

Levels and Seasonal Variability of Pesticides in the Rural Atmosphere of Southern Ontario

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Air samples were collected continuously in Egbert, Ontario, which is in a rural agricultural area north of Toronto, between March 2006 and September 2007 and analyzed for pesticides of both current and historic use. The fungicide chlorothalonil was present in highest abundance with levels exceeding 2000 pg·m⁻³ in the summer. Almost as abundant, with summer time concentrations around 400 to 600 pg·m⁻³, were the herbicides atrazine, alachlor, and metolachlor. Other pesticides in current use, such as trifluralin, pendimethalin, chlorpyrifos, endosulfan, and disulfoton were consistently present at levels approximately 1 order of magnitude lower. Concentrations of banned pesticides (chlordanes and hexachlorocyclohexane) were generally below 10 pg·m⁻³, except for hexachlorobenzene, which was present at the global average of approximately 50 pg·m⁻³. These levels and the fact that they are generally lower than what has been reported for the area previously are in agreement with pesticide usage data for Ontario. Only the concentrations of chlorothalonil, chlorpyrifos, and HCB were correlated with air mass origin, as determined by back trajectory analysis. All pesticides had higher levels during the growing season compared to those in winter, but the ratio of concentrations during the different seasons is much higher for the pesticides in current use. That ratio may aid in distinguishing seasonal variability caused by pesticide application during the growing season from that caused by temperature-driven revolatilization. Higher concentrations of the banned pesticides during 2007 compared to those in 2006 may be due to higher volatilization rates caused by higher surface temperatures consistent with the El Niño Southern Oscillation.

KEYWORDS: Pesticide; atmosphere; seasonal variability; back trajectory; El Niño Southern Oscillation; air mass origin

INTRODUCTION

In agricultural areas such as Southern Ontario, pesticides are widely used to control a variety of insects, weeds, and fungi in an effort to increase crop yields. Although many historically applied organochlorine pesticides (OCPs) have been phased out or banned, as of 2003 Ontario agriculture still relied on over four million kilograms of current-use pesticides (CUPs) every year (1). Previous studies have reported concentrations of OCPs in the Canadian environment (2), showing a trend of declining atmospheric concentrations in response to usage restrictions (3, 4). However, atmospheric concentrations may continue to be influenced by long-term sources such as volatilization from soils (5–8).

A number of studies have reported atmospheric concentrations of CUPs in both North America (9–17) and Europe (18–20). Although some studies have shown that gas-particle partitioning of pesticides is complex and is influenced by a number of environmental factors (18, 20), Yao et al. indicated that CUPs

are mainly found in the gas phase (9), which may influence the selection of air sampling techniques for CUPs. In contrast to banned OCPs, CUP air concentrations are often influenced by local sources (4, 12, 16, 19) as they enter the atmosphere through spray drift during application or from volatilization from soils and plants following application (21). However, air concentrations may also be influenced by long-range transport (LRT) from distant regions (13–15, 22); often both local applications and LRT have a combined influence on atmospheric levels (10, 11, 17). CUPs may also persist in the environment (23), as either the parent compound or as the degradation products, both of which may elicit toxic biological effects (23–25). Thus, the potential for atmospheric LRT raises the potential for contamination in areas remote from their original application (13, 22, 26, 27).

With the exception of Gouin et al. (17), few studies reported the temporal trends of CUPs in the atmosphere with high resolution, yet such data are required to elucidate relationships between areas of pesticide use and potentially vulnerable receptors. In an earlier paper (28), we reported on a measurement campaign of pesticides in the atmosphere which was conducted in an agricultural area of Southern Ontario during 2006 and 2007. While that paper

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presented a comparative evaluation of several air sampling techniques used in that campaign and all of the air concentration data, it did not seek to explain or interpret the levels and their temporal variability (28). The biweekly schedule of the active samples taken during that study allows for a detailed analysis of concentration time trends over two growing seasons and one winter. Specifically, we interpreted the measured seasonal variability of the air concentrations in light of information on the regional use of pesticides and on climate variability during the sampling period. The short-term variability captured by 24 h high air volume sampling was interpreted with the help of calculations of the air mass origin during each sampling period.

