

The influence of salts in carrier water and adjuvants on glyphosate activity

by

Brian Lindsay de Villiers

Submitted in partial fulfillment of the requirements for
the degree PhD: Agronomy
in the Faculty of Natural & Agricultural Science
University of Pretoria

Pretoria

May 2002

TABLE OF CONTENTS

ABSTRACT		1
UITTREKSEL		2
CHAPTER 1	INTRODUCTION	3
1.1	References	5
CHAPTER 2	CHEMICAL COMPOSITION OF CARRIER WATER INFLUENCES GLYPHOSATE ACTIVITY	8
2.1	Introduction	8
2.2	Materials and Methods	9
2.2.1	<i>General procedures</i>	9
2.2.2	<i>Application information</i>	9
2.3	Results and Discussion	12
2.3.1	<i>Antagonism of glyphosate by various natural water carriers</i>	12
2.3.2	<i>Relationship between glyphosate phytotoxicity and individual ions, total dissolved solids, electrical conductivity and total hardness</i>	13
2.3.3	<i>Multiple regression analysis on cations and anions</i>	14
2.3.4	<i>Correlation between individual ions and factors</i>	20
2.4	Conclusions	22
2.5	References	22
CHAPTER 3	CALCIUM AND MAGNESIUM IN SPRAY CARRIERS ANTAGONIZE GLYPHOSATE PERFORMANCE	25
3.1.	Introduction	25
3.2	Materials and Methods	26
3.2.1	<i>General procedures</i>	26
3.2.2	<i>Application information</i>	26
3.3	Results and Discussion	27
3.4	Conclusions	29
3.5	References	29

CHAPTER 4	SURFACTANT, SALTS AND FORMULATION AFFECT GLYPHOSATE RETENTION AND ABSORPTION	31
4.1	Introduction	31
4.2	Materials and Methods	32
4.2.1	<i>General procedures</i>	32
4.2.2	<i>Phytotoxicity experiments</i>	33
4.2.3	<i>Spray retention experiments</i>	34
4.2.4	<i>[¹⁴C]glyphosate absorption experiments</i>	34
4.3	Results and Discussion	36
4.4	Conclusions	43
4.5	References	43
CHAPTER 5	OPTIMIZING GLYPHOSATE PERFORMANCE WITH ADJUVANTS	46
5.1	Introduction	46
5.2	Materials and Methods	47
5.2.1	<i>General procedures</i>	47
5.2.2	<i>Glasshouse study</i>	47
5.2.3	<i>Field study</i>	49
5.3	Results	50
5.3.1	<i>Glasshouse study</i>	50
5.3.2	<i>Field study</i>	51
5.4	Discussion	54
5.5	Conclusions	54
5.6	References	55
CHAPTER 6	SPRAY DROPLET RESIDUALS OF GLYPHOSATE WITH SOUTH AFRICAN ADJUVANTS IN CALCIUM SPRAY CARRIERS	57
6.1	Introduction	57
6.2	Materials and Methods	58
6.2.1	<i>General procedures</i>	58
6.2.2	<i>Application information and SEM technique</i>	58

6.3	Results and Discussion	59
6.4	Conclusions	65
6.5	References	65
CHAPTER 7	GENERAL DISCUSSION AND CONCLUSIONS	66
CHAPTER 8	SUMMARY	68
	OPSOMMING	70
	ACKNOWLEDGEMENTS	72
	APPENDIX	73

The influence of salts in carrier water and adjuvants on glyphosate activity

Brian Lindsay de Villiers

Professor C.F. Reinhardt

Plant Production (Weed Science)

PhD

ABSTRACT

Glyphosate, a non-selective herbicide, is antagonized by salts in the spray carrier and responds to surfactant type and concentration. Glyphosate antagonism by dissolved salts such as calcium and magnesium was verified with natural water carriers and with carriers to which salts were added. Salt antagonism of glyphosate occurred from the formation of complexes that were less absorptive than the formulated isopropylamine glyphosate. Absorption of various salts of glyphosate varied as follows: isopropylamine > acid > ammonium > sodium > calcium. Ammonium sulphate increased the absorption of glyphosate both in distilled water carriers and in water carriers containing calcium chloride. Absorption and retention of glyphosate generally increased as surfactant (nonylphenol ethoxylate) hydrophilic/lipophilic balance (HLB) increased. The optimal HLB for glyphosate absorption was lower when ammonium sulphate was added to the spray carrier. An experimental adjuvant (trade name: Power-Up) that contained nonionic surfactant and ammonium sulphate, increased glyphosate efficacy more than the currently registered South African adjuvants. This could be as a result of increased foliar absorption and/or retention on foliage. The use of acid containing adjuvants was not essential for adequate glyphosate efficacy. Visual assessment of spray droplet residuals on leaves indicated that the appearance of spray droplet residuals was linked to glyphosate efficacy. Thick, amorphous and grainy spray droplet residuals on the leaf surface was an indicator of poor efficacy, whilst thinner, smoother residuals in close contact with the leaf surface was linked to increased efficacy.

The influence of salts in carrier water and adjuvants on glyphosate activity

Brian Lindsay de Villiers

Professor C.F. Reinhardt

Plantproduksie (Onkruidbeheer)

