

## **Influence of Spray Adjuvants on the Behavior of Trifluralin in the Soil**

M. K. Swarczewicz,<sup>1</sup> Z. Mulinski,<sup>1</sup> I. Zbiec<sup>2</sup>

<sup>1</sup>Department of General Chemistry, Agricultural University, Stowackiego 17,  
71-434 Szczecin, Poland

<sup>2</sup>Department of Plant Cultivation and Watering, Agricultural University, Stowackiego 17,  
71-434 Szczecin, Poland

Received: 30 August 1997/Accepted: 17 February 1998

The persistence, degradation and movement of trifluralin in soils have been studied (Reyes and Zimdahl 1989; Corbin et al. 1994; Tiryaki et al. 1997). Trifluralin, like other dinitroaniline herbicides are volatile when applied to a moist soil surface (Savage 1978). A direct relationship has been reported between volatilization of trifluralin and soil water content where trifluralin volatilized more rapidly from a moist soil than from a flooded soil (Savage 1978). Also an increase in the depth of incorporation could increase the persistence of trifluralin by reducing volatilization and photodecomposition (Corbin et al. 1994), therefore soil applied trifluralin is often incorporated.

The Institute of Plant Protection in Poznan, Poland, has been conducting research for the improvement of herbicide efficiency by tank-mixing the herbicides with adjuvants (Adamczewski et al. 1996; Praczyk et al. 1996). One of the beneficial effects of adjuvants, especially surfactants is a reduction in the amount of water available for evaporation from the soil surface (Bayer and Foy, 1982). In several studies it has been observed that the degradation rate depends on the type of herbicide and adjuvant (Khan et al. 1981; Kostowska and Sadowski 1992; Praczyk 1992; Swarczewicz and Mulinski 1996). Further research has shown that the addition of Olejan to the trifluralin applications causes a significant increase of the herbicide degradation rate, both in laboratory and pot-field experiments (Swarzewicz 1996).

This study was conducted to evaluate the effect of the spray adjuvant on the degradation rate of trifluralin under field conditions, and to compare these results with laboratory and pot-field results. In this study trifluralin was tank-mixed with adjuvants such as Atpol, Olejan, Olbras, Adbios and Adpros. The degradation rate of trifluralin in the soil with and without the spray adjuvants was described by a mathematical model for mass transfer accompanied by chemical reaction (Mulinski 1996). The addition of spray adjuvants could reduce volatilization of trifluralin from the soil surface.

---

Correspondence to: M. K. Swarczewicz, Department of Plant and Soil Sciences, University of Massachusetts, Amherst, MA 01003, USA

## MATERIALS AND METHODS

All reagents used were of analytical purity and the solvents were distilled. Reagents used were: methanol, *n*-hexane, anhydrous sodium sulfate, sodium chloride, trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine] from Dow Elanco Limited. The herbicide used was a commercial formulation (EC) of Trifluralin (480 g a.i./l San-Chem Ltd., South Africa). Five different adjuvants produced in Poland were tested in combination with trifluralin (Table).

Field studies were conducted at the Lipnik Experiment Station of the Faculty of Agronomy of the Agricultural University of Szczecin. Soil was proved to be a loamy sand with a composition of 72% sand, 16% silt, and 12% clay, pH 6.5, organic matter content 1.3%, and maximum water holding capacity of 25.4 mL 100 g<sup>-1</sup>). Field experiment was established on May 24 1995, the experiment area being fallow the previous year. The climatological conditions during the experimental period were as follows: May — the month average temperature 12.3°C, the total monthly rainfall 45.2 mm; June — 15.3°C and 82.2 mm; July — 20.4°C and 20.9 mm.

