

Volatilization of Trifluralin, Atrazine, Metolachlor, Chlorpyrifos, α -Endosulfan, and β -Endosulfan from Freshly Tilled Soil

CLIFFORD P. RICE,^{*,†} CRISTINA B. NOCHETTO,[‡] AND PEDRO ZARA[†]

Animal and Natural Resources Institute, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705, and Center for Veterinary Medicine, U.S. Food and Drug Administration, Laurel, Maryland 20708

The volatile and soil loss profiles of six agricultural pesticides were measured for 20 days following treatment to freshly tilled soil at the Beltsville Agricultural Research Center. The volatile fluxes were determined using the Theoretical Profile Shape (TPS) method. Polyurethane foam plugs were used to collect the gas-phase levels of the pesticides at the TPS-defined critical height above a treated field. Surface-soil (0–8 cm) samples were collected on each day of air sampling. The order of the volatile flux losses was trifluralin > α -endosulfan > chlorpyrifos > metolachlor > atrazine > β -endosulfan. The magnitude of the losses ranged from 14.1% of nominal applied amounts of trifluralin to 2.5% of β -endosulfan. The daily loss profiles were typical of those observed by others for volatile flux of pesticides from moist soil. Even though heavy rains occurred from the first to third day after treatment, the majority of the losses took place within 4 days of treatment, that is, 59% of the total applied atrazine and metolachlor and >78% of the other pesticides. Soil losses generally followed pseudo-first-order kinetics; however, leaching due to heavy rainfall caused significant errors in these results. The portion of soil losses that were accounted for by the volatile fluxes was ordered as follows: α -endosulfan, 34.5%; trifluralin, 26.5%; chlorpyrifos, 23.3%; β -endosulfan, 14.5%; metolachlor, 12.4%; and atrazine, 7.5%.

KEYWORDS: Volatility; pesticides; atrazine; metolachlor; chlorpyrifos; endosulfan; trifluralin

Atmospheric loss of agricultural pesticides during application is obviously important to the occurrence of these chemicals at distant locations. There is much information to support the presence of agricultural pesticides at distant sites and as global pollutants (1). As discussed by Wania and Mackay, interactions at surfaces become a critical variable in determining the ultimate behavior of these compounds. Particularly important to the environmental fate of these compounds are the aqueous solubility, vapor pressure, solid-phase partitioning, and chemical persistence. Each of these factors is important to volatile release of pesticides from soil surfaces.

Volatile soil losses of pesticides have been measured for several pesticides in field situations. Losses varied from as low as 1.1% of soil-surface-applied simazine in 24 days to 90% of soil-surface-applied trifluralin lost in 6 days (2). Many factors appear to affect the magnitude of these losses. Important among these are the characteristics of the pesticides themselves, the modes of application (especially whether they are applied subsurface or at the surface), and surface soil moisture status. Jury and associates (3) specifically identified several of the

parameters important to the soil system that regulate volatility, especially temperature, properties of the chemical (solubility and Henry's law constant), soil moisture, and organic carbon content, and they also indicated the interactions that are important for them to affect volatile release within a modeling framework.

A detailed understanding of the complex behavior of localized micrometeorological processes is very difficult to achieve even when simple parameters such as water vapor and temperature are being measured. These studies become even more complex when volatile flux of pesticides is studied because of the analytical problems in obtaining adequate material for quantitative determinations of the compounds being emitted. Adequate sample collection times are typically >30 min, which may be long enough for the microclimate over the field to undergo several important changes; for example, consider intermittent cloud cover, where radiant heating can cause very rapid fluctuations in temperature. Therefore, it can become very difficult to verify and refine any model predictions that do not account for short time intervals. Most of the volatile flux measurement techniques are based upon upward flux rates calculated from gradients of vapor concentration of the pesticides that are measured in turbulent air flowing over treated fields. Newer methods involve adaptation of statistical methods (4), and these have helped to reduce the need for elaborate

* Address correspondence to this author at USDA, ANRI, EQL, Room 225, Bldg. 007, BARC-W, 10300 Baltimore Ave., Beltsville, MD 20705 [e-mail ricec@ba.ars.usda.gov; telephone (301) 504-6398; fax (301) 504-7976].

[†] U.S. Department of Agriculture.

[‡] U.S. Food and Drug Administration.

Table 1. Physical–Chemical Constants for Pesticides Applied in This Study

pesticide	subcooled liquid			
	vapor pressure, mPa	saturated vapor density, ^a mg/L	water solubility, mg/L	Henry's law constant, dimensionless
atrazine	1.3 (14)	1.1×10^{-4}	960 (14)	1.18×10^{-7} (14)
metolachlor	1.7 (14)	2.0×10^{-4}	530 (14)	3.21×10^{-6} (15)
chlorpyrifos	2.2 (14)	3.1×10^{-4}	0.44 (14)	1.30×10^{-4} (15)
trifluralin	9.8 (14)	1.3×10^{-3}	0.82 (14)	4.23×10^{-3} (15)
α -endosulfan	6.1 (16)	1.0×10^{-3}	3.7 (17)	2.72×10^{-3} (15)
β -endosulfan	3.2 (16)	4.9×10^{-4}	21 (17)	3.60×10^{-4} (15)

^a Calculated as vapor density = $PM/(RT)$, where P = vapor pressure, M = molecular weight, R = gas constant, and T = temperature in Kelvin (10).

instrumentation and extensive analytical support that tend to limit the performance of these types of flux determinations. Comparative studies of the various sampling methodologies, particularly aerodynamic versus theoretical profile shape (TPS) methods, demonstrated the utility of the TPS method and established it as a reliable method for monitoring volatile pesticide fluxes. The TPS method offers several advantages over the more classical aerodynamic methods in that it allows measurement of pesticide concentrations in the air to be made at only one height above a field, whereas the other methods require measurement of air concentrations at several heights, more meteorological monitoring, and larger treatment areas (4). Several authors have successfully used the TPS method (5–7). The aerodynamic method continues to be the more popular, however, and several references to it can be found in the literature (8–12).

The purpose of this study was to employ the TPS method to measure the volatile release of pesticides from freshly tilled soil with the view of correlating the release with environmental parameters. Five pesticides were applied: trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine]; atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine]; metolachlor [2-chloro-*N*-(2-ethyl-6'-ethyl-*N*-(2-methoxy-1-methyl-ethyl)acetamide)]; chlorpyrifos (phosphorothioic acid *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) ester]; and endosulfan (a 70:30 mixture of α - plus β -endosulfan) (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dimethanol cyclic sulfite). Their fluxes were studied over the course of 20 days. Inclusion of metolachlor and endosulfan was intended to provide data for these less studied chemicals and to allow comparisons with other chemicals on this list of compounds for which several field volatility studies were available (13).