PhD

UITTREKSEL

Glifosaat, 'n nie-selektiewe onkruidoder, word benadeel deur opgeloste soute in die spuitwater en reageer op benattertipe en -konsentrasie. Glifosaat antagonisme deur opgeloste soute soos kalsium en magnesium is geverifieer met natuurlike waterdraers en draers met bygevoegde chemikalieë. Soutantagonisme van glifosaat het plaasgevind as gevolg van die vorming van komplekse wat minder opneembaar is as die geformuleerde glifosaat isopropielamien. Opname van verskillende soute van glifosaat het as volg gevarieer: isopropielamien > suur > ammonium > natrium > kalsium. Ammoniumsulfaat het die opname van glifosaat bevorder; beide met gedistilleerde water en met waters wat kalsiumchloried bevat het. Opname en behoud van glifosaat op blare het oor die algemeen toegeneem soos die hidrofiliese/lipofiliese balans (HLB) van die benatter (noniel-fenol-etoksilaat) gestyg het. Die optimale HLB vir glifosaatopname was laer wanneer ammoniumsulfaat tot die spuitoplossing gevoeg is. 'n Eksperimentele hulpmiddel (handelsnaam: Power-Up), wat beide 'n nie-ioniese benatter en ammoniumsulfaat bevat, het glifosaateffektiwiteit meer bevorder as die huidige geregistreerde Suid-Afrikaanse hulpmiddels. Dit kan die gevolg wees van verhoogde blaaropname en/of behoud van die spuitstof op die blaaroppervlak. Die gebruik van suurbevattende hulpmiddels was nie krities vir aanvaarbare glifosaat-effektiwiteit nie. Waarneming van spuitdruppelresidue op die blaaroppervlak het aangedui dat die voorkoms van residue 'n goeie indikasie van glifosaateffektiwiteit is. Residue met 'n verdikte, amorge en growwe voorkoms was met swak effektiwiteit geassosieer, terwyl dunner, gladder residue wat in nabye kontak met die blaaroppervlakte was, met verhoogde effektiwiteit verband gehou het.

CHAPTER 1

INTRODUCTION

Glyphosate is a non-selective herbicide that has been used in South Africa for decades. In spite of comprehensive research abroad, there is still a lack of awareness as to the influence of, and remedy for, salt antagonism from water containing high levels of calcium, magnesium and sodium. Enhancement of activity by tank mix adjuvants at low glyphosate rates is also not a priority as is the case in the USA, for instance. The pH is widely regarded as the only true indicator of water quality as far as the efficacy of glyphosate is concerned and acidifiers have been used extensively to overcome salt antagonism. Glyphosate is registered in South Africa for use with the tallow amine ethoxylate surfactants (Grobler, Vermeulen & van Zyl, 2000) and is also widely used with Bladbuff 5. A prescribed method of increasing surfactant concentration in spray solutions has been by combining the 360 g a.i. L⁻¹ (Roundup®) and 180 g a.i. L⁻¹ (Sting®) formulations of glyphosate, whereby more surfactant is added via the high surfactant containing formulation. Ammonium sulphate is registered as an adjuvant for certain glyphosate formulations only when glyphosate is mixed with simazine. Certain glyphosate formulation labels, such as Roundup® CT, even prohibit the use of tank mixed adjuvants.

Glyphosate is highly prone to antagonism from dissolved salts in carrier water (Buhler & Burnside, 1983a) and glyphosate activity is higher in water carriers containing lower salt concentrations (Shea & Tupy, 1984). The nature of the glyphosate molecule makes it prone to complex certain cations, and in so doing, lose a certain amount of its activity (Glass, 1984; Motekaitis & Martell, 1985).

In South Africa, ions such as calcium, magnesium and sodium are frequently encountered at high levels in spray water carriers utilized by farmers (Unpublished ARC-Small Grain Institute survey). Farmers apply glyphosate in relatively high

water volumes, probably to increase the coverage on large weeds but this is a contributing factor to a decrease in efficacy (Buhler & Burnside, 1983a; Buhler & Burnside, 1983b; Nalewaja, Woznica & Manthey, 1990).

In South Africa, few surfactants are registered with glyphosate and mixing formulations with different surfactant concentrations often provides additional surfactant. Numerous studies have indicated that the type of surfactant is of utmost importance to glyphosate activity (Hatzios and Penner, 1985; Nalewaja, Koziara, Matysiak & Manthey, 1995). The ethoxylated amine surfactants have been used successfully with glyphosate (Wyrill & Burnside, 1977) and this is probably the reason for them being registered as tank-mix adjuvants for glyphosate.

Cranmer & Linscott (1991) found that absorption of glyphosate from droplets is dependent on both the glyphosate and the surfactant concentration. To achieve a high glyphosate concentration in the droplet, lower carrier volumes can be used. The selection of the correct application technique and spray volume is important to glyphosate activity. This has an effect on spray coverage but also on glyphosate and surfactant concentration. This may be the reason why high HLB value surfactants cause high glyphosate activity even though these surfactants may reduce droplet spreading on leaf surfaces (Stock & Holloway, 1993).

Ammonium sulphate is tank mixed with glyphosate to overcome antagonistic salts and could also increase glyphosate activity in distilled water. Ammonium sulphate is often recommended at high concentrations (2%), but it was found that 1% of ammonium sulphate applied with glyphosate could overcome antagonistic carriers with a joint calcium and magnesium level of 718 mg L⁻¹ (Nalewaja & Matysiak, 1993a). Nalewaja & Matysiak (1993b) indicated that ammonium sulphate was the most effective ammonium salt to overcome antagonism of salts. Ammonium sulphate was more effective in overcoming calcium chloride antagonism of glyphosate than ammonium nitrate, for instance.

Nalewaja, Matysiak & Freeman (1992) found that close contact between the spray residual and the plant surface is essential for absorption. Spray carrier salts could modify the spray residual in such a way that the adherence to the plant surface is reduced. Surfactants, when applied with water soluble herbicides such as glyphosate, increase droplet spreading and increase the contact with the leaf epidermal surface (Hess & Folk, 1990). Amorphous and grainy glyphosate deposits have been linked to poor efficacy and poor efficacy could be due to reduced absorption as a result of physical entrapment of the herbicide in the spray deposit and to poor contact of the spray droplet residual to the leaf surface. (Nalewaja *et al.*, 1992)

The aims of this study were to:

- Ascertain the extent of antagonism of glyphosate activity by salts in South African water carriers.
- Identify the mechanism of antagonism by ions such as calcium and sodium.
- Explain the efficacy of higher HLB surfactants through absorption and retention studies.
- Identify suitable adjuvants for glyphosate.
- Promote an awareness by the chemical industry and farmers that antagonism of glyphosate is caused by dissolved salts in the water.
- Test and develop EXP94KG1 (trade name: Power-Up) to optimize glyphosate performance in comparison to products such as Armoblen 650, Frigate, Beef-Up As and Bladbuff 5.

