Polymeric Microcapsules of Alachlor and Metolachlor: Preparation and Evaluation of Controlled-Release Properties

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The microencapsulation of alachlor and metolachlor in the polymers cellulose acetate butyrate, ethyl cellulose, poly(methyl methacrylate), and poly(α-methylstyrene) with different emulsifiers is described. The controlled-release properties of these formulations were measured under greenhouse conditions on barnyardgrass, crowfootgrass, smallflower morningglory, and Palmer amaranth. The emulsifiers had little effect on the activity of the herbicides. The herbicidal activities of the poly(methyl methacrylate) and poly(α-methylstyrene) formulations were consistently lower on all weed species when compared to the activities of the cellulose acetate butyrate, ethyl cellulose, and commercial formulations. The ethyl cellulose formulation of alachlor exhibited controlled-release properties. The results with metolachlor were similar to those with alachlor except that none of the metolachlor formulations exhibited efficacy superior to that of the commercial formulation or controlled release properties.

Keywords: *Formulation; microencapsulation; persistence; herbicide activity*

INTRODUCTION

In the past decade, concern over the contamination of groundwater and surface water by pesticides has mounted (Wauchope, 1978; Squillace and Thurman, 1992; Pereira and Hostettler, 1993). Selected pesticides have been detected at extremely low levels in groundwater in isolated locations across the United States. In 1986, the U.S. Environmental Protection Agency disclosed that at least 17 pesticides used in agriculture had been detected in groundwater in 23 states (Cohen et al., 1986). According to a 1988 interim report, 74 different pesticides have been detected in the groundwater of 38 states. Contamination attributable to normal agricultural use has been confirmed for 46 different pesticides detected in 26 states (Williams et al., 1988). Gilliom et al. (1998) detected 75 pesticides at least once in 4800 water samples collected from 20 major river basins and aquifers in the United States during 1993−1995. Occurrence was much more frequent in streams than in groundwater.

The herbicides atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine], cyanazine [2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile], simazine (6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine), metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-traizine-5(4*H*)-one], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] have been frequently implicated in groundwater and surface water contamination (Cohen et al., 1986; Williams et al., 1988; Squillace and Thurman, 1992; Pereira and Hostettler, 1993). According to the National Alachlor Well Water Survey (Holden et al., 1992), within the targeted alachlor use area, alachlor was detected in 0.78% of the private rural domestic wells, atrazine in 11.7%, cyanazine in 0.28%, metolachlor in 1.02%, and simazine in 1.60%. It was estimated that the following amounts of the five major herbicides were discharged into the Gulf of Mexico in 1991: atrazine, 160 metric tons (t); cyanazine, 71 t; metolachlor, 56 t; alachlor, 18 t; simazine, 10 t (Pereira and Hostettler, 1993).

Research must be conducted to reduce the potential for surface water and groundwater contamination and improve public perception of agrichemicals in the environment (Schweizer, 1988). Controlled-release technology, particularly microencapsulation, should be useful in accomplishing this goal (Bahadir and Pfister, 1990; Riggle and Penner, 1990; Seaman, 1990; Williams, 1984; Scher, 1977). Microencapsulated pesticides should be safer to handle, reduce the total amount of pesticide used, and have reduced potential for leaching in the soil

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profile while maintaining effective biological activity. The chief objectives of our research are to develop pesticide formulations that will maintain or increase efficacy on target organisms and that will not have an adverse impact on the environment, particularly groundwater and surface water.

