



# Atmospheric concentrations and loadings of organochlorine pesticides and polychlorinated biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and temporal analysis (1992–2012)<sup>☆</sup>



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## ABSTRACT

Long-term air monitoring data for POPs are required to determine the effectiveness of source reduction measures and factors controlling air concentrations. Air samples were collected between 1992 and 2012 at three sites with different geographical characteristics (Burnt Island, Egbert and Point Petre) in the Canadian Great Lakes Basin (GLB) using high-volume samplers and analyzed for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). Spatial and temporal trends of gas-phase concentrations of OCPs, selected PCB congeners and ΣPCBs (84 congeners) were assessed. Egbert had the highest concentrations of some OCPs due to historical [dichlorodiphenyltrichloroethanes (DDTs), dieldrin, γ-hexachlorocyclohexane (γ-HCH)] and current (endosulfan) applications of these pesticides in the surrounding agricultural cropland. This shows that agricultural areas are a source of OCPs to the GLB. High *o,p'*-/*p,p'*-DDT ratios were determined and an increasing trend was observed at Point Petre and Burnt Island up to 2004; indicating that the GLB is influenced by dicofol-type DDT sources, which have higher *o,p'*-/*p,p'*-DDT ratios than technical DDT. Atmospheric PCB concentrations at Egbert and Point Petre are higher than those measured at Burnt Island, likely due to urban influence and greater populations. Loadings calculations suggest that the atmosphere is a source of α-endosulfan and *p,p'*-DDT to the lakes and the opposite is true for *p,p'*-DDE. Long-term decreasing trends were observed for both OCPs and PCBs; consistent with control measures implemented in North America. Atmospheric PCB concentrations are decreasing relatively slowly, with half-lives in the range of 9–39 years. Chlordane, α-endosulfan, β-endosulfan, dieldrin, and DDT-related substances showed half-lives in the range of 7–13 years. α-HCH and γ-HCH were decreasing rapidly in air, with half-lives of 5 years. Long-term declining trends of PCBs and OCPs suggest that regulatory efforts to reduce emissions to the GLB environment have been effective, but emissions from primary and secondary sources might limit future declines.

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## 1. Introduction

Persistent organic pollutants (POPs) are synthetic organic chemicals that do not degrade readily and are released into the

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environment through various human activities. They are subject to long-range atmospheric transport (Hung et al., 2005; Shen et al., 2005) and can bio-accumulate in organisms, causing undesirable pollution of the ecosystem with long term-effects that are difficult to predict. POPs consist of industrial chemicals such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), and unintentionally emitted pollutants such as polychlorinated dibenzo-*p*-dioxins. Due to their toxicity and widespread occurrence in the environment, POPs remain a major concern for human and

wildlife health. To address this concern, several global and regional conventions and agreements have been developed with the goal of eliminating or reducing emissions of POPs.

OCPs and PCBs were widely used in North America historically (Panshin and Hites, 1994; Shen et al., 2005). PCBs were used in the manufacturing of electrical equipment, heat exchangers, hydraulic systems, and several other specialized applications (Shen et al., 2006). Whereas their production was banned in the late 1970s in North America, emission of PCBs from older electrical and hydraulic equipment still in use and in the waste stream continues. Despite being banned for decades, legacy OCPs, e.g. dichlorodiphenyltrichloroethanes (DDTs), chlordane and technical hexachlorocyclohexane (HCH), are still present in the environment (Tanabe et al., 1983; Hung et al., 2005; Shunthirasingham et al., 2010). Studies in the 1980s suggested that these compounds were delivered to the Great Lakes (GL) by deposition from the atmosphere (Eisenreich et al., 1981; Strachan and Eisenreich, 1988).

To monitor and quantify the atmospheric deposition of pollutants including trace elements and POPs, the Integrated Atmospheric Deposition Network (IADN) was established in 1989 as a joint effort between Canada and the United States of America (USA) in support of the Great Lakes Water Quality Agreement (GLWQA, 2012). One of the main goals of the network is to measure atmospheric concentrations of toxic chemicals in the Great Lakes Basin (GLB) in order to determine their temporal and spatial trends such that the effectiveness of control measures can be evaluated. The other aim of the network is to determine the atmospheric loadings of POPs to the GL. Under this network, air and precipitation samples are collected at one regionally-representative master air monitoring station (with no known local sources) on the shores of each lake and several satellite stations to increase spatial coverage. Canada's air monitoring in the GLB under the Chemicals Management Plan contributes measurement data to IADN. Two decades of air monitoring data of POPs are now available for determining temporal trends which are essential for assessing the effectiveness of source reduction measures and regulatory controls implemented under domestic, e.g. the Canada-Ontario Agreement on Great Lakes Water Quality and Ecosystem Health, and international agreements, such as the GLWQA and the Stockholm Convention (SC) on POPs.

Extensive research has been conducted on the occurrence and temporal trends of POPs in air and precipitation in the GL (Hillery et al., 1997; Cortes et al., 1998; Strandberg et al., 2001; Buehler et al., 2002; Ma et al., 2013; Venier et al., 2016). Observed declines were attributed to past bans and restriction on uses and emissions in North America (Simcik et al., 1999; Chan et al., 2003; Sun et al., 2006a–e, 2007; Vernier and Hites, 2010). However, atmospheric concentrations may continue to be influenced by long term sources such as volatilization from soils (Bidleman et al., 1998; Scheyer et al., 2005; Bidleman et al., 2006). Recent studies reported the presence of various emerging chemicals, e.g. novel flame retardants, in air in the GLB (Salamova and Hites, 2011; Ma et al., 2012; Venier et al., 2012a; Salmova et al., 2014). Continued research on POPs and emerging chemicals in the GLB is important because it is a major economic and recreational resource for Canada and the USA and preserving its unique ecosystem is essential.

In this study, we update the temporal and spatial trends of gas-phase OCP and PCB concentrations in air measured at the Canadian-operated master stations of Burnt Island on Lake Huron and Point Petre on Lake Ontario, and the satellite station of Egbert between the two lakes from January 1992 to December 2012 with 21 years of data. Also, we report for the first time the trends of atmospheric loadings of these substances to the GLB in 1992–2010. This study will provide information on the effectiveness of emission control

strategies and give a better understanding of the behavior and transport of PCBs and legacy OCPs in the GLB.

### 1.1. Experimental procedure and data analysis

**Air Sampling Sites:** Air samples were collected at two regionally-representative remote master stations on Lakes Huron (Burnt Island; 45° 49' 42" N, 82° 56' 53" W) and Ontario (Point Petre; 43° 50' 34" N, 77° 09' 13" W) and at one rural/suburban satellite station on Lake Huron (Egbert; 44° 13' 57" N, 79° 46' 53" W) (Fig. 1). Air samples were collected at Burnt Island and Point Petre from January 1992 to December 2012 and at Egbert from January 1995 to December 2006. Twenty-four-hour air samples were collected once every 6 days from January 1992 to April 1994; then changed to once every 12 days up to December 2012; and once every 36 days thereafter.

