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A captured episode of γ-hexachlorocyclohexane air pollution in the Toronto area after the Canadian lindane ban

Yuan Yao*, Tom Harner, Ky Su, Kenneth A. Brice, Pierrette Blanchard, Jianmin Ma

Science and Technology Branch, Environment Canada, 4905 Dufferin St., Toronto, ON, M3H 5T4, Canada
** Worsfold Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, ON, K9J 7B8, Canada*

ABSTRACT

A Canadian ban on lindane for agricultural use came into effect on December 31, 2004. In the years leading up to this ban, air concentrations of γ–HCH, the active ingredient of lindane, decreased gradually over the Great Lakes region. Typical mean concentrations were about 5 and 10 pg m^{-3} for Lakes Huron and Ontario, respectively, during the summer of 2005. However, during the period June 27–28, 2005, a γ–HCH air pollution episode was captured in Toronto by three independent sampling programs [Episodic Pesticide Transport (EPT) Study, Integrated Atmospheric Deposition Network (IADN) and Canadian Atmospheric Network for Currently Used Pesticides (CANCUP)], with concentrations of 586 and 3 070 pg m^{-3} measured in north and downtown Toronto, respectively – an increase of about two orders of magnitude above typical levels. This episode was not observed at any of the regional IADN sites on the same day, suggesting a localized emission in the city from an unknown and episodic source. This study demonstrates the value in continued monitoring of persistent organic pollutants (POPs) beyond their phase–out period and highlights the importance of combining information from different projects to discover environmental pollution events.

Keywords:
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Corresponding Author:
Yuan Yao
Tel: +1-705-748-1011
Fax: +1-705-748-1625
E-mail: yuanyao@trentu.ca

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1. Introduction

Hexachlorocyclohexane (HCH) is a synthetic organochlorine compound that exists in several chemical forms called isomers. HCH technical grade generally contains five isomers (α–: 60-70%; β–: 5-12%; γ–: 10-12%; δ–: 6-10%; and ε–: 3-4%) (Xiao et al., 2004) and another formulation consisting of at least 99% of the active ingredient, γ–HCH, is known as lindane (Hornstein and Sullivan, 1953). Both formulations have experienced widespread global use over the last 60 years. The use of technical HCH began in 1943 and peaked in 1981 with an estimated annual use of 334 400 t. The cumulative use of technical HCH was estimated to be as high as 6.0 million t (Li et al., 1998). The total global annual use for lindane was estimated to be 5 900 t in 1980 and 4 000 t in 1990 (Li et al., 1996). As a consequence of the widespread and continuous use of HCH products, public concern regarding its ubiquitous presence in the environment led to regulatory action restricting the use of the technical HCH mixture in a number of countries, including Canada, during the 1970s (CEC, 2006).

Whereas the widespread use of technical HCH discontinued in the 1970s, the use of lindane continued until recently. In 2006, for instance, Canada, Mexico and the United States of America established a North American Regional Action Plan (NARAP) aiming at reducing the risks associated with exposure to lindane and other HCH isomers (CEC, 2006). This follows regulatory activity in Canada in December 2004, which banned the use of lindane for agricultural purposes (with an exemption for pharmaceutical uses to control head lice and scabies). In 2005, Mexico committed to phase out all lindane applications and the U.S. implemented a ban on lindane use in agriculture in August 2006. In Canada, the main use (94%) was as a seed treatment on canola in the Canadian Prairies (i.e., Alberta, Saskatchewan, and Manitoba) and it is estimated that 9 000 t was used in Canada over the period 1970–2000, with peak use in 1994 (558 t) (Li et al., 2004). In May 2009, three HCH isomers, namely γ–HCH, α–HCH and β–HCH, were added to the Stockholm Convention's persistent organic pollutants (POPs) list. The classification of the three HCH isomers as POPs is based on strong scientific evidence demonstrating that these substances are persistent, bioaccumulative, cause adverse effects, and have the potential to undergo long-range atmospheric transport.

Lindane has a relatively high vapor pressure ($P_L = 7.57 \times 10^{-2}$ Pa at 25 °C) (Xiao et al., 2004), compared to many other legacy and current–use organochlorine pesticides (e.g., p,p'–DDT: 9.60×10^{-5} Pa at 25 °C; α–endosulfan: 6.3×10^{-3} Pa at 25 °C) (Woodrow et al., 2001; Muir et al., 2004). Consequently, γ–HCH volatilizes readily to the atmosphere after application and exists predominantly in the vapor phase (Ballschmiter and Wittlinger, 1991; Lane et al., 1992; Yao et al., 2008) making it well–suited to undergo long–range atmospheric transport to remote areas such as the Arctic (Bidleman et al., 1995; Hung et al., 2002). The potential of γ–HCH for long–range atmospheric transport is also supported by modeling studies. For example, Beyer et al. (2000) calculated a high characteristic travel distance (CTD) value for γ–HCH in air compared to most other organochlorine insecticides based on a

multimedia box model. Ma et al. (2003) pointed out that the atmospheric loading of γ–HCH to the Great Lakes region over the period of May 1, 1998–April 30, 1999 was mostly attributed to applications of lindane in the Canadian Prairies. In addition, Van Jaarsveld et al. (1997) noted that γ–HCH has the potential for dispersion throughout the hemisphere with most of it destined to end up in large water bodies. This is because γ–HCH is relatively soluble, with a relatively lower Henry's Law constant (1.5×10^{-1} Pa m^3 mol^{-1} at 25°C) compared to other legacy organochlorine pesticides such as hexachlorobenzene (1.03×10^{1} Pa m^3 mol^{-1} at 25°C) and aldrin (1.72×10^{1} Pa m^3 mol^{-1} at 25 °C), and hence it will be scavenged by precipitation (Granier and Chevreuil, 1997). HCH isomers are the most abundant organochlorines in the Arctic Ocean. The highest concentrations of HCH isomers are in the Beaufort Sea and Canadian Archipelago. The elevated residues of HCH isomers in marine mammals of the Archipelago are likely from the high concentrations of HCH isomers in the water (CEC, 2006).

