SURFACTANTS CAN MASK HERBICIDE MIXTURE ANTAGONISM

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Summary The amine formulation of MCPA is well known to be antagonistic to grass and other broadleaf herbicides. Surfactants have been successful in overcoming antagonism in some cases.

In this research the activity of MCPA amine was improved by the addition of surfactant. When MCPA amine and the sulfonylurea, metsulfuron methyl, were mixed the surfactant enhanced the activity of both herbicides masking antagonism between the two herbicides.

INTRODUCTION

Herbicide tank mixtures increase the weed spectrum controlled and save the cost of multiple applications. Though many mixtures are successful, some herbicides antagonize others; reducing activity. Compatibility between herbicides is assessed so that suitable mixtures can be listed on the label. For example recommendations on Hoegrass® (diclofop methyl) are for mixing with low rates of MCPA ester and not with MCPA amine. Phenoxy herbicides have antagonized many grass herbicides (Hatzios and Penner 1985).

Phenoxys may also be mixed with other broadleaf herbicides such as the sulfonylureas. This is an important mixture with 66% of metsulfuron methyl used in the USA being mixed with a phenoxy herbicide. Mathiassen and Kudsk (1993) showed that MCPA dimethylamine salt was antagonistic to sulfonylurea herbicides. However, MCPA iso-octyl ester did not antagonize the activity of metsulfuron methyl (Hollaway *et al.* 1996). Whilst the esters are less antagonistic, regulators have forced the use of non-volatile MCPA amine. Therefore the antagonism caused by the amine formulation must be overcome.

Metsulfuron methyl is normally mixed with a surfactant to improve activity. Likewise the manufacturers recommend use of a surfactant when mixing metsulfuron methyl with MCPA amine. However, MCPA amine does not require the addition of surfactant when used alone.

Surfactant has been shown to mask antagonism between herbicides (Penner 1989) by decreasing the rate needed. When Mathiassen and Kudsk (1993) examined the joint activity of MCPA amine and metsulfuron methyl they did not add surfactant to the mixture. As the surfactant improves efficacy of metsulfuron methyl it may overcome the antagonism between MCPA amine and metsulfuron methyl.

This paper examines the relationship between metsulfuron methyl, MCPA amine and surfactant. The Additive Dose Model (ADM) will be used to investigate the joint activity of the two broadleaf weed herbicides. The use of the ADM is explained briefly in Materials and Methods or in more detail in Green and Streibig (1993).

MATERIALS AND METHODS

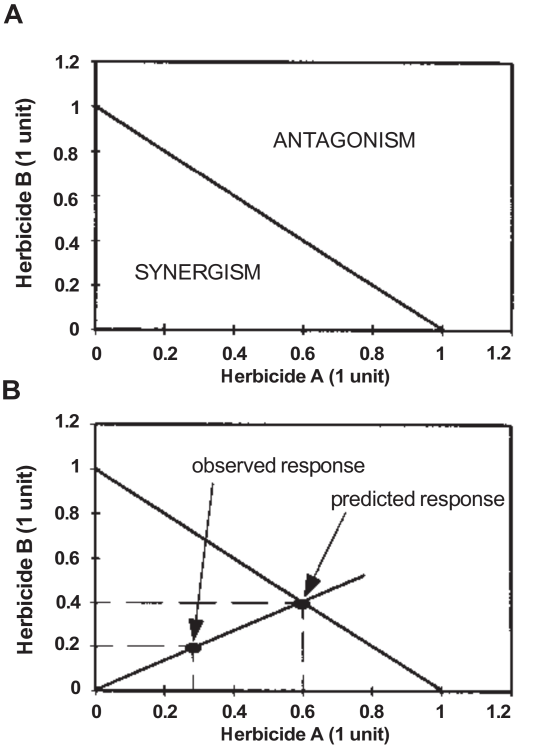
Dose response bioassays were conducted for MCPA dimethylamine salt (± the surfactant BS1000) and metsulfuron methyl applied separately and in a range of mixture ratios. The results compared the activity of MCPA amine with and without BS1000 and these were used to construct Additive Dose Models (ADMs) (Morse 1978). The joint action of MCPA amine and metsulfuron methyl were visually interpreted from the ADMs.

