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Field Comparison of an Eddy Accumulation and an Aerodynamic-Gradient System for Measuring Pesticide Volatilization Fluxes

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■ The field experiment reported here applied the relaxed eddy accumulation (REA) technique to the measurement of triallate (TA) and trifluralin (TF) volatilization from fallow soil. A critical analysis of the REA system used in this experiment is done, and the fluxes are compared to those obtained by the aerodynamic-gradient (AG) technique. The measured cumulative volatilization losses, corrected for the effective upwind source area (footprint), for the AG system were higher than with the REA system. The differences between the methods over the first 5 days of the experiment were 27 and 13% for TA and TF, respectively. A mass balance based on the amount of parent compounds volatilized from soil during the first 5 days of the experiment showed a 110 and 70% and a 79 and 61% accountability for triallate and trifluralin by the AG and REA methods, respectively. These results also show that the non-footprint-corrected AG flux values underestimated the volatilization flux by approximately 16%. The footprint correction model used in this experiment does not presently have the capability of accounting for changes in atmospheric stability. However, these values still provide an indication of the most likely upwind area affecting the evaporative flux estimations. The soil half-lives for triallate and trifluralin were 9.8 and 7.0 days, respectively.

Introduction

There is a variety of techniques that can be used to measure the postapplication volatilization rates of pesticides from agricultural fields, each with its associated advantages and disadvantages (*1*). The aerodynamic-gradient (AG) method is the most frequently used technique for determining field pesticide volatilization rates, but the methodology has not been standardized. This technique has been developed by analogy with the molecular diffusion processes, and its applicability to atmospheric turbulent-transfer processes has been questioned when larger size eddies are present in the flow (*2, 3*). Questions have also been raised about the molecular weight and structure contribution of the pesticide to it's dispersion in turbulent air (*4*). Several investigators have reported good accountability when using the AG technique in pesticide mass balance field experiments (*5, 6*). However, others have indicated that this technique may underpredict the evaporation rate (*7, 8*).

In contrast, the eddy correlation (EC) technique has long been recognized as a more direct approach for measuring atmospheric fluxes of sensible heat, water vapor, and carbon dioxide (*9–13*). Due to the lack of fast-response sensors for agrochemicals it has not been possible to use this technique for estimating pesticide fluxes. Desjardins (*14*) suggested an alternative, the eddy accumulation technique (EA), to overcome this limitation. EA is based on the conditional sampling of air at a rate proportional to the vertical wind velocity. One air sampling inlet collects vapors or particulates associated with updrafts, and the other, vapors or particulates associated with downdrafts. Despite the intrinsic appeal, this technique has not yet been successfully used in the field due to problems related to biased vertical wind velocity measurements, limited accuracy of volume and chemical analysis measurements, and difficulty in controlling the proportional sampling

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valves (*15–17*).

Businger and Oncley (*18*) proposed a relaxation of the eddy accumulation technique (REA). This REA technique samples air conditional to the vertical wind direction but at a constant rate, which significantly simplifies the valving design. The EC, EA, and REA techniques have yet to be applied to the problem of measuring pesticide volatilization. We report here the application of REA to estimate the volatilization flux of two herbicides from fallow soil, its comparison with the AG method, and a calculation of mass balance of the parent compounds based upon the two techniques.

Measurement Techniques

Aerodynamic-Gradient (AG) Technique. The aerodynamic-gradient technique requires accurate measurements of horizontal wind speed, vertical temperature, and pesticide concentration gradients taken above an extended upwind treated area. The treated area requires a uniform, relatively flat, sufficiently large surface to ensure that the measurements are made within the equilibrated surface boundary layer which develops over it. These surface requirements are common to all evaporative flux measurement systems.

The AG pesticides fluxes (P_{AG}) were estimated using a modified form of the Thornthwaite–Holzman equation (*19*) corrected for atmospheric stability conditions, eq 1, where

$$P_{AG} = k^2 \Delta\bar{c} \Delta\bar{u} / \phi_M \phi_P [\ln (z_2/z_1)]^2 \qquad (1)$$

k is the von Kármán constant and $\Delta\bar{c}$ (μg m^{-3}) and $\Delta\bar{u}$ (m s^{-1}) are the average pesticide concentration and horizontal wind speed differences, respectively, between heights z_1 and z_2 (m) above the treated surface. The ϕ expressions ϕ_M and ϕ_P are stability correction functions of the vertical profiles for wind and pesticide concentration in the surface layer, respectively (*20*). The flux estimates assumed that the flux gradient relationships for pesticides were similar to those for water vapor. A more complete description of this theoretical approach is given by Majewski et al. (*21*).

Relaxed Eddy Accumulation (REA) Technique. The relaxed eddy accumulation technique (*18, 22*) is a variation of the eddy correlation technique based on a determination of the pesticide concentration difference between the upward and downward moving air masses. The pesticide fluxes (P_{REA}) for each compound were calculated using eq 2, where A (dimensionless) is an empirical

$$P_{REA} = A s_w (\overline{c^+} - \overline{c^-}) \qquad (2)$$

coefficient, s_w (m s^{-1}) is the standard deviation of the vertical wind speed measured with a sonic anemometer, and $\overline{c^+}$ and $\overline{c^-}$ (μg m^{-3}) are the mean herbicide concentrations associated with the upward and downward moving air masses, respectively.