**Table 1.** Commercial, chemical type of oil, and surfactant trade name of spray adjuvants used in this study

Commercial name	Chemical type of oil	Surfactant trade name
Adbios 85 SL <sup>®</sup>	85% polyethoxylated fatty amine	15% ethoxylated butyl alcohol Turowa Wola*
Adpros 85 SL <sup>®</sup>	85% methylated rape seed oil	15% Atplus 300 F Varichem*
Atpol <sup>®</sup>	83% paraffin oil	17% Atplus 300 F Czechowice*
Olbras 88 EC <sup>®</sup>	88% postrefined fatty acid of rape seed	12% Rokefenol N- 8 Olbrol*
Olejan 85 EC <sup>®</sup>	85% rape seed oil	15% DM, Danmar*

\* Source

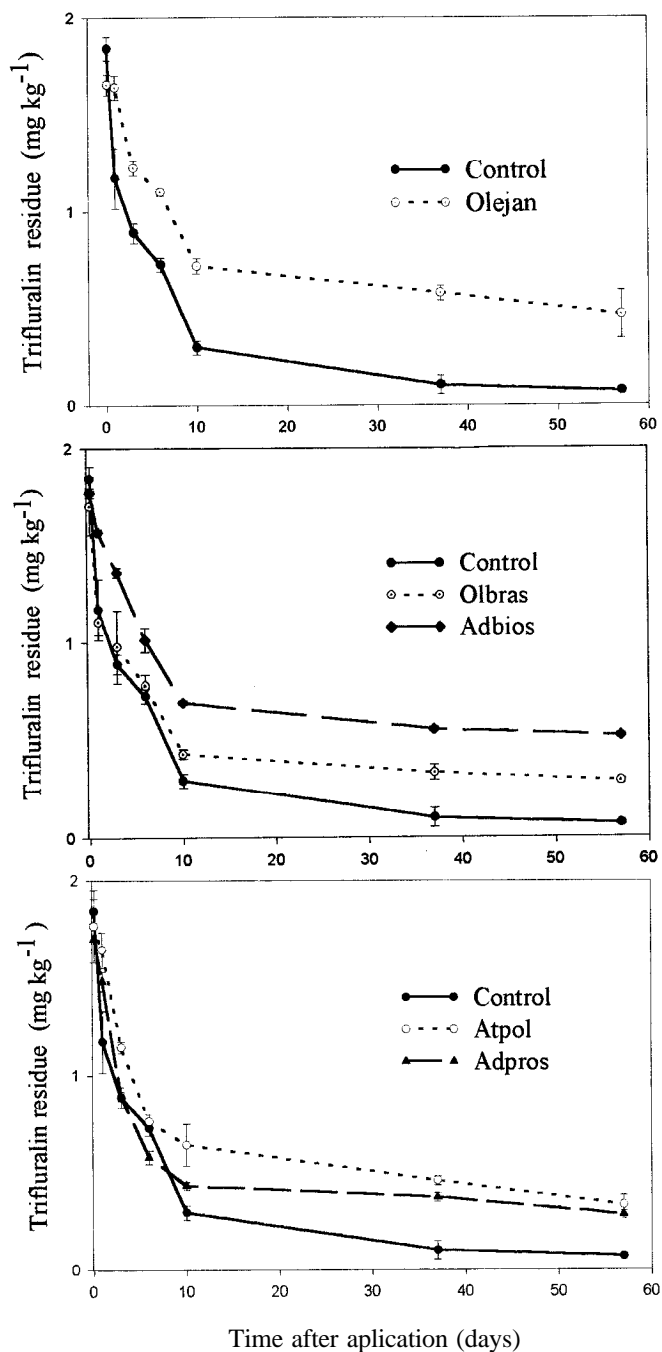
Trifluralin was applied at 2.0 L ha<sup>-1</sup> in 200 L ha<sup>-1</sup> of water to four replicates of 2-by 5-m plots using a plot sprayer. The herbicide-adjuvant mixture was tank mixed before application. Treatments consisted of trifluralin alone and with the addition

