

## Diurnal Variation of Diazinon Volatilization: Soil Moisture Effects

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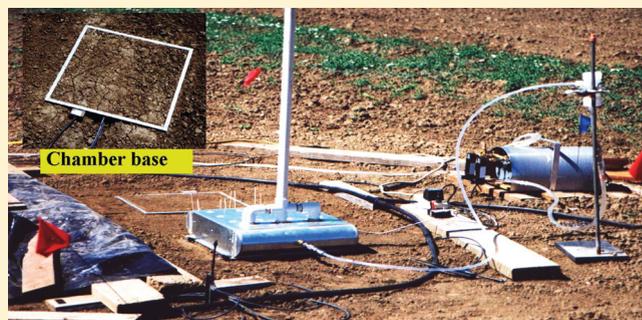
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**S** Supporting Information

**ABSTRACT:** Diurnal variations in diazinon volatilization were monitored in three field experiments conducted with differing soil moisture contents. The highest flux rates in all experiments were recorded just after diazinon application, but the magnitudes of those initial rates differed according to the soil moisture content, with wetter soil producing a higher rate:  $5.6 \times 10^{-4} \mu\text{g cm}^{-2} \text{min}^{-1}$  for initial soil moisture above field capacity,  $8.3 \times 10^{-5} \mu\text{g cm}^{-2} \text{min}^{-1}$  for initial soil moisture at field capacity, and  $2.5 \times 10^{-5} \mu\text{g cm}^{-2} \text{min}^{-1}$  for initially very dry soil. Volatilization decreased during the first day in the two experiments with initially wet soils but remained relatively constant in the experiment with initially dry soil.

The volatilization rate during the first night for the wettest soil remained about an order-of-magnitude higher than that observed for driest soil. When the surface dried in the experiment conducted at the intermediate water content, the volatilization rate and temporal pattern transitioned and became similar to that observed for the initially dry soil. Around noon of the second day, a daily maximum value was observed in the volatilization rate for wet soil, whereas a minimum value was observed for the dry soil, resulting in an order-of-magnitude difference. This study demonstrates the importance of soil moisture on emissions of pesticides to the atmosphere.



### INTRODUCTION

Pesticides are a critical component of modern agriculture. Volatilization is one of the principal processes leading to the dispersion of pesticides in the environment.<sup>1,2</sup> Airborne transport of pesticides poses a risk to persons living near treated fields. To protect public health, there is a need for more information on the important processes and mechanisms that affect pesticide fate and transport under typical field conditions.

Field volatilization rates are controlled by simultaneous interactions between chemical properties, soil and weather conditions, and usage patterns. Past studies found that volatilization exhibits a diurnal cycle that appears to be related to soil–water content and solar radiation<sup>3</sup> or surface soil temperature.<sup>4,5</sup> When soils were wet, the volatilization rates, solar radiation, and soil temperature peaked together at mid-day. However, when soil–water content was low, peak volatilization rates no longer coincided with solar radiation and surface soil temperature.<sup>3–5</sup>

During the past decade several predictive models capable of forecasting hourly emission rates have been developed and tested against measured data.<sup>6–9</sup> These studies found that the order of magnitude of the simulated volatilization flux was in good agreement with the field measurements. However, the timing of the maximum flux rate during the day was not correctly described, probably due to increased sorption under dry soil conditions. This point requires further investigation. Hourly emission rates are very important for determining the risks of acute inhalation toxicity, and thus their accurate estimation is crucial.

This paper presents field data collected during June–July 2000 at a UC-Davis research facility. The study was conducted to measure volatilization rates of diazinon [O, O diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate] after applying to bare soil with differing soil–water contents. This study was a follow-up of a previous study that focused on the effect of initial water content and evaporation condition on the volatilization of soil-incorporated diazinon under isothermal conditions.<sup>10–12</sup> The purpose of the present study was to investigate the effect of soil moisture status on volatilization of diazinon under typical semiarid field conditions. The experiment was designed to obtain detailed information that will aid in testing and improving predictive models. Consequently, we used small field plots and measured volatilization fluxes using flux chambers.<sup>13</sup> The accuracy of the chamber method in comparison to various micrometeorological methods for measuring pesticide volatilization was studied by several investigators.<sup>14–16</sup> It was found that within the limits of estimated uncertainty in volatilization measurement (50% and more<sup>17</sup>), there is a good agreement between flux density values produced with aerodynamic and flux chamber methods. The current study consists of three field experiments, each three days in duration. Over the course of the experiments, diurnal changes

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in volatilization were measured along with changes in soil–water content and soil temperature at two depths. At the end of the experiment, the total amount of diazinon remaining in the soil was measured.