Lindane has been routinely monitored in the Great lakes region and has been the subject of a number of processes and modeling studies (Ma et al., 2003; Sun et al., 2006; Yao et al., 2008). A prominent example is the Integrated Atmospheric Deposition Network (IADN), which was initiated under the Canada–U.S. Great Lakes Water Quality Agreement (GLWQA) during 1988–1990 for monitoring loadings of priority toxic pollutants to the Great Lakes – including: organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and other trace elements present in air and precipitation (Hoff et al., 1996; Buehler et al., 2004; Galarneau et al., 2006). Lindane was added into the IADN's target analyte list in the early 1990s and has been routinely measured in air at Canadian IADN sites since 2000. A more recent monitoring network aimed at current–use pesticides (CUPs) is the Canadian Atmospheric Network for Currently Used Pesticides (CANCUP), which was initiated to investigate pesticide concentrations in air in the diversity of agricultural regions across Canada (Yao et al., 2006). Lindane was targeted in the project to document changes in air following withdrawal of its use in the prairies in 2003 and the phase–out of all agricultural uses in the country in 2004. Additionally, a short–term Episodic Pesticide Transport (EPT) study during the summer of 2005, conducted by Environment Canada with the aim of capturing atmospheric pesticide transboundary transport events, has more recently measured lindane in the Great Lakes region (Yao et al., 2007).

In this paper the time trends of γ–HCH air concentrations at the three Canadian IADN sites are investigated for the period 2000–2005 in order to establish the long–term regional background air concentration for γ–HCH leading up to the Canadian ban in December 2004. Overlapping and supporting results from all three programs demonstrate the occurrence of an intense, 1–day emission episode of γ–HCH on June 27-28, 2005 in the Toronto area.

2. Methods

Detailed sample collection and analysis methods for the IADN program are described in this section. Sampling and analysis details for the EPT and CANCUP studies have been described elsewhere (Yao et al., 2007; Yao et al., 2008). Therefore, only a brief description of the field and laboratory operations for the two programs will be given here.

2.1. Sample collection

Air samples for IADN, CANCUP and EPT were collected by different site operators. During 2000–2005, Canadian air sampling sites operated under IADN included two background/receptor sites at Burnt Island and Point Petre and a rural/agricultural site at Egbert (Figure 1 and Table 1). Twenty–four hour air samples (~350 m^3) were collected on a schedule of 1 in 12 days using high–volume samplers (PS-1, General Metal Works). The sampling head employed a glass fiber filter (GFF, 102 mm diameter, Gelman A/E Microfibre) for particle collection followed by a polyurethane foam (PUF, 7.5 cm × 6.2 cm diameter, Levitt Safety) plug for trapping gas–phase compounds. In 2005, daily air samples, with the same sampling frequency, were also taken at Gage, a site in downtown Toronto and on a buoy situated in western Lake Ontario (Figure 1).

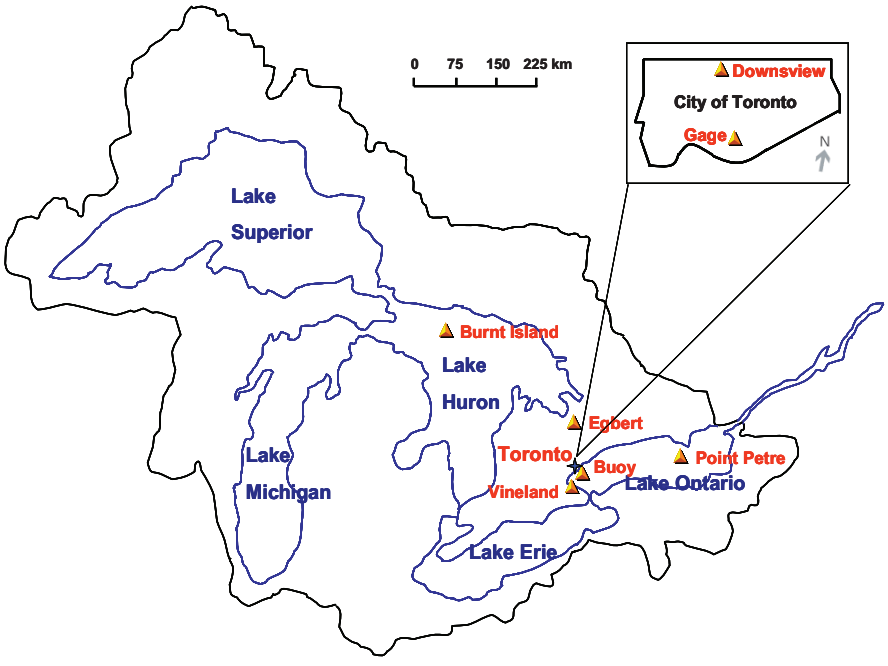

Figure 1. *Map showing air sampling locations in the Great Lakes region.*

Table 1. *Description of the air sampling sites and periods under the three monitoring and research programs in 2005*