1.1 References

- BUHLER, D.D. & BURNSIDE, O.C., 1983a. Effect of water quality, carrier volume, and acid on glyphosate phytotoxicity. *Weed Sci.* 31, 163-169.
- BUHLER, D.D. & BURNSIDE, O.C., 1983b. Effect of spray components on glyphosate toxicity to annual grasses. *Weed Sci.* 31, 124-130.

- CRANMER, J.R. & LINSKOTT, D.L., 1991. Effects of droplet composition on glyphosate absorption and translocation in velvetleaf (*Abutilon theophrasti*). *Weed Sci.* 39, 251-254.
- GLASS, R.L., 1984. Metal complex formation by glyphosate. *J. Agric. Food Chem.* 32, 1249-1253.
- GROBLER, H., VERMEULEN, J.B. & VAN ZYL, K., 2000. A guide to the use of herbicides (17th Edition). Directorate: Agricultural Inputs.
- HATZIOS, K.K. & PENNER, D., 1985. Interactions of herbicides with other agrochemicals in higher plants. *Rev. Weed Sci.* 1, 1-63.
- HESS, D.F. & FOLK, R.H., 1990. Herbicide deposition on leaf surfaces. *Weed Sci.* 38, 280-288.
- MOTEKAITIS, R.J. & MARTELL, A.E., 1985. Metal chelate formation by N-phosphonomethylglycine and related ligands. *Coord. Chem.* 14, 139-149.
- NALEWAJA, J.D. & MATYSIAK, R., 1993a. Optimizing adjuvants to overcome glyphosate antagonistic salts. *Weed Tech.* 7, 337-342.
- NALEWAJA, J.D. & MATYSIAK, R., 1993b. Spray carrier salts affect herbicide toxicity to *Kochia (Kochia scoparia)*. *Weed Tech.* 7, 154-158.
- NALEWAJA, J.D., KOZIARA, W., MATYSIAK, R. & MANTHEY, F.A., 1995. Relationship of surfactant HLB to glyphosate phytotoxicity. in *Pesticide Formulation and Application Systems* 14, 269-277, ASTM STP 1234 Philadelphia PA.

- NALEWAJA, J.D., MATYSIAK, R. & FREEMAN, T.P., 1992. Spray droplet residual of glyphosate in various carriers. *Weed Sci.* 40, 576-589.
- NALEWAJA, J.D., WOZNICA, Z. & MANTHEY, F.A., 1990. Sodium bicarbonate antagonism of 2,4-D amine. *Weed Tech.* 4, 588-591
- SHEA, P.J. & TUPY, D.R., 1984. Renewal of cation-induced reduction in glyphosate activity with EDTA. *Weed Sci.* 32, 802-806.
- STOCK, D. & HOLLOWAY, P.J., 1993. Possible mechanisms for surfactant induced foliar uptake of agrochemicals. *Pestic. Sci.* 38, 165-177.
- WYRILL, J.B. & BURNSIDE, O.C., 1977. Glyphosate toxicity to common milkweed and hemp dogbane as influenced by surfactants. *Weed Sci.* 25, 275-287.

CHAPTER 2

CHEMICAL COMPOSITION OF CARRIER WATER INFLUENCES GLYPHOSATE ACTIVITY (*S. Afr. J. Plant Soil* 10(4), 178-182)

2.1 Introduction

Glyphosate is a non-selective post-emergence herbicide for the control of annual and perennial plants. Phytotoxicity of glyphosate is influenced by factors such as soil moisture, air temperature, weed development stage, humidity and water quality (Buhler & Burnside, 1983a). Phytotoxicity increases when the carrier volume is decreased (O'Sullivan, O'Donovan & Hamman, 1981; Buhler & Burnside, 1983a; Buhler & Burnside, 1983b) and deionized water is used as a carrier (Shea & Tupy, 1984). Nalewaja & Matysiak (1992) found that the activity of glyphosate in combination with the amine formulations of 2,4-D is also affected by water quality.

The antagonism of glyphosate activity by high salt concentrations in water is caused by complex formation of the herbicide with divalent and trivalent cations (Glass, 1984). Mervosh and Balke (1991) found that the complexes that glyphosate forms with metal ions do not inhibit the absorption of glyphosate at cell membrane level but they stated that these complexes may affect the mode of action in plants. However, on the whole plant level, cationic antagonism decreases in the following order: iron > zinc > calcium > magnesium > sodium > potassium (Nalewaja & Matysiak, 1991).

Nalewaja & Matysiak (1991) found that salt antagonism is also influenced by the anion to which the cation is bound. Calcium sulphate at 0.02M reduced glyphosate activity by 30% while calcium chloride at the same concentration of calcium reduced glyphosate phytotoxicity by up to 75%. Sandberg, Meggitt & Penner (1978) also found that calcium chloride inhibited glyphosate phytotoxicity.

They, however, did not include other forms of calcium in their study. Phytotoxicity of glyphosate was not influenced by a water pH ranging from 2.2 to 8.0 (Nalewaja & Matysiak, 1991). Research on water pH involves using buffers to stabilize the pH and therefore data interpretation may be complicated by salt modifications (Nalewaja, Woznica & Matysiak, 1991). Antagonism of glyphosate by certain salts such as sodium bicarbonate, for example, is thus probably not primarily due to a high pH (Shea & Tupy, 1984).

The antagonistic ability of salts in water carriers is not entirely understood at this stage. A comprehensive knowledge of the interactions between salts and glyphosate would promote reliable efficacy of this herbicide. The aim of this study was to determine to what degree specific ions and other factors such as hardness, total dissolved solids and electrical conductivity antagonize glyphosate activity in water used as spray carriers.

