Environ. Sci. Technol. **1998**, *32,* 1032−1038

Aircraft Measurements of the Concentration and Flux of Agrochemicals

T. ZHU,*,† R. L. DESJARDINS,†
J. I. MACPHERSON,‡ E. PATTEY,† AND
G. ST. AMOUR†

Eastern Cereal and Oilseed Research Centre, Agriculture and Agri-Food Canada, Ottawa, Ontario K1A 0C6, Canada, and Flight Research Laboratory, National Research Council, Ottawa, Ontario K1A 0R6, Canada

The use of agrochemicals, such as insecticides and herbicides, is of great environmental concern. To quantify and model the volatilization and deposition of these agrochemicals, measurements of the exchange rates between the atmosphere and different surfaces are required. An aircraft-based air sampling system using the relaxed eddy-accumulation technique for measuring concentrations and fluxes of agrochemicals was developed and tested in June 1993 and July 1994. Atrazine and metolachlor, which are used on corn and soybean crops, were detected in samples collected along flights from Ottawa to southern Ontario. Concentrations as high as 4.6 ng m^{-3} for atrazine and 9.8 ng m^{-3} for metolachlor were found. Fluxes ranged from −1.1 to 2.5 ng m^{-2} s^{-1} for atrazine and from −0.01 to 0.56 ng m^{-2} s^{-1} for metolachlor. These results demonstrate that the aircraft-based relaxed eddy-accumulation approach is a useful method for measuring concentrations and fluxes of agrochemicals at both local and regional scales. Combined with footprint calculations and air mass back-trajectories methods, the fluxes measured with this system should be useful to improve our understanding of the long-range transport of semivolatile organic compounds and their potential impact on various ecosystems.

Introduction

Drift, volatilization, and runoff of many agrochemicals, such as insecticides and herbicides, are well-recognized sources of toxic organic chemicals in the environment. They have also been considered important sources of pollution for the Great Lakes (*1*). To quantify and model the atmospheric transfer of these agrochemicals, measurements of their exchange rates (i.e., vertical flux densities) between air and different surfaces are required. In this paper, flux is used as a simplified term for the vertical flux density.

During the past decade, aircraft-based flux measurements have been obtained for several gases, such as O_3, CO_2, and H_2O, with the eddy-covariance technique (*2, 3*). However, this technique can only be used for gases for which fast response analyzers were available, which is not the case for organic compounds. As a potential solution to this problem, an eddy-accumulation system was developed (*4*). It involves the partitioning of the gas samples into two separate reservoirs based on whether the real time wind-measuring system senses ascending or descending air. The air collected can then be analyzed using a slow response analyzer, such as a gas chromatograph. In the original concept, the air was collected at a rate proportional to the magnitude of the vertical wind velocity, w (*4*). Businger (*5*) suggested a relaxation of this method in which air samples are collected strictly at a constant flow rate but on the basis of the sign of w. The conceptual simplicity of this technique is attractive, because the vertical flux estimate for a trace gas $\overline{w'c'}$ is a simple function of the standard deviation of the vertical wind velocity, σ_w, the difference of the mean concentrations between ascending air ($\overline{c^+}$) and descending air ($\overline{c^-}$), and an empirical constant A (eq 1):

$$\overline{w'c'} = A\sigma_w(\overline{c^+} - \overline{c^-}) \qquad (1)$$

This method (called relaxed eddy-accumulation or REA) has been used on several tower-based systems (*6−8*). It has also been evaluated for airborne flux measurement using numerical simulation (*9*). REA is preferable in the case of agrochemicals because a large volume of air is usually required to obtain a measurable concentration, and there are no fast-response proportional sampling valves capable of handling such high flow rates (300−400 L min^{-1}).

In this paper, we describe an aircraft-based REA sampling system that has been developed to measure the flux of agrochemicals. We also present results obtained during several test flights.

Experimental Section

Sampling System and Flight Path. The aircraft used for the flux measurements was the Twin Otter from the Flight Research Laboratory of the National Research Council of Canada. It is instrumented to measure the three orthogonal components of atmospheric motion over a frequency range of 0−5 Hz. The wind computation methods and a description of the data acquisition system are given by MacPherson (*10*). The vertical wind velocity (w) is calculated and filtered in real time on the aircraft. These data are then used to control three solenoid valves that divert the air sampled through one of two agrochemical absorbers depending on the direction of w or directly to the pump when $-0.1 < w < 0.1$ m s^{-1}, which is the threshold of the deadband. A deadband is a range of vertical wind velocity when no sample is collected. It is used to prolong the life of the valves driven by the REA sampling system and to increase the difference in trace gas concentration between updrafts and downdrafts ($\overline{c^+} - \overline{c^-}$). A schematic of the sampler is shown in Figure 1. The air flows through the inlet at a flow rate of 392 L min^{-1}.

In Ontario, most pesticides used are herbicides. They accounted for 70% of the 7.2 × 10^6 kg pesticides applied to agricultural crops in 1988. From all the herbicides applied in the province of Ontario, 56% were applied in southern Ontario with 30% in western Ontario, 6% in central Ontario, and 8% in eastern Ontario (*11*). On the basis of vapor pressure, water solubility, and the amount applied, five herbicides were selected as target compounds for the experiments: EPTC, butylate, trifluralin, atrazine, and metolachlor (see Table 1). The widest application of EPTC, butylate, and atrazine in Ontario is for the treatment of corn, while metolachlor is used for the treatment of corn and soybeans and trifluralin is used for soybeans.