MATERIALS AND METHODS

A detailed description of sampling and chemical analysis is given in ref 28. Briefly, from March 2006 until September 2007 in Egbert, Ontario (44°13'52"N, 79°46'59"W), a low-volume active air sampler (LV-AAS) was deployed for concurrent 2-week periods throughout the study, while a high volume active air sample (HV-AAS) was taken during the first 24 h of each two week sampling interval. A pump pulled air through a PUF-XAD-PUF sandwich in both samplers, while the HV-AAS also had a glass-fiber filter (GFF) in front of the PUF-XAD-PUF sandwich to sample the atmospheric particulate phase. Sample volumes for the HV- and LV-AAS were 400 and 3 m³·d⁻¹, respectively. Samples were spiked with 10 μL of 100 μg·L⁻¹ each of d¹⁴-trifluralin and d¹⁰-chlorpyrifos prior to extraction in dichloromethane, with recoveries ranging from 95 to 115%. The samples were not recovery corrected. The samples were analyzed by gas chromatography (Agilent 6890 GC) using an Agilent 5973 mass-selective detector in both EI and NCI modes and a DB-5MS column (J&W Scientific; 60 m × 0.25 mm i.d., 0.10 μm film thickness). Laboratory blanks (*n* = 8) and field blanks (*n* = 16) were consistently below the method limit of quantitation (LOQ) of 0.6 pg·m⁻³ (NCI detection) and 24.5 pg·m⁻³ (EI detection). The higher quantitation limits in EI mode resulted in more nondetects for compounds analyzed with EI detection (atrazine, alachlor, methyl isothiocyanate, disulfoton, metolachlor, and simazine) than those analyzed with NCI detection (trifluralin, pendimethalin, chlorothalonil, endosulfan, hexachlorobenzene [HCB], α- and γ-hexachlorocyclohexane [HCH], *trans*- and *cis*-chlordane [TC, CC], and *trans*-nonachlor [TN]).

Back trajectories of air masses arriving at Egbert during the HV-AAS sampling periods were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLOT), from the National Oceanic and Atmospheric Administration (29). Twenty-four hour back trajectories were calculated, arriving at 50 and 200 m above ground level for each HV sampling period. Three trajectories were calculated for each sample (air arriving at the start, end, and middle of the sampling period, the latter of which may be found in Figure S1 of the Supporting Information). In most cases, the three trajectories were similar, allowing each sample to be assigned to one of four directions of air mass origin; the boundaries were defined as areas where none of the back trajectories crossed.

One measure of atmospheric residence is a chemical's characteristic travel distance (CTD), the distance over which a chemical is expected to travel in the atmosphere before its concentration decreases to 1/e of its original value (30). CTDs were calculated for the pesticides using the Transport and Persistence Level 3 (TaPL3) model (31), using physical and chemical properties for each pesticide compiled from the literature (Table 1). TaPL3 is a steady-state fugacity-based model which assumes nonequilibrium conditions and multimedia transport. For CTD calculations, a chemical released to air is transported between a moving Lagrangian cell and non-moving compartments representing soil and/or vegetation, while being subject to degradation loss.

RESULTS AND DISCUSSION

Nine CUPs (trifluralin, pendimethalin, chlorothalonil, α-endosulfan, chlorpyrifos, atrazine, disulfoton, alachlor, and metolachlor) and six historic-use OCPs (HCB, α- and γ-HCH, TC, CC, and TN) were regularly detected at Egbert. Table 1 includes the arithmetic mean and range of air concentrations during the 2006 and 2007 growing periods (May–September). The air concentrations for the chlordane-related substances (*trans*-nonachlor, *cis*-, and *trans*-chlordane) were very close to the LOQ. Other pesticides which were included in the analysis but were not consistently detected include methyl isothiocyanate, diazinon, metribuzin, malathion, and simazine. We also analyzed the GFF from the HV-AAS for the same suite of pesticides but were unable to quantify any in the particulate phase. Only small amounts of α-endosulfan were found, but these were below the LOQs.

When compared to recent studies in the same agricultural area (9, 17), our data indicate that levels of these CUPs in the atmosphere may be decreasing. Ontario pesticide usage data (1) indeed show a continuous decline since 1983. Endosulfan and chlorothalonil are historically among the most highly applied insecticides and fungicides, respectively, in Ontario (1), and both show dramatic drops in air concentrations when compared with those in 2003 (9, 17). The average air concentration of endosulfan during the 2006 and 2007 growing periods is an order of magnitude lower than that in previous studies, which may indicate a large-scale decrease in endosulfan usage around the Egbert site (1). Significant decreases of endosulfan have also been observed in Great Lakes precipitation, most notably at Point Petre (4). The mean air concentration of trifluralin during our study, albeit lower than that in previous reports, is not statistically different. In contrast, pendimethalin air concentrations in 2006–2007 are significantly lower than those reported for 2003 (17) when pendimethalin usage was much greater than that of trifluralin in Ontario (1). These trends are also reflected in our 2006–2007 air concentrations, where year-to-year decreases are present (discussed below). The difference between trifluralin and pendimethalin air concentrations in 2006–2007 cannot be related to differences in their CTD, which are very close, meaning they should have similar atmospheric residence times.

There appears to be no relationship between the average observed air concentrations of a pesticide and its total usage in Ontario agriculture (data presented in Table 1 and ref 1). However, the atmospheric concentration of a pesticide is expected to also depend on its volatility and atmospheric degradability, and the type of application (28). Although only half as much chlorothalonil as pendimethalin is used in Ontario, air concentrations of chlorothalonil are an order of magnitude higher during the application season and reflect its much longer atmospheric half-life (*t*_{1/2air}); pendimethalin is degraded more quickly in air and thus has a much shorter atmospheric residence time. This is reflected by pendimethalin's CTD of 42 km, compared to 3850 km for chlorothalonil. Another example is endosulfan, which is used in much lower amounts than the herbicides, but has air concentrations that are 2–3 times higher. Endosulfan's *t*_{1/2air} is approximately 6 days, while trifluralin and pendimethalin have *t*_{1/2air} values of 0.35 and 2 h, respectively. This leads to a greater residence time of endosulfan in the atmosphere, which is consistent with its much higher CTD. Finally, air concentrations for metolachlor are similar to those of chlorothalonil, even though usage of metolachlor is roughly an order of magnitude higher. Metolachlor's CTD is only 52 km, which is due to its much shorter atmospheric residence time.