Previously, the preparation of β-cyclodextrin complexes of atrazine, metribuzin, and simazine and the evaluation of their efficacy as herbicides under greenhouse conditions were reported (Dailey et al., 1990). The microencapsulation of atrazine by an interfacial polymerization process has been reported (Beestman and Deming, 1983). Formulations of atrazine encapsulated within a starch matrix have exhibited promising controlled-release properties (Trimnell and Shasha, 1990; Carr et al., 1991; Fleming et al., 1992; Mills and Thurman, 1994). The use of cornstarch in the encapsulation of alachlor has also been reported (Wing, 1989; Wing et al., 1991). Boydston (1992) demonstrated that leaching of starch-encapsulated norflurazon [4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2*H*)-pyridazinone] and simazine could be significantly reduced in soil columns. Buhler et al. (1994) showed that starch encapsulation of alachlor, metolachlor, and atrazine could result in weed control levels different from (often less than) those of commercial formulations, depending on weed populations. Riggle and Penner (1987, 1988, 1992) investigated the formulation of alachlor and metribuzin with kraft lignins and observed controlled-release properties. Alginates in combination with various additives show promise in the controlled release of metribuzin (Pepperman et al., 1991; Pepperman and Kuan, 1993; Johnson and Pepperman, 1995a), atrazine (Johnson and Pepperman, 1995b) and alachlor (Pepperman and Kuan, 1995). In a study of the comparative efficacy of formulations of alachlor and metolachlor, an emulsifiable concentrate formulation of alachlor inhibited shoot growth of three grass weed species more than microencapsulated alachlor, but microencapsulated and emulsifiable concentrate formulations of metolachlor caused similar effects (Doub et al., 1988). Finally, several evaluations of microencapsulated formulations of alachlor have been reported (Petersen and Shea, 1989; Huang and Ahrens, 1991; Greene et al., 1992).

We are investigating a number of methods for the microencapsulation of pesticides. Among these is the solvent evaporation process, which yields microcapsules of pesticide incorporated within a polymer matrix. We have reported the preparation and evaluation of polymeric microcapsules of the herbicides atrazine and metribuzin (Dailey et al., 1993). We have also reported on the preparation and evaluation of polymeric microcapsules of cyanazine (Dailey and Dowler, 1995, 1998). Atrazine and metribuzin have been microencapsulated within cellulose acetate butyrate, ethyl cellulose of two different viscosities, and low and medium molecular weight poly(methyl methacrylate) by the solvent evaporation process using two different emulsifiers (Dailey et al., 1993). The preparation of microcapsules of alachlor or metolachlor using these polymers has not been reported previously. In this paper, we will describe the preparation of the polymeric microcapsules and the evaluation of their effectiveness in controlling weeds in the greenhouse, particularly with regard to controlled-release properties.

MATERIALS AND METHODS

Chemicals and Reagents. Alachlor (technical, 94% pure) was provided by Monsanto, St. Louis, MO, and was recrystallized from 95% ethanol at 2 °C, affording material of mp 39.1−41.9 °C (lit. mp 39.5−41 °C) (Hartley and Kidd, 1987). Technical metolachlor was provided by CIBA (now Novartis), Greensboro, NC, and was used without further purification. Samples of the 88% hydrolyzed poly(vinyl alcohol)s Airvol 205 (low viscosity) and Airvol 523 (medium viscosity) were provided by Air Products and Chemicals, Inc., Allentown, PA. Stock 0.5% solutions of Airvol 205 and 523 were prepared by adding the poly(vinyl alcohol) to the vortex of cold stirred water in a steady stream followed by heating at 85 °C for 30 min. The following polymers were purchased from Aldrich Chemical Co., Inc.: 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 100 cP (EC100); poly(methyl methacrylate), low molecular weight (PMML); poly(methyl methacrylate), medium molecular weight (PMMM); poly(α-methylstyrene), medium molecular weight (PMS).

Preparation of Polymeric Microcapsules. In a typical microcapsule preparation, a solution of 2.50 g of herbicide (alachlor or metolachlor) and 10.0 g of polymer in 200 mL of dichloromethane was added slowly to the vortex of 1000 mL of a 0.25% Airvol 205 or 523 solution, stirred at 350 rpm. A Lightnin Model TSR 1516 variable-speed high-torque mixer equipped with a 5.0-cm-diameter six-bladed turbine impeller was used for all stirring. When cellulose acetate butyrate and ethyl cellulose polymers were used in the preparation of alachlor formulations, dichloromethane was heated to 40 °C to effect complete dissolution; for metolachlor formulations, from 30 min to 3 h was required for complete dissolution of these polymers in dichloromethane at room temperature. About five drops of *n*-octanol were added to the stirred emulsion to reduce foaming. Stirring at 350 rpm was continued for 20−24 h, at which time evaporation of the organic solvent was complete as determined by visual observation and examination of a portion of the suspended product under a research microscope. After the stirring was halted, the microcapsules were allowed to settle. The supernatant liquid (including floating solids) was decanted, 1000 mL of distilled water was added, and the mixture was stirred for 1−2 h. The floating solids consisted of agglomerated microcapsules, probably containing entrapped air. After settling, the microcapsules were filtered, allowed to air-dry, and finally dried in a vacuum desiccator until a constant weight was obtained.

