Volatilization of Alachlor from Polymeric Formulations

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Pesticides may be dispersed throughout the environment by several means, including groundwater contamination, surface water contamination, and volatilization with subsequent atmospheric transport and deposition. In earlier research primarily directed at reducing the potential for groundwater contamination, a number of herbicides were microencapsulated within several different polymers. These polymeric formulations were evaluated for efficacy in the greenhouse. In the studies described in this paper, three polymeric alachlor formulations that were the most effective in the greenhouse were evaluated in laboratory volatility studies using pure alachlor and a commercial formulation (Lasso 4EC) for comparison purposes. In a given experiment, technical alachlor, Lasso 4EC, and two polymeric formulations were applied to soil and evaluated in a contained system under 53% humidity with a fixed flow rate. Evolved alachlor was collected in ethylene glycol, recovered with C18 solid phase extraction cartridges, and analyzed by reverse-phase high-performance thin-layer chromatography with densitometry. Duration of the studies ranged from 32 to 39 days. In studies in which all formulations were uniformly incorporated in the soil, total alachlor volatilization from the polymeric microcapsules was consistently lower than that from the alachlor and Lasso 4EC formulations. In studies in which the polymeric formulations were sprinkled on the surface of the soil, microcapsules prepared with the polymer cellulose acetate butyrate released the smallest quantity of volatilized alachlor.

KEYWORDS: Volatilization; alachlor; polymer; microcapsule; ethylene glycol; reverse-phase high-performance thin-layer chromatography; densitometry

INTRODUCTION

Pesticides may be dispersed throughout the environment by several means, including groundwater contamination, surface water contamination, and volatilization with subsequent atmospheric transport and deposition. Volatilization is not just a source of pesticide loss but can be a contributor to environmental pollution of surface water and groundwater, as a consequence of precipitation. Studies have been conducted to determine the volatilization of a variety of pesticides in the field (*1−6*) and the laboratory (*6−14*). Volatilization studies are typically conducted using a volatilization chamber (*3, 7, 9−12*). Microbalances (*8*) and ^{14}C-labeled pesticides (*13, 14*) have also been employed.

The value of microencapsulation in controlling vapor losses has been evaluated for a number of herbicides (*1, 3, 4, 7*). In studies of formulations of chlorpropham, the active ingredient volatilized from the conventional emulsifiable concentrate ∼5 times more rapidly than from a microencapsulated formulation (*1*). Several studies have dealt with the effect of starch encapsulation on the volatilization of atrazine and alachlor (*3, 4, 7*). Wienhold and Gish (*3*) used an acrylic chamber to measure volatilization of the two herbicides in the field using polyure-

thane foam plugs to quantitatively trap the herbicides. In comparison with a commercial wettable powder formulation, starch encapsulation of atrazine reduced volatilization from both conventionally tilled and no-till corn fields. In comparison with a commercial microencapsulated formulation, starch encapsulation of alachlor showed no difference in volatilization from a conventionally tilled field. However, in the no-till field after 35 days, cumulative volatilization from the commercial formulation was 9%, but only 4% from the starch-encapsulated formulation.

In earlier research primarily directed at reducing the potential for groundwater contamination, a number of herbicides were microencapsulated within several different polymers, and the polymeric formulations were evaluated for efficacy in the greenhouse (*15−17*). The studies included polymeric microcapsules of atrazine and metribuzin (*15*), cyanazine (*16*), and alachlor and metolachlor (*17*). Significant losses of alachlor due to volatilization have been reported in field studies (*2*). Encapsulated formulations of alachlor have shown some promise in reducing volatilization (*3, 4*). In this paper, the evaluation of the effectiveness of three selected polymeric formulations in reducing the volatilization of alachlor will be described. The procedure employed, based upon a modification of a literature method (*11, 12*), uses relatively inexpensive equipment.

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Volatilization of Alachlor

J. Agric. Food Chem., Vol. 52, No. 22, 2004 **6743**

Figure 1. Components of system employed in alachlor volatilization experiments.