## EXPERIMENTAL PROCEDURES

The field site was located at a research facility of the University of California at Davis. The soil was Yolo silt loam (fine-silty, mixed, nonacid, thermic Typic Xerorthent), pH of 6.9, and consisted of 35% sand, 47% silt, 18% clay, and 1.48% organic matter. Volatilization rates were measured using flux chambers.<sup>13</sup> Three field plots measuring 2 m × 1.2 m were used for the different experiments. Each plot (see Figure S-1, Supporting Information) contained two chamber bases (40 cm × 40 cm × 6 cm) that served as two replications (Loc1 and Loc2). The chamber bases were inserted 6 cm into the soil. Volatilization rates were measured by alternating the placement of the flux chamber onto one of the two chamber bases.

**Pesticide Properties.** Diazinon is a typical organophosphate insecticide used in a wide variety of home, turf, and agricultural applications. The properties of diazinon are summarized in Table S-1, Supporting Information.

**Pesticide Application.** Diazinon was applied to the bare soil surface by hand spraying at a rate of 1–1.5 kg/ha. The applications were at 10:00, 9:00, and 8:30 for experiments 1, 2, and 3, respectively. The initial volumetric water contents in the surface layer (0–1 cm) were 0.22, 0.075, and 0.29 for experiments 1, 2, and 3, respectively. In experiment 3, 1 mm of water was applied 1 h after spraying. The initial water contents were determined gravimetrically from soil samples collected from the field plot outside the chamber bases.

**Flux Chamber and Volatilization Rate Measurements.** A detailed description of the flux chamber and its performance was given previously.<sup>13</sup> The chamber consisted of a large air inlet (2.5 cm), a main body (40 cm × 40 cm) divided into two sections by a partition plate, five fans, aerodynamic edges, and an air outlet. The entire chamber body was made with 20-gauge galvanized sheet metal. The chamber fans, partition plate, and aerodynamic ends were designed such that air was forced to uniformly sweep over the entire soil surface. A fraction of the air flowing inside the chamber was sampled at the outlet. The air velocity inside the chamber was controlled by fan speed and the outlet flow rate (i.e., suction). In the current study, the fan speed was set at medium, and a vacuum was applied to the outlet that produced a flow rate of 20 L/min. It was shown that under these conditions the chamber accurately measures gas emissions from soil.<sup>13</sup> The pesticide volatilization rate (flux) was calculated using

$$\text{flux} = \frac{Q(C_{\text{out}} - C_{\text{in}})}{A} \quad (1)$$

where  $Q$  is the suction flow rate,  $C_{\text{in}}$  and  $C_{\text{out}}$  are the inlet and outlet concentrations, respectively, and  $A$  (0.16 m<sup>2</sup>) is the soil area covered by the chamber.

**Air Sampling.** Diazinon vapor in the chamber outlet was trapped in a Teflon cap (SAVILLEX Corp. Minnetonka, MN) packed with XAD-4 sorbent (SUPELCO, Inc. Bellefonte, PA) precleaned by the multiple-extraction method.<sup>18</sup> [Mentions of products and trade names are for the benefit of the reader and do not imply a guarantee or endorsement of the product by USDA.] Each cap (4.4 cm i.d. and 12.1 cm length) was filled with 30 mL XAD-4 resin, which was exchanged with fresh material at the end

of each sampling period. Each resin sample was placed into a clean glass jar with a Teflon-lined lid at the end of each sampling period. These samples were then stored on dry ice until transferred to a freezer (−20 °C) for storage until analyzed. The sampling time interval ranged between 30 and 60 min from 8:00 to midnight during each experiment. For experiment 1, no sampling occurred between midnight and 8:00, whereas a 4-hour sampling interval was used during this period for experiments 2 and 3.

