A COMPARISON OF DIFFERENT SALT FORMULATIONS OF MCPA, 2,4-D, 2,4,5-T, PICLORAM AND DICAMBA, AND OF SALT ADDITIVES TO THESE HERBICIDES ON RUBBER VINE

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Summary. Seven salts of five growth regulator herbicides were evaluated on rubber vine, *Cryptostegia grandiflora*. Salts tested were the potassium, sodium, dimethylamine, triethylamine, diethylamine, triethanolamine and diethanolamine of the herbicides MCPA, 2,4-D, 2,4,5-T, picloram and dicamba. Efficacy of the herbicides declined in the order picloram, dicamba > 2,4-D > 2,4,5-T, MCPA. No differences in efficacy were found between salts of these herbicides.

Subsequently, a number of inorganic salts were tested for their usefulness as additives to some of these salt formulations. Sodium and potassium sulphate and nitrate, but not sodium or potassium phosphate, at 0.5% slightly enhanced the activity of the sodium and potassium salts of the above herbicides against rubber vine; salt concentratios of 0.2, 2 and 5% had no effect, indicating an optimum concentration of salt additive between 0.2 and 2%. Increasing concentrations of ammonium sulphate and phosphate from 0.1 to 5% had an increasingly inhibitory effect on the dimethylamine and triethanolamine salts of the above herbicides. The results confirm field observations that autumn treatment of rubber vine is more successful than spraying at other seasons, and this, rather than the use of additives, is the key to improved control of rubber vine with herbicide sprays.

INTRODUCTION

Amine salt formulations of MCPA, 2,4-D, 2,4,5-T, picloram and dicamba are generally less effective than ester or acid formulations of these herbicides (2, 7, 9) and this is the case in control of rubber vine (5, 6). However, the amine salts are considerably less volatile than the esters, and cheaper, so that there would be advantages if a salt formulation could be substituted for an ester with equal effect.

The possible enhancement of herbicidal effects through the addition of inorganic salts or other additives is of considerable interest. Cook and Duncan (3) mention "the possibility...of improving the overall uptake process under a range of environmental conditions", and McWhorter and Jordan (8) found that addition of 0.1M KH_2PO_4 restored the effectiveness of 2,2-DPA/surfactant mixtures to Johnson grass, *Sorghum halepense*, under adverse climatic conditions.

Wilson and Nishimoto (17) found that ammonium sulphate enhanced the activity of picloram on guava, *Psidium guajava*, strawberry guava, *P. cattleianum*, and dwarf beans, *Phaseolus vulgaris*, and note "increased activity might also permit the use of lower rates of picloram, which is both environmentally and economically desirable".

Turner and Loader (14) found several ammonium salts were synergists when added to foliar-applied water soluble herbicides. Certain rates of ammonium sulphate and nitrate increased picloram phytotoxicity in dwarf bean and guava; ammonium nitrate enhanced the effects of MCPA salt on willow, *Salix fragilis*, and poplar, *Populus gelrica*, and increased the activity of mecoprop salt on privet, *Ligustrum ovalifolium*, and *Rhododendron ponticum*. Brady (1) found that ammonium nitrate and phosphoric acid increased the absorption, but not translocation, of the iso-octyl ester of 2,4,5-T in a number of woody species. In fact, translocation as a percentage of chemical absorbed was reduced.

Turner and Loader (15) found several complexing agents enhanced the activity of glyphosate and dichlorprop to *Agropyron repens* and *Stellaria media*, respectively, but not all additives enhanced activity and some were antagonistic. In contrast to the findings of Brady, Turner and Loader (15) did not obtain enhancement of MCPA or mecoprop esters with inorganic additives and conclude that "it is often possible to obtain approximately equivalent results simply by using an ester in place of a salt formulatin" (14, 16).

In contrast to the many herbicidal studies of salts as additives, systematic studies of these herbicides formulated as salts are lacking. Melnikov (9) states that the activity of salts of the aryloxyacetic acids with organic bases is 1.2-1.7 times higher than the activity of alkali metal salts of these acids, but cites no evidence to support this view.

Trials were, therefore, conducted to test the relative efficacy of sodium (Na^+), potassium (K^+) and various amine salt formulations of the above herbicides acids, and to include the use of salt additives to see if this would improve the performance of the salf formulations against rubber vine.

METHODS

<u>Preparation of the herbicides salts</u>. Technical 2,4-D, 2,4,5-T and MCPA were recrystallized from toluene. Technical picloram (91%) and dicamba (81%) were used as received.

The amine salts dimethylamine (DMA), diethylamine (DEA), triethylamine (TEA), deithanolamine (DEOA) and triethanolamine (TEOA) were prepared by adding a slight excess of the appropriate amine to the correct amount of the respective herbicidal acid. The sodium and potassium salts were likewise prepared by adding a slight excess of NaOH or KOH for the sodium and potassium slats, respectively. Distilled water and a nonionic wetting agent (BS100^R) were added to give final concentrations of 10% (picloram) or 20% (w/v) (MCPA, 2,4-D, 2,4,5-T and dicamba) containing 5% (v/v) wetting agent. The Na^+ and K^+ salts of 2,4-D and 2,4,5-T are almost insoluble, so that the spray solutions of these herbicides were prepared directly.

