

Measuring Herbicide Volatilization from Bare Soil

S. R. YATES*

USDA-ARS, GEBJ Salinity Laboratory,
450 W. Big Springs Road, Riverside, California 92507

A field experiment was conducted to measure surface dissipation and volatilization of the herbicide triallate after application to bare soil using micrometeorological, chamber, and soil-loss methods. The volatilization rate was measured continuously for 6.5 days and the range in the daily peak values for the integrated horizontal flux method was from 32.4 (day 5) to 235.2 g ha⁻¹ d⁻¹ (day 1), for the theoretical profile shape method was from 31.5 to 213.0 g ha⁻¹ d⁻¹, and for the flux chamber was from 15.7 to 47.8 g ha⁻¹ d⁻¹. Soil samples were taken within 30 min after application and the measured mass of triallate was 8.75 kg ha⁻¹. The measured triallate mass in the soil at the end of the experiment was approximately 6 kg ha⁻¹. The triallate dissipation rate, obtained by soil sampling, was approximately 334 g ha⁻¹ d⁻¹ (98 g d⁻¹) and the average rate of volatilization was 361 g ha⁻¹ d⁻¹. Soil sampling at the end of the experiment showed that approximately 31% (0.803 kg/2.56 kg) of the triallate mass was lost from the soil. Significant volatilization of triallate is possible when applied directly to the soil surface without incorporation.

Introduction

The occurrence of pesticides in the atmosphere or in water supplies is an important national issue (1, 2). Numerous studies have shown that agricultural use of pesticides can contribute to both atmospheric (3–5) and water contamination (6, 7). Pesticide movement in the soil zone is affected by many interrelated factors such as the pesticide application methods, soil and environmental conditions, and water management practices. It is expected that with an understanding of pesticide fate and transport, and water management, pesticide application practices could be developed that reduce the movement of pesticides outside of the root zone.

In irrigated areas, the application of water can be highly controlled, therefore, it should be possible to minimize pesticide contamination provided an adequate understanding exists of how the management of water affects pesticide transport. This is not necessarily the case in areas where rain is the principal source of water. In these areas, natural factors affect the rate and timing of water application where intense storms coupled to soil characteristics can produce high infiltration rates that can greatly increase the potential for pesticides to reach groundwater. These same factors also cause variations in the moisture content of a soil that can affect the loading to the atmosphere from volatile pesticides (8).

Volatilization is an important route of dissipation for pesticides with large vapor pressures or, similarly, large

Henry's Law constants (5, 9, 10). Volatilization has also been shown to be important for pesticides with low to moderate volatility (11–13). Volatilization reduces the pesticide available for control of pests and reduces the potential for groundwater contamination, but increases contamination of the atmosphere. This poses an increased risk to persons living near treated fields, since many pesticides are considered to be carcinogenic (14). To protect public health, there is a need for more information on the important processes and mechanisms that affect the pesticide fate and transport under typical field conditions.

A field experiment was conducted to measure the volatilization rate of triallate (S-(2,3,3-trichloroallyl) diisopropyl thiocarbamate) after application to a bare soil. Triallate is a selective pre-emergence herbicide used to control wild oats in wheat, barley, and a number of other crops. Triallate has relatively low water solubility and relatively long field half-life, and thus, effective weed control can be maintained for up to 6 months. However, triallate also has a relatively high vapor pressure so loss to the atmosphere is an important route of dissipation. Triallate is somewhat toxic to fish and slightly toxic to birds (15). Therefore, a better understanding of the fate and transport of triallate should yield methods to minimize adverse environmental impacts from its use.

The purpose of this experiment was to obtain information needed to provide a better understanding of the soil and environmental conditions that affect and control the surface volatilization rate in semi-arid agricultural regions. To achieve this, time series' of the volatilization rate, the soil chemical distribution, and ancillary environmental conditions were obtained. Relatively few volatilization experiments have been conducted that include continuous monitoring of the volatilization rate over relatively long periods. Continuous monitoring is necessary if mass-balance information is to be obtained or if the data are to be used to test and improve predictive models.