MATERIALS AND METHODS

Chemicals and Reagents. Technical alachlor (provided by Monsanto, St. Louis, MO) was recrystallized from 95% ethanol, affording material of mp 39.1−41.9 °C [lit. mp, 39.5−41.5 °C (*18*)]. The 88% hydrolyzed poly(vinyl alcohol) Airvol 205 (low viscosity) was provided by Air Products and Chemicals, Inc., Allentown, PA. The following polymers were purchased from Aldrich Chemical Co., Inc., St. Louis, MO: cellulose acetate butyrate, butyryl content 17%, $T_m = 235$ °C (CAB); ethyl cellulose, ethoxyl content 48%, viscosity (5% solution in 80:20 toluene/ethanol) 22 cP [EC22]; ethyl cellulose, ethoxyl content 48%, viscosity (5% solution in 80:20 toluene/ethanol) 100 cP [EC100]. Ethylene glycol, 99+%, was purchased from Aldrich Chemical Co., Inc. HPLC reagent grade dichloromethane and methanol were used as solvents.

Preparation of Polymeric Microcapsules. Using the procedure previously described (*17*), fresh formulations of alachlor were prepared using the polymers CAB, EC22, and EC100 and the emulsifier Airvol 205, giving polymeric formulations designated CAB-205, EC22-205, and EC100-205. These three formulations were the most effective in greenhouse studies and showed controlled-release properties (*17*). In a typical microcapsule preparation, a solution of 1.25 g of alachlor and 5.00 g of polymer in 100 mL of dichloromethane was added slowly to the vortex of 500 mL of a 0.25% Airvol 205 solution, stirred at 350 rpm. Stirring was continued for 24 h, at which time evaporation of the organic solvent was complete. After the stirring was halted, the microcapsules were allowed to settle. The supernatant liquid (including floating solids) was decanted, 500 mL of distilled water was added, and the mixture was stirred for 1.0 h. After settling, the microcapsules were filtered, allowed to air-dry, and finally dried in a vacuum desiccator until a constant weight was obtained.

Laboratory Volatility Studies. Laboratory volatility studies were conducted using purified technical alachlor, a commercial formulation (Lasso 4EC), and the three polymeric alachlor formulations. The percentage of alachlor in these formulations was determined by reverse-phase high-performance thin-layer chromatography (RP-HPTLC) with densitometry (*19*) with the following results: CAB-205, 20.1% alachlor; EC22-205, 17.9%; EC100-205, 18.1%. A total of four volatilization experiments were conducted. In a given experiment, technical alachlor, Lasso 4EC, and two polymeric formulations were evaluated in two contained systems under 53% humidity with a fixed flow rate produced by vacuum. **Figure 1** shows the system employed. For each study of four alachlor formulations, the system had the following components: four Scienceware 250 mL polypropylene gas washing bottles fitted with porous polyethylene disks of 70 μm porosity (Fisher Scientific, Pittsburgh, PA); four 500 mL Erlenmeyer flasks containing the alachlor formulations; four Pyrex gas washing bottles (250 mL capacity) equipped with 12 mm coarse fritted cylinders; one 500 mL Erlenmeyer flask containing anhydrous calcium chloride as desiccant; and one 65 mm direct reading flow meter mounted on a tripod base (Cole-Parmer Instrument Co., Vernon Hills, IL). The experiments were conducted at room temperature (∼25 °C). Each experiment was run in duplicate with a parallel setup of the system components, and results were averaged.

