

Reduced efficacy and enhanced degradation of carbetamide after repeated application in Australia

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Summary

Following reports of poor weed control, the effectiveness of repeated applications of carbetamide and propyzamide in controlling *Lolium rigidum* Gaud. (annual ryegrass) was examined under field conditions. Repeated applications of carbetamide or propyzamide were less effective in controlling *L. rigidum* than an initial application. A single application of carbetamide or propyzamide was sufficient approximately to halve the efficacy of a subsequent treatment with the same herbicide. Laboratory incubations of soil linked the poor performance of carbetamide upon repeated application to an enhanced degradation rate. We conclude that the repeated application of carbetamide or propyzamide results in less effective weed control under field conditions and that this can be partially avoided by rotation between carbetamide and propyzamide.

Introduction

Carbetamide is a soil-acting herbicide used for the control of annual grasses in *Trifolium* spp. (clover) seed crops in Australia. Clover seed producers from the south-east of South Australia reported to us that after 3-4 years of annual carbetamide application, poor control of *Lolium rigidum* Gaud. (annual ryegrass) and other grass weeds was evident. This carbetamide failure was

not due to herbicide resistance in these *L. rigidum* populations (S. J. W. Hole & S. B. Powles, unpubl. obs). One possibility was that carbetamide degraded at a faster rate in soils with a history of carbetamide use (enhanced degradation). Enhanced degradation is evident when a chemical is degraded at a faster rate than when it is applied for the first time (Roeth, 1986). This phenomenon has been reported for a wide range of soil-applied pesticides (Roeth, 1986; Felsot, 1989; Racke & Coats, 1990) and the practical effect of enhanced degradation is decreased efficacy of weed or pest control. To the best of our knowledge enhanced degradation of herbicides has not been reported as a phenomenon in Australia. However, enhanced degradation of soil-applied herbicides has often been reported in the Northern Hemisphere, including the herbicide propyzamide (Walker & Welch, 1991). Carbetamide and propyzamide are structurally dissimilar but have a similar mode of action (mitotic disruption). In Australia these herbicides are registered for annual grass control in clover seed crops, with propyzamide also registered for use in lettuce and turf.

Experiments were conducted to determine whether enhanced soil degradation of carbetamide was the reason for carbetamide failure. Field trials examined the efficacy of both carbetamide and propyzamide in controlling *L. rigidum* upon repeated application. Also, the kinetics of carbetamide degradation as influenced by prior carbetamide treatment were examined under laboratory conditions.

Materials and methods

Experimental sites

Experiments were conducted in two adjacent

Table 1. Pesticide history of field B. Values in brackets are grams of active ingredient per hectare

Year	Crop	Pesticides
1988	Cocksfoot (<i>Dactylis glomerata</i> L.)	Diuron (1,750) Diclofop-methyl (412) Omethoate (29)
1989	Cocksfoot	Diuron (1,800) Simazine (900) MCPA (274) Dicamba (140)
1990	Subterranean clover (<i>Trifolium subterraneum</i> L. cv. Junee)	Carbetamide (2,100) Bromoxynil (300) MCPA (300) Omethoate (29) Haloxypol (31) Sathoxydim (140) Omethoate (35)
1991	Subterranean clover (cv. Junee)	Glyphosate (468) Omethoate (58) Bromoxynil (300) MCPA (300) Carbetamide (2,100)
1992	Subterranean clover (cv. Junee)	Paraquat (188) Diquat (113) Metolachlor (216) Omethoate (35) Carbetamide (2,100) Bromoxynil (300) MCPA (300)
1993	Chinese cabbage	Paraquat (250) Diquat (150) Trifluralin (560) Omethoate (29) Paraquat (125) Diquat (75) Chlorpyrifos (250) Clopyralid (75)
1994	Subterranean clover (cv. Junee)	Paraquat (250) Diquat (150) Pendimethalin (660) Paraquat (188) Diquat (113) Paraquat (100) Metolachlor (324) Diflufenican (20) MCPA (200) Olethodim (72) Methidathion (720)

fields (A & B) near Naracoorte (37 °S, 140.75 °E), in the south-east of South Australia. Field A had no prior history of herbicide application, whereas field B had been sprayed commercially with 2100 g a.i. ha⁻¹ carbetamide annually for 3 consecutive years (1990–92). Soil in field A is a sandy clay loam (silt 7%, clay 23%, pH 4.8), and in field B the soil is a sandy loam (silt 8%, clay

12%, pH 4.9). Herbicide and crop histories for field B are listed in Table 1.