EXPERIMENTAL PROCEDURES

The study was conducted at the Beltsville Agricultural Research Center, Beltsville, MD. The experimental site is situated on the southern corner of the Center's North Farm on a section of active farmland that is free of any overhead obstructions within 100 m of the test site. Within this 100 m unobstructed zone, there was a grassy strip on the west of the treated plot and fallow soil extended over the remainder. Part of the field had remained fallow for 3 years prior to this study. The soil was of the Mattapex series, Mattapex silt loam (fine-silty, mixed, mesic Aquic Hapludults). A 0.2-ha-square field was mold board plowed and disked 2 weeks prior to pesticide application. For the purpose of determining the roughness height of the plot, the micrometeorological conditions above the plot were determined over the next 2 weeks. Just prior to spraying, the field was disked plowed one final time and a final roughness height determination was carried out overnight.

The pesticides were applied on the circular plot with a diameter of 40 m. Spraying with the pesticides occurred between 10:00 and 11:00 a.m. on May 16, 1995. Nominal application rates for the respective pesticides were as follows: 5 lb of active ingredient (AI)/acre (5.6 kg/ha) of atrazine "Nine-O", metolachlor "Dual 8E", and chlorpyrifos

"Dragon"; and 1 lb of AI/acre (1.12 kg/ha) of trifluralin "Treflan 4EC" and endosulfan "Thiodan". Under normal soil applications, both chlorpyrifos and trifluralin are often soil incorporated. The levels were selected to be close to recommended amounts. Actually, 2.5 lb of AI/acre rather than 5 lb of AI/acre is more typical for atrazine, metolachlor, and chlorpyrifos; however, these levels were predetermined to produce analytical extracts with levels of the six pesticides that could all be analyzed simultaneously by electron capture gas chromatography. Some of the important physicochemical properties of the pesticides are listed in Table 1.

Theoretical Profile Shape Method. To determine the volatilization rates of pesticide from the soil surface, the TPS method of Wilson et al. (18) was used. In this method, volatilization rates are calculated from measured pesticide concentrations in the air and wind speed at the center of a circular plot at a height, Z_{inst} , at which the ratio of the horizontal flux to the vertical flux from the ground is minimally affected by atmospheric stability. Z_{inst} is a function of surface roughness and the diameter of the circular plot. Surface roughness is the theoretical height above the surface at which the logarithmically changing wind speed extrapolates to zero at times when air temperature does not change with height. The surface roughness was estimated from wind profiles measured during periods of atmospheric neutrality. Wind speeds were measured with rotating-cup anemometers (C. W. Thornthwaite Associates, Pittsgrove, NJ) at heights of 20, 40, 80, and 160 cm for several days. Air temperatures were measured simultaneously using shielded temperature sensors at heights of 40 and 100 cm. Using these measurements the Z_{inst} height was calculated to be 0.8 m for our plot, which is the value used in our flux calculations. Wilson (18) also provided information on how roughness height relates to the radius for the sampling plot in order to calculate an error for the accuracy of the TPS method. Applying Wilson's method to our plot produced an error value of 4.1%, which can affect source concentration determination (see ref 18).

Air Sampling. Sampling of the air for pesticide residues was accomplished by drawing known volumes of air through polyurethane foam (PUF) plugs, 4 cm diameter \times 4 cm long. The plugs were held in a Teflon tube through which air was drawn using a vacuum pump. Flows were determined using a Gilmont no. 5 rotameter (Cole-Parmer Instrument Co., Chicago, IL), which was calibrated using a bulk gas flow meter. After exposure, the plugs were returned to their sample jars and kept frozen until analysis. Storage losses were monitored by placing spiked foam plugs in the freezer; these were removed and extracted along with the samples. All of the recoveries in these storage control spikes were acceptable (i.e., >95% of the method spike results).

Pesticides were recovered from the plugs by Soxhlet extraction for 8 h with 1:1 (hexane/acetone). All solvents were of residue grade quality. The extracts were concentrated in Kuderna Danish evaporative concentrators to 5 mL and saved in amber bottles. These extracts were typically analyzed directly without dilution or concentration by capillary gas chromatography using an electron capture detector. The analytical instrument was a Hewlett-Packard 5890 series 2 gas chromatograph (Hewlett-Packard Co., Avondale, PA) equipped with a split inlet, 30-m fused silica SP-608 capillary column with a 0.25-mm i.d. and a 0.25- μ film thickness (Supelco Inc. Bellefonte, PA), and an electron capture detector (ECD). The routine GC program was as follows: injector, 270 °C; detector, 300 °C; splitless mode with a 1 min delay; 1 μ L was

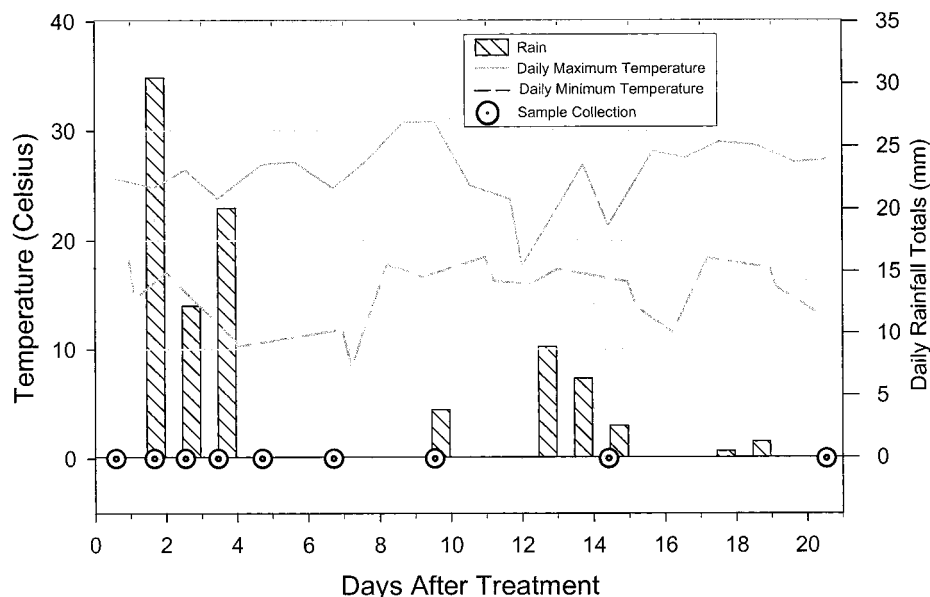


Figure 1. Precipitation events, minimum/maximum temperatures, and sampling times over the 21-day experimental period.