Details on air and precipitation sample collection and chemical analysis is summarized in Wu et al. (2009) and Melymuk et al. (2011). Brief descriptions are given below and more details are given in the Supporting Information (SI).

**Air and Precipitation Sample Collection:** Air samples were collected with a PS-1 high volume air sampler equipped with a glass fiber filter (GFF) and a polyurethane foam (PUF) plug. From January, 2012, two PUF plugs were used in series to collect gas phase organic chemicals at Point Petre to evaluate breakthrough of volatile compounds in summer.

OCP and PCB concentrations were assessed in precipitation samples to estimate wet deposition fluxes to the lakes. Samples were collected at Burnt Island and Point Petre using MIC-B samplers with stainless steel funnel. Dichloromethane (DCM) (250 mL) was used as a sampling medium at the time of collection. Precipitation samples were collected on a biweekly basis in 1992–2001 and changed to once every 28 days in 2001–2004 and monthly samples are now collected since 2005.

**Analysis of Air and Precipitation Samples:** Only gas-phase OCPs and PCBs in air samples were analyzed, due to very low levels found on GFF before 1993 (Blanchard et al., 2008). The PUFs were Soxhlet extracted with hexane; the extracts were dried with anhydrous sodium sulfate; concentrated and fractionated on a Florisil column and analyzed using gas chromatography/electron-capture detection (GC/ECD).

Precipitation samples in DCM were extracted by liquid–liquid extraction, fractionated on a sodium sulfate-silica column, and analyzed by GC/ECD.

Twenty-six pesticides [aldrin, *trans*-chlordane (TC), *cis*-



Fig. 1. Great Lakes Basin sampling stations.

chlordan (CC), *trans*-nonachlor (TN), *p,p'*- and *o,p'*-dichlorodiphenyltrichloroethane (DDT), *p,p'*- and *o,p'*-dichlorodiphenyldichloroethane (DDD), *p,p'*- and *o,p'*-dichlorodiphenyldichloroethylene (DDE), dieldrin, endrin, hexachlorobenzene (HCB),  $\alpha$ - and  $\beta$ -endosulfan (ES), endosulfan sulfate,  $\alpha$ -,  $\beta$ -,  $\delta$ -, and  $\gamma$ -hexachlorocyclohexane (HCH), heptachlor (HEPT), heptachlor epoxide (HEPX), methoxychlor, oxychlordan, mirex, and photomirex], and 84 PCBs (4 + 10, 5 + 8, 6, 7 + 9, 12 + 13, 15 + 17, 16 + 32, 18, 19, 22, 26, 28, 31, 33 + 53, 37 + 42, 41 + 64+71, 44, 45, 47 + 48, 49, 52, 56 + 60+84 + 92, 70 + 76, 74, 77 + 110, 83, 85, 87 + 81, 89, 91, 95 + 66, 97, 99, 100, 101, 105 + 132+153, 114 + 131, 118, 119, 123 + 149, 126, 128 + 167, 135 + 144, 138 + 163, 156 + 171 + 202, 169, 170 + 190, 172, 174, 180, 194 + 205, 199, 201, 206, and 209) were analyzed in air and precipitation samples. All target analytes were quantified using external standard calibration methods.

**Quality Control and Assurance (QA/QC):** Details can be found in Section S1.5. Laboratory and field blanks were processed the same way as samples. Only low blank levels of PCBs and OCPs were found (Table S1). Recoveries from sample and blank PUF spikes were 60–80% for OCPs and 60–80% for PCBs; and from florisisl-column spikes were 90–100% for OCPs and 90–100% for PCBs. The reported data were not blank or recovery corrected. Finally, analysis of common reference standards and matrix spikes were used to provide information about laboratory performance (Wu et al., 2009). HCB was observed to breakthrough in the double-PUF system at Point Petre in the summer, thus is not reported here.

**Data Management:** Concentration data are quality controlled using the interactive SAS-based Research Data Management and Quality Control system™ (RDMQ™) (Sukloff et al., 1995) with flagging capability to ensure consistent data treatment (see Section S1.6 for details).

**Loading Calculations:** A brief overview of the calculations is presented here. The readers are referred to Hoff (1994), Hoff et al. (1996) and Hillery et al. (1998) for additional information. Three main processes influence the net atmospheric flow ( $L$ , in kg/year): wet deposition, dry deposition, and net gas exchange (volatilization and absorption). However, dry deposition cannot be estimated here because only gas-phase concentrations are measured. Therefore, for PCBs and OCPs:

$$L = \underbrace{C_p R_p A}_{\text{Wet deposition}} + \underbrace{[k_{ol}(1-\phi_A)C_A(RT/H)A - k_{ol}(1-\phi_w)C_w A]}_{\text{Gas exchange}} \quad (1)$$

where  $C_p$  (kg/m<sup>3</sup>) is volume-weighted mean precipitation concentrations,  $R_p$  (m/year) is precipitation rate,  $A$  (m<sup>2</sup>) is lake area,  $k_{ol}$  (m/year) is the overall air–water mass transfer coefficient,  $R$  (atm·m<sup>3</sup>/K mol) is the ideal gas constant;  $H$  (mol/atm·m<sup>3</sup>) is the Henry's law constant, and  $C_w$  (kg/m<sup>3</sup>) is water concentration (See Tables S2 and S3 for lake water concentrations; and equations used to calculate  $H$ , respectively). Net gas exchange is the sum of the absorption and volatilization. A positive net value means gas-absorption from air to lake is dominant, whereas a negative value indicates net volatilization from lake. Lake water concentrations are not measured as part of the program, and are provided by other sources (See: Acknowledgments). Lake water concentrations were not available for all years; some data were used for several years before and after the measurements took place. Occasionally, more than one source for water concentrations were available for one year, and the data were pooled by inverse-variance weighting

(Taylor, 1990).

**Temporal Trends and Apparent First Order Halfives:** Temporal trend analysis was performed using the digital filtration (DF) method. DF is a statistical procedure in which temporal trends and seasonal cycles are approximated using a Reinsch-type cubic spline and Fourier components, respectively, by an iterative fitting technique. Detailed descriptions and applications of this method can be found elsewhere (Nakazawa et al., 1997; Hung et al., 2010; Venier et al., 2012b). Outliers more than 3 standard errors away from the fitted curve were rejected after each iterative fit. Long- and short-term variations were then extracted using two Butterworth digital filters with a short-term cutoff period of 4 months, and a long-term cutoff period of 96 months. Variabilities between 4 and 96 months refine the overall seasonal cycle, and those longer than 96 months render the final long-term trend. The cutoff periods, which produced the “best fit” to the specific dataset, were chosen by visual inspection of the fitted seasonal cycle and trend. Non-detects were not included in the determination of temporal trends. Trends and seasonal cycles fitted with the DF method are statistically significant with 95% confidence since they have been statistically “smoothed” using digital filters.

