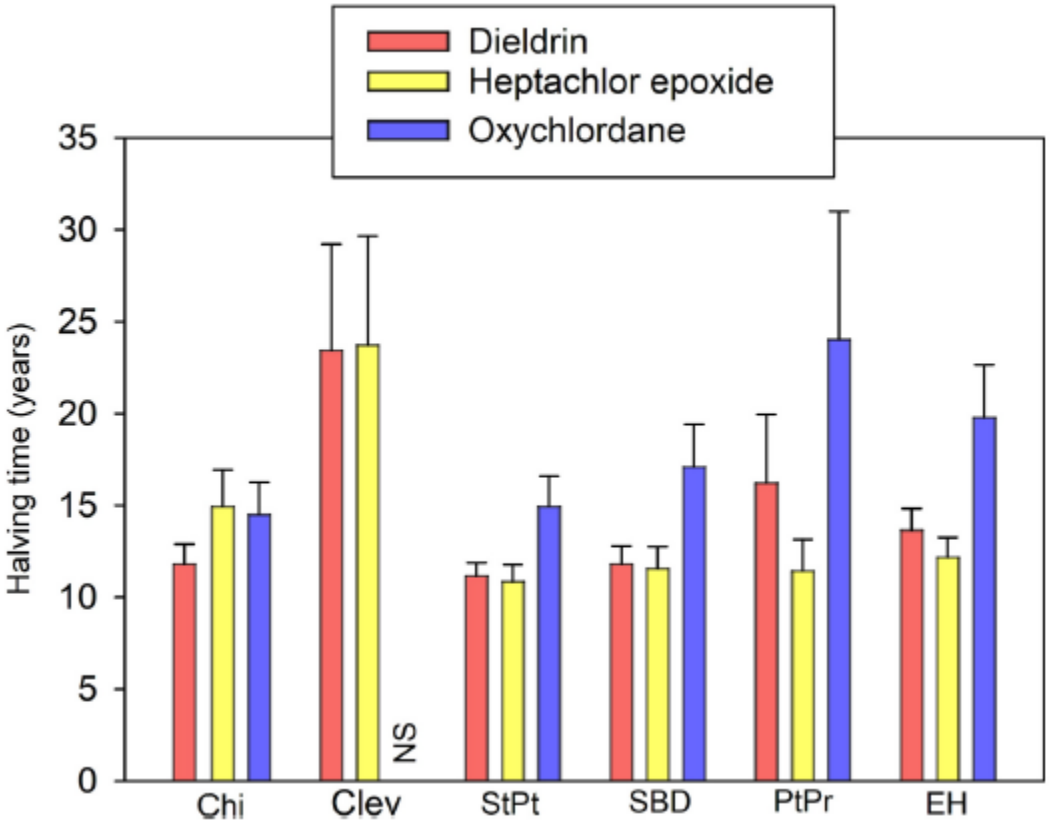

Figure 9. Halving times in years for dieldrin, heptachlor epoxide, and oxychlordane at six sites on the shores of the Great Lakes. The error bars show the standard errors of the coefficients as determined from linear regressions. "NS" indicates that the time coefficient (a3) was not significant at $P < 0.05$. Source: Hites et al., 2024.