Sampling site	Latitude	Longitude	Description	Sampling period
Gage, ON	43°39' N	79°23' W	Downtown Toronto.	IADN: Jun. 2005-Oct. 2005
Downsview, ON	43°40' N	79°37' W	Residential and industrial area.	EPT: Jun. 2005-Jun. 2005 Sep. 2005-Sep. 2005 CANCUP: Jun. 2005-Aug. 2005
Buoy, ON	43°26’ N	79°24’ W	Receptor site on the Lake Ontario.	IADN: May 2005-Oct. 2005
Burnt Island, ON	45°50’ N	82°57’ W	Receptor site on the Lake Huron.	IADN: Jan. 2000-Dec. 2005
Point Petre, ON	43°50’ N	77°09’ W	Receptor site on the Lake Ontario.	IADN: Jan. 2000-Dec. 2005
Egbert, ON	44°14' N	79°47' W	Rural and suburban area, surrounded by fields and mixed forest.	IADN: Jan. 2000-Dec. 2005 CANCUP: May 2005-Jul. 2005
Vineland, ON	43°11' N	79°24' W	Intensive agricultural area (fruit, vegetables, and wine).	CANCUP: Jun. 2005-Aug. 2005

Under CANCUP, air samples were collected continuously from the spring to summer of 2005 at eight mainly agricultural sites across Canada. High–volume air samplers (PS–1, Tisch Environmental, Inc.) were used to collect weekly integrated air samples (~2 500 m^3). Particles were collected with GFFs (102 mm diameter, Pall Life Sciences) and gas–phase compounds were trapped with cartridges containing 10 g of XAD–2 resin (Supelpak 2, Supelco) placed between PUF plugs (75 mm × 37 mm, Supelco). Most relevant to this study are the two rural/agricultural sites at Egbert and Vineland and the urban site at Downsview, in north Toronto, approximately 17 km from the Gage site mentioned above (Figure 1 and Table 1).

For the EPT study, daily air samples (~280 m^3) were collected continuously during two sampling periods (June 22–29 and September 21–30, 2005) at Downsview to capture transboundary pesticide transport events from the southern U.S. A high–volume air sampler equipped with GFF and PUF/XAD/PUF cartridges (same as used in the CANCUP study) were employed. For all three programs, one field blank was collected for each sampling period and samples were stored at low temperature (-20 to 4°C) and in the dark until extraction.

2.2. Sample analysis

Samples collected under IADN, CANCUP and EPT were analyzed by Environment Canada’s Organic Analysis Laboratory (OAL) in Toronto, National Laboratory for Environmental Testing (NLET) in Burlington and Hazardous Air Pollutants (HAPs) laboratory in Toronto, respectively. Under the IADN program, gas–phase (PUF) samples were Soxhlet extracted with hexane for 24 h. The extracts were then dried using anhydrous granular sodium sulfate (12–60 mesh) and filtered with glass fiber filter (Whatman 934–AH). After volume reduction and exchange into isooctane, Florisil column chromatography (60–100 mesh, Supelco PR grade, 2% w/w water–deactivated) was used to remove interferences and fractionate the extracts. γ–HCH was eluted with 15% dichloromethane (DCM)/85% hexane and concentrated to 1 mL, followed by gas chromatography (GC)/electron capture detector (ECD) analysis. An HP5890 GC equipped with dual ^{63}Ni ECD and dual heated splitless/split injection ports was utilized. A DB–5 capillary column (60 m length × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) was used for primary analysis (80°C for 2 min, 15°C min^{-1} to 160°C, 2.5°C min^{-1} to 265°C, then hold for 20 min). A DB–17 column (30 m length × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) was used under the same temperature program conditions to provide confirmatory analysis. Splitless mode injections (1 µL) were made separately onto both columns using an autosampler (HP 7673 series). Ultra high purity helium and nitrogen were used as carrier gas and make–up gas. External method was used for quantitation. To confirm the presence of γ–HCH, mass spectrometry (MS, Agilent 5973N) was also applied in both electron impact (EI) and electron capture negative ion (ECNI) scan modes.

Under the CANCUP project, two surrogate compounds, 1,3–dibromobenzene (1,3–DBB) and endrin ketone, were added to each sample for analyzing organochlorine pesticides prior to Soxhlet extraction. The gas–phase (PUF/XAD/PUF) samples and particle–phase (GFF) samples were extracted together with 400 mL hexane/acetone (50/50 v/v) for 24 h. The extracts were concentrated and solvent exchanged to hexane. After cleanup with silica gel column chromatography, γ–HCH in each sample extract was identified and quantified by GC (HP 5890 Series II)/ECD (Ni^{63}). A DB–5 column (30 m length × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) was used for primary analysis (80°C for 2 min, 4°C min^{-1} to 260°C and hold for 8 min) and a DB–1 column (30 m length × 0.25 mm i.d., 0.25 µm film thickness) was used for confirmation under the same temperature program.

In the EPT study, the gas– and particle–phase samples were spiked with a γ–HCH–d_6 surrogate standard and Soxhlet extracted together with 400 mL hexane/acetone (50/50 v/v) for 24 h. The extracts were reduced in volume by rotary evaporation and exchanged into hexane. The extracts were then cleaned with alumina column and analyzed by GC (Agilent 6890)/MS (Agilent 7683). Negative chemical ionization (NCI) mode was used. A DB–5MS capillary column (60 m length × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) was employed. The temperature program started at 90°C for 1 min, 15°C min^{-1} to 240°C, 6°C min^{-1} to 270°C, then 25°C min^{-1} to 290°C and hold for 6 min.

All laboratory operations were monitored using strict quality assurance/quality control (QA/QC) measures. These included analyzing laboratory blanks, laboratory spikes and standard reference materials, and routine participation in inter–laboratory studies. The average surrogate recoveries were 109% [standard deviation (SD): 22%] for 1,3–DBB, 95% (SD: 19%) for endrin ketone, and 82% (SD: 6%) for γ–HCH–d_6. Field blanks were investigated and the detected quantities were negligible. No recovery or blank correction was applied to the results.