In subsequent discussions, a polymeric microcapsule formulation will be referred to in abbreviated form, such as CAB-205, indicating the use of the polymer cellulose acetate butyrate and the emulsifier Airvol 205.

The herbicidal content of all the polymeric microcapsules prepared was determined by elemental analysis (Galbraith Laboratories, Inc., Knoxville, TN) within 1 month of preparation. On the basis of the amounts of materials used, each of the polymeric microcapsule formulations should contain 20% active ingredient (ai). The herbicidal content of alachlor and metolachlor formulations was calculated on the basis of nitrogen and chlorine microanalyses.

Greenhouse Studies. A 10−10−10 fertilizer was thoroughly mixed at the rate of 1000 kg/ha into an air-dried Tifton loamy sand top soil (fine-loamy, siliceous, thermic, Plinthic Paleudults) with 83% sand, 10% silt, 7% clay, and 1.0% organic matter and placed in 20 × 35 × 9 cm deep galvanized steel flats. The soil was then uniformly moistened by sprinkler from the top and allowed to equilibrate for 24 h. Corn and the selected weed species were then planted in rows 3 cm apart (15−20 seeds per row) per flat. The flats were again lightly moistened with overhead sprinklers and herbicides applied preemergence to crops and weeds. The commercial herbicide formulations were applied with an enclosed chamber sprayer using a Tee Jet 80067 flat fan spray tip, operating at 160 kPa, which delivered a volume of 187 L/ha at 0.45 m/s. Spray height was 46 cm. The controlled-release formulations were weighed for each individual flat, placed in a small paper envelope, and spread evenly over the soil surface by hand. The treated flats were placed in a greenhouse with day length maintained at ~14 h by natural or supplemental fluorescent lighting and the temperature ranging from 20 to 34 °C. The experimental design was a randomized complete block with four replications.

The weed species used in these experiments were barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.] (ECHCG), crowfootgrass (*Dactyloctenium aegyptium*) (DTTAE), smallflower morningglory [*Jacquemontia tamnifolia* (L.), Griseb.] (IAQTA), and Palmer amaranth (*Amaranthus palmeri* S. Wats) (AMAPA). These species were chosen for their extensive occurrence in the southeastern United States (Dowler, 1995) and for their different levels of tolerance to the herbicides alachlor and metolachlor.

There were two series of greenhouse efficacy studies for alachlor. The first series involved 10 16-month-old polymeric alachlor formulations and the weeds barnyardgrass and Palmer amaranth. The initial planting date and herbicide treatment (week 0) was October 3, 1991. The herbicides were applied at two different rates: 2.2 and 4.5 kg of ai/ha. Herbicide activity was measured 21 days after planting by visual observation. Percent control was recorded on a scale of 0 = no effect to 100 = complete kill, as compared to an untreated check. The flats were then allowed to air-dry, the tops of dead plants carefully removed, and the same weeds replanted with minimum soil disturbance 4, 8, 16, and 24 weeks after the initial treatment to determine herbicide persistence or release. The second test involved six 9-month-old polymeric formulations (CAB-205, EC22-205, EC100-205, PMS-205, PMS-523, and PMML-205) on all four weed species. The initial planting date and date of herbicide treatment was September 4, 1992, and the weeds were replanted 4, 8, 14, and 24 weeks after initial treatment.

The same experimental procedure in the greenhouse was followed for metolachlor, except that the application rates were 1.7 and 3.4 kg of ai/ha. The metolachlor experiment was initiated October 29, 1992, with replantings made 4, 8, 14, 24, 30, and 46 weeks after treatment.

Statistical Analysis. Weed seeds were planted five or six successive times during each greenhouse study. The Julian date was determined for each planting in each study. Counting each day of the year produces Julian date values (i.e., December 31 = 365). Counting is continued into the next year if necessary. For each study, a mean Julian date was calculated. The first Julian date value was subtracted from each of the Julian date values including the mean Julian date. The mean was then subtracted from each date value thus obtained, and these new values were used in the regression analyses. All of the data were transformed using SQRT for each weed species each of the observation times and were analyzed using regression analysis techniques [PROC GLM (SAS, 1989)] for graphical presentation. The predicted values were squared to fit on the (0−100%) axis. Intercept, slope, and curvature values were obtained from the regression analysis. Replication effects were also included in the regression model. Each of the regression components and their standard error (SE) were compared with each of the other treatments using the unequal *n*-unequal variance *t*-test (Steel and Torrie, 1960). The significance level was chosen to be $P = 0.05$. The *t*-test results were used to construct the multiple comparison letter arrangements appearing with a group of treatments. A line with an intercept and slope only is significantly different from a line with an intercept, slope, and curvature. For a line containing the curvature component, the slope value given is only for the intercept point.