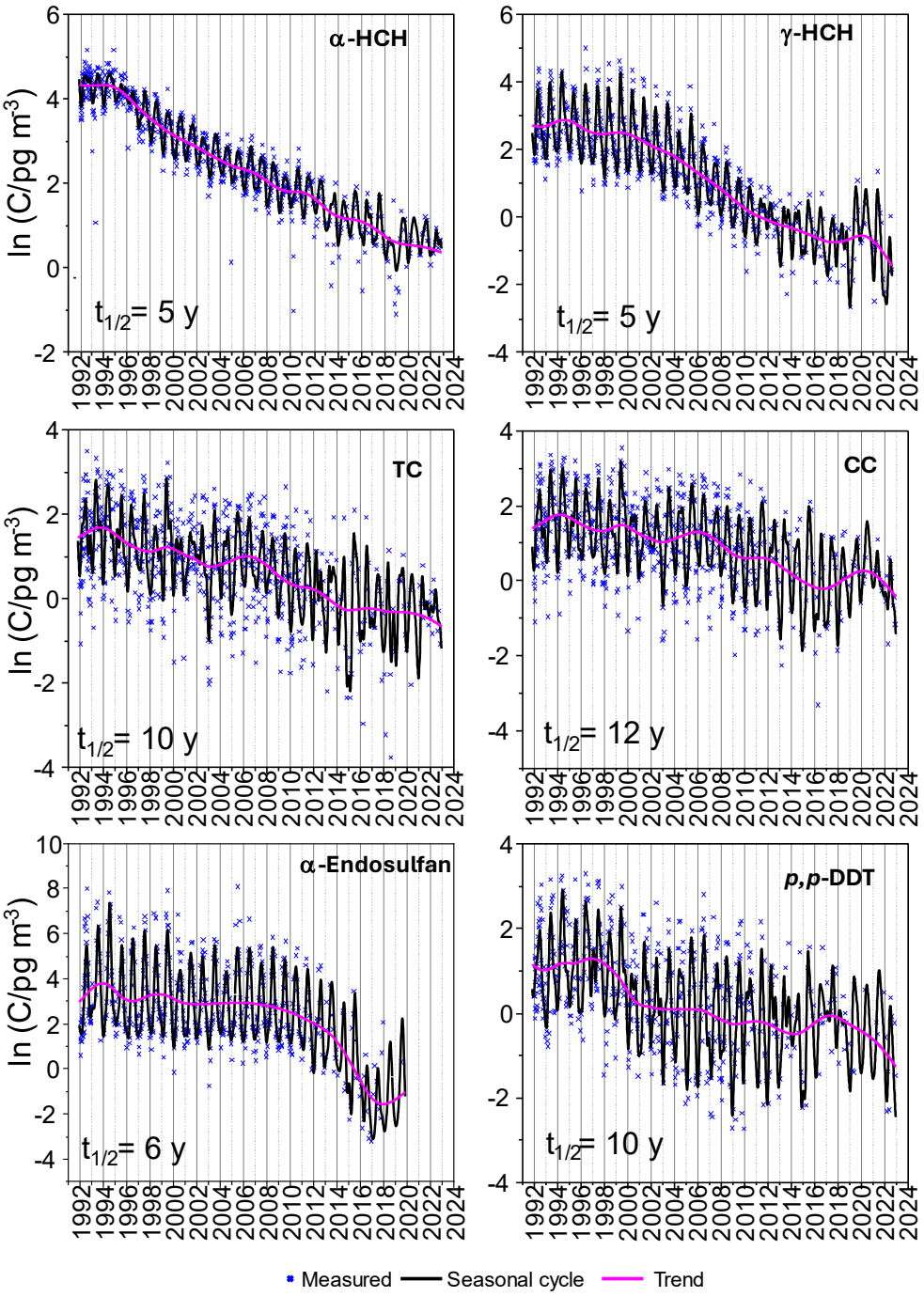

Figure 10. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of α-HCH, γ-HCH, *trans*-chlordane (TC), *cis*-chlordane (CC), α-endosulfan and p,p'-DDT in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method. Source: Hung et al. 2021.