Simulations of the REA technique made with a series of vertical wind speed, water vapor, and air temperature fluctuation measurements using fast-response sensors showed that the A coefficient is nearly constant and equal to 0.59 (*18, 22*). Technical factors make it difficult to sample the air with the same precision using a valve system in place of a fast response sensor. Among them is the lag between the vertical wind speed (w) signal and the valve control caused by the valve response time and the data logger processing time (35–85 ms). These factors cause an underestimation of ($\overline{c^+} - \overline{c^-}$) by diverting a fraction of the up- and downdrafts to the wrong collectors. Under similar atmospheric turbulence conditions, the degree of ($\overline{c^+} - \overline{c^-}$) underestimation is a characteristic of the sampling system and can be accounted for by the adjustment of the coefficient A. The determination of the appropriate adjusted A value (A_s) was achieved in this study by the simultaneous measurement of latent heat flux (E) using the EC and REA techniques and the assumption that the herbicide and water vapor sources had similar distributions. Water vapor fluctuations were measured with a fast-response infrared gas analyzer (*23*). The mean up- and downdraft water vapor concentration measurements ($\overline{q^+}$ and $\overline{q^-}$) (g m^{-3}), were associated with the same filtered w signal which also controlled the pesticide sampling solenoid valve. A_s, which integrates the effects of our system design, was derived using eq 3 and substituted into eq 2.

$$A_s = E_{q,\mathrm{EC}} / s_w (\overline{q^+} - \overline{q^-}) \qquad (3)$$

We assumed that the same coefficient could be used for the two different scalar properties, water vapor and herbicide vapor.

A_s was calculated on an hourly basis for the first 3 days of the experiment. The averaged A_s value was 0.79 ± 0.11. Data logger malfunction during the remaining 2 days of the field experiment prevented q measurements from being taken.

The impact of an error in ($\overline{c^+} - \overline{c^-}$) (eq 2) is linear and can be controlled by the A_s coefficient and the analytical method. The impact of an error in w is not as straightforward and is beyond the scope of this paper. It is essential that errors in w be kept as small as possible.

Corrections for air density fluctuations caused by heat and water vapor fluxes (*24*) were calculated using eq 4,

$$F = F_{raw} + (\rho_c/\rho_a)(0.649 \times 10^{-6} \lambda E + 3.358 \times 10^{-6} H) \qquad (4)$$

where ρ_c/ρ_a is the ratio of the pesticide density in air to the density of dry air, λE (W m^{-2}) is the latent heat flux, H (W m^{-2}) is the sensible heat flux, and F_{raw} (kg m^{-2} s^{-1}) is the calculated field flux. An air temperature of 293 K, an atmospheric pressure of 10^5 Pa, and a water vapor pressure of 10^3 Pa was assumed. The actual measured pesticide air concentration was used for ρ_c. The resulting density ratio governed the outcome of this equation. The effects of air density fluctuations caused by heat and water vapor fluxes on the pesticide fluxes was negligible (<1%). A more detailed description of the impact of density fluctuations on trace gas flux measurements is given by Pattey et. al (*25*).

Fluxes calculated using the AG and REA techniques were corrected to account for the differences in sampling height between the two systems. Since the reference height of each system was different (0.75 m for AG vs 1.75 m for REA), the upwind fetch requirement was also different for the computed fluxes. Beyond the 150-m-radius distance of the treated area, a contribution to the total flux from nontreated area could occur. The herbicide flux contribution associated with the specific (150-m radius) footprint was computed using the equation given by Schuepp et al. (*26*). This correction depends upon the ratio of the horizontal wind speed ($\bar{u}$) to the frictional velocity (u*). Mean hourly wind speed at 1.75 m measured with a sonic anemometer was used for the REA system. A logarithmic wind speed profile with height was assumed to calculate the wind speed at 0.75 m for the AG system. Source area contribution footprints for both systems were calculated daily, and the measured fluxes were adjusted accordingly. The footprint correction calculations showed that the AG and REA flux values needed to be increased by approximately 15 and 35%, respectively (Table I). The differences in the footprint corrections between the two methods ranged from 15 to 20%.

Table I. Contribution of Pesticide-Sprayed Surface to Total Flux for REA System at 1.75 m and AG System at 0.75 m Using the Footprint Equation of Schuepp et al. (*26*)

day	$\bar{u}/u^*$ (s)	contrib,[a] %	$\bar{u}/u^*$	contrib,[b] %
263	13.0 (1.45)	68.5	10.9	87.1
264	10.0 (3.01)	74.6	8.3	90.5
265	15.2 (0.91)	64.6	12.7	85.8
266	14.9 (0.31)	64.6	12.5	85.5
267	13.5 (1.15)	67.5	11.3	87.1
268	14.4 (1.15)	65.5	12.1	86.1

[a] Flux plane height, z = 1.75 m. [b] Flux plane height, z = 0.75 m.

Table II. Physical Properties of the Test Compounds Trifluralin and Triallate[a]

compound	MW	vapor pressure, mPa	water solub, mg L^{-1}
triallate	304.7	16.0 (25 °C)	4 (25 °C)
trifluralin	335.5	13.7 (25 °C)	<1 (27 °C)

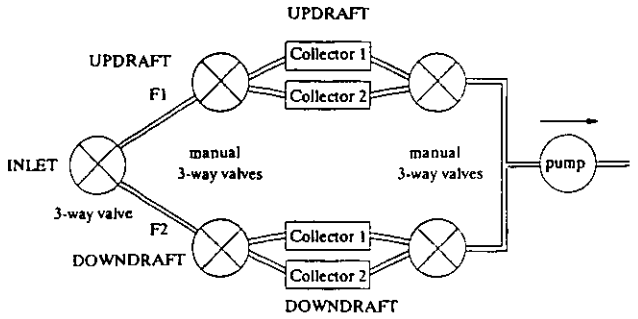
[a] From: *The Pesticide Manual, A World Compendium*, 8th ed.; Worthing, C. R., Ed.; The British Crop Protection Council: Binfield Bracknell, Berks UK, 1987.