Plants Oilseed rape (*Brassica napus* L.) cv. Hyola seeds were sown in Debco® potting mix with necessary nutrients in 10 cm diameter plastic pots. Two seeds per pot were sown 10 mm deep and the potting mix was covered with a 3–5 mm layer of washed river sand to minimize soil water evaporation. Plants were grown in a glasshouse with a summer temperature range of 15–26°C and winter range of 12–25°C. After emergence the plants were thinned for uniformity to one per pot and pots with non-uniform plants were discarded.

Plants were sprayed at the 3–4 true leaf stage approximately two weeks after sowing.

Chemical application A laboratory tracksprayer delivered 64 L ha^{-1} at 200 kPa via three Spraying Systems™ 11001 flat-fan nozzles. Nozzles were spaced 50 cm apart and 35 cm above the plants. The boom traversed the plants at 6 km h^{-1}.

The herbicides, Nufarm MCPA 500 (MCPA dimethylamine salt, 50% a.i.) and DuPont Ally® (metsulfuron methyl, 60% a.i.), were used in this series of experiments. A non-ionic surfactant, ICI Crop Care BS1000® (alcohol alkoxylate, 1000 g L^{-1}), was added to the spray solution at 0.13% spray water volume where metsulfuron methyl was used either alone or in a mixture with MCPA amine. MCPA amine was sprayed both alone and with BS1000 added at the rate of 0.13% to evaluate the influence of surfactant. MCPA amine was applied to



Figures 1A and 1B. The structure of the Additive Dose Model. The ED50s have been set at 1 unit in this example. In 1A the basic structure of the ADM is shown. The area above the isobole represents antagonism and the area below the line represent synergism. In 1B an example of a synergistic mixture of 3 parts Herbicide A to 2 parts Herbicide B is illustrated. The observed response shows that the same 50% level of control was achieved with only half the mixture predicted from the model.

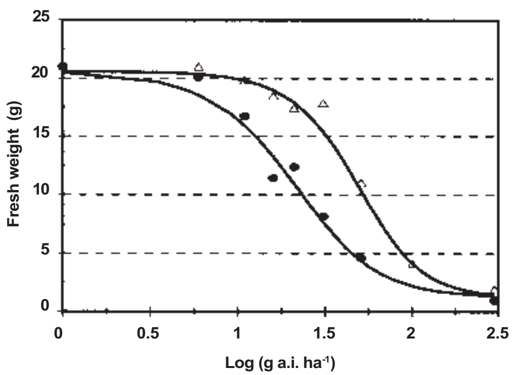


Figure 2. The efficacy of MCPA amine (D) is significantly enhanced by the addition of the surfactant, BS1000 (●).

oilseed rape at 5, 10, 15, 20, 30, 50, 100, 150 and 300 g a.i. ha^{-1}. Metsulfuron methyl was applied at 0.1, 0.13, 0.17, 0.2, 0.4, and 2.0 g a.i. ha^{-1}. The ratio for the tankmix of MCPA amine and metsulfuron methyl that is recommended on the label varies from 140:1 (MCPA amine to metsulfuron methyl) to 350:1. Mixtures of 20:1, 40:1, 100:1, 200:1 and 400:1 were used in this experiment. A minimum of six herbicidal rates were used for each dose response curve. Seven pots were used for all treatments.

A minimum of 28 plants were used for each unsprayed control treatment. The experiment was repeated in full at least once.

Post-spray treatment Plants were kept in their replicates for 24 hours and then returned to the glasshouse and arranged in randomized blocks. Assessment was by shoot fresh weight 14 d after spraying.

Statistical analysis Non-linear regression analysis was used to fit a logistic dose response curve (Streibig 1988) to the data.

The ED50 was defined as the dose required to reduce fresh weight by 50% of the untreated plants, namely halfway between the upper and lower limits of the curve. A 95% least significant interval and standard error were calculated for the ED50.

Additive Dose Model The ADM uses the dose response curves of the individual herbicides to predict their joint action. The ADM was constructed as follows. The ED50 of each herbicide was plotted on the x and y axis of the graph and a straight line isobole was drawn between them. In the example in Figure 1 the ED50s have been set at 1 unit. The line predicts the dose of any mixture which would be required to achieve the same ED50 response. Observed ED50 values were plotted on the graph and compared to the line of predicted response. When less herbicide is required than predicted the response is plotted below the isobole representing 'synergism' (Figure 1A). When more herbicide is required than predicted the response is plotted above the isobole representing 'antagonism'.