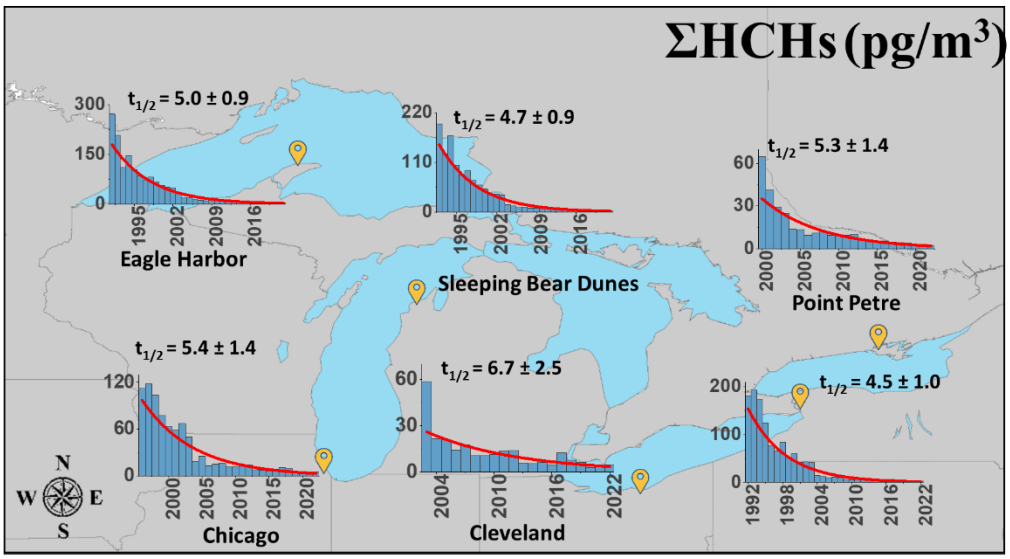

Figure 11a. Temporal trends of the annual median atmospheric concentrations (in pg/m^3) of α- and λ-hexachlorocyclohexane (summed together) in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated. Source: USEPA.

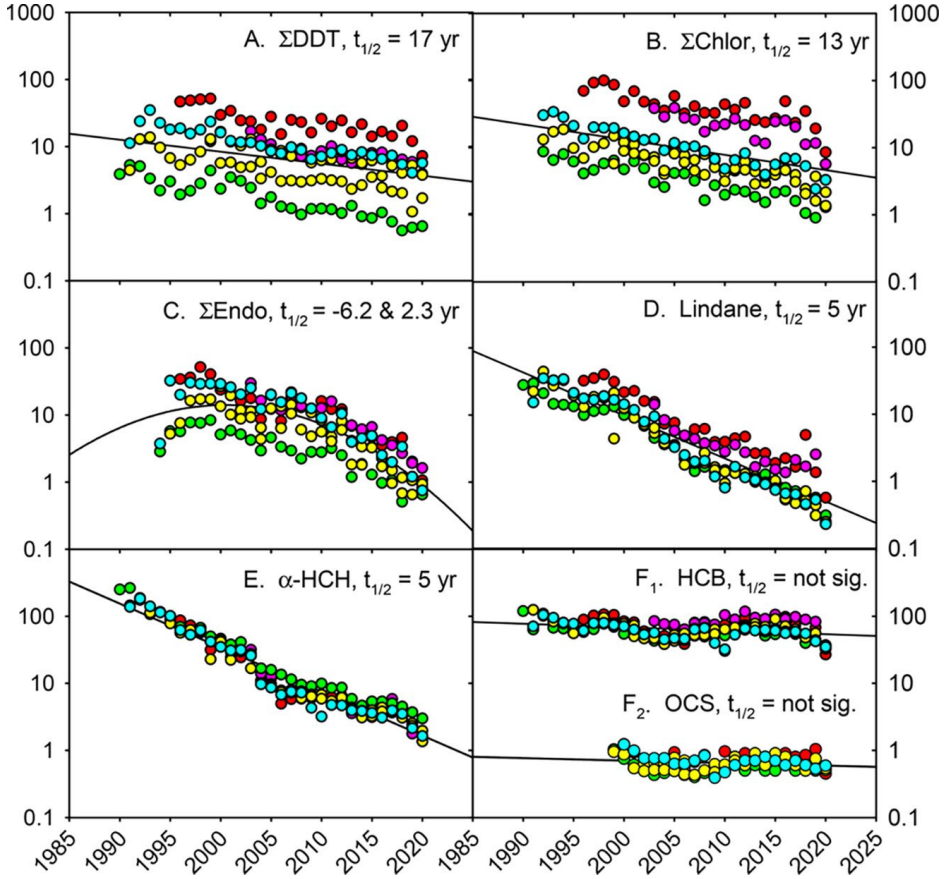

Figure 11b. Annual geometric mean concentrations (in pg/m3) of ∑DDT, ∑Chlor, ∑Endo, lindane (γ-HCH), α-HCH, HCB, and OCS as a function of the six sampling sites on the shores of the North American Great Lakes and sampling year. The symbol color codes are red Chicago, pink Cleveland, cyan Sturgeon Point, yellow Sleeping Bear Dunes and Point Petre, and green Eagle Harbor. The black line shows, in each case, a regression of all the data for each compound(s) as a function of year. The halving times (t1/2) are given for each site except the –6.2 year value for ∑Endo is the doubling time in 1990 (image from Hites and Venier, EST, 2023, DOI: doi=10.1021/acs.est.2c08318).