Upwind source area footprint corrections are very dependent upon atmospheric stability (*27*) and can vary considerably between day and night. The footprint correction model used in the experiment only takes into account small thermal instabilities by a semiempirical adjustment to the ratio of horizontal wind to frictional velocity computed for the daytime conditions of each day. Footprint corrections specific for nighttime conditions were not computed. However, the computed values used still provide an indication of the most likely upwind area affecting the evaporative flux estimations. Footprint corrections during nighttime conditions are generally larger than during daylight hours. Using daytime correction factors on nighttime fluxes avoided potentially large flux errors due to the difficulty in calculating the $\bar{u}/u^*$ ratio at night when $\bar{u}$ is very low. The standard deviation of hourly $\bar{u}/u^*$ values are presented in Table I as information on the $\bar{u}/u^*$ variability. Large errors in the cumulative flux data were minimized since the nighttime fluxes were generally very low. Correcting the measured fluxes for the fetch requirement of each system led to closer overall agreement in flux values between the methods.

Materials and Methods

The experiment was conducted from 20 September (day 263) to 25 September (day 268), 1989, on a 20-ha field located at the Animal Research Center of Agriculture Canada at Ottawa, Canada. The soil type was a Dalhousie clay. A 150-m-radius circular plot (7.1 ha) was inscribed in the approximate center of the field and was treated with trifluralin (TF) and triallate (TA) at a known rate of approximately 2.5 kg ha^{-1} for each active ingredient. These compounds were chosen because of their high volatilization potential based on their vapor pressures (Table II). The compounds were sprayed to the surface as an emulsified aqueous suspension and not incorporated into the soil as is the usual practice. Both air sampling systems were placed within 3 m of the center of the treated area.

At the beginning of the experiment, the field was moist from a light rain received the night before but no standing water was visible. Air sampling began immediately after the completion of the spraying (which lasted 50 min) and 5 d continued for 120 h, with the exception of an approximate 8-h break between days 265 and 266 due to heavy rainfall.



FLOW	F1	F2
0 < W	1	0
W < 0	0	1

Figure 1. Schematic for the relaxed eddy accumulation air sampling system.

Air Sampling and Analysis. Polyurethane foam (PUF) was used as the pesticide vapor trapping medium based upon it's trapping efficiency of >98% for both compounds as reported in the literature (*28*) and confirmed by our own trapping efficiency experiments. The PUF plugs were inserted into Teflon cartridges (Savillex, Minnitonka, MN), which were covered with thick aluminum foil to protect them from sunlight. The actual air sampling periods were of different duration and dependent upon the anticipated volatilization fluxes. They ranged between 1 and 6 h (Table III). Each AG air sampler was aspirated at a rate of approximately 3.0 m^3 h^{-1} using a high-volume air vacuum pumping system. Pesticide air concentration measurements were made at 0.25, 0.40, 0.70, 1.10, 1.60, and 2.26 m above the soil surface. The PUF plugs were changed at the beginning of each sampling period, placed in clean glass jars, sealed with Teflon-lined lids, and refrigerated until analyzed. The horizontal wind speed was measured at the same levels as the air concentration using rotating cup anemometers (C. W. Thornthwaite Assoc., Elmer, NJ). Differential air temperature measurements were made between 0.50 and 1.00 m using a 10-junction copper–constantan thermopile (*29*). Ambient air temperature was measured at 0.75 m using an aspirated, shielded thermistor (Type 107, Campbell Scientific, Logan, UT).

A three-dimensional sonic anemometer–thermometer (DAT-310, Kaijo Denki, Tokyo, Japan) measured w as well as the horizontal wind and temperature at 1.75 m. The signal was monitored at 20 Hz using a data logger (CR-21X, Campbell Scientific, Logan, UT) which controlled a solenoid valve that diverted air flow through one of two absorbers depending on the direction of w (Figure 1). The valve inlet was located at a height corresponding to the midpoint of the vertical wind sensor path (1.75 m) and 0.1 m downwind from the center of the anemometer. The flow rate at the intake was constant at 2.4 m^3 h^{-1} and monitored using a flowmeter with a ±0.2% accuracy and a 1-ms response time. The REA sampling unit consisted of two sets of two Teflon cups connected by switching valves which allowed for continuous operation while one set of PUF plugs was being changed. Teflon tubing (2.25 m × 6.4 mm i.d.) connected the switching valuves to the intake solenoid. The w signal was high-pass filtered at 0.001 Hz with a fourth-order analog filter (Rockland, Model 1022F-02) to minimize potential signal contamination from the horizontal flow components in order to maintain a mean vertical wind speed close to zero.

Before beginning the chemical analytical procedure, the PUF plugs were warmed to room temperature under

Table III. Sampling Day, Time, Duration, and Atmospheric Stability As Described by the Richardson Number (*Ri*), and Herbicide Air Concentrations Used To Calculate the AG and REA Volatilization Fluxes