Experimental Procedures

The field site was located at the University of California's Moreno Field Station. The soil type was a Greenfield sandy loam containing about 1% organic matter. A 30 m radius circle was marked out in the center of a 4 ha field and treated with the pesticide triallate at a target rate of 11.5 kg/ha. Triallate has a field dissipation half-life of approximately 100 d; a Henry's Law constant (K_H) of 0.00045; and an organic carbon distribution coefficient (K_{oc}) of 2400 mL g⁻¹ (16). The pesticide was applied to the field using a tractor-mounted sprayer starting at 0645 h and ending at 0700 h. The initial moisture content of the field was approximately 10–15% (L³ L⁻³). A tractor sprayed in two directions (i.e., N–S and E–W) to ensure that the pesticide was uniformly applied within the field boundary (see Figure 1 in Supporting Information).

Soil Measurements. Soil samples were taken using a coring device 2.5 cm in diameter. Twice each day, a total of 31 samples were collected randomly within the circle to a depth of 1 cm. This information provided an estimate of the triallate mass remaining in the soil at various times after application. Previous simulation modeling using the behavior assessment model (17) indicated that, during the experiment, the mass of triallate would remain within the upper 1 cm if the soil was not irrigated.

Atmospheric Measurements. The concentration of triallate in air was obtained using two polyurethane foam (PUF) plugs (in series) held in a glass tube (18). A vacuum system was used to draw triallate-laden air into the foam at a

* Author e-mail: syates@ussl.ars.usda.gov; phone: 951-369-4803; fax: 951-342-4964.

prescribed flow rate (15 L/min). After each sampling interval, the PUF was stored in a freezer and taken to the laboratory for analysis of the triallate concentration.

Since micrometeorological methods were going to be used to determine the volatilization rate, the site was located in an area of vacant fields to provide a large up-wind fetch. Atmospheric and soil measurements of triallate concentration were collected continuously for a 6-day period. Atmospheric triallate concentrations were obtained at 10, 30, 50, 80, 120, and 170 cm above the soil surface and represent averages over 2-h or 4-h sampling intervals. The 4-h sampling intervals occurred during the nighttime hours of 2000–2400 and 0000–4000. In addition, meteorological measurements of incoming radiation, net radiation, air temperature, wind speed, wind direction, and relative humidity were obtained for each 10 min interval during this period. This information was used to determine the volatilization rate using the integrated horizontal flux (IHF) and the theoretical profile shape (TPS) methods.

Chemical Analyses. The triallate in the PUF was collected using Soxhlet extraction for 2 h at 60 °C with an azeotropic mixture of hexane and acetone (250 mL total solution). The extracts were concentrated to about 10 mL in a rotary evaporator and analyzed on a Varian 3700 gas chromatograph equipped with NP and EC detectors (Varian Instruments, Palo Alto, CA). A HP-608 (30 m × 0.53 mm ID) column (Agilent Technologies, Palo Alto, CA) was used with H₂, N₂, and airflow rates, respectively, of 18, 20, and 20 mL min⁻¹. The injector, oven, and detector temperatures, respectively, were 180, 155, and 250 °C. Extracting triallate from the soil samples followed a similar procedure except the extraction time was 8 h.

A preliminary study was conducted to determine the extraction efficiency and breakthrough of triallate through the PUF material for a 50 L/min airflow rate. After connecting 3 PUF traps in series it was found that the total extraction efficiency was 99–100%; and 99.9% of the triallate mass was captured in the first PUF trap.

Meteorological Measurements. Incoming and net solar radiation were obtained, respectively, using a pyranometer (LI-200S, LI-COR, Inc.) and net radiometer (Q-6, Radiation and Energy Balance Systems, Inc.). Wind speed measurements were taken using six Thornthwaite anemometers (CWT-1806, C. W. Thornthwaite Assoc.) positioned at 0.2, 0.4, 0.8, 1.6, 2.4, and 3.6 m above the field surface. The anemometer mast was located approximately 8.5 m south of the sampling mast (see Figure 1 in Supporting Information). Air temperature measurements were obtained at 0.2 and 0.8 m above the field using two platinum thermometers and two Campbell CS207 (Campbell Scientific, Inc.) relative humidity and temperature sensors. These instruments were housed in white louvered covers and mounted on a weather station mast.

Methods For Measuring The Rate of Volatilization. Three different methods were used to obtain experimental values for the rate of volatilization of triallate from a bare surface soil: micrometeorological, flux chamber, and soil-loss.