RESULTS AND DISCUSSION

The herbicidal content of two "9-month-old" alachlor formulations (19.4 and 22.8%) was determined on the basis of nitrogen analyses. The herbicidal content of the remaining 14 formulations was determined by taking the average of nitrogen and chlorine microanalyses that ranged from 19.7 to 24.8%. The herbicidal content of the seven metolachlor formulations was determined by taking the average of nitrogen and chlorine microanalyses that ranged from 17.0 to 20.3%. The nitrogen and chlorine microanalyses often were not in good agreement. With the exception of PMML formulations, chlorine microanalyses gave higher values. For alachlor formulations the standard error range was from 0.3 to 4.3%. For metolachlor formulations, the range was from 0.2 to 2.0%. On the basis of microanalysis, the alachlor or metolachlor content of all the polymeric microcapsules ranged between 17 and 24.8% (theoretical amount = 20%). In addition, stored samples of four of the "16-month-old" alachlor formulations (EC100-205, EC22-205, CAB-523, and PMML-523) were reanalyzed by reverse-phase high-performance thin-layer chromatography with densitometry (Dailey and Johnson, 1995) 4 years after preparation and original microanalyses. The alachlor content was found to be 80.0−89.8% of original values. None of the developed TLC plates showed any impurities or decomposition products, indicating long-term stability of the microcapsules. The gradual loss of alachlor content over time is probably due to volatilization.

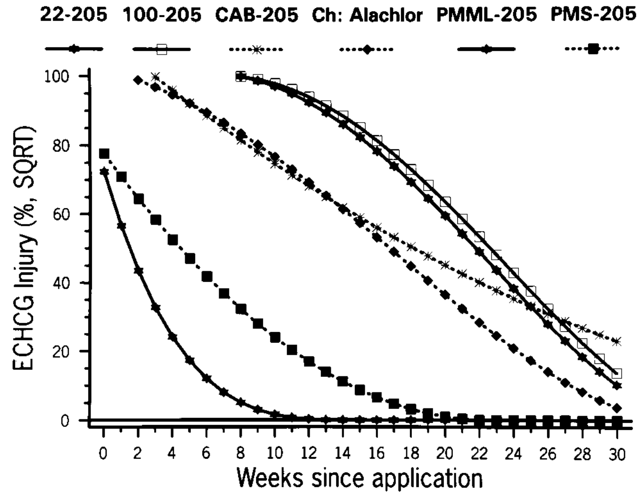

Figure 1. Effect of 9-month-old CAB, PMML, EC, and PMS formulations of alachlor at 4.4 kg/ha on barnyardgrass injury for 30 weeks after application.

The untreated check has zero effect on all weed species at all planting dates, so these data are not shown. As anticipated, the lower rates of application of alachlor (2.2 kg of ai/ha) and metolachlor (1.7 kg of ai/ha) resulted in lower herbicidal activity and reduced length of activity. The controlled-release properties of each formulation were similar to those of high-rate applied formulations. Therefore, data reported herein are for the higher application rate.

The emulsifiers had little effect on the activity of the herbicides in different polymers, so data reported herein are with the emulsifier Airvol 205. The herbicide activities with the polymers (PMML and PMMM) were similar, so only the data for PMML are included herein. In some figures, efficacy data may be indicated only at 4 or 8 weeks after treatment. That level of activity occurred at treatment and was maintained to the time indicated.