		AG method						REA method				
			air concn, $\mu g\ m^{-3}$						air concn, $\mu g\ m^{-3}$			
			trifluralin		triallate				trifluralin		triallate	
day	midpt samplg time	samplg duratn[a]	0.5 m	1.0 m	0.5 m	1.0 m	*Ri*	samplg duratn[a]	up	down	up	down
263	9.63	0.75	41.4	28.4	52.0	35.9	−0.1484					
263	10.00							2.00	27.5	23.6	26.9	17.7
263	10.50	1.00	16.4	11.6	24.0	16.3	−0.1911					
263	11.50	1.00	8.40	5.80	10.50	7.50	−1.0862	1.00	20.69	1.35	12.97	3.97
263	12.50							1.00	11.17	5.23	8.92	4.31
263	13.00	2.00	4.03	2.80	5.00	3.60	−0.1205					
263	13.50							1.00	4.47	5.38	5.16	5.06
263	15.00	2.00	2.45	1.60	3.15	2.15	−0.1246	2.00	0.89	0.70	1.95	1.03
263	17.00	2.00	2.50	1.70	3.45	2.36	−0.0641	2.00	0.69	1.24	1.59	0.99
263	19.00	2.00	11.00	7.04	20.00	12.40	0.1028	2.00	5.13	3.35	7.17	5.29
263	21.00	2.00	15.80	10.60	27.40	18.00	0.0425	2.00	6.69	5.23	9.99	9.03
263	24.00	4.00	16.50	8.30	22.00	11.50	0.1911	4.00	5.45	3.70	6.46	5.10
264	3.50	3.00	14.00	6.37	17.73	8.03	0.4374	3.00	2.58	2.16	2.67	2.71
264	7.00	2.00	13.07	8.72	17.75	11.75	−0.0402	3.00	4.06	3.59	4.85	4.50
264	9.00	2.00	3.51	2.56	3.69	2.73	−0.9996	2.00	1.74	1.55	2.92	1.67
264	11.00	2.00	1.52	1.05	1.63	1.11	−0.1452	2.00	0.61	1.02	1.40	0.87
264	13.50	3.00	0.58	0.39	0.73	0.48	−0.3101	3.00	1.45	0.76	1.71	0.83
264	16.50	3.00	0.93	0.61	0.90	0.60	−0.0291	3.00	0.17	0.51	0.43	0.13
264	21.00	6.00	4.20	2.36	4.82	2.77	0.0636					
265	1.17	2.10	9.39	4.49	9.35	5.10	*c*	7.00	2.86	2.48	3.02	2.66
265	6.50	3.00	6.84	4.86	6.77	4.73	−0.0363	3.00	3.23	2.22	3.02	2.22
265	9.50	3.00	5.21	3.55	4.71	3.21	−0.0140	3.00	3.19	2.49	1.85	1.45
265	13.00	4.00	1.29	0.86	0.99	0.67	−0.0043	4.00	1.46	0.87	0.63	0.29
265	15.50	1.00	14.81	9.87	22.44	15.39	0.0029	1.00	4.94	4.00	4.63	3.00
265	16.50	1.00	*b*	*b*	*b*	*b*	0.0029	1.00	6.22	4.12	8.90	7.43
265	17.50	1.00	19.42	13.27	29.46	20.45	0.0074	1.00	8.28	5.87	10.03	6.12
265	19.00	2.00	12.99	9.12	20.08	13.77	0.0058	2.00	5.24	3.92	7.82	6.06
265	21.17	2.20	8.46	5.57	13.67	9.13	0.0067	2.00	3.36	3.21	5.22	5.17
266	8.00							4.00	0.21	0.22	0.56	0.44
266	8.75	2.60	1.02	0.68	1.86	1.22	−0.0010					
266	11.50	3.00	0.98	0.65	1.77	1.16	−0.0030	3.00	0.26	0.31	0.65	0.49
266	14.50	3.00	0.96	0.62	1.60	1.03	−0.0022	3.00	0.26	≤lod[d]	0.59	0.45
266	17.50	3.00	0.84	0.53	1.18	0.75	0.0022	3.00	0.17	0.09	0.29	0.26
266	20.50							3.00	0.55	<lod	0.45	0.33
266	21.50	5.00	0.75	0.51	1.01	0.66	0.0023					
267	3.00	6.00	0.56	0.37	0.79	0.51	0.0044	8.00	0.09	0.00	0.18	0.15
267	7.50	3.00	0.56	0.37	0.86	0.56	0.0000	3.00	0.39	0.25	0.25	0.19
267	10.50	3.00	0.78	0.51	1.07	0.71	−0.0121	3.00	0.16	1.52	0.38	0.26
267	13.50	3.00	0.51	0.33	0.58	0.36	−0.0218	3.00	0.13	0.09	0.29	0.19
267	16.50	3.00	0.42	0.26	0.45	0.28	−0.0403	4.00	0.09	1.40	0.14	0.10
267	21.00	6.00	0.87	0.55	1.06	0.66	0.2231	3.00	<lod	<lod	<lod	<lod
268	3.00	6.00	0.64	0.36	0.76	0.43	0.2079	6.00	<lod	<lod	<lod	<lod
268	7.00	2.00	1.01	0.66	1.29	0.85	0.0161	2.00	<lod	<lod	<lod	<lod
268	9.00	2.00	0.97	0.63	1.21	0.78	−0.0380	2.00	<lod	<lod	<lod	<lod
268	11.00	2.00	0.43	0.27	0.49	0.30	−0.0262	2.00	<lod	<lod	<lod	<lod

[a] Blank spaces represent overlapping time periods. [b] Sample lost during analysis. [c] No wind speed data. [d] <lod, below analytical limit of detection.

subdued light and then Soxhlet-extracted with 250 mL of hexane (Burdick and Jackson) for 4 h (approximately 20 cycles). The Soxhlet extract was then concentrated or diluted as needed for gas chromatography analysis. The instrument was a Hewlett-Packard 5890 equipped with a ^{63}Ni electron capture detector using argon–methane (95:5) as the carrier gas. A 30 m × 0.53 mm i.d. DB-1 fused-silica wide-bore column was used (J&W Scientific, Folsom, CA). The column temperature was programmed from 175 to 220 °C at 20 °C min^{-1} with a 1 min hold at 220 °C. The injector and detector temperatures were 220 and 300 °C, respectively.