The integrated horizontal flux method (10, 19) assumes the pesticide was applied as a spatially uniform source. The emission rate, i.e., flux density or volatilization rate (mg/m³ s), can be estimated using the period averaged triallate concentration, $\bar{C}(z)$, and horizontal wind speeds, $\bar{u}(z)$, in the atmosphere as a function of height. The volatilization rate, $f_z(0, t)$, is estimated from a statement of mass balance, that is

$$f_z(0, t) = \frac{1}{L} \int_0^{\infty} \bar{u}(\xi) \bar{C}(\xi) d\xi \quad (1)$$

where ξ is an integration parameter representing height and L is the upwind distance between the mast and the field

edge. This equation states that the mass emitted from the soil surface upwind from a sampling point is equal to the mass that passes through a vertical plane located at the sampling point. To use this methodology, the concentration at several heights above the soil surface must be determined, and the distance of the source area upwind from the sampling mast must be known. An advantage of this method over the other flux estimation methods (i.e., aerodynamic method) is that corrections for atmospheric stability are not needed since this approach is based on principals of mass balance.

The theoretical profile shape (TPS) method (20) provides an estimate of the volatilization rate from a field experiment conducted on a circular plot. The TPS method has advantages in that the large fetch requirement is not necessary and only a single-height measurement of the concentration in air and wind speed is necessary. Numerous investigators (10–11, 20–21) have used the theoretical profile shape method, among others, to determine the rate of pesticide from field experiments. The pesticide volatilization rate is obtained from

$$f_z(0, t) = \frac{(\bar{u}\bar{C})}{R_{inst}} \Big|_{Z_{inst}} \quad (2)$$

where average values of the wind speed, $\bar{u}(Z_{inst})$ and triallate concentration in air, $\bar{C}(Z_{inst})$ are obtained at the instrument height, Z_{inst} . The flux density can be obtained by determining the ratio, R_{inst} , of the horizontal to vertical flux at the measurement height using the trajectory simulation method (22). This ratio depends on the surface roughness and the radius of the circular plot but does not depend on the wind speed. Using wind measurements taken prior to the start of the experiment, the roughness length for the experimental field was found to be 0.06 cm. For a 30 m field with a 0.06 cm roughness length, the $Z_{inst} = 0.88$ m and $R_{inst} = 10.9$. See Supporting Information for more information.

Two flux chambers (23–24) were also used to estimate the volatilization rate to provide another independent measurement. Flow-through chambers were used to collect pesticide emissions from the soil surface. The pesticide volatilization rate was calculated using

$$f_z(0, t) = \frac{Q(C_{out} - C_{in})}{A} \quad (3)$$

where Q is the bulk air flow rate (m³ s⁻¹), C_{in} and C_{out} are the inlet and outlet concentrations (g m⁻³), respectively, and A is the soil area covered by the chamber (0.39 m²). To obtain the volatilization rate, 15 L/min of air was passed through the chambers to ensure that the triallate concentration would not build up inside the flux chambers. This resulted in a residence time of less than 3 min.

Each chamber had four openings: three inlet openings to allow air to enter the chamber and one outlet used for sampling. At each inlet, two polyurethane foam plugs (in series) were used to remove ambient triallate from the incoming air stream and resulted in a zero inlet concentration. These plugs were replaced daily. To minimize the affect of placing the chamber on the soil surface, thin metal frames were installed so that the chambers could be moved to one of three positions after each measurement. This procedure allows the soil to re-equilibrate with current environmental conditions and helps to reduce the affect of the chamber being placed on the soil surface.

Results and Discussion

Shown in Figure 1A is a time series of the air temperature measured 0.8 m above the surface of the field during the 6^{1/2}-day experiment, where integer values on the time axis indicate midnight. The overall weather during the experiment

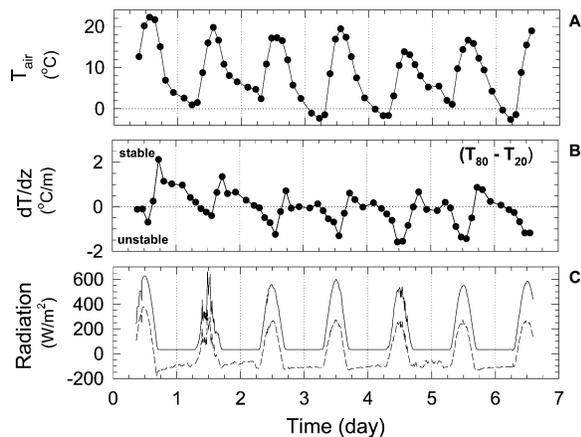


FIGURE 1. Air temperature in °C at 0.8 m height above the soil surface (A), temperature gradient between 0.8 and 0.2 m (B), and incoming (solid line) and net radiation (dashed line) over the course of the experiment (C).

