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COMPARISON BETWEEN MEASURED AND PREDICTED RATES OF PESTICIDE VOLATILIZATION FROM AN AGRICULTURAL FIELD

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ABSTRACT

A field experiment was conducted to measure surface accumulation and volatilization of pesticides as related to their physical and chemical properties in the field. The volatilization rate was measured using several methods. Comparisons are made between the measured and predicted values based on water and solute transport models. The measured and simulated flux compares fairly well, especially at later times, although there was lesser agreement at earlier times. Comparisons between the predicted and measured residual triallate mass in the soil shows a nearly identical dissipation rate (i.e., approximately 115 g/d) starting 8 hours after application. During the first 8 hours, however, there was a sudden decrease in the measure residual mass which was not observed in the simulation. The predicted extent of triallate movement was about 0.25 cm during the first 5 days of the experiment. A description of the experimental methods for obtaining the volatilization rate and comparisons between the experimental values and the model predictions are provided.

INTRODUCTION

The occurrence of pesticides in the atmosphere or in groundwater has become an important national issue (USEPA, 1987; Kaufmann and Matheson, 1990). Volatilization is recognized as an important route for the dissipation of pesticides and related organics from soil. The ability to predict the rate of volatilization in the field for a variety of environmental conditions is paramount in protecting the environment from agricultural pollution. Pesticide movement in the soil zone is closely related to both pesticide properties, environmental conditions, application methods and water management practices. Information is needed that will reduce the movement of pesticides outside of the root zone and determine the factors, which can affect the atmospheric loading from volatile pesticides (Taylor and Spencer, 1990; Spencer and Cliath, 1990).
Recent laboratory experiments have confirmed model predictions that the behavior of volatile organics in soil is controlled by physical and chemical properties, primarily their Henry's law constant. Although these results are important, more information is needed about the behavior of volatile organics in large fields under typical atmospheric conditions. Methods are needed to accurately and efficiently measure the rate of volatilization from the soil surface, to model the transport and fate of volatile organics in heterogeneous porous media and to manage the application of water to minimize the potential for ground water contamination.

One method for developing effective management practices is to use models to compare the environmental impacts that result from various management alternatives (Jury et al., 1984). Before models become useful for estimating the potential for a pesticide to contaminate the environment, it is necessary to understand and be able to predict all routes of transport and dissipation. Volatilization is an important route of dissipation for pesticides with large vapor pressures (or large Henry's constants). Through volatilization, the amount of a pesticide available for control of pests and the potential for ground water contamination is reduced but the potential for contaminating the atmosphere and surface waters is increased. Volatilization can cause an increased risk of illness to persons living down-wind from treated fields (Yates, 1992), since many pesticides are considered to be toxic or carcinogenic (Doull, 1989). Consequently, pesticide transport models should be capable of predicting vapor phase transport as well as the surface volatilization rate under field conditions.

The purpose of this paper is to compare measured volatile flux of the pesticide triallate from a bare field soil with simulated values using a numerical model. The model simulates pesticide transport in a saturated and unsaturated soil and can be used to characterize the environmental fate of volatile pesticides. This model can simulate pesticide leaching to ground water, vapor phase transport and pesticide loading into the atmosphere.

METHODS

The field site was located at the University of California's Moreno Field Station. A 30 m radius circle, containing the Greenfield sandy loam, was treated with the pesticide triallate at a rate of 11.5 kg/ha using 0.520 m^3/ha of water. Physical properties for triallate are presented in Table 1. Atmospheric and soil measurements of triallate concentrations were made between December 14 and 20, 1989. Atmospheric triallate concenaations were obtained at 6 heights above the soil surface and represent averages over a two or four hour sampling interval. In addition, meteorological measurements of incoming radiation, net radiation, air temperature, wind speed, wind direction and relative humidity, were obtained for 10 min intervals during this period. From this information the evaporation rate was determined.

Soil hydraulic properties were determined using a combination of field and laboratory techniques. The van Genuchten (1980)-Mualem (1976) approach for characterizing the moisture-tension and unsaturated hydraulic conductivity relationships were fitted to the experimental data and produced the following values for the residual moisture content, θ_r=0.04; the saturated moisture content, θ_s=0.36; the saturated hydraulic conductivity, K_s=0.14 cm/d; and the van Genuchten (1980) retention parameters: α=0.03, n=1.5 and ℓ=0.5. The saturated hydraulic conductivity was determined from a field experiment where water was ponded on the surface until steady state. Matrix effects were assumed negligible and the final inflow rate was assumed to be due solely to gravity drainage effects.