**Soil Sampling.** Soil samples for determining diazinon residue were taken using rings 5 cm in diameter and 1 cm deep. During the experiments, samples were taken from the sprayed area between the two chamber bases. In experiments 1 and 2 samples from the 0–1 cm soil layer were taken at 1, 10, 27.5, and 33.5 and 0.5, 8, and 51 h after application, respectively. In experiment 3, one soil sample was taken from six soil depths: 0–1, 1–2, 2–3, 3–4, 4–5, and 5–6 cm after 1, 3, 10, and 33.5 h after application. At the end of the experiments ( $t = 58, 72, \text{ and } 58$  h for experiment 1, 2, and 3, respectively) soil samples were taken from soil within each chamber base. In Experiments 1 and 2, two samples were taken from two depths, 0–1 cm and 1–2 cm, and in Experiment 3 one sample was taken from the six soil depths. Control samples were taken about 0.5 h before pesticide application. From each soil sample, 2 to 4 subsamples were taken for extraction and determination of diazinon residual concentrations. The concentrations of the subsamples were then averaged.

**Chemical Analysis.** A complete description of chemical analysis can be found in the Supporting Information.

**Soil Temperature and Moisture Measurements.** The diurnal variation of soil temperature was measured at 2 soil depths (1 and 5 cm) using a Campbell Scientific 101 thermistor probe (accuracy ±0.5 °C from −30 – 53 °C).

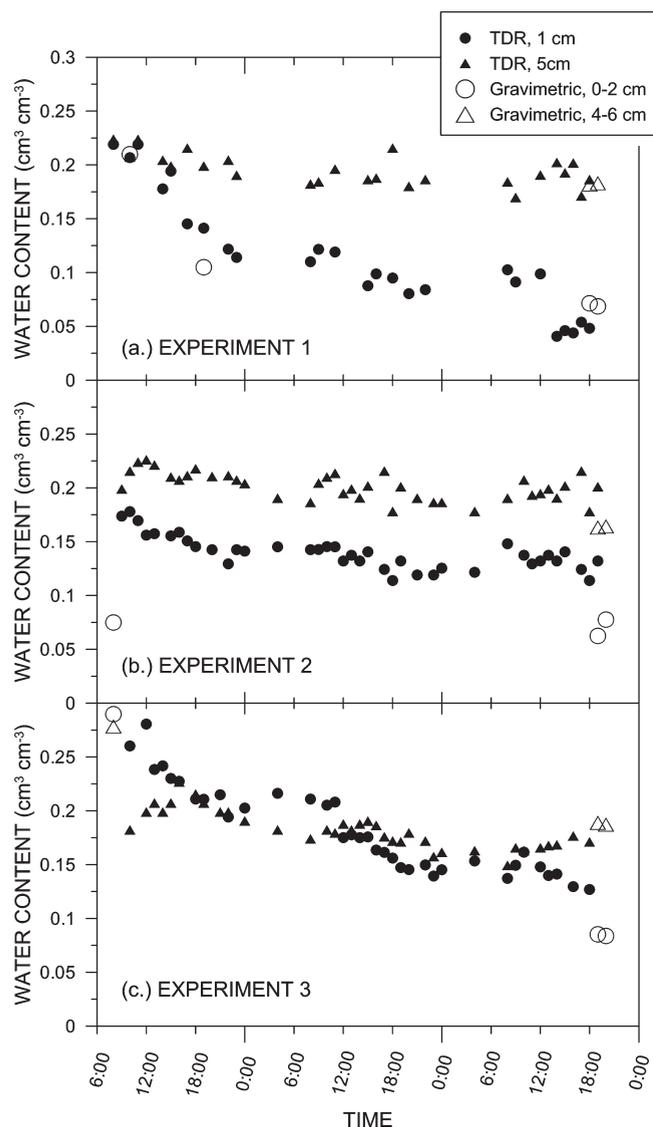
The diurnal variations of soil moisture were measured using Time Domain Reflectometry (TDR). The TDR probes had three-prongs, 15 cm long and 1 cm apart. Four probes were installed horizontally in the soil, within the two chamber frames, at 1- and 5-cm depths. Measurements were made with a Tektronix 1502C equipped with a Tektronix SP232 serial extended function module connected to a laptop computer. WinTDR<sup>19</sup> was used to control, execute, and analyze the measurements. Preliminary measurements were performed to calibrate the TDR probes to the Yolo soil. At the end of the experiments, soil samples from the 0–2 cm and 4–6 cm soil layers within the chamber frames were taken for determination of bulk density and gravimetric moisture.