2.2 Materials and Methods

2.2.1 General procedures

The study was conducted in a glasshouse using bean plants (*Phaseolis vulgaris*) as a bioassay species. Seven seeds were planted 2 cm deep in each 2-L plastic pot in a coarse sand mixture that was covered with a layer of vermiculite before herbicide application. Water and fertilizer was dispensed with an automatic irrigation system that ensured optimal plant vigour. The plants were thinned to four uniform plants per pot one week after emergence. The temperature varied between 15°C (night) and 20°C (day).

2.2.2 Application information

Spray carriers comprised 25 borehole and dam (municipal) samples collected at various locations in the Free State and Northern Cape Province. The 360 g ai L⁻¹ glyphosate isopropylamine formulation, containing a surfactant (Roundup[®],

Monsanto, USA), was applied at a rate of 360 g ai ha⁻¹. The salt content of the carriers is indicated in Table 1. Herbicide solutions were applied with a moving nozzle pot sprayer that delivered 350 L ha⁻¹ at 200 kPa from two 8001 Teejet flat-fan nozzles. The bean plants were treated at the 4-leaf stage and top growth was harvested 19 days after herbicide application. Data are presented as the percentage reduction in fresh mass compared with the untreated control. The experiment had a completely randomized design with treatments replicated four times. Data were subjected to analysis of variance and LSD (Tukey) values were determined at the 95% probability level. Non-linear regression (cations, anions, total dissolved solids and electrical conductivity) and multiple forward additive stepwise regressions (cations and anions) were conducted to identify trends with single ions, factors and with multiple ionic combinations. A correlation matrix and principal component analysis were also conducted prior to multiple regression analysis to determine which ions and factors were inter-correlated so as to ensure dependable results.

Table 1 Chemical analysis of natural water carriers used in this study

Sample no. (Locations in parenthesis)	Ion concentration (mg L ⁻¹)								Other factors		
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	TDS*	TH**	EC***
1 (Deionized)	0.2	0.1	0	0.7	0.4	6.1	0	0	4.5	1	1
2 (Kestell – District)	3.6	0.6	109.0	1.5	12.8	234.9	11.0	1.9	259.8	12	42
3 (Harrismith – Municipal)	10.6	2.6	6.2	2.6	4.3	36.6	14.4	0.6	59.5	37	10
4 (Bethlehem – Danielsrus)	48.4	15.1	59.0	5.6	17.0	262.3	13.9	18.0	308.2	183	48
5 (Bethlehem – Municipal)	35.2	12.5	23.7	5.7	9.6	164.7	14.9	-	185.4	140	31
6 (Bethlehem – Meets)	32.8	6.9	45.2	1.5	21.3	119.0	5.8	71.9	244.9	111	36
7 (Paul Roux – District)	53.4	21.9	153.0	18.4	95.5	372.1	26.9	47.7	608.9	224	91
8 (Warden – District)	33.0	7.5	20.8	2.6	9.6	137.3	6.7	7.4	156.3	114	26
9 (Memel – Municipal)	10.6	5.1	7.7	2.1	7.1	42.7	4.8	0.6	65.5	48	12
10 (Reitz – District)	56.8	18.5	36.7	1.6	42.6	213.5	43.7	4.3	311.0	218	50
11 (Bothaville – Municipal)	79.8	32.7	87.5	19.9	109.0	140.3	257.8	-	656.8	334	90
12 (Vredefort – District)	31.4	14.2	53.4	4.8	23.8	180.0	22.1	27.9	267.5	137	41
13 (Koppies – Municipal)	47.6	23.2	55.5	6.4	40.5	237.9	41.3	-	336.5	215	53
14 (Koppies – Heuningspruit)	38.6	9.2	304.0	3.4	218.0	359.9	110.4	1.9	868.4	135	124
15 (Koppies – District)	54.6	27.4	95.0	33.5	47.6	329.4	56.2	21.1	500.0	249	75
16 (Kroonstad – Municipal)	32.2	14.3	39.6	6.8	25.9	167.8	28.3	0.6	231.7	140	38
17 (Kimberley – Municipal)	45.8	27.4	61.0	17.5	71.7	128.1	153.1	0.6	441.2	227	64
18 (Ritchie – District)	301.4	177.4	383.0	5.1	1043.7	439.2	514.6	66.3	2711.1	1483	351
19 (Rietrivier – Station)	53.6	38.9	36.4	1.4	19.2	326.4	25.4	-	339.0	295	56
20 (Bloemfontein - De Brug)	35.6	57.8	374.5	21.3	252.4	677.1	157.0	46.5	1285.0	327	183
21 (Dealsville – Municipal)	53.4	30.0	30.2	2.9	19.2	311.1	25.9	18.6	336.6	260	51
22 (Hertzogville – District)	196.0	89.1	43.8	9.7	274.4	298.9	118.1	334.8	1215.4	857	166
23 (Hoopstad – District)	78.8	36.6	92.5	5.6	98.0	366.0	35.0	152.5	682.0	348	95
24 (Wesselsbron – Municipal)	79.4	32.3	83.5	19.0	115.7	170.8	263.0	0.6	679.0	332	89
25 (Wesselsbron - District)	48.2	24.4	80.0	4.7	61.8	356.9	17.8	17.4	432.6	221	64

* TDS = total dissolved solids (mg L⁻¹)** TH = total hardness (mg L⁻¹)*** EC = electrical conductivity (mS m⁻¹ at 25 °C)

2.3 Results and Discussion

2.3.1 Antagonism of glyphosate by various natural water carriers

Natural water spray carriers differed in antagonism of glyphosate (Table 2). The difference in phytotoxicity of glyphosate mixed with deionized water (sample no. 1) and with the most antagonistic carrier (sample no. 24) was 72%. Sample no. 24 was not particularly high in salt content but could have contained other foreign material, such as organic matter, that antagonized glyphosate activity. Large differences in antagonistic ability among other carriers was also found. This supported work by Buhler & Burnside (1983b) who found that there is diversity in glyphosate phytotoxicity when the herbicide is applied with different natural water carriers.