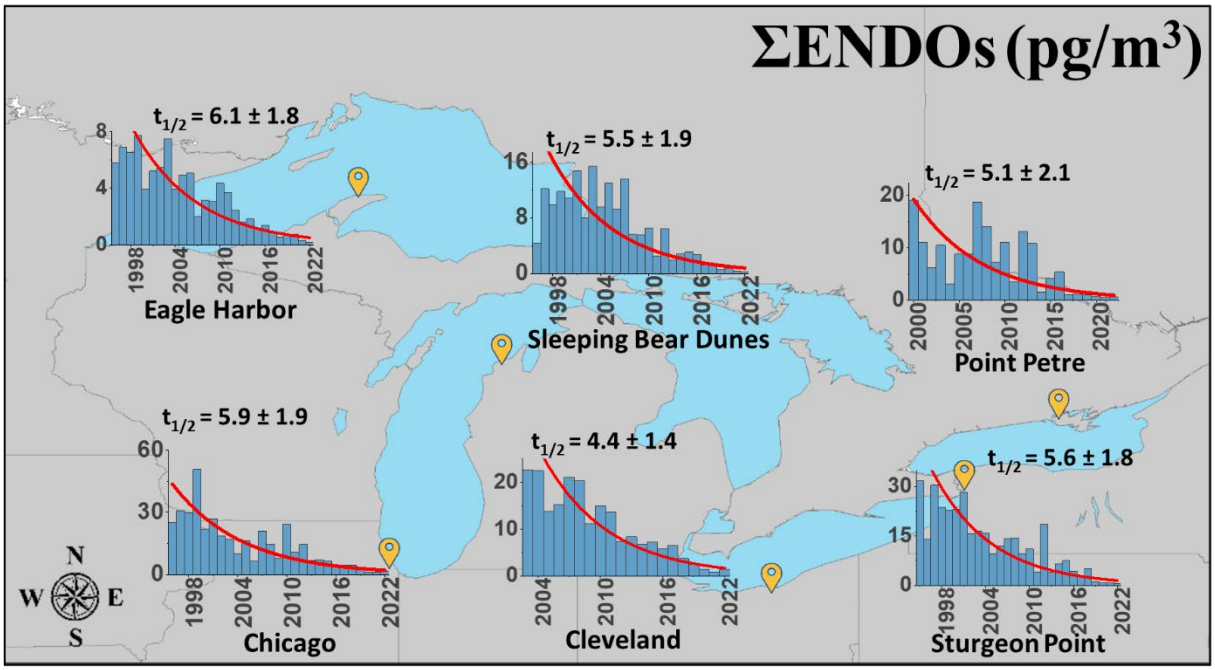

Figure 12. Temporal trends of the annual median atmospheric concentration (in pg/m^3) of total endosulfans (sum of endosulfan I, endosulfan II and endosulfan sulfate) in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time is calculated. Source: USEPA.