**Meteorological Data.** Variations of the meteorological parameters solar radiation, wind speed, air temperature, and humidity were measured 2 m aboveground using a standard meteorological station placed near the site.

## RESULTS AND DISCUSSION

Three scenarios are examined in this study: (1.) Pesticide application on soil at field capacity moisture content, followed by drying conditions (no subsequent additions of water) (Experiment 1), (2.) Pesticide application on extremely dry soil with no subsequent additions of water (Experiment 2); and (3.) Pesticide application on moist soil followed by a minor irrigation (or precipitation) event one hour after pesticide application (Experiment 3).

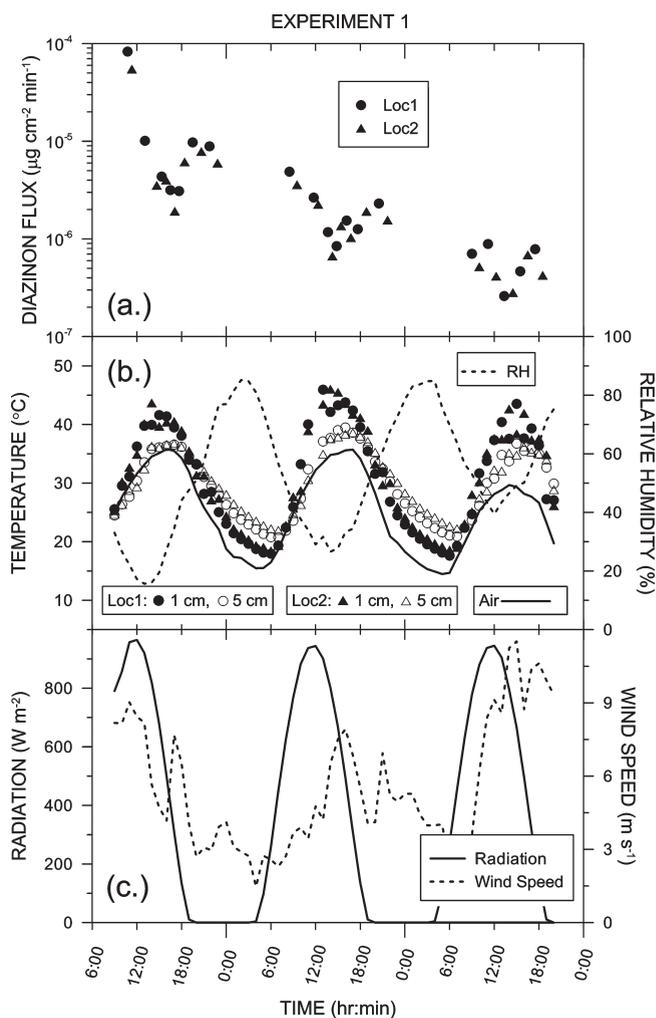
The temporal variations of soil moisture measured at two depths during the three experiments are shown in Figure 1. In Figure 1, reasonable agreement exists between the TDR and gravimetrically determined water contents, except for the 1 cm depth in Experiment 2 (Figure 1b). For all experiments, we



**Figure 1.** Temporal variations of soil moisture measured at two depths (about 1 and 5 cm) during the three days of (a.) Experiment 1, (b.) Experiment 2, and (c.) Experiment 3.

consider the gravimetric data to be more reliable, and consider that data to be the most accurate measurement of the water content. The TDR data, though less accurate, is nevertheless useful for visualizing the time course of the soil–water content during the periods where gravimetric data is not available. Water content data at the soil surface is useful for interpreting the temporal variations in pesticide flux.