For each chemical, an apparent first order half-life ( $t_{1/2}$ ) 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,  $\ln C_A$  (pg/m<sup>3</sup>), and time (year). Some POPs do not necessarily decline linearly or consistently in the first order manner. The half-lives presented here are only used to compare the relative rates of decline among sites.

## 2. Results and discussions

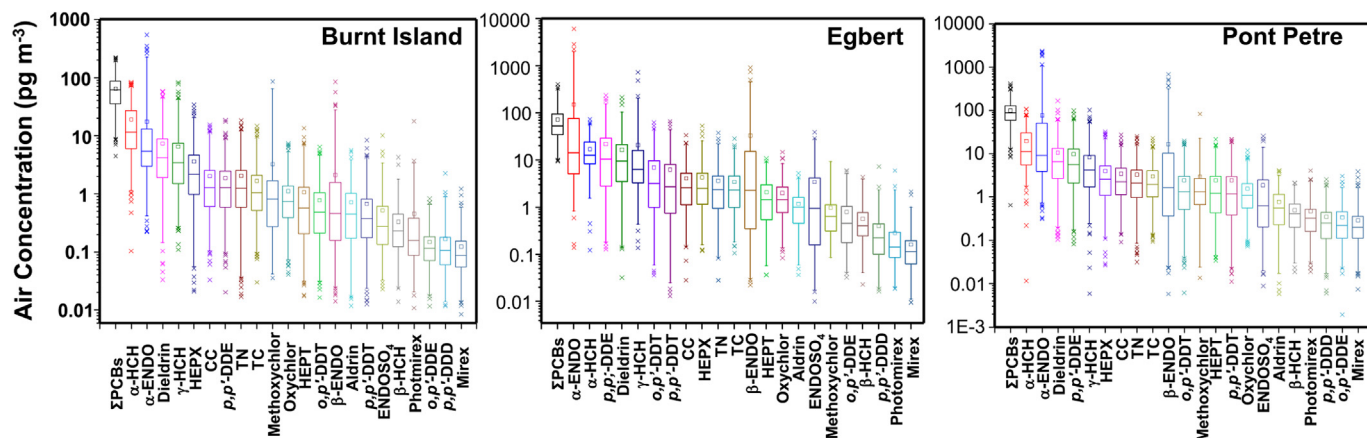
### 2.1. Air concentrations of PCBs and OCPs

Table S4 and Fig. 2 summarize the OCP and PCB concentrations for the GLB. Concentrations have generally declined with time (see temporal trend discussions below). The POPs are arranged from the highest to the lowest median concentrations in Fig. 2. The most abundant POPs at all sites were PCBs with annual average  $\Sigma$ PCBs concentrations ranging 30–130 pg/m<sup>3</sup>. The relative abundance of OCPs is generally  $\alpha$ -HCH  $\approx$   $\alpha$ -endosulfan  $>$  *p,p'*-DDE  $\approx$  dieldrin. The size of boxes and whiskers in Fig. 2 indicates concentration variabilities.  $\Sigma$ PCBs have a relatively small interquartile range, indicative of a slow declining trend (see below) with no major fresh sources in the region. Contrarily, endosulfan-related substances have a large interquartile range, suggestive of high concentration variabilities. Samples taken during 1998 in Egbert and 2005 in Point Petre had the highest concentrations of endosulfan, reflecting its widespread usage. Basic information on the OCPs, their uses and control measures implemented in North America is given in Section S12.

### 2.2. Spatial patterns in the GLB

The three GLB stations have different geographical characteristics which may be reflected in the spatial patterns of OCPs and PCBs. Point Petre is a remote site on Lake Ontario with potential influence from urban centers, e.g. Toronto and Rochester. Also a remote site, Burnt Island is located on the southwestern end of Manitoulin Island in northern Lake Huron which may be influenced by nearby mining/industrial towns of Sudbury and Sault Ste. Marie; while Egbert is located within agricultural cropland (Gouin et al., 2008), close to Toronto, with a large residential population of 244,446 within a 25 km radius of the site (as compared to 48,948 at Burnt Island and 15,996 at Point Petre) (Free map tools, 2015).

Being the most abundant POP in the GLB, PCB levels were similar



**Fig. 2.** Box-and whisker plot of OCP and  $\Sigma$ PCBs air concentrations in the GLB. Boxes represent the interquartile range, bound by the 75th and 25th percentile. Vertical lines indicate the 1 and 99 percentile and outliers  $>1.5 \times$  (interquartile range) are shown individually. Median and arithmetic mean are shown as horizontal bar in the box and a square, respectively.

at Point Petre and Egbert but lower at Burnt Island. The mean air concentrations of  $\Sigma$ PCBs (84 congeners) ranged from 30 to 77  $\text{pg}/\text{m}^3$  at Burnt Island, 52–130  $\text{pg}/\text{m}^3$  at Egbert and 47–130 at Point Petre. Higher PCB concentrations are likely associated with the larger populations at Egbert and proximity to urban sources (e.g. Toronto) for both Point Petre and Egbert. This observation is consistent with Sun et al.'s (2007) suggestion that the source of PCBs around Point Petre could be atmospheric transport from Toronto and Rochester. The USA could be a significant source of PCBs to the GLB as historical PCB consumption was much higher in the USA (~46%) than in Canada (~3%) (Breivik et al., 2002). Lake Ontario could also be a source of PCBs to surrounding areas as volatilization fluxes from lake water (secondary emission) has increased in recent years (see Figs. S18 and S19 and flux trend discussion below). Congener profiles are similar at all sites (Fig. S1), indicating uniform PCB composition in GLB air despite concentration differences. Lower chlorinated PCBs 8, 16 + 32 and 18 were dominant in air which can be explained by their higher volatilities. PCB5+8, PCB18 and PCB28 + 31 are the most abundant congeners in Arochlor 1242 and Arochlor 1016 (Jansson et al., 2011). Arochlors 1260, 1254 and 1242 made up 80% of production between 1957 and 1972 with Arochlors 1248 and 1016 (after 1971) making up most of the remainder (Sather et al., 2001). This usage pattern would explain the observed profile in air samples. Tri- and tetra-homologs made up the largest fraction in air, consistent with historical production and use of the technical mixtures such as Arochlor 1242. The homolog profiles did not change over time, indicating that primary emission sources from existing equipment/waste are still dominant.