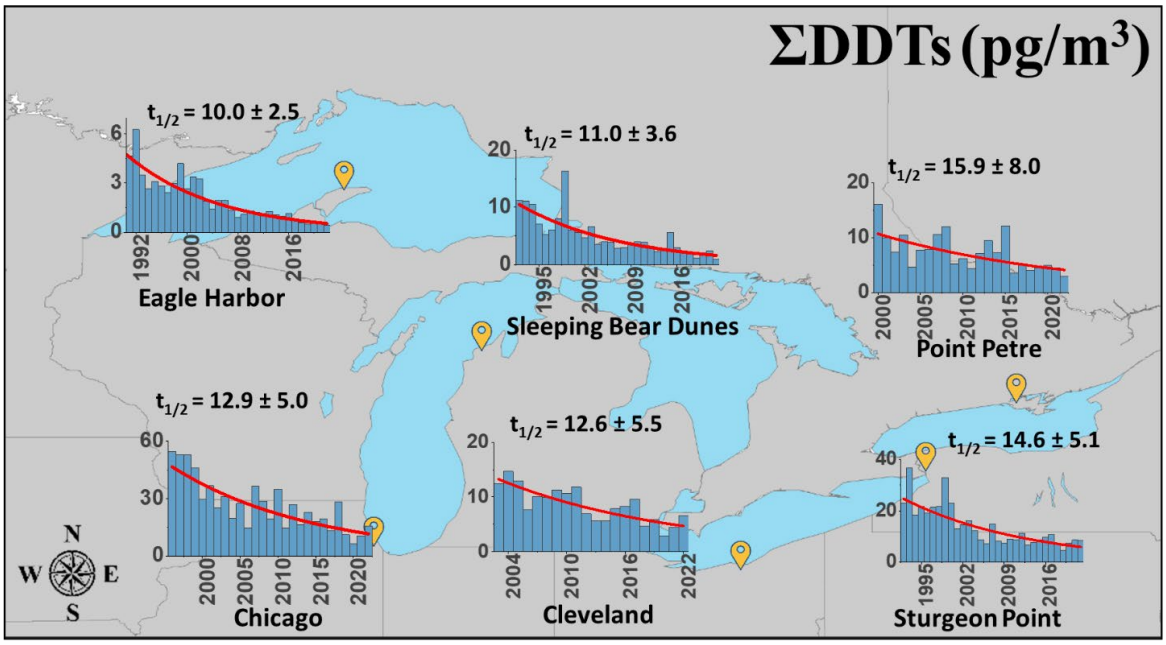

Figure 13. Temporal trends of the annual median atmospheric concentration (in pg/m^3) of total DDTs in the vapor phase at IADN stations. In each plot, the dotted line represents the exponential regression (statistically significant at $p \leq 0.05$), from which the halving time $t_{1/2}$ is calculated. Source: USEPA.