injected into the column at an initial temperature of 120 °C, 2-min hold, then programmed at 3 °C/min to 200 °C, held for 10 min, then programmed at 2 °C/min to 250 °C, and held for 20 min, which made the total run time 83 min. Helium gas was used as the carrier gas at 16 psi initial (~1 mL/min) pressure for 32 min, and then it was decreased at 5 psi/min to a final pressure of 5 psi, which was held for 10 min. The pressure was increased again at 2 psi/min to 16 psi in order to separate metolachlor and chlorpyrifos from each other. Argon methane was used as makeup gas at 31 psi (30 mL/min) for the electron capture mode of operation. The electron capture detector was used for all analytes except when atrazine concentrations fell below the lowest detectable atrazine standard of 0.2 ng/ μ L. With these samples, the extracts were analyzed using the gas chromatograph equipped with a nitrogen–phosphorus (N–P) detector, which had a lower detection range, that is, 0.026 ng/ μ L. Similar column conditions and operating temperatures were employed as discussed with the ECD analyses. The other pesticide lowest detection ranges were as follows: metolachlor, 0.03 ng/ μ L; chlorpyrifos, 0.05 ng/ μ L; trifluralin, α -endosulfan, and β -endosulfan were all detected down to 0.005 ng/ μ L. Mass spectrometer confirmations were carried out on 10% of the samples using a Hewlett-Packard model 5970 GC-MS that was operated in EI mode for atrazine and metolachlor and in NCI mode for trifluralin, α -endosulfan, and β -endosulfan. All initial identifications were found to be correct. The GC column utilized for the mass spectrometer studies was a 30 m long \times 0.25 mm i.d. DB-5MS (J&W Scientific, Folsom, CA) column.

Recovery tests using the PUF sampling system were performed before the experiment was begun and demonstrated that >95% of spiked materials were recovered (with the exception of trifluralin, which consistently averaged 66%) over the range of flows that were used in the study (i.e., 0.33–3.34 m³/h). The range of air volumes sampled was 0.39–10.93 m³ except for the overnight runs, which averaged 21.9 m³. Breakthrough from the front to the back plug was monitored for these higher volumes and never exceeded 5%. Correction of the analytical results for recovery was applied to the trifluralin data, but no corrections were made for the other pesticides.

Soil Samples. Soil samples were collected during the afternoon of each day that air samples were collected. At each sampling period, three triplicate sets of soil plugs (7 cm diameter \times 8 cm deep) were removed and mixed in a ceramic bowl. From each of these composites ~300 g of soil were placed in Teflon-capped jars and labeled for return to the laboratory for processing. Here they were refrigerated at 5 °C and extracted within 2 weeks of collection. Care was taken to secure these samples from each of three equally sized sectors on the outer edge of the circular plot edge in a manner that progressed in a clockwise fashion to ensure that each collection was made from an undisturbed segment of the ring. This procedure was followed so that the results

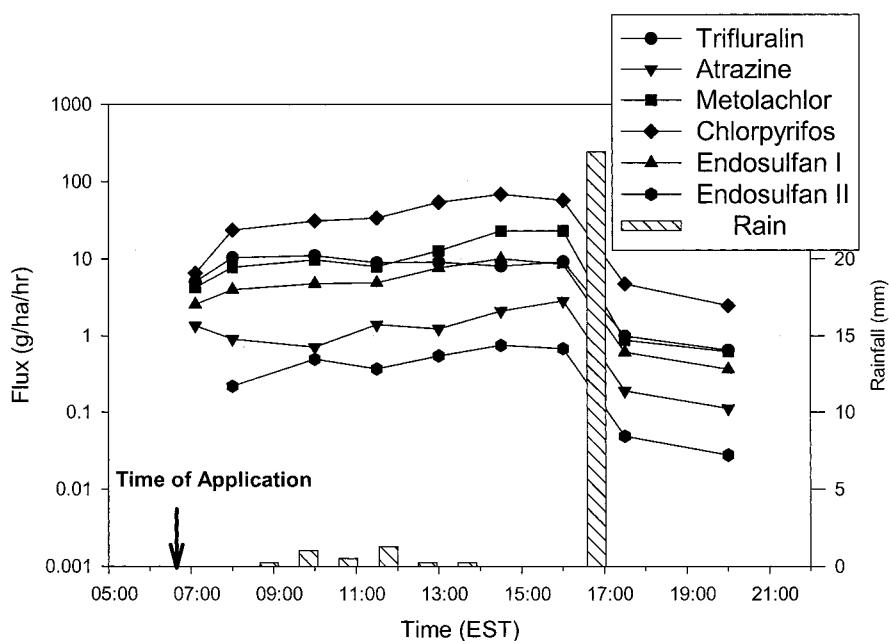
from the three samples could finally be averaged and represent the 0–8 cm soil conditions for the entire plot. Portions of each of the triplicate samples were prepared either for organic matter determination, percent moisture measurement, or pesticide residue analysis. pH was also measured on the fresh soil samples. The pesticides were removed from the soils by extraction via the pulsed-sonication method of the U.S. EPA, Pesticides in Soils and Sludge, SW846-8060 (19). Briefly, the method involves weighing out 30 g wet weight of soil, mixing with 1:1 [acetone/dichloromethane (DCM)], and sonicating. This process was repeated three times, and the mixtures were combined and filtered through a Büchner funnel. The extract volumes were reduced by rotovap and solvent exchanged to hexane. The extracts were directly analyzed for trifluralin by GC as described previously, and the remainder of the analytes were analyzed after Florisil cleanup to remove interferences. Trifluralin recoveries were poor after Florisil cleanup, so this step had to be avoided for this analyte. The Florisil method was adapted from the U.S. FDA (20) as follows. The solvent used to elute the analytes through the Florisil column was 6% ethyl ether/hexane. The columns were 200 mm long \times 10 mm i.d. glass columns packed with 120 mm of oven-activated Florisil. The samples were obtained in 200 mL of eluant, which was solvent exchanged to hexane using Kuderna Danish concentrator methods and adjusted in final volumes to bring the analytes into linear ranges of the appropriate standards, which were all run by ECD-GC. Spike recoveries were as follows: trifluralin (w/o cleaning), 91%; atrazine, 84%; metolachlor, 82%; chlorpyrifos, 92%; α -endosulfan, 106%; β -endosulfan, 97%. Dibutyl chlorindate surrogate recoveries, which were performed on every sample, were all acceptable, averaging >98%.