Soil Sampling and Analysis. A structured sampling of the treated field was done by quadrant and location from the center of the plot (Figure 2). The soil sampling was done at approximately 12-h intervals for the first 3 days, followed by a single morning sampling for each of the remaining 2 days. Triplicate samples consisting of 10 soil cores (2.5 cm diameter × 2.5 cm deep) were taken at each site with adjacent sites composited by quadrant. The depth was adjusted to 7.5 cm after the rainfall on days 265 and 266. As an example, quadrant I contained three composite samples of sites 7 and 13, 8 and 14, and 9 and 15. The soil samples were collected in clean, glass jars with Teflon-lined lids and stored at −20 °C until extracted and analyzed.

The samples were thawed under subdued light to room temperature for at least 2 h before beginning the chemical analytical procedure. The total sample weight was determined, and the soil was passed through a 4.75-mm screen and mixed well. Moisture was determined using 20–30-g subsamples of each well-mixed soil sample. The analytical sample was split into three 20–25-g subsamples for analysis. The moisture content of the analytical sample was brought to ≈10% as needed by adding distilled water and thoroughly mixing. A 100-mL aliquot of a hexane–2-propanol (3:1, v/v) mixture was the extraction solvent. The sample and extraction solvent were blended using a

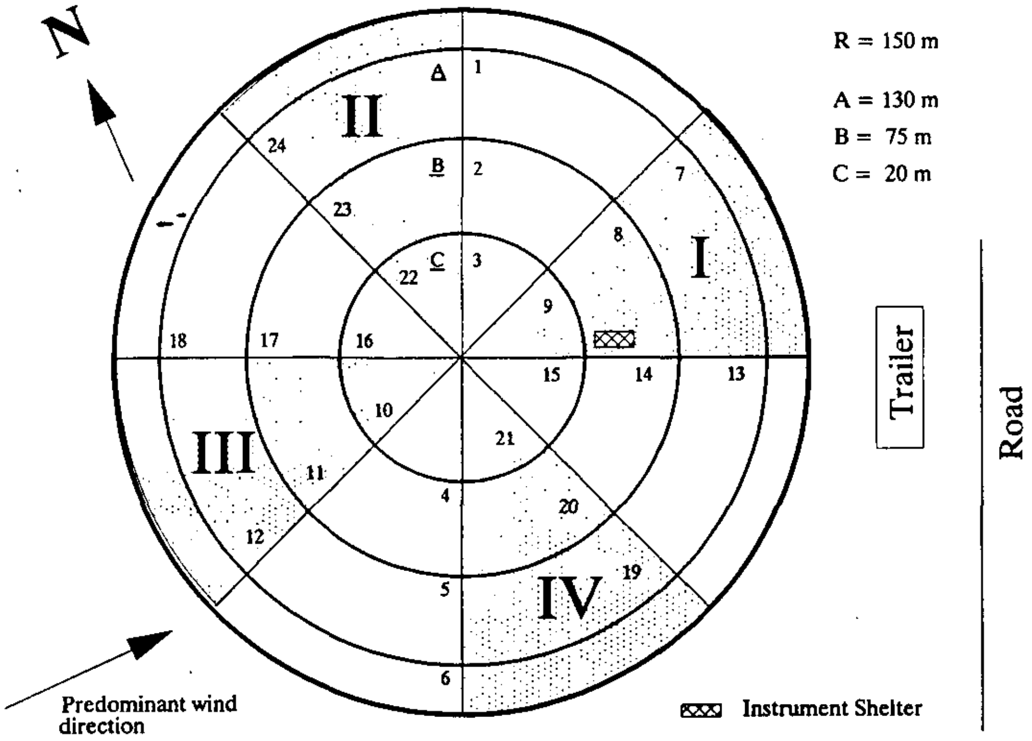


Figure 2. Soil sampling design, indicating quadrants (I–IV) and sites (1–24) selected for sampling.

tissue mincer (Tekmar Co., Cincinnati, OH) for 30–45 s. The mixture was allowed to settle and a 10-mL aliquot was pipeted into a 50-mL volumetric flask containng ≈30 mL of distilled water. The flask was vigorously shaken for 1–2 min. A 5-mL sample of the cleared hexane layer was removed using a volumetric pipet and diluted or concentrated as needed for analysis.

The samples were analyzed using the gas chromatographic conditions described above. The amount of each compound lost from the soil over the 5-day experiment was then compared to the amount measured in the air.

Results and Discussion

A wide range of meteorological conditions occurred during the course of the experiment, ranging from mild, dry, summer-like weather, to windy and rainy, to cold and frosty (Figure 3). This gave us the opportunity to compare the measurement systems over a wide range of weather conditions. The highest pesticide fluxes were observed by both measurement systems during the first 4 h after spraying and during the first hours of the rain event on day 265 (Figure 4a and b). The TA and TF fluxes measured by the AG method showed a very similar pattern throughout the experiment. In general, the evaporative fluxes displayed a pattern of high rates during the early morning hours just after sunrise, diminishing throughout the day, and increased again slightly in the evenings just after sunset. This diurnal pattern tended to follow the moisture content of the top layer of the soil. As the soil surface dried, the evaporative flux decreased. The early morning "blooms" were most likely due to the rewetting of the soil surface by dew formation, while the evening "blooms" were most likely due to the increased movement of soil moisture to the surface driven by the heat energy stored in the soil throughout the day. The large flux value on day 265 coincided with a rainfall of ≈50 mm. These diurnal flux increases also coincided with a change in atmospheric stability conditions, from stable to unstable, or from unstable to stable, as indicated by the temperature gradient and Richardson number (Table III).

