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Amine Salts of Growth Regulator Herbicides Antagonize Paraquat[1]

JOHN T. O'DONOVAN and P. ASHLEY O'SULLIVAN[2]

Abstract. **Amine formulations of 2,4-D [(2,4-dichlorophenoxy)acetic acid] and MCPA {[(4-chloro-*o*-tolyl)oxy] acetic acid} caused a reduction in paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) phytotoxicity to barley (*Hordeum vulgare* L. 'Summit'), wheat (*Triticum aestivum* L. 'Neepawa'), and wild oats (*Avena fatua* L.). Dicamba (3,6-dichloro-*o*-anisic acid) reduced paraquat activity in barley only. Paraquat phytotoxicity was antagonized more by 2,4-D amine at high than at low rates. Higher rates of paraquat relative to a fixed rate of 2,4-D amine overcame the antagonism. Paraquat phytotoxicity was not antagonized by 2,4-D or MCPA amine applied as a separate treatment. The technical components of the 2,4-D- or MCPA-amine formulations were solely responsible for the antagonism. Ester formulations did not affect paraquat phytotoxicity.**

Additional index words. **Herbicide mixtures, formulation components, sequential applications.**

INTRODUCTION

Effective and economical weed control methods are of major importance in zero tillage and/or chemical summerfallow situations. There are two herbicides, glyphosate [*N*-(phosphonomethyl)glycine] and paraquat, presently available for non-selective postemergence control of annual weeds prior to seeding or to crop emergence or throughout the fallow season. Field studies have shown that paraquat at 0.28 kg/ha effectively controlled annual grasses such as barley, wheat, and oats (*Avena sativa* L.), but broadleaf species such as wild turnip (*Brassica campestris* L.) were more tolerant (5). These studies also showed that ester formulations of 2,4-D, MCPA, bromoxynil, and a formulated mixture of bromoxynil and MCPA could be mixed with paraquat at 0.28 kg/ha for a broader spectrum of weed control. However, amine formulations of 2,4-D and MCPA caused a reduction in paraquat phytotoxicity to the annual grass species.

The objectives of this study were to investigate further in the greenhouse the effects of mixing various herbicides with paraquat on the phytotoxicity of paraquat and to offer possible explanations for the antagonism of paraquat activity by formulations of herbicides for broadleaf weed control.

MATERIALS AND METHODS

Barley, wheat, and wild oat were seeded separately in 15-cm-diam pots filled with soil consisting of 39% sand, 53% silt, and 8% clay. The organic matter content was 12.6% and the pH was 6.8. After emergence the plants were thinned to three uniform seedlings/pot. The greenhouse was operated at 22 C day and 18 C night temperature with a 16-h photoperiod consisting of daylight supplemented by 17.2 klux of mixed fluorescent and incandescent light. Each experiment was a randomized complete block design with four replicates.

The herbicides used were the dichloride salt of paraquat[3], dimethylamine salt formulations of 2,4-D[4], MCPA[4], and dicamba[5], an isooctyl ester formulation of 2,4-D[4], an *n*-octanoic acid ester formulation of bromoxynil[4], a commercially formulated mixture of the *n*-octanoic acid ester of bromoxynil, the butoxy ethanol ester of MCPA, and a mixed butyl ester formulation of MCPA[4]. The rates of paraquat and bromoxynil are expressed as active ingredient. The rates of 2,4-D, MCPA, and dicamba are expressed as acid equivalent. Paraquat was applied alone, sequentially, or in a mixture (tank mixture) with commercial formulations of the herbicides for broadleaf weed control. In some experiments, the individual components of the 2,4-D[4]- or MCPA[4]-amine commercial formulations (i.e., the technical dimethylamine salt and the solvent-system components) were applied in combination with paraquat in amounts equivalent to their presence in the complete commercial formulations. In most experiments paraquat was applied at 0.11 kg ai/ha and the herbicides for broadleaf weed control were applied at their recommended field rates (see Tables). All spray applications were made with a motorized pot sprayer in 100 L/ha of distilled water at a pressure of 270 kPa.

Plants were harvested 3 weeks after application and shoot (aerial plant parts) fresh weights were determined immediately after removal at soil level. Most experiments were conducted with 2,4-D amine and MCPA amine, but some involved 2,4-D amine only. All data were subjected to an analysis of variance and treatment means were compared using Duncan's multiple range test.

RESULTS AND DISCUSSION

Under greenhouse conditions, paraquat at 0.11 kg/ha provided complete or almost complete topgrowth control of the grass species. This rate was, therefore, used in most subsequent experiments. The herbicides for broadleaf weed control did not reduce shoot growth significantly in any species 3 weeks after treatment. These herbicides were not therefore, applied alone in subsequent experiments. A statistically significant loss of herbicidal activity in paraquat mixtures compared to paraquat alone was considered an antagonistic interaction.