Figure 1B shows an example of the predicted and actual responses for a mixture of three parts Herbicide A to two parts Herbicide B. The model predicts that 0.6 units of A + 0.4 units of B will be required to achieve 50% control. In this example the actual response (ED50) only required 0.3 units of A and 0.2 units of B. The mixture is synergistic with the actual quantity needed being only half as much as was predicted by the model.

In this experiment two isoboles were constructed the first used the ED50 for MCPA amine alone on the x-axis, the second used the ED50 for MCPA amine + BS1000 on the x-axis.

The straight line which forms the basis of the ADM is not suitable for tests of significance (Morse 1978).

RESULTS

The efficacy of MCPA amine was significantly greater when BS1000 was added to the spray solution. Figure 2 showed that the ED50 for MCPA amine was reduced from 47.7 g a.i. ha^{-1} (s.e. 2.4) to 20.2 g a.i. ha^{-1} (s.e. 2.4) when BS1000 was added. Therefore MCPA amine with BS1000 was 2.4 times more active than MCPA amine sprayed alone. The observed responses for the mixture fell below the predicted isobole on ADM comparing the activity of metsulfuron methyl and MCPA amine (Figure 3 – solid line). This showed that the mixture had greater activity than would be predicted from the activity of either herbicide used alone – synergism.

However when the isobole was moved inwards to show the ED50 of MCPA amine + BS1000 the result was altered. As the x axis co-ordinate of the isobole decreased, it moved closer to the observed data for the mixture. The isobole moved to the left of the observed responses for mixtures with a high ratio of MCPA amine, demonstrating antagonism.

DISCUSSION

The addition of the non-ionic surfactant, BS1000, improved the efficacy of MCPA amine by 2.5 times. Yet surfactant is not normally recommended for use with MCPA amine. Likewise, the surfactant significantly altered interaction of the mixture of MCPA amine and metsulfuron methyl.

From a farmers point of view the mixture of MCPA amine and metsulfuron methyl containing BS1000 should be compared to the activity of the alternative herbicides likely to be used. As an alternative farmers are likely to use either metsulfuron methyl + BS1000 or MCPA amine alone. Comparison of the mixture with these two alternatives (Figure 3 – solid line) showed the mixture to be synergistic.

This result is in direct contrast to Danish researchers, Mathiassen and Kudsk (1993), who showed the mixture to be antagonistic. They suggested that MCPA amine antagonized the metsulfuron methyl, while metsulfuron methyl had no effect on MCPA amine. While these results differ they can be explained.

In our experiments both metsulfuron methyl and all mixtures contained the surfactant, BS1000. Manufacturers recommend the use of surfactant with this mixture. The synergism we observed can be explained by the presence of BS1000 in the mixture. That is, the surfactant masked the antagonism between MCPA amine and metsulfuron methyl. MCPA amine activity was improved by the surfactant which compensated for the loss of metsulfuron methyl activity caused by antagonism. It is likely that the enhancement of both herbicides by the BS1000 was greater than the loss of metsulfuron methyl activity caused by MCPA amine antagonism.

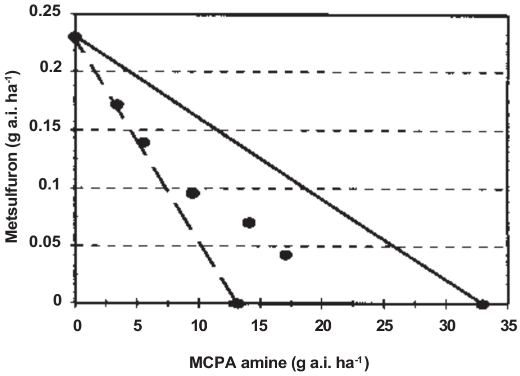


Figure 3. The ADM for MCPA amine and metsulfuron methyl showing the isobole for MCPA (solid line) and MCPA + BS1000 (dash line). The actual mixture responses fall below the solid isobole (synergism) and along or above the dash line (no interaction or antagonism).

To accurately assess the mixture it must be compared to each herbicide with sufficient surfactant added. By comparing the mix to metsulfuron methyl + BS1000 on the y axis and MCPA amine + BS1000 on the x axis the true antagonism at high rates of MCPA amine is observed (Figure 3 – dash line).

Suitable surfactants can mask antagonism in herbicides mixtures in some circumstances. In evaluating a mixture it is essential the activity of all components of the mixture are assessed for their influence on each of the other components.

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