

Volatilization and Wind Erosion of Soil Surface Applied Atrazine, Simazine, Alachlor, and Toxaphene

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The vertical fluxes of alachlor, atrazine, simazine, and toxaphene were measured by air-sampling and aerodynamic measurements over a 24-day period after surface application to a fallow soil in eastern Maryland. The triazines were applied at 1.68 kg/ha as a wettable powder formulation and alachlor and toxaphene at 2.24 and 2.52 kg/ha, respectively, as emulsifiable concentrates. Calculated volatilization losses in the first 21 days were 780 g/ha toxaphene, 420 g/ha alachlor, 40 g/ha atrazine, and 21 g/ha simazine. Daily losses varied with soil moisture content, alachlor and toxaphene volatilization being reduced as the surface soil layers became dry. Daily volatilization patterns of atrazine and simazine indicated that some wind erosion of wettable powder formulation occurred as the surface soil dried, but the amounts transported were small. Volatilization losses of triazines were much smaller than disappearance by chemical degradation. A simple empirical equation was shown to yield estimated volatilization rates that were within about a factor of 10 of field-measured rates for six of eight compounds whose vapor pressures spanned a range of 10^4 .

Glotfelty et al. (1984) have described several field experiments in which the volatilization losses of a number of volatile, nonpolar pesticides were measured after their surface application to fallow soil. They concluded that volatilization rates of those compounds were very rapid from moist soil and that, as long as soil moisture was adequate, long-term losses were controlled by diffusion from the thin layer of soil penetrated by the spray. On the other hand, losses from dry soil were much slower and were controlled by the supply of moisture to the dry surface layer.

The rate of volatilization of pesticides from soil is controlled by a number of intrinsic factors that depend upon properties of the chemical and of the soil. Spencer (1970) showed that the vapor density of pesticides over soil is proportional to the concentration of pesticide in the soil solution and that the proportionality constant was equal to the ratio of pesticide vapor pressure to solubility. In other words, pesticides in the soil solution obeyed Henry's law. The concentration of pesticide in the soil solution is, in turn, a function of soil organic matter and moisture content, as described by the soil/water adsorption coefficient. Spencer therefore concluded that a knowledge of Henry's law coefficients and soil/water adsorption isotherms could be used to predict pesticide volatility from soil.

This concept has been embodied in an empirical rate expression developed by R. L. Swann and co-workers (Swann et al., 1982). In this approach, which is appropriate to soil surface applications, the volatilization rate constant (or specific volatilization rate, day^{-1}), K_v , is given by

$$K_v = Q(P/K_{oc}S) \quad (1)$$

where P = vapor pressure (mmHg), K_{oc} is the soil adsorption coefficient ($\mu\text{g g}^{-1}/\mu\text{g mL}^{-1}$, organic carbon basis), and S is the solubility ($\mu\text{g/mL}$). The empirically determined coefficient, Q , equals 4.4×10^7 .

Jury et al. (1983) proposed a more comprehensive screening model of pesticide volatility using these factors. They conclude that volatilization of compounds for which the nondimensional Henry's law coefficient is much less than 2.5×10^{-5} will be controlled by water evaporation and by vapor movement across the laminar layer at the soil/air boundary. This occurs because the rate of movement of these compounds to the soil surface with evaporating water exceeds their rate of volatilization from the surface. After a period of time, volatilization of these more soluble, less volatile, chemicals should become constant because they accumulate at the surface.

Our objective in the present study was to measure the postapplication losses of several compounds that were less volatile and more polar than had previously been studied in the field. The chemicals chosen, atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], simazine [2-chloro-4,6-bis(ethylamino)-s-triazine], and alachlor [2-chloro-2',6'-diethyl-*N*(methoxymethyl)acetanilide], are all herbicides widely used in corn production. Their Henry's law coefficients, as determined by vapor pressure and solubility, are all 1 order of magnitude or more smaller than the limit value given above. Although not of primary interest, we also included measurements of toxaphene (polychlorocamphene) losses, because, at the time of our study, it was also used extensively in corn production in Maryland. Its use has since been banned.

The volatilization rate of toxaphene from cotton canopies has been described (Willis et al., 1980, 1983; Seiber et al., 1979), but detailed field measurements of the volatilization losses of these four chemicals from soil surface residues have not been reported. We wanted to determine the factors controlling the losses of these compounds and compare the results to those of the earlier study. We also wanted to learn whether the models of pesticide volatility described above could adequately predict losses of these compounds in the field.