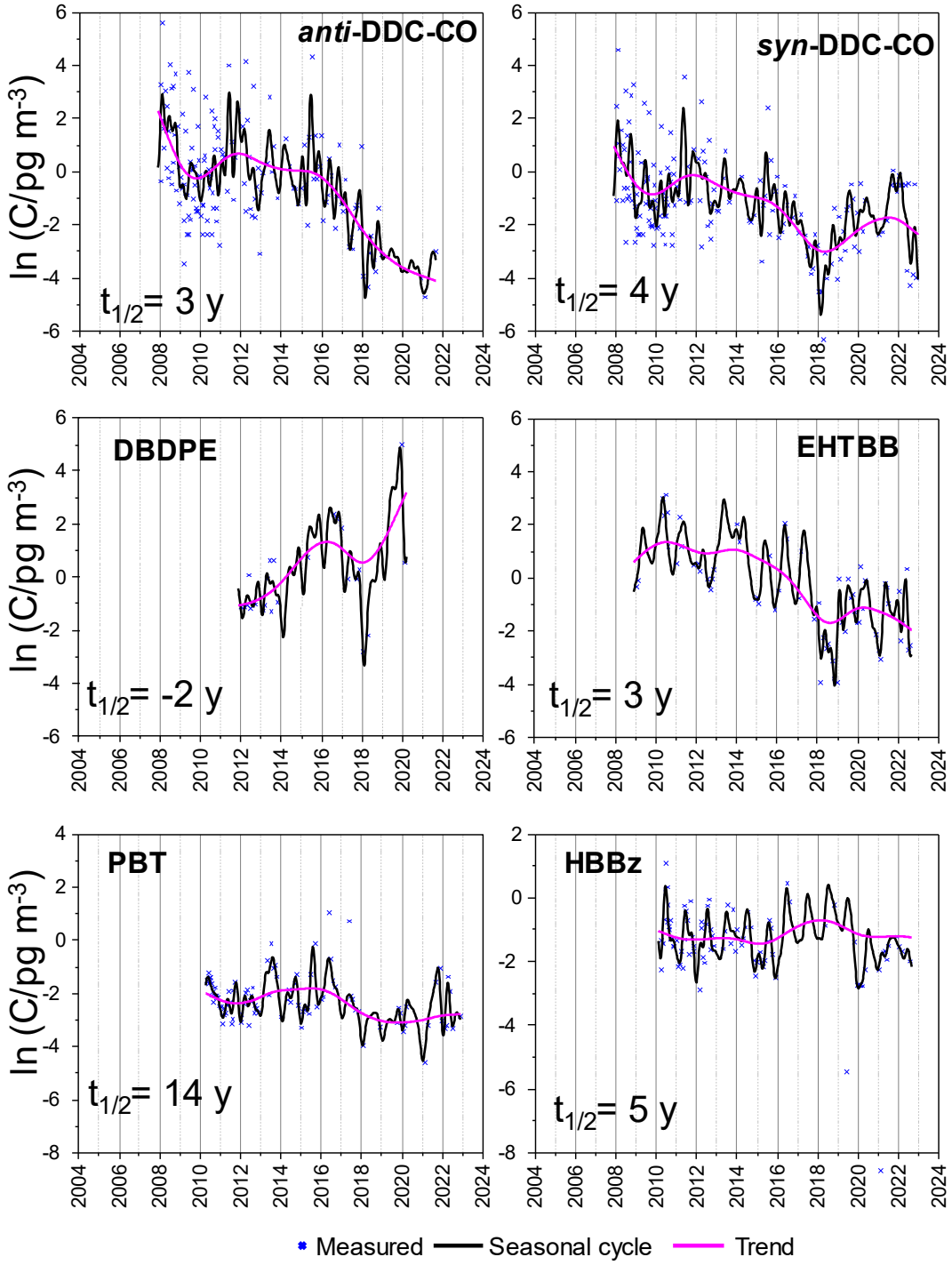

Figure 14. Time trends (red line), seasonal cycles (black line) and measurements (blue cross) of anti- and syn-DDC-CO, DBDPE, EHTBB, HBBz and PBT in air at Point Petre. Time trends and seasonal cycles are generated by the Digital Filtration method. Source: Environment and Climate Change Canada.