of 1.0% (v/v) of Atpol, Olbras, Olejan, Adbios, Adpros, and untreated check, The soil was harrowed to a depth of 10 cm after treatments application. Soil samples were taken at 0, 1, 3, 6, 10, 37, and 57 days after the application of treatments, Twenty-five soil cores (2.5 cm diameter by 20 cm deep) were taken in a random W pattern from each plot. Samples were combined and stored frozen in plastic bags, Prior to extraction the samples were allowed to thaw and trifluralin soil residues then were analyzed using a modified procedure (Savage and Jordan 1980; Corbin et al. 1994; Swarczewicz 1996). One hundred grams of soil was mixed with 200 ml of methanol and gently agitated on a mechanical wrist action shaker for 1hr. Sample was filtered through a Whatman #2 filter paper in a Buchner funnel. After extraction the soil was rinsed with methanol, All methanol fractions were combined in a separatory funnel. Ten ml of 5% (w/v) sodium chloride and 50 ml of distilled n-hexane were added to the methanol in a separatory funnel and shaken to partition the herbicide into the hexane phase. The extraction was repeated twice with an additional 50 ml portion of hexane. The hexane from each extraction was passed through a pad of anhydrous sodium sulfate. Separatory funnel and sodium sulfate were rinsed with hexane to bring the final volume to 200 ml. This extract was evaporated to near dryness at 45° C in an evaporator The trifluralin residue was redissolved in 2 ml of hexane and an aliquot was taken for analysis. Residues were quantified using a Carbo Erba 6000 Vega Seria 2 (“on-column”) gas chromatograph fitted with a FID detector. A glass column DB-5 (0.54 mm x 30 m, 1 µm film thickness, J&W) was used. Injection “on column,” column, and a flame ionization detector temperature were (I) 100° C by 1 min., (II) 40°C/min., (III) 200°C by 10.5 min., and 250°C respectively. Argon was used as carrier gas. Retention time was approximately 9.6 min., and the average recovery was 94.5±4.9% for fortified soil by 10 to 0.05 mg kg<sup>-1</sup>.

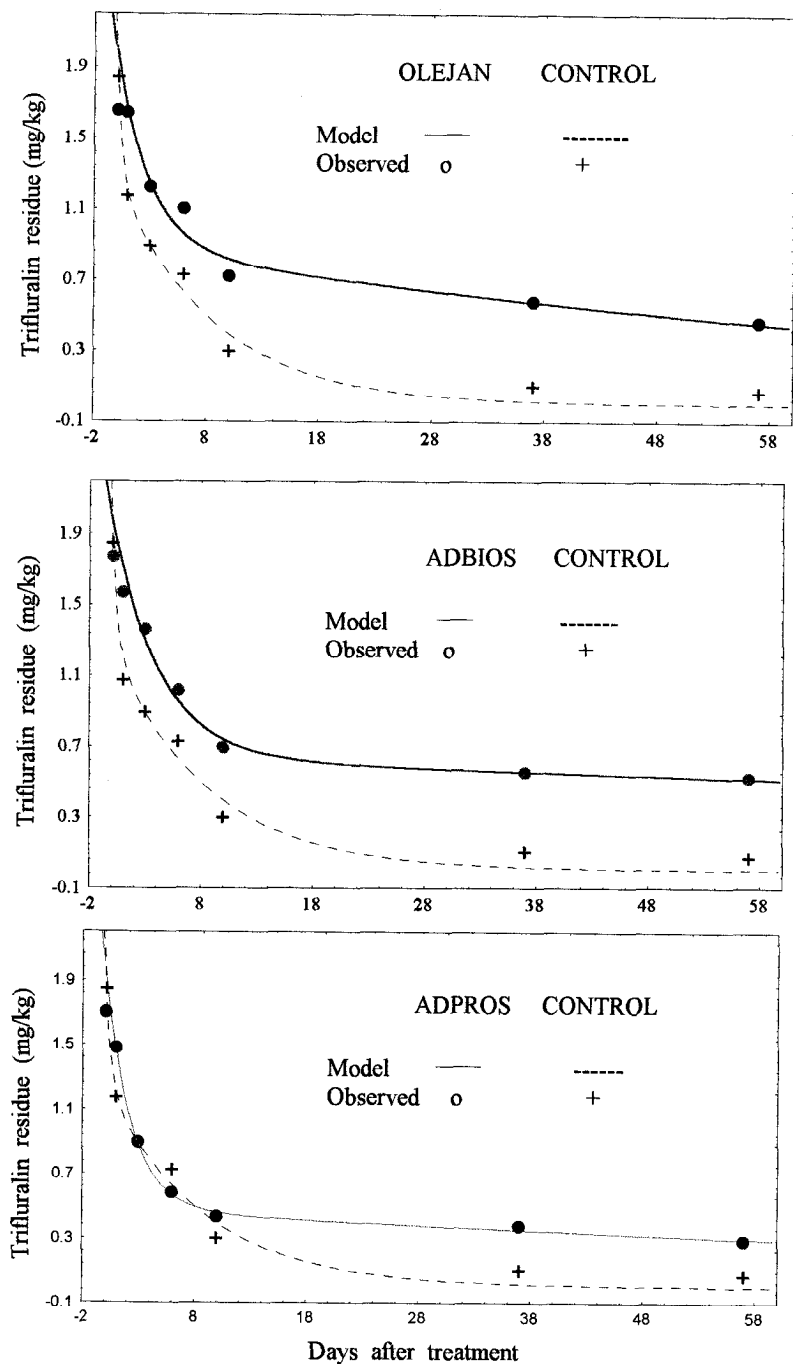
Trifluralin residue data were subjected to analysis of variance. Means were compared using Fishers Protected LSD Test ( $P \leq 0.05$ ). Data from analysis of trifluralin residue indicated an exponential decay of the herbicide over time. The degradation rate of trifluralin in the soil was described by an equation formed by two exponential equations which refer to biphasic degradation of a herbicide in soil (Mulinski 1996). In this new biexponential model the nonlinear regression analysis with Quasi-Newton estimation method was used.