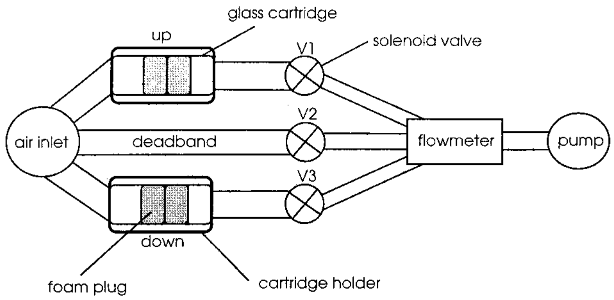
---

[*] Corresponding author: tel: (613) 759-1542; fax: (613) 996-0646; e-mail: zhutong@em.agr.ca.

[†] Agriculture and Agri-Food Canada.

[‡] National Research Council.

S0013-936X(97)00246-0 CCC: $15.00



Flow	up (V1)	deadband (V2)	down (V3)
$w_t < w$	1	0	0
$-w_t \leq w \leq w_t$	0	1	0
$w < -w_t$	0	0	1

w: vertical wind velocity
w_t: deadband threshold level

0: valve close
1: valve open

FIGURE 1. Schematic of the relaxed eddy-accumulation air-sampling system.

Previous studies had indicated that in Ontario the highest atmospheric concentration of trifluralin was observed in June and July (*13*). Due to the weather conditions and schedule constraint on the aircraft, June 16 and June 17 were selected for the sampling in 1993. The aircraft made one flight each day. Fluxes were measured along several transects (Figure 2). Four sets of samples and one field blank were collected during each flight. One set consisted of two cartridges, one for upward and one for downward moving air. The flight path on June 16 was Ottawa−Midland−London−Ottawa at about 160 m over forests and agricultural fields. Samples 93-1, 93-2, 93-3, and 93-4 were collected along the flight. Samples 93-1 and 93-4 were collected over both forests and agricultural regions, while samples 93-2 and 93-3 were primarily over agricultural regions. The sampling duration for each set of sample ranged from 55 to 82 min. The flight on June 17 over Lake Ontario was to study the transfer of herbicides between the atmosphere and the Great Lakes. Samples 93-5, 93-6, 93-7, and 93-8 were collected for a duration of approximately 35 min each at a height of about 50 m.

The measurements in 1994 were carried out between July 4 and July 7. Thirteen sets of data were collected, including long transects over forests and agricultural fields (Figure 3) and short transects over agricultural regions in southern Ontario (Figure 4). The flight on July 4 was to test the sampling system and covered a 10 km segment southwest of Casselman and a 9 km segment east of Casselman. Sample 94-1 was collected at a height of 46 m for a duration of 47 min. On July 5, the aircraft flew from Ottawa to Kitchener at about 167 m over forests and agricultural fields. Samples 94-2 and 94-3, which were collected on the way, had sampling durations of 49 and 45 min, respectively. On the same day, the aircraft flew from Kitchener to Chatham at about 159 m. Sample 94-4 was collected for a duration of 46 min. On July 5−7, samples 94-5, 94-6, 94-7, 94-8, 94-9, and 94-10 were collected when the aircraft flew along short transects over agricultural fields in Essex and Kent Counties, at an altitude of about 30 m (Figure 4). To sample enough air, the aircraft flew over short transects repeatedly for sampling durations ranging from 44 to 73 min. On July 7, sample 94-11 was collected from the Chatham to Kitchener at 166 m for 45 min (Figure 3). Samples 94-12 and 94-13 were collected at 159 m on the way back to Ottawa from Kitchener for durations of 50 and 47 min, respectively.

Trapping and Analytical Method. Polyurethane foam (PUF) was used as the herbicide vapor trapping medium because of the high trapping efficiency for semivolatile organic compounds (*14*). Laboratory test showed that, at flow rate of 392 L min^{-1}, the trapping efficiency of two PUF plugs (6.2 cm diameter by 2.4 cm long) for the five target compounds is higher than 98%. Using Soxhlet extraction, the foam plugs were cleaned with distilled-in-glass solvent (50% acetone and 50% hexane, Caledon Laboratories) for 24 h. Two PUF plugs were inserted into a glass cartridge, which was covered with aluminum foil to protect PUF plugs from sunlight. To collect the air samples, cartridges were inserted into aluminum holders connected to the sampling channels. After the sampling period, the cartridges were covered with aluminum foil and stored at below 0 °C.

To analyze the samples, the PUF plugs were at first warmed to room temperature and then Soxhlet-extracted with 600 mL of hexane (glass-distilled grade, Caledon Laboratories) for 24 h. The extracts were concentrated to 2 mL with a rotary evaporator and then transferred to a Florisil column (8 g of Florisil, 80−100 mesh, 1.2% water by weight, 15 cm length), which had been washed with 40 mL of hexane. The column was eluted with 38 mL of hexane (F1: eluate fraction number 1), 37 mL of hexane−dichloromethane (DCM) (85:15) (F2: eluate fraction number 2), 40 mL of hexane−DCM (40:60) and 40 mL of DCM (F3: eluate fraction number 3), and 50 mL of acetone (F4: eluate fraction number 4). F2 contained trifluralin, F3 contained EPTC and butylate, and F4 contained atrazine and metolachlor. Each Florisil elute was concentrated to 2 mL with a rotary evaporator and was brought to 1.0 mL with a nitrogen flow evaporator.