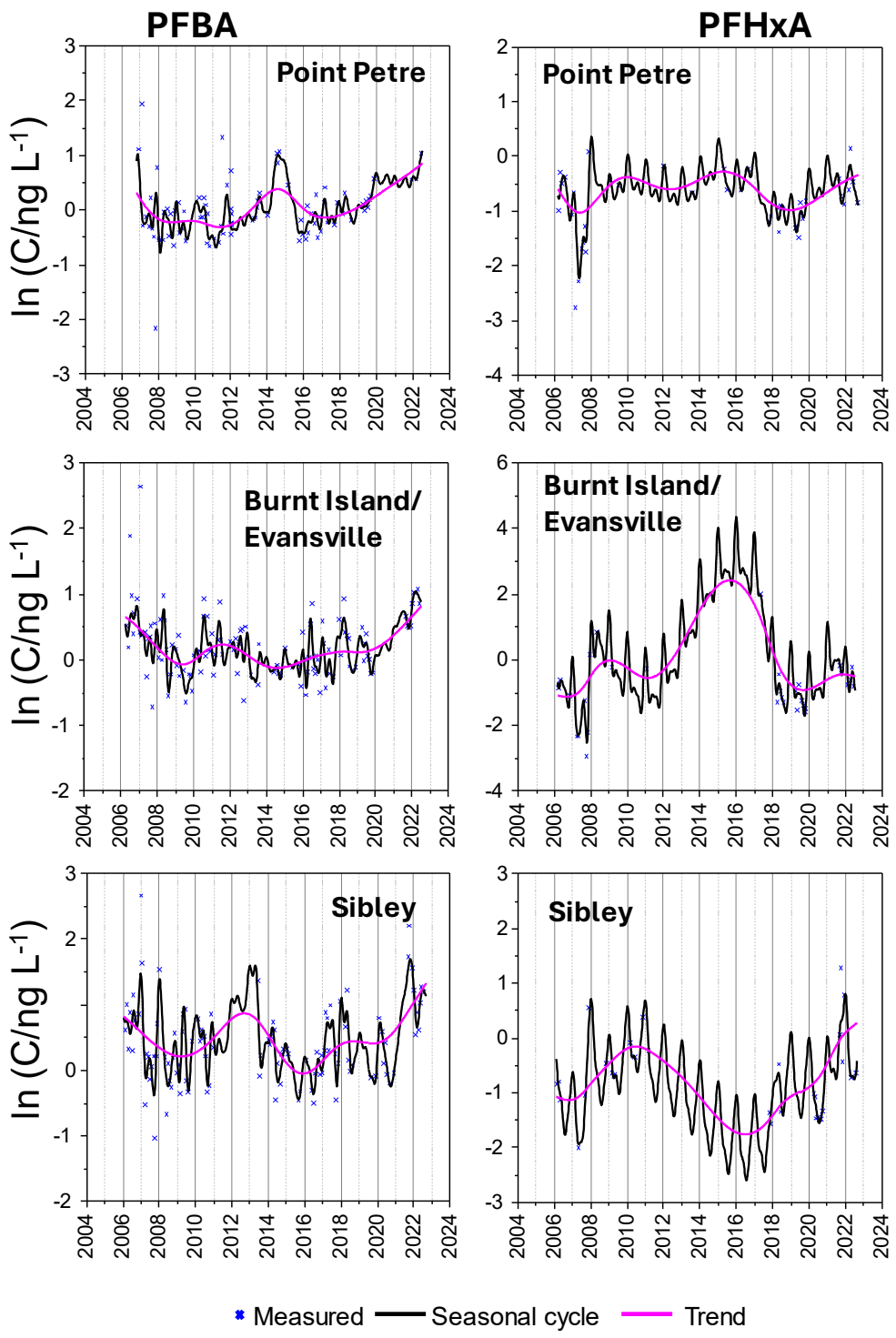

Figure 15. Time trends of PFBA (left) and PFHxA (right) in precipitation collected from Point Petre, Burnt Island/Evansville, and Sibley. The lines showing seasonal cycles and trends were derived from application of the Digital Filtration method on the precipitation data. Source: Environment and Climate Change Canada.