Experiment 1 was performed during the period of June 20–23, 2000. The initial volumetric water content of the soil at the time of application (10:00) was 0.22, which is field capacity of Yolo silty loam.<sup>12</sup> Due to drying, the water content at the soil surface decreased to about 0.11 by 22:00–23:00 of the first day and dropped to 0.09 by noon of the second day (Figure 1a). Chen and Rolston<sup>12</sup> found that for Yolo silty loam, a water content of 0.1 (g/g) represented a threshold value, below which diazinon volatilization dropped off exponentially because of diazinon sorption on the dry soil surfaces. The air–soil partition coefficient measured for this soil is 11,050 m<sup>3</sup>/g.<sup>10</sup> The bulk densities measured for experiments 1, 2, and 3 were 1.23, 1.26,



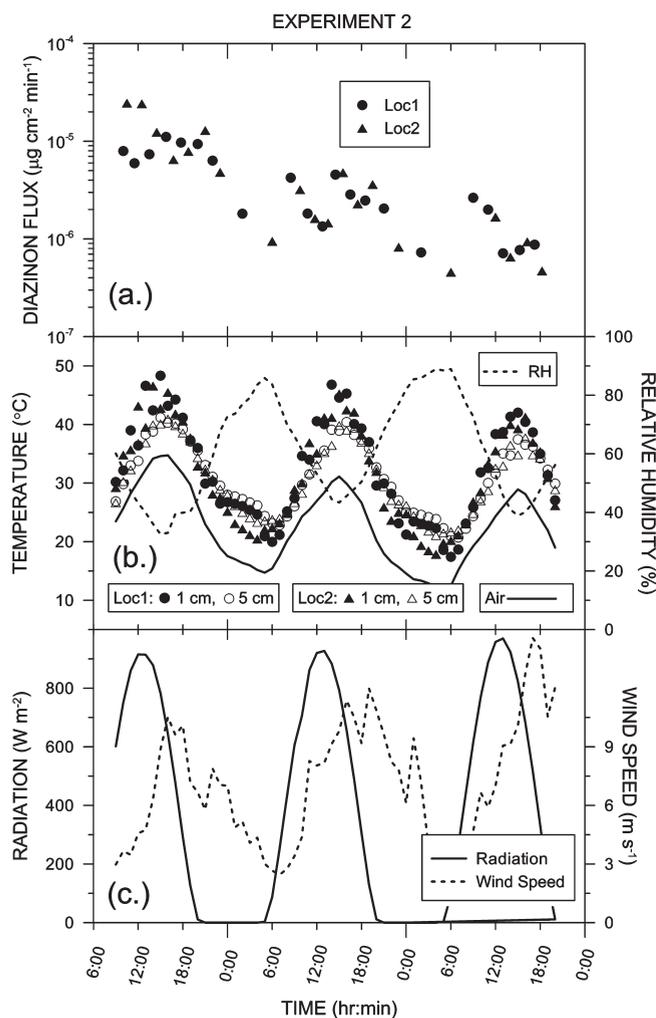
**Figure 2.** Temporal variations of (a.) fluxes, (b.) air temperature, soil temperature at two depths (about 1 and 5 cm) and air relative humidity, and (c.) solar radiation and wind speed, measured during the three days of Experiment 1.

and 1.29, respectively. Accordingly, the corresponding volumetric threshold values for experiments 1, 2, and 3 were 0.123, 0.126 and 0.129, respectively. Thus, in Experiment 1, the water content in the top 1 cm of soil was below the threshold value by the late evening of the first day.

Experiment 2 was performed during the period of June 28–30, 2000. The initial volumetric water content, 0.075, was below the threshold water content. The gravimetric and TDR water contents during this experiment were relatively stable.

Experiment 3 was performed during the period of July 12–14, 2000. The initial volumetric water content, 0.29, was higher than field capacity. Irrigation with 1 mm of water, 1 h after pesticide application, increased the volumetric water content in the upper soil layer to about 0.3. The 1 cm water content at the end of the experiment was about 0.085, below the approximate volumetric water content threshold value for Experiment 3 (Figure 1c).