Untreated controls were included but are not included in the results and analysis.

<u>Experimental design and procedure</u>. Rubber vine seedlings were grown in a glasshouse at Sherwood, Brisbane, in individaul nursery propagating tubes until they were approximately 30 cm tall (approximatley 6 months of age). The best plants were selected for treatment. In Trial 1, the experimental design consisted of 35 treatments (5 herbicides x 7 salts) x 6 replicates x 20 plants/plot (i.e. 4,200 plants), in a randomized black design. All herbicides were used as 0.2% (w/v) solutions in water, except for the more toxic picloram which was used at 0.15%.

In Trial 2 ammonium sulphate and ammonium phospate were applied at concentrations of 0.1, 0.5, 1.0 and 5.0% (w/v). The dimethylamine and triethanolamine salts of MCPA, 2,4-D, 2,4,5-T and dicamba were applied at 0.2% (w/v). Picloram was applied at 0.1% (w/v).

In Trial 3, sodium and potassium sulphate, phosphate and nitrate were applied at concentrations of 0.2, 0.5, 2.0 and 5.0% (w/v). The sodium salts were combined with the sodium salt formulations of the above herbicides, while the potassium salts were combined with the potassium salt formulations. All herbicides were applied at 0.2% (w/v).

Herbicide solutions were applied to the plants using a small pneumatic sprayer fitted with a flat fan nozzle.

The experimental designs in Trials 2 and 3 were a 9x9 and an 11x11 lattice, respectively. Both trials contained three replications with twenty plants/pot. Since it was not feasible to treat all plants at the one time, blocks and replicates of the lattices were separated in time, and thus time was confounded with blocks and replicates in the experimental design. Sets of treatments assigned to a block in the lattice were applied on consecutive days. In Trial 3, replicates were separated by approximately six weeks.

Plants in Trial 1 were sprayed in May, and final measurements taken in October, when surviving plants were showing signs of recovery. In all trials, stem dieback of each plant was measured and calculated as a percentage of the original plant height. Trials 2 and 3 were similarly terminated 3 to 4 months after treatment.

The results were subjected to analysis of variance. Arcsine transformation of the data did not increase the precision of the analysis, so only untransformed values and analyses are reported. In Trials 2 nd 3, the adjusted treatment means were used for calculating the contrasts between treatment combinations and the error mean square of the lattice was used to test for differences between treatments. Since the interactions are not significant, only tables of means are presented.

RESULTS AND DISCUSSION

There were significant differences between herbicides in all these trials, but there was no significant differences between salts of herbicides nor was there a significant interaction between herbicides and salts in any trial.

Table 1. The effect of salt formulations of herbicides on stem dieback of rubber vine

Herbicide	Stem dieback[a] (%)	Formulation	Stem dieback[b] (%)
2,4-D	75	K^+	73
2,4,5-T	66	Na^+	71
MCPA	68	DMA	73
Picloram	75	TEA	70
Dicamba	78	DEA	74
		TEOA	
l.s.d. (P = 0.05)	7.5	DEOA	73
l.s.d. (P = 0.01)	9.9	l.s.d. (P = 0.05)	N.S.

[a]Means across formulations
[b]Means across herbicide treatments

The order of toxicity of the herbicides i.e. picloram, dicamba > 2,4-D > 2,4,5-T, MCPA, is as expected from previous results (6, 7), given that the concentration of picloram used in Trials 1 and 2 was less than that for the other herbicides. The level of herbicide chosen (0.2%) was found in previous experiments to kill some, but not all, seedling rubber vine plants.

Table 2. The effect of ammonium salt additives on stem dieback of rubber vine (%) with amine salts of five herbicides

Herbicides		Dieback[a]	Salt	Dieback[b]	Salt Conc.	Dieback[c]
2,4-D		42.0	$(NH_4)_2SO_4$	36.6	0.1%	39.6
2,4,5-T		32.1	$(NH_4)_3PO_4$	38.3	0.5%	39.3
Picloram		32.7			1.0%	37.5
Dicamba		42.6			5.0%	33.3
MCPA		37.7				
l.s.d	(P = 0.05)	3.7		N.S.		3.3
	(P = 0.01)	4.8		N.S.		4.3

[a]Means across salts and salt concentrations
[b]Means across herbicides and salt concentrations
[c]Means across herbicides and salts

Both anions and cations can affect herbicide absorption and efficacy (1, 10-16, 18). Orgell and Weintraub (10) studied the effects of ionic additives on 2,4-D absorption by bean plants and found decreasing efficacy in the order various amines > lithium > ammonium > potassium > sodium for cations and sulphate > phosphate > nitrate > chloride > borate for anions.