The phytotoxicity of paraquat to barley, wheat, or wild oats was not affected by 2,4-D ester, MCPA ester, bromoxynil, or a formulated mixture of bromoxynil and

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[3] Chipman Chem. Co. Trade Name: Sweep.

[4] Allied Chem. Serv. Ltd.

[5] Velsicol Corp. Canada.

Table 1. Influence of commercial formulations of several herbicides on the phytotoxicity of paraquat to barley, wheat, and wild oats. Combinations were applied as tank mixtures.

Treatment	Application rate	Shoot fresh wt.[a] Barley	Wheat	Wild oats
	(kg/ha)		(g/pot)	
Control		8.4a	5.3a	8.0a
Paraquat	0.11	1.0e	0.6c	1.0b
Paraquat + 2,4-D amine	0.11 + 0.56	4.3c	3.2b	6.7a
Paraquat + 2,4-D ester	0.11 + 0.56	0.7e	0.3c	1.4b
Paraquat + MCPA amine	0.11 + 0.56	5.4b	5.1a	7.7a
Paraquat + MCPA ester	0.11 + 0.56	0.9e	0.7c	1.4b
Paraquat + bromoxynil	0.11 + 0.28	0.5e	0.4c	0.7b
Paraquat + bromoxynil + MCPA	0.11 + 0.56	0.7e	0.2c	1.3b
Paraquat + dicamba	0.11 + 0.11	2.5d	0.8c	1.8b
$S_{\bar{x}}$		0.4	0.4	0.6

[a]Numbers within columns followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

MCPA (Table 1). However, 2,4-D amine and MCPA amine reduced paraquat phytotoxicity to all species. This antagonism of paraquat was greater on wheat and barley with MCPA amine than with 2,4-D amine. Similar reductions in paraquat phytotoxicity caused by amine but not ester formulations of these herbicides have been reported in field studies (5). The reduced antagonism caused by dicamba in barley and lack of antagonism in wheat and wild oats may be related to the lower rate of dicamba (0.11 kg/ha) than that of 2,4-D amine or MCPA amine (0.56 kg/ha). In field studies, 2,4-D amine was considerably more antagonistic to paraquat than dicamba[6].

[6] O'Donovan, J. T. and P. A. O'Sullivan. 1979. Influence of dicamba and 2,4-D amine on the control of rape, barley, wheat and oats with paraquat. Res. Rep., Expert Comm. on Weeds, West. Sect. 3:26.

There was a general trend towards greater antagonism of paraquat phytotoxicity with the technical dimethylamine components of 2,4-D and MCPA amine than with the complete formulations, but differences were significant only for 2,4-D in barley and MCPA in wheat (Table 2). The reason for such differences is unclear at present. The commercial formulations and technical-dimethylamine components of the formulations of 2,4-D amine and MCPA amine (Table 3) reduced the phytotoxicity of paraquat in all species. The solvent-system components of the formulations did not affect paraquat phytotoxicity to the annual grasses.

In barley and wild oats, 2,4-D amine at 0.07 kg/ha and higher rates reduced paraquat phytotoxicity and there were increases in antagonism with higher rates of 2,4-D amine (Table 3). In wheat, 0.56 kg/ha of 2,4-D amine was required for reduction of paraquat phytotoxicity and a further reduction of paraquat phytotoxicity occurred at 0.84 kg/ha.

Higher rates of paraquat relative to a fixed rate of 2,4-D amine appeared to alleviate the antagonism in some cases and antagonism did not occur in any species when the rate of paraquat was increased to 0.28 kg/ha (Table 4).

From a chemical or physical interaction between the herbicides in the spray tank, one would expect increased antagonism with mixtures containing a fixed rate of paraquat and increasing rates of 2,4-D amine and decreased antagonism with increasing rates of paraquat and a fixed rate of 2,4-D amine. The rate of 2,4-D amine required to reduce paraquat activity in wheat (0.56 kg/ha) was greater than that required in wild oats or barley (0.07 kg/ha). The reason for this is unclear at present.

The phytotoxicity of paraquat was reduced by 2,4-D amine and MCPA amine (Table 5) only when these herbicides were applied in mixtures with paraquat. Application of 2,4-D amine or MCPA amine 1 day before, immediately before, or 1 day after paraquat resulted in annual grass control equal to that by paraquat alone. In field studies, O'Sullivan and O'Donovan (5) similarly found that sequential applications of 2,4-D amine and MCPA amine in relation to paraquat did not reduce paraquat activity in annual grasses, whereas

Table 2. Influence of the formulation components of 2,4-D and MCPA dimethylamine at 0.56 kg/ha on the phytotoxicity of paraquat at 0.11 kg/ha to barley, wheat, and wild oats. The herbicide components were applied in amounts equivalent to their presence in the commercial formulation. Combinations were applied as tank mixtures.