EXPERIMENTAL SECTION

Field Site and Pesticide Treatments. The experiment was conducted on a 40-ha field located at the Wye Research and Education Center of the University of Maryland, Queen Anne's County, MD. The site was representative of the coastal plain in that it was essentially flat, with Matapex silt loam soil (Aquic Hapludults) containing 1.5% organic matter. The field had been tilled previously,

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and corn was planted the day before pesticides were applied. The air-sampling and micrometeorological masts were located near the midpoint of the east-west axis, but somewhat north of the center of the field. The distance to the untreated boundary of the field was greater than 200 m in all directions.

On May 25, 1981, atrazine, simazine, alachlor, and toxaphene were applied together as a tank mixture by tractor-mounted sprayer. Atrazine and simazine were applied as wettable powder (WP) formulations at 1.68 kg of a.i./ha each, and alachlor and toxaphene, as emulsifiable concentrates at 2.24 and 2.52 kg of a.i./ha, respectively. At the time of application the soil was warm and very dry, with a south wind of 1.0–1.5 m/s. A small amount of drift was noted. Air-sampling operations began as soon as spraying was finished.

Air Samples. Air samples were taken on the day of application and on the 1st, 2nd, 4th, 9th, 10th, 17th, and 24th days thereafter with use of a sampling mast similar to that described earlier (Turner and Glotfelty, 1977). Air was drawn at about 3.5 m³/h, for periods up to 3 h, through 4.5-cm diameter × 5-cm depth plugs of porous polyurethane foam (PUF) contained in light-shielded sampling probes located at six heights above the soil surface: 20, 30, 50, 80, 120, and 190 cm. Exposed plugs were sealed in glass bottles with Teflon-lined caps and stored at 4 °C prior to analysis.

A similar mast at the same location was used to sample air through 4.2-cm glass fiber filters. The sampling heights and flow periods were the same as the PUF plugs, and flow rates were comparable. Exposed filters were placed in small glass vials with Teflon-lined screw caps and refrigerated prior to analysis.

The pesticides were recovered from the PUF plugs by 6-h Soxhlet extraction (30–40 cycles) using a 1:1 mixture of hexane and acetone. (All solvents were pesticide-residue quality from Burdick and Jackson, Inc.) The extracts were then concentrated to an appropriate volume on Kuderna-Danish evaporative concentrators. Toxaphene was present in sufficiently large quantities to be analyzed directly by gas chromatography as described below. However, Florisil PR column chromatographic cleanup was required prior to herbicide analysis.

After the toxaphene analyses were complete, a small amount of benzene was added and the extracts were evaporated to less than 10 mL. A 2.2-cm-i.d. chromatographic column was packed with 10 g of activated (130 °C overnight) Florisil PR (Floridin Co.). The adsorbent was topped with about 1.5 cm of anhydrous (400 °C overnight) Na₂SO₄. The column was wetted with benzene, and the samples, now in benzene, were applied to the top of the column with small benzene rinses. The elution was continued with benzene until 100 mL had been discarded. Atrazine, simazine, and alachlor were then eluted in one fraction with 150 mL of 5% acetone in benzene. After concentration to an appropriate volume, the herbicides were analyzed by gas chromatography as described below.

Pesticides were recovered from the glass fiber filters by adding 10 mL of 1:1 benzene-acetone to their small glass storage vials, shaking vigorously, and then letting the filters soak for 30 min with occasional shaking. The solvent was then decanted off and the extraction repeated twice more. The combined extracts were then concentrated to an appropriate volume and analyzed directly without further cleanup.

Pesticide Analyses. Alachlor, atrazine, and simazine in air samples were analyzed on a Tracor Model 560 gas chromatograph equipped with a nitrogen-specific Hall 700

A electrolytic conductivity detector. The herbicides were separated on a 1.83 m × 2 mm (i.d.) coiled glass column packed with 3% FFAP on 80–100 mesh Anakrom Q (Analabs, Inc.). Temperatures (°C): inlet, 220; column, 220; detector base, 240; detector furnace, 850. Flow rates: carrier gas, 30–35 mL/min He; reactant gas, 60–100 mL/min H₂; detector solvent (50% 1-propanol in water), 0.5 mL/min. All gases were ultrapure carrier (UPC) grade from Air Products Inc. The limits of quantitation of atrazine, simazine, and alachlor were 5, 5, and 25 ng/m³, respectively.