For each set (up and down) of samples, three units were used for extraction and Florisil elution. One unit was used for PUF plugs collecting upward moving air, and one was used for downward moving air. The third one was for cleaned PUF plugs spiked with a standard solution of the herbicides. Recovery of each herbicide was calculated based on the concentration measurement of the Florisil elute from the third unit. Laboratory tests in 1993 showed that we were able to obtain a 17% recovery for EPTC, 23% for butylate, 40% for trifluralin, 55% for atrazine, and up to 94% for metolachlor. For quantitative analysis, we focused on atrazine and metolachlor, not only because they have the highest recovery and application amount among the five herbicides but also because their existences had been confirmed with GC−MSD (see next paragraph). In the 1993 experiment, recovery of atrazine from PUF plugs ($n = 4$) was 50 ± 11%, and metolachlor was 77 ± 22%. Further tests showed that the recovery of atrazine and metolachlor could be improved by reducing the loss during the transfer of samples at different analytical stages. After optimizing the analytical procedure to reduce the loss of herbicides, the recoveries of atrazine and metolachlor for the analysis of 1994 samples were increased to 97 ± 17% and 100 ± 24% ($n = 12$), respectively. This is quite good, but the reproducibility still needs to be improved.

The presence of the herbicides in the 1993 samples was confirmed by mass spectrometry on a Hewlett-Packard 5890 GC (Model 5970 MSD/Unix Data System) with a DB-5 (30 m, 0.32 mm id) column at Atmospheric Environmental Services, Environment Canada. The herbicides in the 1994 samples were identified based on peak shape and retention time, no confirmation was made with GC−MSD.

Concentrations of herbicides in Florisil elutes were analyzed with a gas chromatograph (Varian 3600) equipped with a thermionic selective detector (TSD) using a DB-5 (30 m, 0.53 mm) column with a helium carrier gas. Herbicide concentrations of the samples were relatively low (<5 pg μL^{-1} for metolachlor). To increase the measurement precision of the herbicide concentration in elutes from the sample PUF plugs and the PUF plugs spiked with standard solution, an automatic thermal desorption unit (ATDU) (Canadian Centre for Advanced Instrumentation, Saskatoon, Saskatchewan) was used to increase the amount of herbicides

TABLE 1. Vapor Pressure, Water Solubility, and Amount Used on Field Crops in Ontario of the Five Target Herbicides

herbicide	vapor pressure[a] (mmHg) at 20 °C	water solubility[a] (ppm) at 20 °C	herbicide used on field crops in Ontario, 1988 (kg)[b]				
			corn	soybeans	beans	canola	total
EPTC	34×10^{-3}	370	230 600		12 780		243 380
Butylate	13×10^{-3}	45	105 890				105 890
Trifluralin	1.1×10^{-4}	0.3		103 080	19 570		122 650
Atrazine	3.0×10^{-7}	33 (at 27 °C)	999 410	350	15 000	30 400	1 045 160
Metolachlor	1.3×10^{-5}	530	712 170	915 170	81 360	1 160	1 709 890

[a] From ref 12. [b] From ref 11.

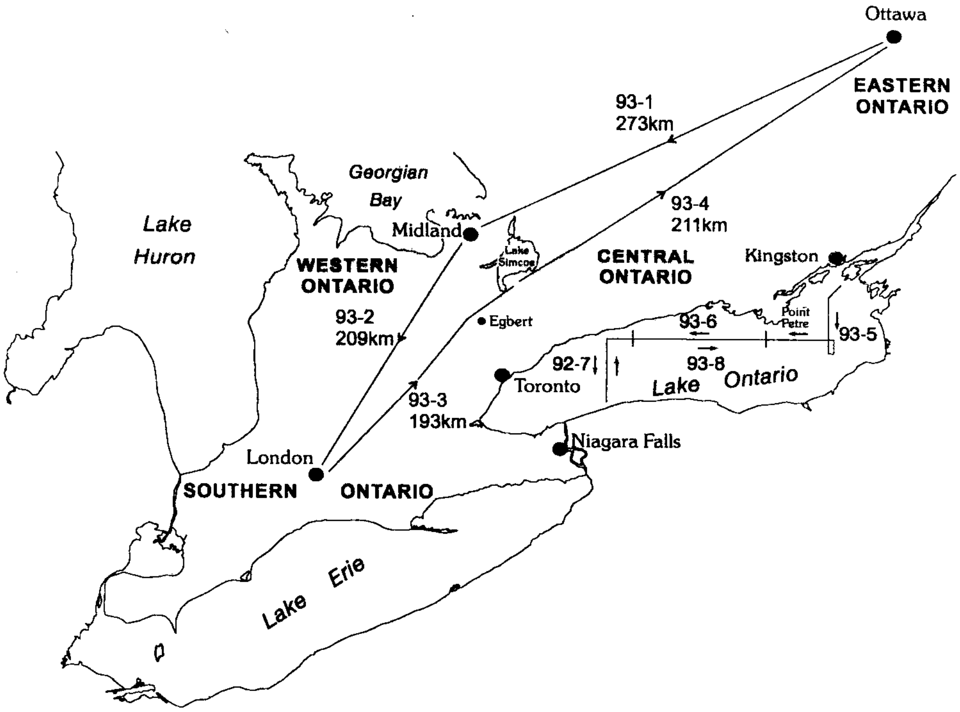


FIGURE 2. Aircraft flight paths across Ontario and Lake Ontario on June 16 and 17, 1993.

injected into the GC. A description of the ATDU has been given by Cessna and Kerr (*15*). With the help of the ATDU, the sensitivity of the analysis was increased by a factor of 50 by spiking 50 μL of sample onto a single glass minitube (2 cm length, 0.5 cm internal diameter) that contained 14 mg of Tenax TA resin. After the solvent vaporized at room temperature, the minitube was inserted into the ATDU, and the herbicides were thermally desorbed at 240 °C for 15 min onto the GC column.