The results of 9-month-old alachlor formulations on barnyardgrass, crowfootgrass, Palmer amaranth, and smallflower morningglory are shown in Figures 1−4. Statistical summary tables of all 9-month-old alachlor

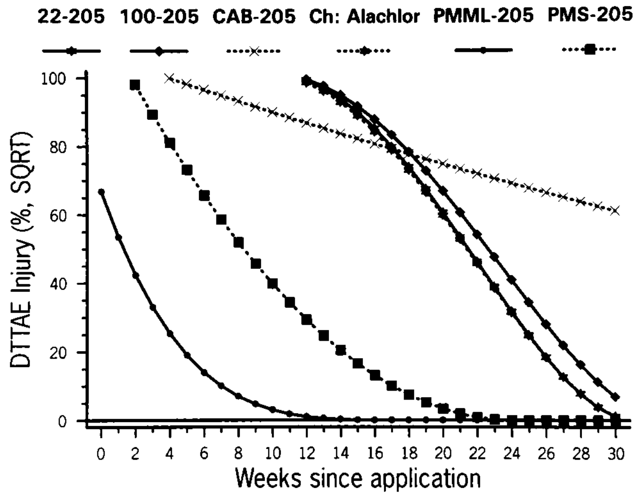

Figure 2. Effect of 9-month-old CAB, PMML, EC, and PMS formulations of alachlor at 4.4 kg/ha on crowfootgrass injury for 30 weeks after application.

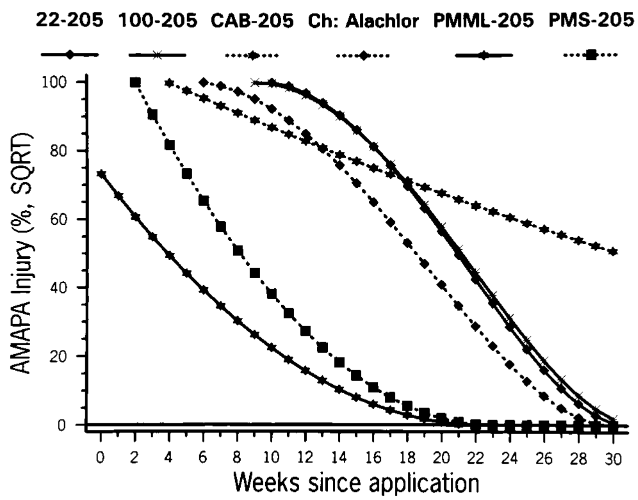

Figure 3. Effect of 9-month-old CAB, PMML, EC, and PMS formulations of alachlor at 4.4 kg/ha on Palmer amaranth injury for 30 weeks after application.

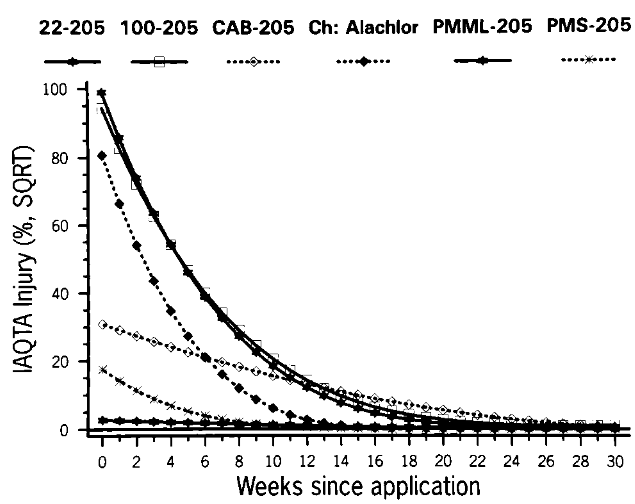

Figure 4. Effect of 9-month-old CAB, PMML, EC, and PMS formulations of alachlor at 4.4 kg/ha on smallflower morningglory injury for 30 weeks after application.

and metolachlor formulations are presented in the Supporting Information. The activity of the PMML and PMS formulations of alachlor was consistently lower on

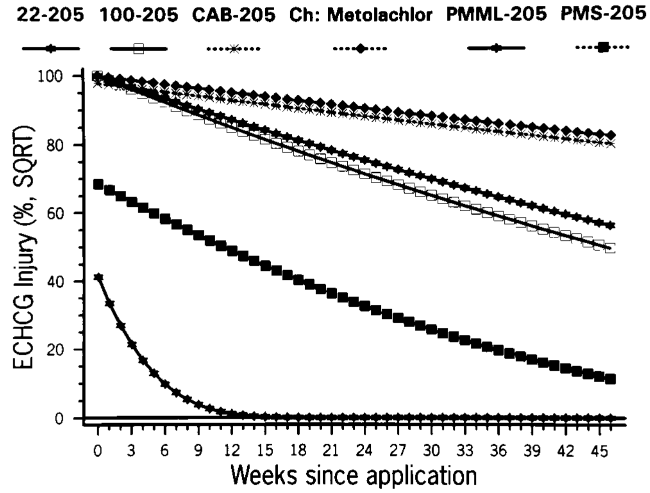

Figure 5. Effect of CAB, PMML, EC, and PMS formulations of metolachlor at 3.4 kg/ha on barnyardgrass injury for 45 weeks after application.