was sunny and dry with occasional thin cirrus clouds present in a southerly direction. The temperature exhibits a typical cyclic pattern with averaged daily peak temperature of 18.2 °C and the averaged daily nighttime minimum temperature of -0.36 °C. The averaged temperature over the entire experiment was 8.8 °C. The temperature behavior was normal for the time of year and was considerably cooler than summertime temperatures when temperature maxima in excess of 40 °C are common (25). Using temperature measurements obtained at 0.8 and 0.2 m above the soil surface, a time series of the temperature gradient can be obtained (Figure 1B). Negative values in this figure indicate that the temperature near the surface is greater than the temperature higher in the atmosphere. The temperature gradient varied ± 2 °C throughout the experiment and negative gradients generally occurred between 0800 and 1400 h and coincided with relatively rapid increases in air temperature.

Except for Day 2, the incoming and net solar radiation had a smooth cyclic character indicative of mostly clear skies (Figure 1C). This can also be seen from the smooth cycles in the temperature pattern shown in Figure 1A. The maximum and average incoming solar radiations, respectively, were 661 and 166 W/m². This is close to values one would obtain using theoretical models of solar radiation in the absence of cloud cover. The dashed line in Figure 1C is the observed net radiation. The observed values had a maximum of 366, a minimum of -172, and an average of -10 W/m².

The wind speed and direction during the experiment are shown in Figure 2. Typical wind patterns for the inland areas of southern California include high daytime wind speeds and a shift between coastal (west) and desert (south and east) influences occurring in the afternoon. A daily pattern forms where winds are predominately from the west during the afternoon when wind speeds are highest. The winds are more moderate and are commonly from the south and east during the night and early morning. The daily maximum wind speeds ranged from a low of about 2 m/s to a high of about 4 m/s. Wind speeds during the middle of the night were generally about 0.6–0.8 m/s. Large changes in relative humidity (Figure 2C) over fairly short time intervals (i.e., days) are common in the inland area due to its proximity to the desert and ocean. The behavior of the wind and relative humidity during the first 2 days of the experiment suggests a weakened ocean influence. During these periods, desert influences dominate and the relative humidity tends to be lower than average conditions. This is often indicated by the so-called Santa Ana winds, relatively dry air and strong winds from the east and southeast.

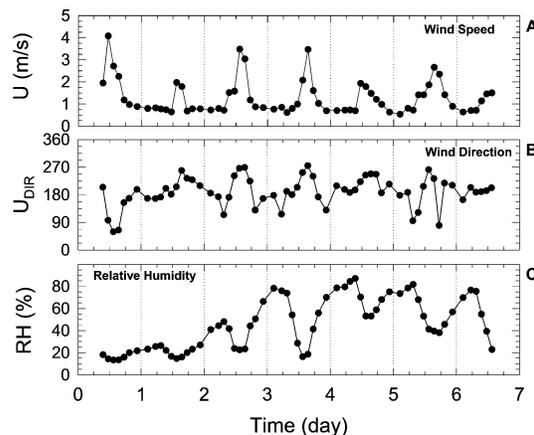


FIGURE 2. Variation in wind speed (A), wind direction (B), and relative humidity (C) with time.

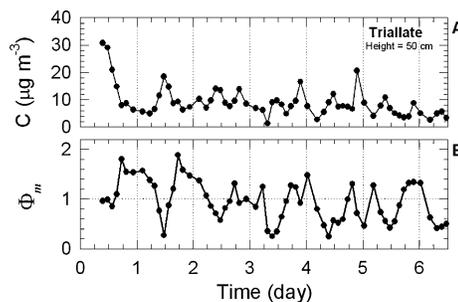


FIGURE 3. Measured triallate concentration in the atmosphere at 50 cm above the soil surface (A). Atmospheric stability, $\Phi = (1 \pm 16 Ri) \pm 0.33$, as a function of time (B), where $Ri = g(\partial T/\partial z)/[T(\partial u/\partial z)^2]$, and T and u , respectively, are the temperature and wind speed (10). The plus sign is used for $Ri > 0$, otherwise the minus sign is used. Values of Φ greater than 1 indicate stable conditions, those less than 1 indicate unstable conditions.

