MECHANISMS OF THE BREAKDOWN OF A PYRIDINE HERBICIDE

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Summary The cause of variation in weed control of a new soil applied herbicide called thiazopyr was investigated with a series of bioassays. Volatilization, UV degradation, leaching and chemical and microbial degradation were considered as potential sources of herbicide loss. Microbial degradation was the main cause for variable weed control. When incubated for 94 days at 25°C in unsterilized soil the activity of thiazopyr decreased to <4% of the activity when applied prior to incubation. A formulation was produced where the active ingredient was impregnated into a control release matrix and combined with additives that protect the herbicide from microbial breakdown. This formulation produced a more reliable and consistent weed control than the commercial emulsifable concentrate (EC).

INTRODUCTION

Thiazopyr is a new residual soil-applied herbicide that controls more than 100 annual grasses and small seeded broad-leaf weeds. Some of these include brome grass (*Bromus* spp.), barnyard grass (*Echinochloa crus-galli* L. Beauv), annual ryegrass (*Lolium rigidum* Gaud), wild radish (*Raphanus raphanistrum* L.), mustard (*Brassica juncea* L. Czernj.), fumitory (*Fumaria* spp.), oxtongue (*Picris echioides* L.), pigweed (*Portulaca oleracea* L.) and sow thistle (*Sonchus oleraceus* L.). It is selective in field crops (cotton, soybeans, sugarcane, sunflowers, maize and rice), pastures (perennial grasses, clover and lucerne), horticultural crops (citrus, soft fruits, nuts and grapes), forests (eucalyptus and conifers) and turf swards. Thiazopyr enters through the root and inhibits cell division by disrupting the formation of spindles in mitotic cells. The symptoms of herbicide activity include reduced root and foliar growth, a thickened root tip, hypocotyl or internodes.

Little is known about the behaviour of thiazopyr EC (emulsifable concentrate) in soil, except that weed control is variable. In some cases it lost activity in a few days while in other cases activity remained for six months. The potential causes of variable weed control include volatilization, UV degradation, leaching, or chemical or microbial degradation. We aimed to identify the cause of variable weed control and then develop a formulation of thiazopyr with consistent and reliable weed control.

MATERIALS AND METHODS

Volatilization, UV degradation, leaching, chemical and microbial degradation of thiazopyr were each measured in situ with a bioassay.

Volatilization from soil was measured by spraying nine doses of thiazopyr on to Mallee Sand (0.1 g water g^{-1} soil) that was contained in two sets (each set included seven replicates at each dose) of pots (100 mm diameter, 100 mm high) which had previously been lined with plastic bags. Thiazopyr was sprayed at doses of 0, 5, 7.5, 10, 12.5, 15, 25 and 60 g a.i. ha^{-1} in a laboratory track-sprayer: a spray boom with three nozzles (Spraying Systems® 11001), spaced at 50 cm intervals traversed the pots at 6 km h^{-1}. Each thiazopyr solution was sprayed at 64 L ha^{-1} at a pressure of 200 kPa. The doses were chosen to produce an incremental decrease in the length of millet roots. Once applied, the thiazopyr in one set of pots was mixed into the soil immediately after being sprayed, while the thiazopyr in the remaining set of pots was mixed into the soil after 48 h: during this time both sets of pots were incubated at 25°C in darkness. The soil was mixed by removing the bag from the pot, trapping air in the bag and then shaking and tumbling by hand for about 15 s, the bag was then reinserted into the pot. After incubation, water was added to the pots to replace that lost through evaporation and then soil was then bioassayed for thiazopyr activity as described below. By mixing the herbicide immediately and 48 h after spraying the loss of thiazopyr was estimated i.e. the difference in the ED50 at 0 h and 48 h indicated the amount of herbicide lost to the atmosphere through volatilization.

UV degradation was measured using a similar method to that described for volatilization. Two sets of pots were sprayed as described previously. One of the sets of were placed under florescent tubes with an UV spectrum while the other set was placed in darkness; each for 48 h at 25°C. The soil was thoroughly mixed after 48 h and bioassayed for herbicide concentration as described below.

Leaching Twelve columns (4 segments of PVC tube, 63 mm diameter × 50 mm height) were each packed with oven dry (40°C) Mallee Sand (<2 mm diameter) to a density of 1.2 g cm^{-3}. A layer of sand ³2 mm diameter)

followed by a filter paper (Whatman 42) were placed onto the packed soil to disperse the herbicide and the irrigation water evenly onto the soil. The columns were attached to a vacuum which exerted -600 kPa to the base of the columns for 2 min every 4 h so that water drained freely. Water was then added to raise the water content of the soil in the columns to 9 per cent. The soil equilibrated for two days, and then enough thiazopyr (4 mL, 7.34×10^{-6} g a.i.) was added to the top of the column so that if it all remained in the top segment the length of roots of millet would be reduced to 10 per cent of that of the untreated controls. All columns were irrigated with an equivalent of 100 mm of rain with a peristaltic pump which delivered 2 mm h^{-1}. The leachate was captured and retained for analysis. Once irrigation ceased, the columns equilibrated for two days before being removed from the vacuum and divided into segments. The soil from each segment was raised to a water content of 10 per cent (g water g^{-1} soil) before being bioassayed for thiazopyr.