Toxaphene in air was analyzed by both packed and capillary column gas chromatography. The bulk of the samples were analyzed on a Tracor Model 560 gas chromatograph equipped with a ⁶³Ni electron capture detector, operated in the pulsed mode with linearized output. The 1.83 m × 2 mm (i.d.) coiled glass column was packed with an equal weight mixture of 1.5% OV-17/1.95% OV-210 on 100/120-mesh Chromsorb W HP (Supelco, Inc.). Temperatures (°C): inlet, 245; column, 220; detector, 325. The carrier gas was 40 mL/min of 95:5 Ar-CH₄.

To aid in estimating the more volatile, early-eluting toxaphene components, air samples from the first several days were also analyzed by capillary gas chromatography. A Tracor Model 565 gas chromatograph equipped with a Hall 700A electrolytic conductivity detector operated in the halogen-specific mode was used for sample analysis. Chromatographic conditions: splitless injection with an initial hold for 2 min at 100 °C, programmed at 10 °C/min to a final temperature of 220 °C; injector, detector base, and furnace temperatures (°C), 240, 240, and 850, respectively; reactant gas, UPC-grade H₂ at 35 mL/min; detector solvent, 1-propanol at about 0.5 mL-min. The toxaphene components were separated on a 15 m × 0.25 mm (i.d.) fused silica SE54 WCOT capillary chromatographic column (J & W Scientific, Inc.) operated with UPC-grade He at 100 cm/s linear gas velocity (about 3 mL/min).

Micrometeorological Observations. The micrometeorological observations allowed computation of the vertical pesticide flux rate (g/ha per h) by the aerodynamic or momentum balance method (Parmele et al., 1972). This method requires vertical gradients of wind speed, temperature, and pesticide vapor density be obtained simultaneously over the soil. Wind speeds were measured at four levels, 21, 57, 98, and 243 cm over the soil, by rotating-cup anemometers (C. W. Thornthwaite Associates, Elmer, NJ). These heights were changed to 59, 100, 160, and 245 cm on the last sampling day (day 24) to accommodate the 40-cm-high corn crop.

Differential air temperature (DT) was obtained from the continuous strip-chart record of the output from a shielded, aspirated, 10-junction thermopile of the type described by Lourence and Pruitt (1969). The DT measurements were used to correct for thermal instability using the KEYPS diabatic correction function (Parmele et al., 1972). The measurement heights were initially at 30 and 80 cm but were changed to 70 and 120 cm on the last sampling day. The geometric mean of the heights at which DT was measured determined the plane through which fluxes were determined. On this basis, the minimum fetch to height ratio was greater than 200.

The weather during the experiment is described in Table I.

RESULTS AND DISCUSSION

Diurnal Volatilization Patterns. The observed hourly flux rates for all the sampling periods are presented in Table II. Several different patterns of diurnal behavior

Table I. Weather during Experimental Operations and Measurements (Day 0 = Day of Application, May 25, 1981)

day	operation	weather	temp, °C	wind, m/s
-6		16.5 mm rain		
0	application	sunny	29-32	S 1.0-2.5
1	air sampling	cloud-clear	23-32	S 1.0-3.0
2	air sampling	sunny	24-31	S 2.5-5.0
3		15.5 mm rain		
4	air sampling	sunny	23-29	var 0.5-2.0
8		23.1 mm rain		
9	air sampling	cloudy	28-32	var 1.0-2.0
11		16.3 mm rain		
16		14.9 mm rain		
17	air sampling	sunny	24-27	SW 2.0-5.5
24	air sampling	sunny	25-27	var 1.5-2.5

Table II. Hourly Vertical Flux Intensities (g/ha per h) for Alachlor, Atrazine, Simazine, and Toxaphene from Soil