While several legacy OCPs, e.g.  $\alpha$ -HCH (a major component of technical HCH), aldrin, TC, CC, TN and HEPT, have shown uniform distribution in GLB air with similar air concentrations at the 3 sites,  $\gamma$ -HCH (main component of pesticide lindane), DDTs, dieldrin and  $\alpha$ - and  $\beta$ -endosulfan showed highest air concentrations at Egbert. For example: (1)  $\gamma$ -HCH was about 3 times higher at Egbert (3.2–49  $\text{pg}/\text{m}^3$ ) than at Point Petre and Burnt Island (0.63–17  $\text{pg}/\text{m}^3$ ). (2) DDTs at Egbert (0.18–35  $\text{pg}/\text{m}^3$ ) were about an order of magnitude higher than in Burnt Island (0.025–3.4  $\text{pg}/\text{m}^3$ ) and twice as high as in Point Petre (0.055–18  $\text{pg}/\text{m}^3$ ) (Table S4), although the dominant isomer was  $p,p'$ -DDE at all sites indicating no fresh sources to the GLB. (3)  $\alpha$ -endosulfan concentrations at Egbert were 39–390  $\text{pg}/\text{m}^3$  with a maximum of 6100  $\text{pg}/\text{m}^3$  observed in 1998 summer, while those at Point Petre and Burnt Island were 12–210 and 1.8–54  $\text{pg}/\text{m}^3$ , respectively. (4) The highest

annual average air concentration of 28  $\text{pg}/\text{m}^3$  of dieldrin was observed at Egbert. Other than endosulfan which is a current-use pesticide (CUP) (to be phased out in the USA and Canada by 2016), other OCPs showing high concentrations at Egbert, e.g. DDTs and dieldrin, have been regulated for decades, although lindane use in agriculture was allowed until 2004 in Canada (Becker et al., 2008) and deregistered in the USA in 2006 (Venier et al., 2012b). High pesticide air concentrations at Egbert probably reflect historical (DDTs, HCHs and dieldrin) and current (endosulfan) applications of these OCPs in the surrounding agricultural cropland. For DDTs, HCHs and dieldrin, secondary emission from environmental sinks, e.g. soil, is probably the major source, while the high levels of endosulfan is probably the result of current applications.

Comparisons of observed isomer ratios of OCPs can provide insight on usage patterns and environmental processes. For instance, the  $\alpha$ -/ $\gamma$ -HCH ratios in air ranged from 1.2–5.1 at Burnt Island, 1.1–4.9 at Point Petre and 0.34–1.5 at Egbert (Table S4); generally lower than that in the technical HCH mixture which is around 4–7 (Shen et al., 2004). This is expected due to a shift in usage pattern from technical HCH to lindane (99%  $\gamma$ -HCH) which would lower the ratio. The ratio was lowest at Egbert suggesting the more intense use of lindane at this location. The  $\alpha$ -/ $\gamma$ -ratio was lower than that in technical HCH at Burnt Island from 1994 to 2008 and at Point Petre from 1992 to 2009. After 2009,  $\alpha$ -/ $\gamma$ -ratios were higher than in the technical mixture. As there are no more new sources of both technical HCH and lindane, the relative rates of atmospheric removal processes of the two isomers, e.g. degradation and deposition to surfaces, would be reflected in the ratio.

Decreasing  $p,p'$ -DDT/ $p,p'$ -DDE ratios at all 3 sites over time (Fig. S2) indicates a more weathered DDT signature in the GLB, but the decline has leveled off at Burnt Island since 2005 and Point Petre since 2000. Both technical DDT and DDT-containing dicofol (a CUP) may introduce DDT into the environment. As technical DDT contains less  $o,p'$ -DDT (~15%) than  $p,p'$ -DDT (~85%), and dicofol has a reverse proportion (Qiu et al., 2005), input of DDTs from dicofol may be distinguished from technical DDT by higher  $o,p'$ -/ $p,p'$ -DDT ratios. The annual mean  $o,p'$ -/ $p,p'$ -DDT ratios were 0.9–2.8 at Burnt Island, 1.1–3.2 at Egbert and 0.91–2.2 at Point Petre (Table S4). These values are higher than those predicted for soil emissions across North America of 0.61–1.27; and that estimated from evaporation of technical DDT with WHO composition of 0.72 [Bidleman et al., 2013; values converted from  $p,p'$ -DDT/( $p,p'$ - +  $o,p'$ -DDT)]. USA-manufactured dicofol is restricted to <0.1% residual DDT since 1986 (Qiu et al., 2005), but dicofol manufactured

elsewhere can contain higher proportions. The *o,p'*-DDT/*p,p'*-DDT ratios showed an increasing trend at Point Petre and Burnt Island up to 2004, suggesting increased atmospheric transport of dicofol-type DDT to GLB; however, slow declining trends were observed after 2005 (Fig. S4).

The calculated  $\alpha$ -/ $\beta$ -endosulfan ratios (Table S4) were almost always higher than the ratio of 2.3 in the technical mixture (Shunthirasingham et al., 2010), suggesting that during atmospheric transport  $\beta$ -endosulfan is being preferentially lost.  $\beta$ -endosulfan has a lower Henry's Law Constant than  $\alpha$ -endosulfan (Shen and Wania, 2005) and will therefore partition more readily to the aqueous phase, resulting in greater potential for precipitation scavenging and greater gas partitioning from air into the lakes.

### 2.3. Temporal trends of PCBs and OCPs

Temporal trends of PCBs and OCPs are assessed with 21 years of data from 1992 to 2012 at Point Petre and Burnt Island (Figs. 3–6 and S3–S8). Trends are also developed for Egbert for continuous data from 1995 to 2006 (Figs. S9–S12). Since data after 2006 are not available, recent trends cannot be determined and the shorter trends are not directly comparable to those from Point Petre and Burnt Island. Thus, discussions here will focus on trends at the two master stations. Sun et al. (2006e, 2007) and Salamova et al. (2015)

have previously assessed temporal trends at Burnt Island (1993–2003), Point Petre (1993–2003) and Point Petre (1991–2013), respectively, using the linear regression method with temperature-corrected partial pressure at 288 K. Venier et al. (2012b) have shown that half-lives developed with a similar method as Sun et al.'s, the modified Clausius–Clapeyron equation, are comparable to those determined using DF. Half-lives developed in this study are compared with Sun et al.'s and Salamova et al.'s results in Table S5.

**OCPs:** General declining trends with half-life longer than 10 years (Table S5) can be seen for most legacy OCPs, such as the chlordanes (TC, TN, CC, oxychlordane) and dieldrin (Figs. 3, S3, and S4), as many of them have already been banned for long periods of time in North America. The half-lives of these compounds are generally similar to those reported by Sun et al. (2006e) (Table S5) but slightly longer. With 9 more years of data, some of these OCPs have started to level off, especially after 2008 at Burnt Island, including TN, TC, HEPT, aldrin and dieldrin, indicating that they have now approached steady state with the surrounding environment.