Table 1. Mean Air Concentrations and Range ($\mu\text{g} \cdot \text{m}^{-3}$) for Selected Pesticides at Egbert, Ontario in 2006–2007, along with Previously Reported Levels and Usage Data^a

	C _G 2006–2007		2006–2007		Gouin(17)		Yao(9)		2003		P _L ^{d,e} (Pa)	k _{OH} ^f (cm ³ molec ⁻¹ s ⁻¹)	t _{1/2} (air) (h)	CTD (km)	C _w	C _G / C _w
	mean ^b	range ^c	May–Sept 2003	July–Aug 2003	usage(1) (kg)	usage(1) (kg)	usage(1) (kg)	usage(1) (kg)								
trifluralin	41.2 ± 14.1	4.8–120.8	50	91.1	16,889	16,889	9.8 × 10 ^{-3d}	2.4 × 10 ⁻¹¹	0.35	7.3	8.7 ± 0.6	4.74				
pendimethalin	29.6 ± 12.8	3.6–91.3	140	N.A.	85,334	85,334	9.6 × 10 ^{-3d}	3.0 × 10 ⁻¹¹	2.0	42.5	2.0 ± 0.1	14.80				
chlorothalonil	918 ± 427	8.5–2845	1740	5200	38,570	38,570	8.0 × 10 ^{-5d}	6.2 × 10 ⁻¹⁵	528	3850	59.9 ± 3.7	15.33				
endosulfan	92.1 ± 39.1	1.8–321	820	717	3,698	3,698	6.3 × 10 ^{-3d}	8.2 × 10 ⁻¹²	157	3240	16.8 ± 1.2	5.48				
chlorpyrifos	41.6 ± 14.6	6.7–121	65	378			3.1 × 10 ^{-3d}	9.2 × 10 ⁻¹¹	14	290	15.7 ± 1.8	2.65				
atrazine	587 ± 48	352–823	N.A.	N.D.	513,950	513,950	9.6 × 10 ^{-3d}	2.7 × 10 ⁻¹¹	2.6	54.2	N.D.					
disulfoton	50.7 ± 4.7	27.5–67.4	N.A.	N.A.	12,394	12,394	9.9 × 10 ^{-2d}	1.3 × 10 ⁻¹⁰	10	207	N.D.					
alachlor	468 ± 99	125–900	N.A.	665			4.4 × 10 ^{-3d}	4.5 × 10 ⁻¹¹	2.2	50.6	N.D.					
metolachlor	513 ± 78	145–822	N.A.	129	542,628	542,628	2.4 × 10 ^{-3d}	5.6 × 10 ⁻¹¹	2.5	51.9	N.D.					
HCB	47.1 ± 17.8	0.71–133	N.A.	50.7			9.4 × 10 ^{-3e}	1.7 × 10 ⁻¹⁴	3800	67300	23.7 ± 1.39	1.99				
α-HCH	9.9 ± 3.5	0.69–26.2	21	45.7			2.4 × 10 ^{-1e}	5.7 × 10 ⁻¹³	2.5	47.8	5.2 ± 0.3	1.90				
γ-HCH	8.7 ± 3.3	1.38–25.1	70	17.5			7.7 × 10 ^{-2e}	6.9 × 10 ⁻¹²	2.3	47.8	2.5 ± 0.1	3.48				
trans-chlordane	6.2 ± 1.5	0.87–20.2	N.A.	6.7			3.9 × 10 ^{-3e}	5.0 × 10 ⁻¹²	12	249	3.3 ± 0.1	1.88				
cis-chlordane	7.9 ± 1.8	0.98–56.4	N.A.	6.4			3.0 × 10 ^{-3e}	5.0 × 10 ⁻¹³	12	249	4.1 ± 0.2	1.93				
trans-nonachlor	5.9 ± 1.8	0.83–31.5	N.A.	N.A.			2.9 × 10 ^{-4e}	5.6 × 10 ⁻¹²	12	249	3.7 ± 0.1	1.59				

^aThe pesticides' vapor pressure (P_L; vapor pressure for the liquid phase at 25 °C; sub-cooled P_L is used for pesticides which are normally solid under ambient conditions), OH radical reaction rate constant (k_{OH}), half-life in air (t_{1/2}), and calculated characteristic travel distance (CTD) are also presented. Parameters for the CTD calculations can be found in the Supporting Information. Average air concentrations (pg m⁻³) for selected pesticides during spring- and summer-time growing periods (C_G), winter months (C_w), and the ratio of the two averages are provided. N.A.: not analyzed. N.D.: not detected. ^bData are the arithmetic means of both active sampling techniques during growing periods (May–September). ^cMinimum and maximum air concentrations during growing periods. ^dLiterature-derived values (LDV) compiled by Muir et al. (26). ^eFinal adjusted values (FAV) compiled by Shen and Wania (40). ^fValues calculated using EPI Suite property estimation software, available from the US EPA.