Herbicide application

Carbetamide (Rhône-Poulenc, Carbetamex 700 g a.i. kg⁻¹ WP) and propyzamide (Rhom and Haas, Kerb 50WP, 500 g a.i. kg⁻¹ WP) were

applied using a propane pressurized hand-held sprayer of 2 m boom width (250 kPa) fitted with flat fan nozzles (Hardi 4110-10). Sprayer output was 125 L ha⁻¹ when moving at 1.0 m s⁻¹ at a height of 40 cm above the plant canopy. Each plot was sprayed twice, giving a total water volume of 250 L ha⁻¹. In 1993, natural rainfall served to move the carbetamide into the soil and in 1994 an irrigation system was used.

Effect of a single carbetamide treatment on subsequent carbetamide efficacy (1993 experiment)

The experimental design was a randomized complete block with three replicates conducted in both fields A and B. Half of the plots at both sites were initially treated on June 19 with carbetamide (2100 g a.i. ha⁻¹), the remaining plots were left unsprayed as controls. This herbicide treatment controlled annual grass spp., including *L. rigidum*, when assessed 28 days later (results not presented). To assess a second herbicide treatment, 120 *L. rigidum* seedlings (one leaf) were transplanted into each plot. When seedlings reached the 4- to 6-leaf stage (September 30) all plots were sprayed with carbetamide (2100 g a.i. ha⁻¹). Twenty *L. rigidum* plants in each plot were covered to act as unsprayed controls such that other environmental influences on plant mortality could be excluded. Plant mortality was assessed by the presence/absence of new growth 28 days after spraying.

Effect of carbetamide and propyzamide application on subsequent carbetamide and propyzamide efficacy (1994 experiment)

This randomized block experiment was conducted in field B, which had been commercially treated with carbetamide once annually in the winters of 1990-92. Each of the four replicates consisted of nine 10 m by 2 m plots. Initial treatment was made to the nine plots within each block on July 10, three with carbetamide (2100 g a.i. ha⁻¹), three with propyzamide (1000 g a.i. ha⁻¹), and three remaining unsprayed. To assess a second herbicide application, 128 *L. rigidum* seedlings were transplanted into each plot. When the *L. rigidum* plants were at the 3- to 4-leaf stage (September 25), plots were treated with either carbetamide (2100 g a.i. ha⁻¹) or propyzamide (1000 g a.i. ha⁻¹), or remained un-

sprayed. These treatments were applied so as to generate the nine possible combinations of initial and final treatments. Plant mortality was assessed 28 days after the second treatment.

Enhanced degradation of carbetamide in laboratory incubations of soil

Four replicate 5-kg soil samples were collected to a depth of 10 cm from field B. From each sample, equivalent to 150 g of oven-dry soil was weighed into 10 disposable plastic containers. Moisture content of the soil in each container was raised to 15% (wt/wt). Half the containers of soil from each replicate were treated with 1 mL of an aqueous carbetamide solution (3.0 g L⁻¹ technical grade, 93.9%, Rhône-Poulenc) to give a final soil concentration of 20 mg kg⁻¹. Remaining containers were treated with 1 mL of water. Soil in each container was then thoroughly mixed by emptying into a plastic bag, which was shaken for 30 s. Soil was returned to the same container, to which a clip-on lid was fitted to minimize evaporation. Containers of soil were then incubated at 15 °C. After 56 days all of the soil samples were treated with 20 mg kg⁻¹ carbetamide and mixed as described previously. Containers were removed at weekly intervals to determine residual carbetamide. These samples were mixed as described previously and a 25-g subsample taken and frozen until analysis.

Residual carbetamide was determined by high-performance liquid chromatography (hplc) following extraction with acetonitrile. Frozen 25-g subsamples were placed into 250-mL polypropylene bottles with 25 mL of acetonitrile. After shaking for 1 h on a rotary shaker at 150 rpm, the samples were allowed to stand for 10 min. Approximately 2 mL of the supernatant was then filtered through a syringe-tip filter (nylon 0.2 µm). Filtrate (100 µL) was then injected on to a reverse-phase C₁₈ column (250 × 4.6 mm, Exsil 100/5 µm ODS). Carbetamide was eluted by a 10-100% acetonitrile-water gradient over 15 min at a flow rate of 1.2 mL min⁻¹. Detection was made by UV absorption at 233 nm with a retention time of 10.5 min.

Statistical analysis

An analysis of deviance was performed to compare field trial treatments using Genstat 5. A binomial error distribution was assumed. Large

differences were found between the treatment means; hence the means and standard errors as calculated by GENSTAT 5 were plotted.

Laboratory incubation data were used to generate means and standard error values. These were expressed as the percentage of the respective mean value at the time of the second carbetamide addition.