$\alpha$ - and  $\gamma$ -HCH showed the fastest rates of decline (Fig. 3), with similar half-lives of 4–5 years (Table S5). The rapid declines observed for  $\alpha$ - and  $\gamma$ -HCH are consistent with the high volatilities of these chemicals. The half-lives of  $\alpha$ -HCH and  $\gamma$ -HCH are similar to

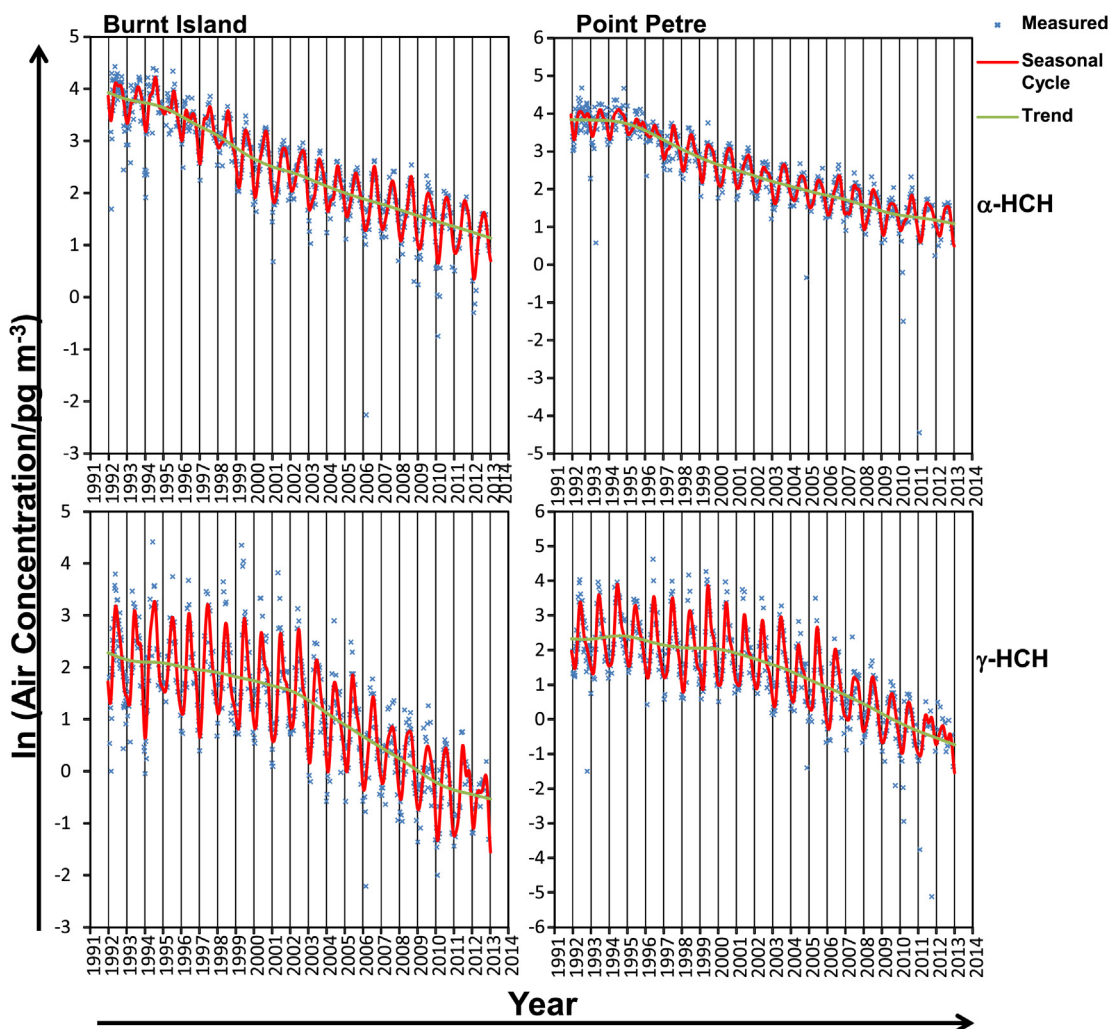


Fig. 3. Trends of  $\alpha$ -HCH and  $\gamma$ -HCH at Burnt Island and Point Petre.

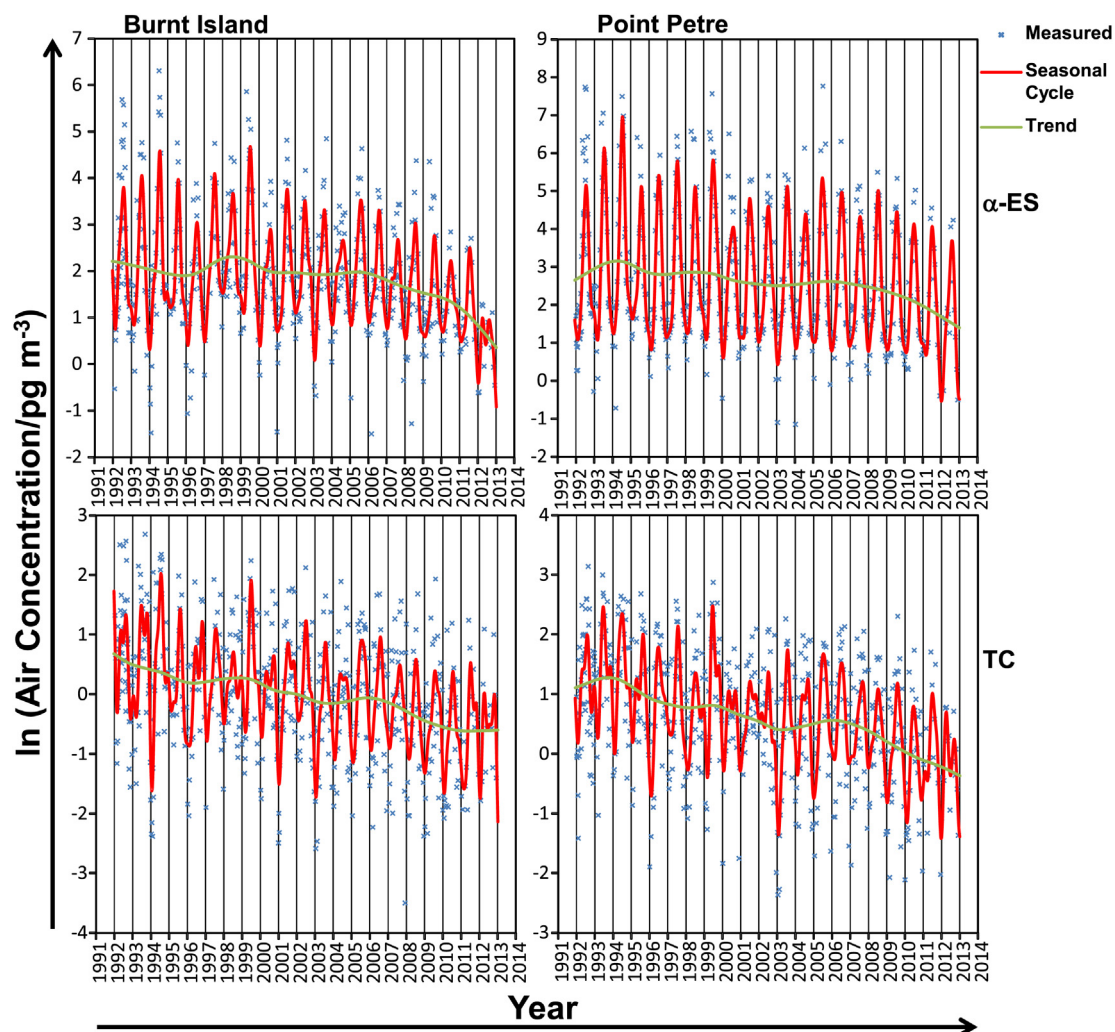


Fig. 4. Trends of trans-chlordane (TC) and  $\alpha$ -endosulfan ( $\alpha$ -ES) at Burnt Island and Point Petre.