Treatment	Shoot fresh wt.[a] Barley 2,4-D	Barley MCPA	Wheat 2,4-D	Wheat MCPA	Wild oats 2,4-D	Wild oats MCPA
			(g/pot)			
Control	7.7a	8.0a	6.3a	5.9a	6.4a	6.5ab
Paraquat	1.5d	1.3b	0.8c	0.7c	0.3b	1.2c
Paraquat + commercial formulation	3.9c	7.9a	3.6b	4.8b	5.5a	6.3ab
Paraquat + technical 2,4-D or MCPA dimethylamine	5.0b	8.2a	3.8b	6.1a	6.6a	7.3a
Paraquat + solvent system for 2,4-D or MCPA dimethylamine	1.6d	1.2b	0.2c	0.6c	0.5b	1.4c
$S_{\bar{x}}$	0.3	0.5	0.3	0.3	0.5	0.3

[a]Numbers within columns followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

Table 3. Influence of various rates of the commercial formulation of 2,4-D dimethylamine on the phytotoxicity of paraquat at 0.11 kg/ha in barley, wheat, and wild oats. Combinations were applied as tank mixtures.

Treatment	2,4-D rate	Shoot fresh wt.[a] Barley	Wheat	Wild oats
	(kg/ha)	(g/pot)		
Control	...	9.3a	7.5a	7.6a
Paraquat	...	3.2e	1.8c	1.7d
Paraquat + 2,4-D	0.04	3.3e	2.0bc	2.4d
Paraquat + 2,4-D	0.07	4.7d	1.4c	5.6c
Paraquat + 2,4-D	0.11	5.1cd	1.0c	6.0bc
Paraquat + 2,4-D	0.28	6.0c	3.2bc	6.5b
Paraquat + 2,4-D	0.56	7.5b	4.2b	6.9ab
Paraquat + 2,4-D	0.84	7.5b	8.3a	7.5a
$S_{\bar{x}}$		0.4	0.7	0.3

[a]Numbers within columns followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

Table 4. Influence of a fixed rate of commercial formulation of 2,4-D dimethylamine (0.56 kg/ha) on the phytotoxicity of various rates of paraquat to barley, wheat, and wild oats. Combinations were applied as tank mixtures.

Treatment	Application rate	Shoot fresh wt.[a] Barley	Wheat	Wild oats
	(kg/ha)	(g/pot)		
Control	...	8.4a	6.6a	5.3a
Paraquat	0.04	6.3bc	4.4b	5.6a
Paraquat	0.07	4.1ef	2.3c	2.6b
Paraquat	0.11	2.5f	0.6d	2.1b
Paraquat	0.14	0.5g	0.2d	1.3b
Paraquat	0.28	0.3g	0.1d	1.1b
Paraquat + 2,4-D	0.04 + 0.56	7.9ab	6.1a	5.1a
Paraquat + 2,4-D	0.07 + 0.56	7.2abc	5.7a	5.7a
Paraquat + 2,4-D	0.11 + 0.56	4.8cd	4.6b	4.3a
Paraquat + 2,4-D	0.14 + 0.56	3.1f	4.0b	5.2a
Paraquat + 2,4-D	0.28 + 0.56	0.4g	0.4c	1.0b
$S_{\bar{x}}$		0.6	0.4	0.6

[a]Numbers within columns followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

tank mixtures of these herbicides with paraquat resulted in antagonism.

These results indicate that antagonism of paraquat activity by 2,4-D amine and MCPA amine is probably due to a chemical or physical interaction between the herbicides in the tank or on the leaf surface. Antagonism of glyphosate phytotoxicity caused by a number of herbicides for broadleaf weed control in annual grasses has been demonstrated (4). Antagonism of glyphosate activity by 2,4-D amine, 2,4-D ester, and bromoxynil was subsequently shown to be due in part to reduced uptake and translocation of ^{14}C-labeled glyphosate (3). However, because paraquat activity is reduced by amine but not ester formulations, a different mechanism of antagonism may be involved. Little information is available in the literature on interactions between paraquat and growth regulator-type herbicides. Hall and Brady (2) showed that 2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid] and dicamba reduced paraquat uptake in several woody plants. Bailey and Davison (1) found that 2,4-D amine decreased necrosis caused by paraquat in *Convolvulus arvensis* L. This may indicate that 2,4-D amine interferes with paraquat-induced breakdown of cell membranes. Paraquat has been shown to form complexes with a number of organic molecules including amines and phenols (6). In the present study, complex formation between paraquat and the technical components of 2,4-D, MCPA, or dicamba amines may result in reduced paraquat uptake and/or a new biologically inactive herbicide complex may be formed.