Organic carbon content of the soils was determined using a Leco model CNS-2000 instrument. The samples were dried and combusted for organic carbon determinations according to the manufacturer's instruction with the modification that AlO₃ was added to suppress splattering during combustion.

Micrometeorological Measurements. Throughout the study, wind speed profiles were measured at four heights, 0.2, 0.4, 0.8, and 1.6 m (this allowed continuous verification of the Zinst height throughout the experiment), and a weather station continuously monitored wind speed, direction, temperature, humidity, rain, radiation intensity, soil moisture (5 cm depth), and soil temperatures (just below the surface and surface temperature). All of the data output was collected by a data logger. Backup meteorological data were also collected by the USDA Farm Operations Manager, and these data were used for verification of our separate data. Figure 1 shows the temperatures and rainfall over the course of the experiment. Radiation measures were made using photosensors.

Table 2. Percentage of Nominal Application Lost to Volatility

days measured or estimated	trifluralin	atrazine	metolachlor	chlorpyrifos	α -endosulfan	β -endosulfan
first 5 days	12.5	2.12	3.85	8.18	9.08	2.07
estimated after 21 days	14.1	3.57	6.49	10.43	11.09	2.54

**Figure 2.** Volatile flux of pesticides on the first day after application, 7:00 a.m. to 8:00 p.m.

RESULTS AND DISCUSSION

Volatile Flux. Table 2 summarizes the overall flux losses for the first 5 days after treatment and for the full 21 days of the experiment. Trifluralin was lost in the greatest amount relative to that applied, 12.5% after 5 days and 14.1% after 21 days. Second to trifluralin for volatile flux losses was α -endosulfan, of which 9% of the nominal applied amount was lost after 5 days and 11% after the 21 days. The flux losses for atrazine and chlorpyrifos can be compared to flux determination carried out for these compounds by Whang et al. (6). Whang's first 4-day flux values for these two compounds were, respectively, 0.7 and 7% for atrazine and chlorpyrifos, and for the last day of their experiment (26 days after treatment) they found 1.9 and 12% flux losses versus their nominal application amounts. Our values for volatile losses for the two compounds went from 2.1% of nominal application for atrazine on day 5 to 3.6% on day 21 and the respective amounts for chlorpyrifos in this study were 8.2–10.4%. Thus, our relative fluxes were similar to those of Whang et al. (6); however, the total amounts were higher. The higher fluxes observed here could represent the higher overall temperature experienced in our study versus the Whang study. In general, our flux losses appear to fall in line with the values summarized by Taylor and Gloflety (2) when the surface-applied and freshly tilled data are singled out. For example, they reported data for loss of atrazine from fallow silt loam of 2.4% in 24 days and trifluralin losses of 50% in 7.5 h for moist fallow silt loam. Alachlor, an acetanilide class of herbicide like metolachlor, was reported to volatilize to 26% of the applied amount in 24 days when applied to fallow silt loam, and Prueger et al. (8) determined that 6% of banded applications of metolachlor was lost through volatilization and 22% was lost when broadcast applied.

The greatest losses due to volatile flux of all of the pesticides occurred either during the remaining part of the day of

application (day 0) (atrazine) or the day immediately following application, day 1 (all of the other chemicals). On the day following application, it rained at 5:00 p.m. This rain appears to have abruptly stopped the flux that was taking place at that time (Figure 2). The typical shape should have been a more rounded drop off as was observed on days without rain and which were observed by Whang et al. (6) in their volatility studies. A volatility flux for day 4 was much reduced compared with the losses observed immediately after treatment, day 0, and on day 1. This trend was also observed by Whang et al. (6) for their conventionally tilled plots. Daily fluxes for the other sampled days were similar in appearance to that observed for day 4; however, the amounts steadily declined. Overnight sampling indicated that there were not appreciable volatile losses occurring overnight and that the process was largely driven by increasing temperatures during the daytime and the atmospheric instability that accompanies the increases in solar radiation at that time. Atmospheric instability, especially in the surface boundary layer, generally implies that the air mass is well mixed. This creates a concentration gradient between the high concentration at the soil surface and the near zero concentrations in the overlying air. Typical flux patterns from moist soil have been described as a log disappearance process, that is, daily flux profiles that increase after sunrise to a maximum at early afternoon and then decline by sunset. However, marked deviations from this pattern have also been demonstrated from several field studies where this affect appears to be linked to soil moisture. In these cases there is often a diurnal curve, where the highest rates are observed in the morning and evening. Taylor (13) explained that the increases in evening fluxes are due to moistening of the soil surface by dew formation, which persists through the night until it is evaporated after sunrise. As pointed out by Gloflety et al. (10) the soil moisture state is also related to the soil type, because sandy soils will dry more

Table 3. Moisture Content of Surface Soil (0–8-cm Depth) as Percentage of Dry Weight

day	moisture content		organic carbon content	
	av, %	RSD ^a	av, %	RSD
0	14.91	0.081	1.09	0.088
1	18.32	0.102	1.15	0.118
2	21.53	0.193	0.98	0.190
3	23.19	0.230	1.09	0.250
4	20.00	0.173	0.87	0.151
6	16.27	0.198	0.81	0.160
9	12.62	0.022	0.80	0.018
14	16.80	0.202	1.03	0.209
20	11.32	0.144	0.92	0.132

^aRSD, relative standard deviation of three replicates.

quickly than silt loam soils that were compared in their study. This drying phenomenon did not appear to impact the flux profiles observed in this study or that of Whang et al. (6), which appears to be most comparable to this study. Naturally, the top few millimeters of soil at the surface can dry and cut off volatility; however, with the deeper soil moistures typically > 15% as were observed in this study (Table 3), the underlying water appears to slowly rewet the surface and prevent complete cessation of volatile release. Majewski et al. (21) described a study in which they observed sufficient drying of the soil surface to see reductions in volatile losses of trifluralin and triallate. Their soil surface conditions were such that the 0–2.5-cm layer of the surface had moisture levels < 15% 6 h after treatment, and the moisture level did not increase again until after a rain event 4 days later; at this point rapid volatile release of the chemicals started again.