Chemical and microbial degradation Eight concentrations of thiazopyr were each added in duplicate to sterile Mallee Sand. One duplicate was incubated at 30°C and the other at 15°C for 94 days. Sub-samples were analysed at intervals for thiazopyr activity with the bioassay described previously. The ED50 for each treatments were plotted to indicate the change in activity over time. Microbial breakdown of the herbicide was also measured by incubating soil at 30°C and 15°C over 94 days but the soil was not sterilized. Again the activity of the herbicide was measured with the bioassay described below.

Bioassay Once treated, the soil (200 g) was dispensed into each of seven petri dishes. Six millet (*Echinochloa utilis* L.) seeds were sown in each petri dish which were then incubated at 30°C for three days. The length of roots in each dish were measured. A logistic curve was fitted to the dose-response of millet roots to herbicide concentration and ED50 for each treatment were calculated.

Soil Mallee Sand (Uc 5.1; Badawy 1982) was used in each experiment after it was sieved (2 mm diameter) and oven dried (40°C). Coarse sand, fine sand, silt, clay and organic matter made up 0.617, 0.328, 0.0071, 0.053 and 0.0098 g g^{-1} soil, respectively. The pH of a 1:5 soil-water suspension was 6.6. This soil has a low organic matter and clay content and because herbicides predominantly bind to these fractions, the potential for volatilization and leaching will be accentuated compared with soil with a high organic matter and clay content.

Statistics A logistical dose-response curve was fitted to the data with non-linear regression analysis (Streibig 1988). An ED50 (the point of inflection of the logistic curve) was calculated for each herbicide dose response curve i.e. the rate of herbicide required to reduce the length of millet roots to half that of the untreated roots.

RESULTS AND DISCUSSION

Volatilization of the herbicide accounted for a 10 per cent loss of activity. The conditions in which the herbicide was volatilized strongly favoured volatilization and so a 10 per cent loss in activity was not considered significant. Under similar conditions, trifluralin lost more than 75 per cent in activity (unpublished results).

UV radiation of soil had no effect on the activity of the herbicide and so we concluded the molecule was stable to UV light i.e., the activity of the herbicide was the same whether it was irradiated with UV light or kept in darkness (results not shown).

Leaching The herbicide did not leach. The herbicide was not detected in the leachate nor the bottom three segments of the packed column (results not shown).

Chemical degradation Thiazopyr may loose activity through chemical hydrolysis of the functional groups of the herbicide molecule in a similar manner to the sulfonylurea herbicides. Because the rate of chemical hydrolysis of molecules was an exponential function of temperature (Blacklow and Pheloung 1991) we identified whether thiazopyr was degraded through chemical hydrolysis by measuring the activity of thiazopyr over time at different temperatures. The herbicide did not degrade chemically. After incubation at either 30°C and 15°C for 94 days the activity of had not declined (results not shown).

Microbial degradation was the major source of loss (Figure 1). During the 94 days of incubation the ED50 of the thiazopyr EC increased from 17 ng a.i. g^{-1} soil initially to 500 ng a.i. g^{-1} soil at 94 days. These results explain why the weed control of the herbicide varied widely from location to location. In soils with high microbial activity the herbicide would have a short period of weed control whereas in soil with a low microbial activity the herbicide would extended the period of weed control.

Formulation development Once we identified that the weed control of the herbicide was negatively correlated with microbial activity, a matrix (i.e. a control release (CR) carrier in which the herbicide was impregnated) and additives with properties that protected thiazopyr from microbial attack was produced. Microbial

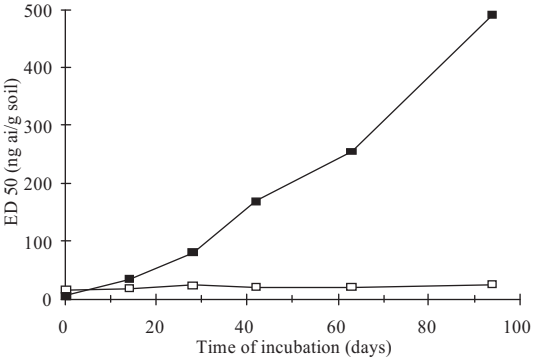

Figure 1. The activity of thiazopyr EC in sterile (open symbols) and unsterile (closed symbols) Mallee Sand.

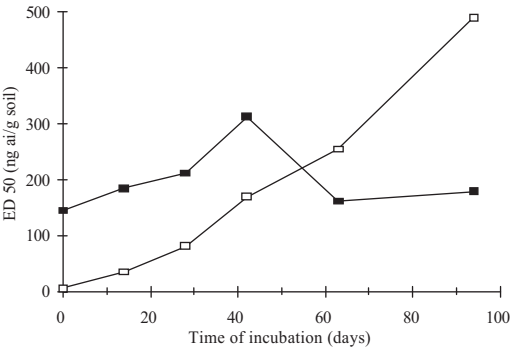

Figure 2. The activity of thiazopyr EC (open symbols) and thiazopyr CR (closed symbols) in unsterilized Mallee Sand.

degradation of thiazopyr was measured as described for the EC formulation. Initial activity of the thiazopyr CR was lower (i.e. larger ED50) than thiazopyr EC (Figure 2), however, continual release of thiazopyr CR produced a more reliable and consistent weed control than the thiazopyr EC. After 94 days, the activity of thiazopyr CR was more than 2.5 times as active as thiazopyr EC (Figure 2).

CONCLUSIONS

The knowledge of the biological parameters which affect the performance of thiazopyr has lead to the development of a thiazopyr formulation with improved performance and reduced risk to the environment. This research demonstrates the benefits of understanding the behaviour of the herbicides in a biological system and a close interaction between our biological research and development team and the chemistry formulation team.

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