The pesticide was applied to a pre-irrigated field using a tractor-mounted sprayer. The initial moisture content of the field prior to spraying was approximately 15%. No additional water was added to the field during the experiment. Assuming that piston flow governed the pesticide movement into the soil during application, the penetration would be approximately 0.3 mm and at a total concentration of 3.83 x 10^{-3} g/cm'.

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. The simplest method used for measuring the rate of emission of volatile compounds is the flux chamber method (Schmidt and Balfour, 1983; DuPont and Reineman, 1986; Clendening, 1988; Clendening et al. 1990). The flux chamber is a closed system device that allows pesticide emissions from a small surface area to be collected. To calculate the pesticide flux using this method the pesticide mass, the continuous and uniform flow rate and the surface area sampled must be determined.

The aerodynamic method uses atmospheric gradients of wind speed, temperature and concentration to provide a measurement of the pesticide flux from the soil surface (Parmele et al., 1972). The method requires a spatially uniform source and a relatively large upwind fetch to assure that the gradients are fully developed. The method was originally developed for use under neutral atmospheric conditions. Using empirical factors, however, the method can be extended to stable and unstable conditions.

The theoretical profile shape method has been recently described by Wilson et al. (1982) as a method to determine the gaseous mass transfer from field experiments conducted on a circular plot. The theoretical profile shape method has advantages over the aerodynamic method in that 1) the large fetch requirement is not necessary, 2) measurements of the air concentration and wind speed are necessary only at one height and 3) the placement of the sensor is located at a position insensitive to the atmospheric stability so temperature and wind gradients are unnecessary. A disadvantage of this method is that the shape of the field must be circular or at least quasi-circular, which is uncommon. This approach is based on the trajectory simulation model described by Wilson et al. (1981 a,b,c). Wilson et al. (1983). Majewski et al. (1989) and Majewski et al. (1990) have used the theoretical profile shape method, among others, to determine the rate of pesticide and ammonia volatilization from field experiments. The pesticide flux is estimated from the ratio of the horizontal to vertical flux using the trajectory simulation model. This ratio depends on the surface roughness and the radius of the circular plot but does not depend on the wind speed.

Simulating Pesticide Transport And Fate

The model that simulates the environmental transport and fate of volatile pesticides couples the Richard's equation for unsaturated water flow to a modified form of the advection-dispersion equation describing transport of volatile pesticides. The subsurface transport of volatile pesticides and the flux of pesticides into the atmosphere is described by a more general form of the behavior assessment model of Jury et al. (1983). The approach assumes that transport occurs in one-dimension, that vapor partitioning follows Henry's Law and that the pesticide is subject to linear equilibrium adsorption and first-order decay.

The Richard's equation, which governs water movement in an unsaturated soil, is where $\phi(z,t,\theta)$ is the matric potential, $C_s(\phi)$ is the specific moisture capacity and $K(\phi)$ is the unsaturated hydraulic conductivity. The boundary conditions at the surface and at depth are,

$$C_s(\phi)\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial z}\left[K(\phi)\frac{\partial\phi}{\partial z}\right] - \frac{\partial K(\phi)}{\partial z} \tag{1}$$

respectively

$$-K(\phi)\frac{\partial\phi}{\partial z} + K(\phi)\big|_{z=0} = Q_o(t) \tag{2}$$

$$\frac{\partial\phi}{\partial t}\Big|_{z=L} = 0 \tag{3}$$

where Q(t) is the water flux at the surface boundary, is negative for evaporation and is obtained from estimates of the evaporation rate as a function of time using meteorological data.