Plots of the volatile losses as a percentage of the nominally applied pesticides (Figure 3) depict loss curves that are similar to those offered by Whang et al. (6). The difference between Whang's results and our study is that here there was an initial increase in volatile flux on the day following application and then a much more rapid decline in flux than observed by Whang and associates. They carried out their study earlier in the year, and the more gradual losses observed by them may have been due to the generally lower temperature fluctuations that they observed over the day–night cycles. Another way of looking at the loss curve was to consider the specific volatility

(percentage volatilized based on that remaining at each sampling time). In this case the slope for decrease in volatile loss was actually lower than observed by Whang and associates. This suggests that the apparent rapid decline in volatile losses observed here could be explained by leaching into the soil surface caused by the high rainfall that was experienced during the early few days of our study. From a comparison of the rates of loss for the two isomers of endosulfan (Figure 3), it appears that β -endosulfan was lost more slowly than α -endosulfan. There is evidence from studies of the volatile release of these two isomers from water that β -endosulfan converts to α -endosulfan during the actual water to air transfer process (15). Thus, there was a higher relative amount of α -endosulfan observed over the treated plot than of β -endosulfan starting on the third day, and the differences became even greater as the experiment progressed.

Soil Loss Results. A summary of the soil residue data is contained in Table 4. Comparing the residue data for the respective pesticides with the nominal concentrations on day 0 indicates that the recoveries were generally higher than predicted except for trifluralin, for which the measured amount was 69% of the expected level. The respective percent recoveries of nominal applied values for the other pesticides were 102% atrazine, 103% metolachlor, 112% chlorpyrifos, and 109% for total endosulfan (104% α -endosulfan and 120% for β -endosulfan). These results were adjusted for moisture fluctuations over the course of the experiment (Table 3) and also for bulk density changes, assuming that the initial bulk density was low due to recent tillage and that it increased through the course of the experiment, especially due to the onset of several periods of rain early in the study.

There are two possible explanations for the lower apparent amounts of trifluralin recovered from the soil. One is the high vapor pressure for trifluralin, 9.8 mPa (Table 1), and thence its high volatility, which could have accounted for significant losses during application, and, second, is the compound's susceptibility to photolytic breakdown [$t_{1/2}$ of 9 h in water (22)]. Unaccounted losses were also observed by Majewski et al. (21), which they ascribed to possible vapor-phase photolysis losses. These two factors may also account for the low but consistent recoveries (62%) that were observed for the polyurethane foam spike

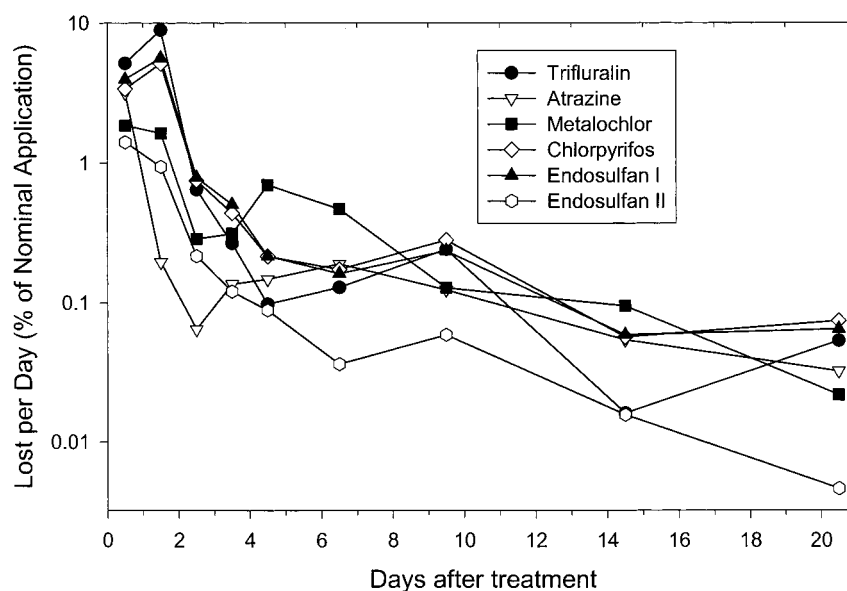
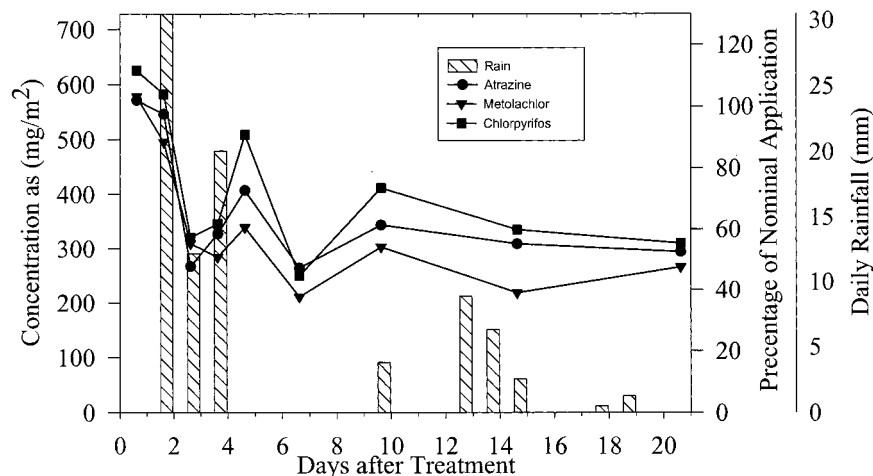


Figure 3. Progressive loss of pesticides from a field treated with five pesticides, presented as a percentage of the nominal amounts applied.