Table 2 Percentage reduction in fresh shoot mass of bean plants treated with glyphosate mixed with different water carriers

Water sample numbers and percentage control									
No.	%	No.	%	No.	%	No.	%	No.	%
1 ¹	84.8	2	42.2	3	64.0	4	20.1	5	32.3
6	37.9	7	40.8	8	35.8	9	72.3	10	42.5
11	27.0	12	32.4	13	29.5	14	31.6	15	26.4
16	57.4	17	38.8	18	16.5	19	17.6	20	20.3
21	24.2	22	15.7	23	15.3	24	13.1	25	25.4

LSD_T(0.05) Carriers = 17.53

¹Glyphosate mixed with deionized water

2.3.2 Relationship between glyphosate phytotoxicity and individual ions, total dissolved solids, electrical conductivity and total hardness

Figures 1-11 illustrate relationships with the most important ions, total dissolved solids, electrical conductivity and total hardness. Trends were fitted best by a linear divided by a linear regression line [$a + b/(1 + dx)$]. Antagonistic cations were calcium [$5.47 + 71.3/(1 + 0.0392x)$], sodium [$20.63 + 67.9/(1 + 0.1091x)$] and magnesium [$9.66 + 59.84/(1 + 0.0912x)$] when evaluated individually (Figures 1-3). These cations accounted for 64.2%, 61.2% and 59.7% of the variance respectively. This confirmed research results of Stahlman & Phillips (1979) and Nalewaja & Matysiak (1991), that indicated that these cations are the principal antagonists of glyphosate in association with specific anions.

Antagonistic anions were bicarbonate [$10.72 + 83.5/(1 + 0.01476x)$], chloride [$21.85 + 70.7/(1 + 0.216x)$] and sulphate [$22.52 + 62.8/(1 + 0.226x)$] (Figures 5-7). These anions accounted for 70.1%, 57.7% and 49.2% of the variance respectively. These results confirmed the findings of Buhler & Burnside (1981) who found that bicarbonate was an important antagonist of glyphosate in natural water carriers. Percentage variance accounted for by both potassium [$27.01 - 41.4/(1 - 2.47x)$] (Figure 4) and nitrate [$18.9 + 24.5/(1 + 0.071x)$] (Figure 8) was non-significant. Iron and zinc were not tested as they were absent in most of the carriers. Further antagonistic factors were total dissolved solids [$12.86 + 77.93/(1 + 0.00913x)$], electrical conductivity [$11.07 + 81.1/(1 + 0.0547x)$] and total hardness [$5.16 + 69.2/(1 + 0.00833x)$] (Figures 9-11). These ionic factors accounted for 73.8%, 73.0% and 65.9% of the variance respectively. Buhler & Burnside (1983b) also found that water with high levels of dissolved solids antagonized glyphosate. Shilling & Haller (1989) reported that optimum glyphosate activity is attained with water low in salts.

2.3.3 *Multiple regression analysis on cations and anions*

Multiple regression analysis with the four cations indicated that calcium and magnesium in combination constituted 24% of a possible 28% in variance. This is in agreement with the findings of Shilling & Haller (1989) who reported that calcium and magnesium in the presence of carbonates (hard water) antagonize glyphosate. Bicarbonate constituted 41% of a possible 55% in anionic variance. This corroborated the research of Buhler & Burnside (1981) who found that bicarbonate is the most antagonistic anion. Chloride, sulphate and nitrate constituted the remaining variance when present with bicarbonate.

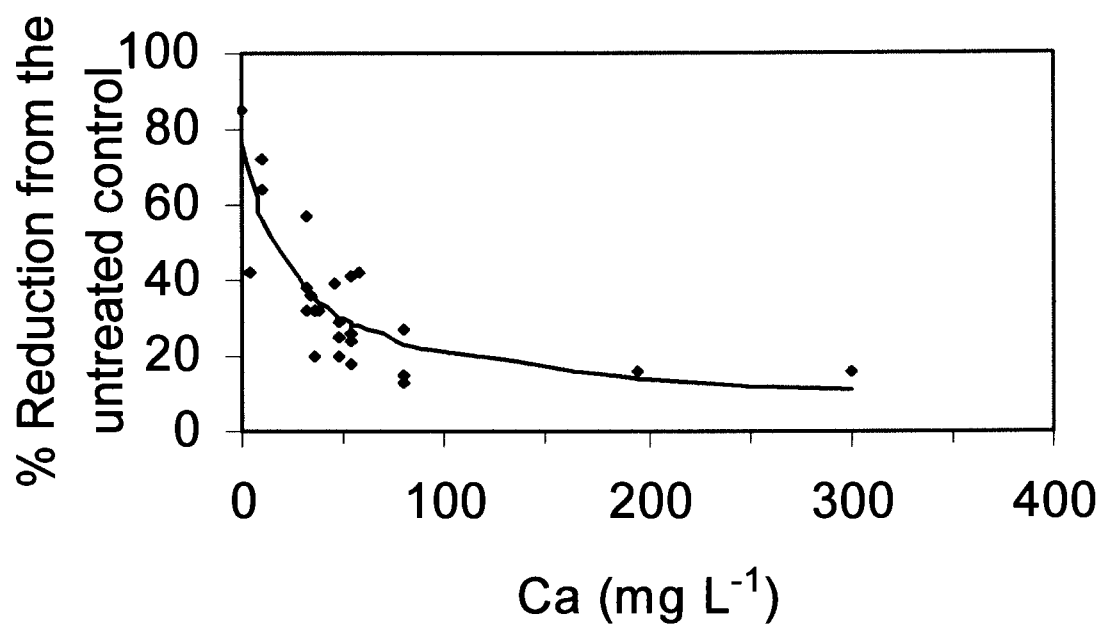


Figure 1 ($R^2 = 0.642$)