The equation that describes transport under unsaturated conditions is

$$\frac{\partial\theta C}{\partial t} + \rho_b\frac{\partial S}{\partial t} + \frac{\partial\eta G}{\partial t} = \frac{\partial}{\partial z}\left[\theta D_\ell\frac{\partial C}{\partial z} + \eta D_G\frac{\partial G}{\partial z} - qC\right] - \mu_\ell\theta C - \mu_s\rho_b S - \mu_G\eta G \tag{4}$$

where D, and Do are the liquid dispersion and vapor phase diffusion coefficients, respectively, and μ is a first-order degradation coefficient. The subscripts: ℓ, s and G indicate liquid, solid, and gaseous phases, respectively. The boundary conditions at the surface and lower boundaries are:

$$\begin{gathered}-D_E\frac{\partial C}{\partial z}\Big|_{z=0} + qC\big|_{z=0} = -H_E C\big|_{z=0} \\ \frac{\partial C}{\partial z}\Big|_{z=L} = 0\end{gathered} \tag{5}$$

where Da = $\theta D_\ell + K_H\eta D_G$ is the effective dispersion coefficient and Ha = $D_G^{air} K_H/b$ is the effective mass transfer coefficient which describes vapor transport across a stagnant boundary layer, b, located at the soil surface and K_H is the Henry’s Law constant.

RESULTS

For the simulation, the initial triallate concentration was assumed to be restricted to the upper 0.03 cm, as described above. Therefore, the triallate liquid phase concentration in this region was equivalent to a concentration of 9.6×10^{-5} g/cm’ which is greater than the solubility of triallate in water. For purposes of calculating the volatilization rate at nodes where this condition was observed, the flux was determine using the saturation value for triallate in water. Selected simulation parameters are shown in Table 2.

Shown in Fig. 1 is a time series of the calculated evaporation rate at the field site during the experimental period. This figure demonstrates a cyclic behavior with peaks occurring predominately during the midday and low values at night. The daily values for the evaporation rate ranged from a low of approximately 0.1 cm/day to a high of approximately 0.24 cm/day on the fifth day. Several discrepancies from expected behavior can be observed in Fig. 1. First, are the very low values for the evaporation rate during the early afternoon on the first and second days. Second, are the relatively high values occurring at approximately midnight of the last two days. Relatively high values also occurred on other nights, as well, but are not so pronounced. These discrepancies are probably due to instrumentation errors and/or difficulties in accurately measuring the gradients in temperature and wind speed, required when using the aerodynamic method to estimate the evaporation rate.

Shown in Fig. 2 is a comparison of the average measured volatilization rate resulting from the three methods with the simulated rate using Eqs. 1 to 5 (heavy solid line). The dotted lines indicate the plus and minus one standard deviation from the average measured value for the volatilization rate (solid line). It is clear from this figure that the overall behavior of the flux has been fairly well predicted, especially at later times. Two discrepancies occur at earlier times. The most important is the large disagreement between the measured and simulated flux during the first few hours. During this time, the rate of volatilization is typically the greatest value observed over the entire experiment. The simulated flux during this time period, however, is rather low. This may be caused by the failure of the meteorological instruments, erroneous values for the evaporation rate, which strongly affect the boundary layer thickness, or possibly some other process is at work at early times that is not accounted for in the pesticide transport model. The other discrepancy occurs during the middle of the second day, when the simulated flux decreases sharply compared to the measured values. Since the simulated values are increasing as time approaches noon and decreasing during the evening (after the midday low values) in accordance with the measured values, the discrepancy is probably due to errors in the measured evaporation rate (see low evaporation rates during this time period in Fig.1). Shown in Fig. 3 is the residual triallate mass in the soil at various times during the experiment. The initial mass applied to the 0.29 ha field was determined to be 3.35 kg. The solid line indicates the predicted mass remaining in the soil; whereas, the dashed line is a regression line for the measured mass using all measured data except the initial value. The discrepancy between the two lines during the first several hours is attributed, in part, to the low simulated flux values (Fig. 2). The slopes of the two lines are almost identical, at approximately 115 g/d. The difference in mass between the simulated and measured values (i.e., the distance between the two lines) is approximately 440 grams and, since the slopes of the lines are approximately equal, appears to be due to early-time behavior. The measured mass that volatilized from the field during the first 8 hours of the experiment ranged from 64 to 261 g (mean=151 g, standard deviation=78 g for three measurement methods). The simulated mass volatilized during the same time period was 17 g. Clearly, if the simulation represented the measured volatilization rate more closely, the deviations between the lines would be approximately in the range 179 to 376 g. It is unclear what factor or group of factors is causing the remaining difference. There are a number of possible explanations. For example, if the initial soil concentration is inaccurate with the initial value higher than what was actually present in the soil, this would cause the appearance of a sudden decrease in concentration at the second sampling time (first sampling after initial values were obtained). Although a sudden decrease in concentration is observed, there is no evidence that the initial concentration is in error. In fact, the initial concentration is very close to the value expected from the application rate. Another possible explanation is that the extraction procedure may be less than 100 percent efficient. This would cause reduced apparent concentrations in the soil samples that would not be accounted for in the simulation. If this occurred, however, it would be expected that the initial value would also be reduced by the same fraction, unless the extraction efficiency changes in a time-dependent manner. Since the simulation uses this initial value as the starting concentration and the observed decrease occurred approximately eight hours after the application of triallate, such an error would not be a likely cause. of the observed behavior.