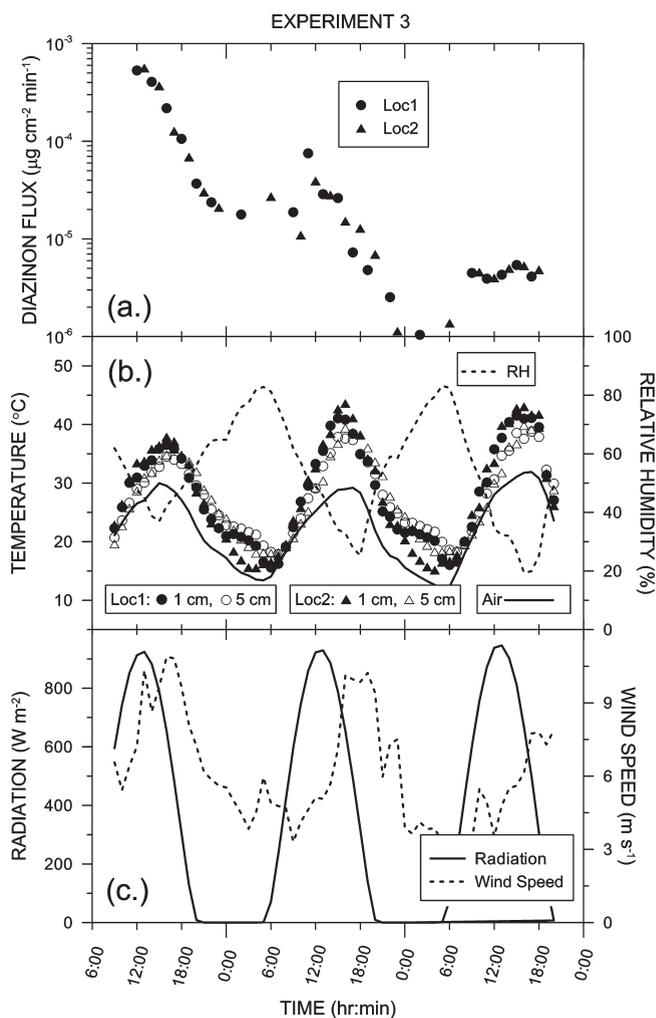
The temporal variations of diazinon fluxes, meteorological parameters (solar radiation, air temperature, air relative humidity, and wind speed) and soil temperature at two depths (1 and 5 cm) measured during Experiments 1–3 are given in Figures 2–4, respectively. Generally, diazinon fluxes measured at the two locations (Loc1 and Loc2) followed the same pattern and served



**Figure 3.** Temporal variations of: (a.) fluxes, (b.) air temperature, soil temperature at two depths (about 1 and 5 cm) and air relative humidity, and (c.) solar radiation and wind speed, measured during the three days of Experiment 2.

as two replications for the soil moisture conditions (Figures 2a, 3a, and 4a). This behavior supports the reliability of the measured fluxes. The maximum solar radiation, measured at 12:00, was about  $915\text{--}970\text{ W m}^{-2}$  (Figures 2c, 3c, and 4c). The air temperature, relative humidity, and wind speed, respectively, varied between  $12\text{--}36\text{ }^{\circ}\text{C}$ ,  $16\text{--}89\%$ , and  $1.2\text{--}14.6\text{ m s}^{-1}$  (Figures 2, 3, and 4). The soil temperature varied between  $13\text{--}47\text{ }^{\circ}\text{C}$  depending on soil depth and moisture conditions. Larger diurnal variations in soil temperature were observed at shallow depths ( $\sim 1\text{ cm}$ ) and for dryer soil conditions (Figures 2b, 3b, and 4b).

**Moisture Effect on Diazinon Volatilization.** Different volatilization curves were obtained for the three experiments (Figures 2a, 3a, and 4a). The curves differ in their temporal patterns and in their magnitudes. In all cases, volatilization was highest in the hours after application. The initial flux rates correlated with the initial soil moisture content, with wetter soil conditions producing a higher flux rate:  $5.6 \times 10^{-4}\text{ }\mu\text{g cm}^{-2}\text{ min}^{-1}$  (Experiment 3)  $> 8.3 \times 10^{-5}\text{ }\mu\text{g cm}^{-2}\text{ min}^{-1}$  (Experiment 1)  $> 2.5 \times 10^{-5}\text{ }\mu\text{g cm}^{-2}\text{ min}^{-1}$  (Experiment 2). In Experiment 2, with initially very dry soil, the flux was relatively consistent throughout the first day. In Experiments 1 and 3, with high initial soil moisture, volatilization decreased steadily throughout the first afternoon and evening.