A more typical pattern occurs after 2 days when the relative humidity is low near solar noon (i.e., approximately 20%) and high after midnight (i.e., approximately 80%). Overall, the relative humidity was generally below 80% and averaged approximately 50%. Average relative humidity during the first 2½ days was 25%, but 59% thereafter, indicating a significant change. The daily maximum relative humidity also changed from 51% to 88% after 2.5 days. Taken together, the wind speed, wind direction, and relative humidity suggests that a change in the weather pattern occurred with more typical conditions occurring after 2.5 days.

Initial atmospheric concentrations were high, with values above 20 µg/m³ during the first 6 h after application (Figure 3A). The values then decreased rapidly during the first day. Later, the rate of dissipation was slower with daily low concentrations of 6–8 µg/m³. The high concentration of triallate in the atmosphere at the start of the experiment is primarily due to the method of application of triallate to the soil surface and lack of incorporation into the soil. This leads to a condition where the availability of chemical is initially highest and is slowly reduced as sorption, diffusion, and volatilization reduce the chemical concentration.

The stability of the atmosphere is shown in Figure 3B. Unstable atmospheric conditions are indicated by Φ values less than 1.0 in Figure 3B, which generally occur during the day when the temperature difference in the atmosphere is as much as -1.5 °C. During the night, neutral to stable conditions were present with the temperature at a height of 0.8 m generally no more than 1.0 °C warmer than that at 0.2 m. For stable conditions, mixing in the atmosphere is suppressed and higher concentrations near the soil surface

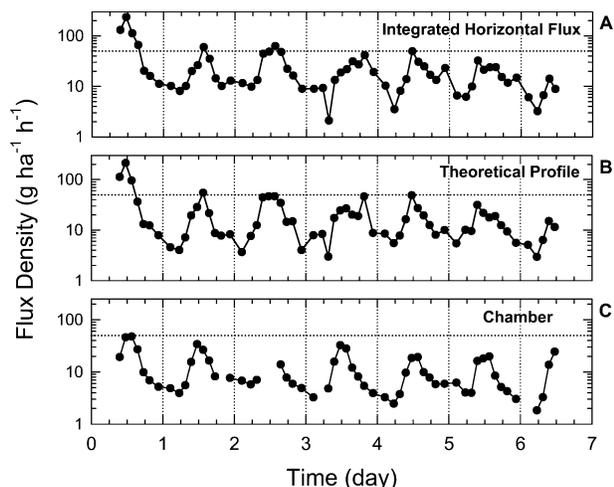


FIGURE 4. Volatilization rate ($\text{g ha}^{-1} \text{h}^{-1}$) as a function of time (day) after application for integrated horizontal flux (A), theoretical profile shape (B), and chamber (C) methods. Note low values for chamber method at early times.

can reduce concentration gradients at the soil–atmosphere interface. In general, this yields lower volatilization rates compared to neutral or unstable atmospheric conditions and the reduced mixing causes an increase in chemical concentration in the atmosphere. Generally, during the middle part of the day the atmosphere may be unstable (i.e., $\Phi(z) < 1$). Low atmospheric concentrations occur for unstable conditions, where buoyancy forces dominate diluting of the chemical concentration.

There can be a strong relationship between concentration in air and atmospheric stability, $\Phi(z)$, where relatively high measured concentrations in air occur during periods of stable atmospheric conditions. However, this behavior is not clearly observable in Figure 3. Yates et al. (25) showed that for very volatile methyl bromide under tarped conditions, atmospheric concentration was highly correlated with atmospheric stability, with high concentration occurring during stable periods and low concentration during unstable periods. However, when a low to moderately volatile herbicide is applied to the soil, it has been reported that evaporation of water plays an important role in the volatilization process (26). Jury et al. (17) demonstrated that evaporation helps to control movement of herbicide into the atmosphere, so periods with low energy input (i.e., nighttime) may not have sufficient energy to significantly evaporate water and move chemical to the surface and into the atmosphere. For situations where evaporation plays a significant role controlling volatilization, one would not expect a high correlation between atmospheric stability and concentration.

Shown in Figure 4 is a time series of the volatilization rate at the field site during the experimental period. The three methods, integrated horizontal flux (IHF), the theoretical profile shape (TPS), and flux chamber, show similar cyclic behaviors with peaks occurring predominately during the midday and low values at night. The maximum daily volatilization rate for each method occurred on the first day and ranged from approximately $50 \text{ g ha}^{-1} \text{h}^{-1}$ (chamber method) to more than $200 \text{ g ha}^{-1} \text{h}^{-1}$ (theoretical profile shape and IHF methods). The minimum daily volatilization rates were generally less than $5\text{--}10 \text{ g ha}^{-1} \text{h}^{-1}$ with the chamber method producing slightly lower values than the other methods.