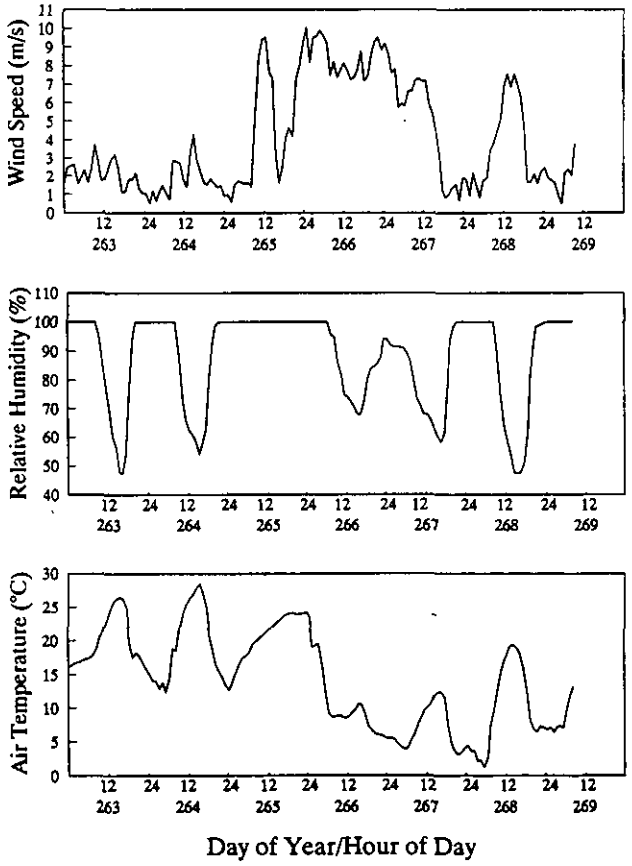


Figure 3. Air temperature, relative humidity, and wind speed conditions during the experiment.

The pattern of volatilization rate dependence on soil moisture has been observed by others (*5–8*, *21*, *30*, *31*) and can be partially explained by the effect of water molecules displacing the herbicide molecules from the soil's active adsorptive sites (*32*). The large AG flux value on day 265 may, at first, appear to be an anomaly, but there is nothing

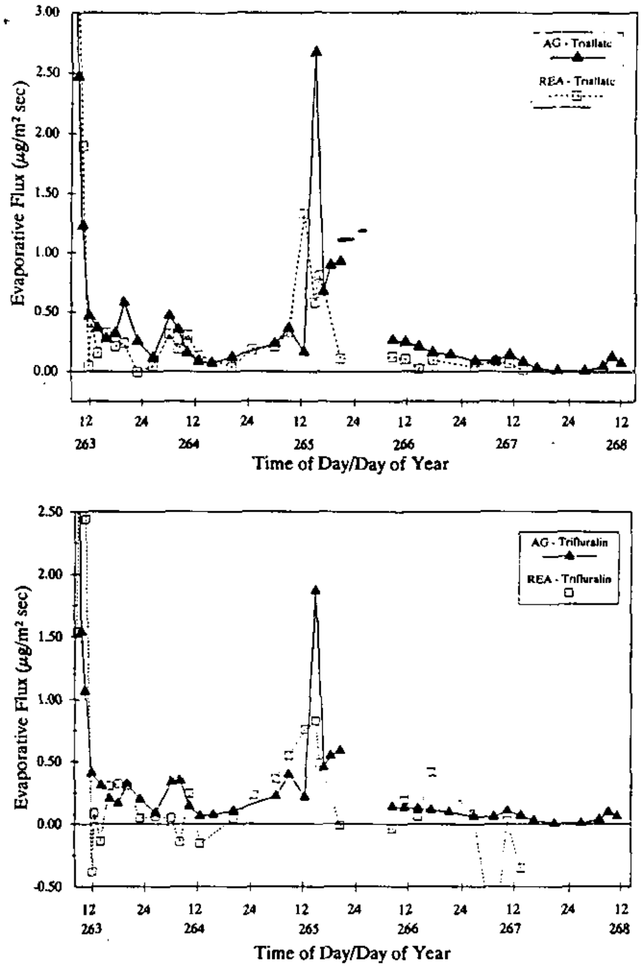


Figure 4. Evaporative flux of (a) triallate and (b) trifluralin with time measured by the aerodynamic-gradient and the relaxed eddy accumulation systems.

in the data to suggest this. The wind speed throughout the sampling period was high (5.9–7.5 m s^{-1} at 1.1 m) but reasonably steady. The ambient temperature dropped ≈5 °C (25.4–21.1 °C), but the temperature gradient was fairly constant (0.119 ± 0.037). These meteorological values are not unusual. After the storm on day 265, a cold front moved in with freezing temperatures at night and very cold days. On day 266, the AG evaporative flux declined steadily throughout the day regardless of the change in atmospheric stability conditions. The soil surface was moist throughout the day. The cold ambient temperatures acted to reduce the effective vapor pressure of the two compounds which, in turn, reduced their volatilization rates.

The temporal pattern of TA fluxes measured by the REA system was similar to that obtained by the AG technique. On day 266 the REA TA fluxes were about half those of AG (Figure 4a). These lower flux estimates were attributed to the high wind velocities observed on that day (Figure 3) which increased the high-frequency component of the w fluctuations. These faster w fluctuations, most likely, increased the impact of the lag between the w signal and the valve control, which resulted in an underestimation of $(\overline{c^+} - \overline{c^-})$. Since A_s was determined under the conditions that occurred in the first 3 days of the experiment when the horizontal wind was less, it could not totally account for the system behavior at higher wind speeds.