## RESULTS AND DISCUSSION

The data indicates a less rapid dissipation of trifluralin were applied with spray adjuvants (Figure 1). Effect distinctly appeared 3 day after treatment with Olejan or Adbios. For the rest of the adjuvants a significant influence on the trifluralin persistence after 10 d was noticed (Fig. 1). Trifluralin residue in the soil with Adbios was found to be  $29.9 \pm 1.9\%$  57 d after application in the loamy sand,  $26.7 \pm 7.2\%$  with Olejan,  $19.1 \pm 2.9\%$  with Atpol,  $16.6 \pm 0.6\%$  with Olbras, and  $16.3 \pm 1.1\%$  with Adpros, and  $3.9 \pm 0.5\%$  for trifluralin alone.



**Figure 1.** Trifluralin dissipation in a loamy sand in the presence of spray adjuvants under field conditions. Bars at each sampling date indicate 95% confidence interval of trifluralin residue



**Figure 2.** Observed values for the biexponential equation for trifluralin without spray adjuvant (control) and in the presence of spray adjuvants under field conditions

Results were comparable with the laboratory conditions (Swarcewicz, 1996) which showed  $49.1 \pm 1.6\%$  of trifluralin residue with Olejan,  $40 \pm 0.9\%$  with Adbios,  $40.9 \pm 1.8\%$  with Atpol, and  $38.6 \pm 3\%$  in the control at 50 days after treatment, In the pot-field experiment  $36.6 \pm 6.5\%$  trifluralin was found with the Adpros,  $31.8 \pm 2.1\%$  with Adbios,  $24.6 \pm 5\%$  with Olejan, and  $11.7 \pm 2.3\%$  in the control (Swarcewicz 1996).

Activity and persistence of trifluralin in the field were show to be more variable than in the laboratory or pot experiments. One factor which might account for the increased variability in the field is the uneven distribution of the herbicide over the soil surface. The field data (Fig.1) shows a similar relationship between herbicide and adjuvant as obtained in the laboratory or pot-field experiments.

The disappearance curves of the herbicide from the soil consist of two phases. The first is a rapid decomposition phase, followed by a second phase characterized by decomposition at a slower, ever-decreasing rate. Savage and Jordan (1980) described the degradation rate of trifluralin by two separate first-order kinetic equations. At the first phase the half-life for trifluralin was 2 d, and in the second, 50 to 70 d, depending on the soil type. A biexponential equation which resulted from integration of the first-order and second-order differential rate equations was used by Reyes and Zimdahl (1989). This model described degradation of trifluralin data better than the first-order kinetic model. Use of new empirical equation (Mulinski 1996) to describe dissipation of trifluralin in soil was done for the first time by Swarcewicz (1996) with a general mathematical model for mass transfer accompanied by a chemical reaction. The equation used was:

$$C = C_0 [(1-Y) \exp(-k_1t) + Y \exp(-k_2t)]$$

where  $t$  = time,  $C$  = concentration,  $C_0$  = initial concentration, and  $k_1$  and  $k_2$  are rate constants,  $Y$  = simulated data from model.

Figure 2 shows this biexponential equation with more accurate descriptors of trifluralin dissipation than that previously used (Savage and Jordan 1980; Reyes and Zimdahl 1989; Corbin et al. 1994). The values of the coefficient of regression were between 0.96 -0.99.