Table 4. Initial Soil Residues, Regression Coefficients of Their Disappearance, Correlation Coefficient for First-Order Curve Fit, and Average Daily Percentage Disappearance of Trifluralin, Atrazine, Metolachlor, Chlorpyrifos, α -Endosulfan, and β -Endosulfan from Freshly Tilled Soil

	trifluralin	atrazine	metolachlor	chlorpyrifos	α -endosulfan	β -endosulfan
nominal amount (mg/m ²)	112	560	560	560	78.4	33.6
measured amount (expressed as mg/m ²)	77.1	571	578	625	81.6	40.3
% of nominal	69	102	103	112	104	120
Computed Loss Rates ^a						
soil first-order loss coefficient	0.051	0.055	0.060	0.049	0.038	0.026
correlation coefficient	-0.57	-0.32	-0.51	-0.52	-0.60	-0.76
Average Percent Daily Disappearance ^b						
av measured % daily disappearance (first 10 days)	5.90	4.65	5.77	4.69	4.77	3.98
calcd av % daily disappearance, first 10 days	6.91	7.17	7.51	6.76	5.83	4.50

^a Based on the equation $\log C/C_0 = -bt$, where t is time in days. ^b Based on losses calculated from average percent loss after the first 10 days.

**Figure 4.** Loss of pesticides (atrazine, metolachlor, and chlorpyrifos) from soil over the 21-day monitoring period, compared against rain events.

experiments. Vapor-phase photolysis has been studied by Woodrow et al. (23), and half-lives of 20 min were measured.

The time course of the soil residue losses is shown graphically in **Figures 4** and **5**. The rates of disappearance were each typical of an exponential loss process (6, 21); however, there were some consistent and apparently anomalous dips in concentration at sampling days 2, 3, and 6. These appear to coincide with occurrences of rain on these days. A possible explanation for these apparent losses and then recoveries back into the sampled 0–8 cm surface layer of the sampled soil plugs was that the surface-applied chemicals were leached below the sampling depth and then migrated back up into the surface layer when surface evaporation started after the rain event [i.e., the “wick effect” (13)]. Some deeper cores were collected on days 6 and 14. An average of 12–17% of the above layer amounts was measured in these deeper samples, which supports the likelihood that leaching to deeper depths was occurring. An important objective of this study was to assess the availability for volatilization of the surface-applied pesticides and not attempt to account for all of the loss processes such as subsurface leaching. The equation $\log C/C_0 = -bt$, where C is the final concentration, C_0 is the initial concentration, b is the rate coefficient, and t is the time in days, was used to produce computed loss rates and provide their correlation coefficients that are shown in **Table 4**. Generally, the data fits were rather poor, that is, <0.60 for all of the pesticides except for β -endosulfan. One possible explanation for the poor fit of the data was that surface concentrations were being lost to subsurface percolation (this will be discussed more later). The rate coefficients (regression coefficients) describing the loss for atrazine and chlorpyrifos were higher than those reported by

Whang et al. (6), that is, 0.055 versus Whang’s 0.012 for atrazine. Our value of 0.049 for chlorpyrifos was also higher than Whang’s value of 0.015. Our coefficient for trifluralin was 0.051, whereas the value from Majewski et al. (21) for their soil was 0.10, yielding a much shorter half-life value of 7.7 days versus a calculated half-life of 13.5 days for this study. The slower losses of trifluralin observed in this study could be due to the fact that the advent of rain drew the material too deeply into the soil and also made it less available to volatilize as compared to what was observed by Majewski et al. (21). The higher soil losses observed in our data versus Whang’s results could reflect the warmer daytime temperatures in our study. These higher temperatures would support more rapid degradation processes than were experienced by Whang et al. (6). The average maximum high air temperatures in the Whang study were generally <20 °C for the first 10 days after treatment, whereas our maximum air temperature were generally ≥ 25 °C during this period.

From an examination of the effect of rain on the observed soil pesticide levels, there appears to be a direct relationship between the measured levels of the pesticides and the first three rain events that occurred over days 1, 2, and 3 of our study. The rain that started at 5:00 p.m., 27 mm of rain, on the first full day after application (**Figure 4**) appears to have initiated a steep drop in the amount of all of the residues that were recovered in the collected 0–8-cm soil cores. Then on the second day it rained again between 2:00 and 3:00 p.m., 11.4 mm of rain, and finally it rained again from 12:00 midnight until 5:00 a.m. of the next day. During this second rainy period the soil residues continued to decline (trifluralin and metolachlor) or rose slightly (atrazine, chlorpyrifos, and total

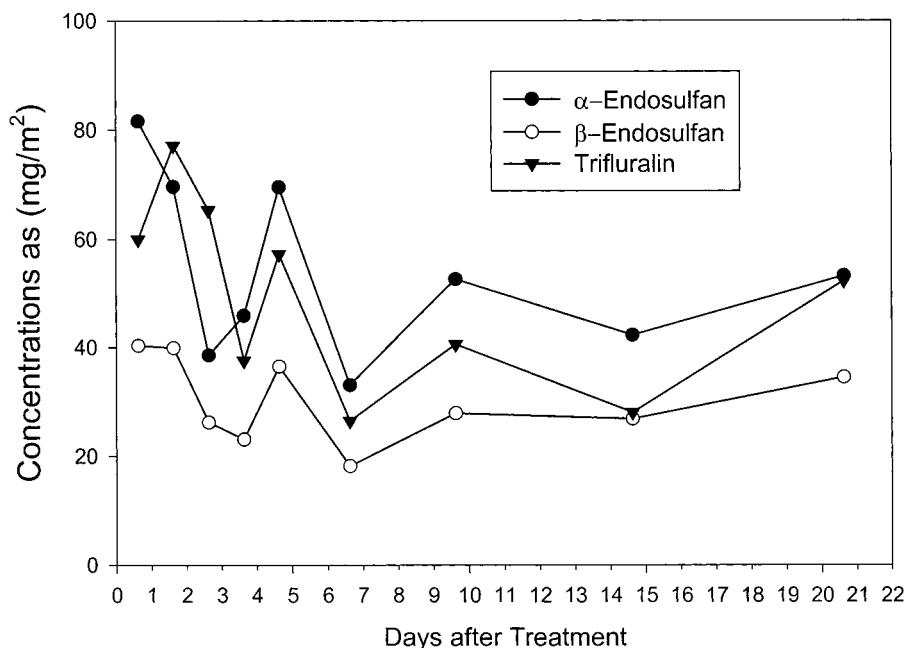


Figure 5. Soil residue losses of α - and β -endosulfan and trifluralin over the 21-day monitoring period.