sampling period	hourly flux intensities, g/ha per hr			
	alachlor	atrazine	simazine	toxaphene
day 0				
1530-1740	3.0	0.11	0.042	5.9
1750-1930	1.7	0.087	0.018	1.9
1940-2130	2.4	0.036	0.014	2.4
day 1				
0530-0730	2.1			9.6
0740-0930	1.1	0.049		6.6
0940-1130	1.2	0.15		7.2
1140-1330	1.5	0.46	0.083	4.6
1340-1530		0.41	0.051	3.5
1545-1720	2.1	0.46	0.11	7.8
1730-1920	1.7	0.31	0.12	12.5
1930-2120	0.81	0.092	0.037	1.0
day 2				
0500-0700	3.1	0.027		1.7
0710-0900	1.9	0.059	0.14	3.2
0910-1100	0.97	0.090	0.058	2.8
1110-1300	1.4	0.18	0.28	
1310-1500	0.46	0.12	0.068	2.8
1510-1700	0.68	0.13	0.092	2.6
1710-1900	1.0	0.11	0.10	2.2
1910-2100	0.70	0.074	0.036	
day 4				
0545-0800	0.96	0.046		1.5
0815-1000	2.4	0.16	0.013	1.7
1010-1200	3.4	0.21	0.012	1.5
1210-1400	6.2	0.24	0.056	3.4
1410-1600	8.1	0.27	0.11	4.0
1610-1700	4.8	0.20	0.053	1.5
day 9				
1615-1810	1.7	0.079	0.019	2.3
1820-2000	0.94	0.069		1.3
day 10				
0600-0755	0.18	0.11		0.39
0800-0955	0.47	0.042	0.019	1.0
1000-1155		0.077	0.023	1.5
1200-1355	3.1	0.27	0.064	2.8
1400-1600	2.0	0.28	0.063	2.3
day 17				
0620-0900	0.90	0.13	0.056	0.63
0905-1200	0.84	0.15	0.10	2.7
1210-1430	1.4	0.33	0.34	3.1
1440-1800	0.48	0.13	0.086	1.1
day 24				
0915-1215	0.22	0.12	0.083	1.6
1225-1520	0.17	0.061	0.064	1.2
1530-1800	0.24	0.017	0.021	1.2

are evident. When the soil surface was moist, on days 4, 9, 10, and 17, the volatilization rates of all the compounds were greatest about midday or in the early afternoon. On days 1 and 2, when the surface was dry, the alachlor and toxaphene rates were higher in the early morning or evening hours than at midday.

In earlier work with compounds of lower solubility and higher vapor pressure, Glotfelty et al. (1984) found that

Table III. Ratios of the Observed Volatilization Rates of Surface-Applied Alachlor, Atrazine, and Simazine on Days with Wet (Days 4 and 10) and Dry (Day 2) Surface Soil

sampling period	day		
	2	4	10
Alachlor/Atrazine			
1	115	21	1.6
2	33	15	11
3	11	16	
4	7.7	26	11
5	3.8	30	7.1
6	5.2	24	
7	9.1		
8	9.5		
Simazine/Atrazine			
1			
2	2.4	0.08	0.45
3	0.6	0.06	0.30
4	1.6	0.23	0.24
5	0.6	0.41	0.22
6	0.7	0.26	
7	0.9		
8	0.5		
mean			
std dev	1.04 ± 0.70	0.21 ± 0.15	0.30 ± 0.10

volatilization rates of pesticides from moist soils varied with the solar energy input to the surface, being highest about noon or early afternoon. If, however, the surface layer of soil became dry, volatilization was dramatically reduced so that minima occurred near noon and the highest rates occurred in the morning and evening as the soil surface was remoistened, either by dew formation or by upward movement of soil moisture to the cooler surface. This pattern reflects the well-known reduction in the vapor pressure of pesticide compounds caused by increased adsorption on dry soil surfaces (Spencer, 1970; Taylor and Glotfelty, 1988). The alachlor and toxaphene behavior in the present experiment are entirely consonant with this interpretation and the earlier observations.

Wind Erosion of Triazines. The triazine data show a different pattern. Noon and afternoon maxima are evident on days 4, 10, and 17 when the soil was moist, although the concentration ranges are much less than the more volatile alachlor. On days 1 and 2 when the soil was dry and the losses of alachlor and toxaphene were suppressed during the midday period, the apparent volatilization of the triazines remained essentially constant or rose slightly. These differences in behavior are illustrated in Figure 1: Figure 1a shows the similarity of alachlor and atrazine on moist soil, and Figure 1b shows the difference between them on dry soil. These contrasts are also clear in the data of Table III, which presents the ratios of the flux rates of alachlor to atrazine and simazine to atrazine for each sampling period. On the days of moist soil, 4 and 10, the alachlor to atrazine ratio remains fairly constant or rises slightly during the midday period, indicating that the volatilization of both compounds was changing in the same way, although of course the atrazine rate was much less than the alachlor. During day 2, when the soil became dry, the ratio showed a midday minimum, indicating that the losses to the air were controlled by different mechanisms: As noted above, the atrazine rate remained essentially constant while the alachlor rate fell to very low values (Table II). In contrast, the simazine to atrazine ratio showed little diurnal variation on any of the days, suggesting that these two herbicides always behaved in the same way.