Shown in Fig. 4 is the simulated soil concentration as a function of depth after 1 and 5 days. During this simulation, the soil zone containing the pesticides was restricted to the upper 0.25 cm. Daily soil samples were obtained to a depth of 3.0 cm. Since no irrigation water was applied to the field during the experiment, it is unlikely that the pesticide moved passed the 3.0 cm depth sampled.

CONCLUSIONS

A model describing the environmental fate of volatile pesticides has been developed by combining a more general solution to transport of volatile pesticides described by Jury et al. (1983) with the Richard’s equation characterizing unsaturated flow of water in soils. A field experiment was conducted to obtain atmospheric concentration of triallate above a field. These data were used to determine the flux of pesticide moving from the soil surface to the atmosphere using three methods. Other meteorological data were obtained to produce estimates of the evaporation rate from the field.

The simulated values of the ttiallate flux have a similar magnitude as the measured values and were in agreement with the measured values during the latter portion of the experiment. Discrepancies were observed at early time, especially during the first few hours of the experiment, and were attributed, primarily, to inaccuracies in the estimated values for the evaporation rate, during this time period. It is also possible that other mechanisms may be acting immediately following triallate application that are not accounted for in the simulation. More research is necessary to determine if other processes are occurring, and if so, to develop definitions of the mechanisms and include them into models so that the transport of volatile pesticides will be adequately simulated throughout all phases of the volatilization process.

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Table 1. Physical Properties of Triallate

Half life	82’	days
Henry’s Constant, K_H	0.00045’	
Organic Carbon Distribution Coefficient, K_{oc}	2400	
Saturated Vapor Density	$1.80\mathrm{x}10^{-9\dagger}$	g/cm^3
Solubility	$4.0\mathrm{x}10^{-6\dagger}$	g/cm’
Molecular Weight	304.7	

† - Data from Wauchope et al. (1992)

Table 2. Selected Simulation Parameters

Bulk Density, ρ_b	1.65	g/cm^3
Diffusion. liquid. D.	$2.986\mathrm{x}10^{-4}$	cm^2/min
Diffusion, vapor, D_v	2.986	cm^2/min
Fraction Organic Carbon, f_{oc}	1.0	%
Incorporation Depth	0.03	cm
Triallate Application Rate	11.5	kg/ha
Triallate Mass Applied	3.35	kg
Moisture Content of Soil, θ	0.15	
Porosity	0.38	

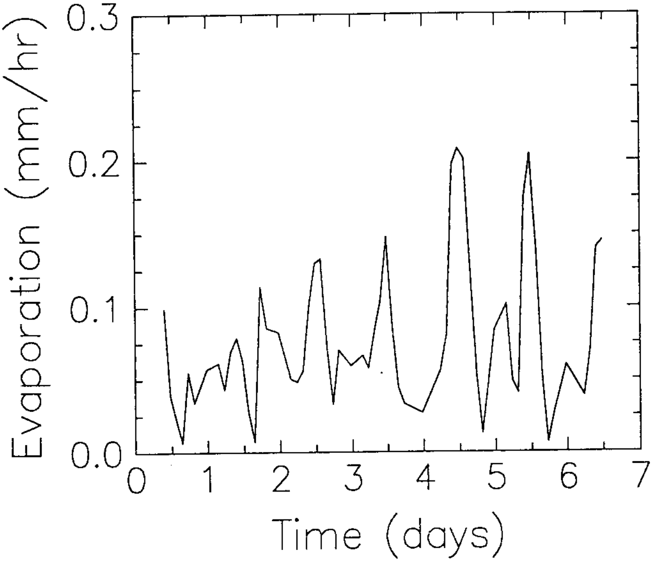

Figure 1 Time series of the evaporation rate at the experimental site.