those reported by Salamova et al. (2015) at Point Petre. Sun et al. (2006e) reported a longer half-life for  $\gamma$ -HCH between 1990 and 2003 at Burnt Island and Point Petre of 7.7 and 7.8 years, respectively (Table S5). Previously observed slower decrease of  $\gamma$ -HCH was probably due to the continuing usage of lindane in North America until the mid-2000s. The declining trends of  $\gamma$ -HCH have apparently accelerated at both sites around 2004 and continued until 2012 (Fig. 3), similar to Venier et al.'s (2012) observation at 2 USA IADN sites (Chicago and Eagle Harbor) that  $\gamma$ -HCH declined more rapidly after ~2002 than in the 1990s.  $\alpha$ - and  $\gamma$ -HCH tend to maximize over the summer which is consistent with enhanced volatilization during warmer periods.

Slow declining trends for atmospheric endosulfan-related compounds was observed at all sites (Fig. 4 and S5), with half-lives of 13 years for  $\alpha$ -endosulfan, 9–11 years for  $\beta$ -endosulfan and 8–10 years for endosulfan sulfate (Table S5).  $\alpha$ -endosulfan concentrations were quite steady with no increasing or decreasing trend until about 2008 when the levels started to decline up to 2012 (Fig. 4). This special feature reflects its current usage. The decline in more recent years is consistent with USA and Canada's phase-out action which started in 2010 (Health Canada, 2011). Highest concentrations are measured during the spring/summer months when the pesticide was applied.

No studies so far have reported long-term trend of mirex in the

GLB. Here, we found slow declining trend of mirex in air at Point Petre, with half-lives of 11 years and for Burnt Island, declining trend of mirex was observed up to the end of 2005, followed by an increase in concentrations (Fig. S5) with no apparent reasons. Soil is likely the source of mirex to the atmosphere. However, changes in temperature over time at this site cannot explain the increasing concentrations (Fig. S13). Shorter half-lives (6–7 years) were observed for its metabolite phtomirex. The decline started to level off for both compounds at Point Petre and only for phtomirex at Burnt Island.

DDT-related compounds showed decreasing trends (Figs. S6 and S7) at all sites with half-lives ranging from 7 to 12 years (Table S5). *p,p'*-DDT tends to decline faster than other isomers indicating decline of fresh sources despite its allowance for use for malaria control in some tropical countries. Our results are consistent with the studies by Sun et al. (2006e), Venier and Hites (2010) and Salamova et al. (2015), who reported decreasing trends for the DDT-related substances with halving times of 9–16 years.

**PCBs:** PCB concentrations showed slower rate of decline than OCPs (Figs. 5, 6 and S8) with half-lives of 9–39 years (Table S5) similar to those reported by Sun et al. (2007), Venier and Hites (2010) and Salamova et al. (2015) of 8–26 years. Despite PCBs were banned for more than 40 years, there are still large amounts of PCBs in transformers, capacitors and other electrical equipment

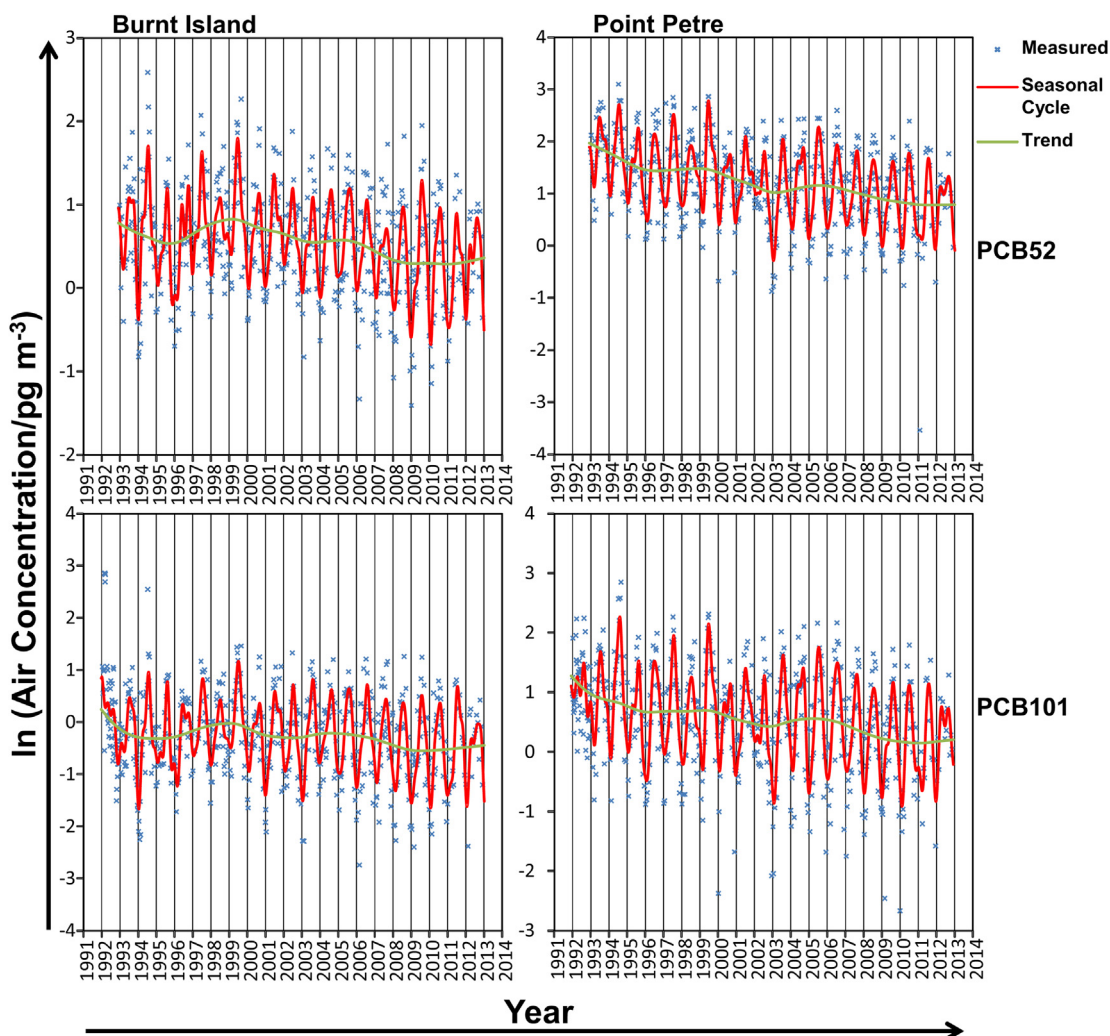


Fig. 5. Trends of PCB52 and PCB101 at Burnt Island and Point Petre.

and building material, which are major sources that sustain their levels in air.