WP formulations such as those used to apply atrazine and simazine in the present experiment appear to be

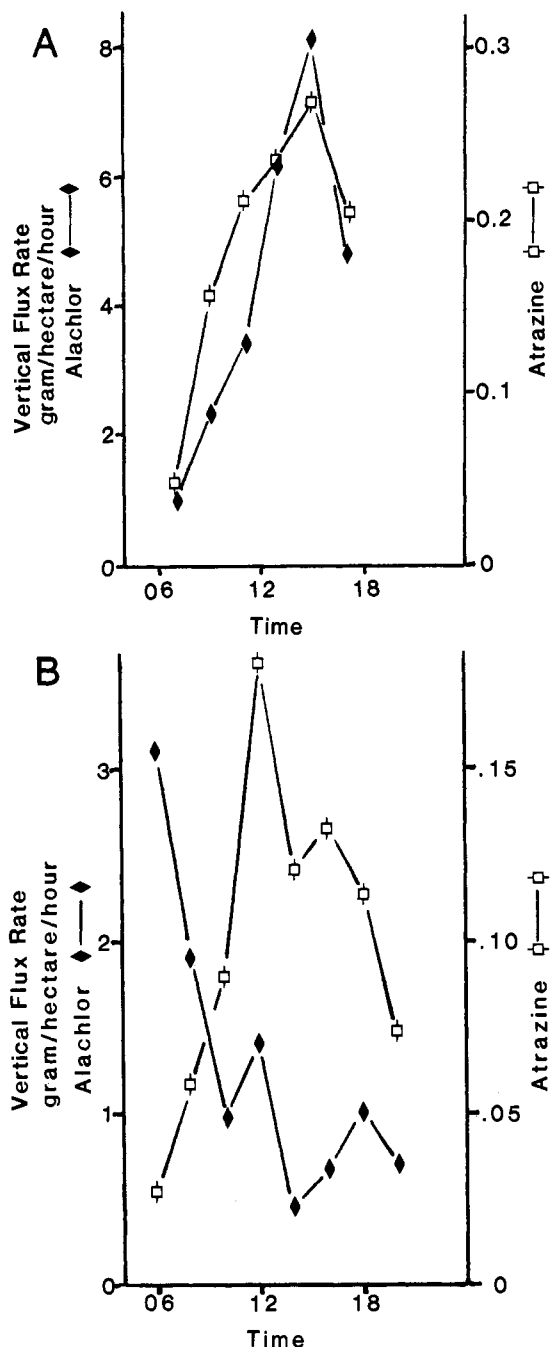


Figure 1. Comparison of alachlor and atrazine losses from wet and dry soil: (A) flux intensities from moist soil on day 4; (B) flux intensities from dry soil on day 2.

susceptible to wind erosion when the soil is dry. Glotfelty (1981) showed that when dacthal (dimethyl 2,3,5,6-tetrachloroterephthalate) was applied in a WP formulation to bare soil, part of the loss was due to wind erosion of the formulation powder. During windy periods in the field, as much as 30% of the airborne dacthal was retained by glass fiber filters. During calm periods less than 2% was retained. The amounts retained during calm periods in the field were equivalent to those retained when glass fiber filters were exposed to dacthal vapor in laboratory experiments. The results obtained from the glass fiber filters in the present experiment were unfortunately inconclusive. The triazines are retained by the filters from both the vapor and particulate-borne forms (alachlor and toxaphene could not be detected on the filters). Evidence for erosion transport of the WP formulation can however be obtained by comparing the simazine to atrazine ratios presented in

Table IV. Observed Daily and Three-Week Losses of Surface-Applied Pesticides to the Atmosphere.

day	soil condition	loss, g/ha per day			
		alachlor	atrazine	simazine	toxaphene
1	dry	22	3.6	1.3	115
2	dry	19	1.5	1.6	37
4	moist	48	2.1	0.5	25
10	moist	20	1.5	0.4	16
17	moist	10	2.0	1.6	21
24	dry	2	0.6	0.5	11
mean daily loss (g/ha)		20	1.9	1.0	37
estd loss (g/ha) (days 1-21)		420	40	21	780
fraction of applicn lost in 21 days (%)		19	2.4	1.3	31