3. Results and Discussion

3.1. Historical trend of γ–HCH air concentrations in the Great Lakes atmosphere

The long–term air concentration for γ–HCH in the Great Lakes region is presented in Figure 2 for the three Canadian IADN sites (Burnt Island, Point Petre and Egbert) during 2000–2005. Ranges and average concentrations of airborne γ–HCH measured by IADN, CANCUP and EPT are summarized in Table 2. For comparison, γ–HCH air concentrations in the Canadian atmosphere reported by other studies are also given in Table 2. Air concentrations for γ–HCH, which exists predominantly in the gas–phase, exhibited seasonality with the highest air concentrations occurring during the late spring to early summer. This is consistent with the application of lindane–treated crop seed in the growing season. Air concentrations at all these sites decreased gradually. Overall, annual average concentrations at Burnt Island, Point Petre, and Egbert in 2005 were over 35% lower than 2000 levels (the highest difference is at Point Petre, at 50%), reflecting the decrease in lindane use in Canada during this period.

Among the three sites, highest air concentrations of γ–HCH were at Egbert, being consistent with the fact that Egbert is an agricultural site surrounded by croplands, while Burnt Island and Point Petre are background, lakeside receptor sites and exhibit much lower air concentrations of γ–HCH. Similar seasonal variations and time trends were found for γ–HCH in precipitation samples collected at several IADN sites including Brule River, Eagle Harbor, Chicago, Burnt Island, and Point Petre from 1998 through 2004 (Sun et al., 2006). Previously, Simcik et al. (2000) reported decreasing trends of γ–HCH concentrations in rain collected over Lakes Superior, Michigan, and Erie during 1991–1997. Results for the Burnt Island, Point Petre and Egbert sites establish a long–term background for the regional atmosphere. No highly elevated air concentrations were observed over the period 2000–2005. Peak air concentrations of γ–HCH for the three sites are 48 pg m^{-3} at Burnt Island in 2001, 56 pg m^{-3} at Point Petre in 2000, and 167 pg m^{-3} at Egbert in 2001. These peaks are linked with lindane application in the region in the past. The annual mean concentrations for 2001 are 8 pg m^{-3} at Burnt Island, 10 pg m^{-3} at Point Petre and 23 pg m^{-3} at Egbert, being comparable with yearly integrated air concentrations from passive air sampling at the same sites (Burnt Island: 21 pg m^{-3}; Point Petre: 35 pg m^{-3}) during the summer 2000 to summer 2001 (Shen et al., 2004). The daily air concentration of γ–HCH in the Great Lakes region from 1993 through 2005 ranges from ND (< 0.1) to 83 pg m^{-3} for receptor sites (Buoy, Burnt Island, Point Petre, Lake Ontario), from 0.4 to 167 pg m^{-3} for rural sites (Egbert, Vineland), and from 6 to 61 pg m^{-3} for urban sites (Downsview, Gage), except two extremely high values (586 pg m^{-3} at Downsview and 3 070 pg m^{-3} at Gage) that were observed in Toronto on June 27–28, 2005 (see discussion below). The highest regional air concentration prior to 1990s was measured by Hoff et al. (1992) at the Egbert site during July 1988–September 1989 (see Table 2).

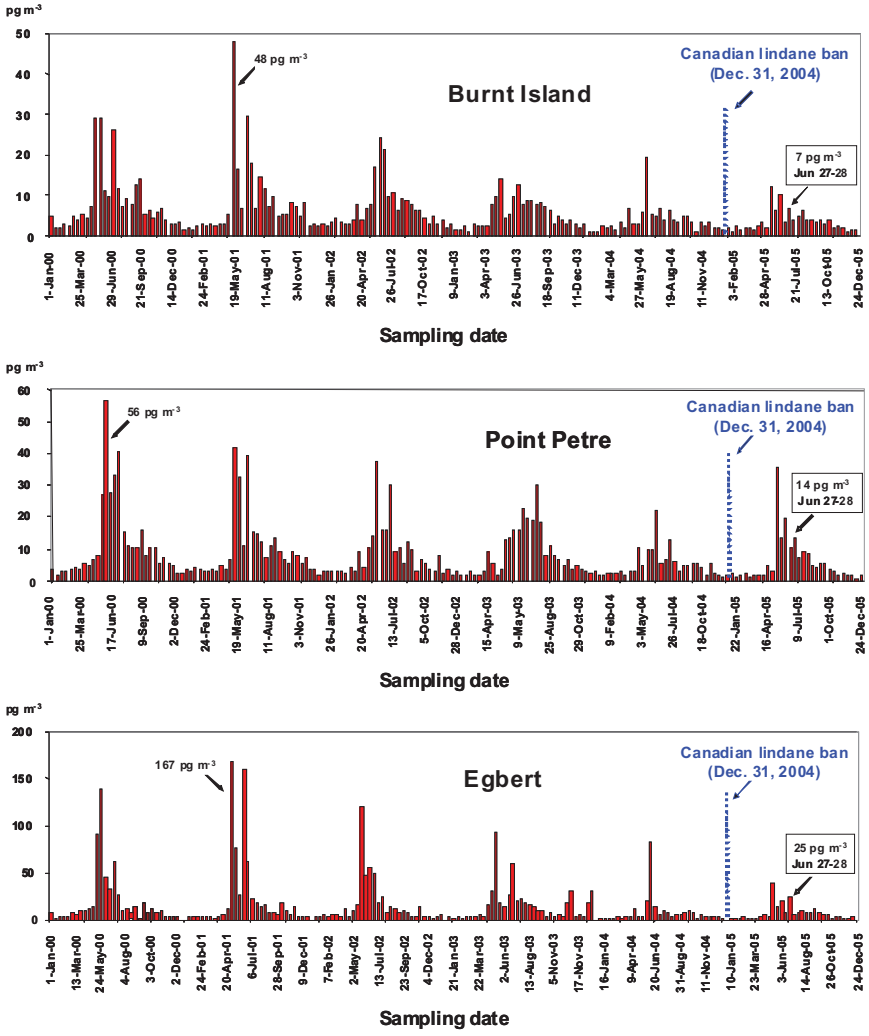

Figure 2. Time trends in gas-phase concentrations (pg m^{-3}) of γ–HCH at the three Canadian IADN sites (Jan. 2000–Dec. 2005). Sampling was conducted on a cycle of every 12 days.