Each polypropylene gas washing bottle served as a humidifier and contained 100 mL of constant-humidity solution of $Mg(NO_3)_2 \cdot 6 H_2O$, providing an intermediate relative humidity of 53%. Volatilization rates have been observed to be higher from moist soil than from dry soil (*7*). The humidifier was connected to a flask containing soil and an alachlor formulation. Each flask contained 100 g of dry Evesboro Ap soil to which was homogeneously incorporated 7.7 g of water to achieve 80% of field capacity (one-third bar) (*20*). Alachlor was applied at a rate of 8 mg of active ingredient/100 g of dry soil. Purified technical alachlor was uniformly incorporated as a solution in 5.0 mL of methanol, and the methanol was allowed to evaporate before water was added. The commercial formulation Lasso 4EC was applied in 5.0 mL of water, and additional water was added to attain a total of 7.7 g. In all four experiments duplicate samples of alachlor, Lasso 4EC, and EC22-205 were used. In experiments I and III, duplicate samples of EC100-205 were used; in experiments II and IV, duplicate samples of CAB-205 were used. In experiments I and II, the polymeric alachlor formulations were uniformly incorporated in the soil; in experiments III and IV, the polymeric alachlor formulations were sprinkled on the surface of the soil. Each sample flask was connected to a Pyrex gas washing bottle containing 70 mL of ethylene glycol for collection of evolved alachlor. A set of four Pyrex bottles was connected to the flask containing calcium chloride desiccant, which was in turn connected to the house vacuum with a flow rate set at 1.2 L/min. After 1 day (24 h), the vacuum was turned off and the ethylene glycol solutions were collected for subsequent analysis and replaced with fresh ethylene glycol. Within 10−20 min, the vacuum was reapplied at flow rate of 1.2 L/min. After an additional 3 days, the collection of ethylene glycol samples was repeated. The process was subsequently repeated at 7 day intervals. Duration of the studies ranged from 32 to 39 days.

Isolation of Volatilized Alachlor. Evolved alachlor was recovered from ethylene glycol with C18 solid-phase extraction cartridges (Sep-Pak Plus, Millipore Corp., Marlborough, MA) according to the following protocol: (1) elute cartridge with 5 mL of methanol; (2) elute with 5 mL of water; (3) load the sample dissolved in a 50:50 mixture of ethylene glycol and deionized water (140 mL); (4) elute with 5 mL of water; (5) elute alachlor with 2 mL of methanol followed by 3 mL of dichloromethane into a 2 dram vial; (6) remove solvent under air current; (7) dissolve residue in 100 μL of methanol for alachlor quantification by RP-HPTLC with densitometry. All elutions were performed using syringes. A 60 mL syringe was used to load the 50:50 ethylene glycol/water mixture. The isolation protocol was followed on known concentrations of alachlor in ethylene glycol in order to determine its effectiveness. Duplicate extraction cartridges were used for each of three amounts of alachlor, and the extracted alachlor was determined by RP-HPTLC with densitometry (as described below). In the event, 99.4% of 125 μg of alachlor was recovered, 92% of 250 μg was recovered, and 87% of 375 μg was recovered. Because 125 μg greatly exceeds evolved alachlor in any of the volatilization experiments, extraction was considered to be quantitative.

Determination of Volatilized Alachlor. Evolved alachlor was analyzed by RP-HPTLC with densitometry (*19*). TLC was performed on C18 high-performance reverse-phase Uniplates (10 × 20 cm, 150 μm thickness, scored, RP18F; Analtech Inc., Newark, DE) as described previously (*19*). A standard solution of alachlor (0.10 μg/μL) was obtained by dissolving 10.0 mg of alachlor in 100 mL of methanol. Standards and sample solutions were drawn into microcapillary pipets and applied with a Nanomat III (Camag, Inc.). Each plate was spotted with 1.0, 2.0, 3.0, and 4.0 μL of standard solution and with 8.0 μL of each sample solution in duplicate. Each plate was developed using MeOH/H$_2$O (85:15) as mobile phase. Following drying, the plates were scanned at 200 nm with a variable-wavelength Shimadzu CS9000U dual-wavelength Flying Spot scanner. RP-HPTLC standard curves were analyzed by linear regression analysis. Taking into account the original volume of 100 μL of solvent, the calculated sample concentrations (micrograms) were multiplied by a factor of 12.5 to give the total evolved alachlor for a given sample. The means of the values for duplicate sample spottings were calculated for final data presentation.