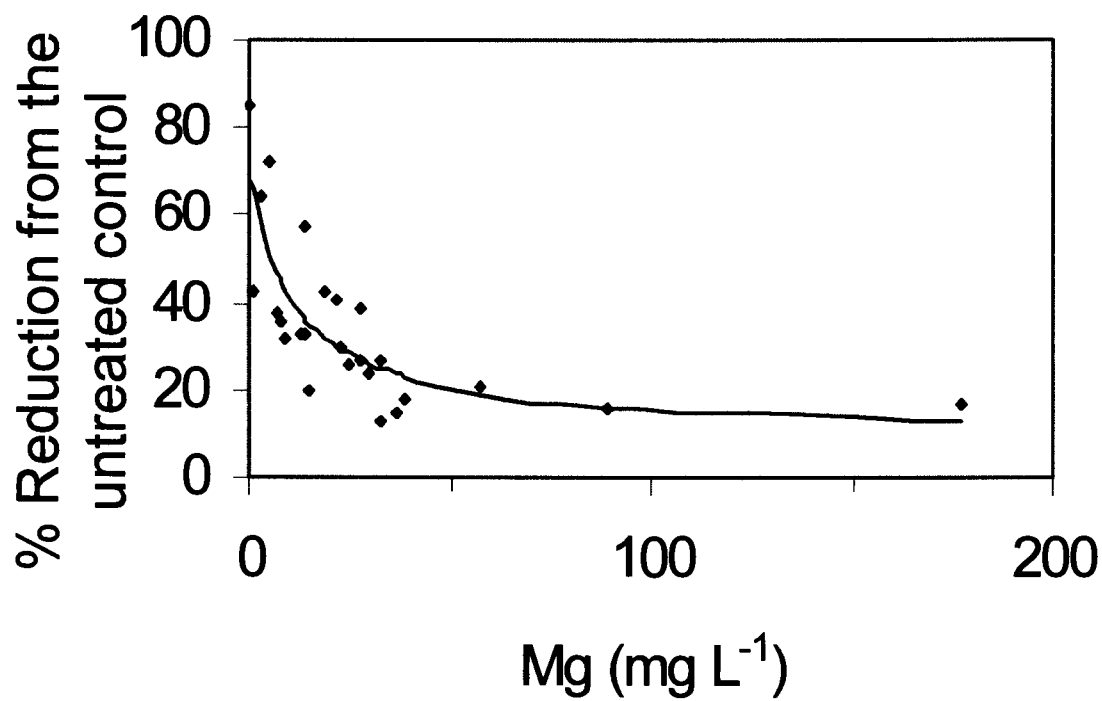


Figure 2 ($R^2 = 0.597$)

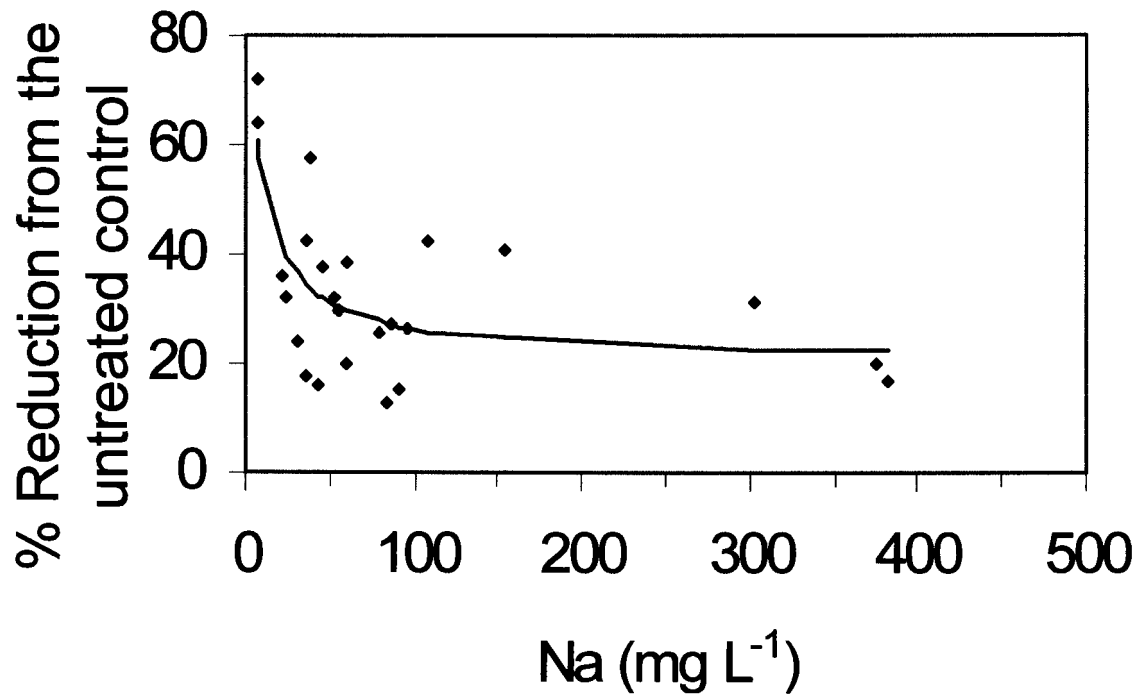


Figure 3 ($R^2 = 0.612$)