Table 2. *Ranges and mean concentrations (pg m^{-3}) of γ–HCH in the Canadian atmosphere measured in this study and other studies*

Sampling location	Site type	Sampling time	Sample type	Conc. range	Mean conc.	Ref.
Gage, ON	urban	Jun. 05-Oct. 05	daily, active	15 – 3 070	329	this study
		Apr. 01-Jun. 01	2-month, passive		225	Motelay-Massei et al., 2005
		Jul. 00-Oct. 00	3-month, passive		52	Harner et al., 2004
Downsview, ON	urban	Sep. 05-Sep. 05	daily, active	6 – 11	8	this study
		Jun. 05-Jun. 05	daily, active	10 – 586	101	this study
		Jun. 05-Aug. 05	weekly, passive	40 – 396	139	Yao et al., 2008
		Apr. 01-Jun. 01	2-month, passive		170	Motelay-Massei et al., 2005
		Jul. 00-Oct. 00	3-month, passive		26	Harner et al., 2004
Lake Ontario, ON	Lake Ontario	May 93-Oct. 93	daily, active	25 – 83	50	Ridal et al., 1996
Buoy, ON	Lake Ontario	May 05-Oct. 05	daily, active	< 0.1 – 20	7	this study
Burnt Island, ON	Lake Huron	Jan. 00-Dec. 05	daily, active	0.7 – 48	6	this study
		Summer 00-Summer 01	yearly, passive		21	Shen et al., 2004
Point Petre, ON	Lake Ontario	Jan. 00-Dec. 05	daily, active	0.5 – 56	8	this study
		Summer 00-Summer 01	yearly, passive		35	Shen et al., 2004
Egbert, ON	rural	Jan. 00-Dec. 05	daily, active	0.4 – 167	15	this study
		May 05-Jul. 05	weekly, active	28 – 126	73	Yao et al., 2008
		May. 04-Jul. 04	weekly, active	10 – 102	34	Yao et al., 2008
		Apr. 01-Jun. 01	2-month, passive		1 020	Motelay-Massei et al., 2005
		Jul. 00-Oct. 00	3-month, passive		40	Harner et al., 2004
		Jul. 88-Sep. 89	daily/2-day, active	4 – 820	60	Hoff et al., 1992
Vineland, ON	rural	Jun. 05-Aug. 05	weekly, active	8 – 139	74	Yao et al., 2008
		May 04-Jul. 04	weekly, active	1 – 118	54	Yao et al., 2008
Abbotsford, BC	rural	May 05-May 05	weekly, active	26 – 62	43	Yao et al., 2008
		Apr. 04-Jun. 04	weekly, active	9 – 80	54	Yao et al., 2008
Bratt's Lake, SK	rural	May 05-Jul. 05	weekly, active	58 – 120	90	Yao et al., 2008
		May 04-Aug. 04	weekly, active	23 – 143	71	Yao et al., 2008
		May 03-Aug. 03	weekly, active	69 – 479	171	Yao et al., 2006
Hafford, SK	rural	May 03-Aug. 03	weekly, active	< 0.1 – 244	141	Yao et al., 2006
Waskesiu, SK	rural	May 03-Aug. 03	weekly, active	< 0.1 – 220	69	Yao et al., 2006
Canola field, SK	rural	May 98-Aug. 98	weekly, active	< 100 – 7 400		Waite et al., 2001
		May 97-Jul. 97	weekly, active	3700 – 16 100		Waite et al., 2001
St. Anicet, QC	rural	Jun. 05-Jun. 05	weekly, active	< 0.2 – 285	155	Yao et al., 2008
		May 04-Jun. 04	weekly, active	11 – 916	245	Yao et al., 2008
		Mar. 94-Dec. 95	daily, active	5 – 552	101	Garmouma and Poissant, 2004
Baie St. Francois, QC	rural	Jun. 05-Jun. 05	weekly, active	< 0.2 – 180	91	Yao et al., 2008
		May 04-Jun. 04	weekly, active	13 – 878	282	Yao et al., 2008
Villeroy, QC	rural	Jan. 93-Dec. 95	daily, active	8 – 269	42	Garmouma and Poissant, 2004
		Jun. 92-Dec. 92	daily, active	< 1 – 368	37	Poissant and Koprivnjak, 1996
Kensington, PEI	rural	Aug. 05-Sep. 05	weekly, active	3 – 115	66	Yao et al., 2008
		Jun. 04-Sep. 04	weekly, active	2 – 88	32	Yao et al., 2008
Resolute Bay, NWT	Arctic	Aug. 92	4-day, active		10	Bidleman et al., 1995
Little Fox Lake, NWT	Arctic	Jul. 02-Jul. 03	weekly, active	2 – 10	5	Su et al., 2006
Alert, NWT	Arctic	Jan. 00-Dec. 01	weekly, active	0.4 – 19	6	Su et al., 2006
		Summer 00-Summer 01	yearly, passive		6	Shen et al., 2004
		Jan. 93-Dec. 97	weekly, active	0.1 – 55	9	Hung et al., 2002