Experimental Design. For each experiment, the experimental design was a split plot with four alachlor formulations as the main unit treatment. The main unit had a randomized complete block design with two replications for each main unit treatment. Measurements were taken over time, and time was a repeated measure subunit. For experiment I, cumulative volatilized alachlor from each of the four formulations was measured over six time periods ranging from 1 to 32 days. For the other three experiments, cumulative volatilized alachlor was measured over seven time periods ranging from 1 to 39 days. In analysis of the data, a quadratic or linear trend was used to predict alachlor as a function of time for each formulation (*21*). First, an *F* test ($P \leq 0.10$) was used to decide if the quadratic or linear trend should be used for the time effect. Then an *F* test ($P \leq 0.10$) was used to compare slopes among the formulations. If there was no evidence that the trends were different for each formulation, then the same trend was used for all formulations. From this analysis, volatilized alachlor for each formulation was predicted at a specified time. LSD tests ($P \leq 0.10$) were used to compare predicted volatilized alachlor among formulations. If the slopes were different for each formulation, then differences between predicted volatilized alachlor will be dependent on the specified time.

RESULTS AND DISCUSSION

In these studies, the effect of encapsulation of alachlor in cellulose acetate butyrate and two ethyl cellulose polymers on volatilization was evaluated, using pure alachlor and a commercial formulation (Lasso 4EC) for comparison purposes. The microcapsules were prepared according to the solvent evaporation process, which distributes the herbicide within a polymeric matrix. Upon microscopic evaluation, the microcapsules were spherical in shape and varied in size from about 140 to 575 μm in diameter (typically, 350−400 μm). There were no observable changes in the microcapsules after 1 month. The results of the four volatilization experiments are shown in **Figures 2−5**. In experiments I (**Figure 2**) and II (**Figure 3**), all four formulations were incorporated in the soil. In experiments 3 (**Figure 4**) and 4 (**Figure 5**), the polymeric formulations were sprinkled on the surface of the soil. In all experiments, 8 mg of active ingredient was applied to the soil. Evolved alachlor was measured after the first and fourth days of the experiment and subsequently at 7 day intervals. Experiment I was conducted for 32 days, whereas the other three experiments were conducted for 39 days.

After the first day in all four volatilization studies, greater alachlor volatilization occurred from soil samples containing pure alachlor and the commercial formulation than from those containing polymeric formulations. The same trend continued through the fourth day, with one exception (EC22-205, **Figure 5**). In general, the amount of incremental volatilized alachlor from the polymeric formulations increased relative to alachlor and Lasso 4EC after a cumulative elapsed time of 11 days and subsequent time intervals.
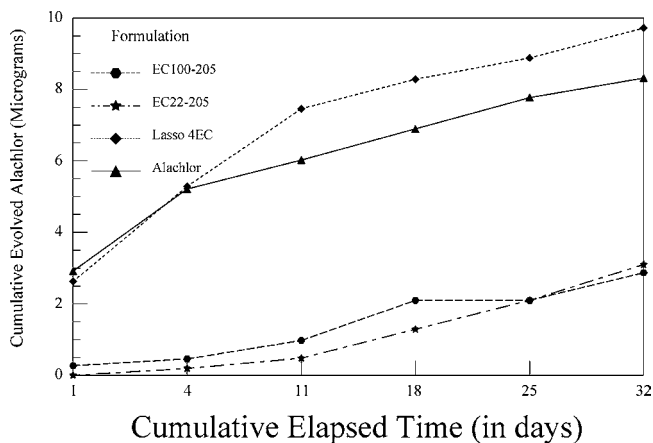

Figure 2. Volatilization from alachlor formulations, results of experiment I. All formulations were incorporated in the soil.
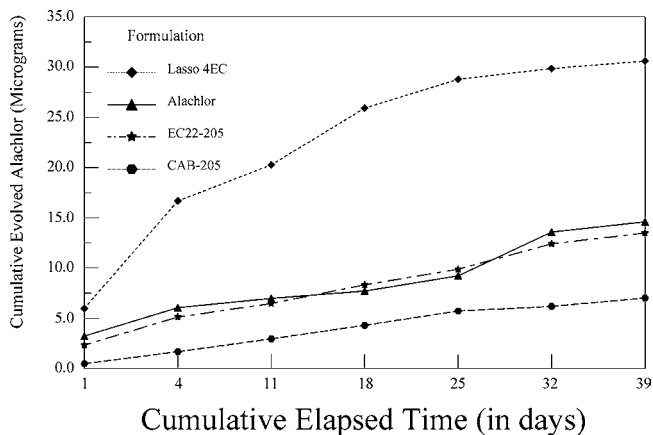