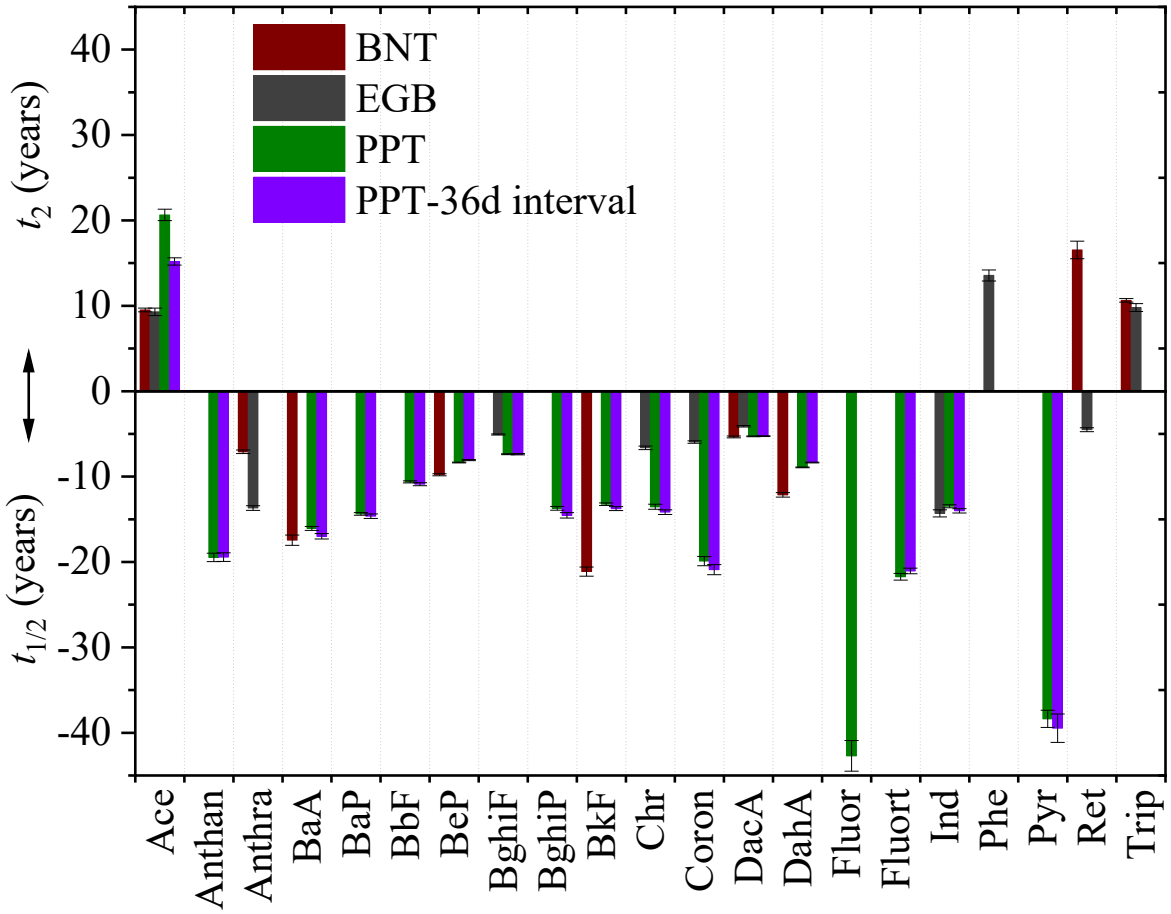

Figure 16. Halving ($t_{1/2}$) and doubling (t_2) times of PAHs in air collected from Burnt Island (BNT), Egbert (EGB) and Point Petre (PPT). PPT-36d interval represents rates of change for PPT site using consistent 36-day interval for the pre-2012 data. Otherwise, 12-day interval sampling data was used for PPT.Only significant increasing or decreasing trends are presented. List of abbreviations: Acenaphthene (Ace), Anthanthrene (Anthan), Anthracene (Anthra), Benz[a]anthracene, (BaA),Benzo[a]pyrene (BaP),Benzo[b]fluoranthene (BbF), Benzo[e]pyrene (BeP),benzo[g,h,i]fluoranthene (BghiF), Benzo[g,h,i]perylene (BghiP),benzo[k]fluoranthene (BkF), Chrysene (Chr), Coronene (Coron), Dibenz[a,c]anthracene (DacA), Dibenz[a,h]anthracene (DahA), Fluorene (Fluor), Fluoranthene (Fluort), Indeno[1,2,3-c-d]pyrene (Ind), Phenanthrene (Phe), Pyrene (Pyr), Retene (Ret), Triphenylene (Trip). Source: Li et al., 2021.

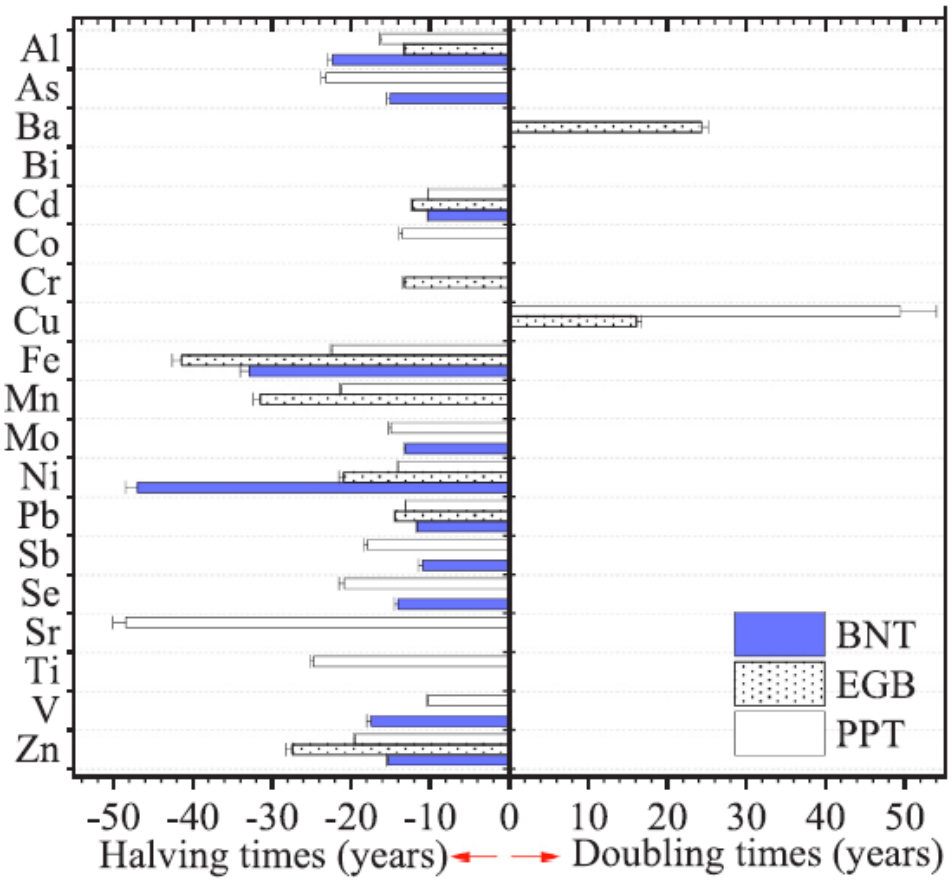

Figure 17. Halving ($t_{1/2}$) and doubling (t_2) times of metals in Burnt Island (BNT), Egbert (EGB) and Point Petre (PPT). List of abbreviations: Aluminum (Al), arsenic (As), barium (Ba), bismuth (Bi), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Source: Li et al., 2020.