Seasonal Variability of Pesticide Air Concentrations. A comparison between air concentrations determined by HV- and LV-AAS showed poor agreement for a given sampling interval (28). Aside from experimental error, it is believed that this was due in part to the difference in sampling duration between the two systems, whereby the HV-AAS collected a 24 h sample once every two weeks, and the LV-AAS collected a continuous two-week sample. In order to better resolve the seasonal time trends of pesticides in the atmosphere, the concentrations of a pesticide for each 2-week sampling interval from both HV- and LV-AAS were averaged (original air concentration data can be found in ref 28). The moving averages of these data are then calculated from the data for each sampling period, along with the data from the periods immediately preceding and following that time period. This has the effect of smoothing out the temporal trends, removing some of the short-term variability found only in the HV-AAS and allows us to focus on the variability on the scale of months. These moving averages are displayed in **Figure 1**.

Air concentrations of both CUPs and OCPs are low during the winter and rise during the warmer seasons. For OCPs such as HCB and α-HCH, which have no current applications, this seasonal pattern is presumably due to temperature controlled air–surface exchange. Whereas this seasonal trend is also apparent for CUPs, their spring- and summer-time air concentrations increase to a much greater extent than can be attributed to seasonal temperature changes. In fact, the data for some CUPs (alachlor, metolachlor, atrazine, and disulfoton) display no gradual increase and decline in concentrations at all, but rather a switch on/switch off pattern with nondetects in winter and much higher levels during the growing seasons (April–October). The time trends of the CUP air concentrations thus appear to be controlled by periods of pesticide application, which greatly outweigh the influence of temperature on atmospheric concentration.

Precipitation may also influence atmospheric concentrations of pesticides by efficiently scavenging pesticide vapors from the atmosphere. Complete precipitation data are not available for Egbert, but for a station in Barrie, a city approximately 15 km northeast of the sampling site, average precipitation amounts were compiled for the 48-h period preceding the end of each HV-AAS sampling period and regressed against the air concentrations for each pesticide. These plots show no meaningful correlation (Figure S1, Supporting Information), and similar results were found when comparing HV-AAS air concentrations with 5-day precipitation averages and LV-AAS air concentrations with 14-day precipitation averages. This indicates that the occurrence of precipitation is not a strong influence on atmospheric pesticide concentrations at Egbert.

Current-Use Herbicides. Trifluralin and pendimethalin are selective, pre-emergence dinitro-aniline herbicides used to control many annual grasses and broadleaf weeds. They are often applied in the early stages of the growing season (typically April–June) in Southern Ontario, although applications may follow throughout the season (until October) to continue controlling the growth of unwanted plants (32). Trifluralin concentrations (**Figure 1**) follow the typical usage pattern for herbicides, peaking in June while continuing to be elevated throughout the summer. Trifluralin continued to be found in low concentrations throughout the fall of 2006 until the spring of 2007. In 2007, trifluralin air concentrations followed a similar trend, with a notable decrease during June 2007, indicating a possible lapse in application during that period. There is no simple meteorological explanation because neither temperature nor precipitation during June 2007 was significantly different from the year before.