Results and Discussion

Table 2 summarizes the sampling conditions, surface temperature, and standard deviation of vertical wind velocity. In 1993, the flight on June 16 from Ottawa to London covered a large variety of land surfaces, including forests and agricultural fields. During this flight the standard deviation of the vertical wind ranged from 0.69 to 1.19 m s^{-1}. Under these conditions, 90% of the time air either passed through the up or the down absorber. The volume of air sampled ranged from 9 to 16 m^3. On June 17, during the flight over Lake Ontario, air turbulance was considerably weaker. Most of the time the standard deviations of vertical wind velocity (σ_w) was less than 0.1 m s^{-1}, which was the setting of the deadband threshold level. Hence, more than 82% of the time no air sample was collected; therefore, less than 1 m^3 of air was passed through the PUF plugs.

In 1994, the sampling duration for most samples ranged from 44 to 53 min, except sample 94-10 (73 min). For samples taken over short segments (94-1, 94-5, 94-6, 94-7, 94-8, 95-9, 94-10), σ_w ranged from 0.34 to 0.59 m s^{-1}, and the flight level was about 30 m. For these cases, 72–85% of the time air was either collected in the up or in the down sample, and the sampled volumes ranged from 6.4 to 12.3 m^3. For samples taken over long transects (94-2, 94-3, 94-4, 94-11, 94-12, 94-13), σ_w ranged from 0.73 to 0.99 m s^{-1}, and 88–90% of the time air was either collected in the up or in the down sample. The sampling volumes ranged from 6.7 to 9.7 m^3, and the flight level was about 160 m.

Concentrations and fluxes of atrazine and metolachlor in the aircraft-based samples along different transects over Ontario are listed in Table 3. Fluxes were calculated with eq 1. Because a threshold of ±0.1 m s^{-1} was set for the deadband, a value of 0.56 was used for the empirical constant *A* (*9*). No correction for density fluctuation was made, as it is negligible for herbicide (*16*). The concentrations shown in Table 3 are mean values of three replicates of GC analysis with their standard deviations. The fluxes were calculated based on the mean concentrations. The errors of the fluxes were estimated solely from the standard deviation of the concentration analysis.

Apart from the precision of GC analysis, the uncertainty of the flux is also caused by factors, such as the low reproducibility of sample recovery in the Soxhlet extraction and Florisil fraction processes.

The analysis of all the field blanks taken for the flights on June 16–17, 1993, and July 4–7, 1994, showed no trace of the

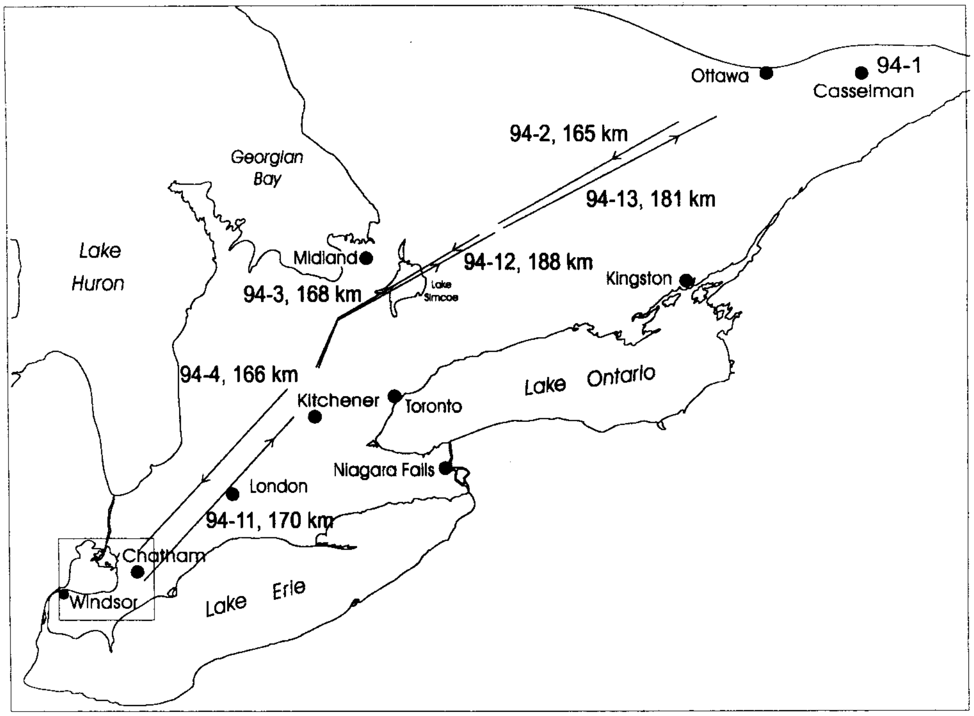


FIGURE 3. Aircraft flight paths across Ontario during July 1994. The short transects in the region between Windsor and Chatham are showed in Figure 4.