At early time periods, the IHF and TPS methods produce very high values (i.e., $>200 \text{ g ha}^{-1} \text{h}^{-1}$) for the triallate flux density (see Figure 4A and B). These values are 2–4 times higher than values from the chamber method. The high flux values at the beginning of the experiment result from a

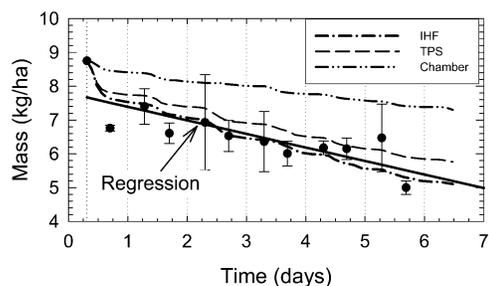


FIGURE 5. Triallate mass in the soil with time. Filled circles are measured values, solid line is a regression relationship, and dashed lines are estimates of the mass remaining in the soil from the volatilization measurements.

combination of high atmospheric concentrations (Figure 3A), near neutral atmospheric stability (dotted line in Figure 3B), and high wind speeds (Figure 2). The TPS method produces values that are proportional to the average wind speed and concentration during the sample interval, so simultaneously high values lead to larger volatilization rates. The IHF method integrates wind speed and concentration so it too would yield large flux values for large wind speed and concentration. In addition, a weather pattern occurred during the first 16 h after application with relatively warm, dry winds from the east (Figure 2) and relatively high wind velocity. The relatively dry airmass (Figure 2C) probably increased volatilization of triallate immediately after application by increasing water evaporation at the soil surface (17) and liberating triallate from the water phase, compared to later in the experiment.

The low values for the chamber method are most likely due to several factors related to the presence of the chamber on the soil surface. A chamber can affect surface evaporation, temperature near the soil surface, and concentration gradients near the soil surface (24). This has often led researchers to question the validity of chamber measurements of pesticide flux from soil surfaces. This is also the reason that the experimental protocol used in this experiment included moving the chamber to one of three different locations after each measurement period. This tends to reduce the influence of the chamber on the soil–atmospheric micro-environment. However, even with this precaution, the chamber method appears to underestimate the volatilization rate and cumulative emissions. All the methods produce daily maximum volatilization rates that slowly decrease over the course of the experiment, but at a much reduced rate compared to the first day.

For later time periods, the chamber flux density values are on average approximately 25% less than those of the IHF and TPS methods. Similar observations were made by Yates et al. (10) for methyl bromide emissions and by Majewski et al. (11) for chlorpyrifos. The correspondence between the IHF and TPS volatilization rates suggest that these are a more accurate representation of the volatilization rate compared to the chamber method. However, it may be difficult to demonstrate this definitively, since uncertainty in volatilization measurements has been estimated to be 50% or more (27).

Shown in Figure 5 is the triallate mass in the soil at various times during the experiment. The points shown in Figure 5 are the measured soil triallate concentrations and the first data point (8.75 kg/ha) was taken immediately after application. This value is comprised of one composite sample value consisting of 31 soil cores randomly taken from the field plot. The other points shown in Figure 5 are the average of three composite samples, each consisting of 31 soil cores. It is clear from the error bars that soil spatial variability can be problematic even when combining numerous soil cores into a single composite sample. This observation is consistent

with numerous reports in the literature of high variability in soil solute concentration measurements (28).

The straight solid line shown in Figure 5 is a regression line obtained using the measured values after the start of the experiment. The rate of disappearance of chemical from the soil can be obtained from the slope of the regression line and is $400 \text{ g ha}^{-1} \text{ d}^{-1}$. Since the first data point consists of only one composite sample value, it has higher uncertainty than the other values shown in Figure 5. Further, the initial rate of volatilization is very high during the first few hours. Excluding the first two data points from the regression yields a lower dissipation rate of $334 \text{ g ha}^{-1} \text{ d}^{-1}$ and may be more representative of the loss rate during most of the experimental period.

If it is assumed that soil degradation is small compared to the amount of triallate lost to the atmosphere, the cumulative volatilization from each method can be compared to estimate the rate of chemical disappearance from soil. Since the triallate degradation half-life, $\tau_{1/2}$, has been reported to be approximately 80–100 d (16), degradation during the first 6 days after application would be less than 5%. This indicates that volatilization is the primary mechanism causing the disappearance of triallate in the field soil.