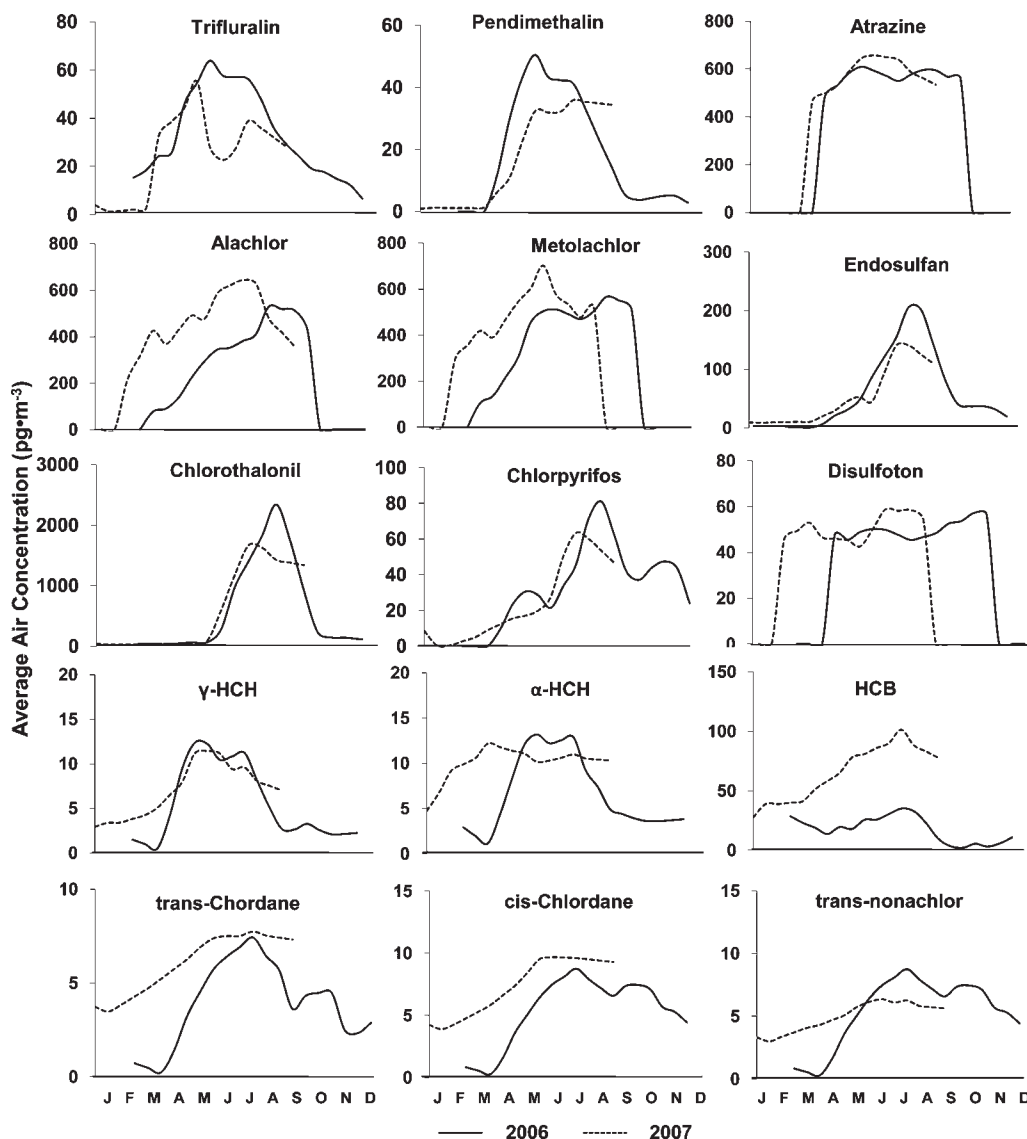


Figure 1. Moving averages of air concentrations determined by both active air samplers at Egbert, Ontario, from 2006–2007 for select current- and historic-use pesticides.

Pendimethalin, which is very similar in properties to trifluralin and has similar uses (32), unsurprisingly showed a similar pattern of air concentrations during both years. In 2006, the air concentrations peaked at the end of May but indicated continued use throughout the growing period. In 2007, the trend was not significantly different, although overall air concentrations were somewhat lower than those in the previous year, suggesting a drop in this pesticide's usage around the Egbert sampling site. Although the observed trend is not statistically significant, decreasing pendimethalin usage would help explain why pendimethalin air concentrations are now lower than those of trifluralin. Current usage data are not available for Ontario to confirm if pendimethalin usage is indeed decreasing.

Atrazine is a widely used triazine herbicide, which targets both pre- and postemergent broadleaf weeds. Alachlor and metolachlor are structurally similar chloracetanilide herbicides, which may be mixed with other pesticides such as atrazine and trifluralin to provide wider protection against pests (32). These three herbicides follow similar trends through 2006–2007, with elevated air concentrations during the spring and summer and levels close to or below quantitation limits during most of the winter months (Figure 1). Atrazine concentrations are the most

consistent between the two years, with overall averages remaining nearly identical through the two growing seasons. These air concentrations are also consistent with previous studies performed in the same region (12, 28). Alachlor and metolachlor show very similar trends in their respective air concentrations, which is to be expected given their similar structure and agricultural uses. Both chemicals are found in the atmosphere throughout the 2006 growing period, with a rise in air concentrations toward the end of the 2006 summer, indicating a surge in usage during this period. In 2007, the air concentrations increase earlier than those in 2006 and also decrease starting in late July 2007, indicating that the 2007 applications occurred earlier than those in the previous year but that the overall usage appears to be of about the same amount.

Current-Use Insecticides and Fungicides. Endosulfan is a neurotoxic organochlorine insecticide of the cyclodiene family of pesticides. It is used in agriculture around the world to control insect pests, and its application is linked to the emergence of the insects which are targeted; as such, it may be applied at different times throughout the growing season (32). Air concentrations increased starting in June 2006 and continued to be high until mid-September 2006 (Figure 1), indicating that endosulfan is in

continuous use throughout the summer. This usage trend is repeated during the 2007 summer, although the air concentrations peak in late June–early July and are then lower through to the end of August, indicating that the amount of endosulfan applied may have been less overall in 2007. This also agrees with earlier findings that endosulfan usage is decreasing in Ontario (1, 4). Interestingly, the HV-AAS from October 27 and November 21, 2006 show what may be a late fall application of endosulfan (concentrations rise to $68 \text{ pg}\cdot\text{m}^{-3}$ from less than $30 \text{ pg}\cdot\text{m}^{-3}$ during September).