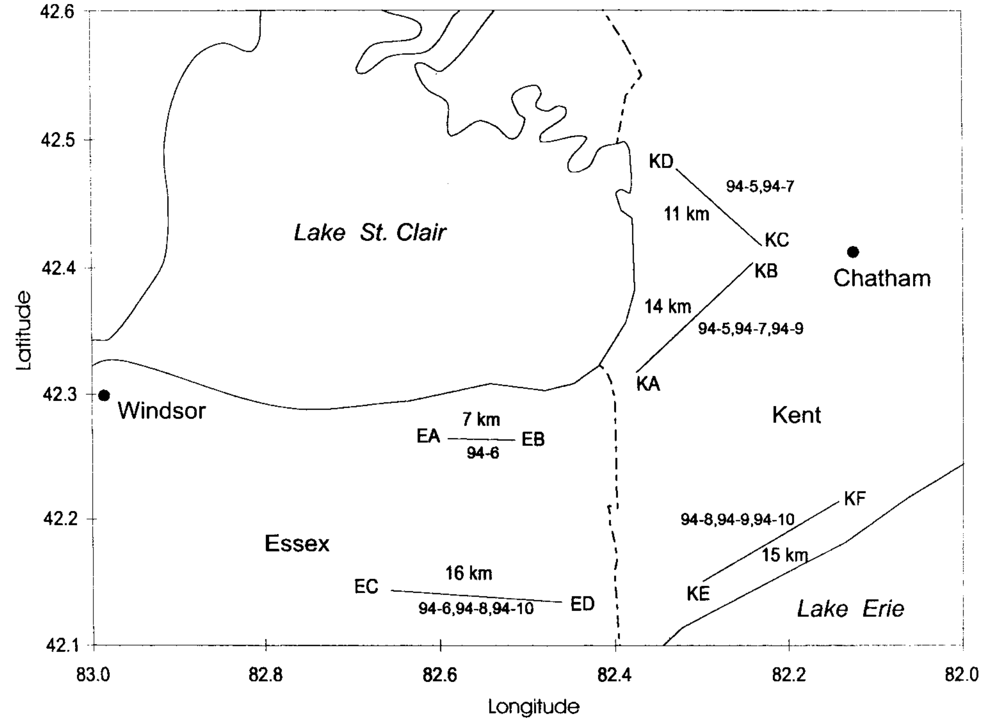


FIGURE 4. Short aircraft transects over Essex and Kent Counties in the region between Windsor and Chatham during July 1994.

five target herbicides. Among the five target herbicides, only atrazine and metolachlor were identified in the samples taken on June 16, 1993, and observed in seven samples taken in 1994. The detection of atrazine and metolachlor is consistent with the fact that atrazine and metolachlor are the two herbicides used in the largest quantities in Ontario. It has been estimated (*11*) that 10^6 kg of atrazine and 1.7×10^6 kg of metolachlor were used in Ontario in 1988, compared to 2.4×10^5 kg of EPTC, 1.1×10^5 kg of butylate, and 1.2×10^5 kg of trifluralin (see Table 1). Table 1 shows that the vapor pressures of EPTC, butylate, and trifluralin are higher than those of atrazine and metolachlor. A herbicide with a higher vapor pressure tends to have a higher volatilization rate from soil. Among the five herbicides, trifluralin has a moderate vapor pressure (1.1×10^{-4} mmHg). Its soil half-life has been determined to be 7 days (*6*). As most of the herbicides are applied in April and May, we can expect that the volatilization of EPTC, butylate, and trifluralin from soil was negligible

TABLE 2. Sampling Conditions, Surface Temperature, and Standard Deviation of the Vertical Wind Velocity (σ_w) during the Measurements in 1993 and 1994

sample	flight path	date	height (m)	sampling time (Local)		duration (min)	REA fraction (%)		volume (m^3)		σ_w ($m\ s^{-1}$)	surface temp (°C)
				begin	end		up	down	up	down		
93-1	Ottawa−Midland	6/16/93	163	11:21	12:43	78.67	40.9	51.7	12.6	15.9	1.19	15.2
93-2	Midland−London	6/16/93	167	14:21	15:22	59.97	41.6	51.1	9.78	12.0	1.03	24.5
93-3	London−Ottawa	6/16/93	170	16:22	17:18	55.19	41.5	47.5	8.98	10.3	0.92	22.4
93-4	London−Ottawa	6/16/93	171	17:22	18:21	58.85	38.5	43.2	8.88	9.97	0.69	17.0
93-5	Lake Ontario	6/17/93	49	14:28	15:00	31.95	5.5	6.3	0.55	0.65	0.07	11.3
93-6	Lake Ontario	6/17/93	50	15:02	15:35	32.00	9.2	8.8	0.92	0.88	0.10	9.7
93-7	Lake Ontario	6/17/93	46	15:39	16:14	35.37	6.7	6.7	0.74	0.74	0.09	9.5
93-8	Lake Ontario	6/17/93	48	16:17	16:51	34.28	1.6	1.8	0.17	0.19	0.05	10.0
94-1	Casselman	7/4/94	46	14:32	15:55	46.97	42.2	43.9	7.77	8.09	0.59	24.6
94-2	Ottawa−Kitchner	7/5/94	166	13:33	14:29	48.71	44.3	46.2	6.72	7.02	0.99	20.7
94-3	Ottawa−Kitchner	7/5/94	167	14:31	15:19	45.00	40.4	49.7	7.13	8.77	0.93	26.3
94-4	Kitchner−Chatham	7/5/94	159	16:36	17:26	45.52	38.6	49.2	6.89	8.78	0.73	25.9
94-5	KB−KA KC−KD	7/5/94	29	17:27	18:42	52.88	36.2	36.2	7.50	7.51	0.34	24.6
94-6	EA−EB EC−ED	7/6/94	30	10:24	11:40	47.64	38.1	44.4	7.11	8.29	0.51	25.5
94-7	KA−KB KC−KD	7/6/94	30	11:42	12:57	51.69	40.1	43.1	8.12	8.74	0.50	31.2
94-8	EC−ED KE−KF	7/6/94	31	14:41	15:56	52.28	38.2	44.5	7.84	9.12	0.51	32.0
94-9	KA−KB KE−KF	7/6/94	33−170	15:58	17:06	43.50	37.2	41.9	6.35	7.14	0.48	29.4
94-10	EC−ED KE−KF	7/7/94	31	10:12	11:57	73.44	37.8	42.5	10.88	12.25	0.46	25.0
94-11	Chatham−Kitchner	7/7/94	166	11:58	12:45	45.18	39.4	49.0	6.98	8.67	0.76	27.1
94-12	Kitchener−Ottawa	7/7/94	159	13:48	14:41	50.32	40.8	49.0	8.04	9.66	0.93	27.9
94-13	Kitchener−Ottawa	7/7/94	159	14:43	15:33	47.00	40.6	47.8	7.47	8.81	0.81	26.6