Results

Effect of a single carbetamide treatment on subsequent carbetamide efficacy (1993 experiment)

Figure 1A shows that application of carbetamide resulted in 88% mortality of *L. rigidum* seedlings when applied to plots within a field that had never been treated with carbetamide. However, at this same site, on plots pretreated once only with carbetamide, the mortality of *L. rigidum* seedlings treated with carbetamide was only 51%. Similar results were obtained in field B, which had been treated in previous seasons with carbetamide. Figure 1B shows that application of carbetamide resulted in 89% mortality of *L. rigidum* seedlings on control plots that received no carbetamide pretreatment. Mortality of *L. rigidum* seedlings treated with carbetamide was only 63% on plots that had been pretreated with carbetamide 103 days earlier. Therefore, although carbetamide causes high mortality when first applied to the soil, there is a loss of herbicidal efficacy upon repeated application, even after only a single previous treatment (Fig. 1A). At both sites, mortality of *L. rigidum* plants that were covered at the second time of carbetamide application, and thus not treated, was less than 4%.

Effect of carbetamide and propyzamide application on subsequent carbetamide and propyzamide efficacy (1994 experiment)

Experiments conducted in 1994 confirmed the results obtained in 1993 with carbetamide and examined the efficacy of repeated propyzamide application. In 1994, application of carbetamide to *L. rigidum* seedlings in previously untreated plots resulted in 97% mortality (Fig. 2 A). However, on plots pretreated earlier in the season with carbetamide, a second carbetamide treat-

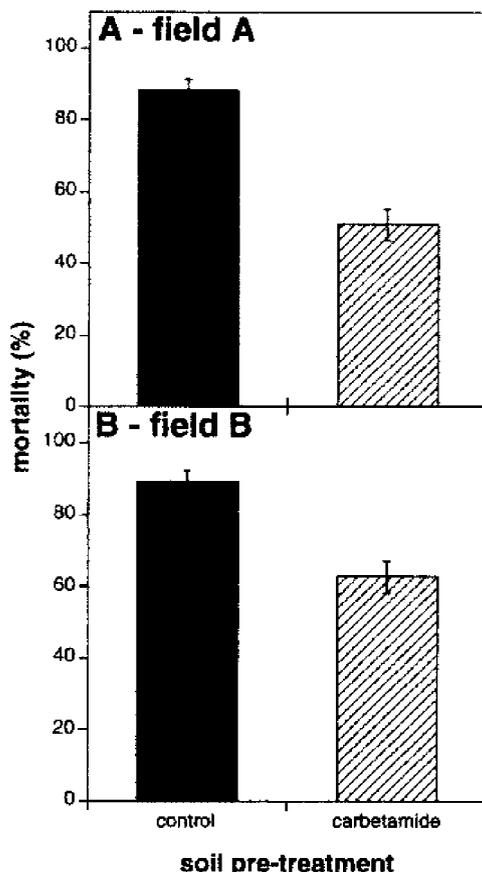


Fig. 1. Percentage mortality of *L. rigidum* in fields A and B following carbetamide application on plots pretreated once with the same herbicide (hashed bar) compared with plots treated only once. Standard errors of the means are indicated by vertical bars.

ment (77 days later) resulted in only 60% mortality. A similar result was found for propyzamide, a herbicide with a similar mode of action. Figure 2B shows that application of propyzamide to previously untreated plots resulted in 99% mortality of *L. rigidum* seedlings. In plots pretreated once with propyzamide, a second propyzamide treatment resulted in only 33% mortality. Therefore, for both carbetamide (Figs 1 and 2A) and propyzamide (Fig. 2B), repeated application results in decreased efficacy.

The 1994 experiment examined whether pretreatment with carbetamide reduced the subsequent efficacy of propyzamide, and vice versa. Rotation between carbetamide and propyzamide, in either order, resulted in high *L. rigidum* mortality (96–97%) from the second herbicide treatment. Figure 2 shows that, al-