3.2. Air pollution episode of γ–HCH in Toronto after lindane ban

The Canadian lindane ban became effective on December 31, 2004 (see Figure 2). After that, γ–HCH was still detected in the atmosphere over the Great Lakes region under the IADN program (Figure 2), presumably the result of residual chemical cycling between different environmental compartments – soil, water and air. In addition, atmospheric transport from other source regions outside Canada might be another reason for this. For 2005, the peak levels of γ–HCH measured at Burnt Island, Egbert and Point Petre were 12, 39 and 35 pg m^{-3}, respectively. The average concentrations for the period of April–September, 2005 were 5, 10, and 12 pg m^{-3} for Burnt Island, Point Petre, and Egbert, respectively. These results can be used to establish the "baseline" value for γ–HCH air concentrations in the Great Lakes basin during spring to summer following the ban on lindane.

On June 27–28, 2005 an intense, 1–day peak in the γ–HCH air concentration was detected at two sites in Toronto by the three independent studies. The EPT study reported a concentration of 586 pg m^{-3} for Downsview on its sixth consecutive day of sample collection. The atmospheric concentrations were approximately 20 times lower on the day prior to and after the episode – 26 and 38 pg m^{-3}, respectively (Figure 3). On the same day, an air sample was also collected under the IADN program that was operating at the Gage site in downtown Toronto. An even higher γ–HCH air concentration of 3 070 pg m^{-3} was reported. This concentration is more than 100 times higher than measured air concentration values for γ–HCH at this site prior to (16 pg m^{-3} on June 15) and after (15 pg m^{-3} on July 9) the episode. Under CANCUP, a week–long air sample was collected at Downsview (same field site as in the EPT study) during June 23–30, 2005, capturing the period of the air episode on June 27–28. Despite the dilution effect of a time–integrated sample, an exceptionally high air concentration of 396 pg m^{-3} was observed. This was the highest value reported under CANCUP for the 2005 sampling year for all agricultural sites across Canada (Table 2) (Yao et al., 2008). Air concentrations of γ–HCH measured at Canadian agricultural sites in 2005 were substantially lower compared to previous years, reflecting reduced use of lindane and the lindane ban that took place in December 2004.

Interestingly, no elevated concentrations of γ–HCH were detected at the IADN regional background sites and the buoy site

over Lake Ontario, indicating that this was a localized emission event in the Toronto area (Figure 4). Air concentrations of γ–HCH at Burnt Island, Point Petre and Egbert on June 27–28 were 7, 14 and 25 pg m^{-3}, respectively. This is consistent with long term trends at these sites (Figure 2). Similarly, a low concentration of 10 pg m^{-3} was reported over Lake Ontario from the buoy sample. Further implication of a localized, Toronto emission source of γ–HCH comes from analysis of air parcel back trajectories covering the period of the episode. This approach has been used to relate episodes of elevated air concentrations of POPs (Subhash et al., 1999; James et al., 2001) and CUPs (Yao et al., 2007; Primbs et al., 2008) to potential regional sources, but not for identification of a local source as back trajectories are too uncertain at this scale.

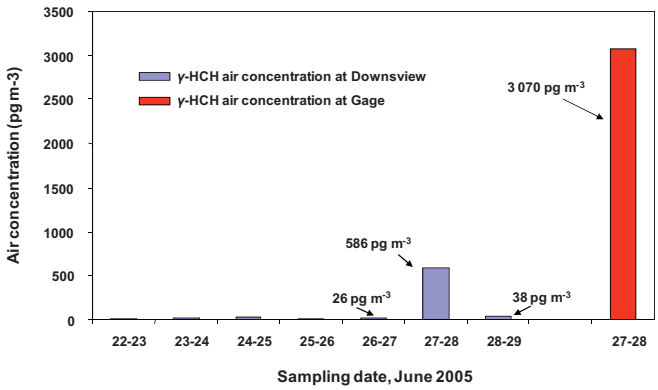

Figure 3. *Air concentrations of γ–HCH at the Downsview and Gage sites in Toronto showing the captured pollution event on June 27-28, 2005.*

In this study, back trajectory analysis was used to identify the possibility that the episode was due to long–range atmospheric transport from somewhere outside of Toronto. Figure 4 shows three–day air parcel back trajectories ending at the Downsview site at a 10 m altitude, calculated every 6 hours during June 27–28 using the Canadian Meteorological Center (CMC) trajectory model (Yao et al., 2007). Prior to arriving in Toronto, a large portion of the sampled air mass traveled across the Canadian–side lakeshores of Lake Superior and Lake Huron, then crossed south over Lake Ontario before returning north to Toronto, passing very near the location of the buoy. The trajectory analysis also showed air flow from northern Pennsylvania and western New York states, which passed the buoy site, where the episode was not detected, before arriving in the city. The back trajectories do not indicate an obvious agricultural source because they did not pass the major lindane use areas in Canada (in the past – Alberta, Saskatchewan and Manitoba) (Li et al., 2004) and the U.S. (e.g., Oklahoma, Georgia, Alabama and South Carolina) (USGS, 1997).