Chlorothalonil is a broad spectrum chloronitrile fungicide with long residual activity. As a fungicide, it is normally applied during the middle of the growing season as a preventative measure against fungal infection during the warmer humid days of the summer (32). The air concentration trends of chlorothalonil appear very similar to those of endosulfan, indicating that their usage patterns around the Egbert station may be very similar. The lower chlorothalonil air concentrations in 2007 also indicate a lower usage in the second year, again agreeing with the overall trend of decreasing usage in Ontario (1).

Chlorpyrifos is an organophosphate insecticide, which may be applied at different times during the growing season to control various types of pests (32). Indeed, this appears to be reflected in the air concentrations for both 2006 and 2007, where both peaks and valleys are present in the air concentration trends. In 2006, there are significant peaks in air concentrations both in late April–early May and again in August. In 2007, there is a more gradual increase in the spring and a slightly earlier summer peak. Overall, the air concentrations in 2007 are somewhat lower than those in 2006. Both sampling systems show a curious increase in air concentrations during late October–early November, well after the traditional growing period. Temperatures did not rise drastically during this time, discounting a temperature-based increase, which would also have been apparent in some of the other pesticides' air concentrations during this period. It is not clear what caused this late concentration peak for chlorpyrifos.

Disulfoton is an organophosphate insecticide which is applied to a wide variety of field crops (32). The disulfoton air concentrations have a similar trend to those of atrazine, alachlor, and metolachlor, partially because air concentrations are only above detection limits during the spring and summer, while levels fall close to or below quantitation limits during most of the winter months (Figure 1). The air concentrations are elevated during June and September 2006 and then start to rise early in 2007 but fall below $10 \text{ pg}\cdot\text{m}^{-3}$ in August 2007. This trend indicates two periods of use in the 2006 growing season and earlier application in 2007 but little to no use during the end of the 2007 growing season. However, disulfoton air concentrations are an order of magnitude lower than those of the three herbicides, atrazine, metolachlor, and alachlor, which are mainly a function of its much lower usage in Ontario (1).

Legacy Pesticides. Hexachlorobenzene (HCB) is a fungicide formerly used as seed treatment. Chlordane, a mixture of mainly α - and γ -isomers and several side-products, is an insecticide which was used until 1988, primarily for termite control. Lindane, which is an insecticide consisting mainly of γ -hexachlorocyclohexane (HCH), until recently still had agricultural uses in some developing nations. These chemicals have now all been banned under the Stockholm Convention yet are typically found as persistent residues in the environment (33, 34). As there are currently no applications of these chemical in Canada or the USA, their air concentration variability is presumably related to volatilization from soils. Indeed, their concentrations rise during the warmer months of the year and decrease to lower levels during the cold winter months (Figure 1). Clausius–Clapeyron plots of

In C_{air} vs $1/T$ indicate that this is the case, although only *cis*-chlordane and *trans*-nonachlor have an $r^2 > 0.5$ (details in Figure S2 and Table S2 of Supporting Information). The CC plots of *trans*-chlordane and γ -HCH have relationships similar to the CC plots of *cis*-chlordane and *trans*-nonachlor but more variability, which is not completely explained by variations in air temperature. The regression is poorest for HCB and α -HCH, which may be due to the higher air concentrations observed for both chemicals during 2007. Legacy pesticide air concentrations do not change as dramatically throughout the year as those of the CUPs, which is in agreement with previous studies (12). Expressed quantitatively, the ratio of average air concentrations during the growing season (C_G , April–September) to the concentrations during the winter (C_W) is smaller for the legacy OCPs (less than 2) than for any of the CUPs (Table 1).

Remarkably, the concentrations of the two HCHs and of the three chlordane-related substances are all higher during the first five months of 2007 compared to those in the period from February to May 2006. This difference is particularly pronounced for *cis*- and *trans*-chlordane and α -HCH. During the summer, their concentrations in the two years of sampling are more similar. HCB also shows lower levels in 2006 compared to that in 2007, but the largest difference occurs during summer, i.e., is delayed by three to four months relative to the other legacy OCPs. Could there be a difference in the rate of volatilization of legacy OCP in 2007 compared to that in 2006, which could result in such differences in air concentrations?

Recently, it has been shown that the air concentrations of OCPs, including HCB, in the Canadian atmosphere can be positively influenced by the El Niño Southern oscillation (ENSO) (35–37). During an El Niño event, warmer equatorial waters in the Pacific Ocean extend from the western coast of South America to the International Date Line. Because of prevailing winds, this leads to elevated surface air temperatures across Western Canada that extend toward the western Great Lakes. Higher surface air temperatures in these areas, it has been argued, can lead to increased volatilization of pesticide residues to the atmosphere, even during the colder winter months (35). El Niño events are recorded by the Multivariate ENSO Index (MEI). The most recent El Niño event occurred during our study, beginning in September 2006 and ending in late January 2007, as indicated by the MEI for that period (Figure 2, bottom panel). This results in higher than average surface air temperatures across Western Canada and into Western Ontario. Even in Egbert, November and December 2006 were much warmer than the following year (Figure 2, top panel).