endosulfan). Once this stint of rain ended, it was apparent that all of the pesticides began to increase in the 0–8-cm layer of soil; thus, they all appeared to be drawn toward the surface as the “wick” effect took place. The second dip in all of the residue levels that occurred from day 4 until day 6 (Figures 4 and 5) does not appear to have any leaching-induced connection and may just represent natural variations in sampling differences or the fact that volatile releases picked up again on the fourth day. For metolachlor and atrazine, there was an increase in volatile flux on days 4 and 6 versus day 3 (Figure 3). The increase in daily fluxes was 40–60% higher for these two pesticides on these days versus the third day. Such increases in volatile flux, however, could not account for the increased soil losses after day 4 that were observed for chlorpyrifos, trifluralin, and endosulfan; therefore, some unknown processes other than increased volatility appear to be responsible here. It also could be possible that there was a significant flux of all of these compounds on day 5; however, this cannot be verified because flux samples were not collected on this day. Another possibility would be rapid degradation, but there is no reason to expect that this would be any more rapid over this period than at any other time. Irreversible binding has also been documented for some soil-applied chemicals (24). Regardless, there is too much scatter in the data to ascribe any real significance to the small loss differences that appeared over this period. It is true that there was a great deal of variability in the data because the relative standard deviations of the mean soil values presented in Table 3 and Figures 4 and 5 all were very high, typically exceeding 0.5 for the three samples that were averaged at each time period. The variability was especially high for the samples collected on day 6 (Figure 6). Once again, from this figure it is clear that there was a large deviation of the data from the exponential regression plots for the soil residues collected on days 2, 3, and 6. This plot for metolachlor is representative of what occurred with all of the pesticides and indicates that something unusual was causing this.

The soil residue losses for trifluralin and α - and β -endosulfan are shown in Figure 5. The two pesticides appear to behave similarly, except for a lower initial level of trifluralin and the fact that the level of trifluralin increased 1 day after application; this increase, however, was not statistically significant from the

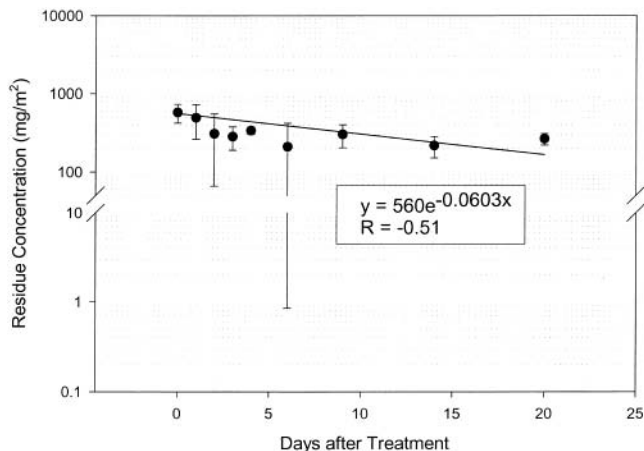


Figure 6. Soil residue losses of metolachlor expressed as an exponential loss curve.

initial value. Both endosulfan isomers and trifluralin increased slightly in amount from day 14 to day 20, which was also observed for atrazine; this may be due again to expression of the wick effect, because some reversal in transport back into the sampled zone may have occurred after the rain events that occurred on the 13th through 14th days following application.

The soil loss of both α -endosulfan and β -endosulfan (Figure 5) behaved similarly except for the last three sampling times. It appears that α -endosulfan was being lost in greater amounts than β -endosulfan. This may have some connection to the fact that α -endosulfan is more volatile than β -endosulfan and therefore is lost more readily. Furthermore, β -endosulfan is 5.7 times more soluble than α -endosulfan (Table 1) and should have been more susceptible to movement into and out of the active surface zone due to the wick effect. The combination of these features could possibly explain the divergence in the percentage of nominal amounts of the two isomers of endosulfan that were observed on the last day of the experiment; however, it should be recognized that these differences are small and not statistically supportable.

Comparison of Volatility versus Soil Loss. Table 5 summarizes the soil reduction and the volatile flux information

Table 5. Total Soil Residue Loss and Fraction of This That Was Measured as Volatile Flux

source of loss	trifluralin	atrazine	metolachlor	chlorpyrifos	α -endosulfan	β -endosulfan
total soil residue loss, mg/m ²	59.74	266	294	251	25.0	5.88
soil loss as % of nominal application amount	53.3	46.5	50.9	40.0	30.9	14.6 ^a
residue loss accounted for by volatilization, %	26.5	7.5	12.4	23.3	34.5	14.5 ^a

^a Calculated from the actual amount lost, not nominal loss as indicated by row heading (necessary because nominal amount was 0% lower than measured value at time zero).

together and presents the data as the proportion of the soil loss that can be ascribed to volatility. These data show that although trifluralin was still lost in highest amounts (26.5% of the total soil loss), the relative importance of volatility to the measured soil losses of chlorpyrifos and α -endosulfan also became more important when viewed this way. Of the total loss accounted for in the soil, volatile flux of metolachlor accounts for 12.4% and atrazine, 7.5%. The percentage of β -endosulfan loss that was measured as volatile flux was calculated differently from the other pesticides that are presented in **Table 5**, that is, loss relative to nominal amount applied. α -Endosulfan flux was >4 times higher than β -endosulfan and represented a higher percentage of the soil loss of the total endosulfan, even higher than the percentage composition that α -endosulfan constitutes of the technical mixture (70:30 α -/ β -endosulfan). This further supports the fact that the volatility of β -endosulfan is less than that of α -endosulfan.

The relative volatility values were close to those reported by Whang et al. (6) for freshly tilled soil in their experiment. Whang's values were 23% for chlorpyrifos and 4.4% atrazine, and the respective values here were 23.3 and 7.5%. Majewski et al. (21) found the loss of trifluralin from a fallow soil surface application to range from 61 to 70% of the soil-monitored losses during the first 5 days of their experiment. These are much higher than observed here; however, they experienced no rain until 3 days after application, which may have kept the trifluralin in more immediate contact with the air for greater flux removal. Their soil type was Dalhousie clay; and this may also have caused them to observe higher volatile losses. Others have reported higher volatile losses of trifluralin than observed in this experiment (2).