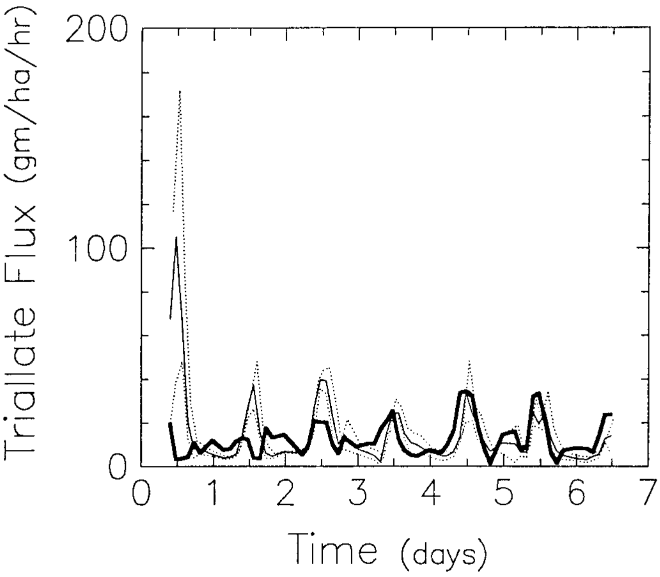

Figure 2 Comparison of measured and simulated volatilization rates for triallate. The thin-solid and dotted lines, respectively, are the average and the plus and minus one standard deviation from the average measured volatilization rate. The heavy solid line is the simulated volatilization rate.

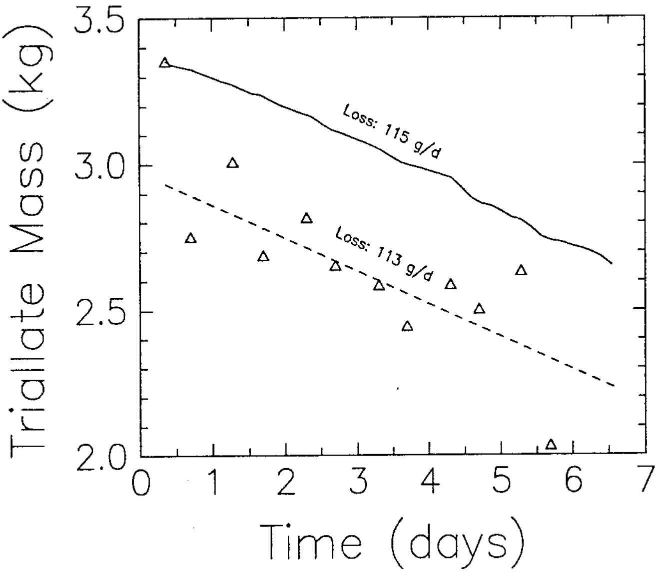

Figure 3 Cumulative triallate mass in the soil profile during the experiment. The dashed line is a regression line for the measured triallate mass using all data (points) except the initial value. The solid line is the simulated residual mass.

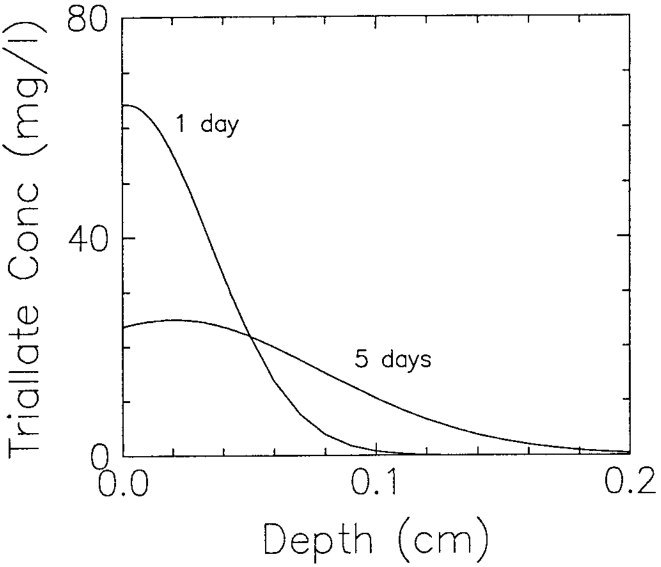

Figure 4 Simulated soil concentration in the soil profile at one and five days.