Table 3. The effect of potassium salt additives on stem dieback of rubber vine (%) with potassium salts of 2,4-D, 2,4,5-T, MCPA, piclorm and dicamba

Herbicides		Dieback[a]	Salt	Dieback[b]	Salt Conc.	Dieback[c]
2,4-D		70.2	K_2SO_4	71.6	0.2%	71.1
2,4,5-T		58.3	K_3PO_4	66.7	0.5%	73.1
Picloram		81.8	KNO_3	71.8	2.0%	68.3
Dicamba		78.8			5.0%	67.6
MCPA		61.0				
l.s.d.	(P = 0.05)	5.9		4.6		5.3
	(P = 0.01)	7.8		6.0		6.0

[a]Means across salts and salt concentrations
[b]Means across herbicides and salt concentrations
[c]Means across herbicides and salts

Brady (1) found both nitrate and phosphate to be effective in increasing 2,4,5-t absorption by leaves of four tree species; Turner and Loader (14) found ammonium sulphate and citrate were more active than ammonium nitrate and chloride in mixtures with picloram. Wilson and Nishimoto (18) found ammonium sulphate, nitrate, chloride and phosphate to be more effective than ammonium carbonate or molybdate in enhancing picloram activity; ammonium sulphate was the only one of six sulphate salts tested to increase absorption.

The experiments reported here specifically avoided mixing cations (Na^+, K^+, $NH_4{}^+$) in order to look for enhanced activity conferred by either cations or anions. The choice of salts was also dictated to a degree by the price and availability of both the herbicide salts and the salt additives. Despite the fact that considerable success has been achieved with ammonium salts, particularly ammonium sulphate in mixtures with potassium salts of the growth regulator herbicides, the successful use of other additives such as organic phosphates and complexing agents (13, 16) and/or ammonium salts with a number of non-growth regulator herbicides (3, 13, 15, 16) suggested that here was no *a priori* reason why ammonium sulphate and phosphate would not effect the same enhancement with the amine salts of 2,4-D etc. or the sodium and potassium salts not enchance their respective salts of these herbicides.

As can be seen from the tables, the only favourable result obtained was an enhancement of the herbicides at a concentration of 0.5% additive in trial 3, suggesting an optimum concentration of additive somewhere between 0.2 and 2%. This result is consistent with that found for ammonium sulphate enhanced absorption of picloram by strawberry guava (18). Also in trial 3, nitrate and sulphate gave superior results to phosphate ($P = 0.05$), while in trial 2 both sulphate and phosphate decreased the activity of their herbicide with increasing concentration of additive, giving the linear relationship

$$Y = 39.5-1.26X \qquad (r = -0.985^{***})$$

where Y = % dieback and X = concentration of ammonium salt

There are a number of possible reasons for these results. Turner and Loader (13, 14) found that not all herbicides/additive/plant combinations were synergistic; many herbicide plus additive combinations had no effect, or were antagonistic. It may be that such combinations just do not work on rubber vine.

Another possible explanation lies in the rates of herbicides plus additives used. Turner (13) and Turner and Loader (14, 15, 16) used sub-lethal rates of herbicides in their experiments; herbicides were intended to injure but not kill the test plants. Examination of their data and that of Wilson and Nishimoto (17, 18) leads to the conclusion, as noted by Wilson and Nishimoto (17), that whereas the use of additives may give an enhanced early response, the apparent differences become negligible with increasing rates of herbicide and time after treatment. Similarly, differences between the amine salt and ester formulations of 2,4-D are reduced as the rate of herbicide is increased (2). Again, there was an interaction with weed species.

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In summary:

1. Differences between formulations are more marked at sublethal concentrations

2. The effects of additives are often more marked at sublethal concentrations

3. Herbicide-additive effects are highly species dependent and such species-herbicide-additive interactions can be affected also by climatic variables, with the result that the best combinations of herbicide plus additives may only restore the efficacy of mixtures to that already to be found by application of properly formulated herbicides under suitable

conditions

4. Short-term responses such as absorption after 24 or 48 hours, or stem twisting, do not necessarily mirror herbicidal effectiveness weeks or months later.

The fact that no differences were found between salts of the various herbicides tested, reinforces the conclusion that such differences are minimal at lethal concentrations or doses of active ingredient.

Trial 2 was set out in spring (October); the general mean for Trial 2 is 37% dieback. Treatment times for replicates 1, 2 and 3 in trial 3 correspond to spring, summer, and autumn, respectively, and the respective means are 55, 56, and 80%. The mean for Trial 1, also applied in autumn, is 73%. Autumn treatment of rubber vine is more successful in the field (5), and the results here tend to confirm that observation.

From a practical point of view, the prospects of enhanced herbicide salt activity would have the following advantages i) reduced costs, ii) reduced herbicide rate with consequential environmental benefits and iii) reduced non-target damage resulting from herbicide drift and/or volatility. However, the results suggest that the benefits to be gained by the use of additives with salt formulations are not so great as those obtained through the use of ester formulations or the timing (choice of season) of application.

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