For Burnt Island, declining trend of PCB28 was observed up to end of 2009, followed by an increase in concentrations (Fig. S8). The reason is unknown. Other congeners showed slow declining trends between 1992 and 2008, but the decline has leveled off after 2009. PCBs showed faster rates of declines at Point Petre than at Burnt Island. The effective reduction efforts around Lake Ontario may have led to a faster rate of decline at Point Petre and the colder water temperatures and large volume of Lake Huron, which acts as a secondary emission source, may have caused slower PCB decline at Burnt Island (Sun et al., 2007).

Shorter half-lives were observed for the heavier PCB, especially PCB180 with  $t_{1/2} \approx 9$  years (Table S5). This may be due to the fact that only gas-phase concentrations are reported here and heavier congeners such as PCB180 have higher tendency to partition to particles with shorter transport distances. Earlier studies showed faster declines of PCBs in air at USA IADN sites, e.g.  $2.7 \pm 1.4$  year in Chicago (1993–1997) (Simcik et al., 1999), and rapid decline of PCBs was observed in trout in the GL (1974–1995) (Hicklerly et al., 2006). More rapid decline of PCB concentrations in the GL region in the 1980s and 1990s likely reflect the rate of decline in primary emissions. Slower rates of decrease for PCBs now may indicate its approach to steady state with existing PCB-containing material in GLB.

#### 2.4. Flux trends of OCPs and PCBs at the Canadian Great Lakes Basin

Flux trends of OCPs and PCBs to Lakes Huron and Ontario estimated using air and precipitation concentrations measured at Burnt Island and Point Petre and lake-wide averaged water concentrations are summarized in Figs. 7 and S14–S19. When the trend and seasonal cycles are discontinuous in the figures, it indicates that the measured concentrations in these three media were either below detection or not available. Gas absorption fluxes of legacy OCPs, e.g.  $\alpha$ -HCH, dieldrin, chlordanes,  $p,p'$ -DDT, DDD and DDE, and  $\Sigma$ PCBs, have declined over time as air concentrations have declined (green line in figures). Wet deposition fluxes (blue line in figures) have only declined slightly (e.g. for  $\alpha$ -HCH,  $p,p'$ -DDE and  $\Sigma$ PCBs); or remained more or less unchanged (e.g. CC, TN) over time; or were too low to assess trends (e.g.  $p,p'$ -DDD and DDT). Volatilization from the lakes (negative fluxes indicated by yellow line in figures) is now dominant for these legacy compounds. For  $\alpha$ -HCH and dieldrin, volatilization fluxes have decreased over time, and for the DDTs and chlordanes, they have stabilized in recent years, as the air–water exchange approaches a steady state. In contrast, volatilization has become more important for  $\Sigma$ PCBs in recent years. The atmosphere has typically been a source of  $p,p'$ -DDT to the lakes, whereas the lakes are a source of degradation product  $p,p'$ -DDE to the atmosphere. While the deposition fluxes of  $p,p'$ -DDT have declined over time, volatilization fluxes for  $p,p'$ -DDE

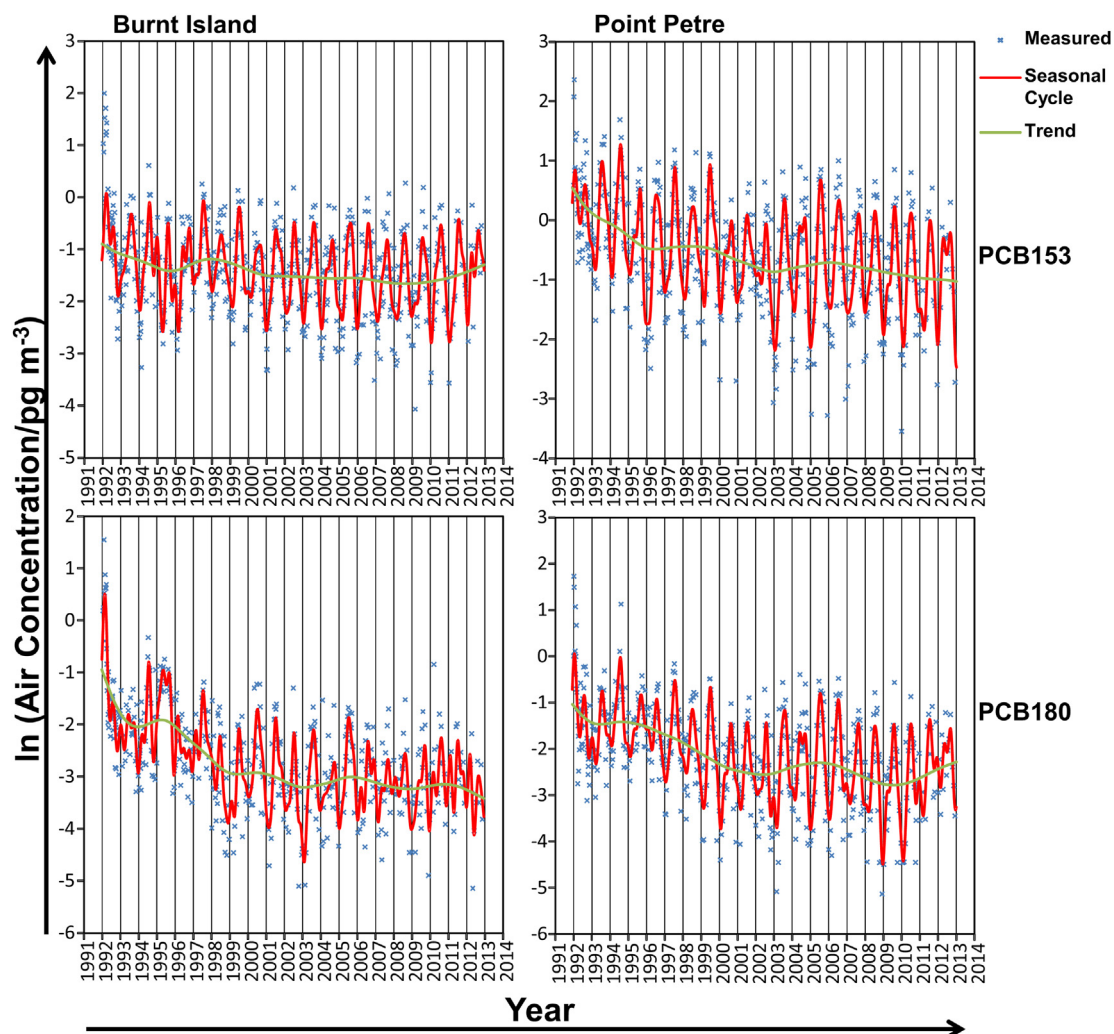


Fig. 6. Trends of PCB153 and PCB180 at Burnt Island and Point Petre.

have not, and in fact has become more important for Lake Ontario, providing an explanation for why *p,p'*-DDE was the major isomer observed in air.