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Table 5. Influence of timing of application of the commercial formulation of 2,4-D and MCPA dimethylamine at 0.56 kg/ha, on the phytotoxicity of paraquat at 0.11 kg/ha in barley, wheat, and wild oats.

Treatment	Shoot fresh wt.[a] Barley 2,4-D	Barley MCPA	Wheat 2,4-D	Wheat MCPA	Wild oats 2,4-D	Wild oats MCPA
	(g/pot)					
Control	7.5a	7.3a	6.4a	6.3a	8.4a	7.0a
Paraquat	2.7c	1.3b	0.9c	0.6b	0.6c	1.2b
2,4-D or MCPA 1 day before paraquat	1.6c	1.4b	0.5c	1.0b	1.3c	1.5b
2,4-D or MCPA in a mixture with paraquat	5.6b	7.0a	2.6b	5.5a	4.9b	7.3a
2,4-D or MCPA immediately before paraquat	2.2c	1.1b	0.6c	1.1b	0.9c	1.6b
2,4-D or MCPA 1 day after paraquat	1.8c	1.4b	0.5c	0.8b	1.1c	1.2b
$S_{\bar{x}}$	0.5	0.4	0.3	0.4	0.6	0.4

[a]Numbers within columns followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

components of 2,4-D, MCPA, bromoxynil, and bromoxynil plus MCPA were supplied by Allied Chem. Serv. Ltd. We gratefully acknowledge the technical assistance of F. Brook, T. Williams, and D. Reader, and C. Caldwell, who critically reviewed the manuscript.

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Fate of 3,4-Dichloroaniline in a Rice (*Oryza sativa*)-Paddy Microecosystem[1]

ALLAN R. ISENSEE, DONALD D. KAUFMAN, and GERALD E. JONES[2]

Abstract. The fate of 3,4-dichloroaniline (DCA), a major metabolite of the herbicide propanil (3′,4′-dichloropropionanilide), in rice (*Oryza sativa* L.), soil, water, and aquatic organisms was determined in rice-paddy microecosystems. Soil, treated with 10 ppm DCA, was placed in glass chambers, planted to rice, then flooded when the rice reached the two-leaf stage. After flooding, four species of aquatic organisms were added. The concentration of DCA and metabolites in soil, rice, water, and aquatic organisms was determined over a period of time. A maximum of 2.8% of the total radioactivity applied to soil desorbed or leached into water. DCA recovered from water decreased from 12 to 1% of the total radioactivity in water between 1 and 30 days after flooding. Between 10.5 and 18.5% of the radioactivity remaining in soil at the end of the experiments was extractable. Of the radioactivity recovered, between 5 and 11% was DCA, and up to 6 to 19% was 3,3′,4,4′-tetrachloroazobenzene (TCAB), these percentages being dependent on exposure time. Rice accumulated 0.5% or less of the total radioactivity in soil. Only 35 to 55% of the accumulated radioactivity was extractable. Very small amounts of radioactivity were accumulated by aquatic organisms.

Additional index words. Soil leaching, metabolism, plant uptake, accumulation.

INTRODUCTION

The rapid formation of DCA in soil from propanil (5) and other aniline-based pesticides has led to extensive research to determine the fate of this metabolite in soil and plants. In soil, large amounts of DCA are bound to soil particles (2), which makes it unavailable for immediate metabolism or plant uptake. Some of the DCA in soil undergoes biochemical condensation to TCAB (1). Even though other metabolites have been found in soil, TCAB appears to be the major product occurring in soils treated initially with DCA. Kearney et al. (7) demonstrated that the degree of condensation of DCA to TCAB increased logarithmically as the initial DCA concentration increased. Subsequent studies with propanil-treated rice soils (8) demonstrated the presence of TCAB at soil depths down to 30 cm. The highest TCAB concentration was present at the 0 to 10 cm depth.

In rice plants, propanil is rapidly taken up by the roots, metabolized to DCA, which is translocated to the tops, and then converted to metabolites such as glycosyl conjugates (3). Yih et al. (12) found that propanil applied directly to rice leaves is also converted to DCA, the major portion of which is complexed with polymeric cell constituents. Still (10) found only trace amounts of radioactivity in rice seedlings growing in nutrient solutions with ^{14}C-TCAB.

This study was undertaken to evaluate further the fate

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[2] Res. Plant Physiol., Res. Soil Microbiologist and Chem., Sci. Ed. Admin., Agric. Res. Serv., U.S. Dep. Agric., Pestic. Degrad. Lab., Beltsville, MD 20705.