The time period of largest concentration difference (February to May 2007 for most OCPs, March to August 2007 for HCB) does not coincide with the maximum MEI (September 2006 to January 2007) but seems to be delayed by 4 to 5 months (or even 7 to 8 months in the case of HCB). Such a delay is consistent with a delay of up to half a year found in correlations between warmer equatorial waters in the Pacific Ocean and elevated concentrations of α -HCH and HCB in the Great Lakes atmosphere (37). A longer delay for HCB can be rationalized by the much longer atmospheric residence time of HCB (> 1 year due to very low k_{OH} and high air–water partition coefficient) compared to that of the other OCPs (weeks to months). To further investigate, we used the CoZMo-POP-2 model (Coastal Zone Model for Persistent Organic Pollutants, version 2), which is a level-IV nonsteady-state multimedia fate model, which allows the estimation of multimedia transport without assuming equilibrium partitioning between compartments (38). Simple calculations with the CoZMo-POP model indeed suggest that for a chemical with such a high atmospheric residence time as HCB, a temporary increase in the

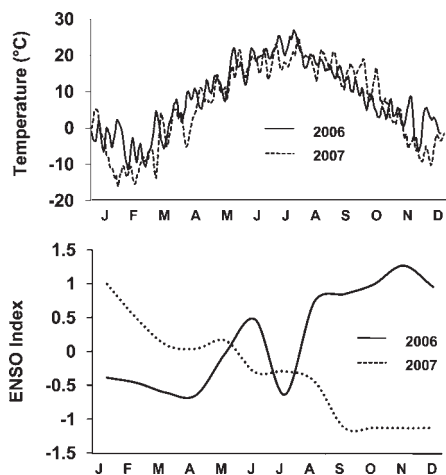


Figure 2. Daily temperature in Egbert, Ontario (top panel); monthly ENSO index (bottom panel).

rate of volatilization from high air temperatures would be reflected in a temporary air concentration increase approximately 2 months later (plots found in Figure S3 of the Supporting Information). The fact that the elevated concentrations for HCB occur two to three months after the elevated concentrations of legacy pesticides with lower atmospheric residence times is thus consistent with enhanced volatilization being responsible for higher levels in 2007 compared to those in 2006.

Short-Term Concentration Variability and the Influence of Air Mass Origin. The presence of pesticides in air is often directly related to the application of pesticides in an agricultural region, either from spray drift or volatilization from plants or soils after application. However, for chemical species which have an appreciable lifetime in the atmosphere, transport through atmospheric movement is a possible factor in explaining temporal trends. During the 2006–2007 growing seasons (May–September), we calculated back trajectories of the air mass arriving during each sampling period and compared with the HV-AAS air concentrations to determine if air mass origin influenced the air concentrations at Egbert. Trajectories corresponding to periods of low air concentrations for all analytes were discarded from the analysis; the remaining trajectories were noted to fall into four distinct categories based on the direction from which they arrived at the Egbert sampling site (Figure 3). Boundaries in Figure 3 were placed in locations where the back trajectories rarely crossed. Air arrived from directly north of Egbert on five sampling events; from either Eastern Ontario or eastern US states on three dates; air parcels arrived from areas west of Egbert or the western Great Lakes on eleven dates; and air traveled from south of Egbert on seven dates.

Chlorothalonil concentrations show one of the strongest relationships with air mass origin, with average concentrations of $72 \text{ pg} \cdot \text{m}^{-3}$ when air arrives from the north, which is an order of magnitude smaller than that during days when the air arrives from the west or south (Figure 4). Chlorothalonil is widely used to protect tomato plants from mold contamination and is also used during the production of tobacco (32); the majority of these crops are produced in areas to the southwest of Egbert (39), which helps explain why air concentrations are elevated when the air arrives from these directions, although they are not statistically different from the average air concentration ($p > 0.05$). Of all the pesticides analyzed, chlorothalonil shows the most significant difference between periods when the air arrives from the north and all other periods, indicating that very little chlorothalonil is used in areas to the north of Egbert and that air concentrations



Figure 3. Categories of air parcel back trajectories, on the basis of the direction of travel prior to arrival at the Egbert sampling site. Back trajectories were calculated with the HYSPLIT model (29).

are dominated by applications in all other regions. Chlorpyrifos is also used during the production of tobacco in the same regions as chlorothalonil, and there is a significant elevation of chlorpyrifos air concentrations when the air arrives from south of Egbert.

Endosulfan is used in a wide variety of crops, including grains, vegetables, and fruits, with the highest use in barley and wheat producing counties to the west of Egbert (39). We see that air concentrations are elevated when the arriving air parcel has passed through areas to the west of Egbert (Figure 4), although this difference is not statistically significant ($p > 0.05$). At times, the air concentrations are also elevated when the air arrives from areas to the east and south of Egbert, areas which also have high wheat production. Because of endosulfan's large CTD value, it is also possible that air concentrations at Egbert are influenced by more distant regions, such as the Canadian Prairies or the northern United States, and thus, the lower levels observed in Egbert during 2006–2007 may also indicate less usage in these areas.