**Figure 4.** Temporal variations of: (a.) fluxes, (b.) air temperature, soil temperature at two depths (about 1 and 5 cm) and air relative humidity, and (c.) solar radiation and wind speed, measured during the three days of Experiment 3.

The decrease in the flux rate for Experiment 3 (wettest soil) was relatively smooth and steady (Figure 4a). In Experiment 1 (Figure 2a), the flux dropped very sharply until about 17:00 and then increased until about 20:00–22:00. Since flux data were not collected in Experiment 1 between 23:00 and 8:00, volatilization pattern and magnitude during this interval are unknown. The rapid decrease in Experiment 1 was such that by the late afternoon and early evening hours of the first day, Experiments 1 and 2 exhibited similar volatilization rates and patterns. This finding supports the previously mentioned observation that by late afternoon of the first day the water content at the soil surface layer in Experiment 1 had decreased below the moisture threshold. The volatilization rates observed for Experiment 3 during the first night were about an order of magnitude higher than those observed for Experiment 2 and presumably Experiment 1, based on similarity in volatilization pattern and magnitude during 18:00–23:00 of the first day and 8:00–12:00 of the second day.

Around noon of the second day, a daily maximum value was observed in the volatilization rate for Experiment 3, while a minimum value was observed in Experiments 1 and 2. Similar volatilization rates were observed for Experiments 1 and 2 during

the morning and afternoon hours. Later, during the late evening of the second day, the volatilization rates observed for the three experiments were similar. This behavior was also observed on the third day except that a slight minimum was observed at 12:00 for experiment 3. Characteristic peaks around 8:00 and 20:00 were observed in experiments 1 and 2. Another peak around 14:00–15:00 was observed in experiment 2.

The temporal behavior in the volatilization curves is believed to be due to the effect of soil–water content on diazinon sorption to soil particles.<sup>3,4,9</sup> Measurements of vapor pressure of pesticide (dieldrin, lindane, DDT, and trifluralin) in soil at various water content conclusively demonstrated that the greater volatilization from wet than from dry soils is due mainly to an increased vapor pressure resulting from displacement of chemicals from soil surface by water.<sup>20–23</sup> The vapor pressure of these pesticides dropped to very low values when the water content was decreased below that equivalent to approximately one molecular layer. Vapor pressures increased to their original values upon rewetting the air-dry soil, indicating that the drying effect is reversible. Furthermore, Spencer and Cliath<sup>24</sup> found a significant increase in the volatilization rates of dieldrin from dry soil after exposure to high relative humidity. Chen and Rolston<sup>12</sup> examined the influence of initial soil–water contents and evaporation conditions on diazinon volatilization under isothermal conditions. The evaporation conditions were varied by passing wet air or dry N<sub>2</sub> alternately across the soil surface. Their results showed increased diazinon volatilization when moist air was swept over the surface and a significant reduction in volatilization when dry N<sub>2</sub> was swept. Prueger et al.<sup>4</sup> found that metolachlor volatilization flux from dry soil surfaces increases with increasing relative humidity. It should be mentioned that soil–water content effects are especially important in adsorption of relatively nonpolar organic chemicals by soil.<sup>25</sup>

These studies show that water content affects volatilization through its effect on pesticide sorption. Under fairly wet conditions, where volumetric water content at 1 cm depth was in the range of 0.29 to 0.15 (Experiment 3 days 1 and 2), volatilization follows Henry's law and increasing soil temperature results in higher volatilization rates; at day 2 between 10:00 to 12:00 the volatilization rates increased from  $1.09 \times 10^{-5}$  to  $3.9 \times 10^{-5} \mu\text{g cm}^{-2} \text{min}^{-1}$  while soil temperature at 1 cm increased from 25 to 32.6 °C. On the other hand, in dry soils (Experiments 1 and 2) when soil–water content is below a threshold value, volatilization is controlled by sorption of pesticide vapor at the presumably air–solid interfaces; and any additional water (vapor or liquid) results in higher volatilization rates due to decreasing sorption. Water can be supplied by condensation as a result of high RH and low surface temperatures, by upward transport of water vapor from the deeper soil, or by some combination of both mechanisms. These mechanisms might explain the small peaks observed in experiments 1 and 2 around 8:00 and 20:00. The peak at 8:00 may be a result of combined effect of sorption decrease as a result of water condensation during night hours (high RH and low soil temperatures) and soil temperature increase due to solar radiation. At 20:00, the first hour of darkness, a water condensation at soil surface can accrue due to increase on air RH and decrease of soil surface temperature.