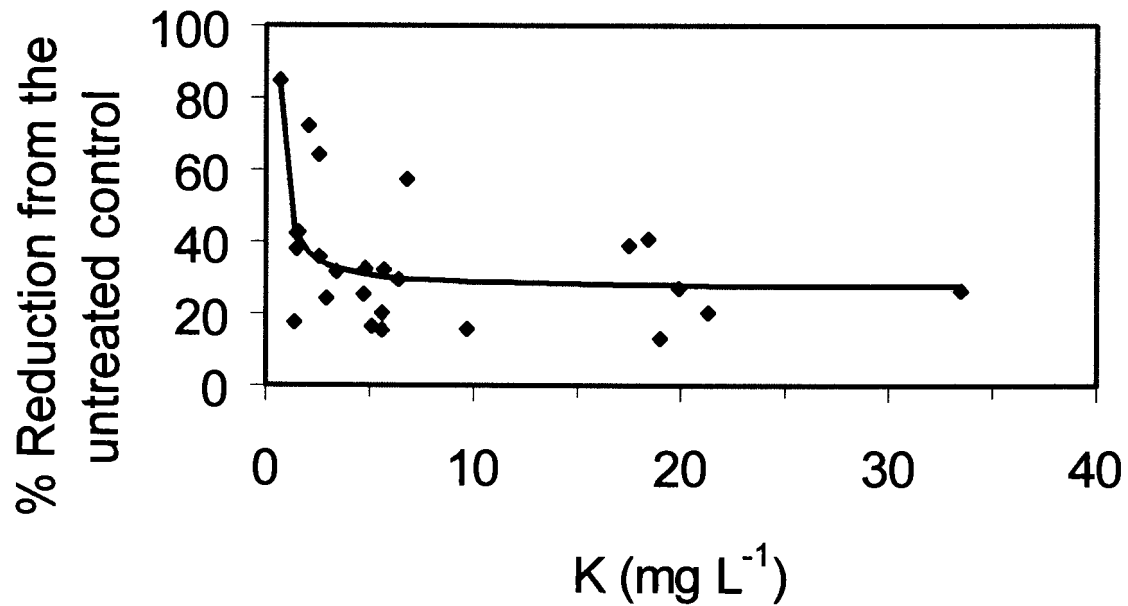


Figure 4 ($R^2 = 0.329$)

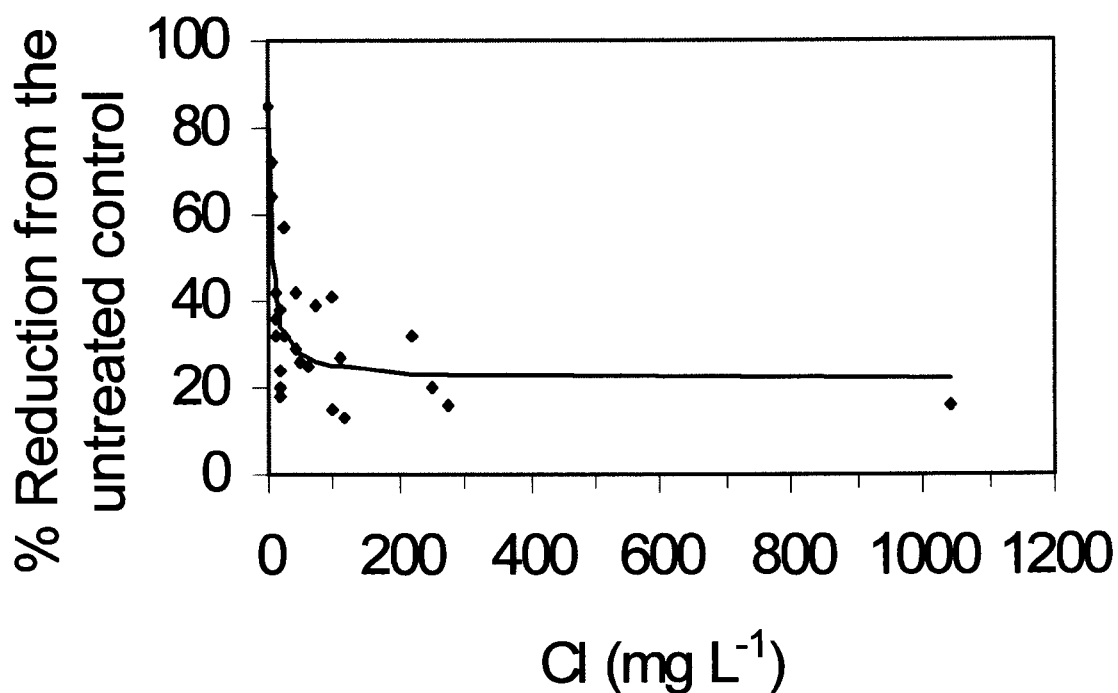


Figure 5 ($R^2 = 0.577$)