In addition, a global atmospheric transport model, Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP, Zhang et al., 2008) was employed to assess source–receptor relationship in accordance with this event. Figure 5 shows the modeled daily air concentration at 3000 m height during June 23–28. Higher air concentrations were identified over the Canadian Prairies – the major emission source due to historical use over North America (Li et al., 2004; Zhang et al., 2008). The eastward atmospheric transport from this source region to east Canada under prevailing westerly wind at this atmospheric level formed an atmospheric pathway for lindane, as illustrated by a concentration plume extending from the Prairies to east Canada. However, during this period the eastern Great Lakes region covering metropolitan Toronto was not within the center of the plume. The modeled air concentrations were in general lower than 20 pg m^{-3}. This demonstrates that the event observed in Toronto was not attributed to long–range atmospheric transport from outside of Toronto. The episodic nature of this event suggests that it is likely due to incidental use or leak of lindane in the city beyond the phase–out period. The observed gradient in γ–HCH air concentrations described previously suggests that the source was probably in the downtown area.

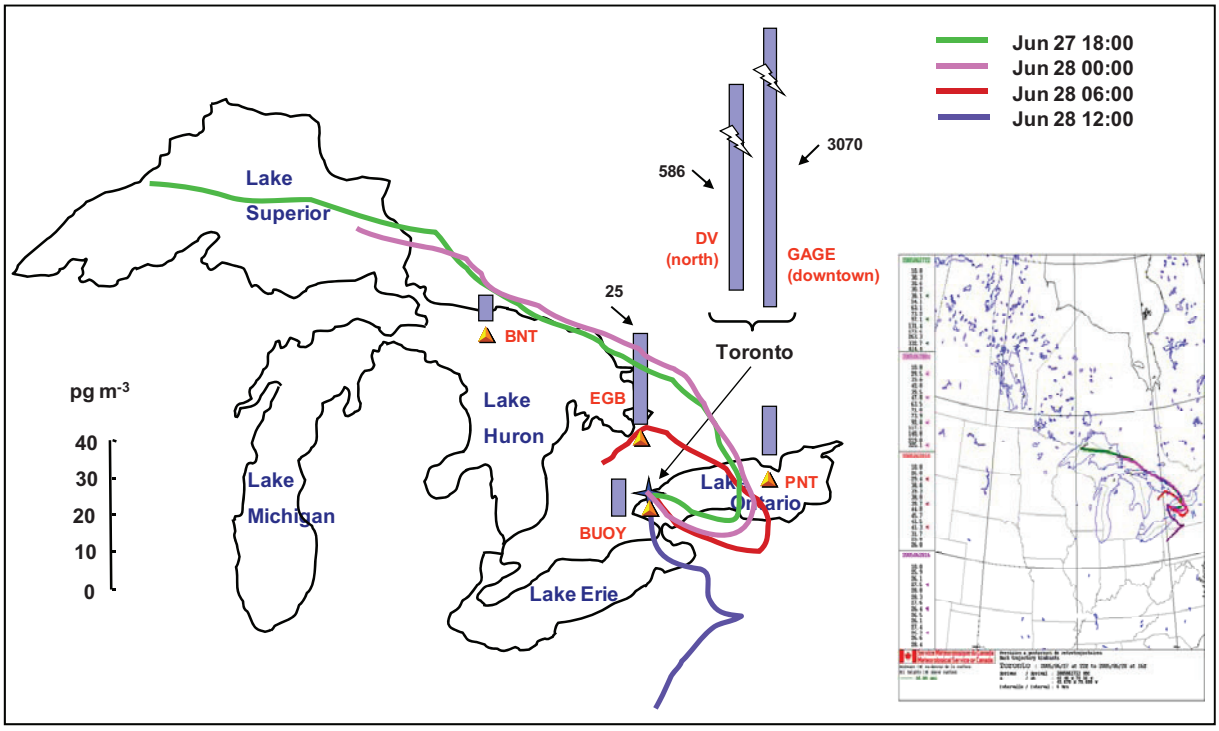

Figure 4. *Spatial distribution of γ–HCH concentrations in the atmosphere in the Great Lakes region on June 27–28, 2005 (BNT: Burnt Island; EGB: Egbert; PNT: Point Petre; DV: Downsview). Lines show 3–day air parcel back trajectories arriving at Downsview at a 10 m altitude. The color of the trajectories refers to the corresponding ending time (EST) at the site. Note the scale offset for the bars representing DV and Gage.*