The dashed lines in Figure 5 are the cumulative loss rates using the volatilization measurements and the initial soil concentration. Both the soil concentration and volatilization measurements demonstrate a rapid loss of triallate during the first few hours, which indicates experimental consistency. Fitting a regression line to the cumulative volatilization loss versus time curve gives triallate volatilization loss rates of 205, 395, and $482 \text{ g ha}^{-1} \text{ d}^{-1}$, for the chamber, theoretical profile shape, and integrated horizontal flux methods, respectively. The average triallate loss from all the volatilization methods is $361 \text{ g ha}^{-1} \text{ d}^{-1}$. This value compares well with the rate of chemical disappearance due only to volatilization obtained from the soil measurements, which is $340 \text{ g ha}^{-1} \text{ d}^{-1}$. This degradation-corrected disappearance (i.e., volatilization) rate was obtained by correcting the soil triallate concentration measurements for degradation losses using a half-life, $\tau_{1/2} = 100 \text{ d}$, and obtaining the slope of the regression relationship. The average temperature during the experiment was $8.8 \text{ }^\circ\text{C}$ and by the end of the experiment approximately 31% of the applied triallate was lost. In laboratory experiments using a sandy loam soil, Taberner et al. (13) found that cumulative triallate volatilization ranged from 14% when the experiment was conducted at $5 \text{ }^\circ\text{C}$ to 32% when the experiment was conducted at $15 \text{ }^\circ\text{C}$. The measured triallate loss is also somewhat higher than the value reported by Smith et al. (29) who found that 21% of the applied triallate volatilized from a granular formulation during a 24 day test period and that the loss rate was highly correlated with rainfall. It should be noted that the materials and conditions used in these studies were quite different from those observed during this field study.

This study illustrates the importance of obtaining a continuous time series for the volatilization rate. Only then can important information concerning the experiment be obtained. In addition, a continuous time series is needed to provide information for modeling. Without complete knowledge of the pesticide behavior, it would be difficult to judge the accuracy of simulations of the fate and transport in soil, or to have knowledge of processes that are required to make an accurate simulation algorithm.

Acknowledgments

The use of trade, firm, or corporation names in this research article is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the United States Department of Agriculture or

the Agricultural Research Service of any product or service to the exclusion of others that may be suitable.