The role of adjuvants in herbicide decomposition under field conditions is not well understood. These studies suggest that the influence of a spray adjuvant on degradation of trifluralin in soil is more significant during the second phase of the experiment, contrary to the data from the laboratory and the pot-field experiments where this effect was observed at 2 to 3 d. Olejan, as compared with Olbras which had a far greater effect on persistence of herbicide in soil. The composition of spray adjuvant may have considerable impact on herbicide persistence in the soil.

Rapid evaporation of trifluralin from the soil surface results in economic losses and undesirable presence of this herbicide in the air which may be hazardous to live organisms. The use of spray adjuvants may provide some protection against the

evaporation of trifluralin. More information is need about behavior of herbicide-adjuvant in the soil and influence their combination on herbicidal activity.

*Acknowledgments.* Many thanks are expressed to K.Adamczewski and T. Praczyk for their valuable input and support.

## REFERENCES

- Adamczewski K, Urban M, Kuzior S (1996) Enhancing the herbicidal spectrum and activity of sulfosulfuron by tank-mixing with adjuvants In: Proc. Second International Weed Control Congress, Copenhagen, 25-26 June, Brown H et al (eds), vol.4, Dep. of Weed Control & Pesticide Ecology, Flakkebjerg, DK-4200 Slagelse, Denmark, pp 813-818
- Bayer DE, Foy CL (1982) Action and fate of adjuvants of adjuvants in soils. In: Hodgson RH, Maryland F (eds) Adjuvants for herbicides, Weed Sci Soc America, Champaign, Ill, pp 84-92
- Corbin Jr.BR, McClelland M, Frans RE, Talbert R, Horton D (1994) Dissipation of fluometuron and trifluralin residues after long-term use. *Weed Sci* 42: 439-445
- Khan SU, Marrige PB, Hamill AS (1981) Effects of atrazine treatment of a corn field using different application methods, times, and additives on the persistence of residues in soil and their uptake by oat plants. *J Agric Food Chem* 29: 216-219
- Kostowska B, Sadowski J (1992) The influence of adjuvants on atrazine degradation in plants and soil. In: Proc 32 Scientific Session Inst Plant Protection, vol. 1, Institute of Plant Protection, Poznan, pp 260-267 (in Polish)
- Mulinski Z (1996) Persistence and fate of EC formulated pesticides in water. General mathematical model for mass transfer accompanied by chemical reaction. *Pest Sci*, in press.
- Praczyk T (1992) Methyl esters of fatty acid and rape seed oil as additive of herbicidal activity of atrazine, bentazon and penmedipham. PhD Thesis, Institute of Plant Protection, Poznan (in Polish)
- Praczyk T, Stachecki S, Wachowiak M (1996) Control of volunteer winter oilseed rape by triflurosulfuron-methyl applied with surfactants and oil adjuvants In: Proc. Second International Weed Control Congress, Copenhagen, 25-26 June, Brown H et al (eds), vol.4, Dep. of Weed Control & Pesticide Ecology, Flakkebjerg, DK-4200 Slagelse, Denmark, pp 911-916
- Reyes C, Zimdahl RL (1989) Mathematical description of trifluralin degradation in soil. *Weed Sci* 37: 604-608.
- Savage KE (1978) Persistance of several dinitroaniline herbicides as affected by soil moisture *Weed Sci* 26:465-471
- Savage KE, Jordan TN (1980) Persistence of three dinitroaniline herbicides on the soil surface. *Weed Sci* 28: 105-110

- Swarcewicz M (1996) Effect of oil adjuvants on trifluralin persistence in a sandy soil. *Zeszyty Naukowe Akademii Rolniczej Szczecin* 173, *Rolnictwo* 63: 211-217 (in Polish)
- Swarcewicz M, Mulinski Z (1996) Effect of spray adjuvants Atpol and Olbras on atrazine fate in soil and water. In: *Proc. Second International Weed Control Congress*, Copenhagen, 25-26 June, Brown H et al (eds), vol. 1, Dep. of Weed Control & Pesticide Ecology, Flakkebjerg, DK-4200 Slagelse, Denmark, pp 343-348
- Tiryaki O, Gözek K, Khan SU (1997) <sup>14</sup>C-Residues of trifluralin in a soil and their uptake by carrots. *Bull Environ Contam Toxicol.* 59: 58-64.