Conclusions. The approach used here was to attempt to minimize environmental variables as much as possible in the study of the volatile flux of a series of pesticides. This was successfully accomplished by simplifying the soil interactions and studying some "model compounds" such as atrazine and trifluralin to be compared with the less studied compounds, metolachlor, chlorpyrifos, and endosulfan. The soil factors were minimized by application of the pesticides to freshly tilled soil that was characterized by soil moisture and soil organic matter content. Environmental factors were carefully monitored to relate as many variables as possible to the observed flux behavior. The TPS method proved to be very appropriate for the study. The results for the model compounds agreed well with published findings. Many of the properties required as variables in the Jury model were determined in this study. Field-observed flux values were produced for metolachlor and for the two isomers of endosulfan, α -endosulfan and β -endosulfan. This was one of the first detailed field studies of the volatile flux of these compounds. The data for the model compounds, atrazine, chlorpyrifos, and trifluralin, validated other studies carried out on these compounds and also provided further evidence for the important role that event-based meteorological conditions (especially rainfall and temperature) and soil condition (type and moisture status) play in effecting the volatile releases of

semivolatile organic compounds. The data further support the need to establish generalized methods to gauge critical factors impacting conditions that prevail during the earliest periods after spray applications. The need exists to characterize these factors as boundary conditions in modeling the combined impact of initial volatile fluxes of pesticides. The range of possibilities is great, but generally the process should lend itself to parametrizing over large land masses on a first-cut basis.

LITERATURE CITED

- (1) Wania, F.; Mackay, D. Tracking the Distribution of Persistent Organic Pollutants. *Environ. Sci. Technol.* **1996**, *30*, 390A–401A.
- (2) Taylor, A. W.; Glotfelty, D. E. Evaporation From Soils and Crops. In *Environmental Chemistry of Herbicides*; Grover, R., Ed.; CRC Press: Boca Raton, FL, 1988; pp 89–129.
- (3) Jury, W. A.; Spencer, W. F.; Farmer, W. J. Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity. *J. Environ. Qual.* **1984**, *13*, 567–572.
- (4) Majewski, M. S.; Glotfelty, D. E.; Paw, U. K. T.; Seiber, J. N. A Field Comparison of Several Methods for Measuring Pesticide Evaporation Rates from Soil. *Environ. Sci. Technol.* **1990**, *24*, 1490–1497.
- (5) Jenkins, J. J.; Cooper, R. J.; Curtis, A. S. Comparison of pendimethalin airborne and dislodgeable residues following application to turfgrass. In *Long Range Transport of Pesticides*; Kurtz, D. A. E., Ed.; Lewis Publishers: Chelsea, MI, 1990.
- (6) Whang, J. M.; Schomburg, C. J.; Glotfelty, D. E.; Taylor, A. W. Volatilization of fonofos, chlorpyrifos, and Atrazine from conventional and no-till surface soils in the field. *J. Environ. Qual.* **1993**, *22*, 173–180.
- (7) Majewski, M.; Glotfelty, D. E.; Seiber, J. N. A comparison of the Aerodynamic and the Theoretical-Profile-Shape methods for measuring pesticide evaporation from soil. *Atmos. Environ.* **1989**, *23*, 929–938.
- (8) Prueger, J. H.; Hatfield, J. L.; Sauer, T. J. Field-scale metolachlor volatilization flux estimates from broadcast and banded application methods in central Iowa. *J. Environ. Qual.* **1999**, *28*, 75–81.
- (9) Majewski, M. S.; McChesney, M. M.; Woodrow, J. E.; Prueger, J. H.; Seiber, J. N. Organic chemicals in the environment. *J. Environ. Qual.* **1995**, *24*, 742–752.
- (10) Glotfelty, D. W.; Taylor, A. W.; Turner, B. J.; Zoller, W. H. Volatilization of Surface-Applied Pesticides from Fallow Soil. *J. Agric. Food Chem.* **1984**, *32*, 638–643.
- (11) Ross, L. J.; Johnson, B.; Kim, K. D.; Hsu, J. Prediction of methyl bromide flux from area sources using the ISCST Model. *J. Environ. Qual.* **1996**, *25*, 885–891.
- (12) Yates, S. R.; Gan, J.; Ernst, F.; Mutziger, A.; Yates, M. V. Methyl bromide emissions from a covered field: I. Experimental conditions and degradation in soil. *J. Environ. Qual.* **1996**, *25*, 184–192.
- (13) Taylor, A. W. The Volatilization of Pesticide Residues. In *Environmental Behaviour of Agrochemicals*; Roberts, T. R., Kearney, P. C., Eds.; Wiley: London, U.K., 1995; Chapter 6, pp 257–306.
- (14) Majewski, M. S.; Capel, P. D. *Pesticides in the Atmosphere*; Ann Arbor Press: Chelsea, MI, 1995.

- (15) Rice, C. P.; Chernyak, S. M.; Hapeman, C. H.; Bilboulia, S. Air–Water Distribution of the Endosulfan Isomers. *J. Environ. Qual.* **1997**, *26*, 1101–1106.
- (16) Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T. Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data. *J. Chem. Eng. Data* **1990**, *35*, 232–237.
- (17) Cotham, W. E.; Bidleman, T. F. Laboratory investigation of the partitioning of organochlorine compounds between the gas phase and atmospheric aerosols on glass fiber filters. *Environ. Sci. Technol.* **1992**, *26*, 469–477.
- (18) Wilson, J. D.; Turtell, G. W.; Kidd, G. E.; Beuchamp, E. G. Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere. *Atmos. Environ.* **1982**, *16*, 1861–1867.
- (19) U.S. EPA. *Replacement Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd ed.; U.S. GPO: Washington, DC, 1992.
- (20) U.S. Food and Drug Administration. *Pesticide Analytical Manual*; U.S. GPO: Washington, DC, 1989; Vol. I.
- (21) Majewski, M.; Desjardins, R.; Rochette, P.; Pattey, E.; Seiber, J.; Glotfelty, D. Field Comparison of an Eddy Accumulation and an Aerodynamic-Gradient System for Measuring Pesticide Volatilization Fluxes. *Environ. Sci. Technol.* **1993**, *27*, 121–128.
- (22) Wauchope, R. D.; Butler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W. M.; Burt, J. P. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1–164.
- (23) Woodrow, J. E.; Crosby, D. G.; Mast, T.; Moilanen, K. W.; Seiber, J. Rates of Transformation of Trifluralin and Parathion Vapors in Air. *J. Agric. Food Chem.* **1978**, *26*, 1312–1316.
- (24) Mersie, W.; Liu, J.; Seybold, C.; Tierney, D. Extractability and degradation of atrazine in a submerged sediment. *Weed Sci.* **1998**, *46*, 480–486.

Received for review November 29, 2001. Revised manuscript received April 18, 2002. Accepted April 19, 2002. This work was funded in part by an interagency agreement from the U.S. EPA, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park (Contract DW 12936572).

JF011571T