The REA TF fluxes showed more variability than the REA TA values. During days 265 and 266, two periods showed much lower fluxes than those obtained by the AG

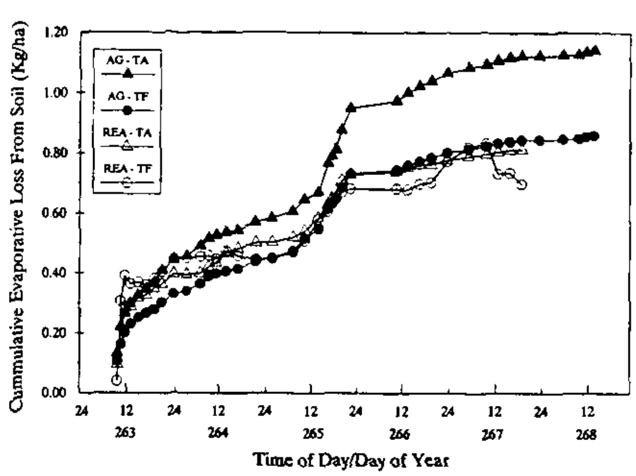


Figure 5. Cumulative evaporative flux of triallate and trifluralin with time measured by the aerodynamic-gradient and the relaxed eddy accumulation systems.

technique, and negative fluxes were measured during seven periods in the experiment (Figure 4b). Since the vertical air concentration gradient of TF was negative throughout the sampling height during the periods of negative flux measurements, we would expect the fluxes to be directed away from the surface and, by convention, result in a positive REA TF flux value. It is unclear why TF behaved differently from TA since both herbicides were sampled simultaneously and analyzed with the same procedure and equipment. An explanation could be linked to the sensitivity of TF to sunlight-induced UV photolysis (*33*) since all periods of underestimation occurred during daylight hours. If photolysis was a major factor, it would also have affected the corresponding AG flux value. The effect of a vapor-phase photoproduct gradient on the AG system would be a reduction of the TF concentration with height, thereby increasing the apparent concentration gradient of the parent compound and resulting in a greater TF flux value. However, the actual photoproduct source may be difficult to identify since photolysis can occur in the vapor phase as well as on the soil surface. Also, these photoproducts may be the same as those formed by aerobic decomposition in the soil (*34*). Since this experiment compared the parent TF compound only, the photolytic effects on the overall flux results should be similar in both methods. There are, however, several factors associated with the REA sampler design itself that may have contributed to the odd TF behavior. The majority of the intake system was Teflon, but it was over 2 m long and herbicide vapor adsorption to the inside walls of the tubing was likely. In addition, several brass and stainless steel joints and valves were used and the solenoid valve was not Teflon. These factors may have contributed to a preferential TF degradation and/or adsorption within the REA system itself during certain conditions. Also, the assumption that the A_s coefficient is similar for different scalar properties may not have been entirely valid, especially as the moist soil surface dried unevenly. The EC energy balance closure calculations indicated that the fluxes appear to be underestimated by 5–10%.

Figure 5 shows the cumulative volatility losses of TA and TF for both the REA and the AG flux measurement systems. The cumulative TF volatility losses had some slight discrepancies due to the negative fluxes computed with the REA system. Over the first 5 days of the experiment, the difference in cumulative TF volatility between the two methods was 13%. If the negative fluxes are excluded, the cumulative difference is less than 1%. A cumulative difference of 27% was observed in the volatility losses for

Table IV. Total Averaged Concentration and Standard Deviation (s) of Trifluralin (TA) and Triallate (TF) in the Soil and Total Averaged Volumetric Moisture Content (M) and Standard Deviation (s) of the Soil SUrface

day	time, h	TF (s), kg ha^{-1}	TA (s), kg ha^{-1}	M (s), %
263	10.80	2.66 (0.26)	3.37 (0.29)	17.25 (2.98)
263	16.00	1.88 (0.29)	2.74 (0.38)	14.24 (3.03)
264	07.00	2.00 (0.31)	2.96 (0.29)	14.22 (2.16)
264	17.50	1.55 (0.28)	2.26 (0.38)	12.02 (2.50)
265	06.75	1.76 (0.15)	2.72 (0.48)	12.61 (2.37)
265	17.50	1.65 (0.25)	2.53 (0.39)	24.04 (3.65)
266	10.00	1.55 (0.29)	2.32 (0.42)	32.24 (3.45)
267	08.50	1.46 (0.70)	2.35 (0.88)	28.42 (1.91)
268	09.00	1.38 (0.24)	2.12 (0.33)	24.53 (2.02)

19.95

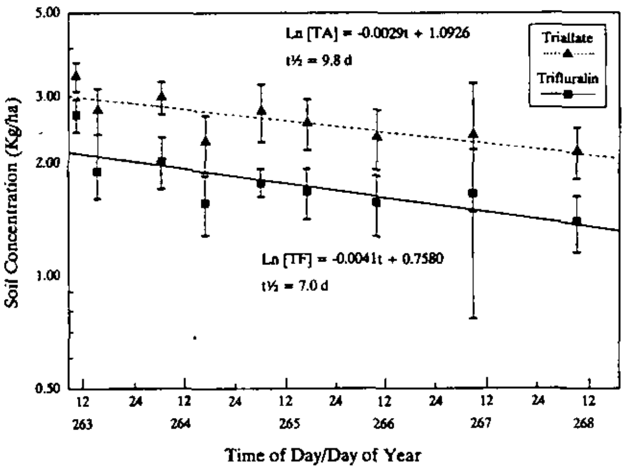


Figure 6. Soil concentration decline with time for triallate and trifluralin.

TA. This difference was due mainly to the lower measured REA fluxes during the rainfall on day 265 and on day 266.