When lindane was still used in North America, the atmosphere continued to be the dominant source of  $\gamma$ -HCH into the lakes until 2003, when the lakes became a source of  $\gamma$ -HCH into the atmosphere. This change could be attributed to the regulation of lindane in North America in the early 2000s. Since then, the net air–water exchange fluxes for both lakes were approaching steady state. This is the result of significant decreases in  $\gamma$ -HCH concentrations in both air and lake water since 2002. Higher fluxes into the lakes were observed in the warmer months (spring and summer) for  $\gamma$ -HCH corresponding to usage and tillage patterns which release pesticides from soils.

Net flux of current-use  $\alpha$ -endosulfan was generally positive; the atmosphere was a source of  $\alpha$ -endosulfan into the lakes. Highest values were observed during the spring/summer months when the pesticide was applied.

### 3. Conclusions

Air monitoring in the GLB operated since 1992 provided the necessary temporal trends for assessing effectiveness of the SC and other national and international control measures. Monitoring at

multiple regionally-representative stations, also allows for the assessment of spatial differences, e.g. the agricultural site of Egbert versus urban influence on Point Petre versus the more remote concentration patterns observed for Burnt Island; and the co-located precipitation measurements made possible the assessment of atmospheric loadings to the GL. In gauging the success of chemical management initiatives, a big-picture approach is needed. Although air is designated as a core medium for monitoring under the SC because most POPs are subject to atmospheric transport, for a complex environment such as the GL, it is necessary to take into account factors other than regulatory controls that would influence trends, e.g. environmental partitioning and degradation processes, volatilization from sinks and waste streams. There are knowledge gaps, e.g. whether environmental reservoirs act as sources or as sinks, whether primary or secondary sources are controlling air concentrations of POPs. The long-term monitoring plans should provide an opportunity to investigate these processes, e.g. conducting soil and water measurements, at the same locations as the air and precipitation measurements.

In summary, the long-term air monitoring data (1992–2012) at the GLB show that the levels of legacy pesticides, CUP (endosulfan) and PCBs have declined in the atmosphere of the GLB. Decreasing trends in air follow historic decreases in emissions, but the decreases have started to level off for some POPs approaching a steady



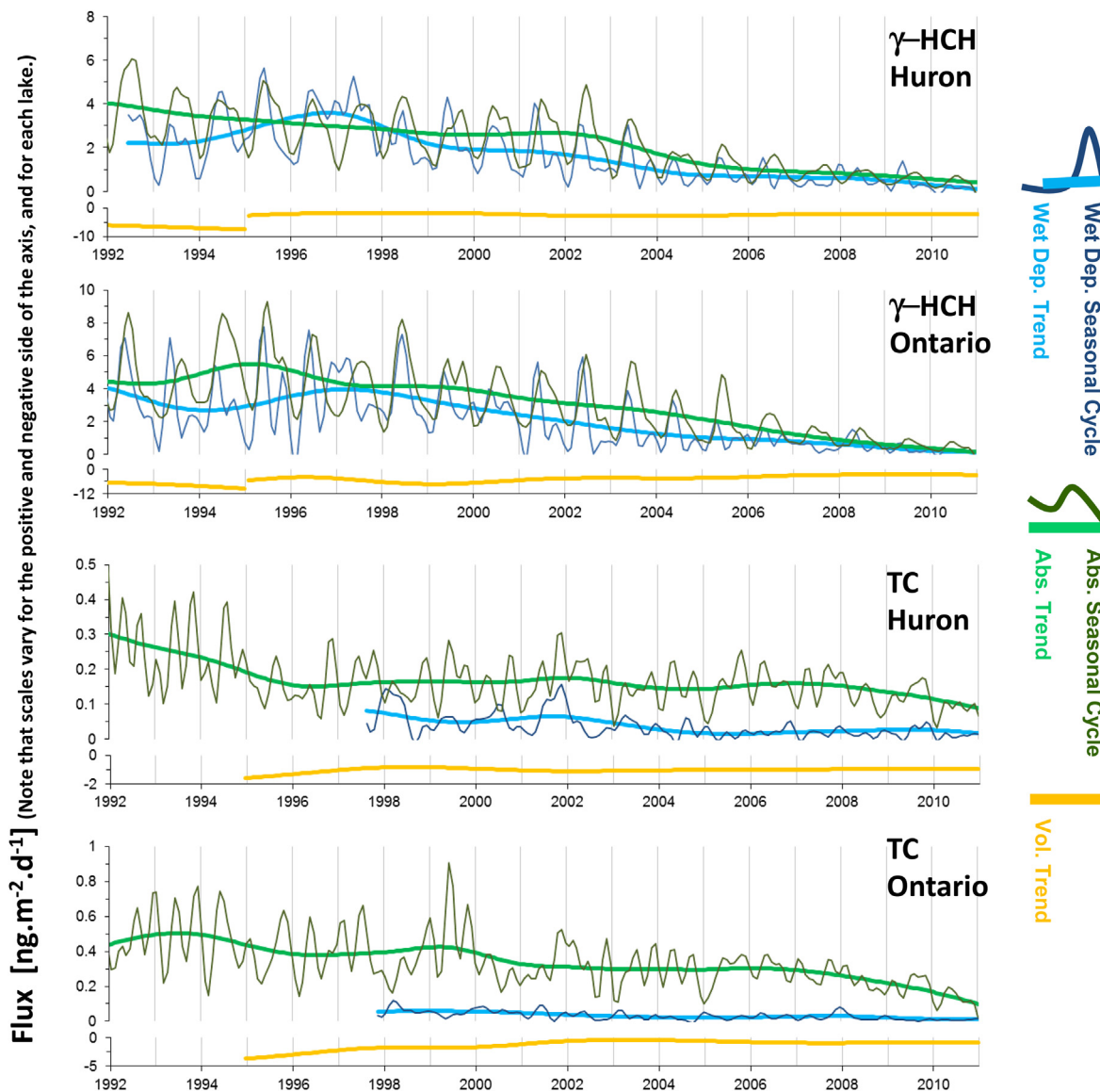


Fig. 7. Flux trends of  $\gamma$ -HCH and trans-chlordane for Lakes Ontario and Huron.

state with the environment. This suggests that atmospheric concentrations are being less driven by the primary sources and more by environmental processing and partitioning. The long-term trends of OCPs and PCBs found in this study suggest that regulatory efforts to decrease emission of these compounds in North America have been effective. Air monitoring in the GLB provides sound scientific results to support policy-making and insights into the atmospheric behavior of POPs in the GLB environment.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.01.039>.

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