all weed species when compared to the other polymeric formulations or alachlor 4EC. The CAB-205 formulation exhibited definite controlled-release properties on Palmer amaranth and crowfootgrass (Figures 2 and 3). The EC22 and EC100 formulations produced activity similar to that of the alachlor 4EC formulation. The EC22, EC100, and CAB formulations were comparable or superior to the commercial formulation in herbicide activity at all planting dates. At 14 weeks, EC100-205 was more active than alachlor 4.0EC on barnyardgrass, and at 24 weeks, it was more active on both barnyardgrass and Palmer amaranth. The results from Figures 1−4 would indicate that crowfootgrass is the weed species most susceptible to alachlor, followed by Palmer amaranth, barnyardgrass, and smallflower morningglory.

Results of greenhouse studies on the effectiveness of the 16-month-old polymeric formulations of alachlor on barnyardgrass and Palmer amaranth are presented as figures and summary statistical tables in the Supporting Information. The EC and CAB formulations were comparable to the commercial alachlor formulation on Palmer amaranth. The PMML injured Palmer amaranth at 0 weeks, but this activity decreased rapidly. Barnyardgrass was only slightly injured by PMML-205 at 0 weeks. The EC100 and CAB formulations exhibited less herbicidal activity on barnyardgrass than the commercial formulation 8 and 16 weeks after treatment. Activity of all formulations had ceased 24 weeks after treatment on both barnyardgrass and Palmer amaranth. Although a direct comparison to efficacy on barnyardgrass and Palmer amaranth could not be made, the 9-month-old formulations tended to have higher activity than the 16-month-old formulations, especially 14 weeks or more after application.

The results for polymeric microcapsule formulations of metolachlor showed the same general trend as polymeric formulations of alachlor. The activities of PMML and PMS formulations were lower on all weed species. The herbicidal activity of PMMM formulations had disappeared 14 weeks after application. In general, EC22, EC100, and CAB formulations of metolachlor resulted in herbicidal activity similar to that of the metolachlor 8EC commercial formulation. There was no evidence of controled-release properties from any of the polymeric microcapsule formulations (Figures 5−8).

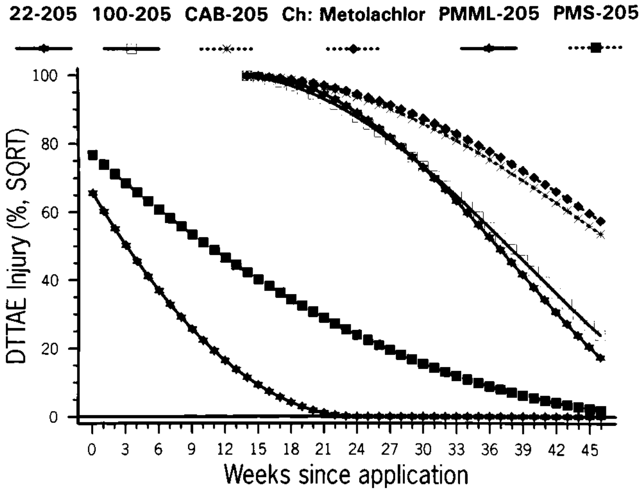

Figure 6. Effect of CAB, PMML, EC, and PMS formulations of metolachlor at 3.4 kg/ha on crowfootgrass injury for 45 weeks after application.