Mass Balance. Table IV and Figure 6 show the overall soil dissipation for TA and TF over the 6-day study period. Both compounds showed a log-linear relationship between soil concentration and time. The resulting soil half-lives ($t_{1/2}$) were 9.8 and 7.0 days for TA and TF, respectively. The measured cumulative volatilization of the AG system (footprint-corrected) accounted for 110 and 70% of the quantity lost by soil for TA and TF, respectively, over the first 5 days of the experiment. The corresponding REA system values were 79 and 61%. The non-footprint-corrected AG results accounted for 74 and 54% of TA and TF loss from the soil by volatilization. These results indicate that the non-footprint-corrected AG system may be underestimating the evaporative losses by approximately 16%.

The low TF accountability by both flux measurement systems may be due to vapor-phase photolysis of this compound. The degradation products were not analyzed for. Triallate, on the other hand, is very stable to photolysis, and this fact is reflected in the good TA soil loss accountability by volatilization. Also contributing to the observed differences in the mass balance of both compounds could be the leaching of the herbicides below the 7.5-cm soil sampling depth and run off. These dissipative pathways were not monitored.

Conclusion

This experiment showed that measuring pesticide field volatilization is possible using a relaxed eddy accumulation system. Fluxes measured by this approach showed a temporal pattern similar to those obtained by the aerodynamic gradient technique. However, it was observed that the reaction time of the valve control to changes in w caused flux underestimation. In this experiment, the REA empirical coefficient could be independently determined through the measurement of latent heat fluxes with an eddy correlation system and the assumption of similar vapor behavior of the herbicides and water. If one wants to use the REA technique in the absence of such measurements, the valve control reaction time will need to be minimized if the 0.59 value is to be used (*18, 22*).

The overall comparison of the two pesticide evaporative flux determination methodologies was encouraging, with good accountability of the amount of material lost from the soil by volatilization. Part of the REA underestimation can be attributed to the adsorption of the herbicides to the intake tubing and valves. However, it is recognized that refinements in the REA system need to be made. Planned modifications are to shorten and make the intake system entirely of Teflon to minimize any chemical adsorption and/or reaction within the system and to heat the intake tubes. Further experiments should aim at testing the REA system under conditions of smaller vertical pesticide air concentration gradients and where footprint corrections are not as large. This REA technique should also be applied to aircraft-based sampling over long trajectories, where observations at one level preclude the use of gradient techniques.

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Absorption of NO Promoted by Strong Oxidizing Agents: Organic Tertiary Hydroperoxides in *n*-Hexadecane

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■ The selective removal of nitric oxide from gas streams was investigated using 3,6-dimethyl-3-octyl hydroperoxide, *p*-menthanyl hydroperoxide, pinanyl hydroperoxide, and cumenyl hydroperoxide in solutions of *n*-hexadecane (cetane). The influence of different variables such as temperature, gas stream flow rate (or residence time), and concentration of hydroperoxide compounds on rate of NO removal was evaluated. The NO reacted with the hydroperoxides to produce alkyl nitrates. These are easily hydrolyzed with ammonium hydroxide to ammonium nitrate and the alcohol. The hydroperoxides used in this study were selected to be inexpensive, be commercially available, have a relatively low vapor pressure to avoid loss of reagent when in contact with hot flue gas, and be easily regenerated. Under the same conditions, cumenyl and pinanyl hydroperoxide removed NO faster than the other two organic hydroperoxides tested. The highest rates of NO removal were obtained at the highest temperatures, concentrations, and residence times.

Introduction

Nitrogen oxides (NO_x) are mixtures of compounds of nitrogen and oxygen generally found in effluents from combustion sources. The predominant NO_x compounds are NO and NO_2. They are formed as a result of the reactions of atmospheric nitrogen with atmospheric oxygen at very high temperatures. Also, large quantities of NO_x are formed from the oxidation of nitrogen compounds found in fuel or in wastes being incinerated. More than 90% of NO_x emitted from stationary combustion sources consist of NO, which is relatively insoluble in inorganic aqueous solutions. Finding a way to control NO is essential for the prevention of NO_x pollution, one of the major sources of acid rain.

One of the most difficult problems related to pollution control from boilers and incinerators is reducing the emissions of the oxides of nitrogen. The NO_x emissions that result from the high-temperature oxidation of the nitrogen in the combustion air can be partly controlled by combustion modification techniques and by postcombustion methods. Postcombustion methods include selective catalytic reduction (SCR), thermal NO_x removal, and scrubbing. Research on NO_x-scrubbing processes has shown that these processes require expensive oxidation reagents and may present special disposal problems because of high concentrations of chlorides, nitrates, and nitrites in the aqueous effluents. However, scrubbing promises to be less expensive than competing posttreatment technologies and has the advantage that the same scrubber could be used to control other acid gases and particulates.

No specific techniques have been developed for controlling the extremely high concentration of NO_x emissions that results from the oxidation of nitrogen compounds found in industrial and agricultural substances being incinerated. SCR systems have not been demonstrated for high NO_x concentrations and are easily poisoned by substances present in hazardous wastes. In the case of industrial incineration, NO_x emissions resulting from nitrogen compounds have been found in excess of 8000 ppm (*1*). In addition to NO_x, scrubbers should be designed to control other acidic effluents such as oxides of sulfur (SO_x), hydrogen chloride (HCl), phosphorus pentoxide (P_2O_5), and inorganic particulate matter containing transition metals (*2, 3*).

A number of aqueous inorganic solutions have shown high capacity for NO_2 absorption, but NO is absorbed with difficulty. Consequently, a method to oxidize NO to NO_2 or an equivalent oxidized state of nitrogen is required to substantially reduce NO_x emissions. Aqueous solutions of a number of oxidizing agents have been studied to determine their effectiveness in removing NO_x and SO_x from

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