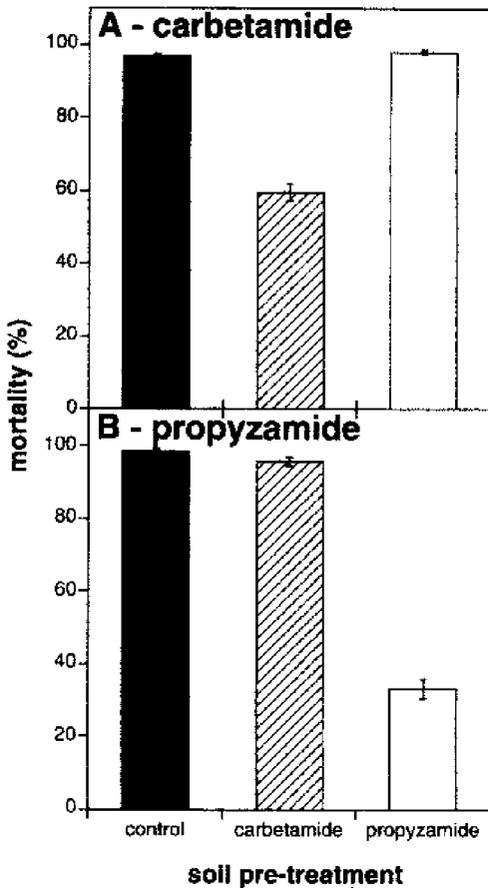


Fig. 2. Percentage mortality of *L. rigidum* following carbetamide (A) or propyzamide (B) application on plots pretreated once with carbetamide (hashed bar) or propyzamide (white bar), or plots that were initially untreated. Standard errors of the means are indicated by vertical bars.

though having similar modes of action as herbicides, carbetamide (Fig. 2A) and propyzamide (Fig. 2B) acted independently. Thus, pretreatment with one herbicide did not affect the subsequent efficacy of the other herbicide.

Enhanced degradation of carbetamide in laboratory incubations of soil

The kinetics of carbetamide degradation in soil samples taken from field B and incubated under controlled conditions clearly demonstrates that carbetamide is degraded at a faster rate upon repeated application (Fig. 3). After 7 days, only 8% of the applied carbetamide remained in the soil pretreated with carbetamide, whereas there was 78% remaining in the control soil.

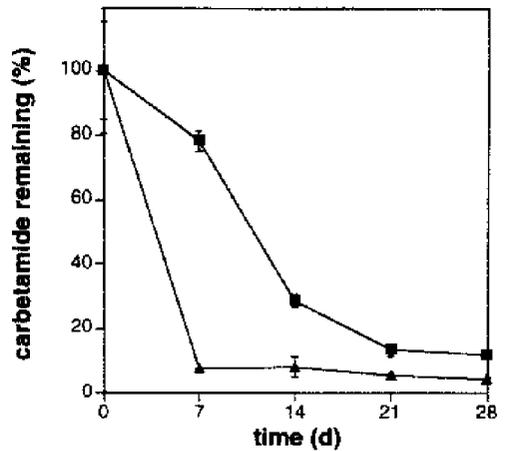


Fig. 3. Degradation of carbetamide in soil not treated with carbetamide (■) and soil treated with carbetamide 56 days earlier (▲). Standard errors of the means are indicated by vertical bars.

Discussion and conclusions

The results presented in Figs 1 and 2 confirm the observation by farmers that repeated application of carbetamide is associated with a decline in weed control efficacy. In addition, Fig. 2 establishes that the efficacy of propyzamide is also decreased upon repeated application. Figure 3 shows that the reduced efficacy of carbetamide upon repeated application is due to an enhanced rate of degradation in the soil. This is the first reported evidence of enhanced carbetamide degradation and is the first report in Australia of enhanced degradation of any herbicide. Given that enhanced degradation of propyzamide has been reported previously (Walker & Welch, 1991), the likely cause of reduced propyzamide efficacy upon repeated application (Fig. 2) is also enhanced degradation.

Management of enhanced herbicide degradation can often be achieved by decreasing the frequency at which the herbicide is applied (Roeth, 1986). As herbicides are a key strategy in the control of weeds in modern agriculture, a decrease in application frequency can be achieved by rotation of chemically dissimilar herbicides (Drose *et al.*, 1990). The experiment conducted in 1994 (Fig. 2) clearly demonstrated that rotation between carbetamide and propyzamide maintained excellent weed control. Therefore, in commercial situations, rotation between carbetamide and propyzamide may provide more

effective weed control than if either herbicide is used exclusively (assuming that there is no carry-over effect of this 2-year rotation). Also, this result implies that these two herbicides are degraded by different soil microbes and/or different pathways. Whereas the benefit of herbicide rotation was demonstrated in this study, other weed control methods may also be of benefit in a system in which enhanced degradation is a problem.

The experiments reported here demonstrate that enhanced degradation of carbetamide is the cause of reduced carbetamide efficacy upon repeated application. Also, enhanced degradation of propyzamide is likely under Australian conditions. Based upon our observations of poor weed control owing to enhanced carbetamide degradation, we consider that users of these herbicides will have to modify the frequency at which they are applied in order to maintain effective weed control. Further research is required to determine the minimum length of time necessary between applications of these herbicides if effective weed control is to be maintained.

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