Figure 3. Volatilization from alachlor formulations, results of experiment II. All formulations were incorporated in the soil.
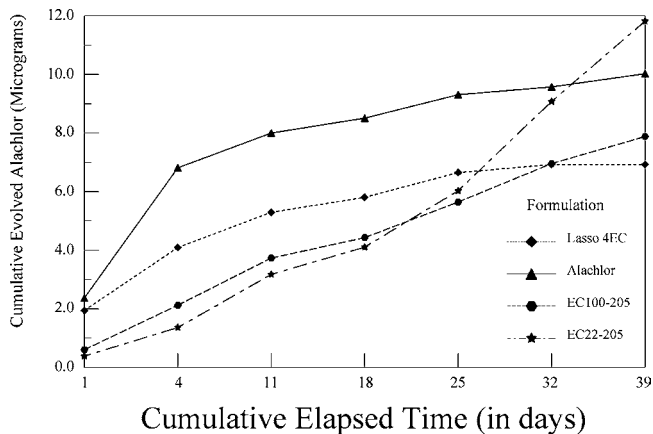

Figure 4. Volatilization from alachlor formulations, results of experiment III. Alachlor and Lasso 4EC formulations were incorporated in the soil. Polymeric formulations were sprinkled on the surface of the soil.

Table 1 shows the total alachlor evolved (in micrograms) for each formulation for the duration of the four volatilization experiments. Variability was observed from experiment to experiment, but there were some consistent trends. In experiment II, alachlor evolved from Lasso 4EC greatly exceeded volatilized alachlor from the other three formulations. In experiment IV, volatilization from the EC22-205 formulation was much higher. Volatilization from Lasso 4EC exceeded volatilization from pure alachlor with the exception of experiment III. In studies in which all of the formulations were incorporated in the soil (experiments
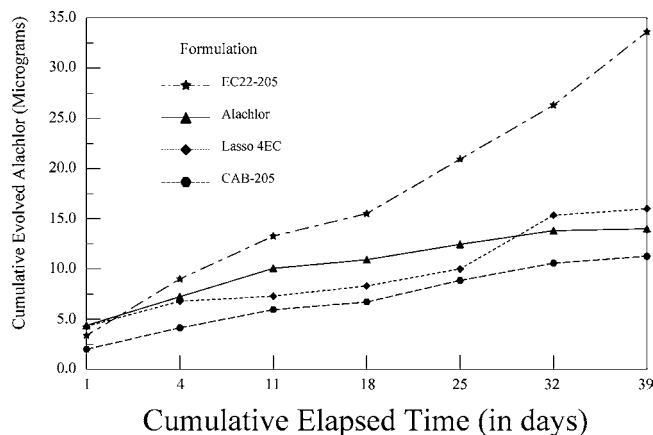
Volatilization of Alachlor

J. Agric. Food Chem., Vol. 52, No. 22, 2004 **6745**

Figure 5. Volatilization from alachlor formulations, results of experiment IV. Alachlor and Lasso 4EC formulations were incorporated in the soil. Polymeric formulations were sprinkled on the surface of the soil.

Table 1. Total Alachlor Volatilized for Four Experiments Comparing Four Alachlor Formulations per Experiment[a]

formulation	expt I	expt II	expt III	expt IV
Alachlor	8.32[a]	14.61	10.02	14.00
Lasso 4EC	9.72	30.61	6.93	15.98
EC22-205	3.10	13.48	11.82	33.62
EC100-205	2.87		7.88	
CAB-205		7.02		11.27

[a] Total evolved alachlor is measured in micrograms (μg).

I and II), total alachlor volatilization from the polymeric microcapsules was consistently lower than that from the alachlor and commercial formulations. In studies in which the polymeric formulations were sprinkled on the surface of the soil (experiments III and IV), total alachlor volatilization from the CAB formulation was lower than that from the alachlor and Lasso 4EC formulations. Volatilization from the EC100 formulation was comparable, and volatilization from the EC22 formulation was higher. Overall, total volatilized alachlor was low for all of the experiments, ranging from 2.87 μg (0.036% of the original 8.0 mg) to 33.62 μg (0.42%). In contrast, cumulative volatilization of alachlor after 35 days ranged from 4 to 14% in field studies (*3*). In studies using agroecosystem chambers, cumulative volatilization of alachlor after 35 days ranged from 2 to 32% depending on formulation and temperature (*7*).