TABLE 3. Concentrations and Fluxes of Atrazine and Metolachlor Measured in 1993 and 1994 in the Province of Ontario

	concentration ($ng\ m^{-3}$)					
	atrazine		metolachlor		flux ($ng\ m^{-2}\ s^{-1}$)	
sample	up	down	up	down	atrazine	metolachlor
93-1	N/D[b]	N/D	0.13 ± 0.05	0.14 ± 0.06	N/D	−0.01 ± 0.07
93-2	3.46 ± 0.06	5.38 ± 0.01	0.10 ± 0.02	0.13 ± 0.07	−1.11 ± 0.04	−0.02 ± 0.05
93-3	7.2 ± 0.9	2.4 ± 0.1	0.52 ± 0.02	0.44 ± 0.05	2.5 ± 0.5	0.04 ± 0.04
93-4	0.11 ± 0.01	0.109 ± 0.001	0.37 ± 0.02	0.36 ± 0.03	0.000 ± 0.004	0.004 ± 0.020
94-4	∼1	∼0.8	2.29 ± 0.06	0.90 ± 0.02	N/D	0.56 ± 0.03
94-5	∼1	∼1	2.00 ± 0.09	1.47 ± 0.02	N/D	0.11 ± 0.02
94-6	∼0.6	∼0.6	9.79 ± 0.08	8.0 ± 0.4	N/D	0.50 ± 0.14
94-7	1.30 ± 0.05	1.17 ± 0.03	0.38 ± 0.02	0.19 ± 0.01	0.04 ± 0.02	0.06 ± 0.01
94-10	∼0.7	∼0.4	∼2	∼1	N/D	N/D
94-11	∼0.6	∼0.5	N/D	N/D	N/D	N/D
94-12	∼1	∼0.9	N/D	∼1	N/D	N/D

[a] The concentrations shown here are mean values of three replicates of GC analysis together with standard deviations. The errors of the fluxes were estimated solely from the standard deviation of the concentration analysis. [b] N/D, not detected.

when we conducted the measurements in June and July. Once in the air, the lifetimes of these herbicides are determined by many processes, such as long-range transport to other locations, chemical reactions, and wet and dry depositions. Due to these processes, the air concentrations of EPTC, butylate, and trifluralin in June and July might be lower than the detection limits of our system.

Because of the relatively small volume sampled and relatively low atmospheric concentration of herbicide over Lake Ontario, none of the five target herbicides were observed in the aircraft-based samples taken on June 17, 1993. During the flights in 1993, air samples were also taken on the ground at Egbert and Point Petre by scientists of Environment Canada. All of the five target compounds were found in these samples. This is not surprising considering the larger volume of air sampled (70 m^3).

Flux measurements, at a given height, are based on the observation of molecular concentration contributed from an infinite number of surface point sources and are primarily affected by sources upwind. A meaningful interpretation of fluxes measured with aircraft, over nonuniform terrain, must therefore consider the relative contribution from nonhomogeneous distribution of upwind sources. With the help of footprint function FP, the contribution of upwind sources $Q(x,y,0)$ to the aircraft measured flux $F(0,0,z)$ at a given height z can be defined by

$$F(0,0,z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(x,y,0)\ \mathrm{FP}(x,y,z)\ \mathrm{d}x\ \mathrm{d}y \qquad (2)$$

where $\mathrm{FP}(x,y,z)$ denotes footprint function.