Table III. According to eq 1, the ratio of the volatilization rates of simazine and atrazine from moist soil should be 0.17. The data in Table III show average values of 0.21 ± 0.15 and 0.30 ± 0.10 for this ratio on days 4 and 10 when the soil was moist. This suggests that vapor losses were dominant on these days, when maximum flux rates of both triazines, as also of alachlor and toxaphene, were observed in the early afternoon hours. On day 2, when the soil was dry and the windspeed higher, the average value of the ratio was 1.04 ± 0.70 . Since their application rates were the same, this is very close to the ratio to be expected from wind erosion of the applied formulation.

The results of the present experiment are therefore consistent with the following hypothesis: When the soil surface is moist, atrazine and simazine that have been applied to the soil surface in a WP formulation are lost to the atmosphere by volatilization; when the soil is dry, the WP formulation is subject to wind erosion that carries herbicides still associated with the formulation into the atmosphere. This is important in that losses from moist soil can be predicted from a knowledge of the physico-chemical properties of the herbicides, whereas losses from dry soil cannot.

The small amounts of triazines found in the air suggest that the amount of pesticide that may enter the atmosphere by wind erosion of a WP formulation will be small in comparison to that injected by true molecular evaporation of pesticides of substantially higher vapor pressures. It may be noted that wind speeds as high as those necessary for severe soil erosion are not necessary to produce the observed effects. The fine clay particles that carry the two herbicides in the formulation remain exposed on the soil surface. After moisture applied with the spray dissipates, the powder is left as a deposit of fine dusty material of high herbicide content, which is liable to be disturbed much more readily than the soil surface itself. Removal of a very small fraction of the formulation from the surface will give pesticide fluxes similar to those recorded in Table II.

Daily and Longer Term Losses. The total losses for each day of observation, calculated as the sum of the products of the flux rates and sampling times for all the periods in each day, are presented in Table IV. Estimates of the evaporation losses from the 1st through the 21st days, calculated from the average losses on all the sampling days, are also included. The latter figures indicate that the residues of alachlor and toxaphene were substantially reduced by volatilization during the first 3 weeks after application. The losses of both atrazine and simazine were much smaller, and their dissipation by volatilization probably can be neglected in comparison with their dis-

Table V. Pesticide Physical Properties and Comparison of Volatilization Rate Constants Measured in the Field with Those Estimated by Equation 1

physical property or rate const	compound			
	atrazine	simazine	alachlor	toxaphene
vapor pressure (mmHg)	6.6 (10 ⁷) ^a	1.5 (10 ⁻⁸) ^a	2.2 (10 ⁻⁵) ^b	1.0 (10 ⁻⁶) ^c
water solubility (μg/mL)	32 ^d	5 ^d	242 ^b	0.4 ^e
soil ads coeff (org C basis) (μg g ⁻¹ /μg mL ⁻¹)	163 ^f	138 ^f	82 ^f	9.9 (10 ⁴) ^h
volatilization rate const, ×10 ⁻³ day ⁻¹ estd from eq 1	6	1	49	1
measd from Table IV	1.1	0.6	9	15

^aFriedrich and Stambach, 1964. ^b*Herbicide Handbook*, 1974. ^cSeiber et al., 1981. ^dFreed, 1976. ^eSanborn et al., 1976. ^fRao and Davidson, 1980. ^gAverage for soils 2-7, Table 3 in Weber and Peter (1982). ^hMcDowell et al., 1981.

appearance by chemical degradation. Even though they are not very volatile, atrazine and simazine losses from the treated area by atmospheric transport are roughly equivalent to their reported losses by surface runoff (Wauchope, 1978).

Comparison with Projected Volatilization Rates. Estimated volatilization rate constants calculated for the four pesticides by eq 1, together with the selected values of the physical constants upon which the estimates are based, are presented in Table V. If this equation is viewed critically, it is clear that it fails to take into account a number of factors that may influence pesticide volatilization, such as the organic matter content of the soil, the pesticide concentration in the soil, the soil moisture content, and so forth. Furthermore, field-measured volatilization rates are not constant, as is implied by eq 1, but rather vary markedly over a diurnal cycle. Therefore, at best, eq 1 can only approximate average volatilization losses over long time periods. Finally, it is questionable whether first-order kinetics are an adequate description of volatilization losses from soil surface applications (Glotfelty et al., 1984).