The general observation that, in volatilization experiments in which all formulations were incorporated in the soil, evolved alachlor from the alachlor and Lasso 4EC formulations substantially exceeded that from the polymeric formulations only through the first 4 days could indicate increased degradation of the microcapsules with passage of time. When the polymeric microcapsules were sprinkled on the surface of the soil, the EC22 formulation appeared to be the most susceptible to degradation and the CAB formulation the least.

Considerable variability was observed for the same formulation from experiment to experiment. In addition, apparent anomalous results were obtained for Lasso 4EC in experiment II and for EC22-205 in experiment IV. A definite cause or causes of the discrepancies could not be determined. However, possible contributing factors include fluctuations in room temperature and the vacuum-induced flow rate and variations of the microbial content of the soil samples. Although all soil samples came from the same source, variations of microbial content from sample to sample could result in differences in degradation of the polymeric microcapsules. In addition, errors could be introduced during the periodic collection and replacement of ethylene glycol samples.

Statistical Analysis. The results of experiment I indicated a linear trend for predicting alachlor as a function of time. There was not a significant difference between the trends used for each formulation ($F = 1.3$, $P = 0.2875$). LSD ($P \leq 0.10$) comparisons of predicted alachlor indicated that the alachlor and Lasso 4EC formulations were not significantly different and that the EC100 and EC22 formulations were not significantly different, but the alachlor and Lasso 4EC formulations exhibited significantly higher volatilization ($P < 0.0001$) than the EC100 and EC22 formulations.

The results of experiment II indicated a quadratic trend for predicting alachlor as a function of time. The trend for Lasso 4EC was significantly different ($P \leq 0.10$) from the trend for the other three formulations. Therefore, a different trend was used for each formulation, and differences between formulations will vary over time. LSD ($P \leq 0.10$) comparisons of predicted volatilized alachlor showed that for time periods of 10, 20, and 30 days, the Lasso 4EC formulation exhibited significantly higher volatilization ($P < 0.0001$) than the other three formulations. In addition, the CAB formulation was significantly less volatile ($P < 0.02$) than the other formulations for all three time periods.

The results of experiment III indicated a linear trend for predicting alachlor as a function of time. The trend for EC22-205 was significantly different from the trend for the Lasso 4EC and alachlor formulations. Therefore, a different trend was used for each formulation, and differences between formulations will vary over time. LSD ($P \leq 0.10$) comparisons of predicted volatilized alachlor showed that the alachlor formulation exhibited significantly higher volatilization than the other three formulations for time periods of 10 and 20 days and that the alachlor formulation exhibited significantly higher volatilization than the Lasso 4EC and EC100 formulations at 30 days.

The results of experiment IV indicated a linear trend for predicting alachlor as a function of time. The trend for EC22-205 was significantly different ($P \leq 0.10$) from the trend for the other three formulations. Therefore, a different trend was used for each formulation and differences between formulations will vary over time. LSD ($P < 0.10$) comparisons of predicted volatilized alachlor showed that for time periods of 10, 20, and 30 days, the EC22 formulation exhibited significantly higher volatilization ($P < 0.10$) than the other three formulations. In addition, the CAB formulation was significantly less volatile ($P < 0.10$) than the other formulations for the time periods of 20 and 30 days and than the alachlor and EC22 formulations for 10 days. There was no significant difference between the alachlor and Lasso 4EC formulations for any of the time periods.

Conclusions. The overall results suggest that microencapsulation of alachlor with selected polymers can reduce volatilization, particularly when the formulation is incorporated in the soil for a direct comparison with the commercial formulation and during the first 4 days after application. When the polymeric microcapsules were sprinkled on the surface of the soil, microcapsules prepared with the polymer cellulose acetate butyrate released the smallest quantity of volatilized alachlor. Overall, the CAB formulation showed the most potential for reducing volatilization of alachlor. Statistically, it was significantly less volatile than the other formulations in both experiments II and IV.

Dailey

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