The footprint function can be calculated based on wind velocity, atmospheric stability, and surface roughness. A number of studies to calculate footprint function for aircraft flux measurements has recently been carried out (e.g., refs 17 and 18). Kaharabata et al. (*18*) showed that aircraft-based flux measurements are influenced by sources located up to several kilometers upwind, depending on the observation height and stability conditions. For unstable conditions, 80% of the flux is contributed by sources located in the first 2 km, and about 50% of the flux contribution come from sources in the first kilometer for a sampling height of 100 m. For neutral conditions, the footprint expands greatly, so that only 50% of the flux contribution comes from the nearest 5 km. The flux observed at greater height (300 and 500 m) have a considerably expanded footprint. At this level, mesoscale contribution, large-scale advection, possibly boundary-layer characteristics left over from the previous day, and even synoptic scale disturbances may affect flux observations.

In both years, all the samples collected over the short transects were from repeated passes at about 30 m over relatively uniform agricultural fields. At this level, most of the flux contribution came from sources located within a few kilometers from the flight path. The results of such measurements can be used to validate process models that simulate the air−surface exchange processes at local scale.

Due to flight regulations, all the long transects had to be flown at about 160 m. At this level, flux measurements can still be associated to surface sources. However, over long transects the contribution from surface sources are very complicated. These transects contain a wide range of ecosystems, such as forests, agricultural fields, and lakes, etc. Consequently, such measurements are a spatial integration of several sources and sinks. It is therefore difficult to obtain local surface source information. On the other hand, these flux measurements provide a spatial average of the air−surface exchange rate at a regional scale. This information can be used to validate large-scale models dealing with regional emissions and depositions and long-range transport of herbicides.

In 1993, sample 93-1 was collected during the flight from Ottawa to Midland (Figure 2) across eastern and central Ontario at a height of 163 m. About 20% of the flight was over agricultural fields and 80% was over forests, where herbicides were not used. The concentration of atrazine was below the detection limit. The concentration and flux of metolachlor were 0.14 ng m^{-3} and $-$ 0.01 ng m^{-2} s^{-1}, respectively. The metolachlor flux associated with samples 93-1, 93-2, and 93-3 were smaller than the error; hence, we have no confidence in the sign of these fluxes. Sample 93-2 was collected during the flight from Midland to London at a height of 167 m, across western and southern Ontario, where the greatest amounts of atrazine and metolachlor are applied in the province. Eighty percent of the flight was over agricultural fields. While the concentration of metolachlor was almost the same as that of the transect from Ottawa to Midland, the concentration of atrazine was much higher. The negative flux of atrazine indicates that, along the flight path, more atrazine was deposited to than emitted from the surface. Sample 93-3 was taken during the flight between London and Lake Simcoe at a height of 170 m, also across southern and western Ontario, with about 80% coverage of agricultural fields. Atrazine and metolachlor in sample 93-3 had the highest concentrations and fluxes of the four samples. This is primarily due to the high use of these two herbicides in southern and eastern Ontario. Sample 93-4 was collected during the flight from Lake Simcoe to Ottawa at a height of 171 m, across central and eastern Ontario, with 80% coverage of forests and 20% agricultural fields. Along this flight path, the concentration of metolachlor (0.37 ng m^{-3}) was very close to that of the 93-3 sample(0.44 ng m^{-3}). The concentration of atrazine along the 93-4 path is much smaller than that along path 93-2 and 93-3, and a zero flux was observed. This is most likely because the amount of atrazine emitted was very close to that deposited along that flight path.

In the 1994 samples, atrazine and metolachlor were observed mostly in those samples taken along the short segments over agricultural fields. Due to the interference of an unknown peak, we were unable to quantify atrazine concentration in most of the samples. Therefore, only a rough estimation of its concentration is given, and only one flux value was calculated. The interference for metolachlor was not as serious as for atrazine, and we were able to calculate its flux. It is interesting to note that metolachlor was only observed from the samples taken over the short transects over agricultural fields. While the concentration of atrazine was changing around 1 ng m^{-3}, the concentration of metolachlor showed large variations over various transects, from 0.2 ng m^{-3} for sample 94-7 in Kent County (KA-KB, KC-KD) (Figure 4) to 9.8 ng m^{-3} for sample 94-6 over Essex County (EA-EB, EC-ED) (Figure 4). The same was true for the flux of metolachlor, which changed from 0.06 for sample 94-7 to 0.50 ng m^{-2} s^{-1} for sample 94-6. This is mostly due to the fact that the metolachlor concentration and flux were under strong influence of local sources, which are a function of the amount of metolachlor applied and the local environmental conditions.

It is interesting to note that contrary to the results of 1994, the results of 1993 showed large variations in the concentration of atrazine, while the variations in the concentration of metolachlor were much smaller. The difference between the results of 1994 and 1993 could be attributed to the fact that the samples collected on June 16, 1993, were from long transects at regional scale, while most samples collected in July 1994 were from short transects at local scale. Samples 93-1 and 93-4 were collected in eastern and central Ontario and had only 20% coverage of agricultural area. Southern Ontario is the most intensive agricultural area in Ontario, and most of the atrazine and metolachlor used in Ontario were applied there. The atrazine and metolachlor found in samples 93-1 and 93-4 were likely coming from the sources in southern Ontario through long-range transport. Samples 93-2 and 93-3 were taken between southern and western Ontario with about 80% coverage of agricultural fields. They were closer to southern Ontario than samples 93-1 and 93-4 and might be under stronger influence from the emission of the sources in southern Ontario. During long-range transport, herbicide concentrations are subjected to the influence of many factors, such as photodissociation, oxidation reactions, and wet and dry deposition. Because of its low vapor pressure (3×10^{-7} mmHg, at 20 °C) (see Table 1), atrazine can be easily adsorbed at the ground surface. Low vapor pressure of atrazine can also result in high particulate/gas partition. Once in particulate phase, atrazine can deposit faster to the surface through both wet and dry processes than when it is in gas phase. Particulates containing atrazine can be trapped by PUF plugs and therefore cause errors in the concentration results. At this point, no attempt has been made to separate particulate from gas phase. The large variations in concentrations and fluxes of atrazine indicate strong local influence, possibly related to wet and dry deposition. In comparison to atrazine, metolachlor has a much higher vapor pressure (1.3×10^{-5} mmHg, at 20 °C). Along each transect, metolachlor had a very small flux, with its concentration along the transects 93-3 and 94-4 slightly higher than that along the transects 93-1 and 93-2. This indicates that local influence was of minor importance and that metolachlor was well mixed in the atmosphere and transported long distances.