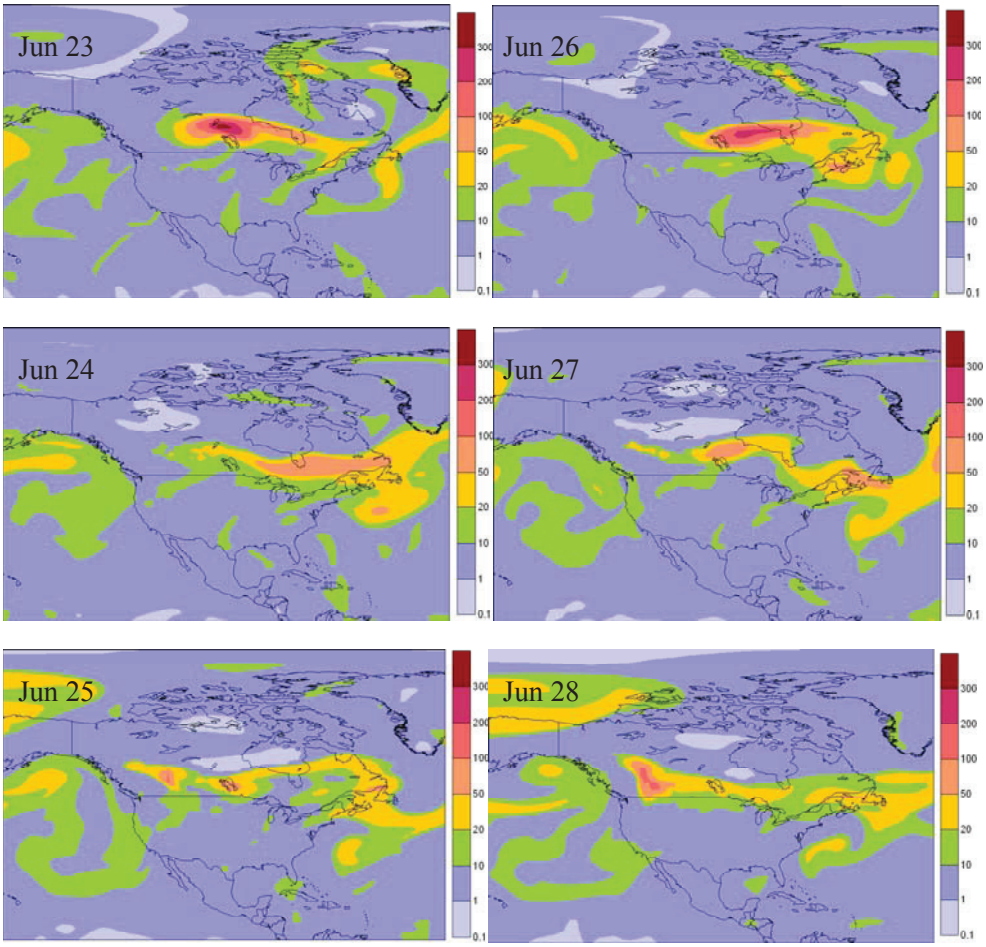

Figure 5. *CanMETOP modeled lindane atmospheric concentrations at 3000 m altitude during June 23-28, 2005.*

A simple box model was applied to estimate the magnitude of the emission to the atmosphere that could account for this episode. This was done assuming that the elevated air concentrations were largely confined to an area about the size of Toronto – a rectangular box, 20 km by 20 km and 1 km in height with a volume of 4.0×10^{11} m^3. The amount of γ–HCH passing through the box over one day was then estimated as:

$$E = C\,V\,S \qquad (1)$$

where E (kg day^{-1}) is the γ–HCH emission in the Toronto area during the episode; C is the average daily air concentration in the area (1 830 pg m^{-3}) that was calculated as the mean for results measured at the Downsview (586 pg m^{-3}) and Gage (3 070 pg m^{-3}) sites; V is the volume of the box (4.0×10^{11} m^3); and S is the speed of horizontal motion of air parcel passing through the box that was calculated to be 10 volume day^{-1} based on a horizontal wind speed of 2.4 m s^{-1} (calculated with wind speed data measured during the sampling period). The result is an estimated emission of 7.3 kg.

Furthermore, forward air parcel trajectories were calculated by Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model. The trajectories indicate that air masses during this episode were transported to the northeast (see Figure 6). Some of these air masses may have impacted the regional IADN sites. Interestingly, the measured air concentration of γ–HCH at Egbert on June 27–28 (25 pg m^{-3}) was the second highest level observed at the site in 2005. Similarly, the air concentrations at Burnt Island (7 pg m^{-3}) and Point Petre (14 pg m^{-3}) were the third highest values reported for the sites in 2005 (Figure 2).

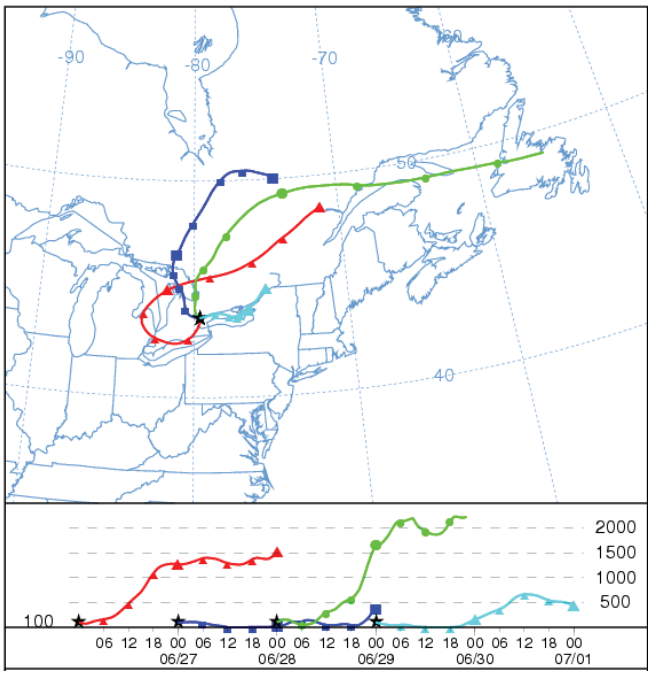

Figure 6. *Two–day forward trajectories (100 m altitude) for air masses originating in Toronto covering the period of the episode.*

4. Conclusions

The historical trends of γ–HCH air concentrations at three Canadian IADN sites are presented for the first time for the period 2000–2005. The results establish a long–term regional background air concentration for γ–HCH leading up to and following the Canadian lindane ban in December 2004. Furthermore, this paper reveals the occurrence of an intense, 1–day γ–HCH air pollution event in the Toronto area after the ban on lindane. The finding is corroborated by three separate monitoring and research programs and further validated by several years of ongoing air measurements conducted in the Great Lakes region. This work demonstrates the value in continued monitoring of POPs even after they have been banned as new and unsuspecting sources may arise. In addition, the approach used in this study highlights the importance of integrating scientific information from different projects considering the possibility that such an episode might not be effectively captured by a single monitoring or research program as many of them only target toxic pollutants intermittently or only at limited locations. The episode is of significance because of its magnitude and the fact that it occurred over a large urban area after the official ban on lindane and with no previous or known sources, shedding light on the difficulties of compliance with and implementation of chemicals law.

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