Further research on the effects of moisture on diazinon volatilization under field conditions should include a comparison of measured data with model predictions and a related sensitivity analysis for model discrimination. The analysis should include a comprehensive nonisothermal model<sup>26</sup> with an expression for

vapor sorption at the solid–gas interface<sup>10</sup> and various approaches for heat and moisture transport. Neither Henry's Law or a simple linear sorption relationship apply when predicting a pesticide's vapor concentration at low soil–water contents since the vapor sorption of volatile organic compounds (VOCs) onto soils and soil materials in the dry region (water content < about 4 or 5 layers of water molecule coverage to oven-dry) increases exponentially with decreasing water content.<sup>27–30</sup> It is believed that in the nonlinear partitioning region, the change of soil sorption capacity for organic vapor is the result of competition between water molecules and organic molecules for sorption sites on soil particles, with water molecules sorbed preferentially.<sup>31,32</sup> The volatilization curves measured in Experiments 1 and 2 suggest that the conditions in these experiments were very likely affected by the nonlinear behavior of vapor–liquid-sorption process, where, a change in the partition coefficient  $K_D'$  (=the organic chemical content in soil/the organic vapor concentration in soil air) is affected by the water vapor sorption characteristics. This relation for diazinon and Yolo silt loam was evaluated and measured.<sup>10</sup> Chen and Rolston<sup>12</sup> showed that including vapor sorption at the solid–gas interface had a crucial rule in predicting diazinon volatilization rates under dry soil conditions.

**Soil Residues.** Soil residues of diazinon measured over the course of the three experiments are summarized in Table S-2, Supporting Information. Data for Experiment 1 suggest a non-uniform application since there is a relatively large variation among values measured for different soil samples collected 1 and 10 h after application (i.e., coefficient of variation, CV, of ~35%). The deviation between the subsamples taken for extracts was less than 5% (data not shown), and thus the variability was not due to extraction or analytical techniques. The residue values for samples taken 27.5 h after application were higher than those recorded for 1 h after application and the CV was 28%. The reason for the higher values is not known, although similarly high values were found for the two chamber bases at the end of the experiment. The residue data for Experiment 2 indicate that pesticide application outside the chamber bases was more uniform (CV from 15 to 20%). However, the chamber base values recorded for Loc2 were about 1.7 higher than those obtained for Loc1. Nevertheless, the decrease in soil residue over time was noticeable. The decrease in soil residue observed in Experiments 2 (dry soil conditions) and 3 (wet soil conditions) was similar, to about 0.26–0.48 of initial values. In all three experiments, very small amounts of diazinon were measured in the 1–2 cm layer (less than 5% of the initial surface layer values), and no diazinon was detected below this depth. This suggests that the migration of diazinon below the 0–1 cm layer was insignificant. This observation follows the results of Jury et al.<sup>33</sup> who showed that diazinon has relatively low convective (category 2 that represents moderate mobility) and diffusive (category 1 that represents insignificant diffusive mobility) mobility times. In the absence of irrigation, migration in soil would be negligible over a 3-day time period.

**Chamber Effect on Volatilization Flux.** The soil temperature diurnal variation is accompanied by small fluctuations due to the effect of the flux chamber on soil temperature during the daylight hours (Figures 2b–4b). The extent of the effect depends on the time of day and soil moisture. The greatest effect was measured for dry soil at mid-day (Figure 3b). During the night time, the chamber prevented long wave emissions from the soil and increase the soil temperature (Figures 3 and 4).

Pesticide volatilization is a dynamic process affected by many fate and transport mechanisms and prevailing soil and atmospheric conditions. The effect of soil–water content has been shown to play an important role in affecting pesticide sorption and, in turn, volatilization. Further study is needed to refine process models and to develop predictive tools that realistically simulate pesticide volatilization under highly variable soil temperature and moisture conditions.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Description of the field setup, diazinon properties, soil residue, and chemical analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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