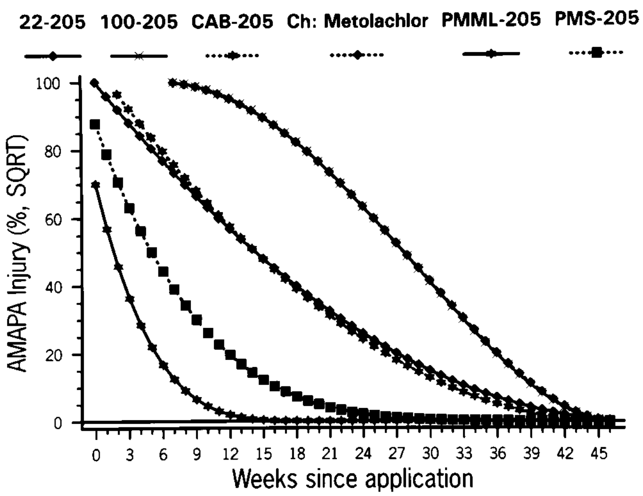

Figure 7. Effect of CAB, PMML, EC, and PMS formulations of metolachlor at 3.4 kg/ha on Palmer amaranth injury for 45 weeks after application.

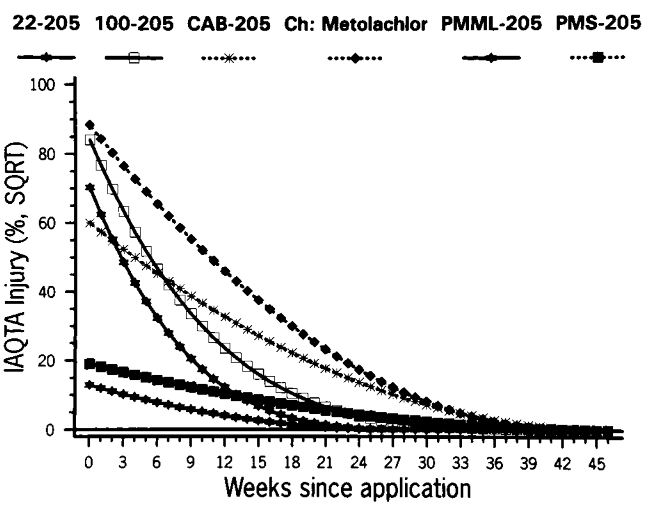

Figure 8. Effect of CAB, PMML, EC, and PMS formulations of metolachlor at 3.4 kg/ha on smallflower morningglory injury for 45 weeks after application.

In the control of barnyardgrass and crowfootgrass (Figures 5 and 6), the CAB formulation exhibited activity very similar to that of the metolachlor 8EC commercial formulation 14 or more weeks after application. However, the activity of the EC22 and EC100 formulations decreased significantly. In treatments of Palmer amaranth (Figure 7), EC100-205 was comparable to metolachlor 8EC throughout the study, EC22-205 was comparable through week 24, and CAB-205 was comparable through week 8. None of the metolachlor formulations, including metolachlor 8EC, showed any activity after 46 weeks. None of the metolachlor formulations controlled tolerant smallflower morningglory after 30 weeks. For the first 24 weeks of the study, none of the polymeric formulations were as active as metolachlor 8EC, but EC100-205 exhibited the highest activity, followed by the CAB and EC22 formulations (Figure 8). The results for metolachlor controlled-release applications would indicate that barnyardgrass is more susceptible to metolachlor, followed by crowfootgrass, Palmer amaranth, and smallflower morningglory.

CONCLUSIONS

In herbicidal efficacy studies of polymeric microcapsules of alachlor, formulations using ethyl cellulose and CAB were generally at least as effective as the commercial formulation. Best results were obtained with the 9-month-old ethyl cellulose formulation EC100-205, which was significantly more active than the commercial formulation and exhibited controlled-release properties. The 9-month-old formulations had measurably higher activity than the 16-month-old formulations, suggesting loss of activity over time under storage conditions (20−34 °C).

In herbicidal efficacy studies of polymeric microcapsules of metolachlor, formulations using ethyl cellulose and CAB were generally comparable in activity to the commercial formulation at the 3.4 kg/ha application rate. Best results were obtained with CAB-205 and the ethyl cellulose formulation EC100-205, which also was the most effective of alachlor formulations.

The findings as to relative effectiveness of the polymeric microcapsules were generally in agreement with results we obtained previously with polymeric microcapsules of atrazine and metribuzin (Dailey et al., 1993). However, none of the metolachlor formulations exhibited efficacy superior to the commercial formulation or controlled-release properties, as was the case with some atrazine and alachlor formulations.

Supporting Information Available: Figures for activity of 16-month-old formulations of alachlor on barnyardgrass and Palmer amaranth and statistical summary tables for all alachlor and metolachlor formulations on all weed species are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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