Supporting Information Available

A schematic of the field site and a description of the theoretical profile shape method including a figure that shows how Z_{inst} and R_{inst} were obtained. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Kaufmann, C.; Matheson, N. *Protecting Groundwater from Agricultural Chemicals: Alternative Farming Strategies for Northwest Producers*; Alternative Energy Resources Organization: Helena, MT, 1990; 28 pp.
- (2) USDA. *Reducing Pesticide Risk, Proceedings of the Reducing Pesticide Risk Workshop*; Agricultural Research Service: Washington, DC, January, 1999; 62 pp.
- (3) Van den Berg, F.; Kubiak, R.; Benjey, W.; Majewski, M.; Yates, S. R.; Reeves, G.; Smelt, J.; van der Linden, A. Emission of pesticides into the air. *Water, Air Soil Pollut.* **1999**, *115*, 195–218.
- (4) Prueger, J. H.; Gish, T. J.; McConnell, L. L.; Mckee, L. G.; Hatfield, J. L.; Kustas, W. P. Solar radiation, relative humidity, and soil water effects on metolachlor volatilization. *Environ. Sci. Technol.* **2005**, *39*, 5219–5226.
- (5) Cryer, S. A. Predicting soil fumigant air concentrations under regional and diverse agronomic conditions. *J. Environ. Qual.* **2005**, *34*, 2197–2207.
- (6) U.S. EPA *Agricultural Chemicals in Ground Water: Proposed Pesticide Strategy*; Office of Pesticides and Toxic Substances: Washington, DC, December, 1987; 150 pp.
- (7) McConnell, L. L.; Harman-Fetcho, J. A.; Hagy, J. D. Measured concentrations of herbicides and model predictions of atrazine fate in the Patuxent River Estuary. *J. Environ. Qual.* **2004**, *33*, 594–604.
- (8) Taylor, A. W.; Spencer, W. F. Volatilization and vapor transport processes. In *Pesticides in the Soil Environment: Processes, Impacts and Modeling*; Soil Science Society of America Book Series, No. 2; SSSA: Madison, WI, 1990; Chapter 7, pp 213–269.
- (9) Yagi, K.; Williams, J.; Wang, N. Y.; Cicerone, R. J. Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigations. *Science* **1995**, *267*, 1979–1981.
- (10) Yates, S. R.; Ernst, F. F.; Gan, J.; Gao, F.; Yates, M. V. Methyl Bromide Emissions from a Covered Field. II. Volatilization. *J. Environ. Qual.* **1996**, *25*, 192–202.
- (11) Majewski, M. S.; 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.
- (12) Baker, J. M.; Koskinen, W. C.; Dowdy, R. H. Volatilization of EPTC: simulation and measurement. *J. Environ. Qual.* **1996**, *25*, 169–177.
- (13) Taberner, M. T.; Alvarez-Benedi, J.; Atienza, J.; Herguedas, A. Influence of temperature on the volatilization of triallate and terbutryn from two soils. *Pest Manage. Sci.* **2000**, *56*, 175–180.
- (14) Doull, J. *Pesticide Carcinogenicity; Carcinogenicity and Pesticides: Principles, Issues and Relationships*; American Chemical Society: Washington, DC, 1989; 246 pp.
- (15) Gowan Company. *Ecological Information Summary for Far-Go (triallate)*; Material Safety Data Sheet, Revision 7/19/2005; Gowan Co.: Yuma, AZ, 2005.
- (16) Wauchope, R. D.; Buttler, 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*, 1–155.
- (17) Jury, W. A.; Spencer, W. F.; Farmer, W. J. Behavior assessment model for trace organics in soil: 1. Model description. *J. Environ. Qual.* **1983**, *12*, 558–564.
- (18) Turner, B. C.; Glotfelty, D. E. Field air sampling of pesticide vapors with polyurethane. *Anal. Chem.* **1977**, *49*, 7–10.
- (19) Majewski, M. S.; Glotfelty, D. E.; Paw, 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.
- (20) Wilson, J. D.; Thurtell, G. W.; Kidd, G.; Beauchamp, E. Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere. *Atmos. Environ.* **1982**, *16*, 1861–1867.
- (21) Ferrari F.; Trevisan, M.; Capri, E. Predicting and measuring environmental concentration of pesticides in air after soil application. *J. Environ. Qual.* **2003**, *32*, 1623–1633.

- (22) Wilson, J. D.; Thurtell, G. W.; Kidd, G. E. Numerical simulation of particle trajectories in inhomogeneous turbulence, I: Systems with constant turbulent velocity scale. *Boundary Layer Meteor.* **1981**, *21*, 295–313.
- (23) Hollingsworth, E. B. Volatility of trifluralin from field soil. *Weed Sci.* **1980**, *28*, 224–228.
- (24) Clendenning, L. D. A field mass balance study of pesticide volatilization, leaching and persistence. Ph.D. Thesis, Department of Soil & Environmental Sciences, University of California, Riverside, CA, 92521, 1988; 221 pp.
- (25) Yates, S. R.; Ernst, F. F.; Gan, J.; Gao, F.; Yates, M. V. Methyl Bromide Emissions from a Covered Field. I. Experimental Conditions and Degradation in Soil. *J. Environ. Qual.* **1996**, *25*, 184–192.
- (26) Spencer, W. F.; Cliath, M.; Jury, W. A.; Zhang, L. Z. Volatilization of Organic-chemicals From Soil as Related to their Henry's Law Constants. *J. Environ. Qual.* **1988**, *17*, 504–509.
- (27) Majewski, M. S. Error evaluation of methyl bromide aerodynamic flux measurements. In *Fumigants: Environmental Fate, Exposure, and Analysis*; Seiber, J. N., Knuteson, J. A., Woodrow, J. E., Wolfe, N. L., Yates, M. V., Yates, S. R., Eds.; ACS Symposium Series 652; American Chemical Society: Washington, DC, 1997; pp 135–153.
- (28) Jury, W. A. *Spatial Variability of Soil Physical Parameters in Solute Migration: A Critical Literature Review*; Electric Power Research Institute Interim Report EA-4228, Project: 2485-6; EPRI: Palo Alto, CA, September 1985; 66 pp.
- (29) Smith, A. E.; Kerr, L. A.; Caldwell, B. Volatility of ethalfluralin, trifluralin, and triallate from a field following surface treatments with granular formulations. *J. Agric. Food Chem.* **1997**, *45*, 1473–1478.

Received for review January 26, 2006. Revised manuscript received March 15, 2006. Accepted March 22, 2006.

ES060186N