These are the first published results of agrochemicals fluxes using an aircraft-based relaxed eddy-accumulation sampling system. They demonstrate that this approach is a promising method for measuring concentrations and fluxes of agrochemicals at both local and regional scales. Combined with other methods, such as footprint calculation and air mass back-trajectories method, the fluxes measured with this system should be useful to improve our understanding of the long-range transport of semivolatile organic compounds and their impact on various ecosystems. It should also be useful to validate models that simulate the emission and deposition of semivolatile organic compounds over different scales. Further developments of the sampling system, such as increasing the volume sampled and separating particulate from the gas phase should improve the value and accuracy of this technique.

Acknowledgments

This study was supported by funding from the Agriculture and Agri-Food Canada Great Lakes Water Quality Program. We are grateful to Mr. K. Brice and Dr. R. Hoff (AES, Environment Canada) for their valuable help in the GC−MS identification of herbicides and for providing ground-based samples. Special thanks are also due to the staff of the Institute for Aerospace Research of the NRC, Ottawa, for their technical assistance in collecting the aircraft-based data. We also thank D. Dow (ECORC, Agriculture and Agri-Food Canada) for his assistance in testing the high volume sampler on the aircraft.

Literature Cited

(1) Rapaport, R. A.; Eisenreich, S. J. *Environ. Sci. Technol.* **1988**, *22*, 931−941.
(2) Desjardins, R. L.; MacPherson, J. I. In *Exchange of Trace Gases between Terrestrial Ecosystem and the Atmosphere*; Andrea, M. O., Schimel, D. S., Eds.; John Wiley & Sons Ltd.: New York, 1989; pp 135−152.
(3) Desjardins, R. L.; MacPherson, J. I.; Neumann, H.; Den Hartog, G.; Schuepp, P. H. *Atmos. Environ.* **1995**, *29*, 3147−3158.
(4) Desjardins, R. L. *Ph.D. Dissertation*, Cornell University, No. 73-74 University Microfilms, 1972, Ann Arbor, MI.
(5) Businger, J. A. *J. Climate Appl. Meteorol.* **1986**, *25*, 1100−1124.
(6) Majewski, M.; Desjardins, R.; Rochette, P.; Pattey, E.; Seiber, J.; Glotfelty, D. *Environ. Sci. Technol.* **1993**, *27*, 121−128.
(7) Pattey, E.; Desjardins, R. L.; Rochette, P. *Boundary-Layer Meteorol.* **1993**, *66*, 341−355.
(8) Pattey, E.; Cessna, A. J.; Desjardins, R. L.; Kerr, L. A.; Rochette, P.; St. Amour, G.; Zhu, T.; Headrick, K. *Agric. Forest Meteorol.* **1995**, *76*, 201−220.
(9) MacPherson, J. I.; Desjardins, R. L. In *Proceedings of the Seventh AMS Symposium on Meteorological Observations and Instrumentation*, New Orleans, LA, January 14−18, 1991; pp 6−11.
(10) MacPherson, J. I. *NRC, NAE Laboratory Technical Report LTR−FR-109*; February 1990.
(11) Moxley, J. *Survey of pesticide use in Ontario*; Economics Information Report No. 89-08; Economics and Policy Coordination Branch, OMAF: 1989.
(12) Colby, S. R.; Hill, E. R.; Humburg, N. E.; Kitchen, L. M.; Lym, R. G.; McAvoy, W. J.; Prased, R. *Herbicide Handbook*, 6th ed.; Weed Science Society of America: Champaign, IL, 1989.
(13) Hoff, R. M.; Muir, D. C. G.; Grift, N. P. *Environ. Sci. Technol.* **1992**, *26*, 266−272.
(14) Turner, B. C.; Glotfelty, D. E. *Anal. Chem.* **1977**, *49*, 7−10.
(15) Cessna, A. J.; Kerr L. A. *J. Chromatogr.* **1993**, *642*, 417−423.
(16) Pattey, E.; Desjardins, R. L.; Boudreau, F.; Rochette, P. *Boundary-Layer Meteorol.* **1992**, *59*, 195−203.
(17) Schuepp, P. H.; Macpherson, J. I.; Desjardins, R. L. *J. Geophys. Res.* **1992**, 97, 18,455−18,466.
(18) Kaharabata, S. K.; Schuepp, P. H.; Ogunjemiyo, S.; Shen, S.; Leclerc, M. Y.; Desjardins, R. L.; MacPherson, J. I. *J. Geophys. Res.* **1997**, *102*, 29,113−29,124.

Received for review March 17, 1997. Revised manuscript received October 23, 1997. Accepted January 22, 1998.

ES970246C