Nevertheless, comparison of the calculated volatilization rate constants in Table V with the average daily values listed in Table IV shows that eq 1 correctly predicts the relative volatility of alachlor, atrazine, and simazine and is within a factor of about 5 of their respective absolute volatilization rates. The volatilization rate of toxaphene is underestimated by a large margin.

Several points must be borne in mind in this comparison. First, eq 1 predicts evaporation under "free" conditions, whereas the average observed rates are weighted by data obtained on days when volatilization was partly inhibited by adsorption on dry soil. Second, as noted above, the triazine concentrations include an unknown fraction of particulate-borne material, so that the vapor-phase concentrations and volatilization rates are lower than those given in Tables III and IV: The amount of this error is not known. Third, the significance of the toxaphene data is uncertain, because this insecticide is not a pure compound but a mixture of many molecular species of differing vapor pressures. The higher than predicted volatilization rate of toxaphene corresponds to the rapid loss of the more volatile fractions, so that the average values calculated over the 24-day period are further distorted by the change in composition of the residues. Similar effects have been described by Willis et al. (1983) and Seiber et al. (1979).

Our field data for alachlor, atrazine, and simazine suggest that the value for the factor Q in eq 1 should be about 8×10^6 . As a further test, we used this value of Q to calculate the apparent first-order volatilization rate constants for several pesticides that had been applied to the surface of fallow soil in an earlier study (Glotfelty et al., 1984). Calculated (measured) volatilization rate constants (day⁻¹): trifluralin, 0.7 (2-6); lindane 0.01 (3); chlordane, 1 (0.3); heptachlor, 5 (3). The calculated and field-measured rate constants are in reasonable agreement for all

the compounds except lindane.

Thus, our data show that eq 1, with $Q = 8 \times 10^6$, yields volatilization rate constants that are within a factor of about 10 of field-measured values for six of eight pesticides having volatilities different by a factor of 10⁴. Equation 1 therefore appears to be useful for making rough estimates of the volatilization rates of surface-applied pesticides, provided its limitations are recognized. The major advantage is that it is a simple, straightforward calculation. A complex model such as that proposed by Jury et al. (1983) would be needed to adequately take into account all the factors that influence pesticide volatilization from soil.

SUMMARY

When soil surfaces were moist, the volatilization rates of alachlor, atrazine, simazine, and toxaphene showed noonday or early afternoon maxima, indicating that they were all responding in a manner similar to the solar energy input, that is, to soil heating and increased atmospheric turbulence. On days when the soil surface became dry, the volatilization of alachlor and toxaphene was greatly reduced by increased adsorption of the pesticides onto the dry soil, with midday and afternoon volatilization rates being less than those observed in the morning and evening. On days of soil drying, the concentrations of atrazine and simazine found in the air did not decrease during the afternoon in parallel with the alachlor and toxaphene, suggesting that these compounds were injected into the air by wind erosion of the fine wettable powder formulation remaining on the dry soil surface. The amounts of pesticide transported in this way were however small, amounting to less than about 1% of the amounts applied.

The measured volatilization rates indicated substantial losses (31%) of surface-applied toxaphene residues within a 21-day period, with a more rapid loss of the most volatile fraction. Nineteen percent of the alachlor was lost in the same period. Atrazine and simazine losses, by both volatilization and erosion, were 2.4% and 1.3%, respectively, suggesting that the atmospheric losses of these herbicides are too small to cause reductions in their herbicidal activity.

A simple empirical equation relating volatilization rate to vapor pressure, solubility, and soil organic carbon adsorption coefficient correctly estimated the relative volatilities of alachlor, atrazine, and simazine and was within a factor of about 5 of their actual field-measured rates. When the equation was applied to data from earlier work, the estimated volatilization rates were within a factor of 10 of measured volatilities for six of eight compounds covering a wide volatility range. Toxaphene was not correctly estimated because it is a mixture having a range of volatilities. While a more complex model would be required to adequately take into account all the factors controlling pesticide volatilization, the simple empirical equation appears to be useful for estimating volatilization rates of surface-applied pesticides from moist soil, provided

its limitations are recognized.

Registry No. Atrazine, 1912-24-9; simazine, 122-34-9; alachlor, 15972-60-8; toxaphene, 8001-35-2.

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