There is no significant difference in the air concentrations with respect to the origin of the arriving air parcel for a number of chemicals which are used on crops in the areas surrounding Egbert. Trifluralin and pendimethalin are used in the production of canola, soy, and corn, three crops which are produced in many of the counties surrounding Egbert (39). Atrazine finds highest use on corn crops, with nearly 500,000 kg applied to this Ontario crop in 2003 (1). Although corn is grown throughout Southern Ontario, its highest production is in counties to the south and west of the Egbert site, which correlates with the elevated air concentrations seen during periods of air delivery from these regions (Figure 4). Alachlor and metolachlor are both used in the production of corn and soybeans, in approximately equal portions per crop. There appears to be no significant difference in the air concentrations of any of these chemicals based on the origin of the arriving air parcel.

Disulfoton air concentrations show a much different correlation to the air back trajectories than the other CUPs. The lowest air concentrations occur during periods when the air originates from areas south and/or west of Egbert, while the highest levels are found when the air arrives from either the north or east. Disulfoton is often used in lower production vegetable crops such as lettuce, cauliflower, and broccoli (32). Although these crops are grown in areas to the south and west of Egbert, the correlation in Figure 4 indicates that disulfoton air concentrations are influenced more strongly by local applications in regions to the north and east. Barrie, a city of approximately 177,000 residents, lies in this direction, and disulfoton air concentrations may be due to a combination of agricultural and domestic applications in this area.

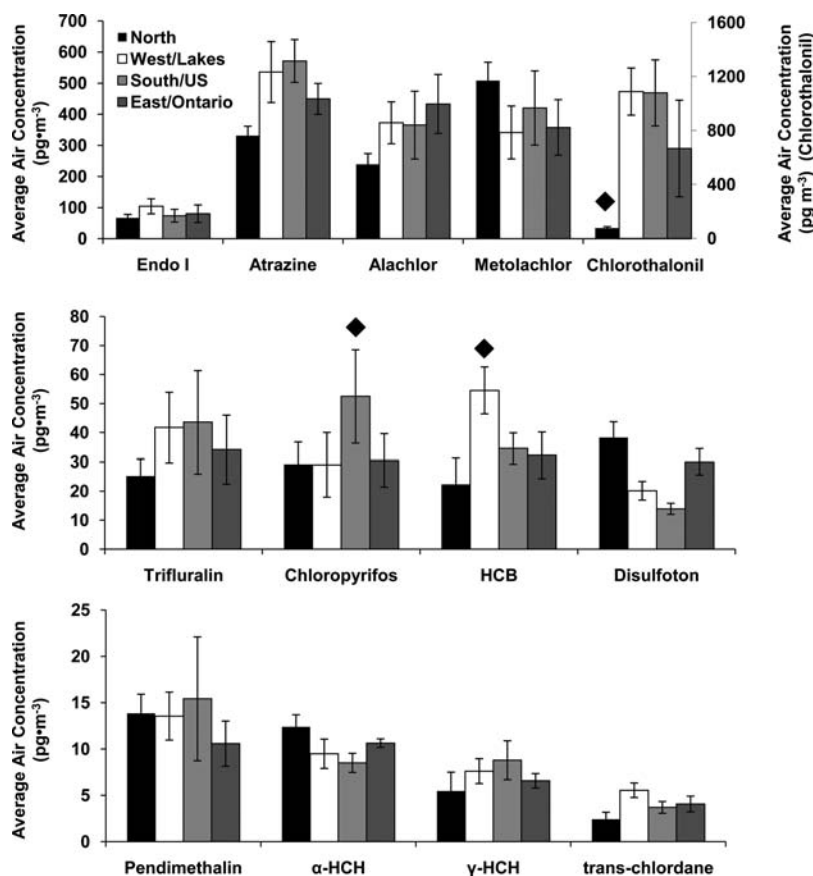


Figure 4. Average air concentrations for selected pesticides during sampling periods in which the air parcel at Egbert originates from the North, West/Great Lakes, South/US, and East/Ontario. The black diamonds (◆) indicate sample sets which are significantly different from the chemical's average air concentration ($p > 0.05$).

Air mass origin has little influence on the air concentration of the legacy pesticides. α - and γ -HCH, and the chlordanes all show no significant difference in air concentrations regardless of the direction from which the air arrives at the Egbert sampling station. Since all these periods were during the warmer growing season, the warmer temperatures are the main factor in the air concentrations of these chemicals, not the direction of the arriving air. HCB is the one legacy pesticide which shows a correlation between the air parcel back trajectory and local air concentrations. The HCB air concentrations are elevated above the summer averages at Egbert on days when the air arrives from the west, often having passed over the Great Lakes. This may be related to our earlier discussion that the elevated HCB air concentrations during the 2007 summer are related to higher surface air temperatures in regions to the west of Egbert.

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Supporting Information Available: Physical properties for selected pesticides, used to calculate the Characteristic Travel Distance; Clausius–Clapeyron plots for OC pesticides and regression coefficients; plots of HCB and α -HCH air concentration vs temperature in CoZMo-POP; air concentrations of infrequently detected pesticides; and air mass back trajectories. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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