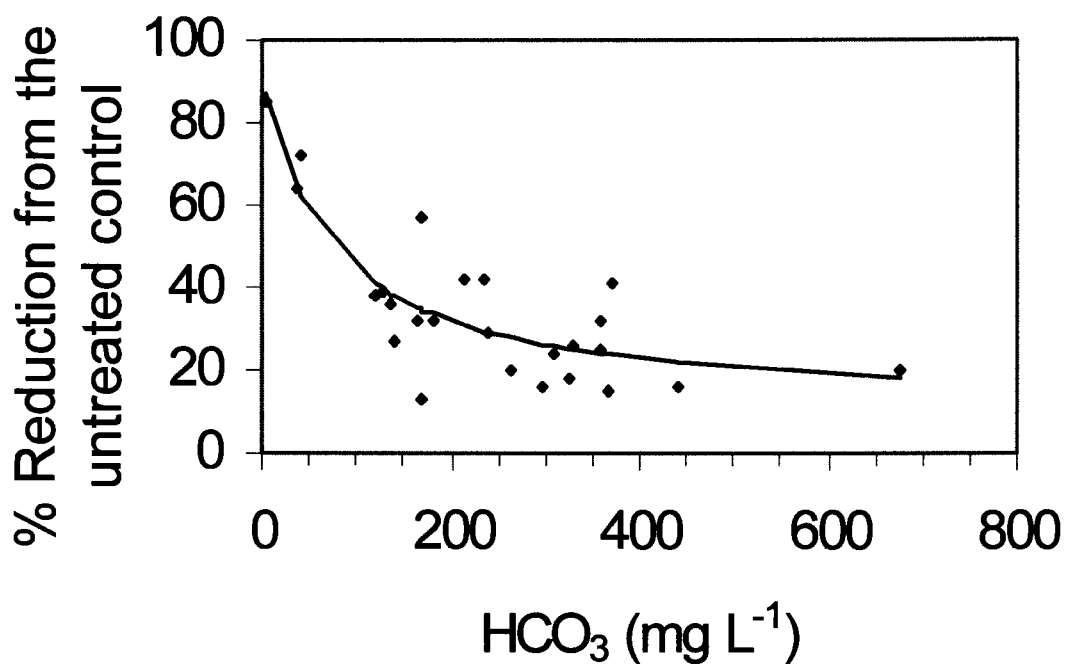


Figure 6 ($R^2 = 0.701$)

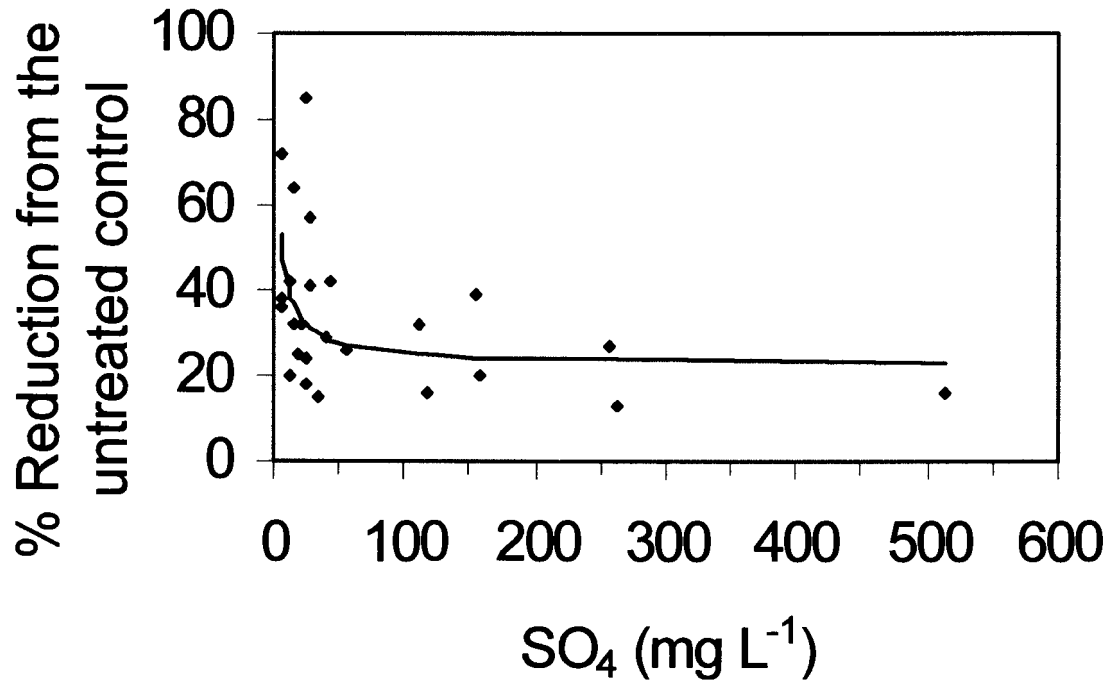


Figure 7 ($R^2 = 0.492$)

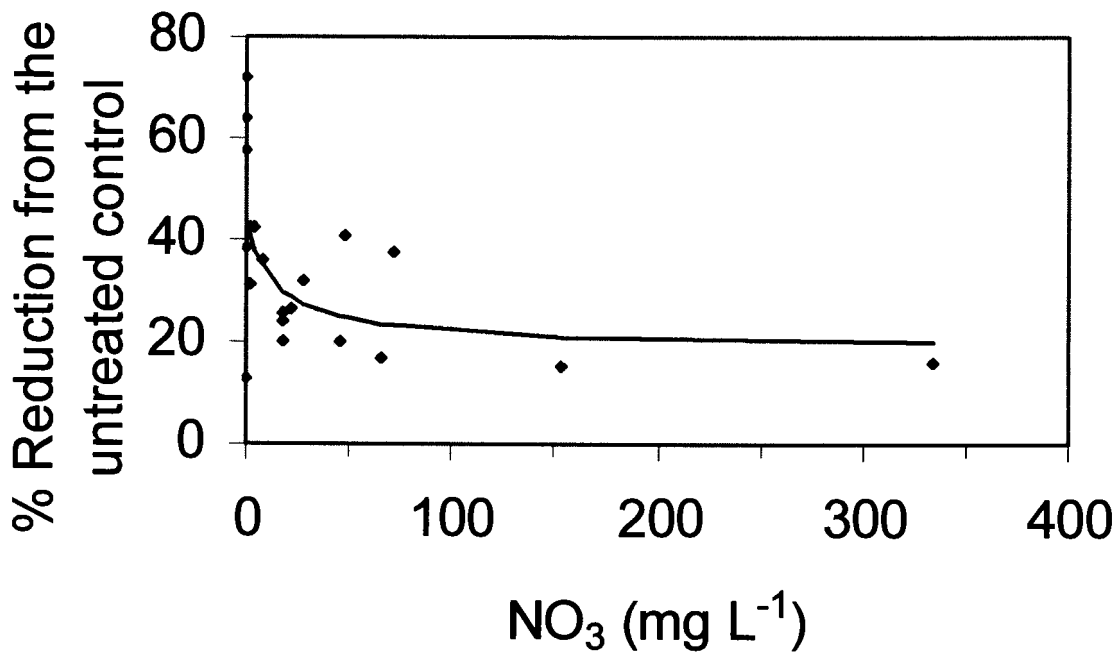


Figure 8 ($R^2 = 0.151$)

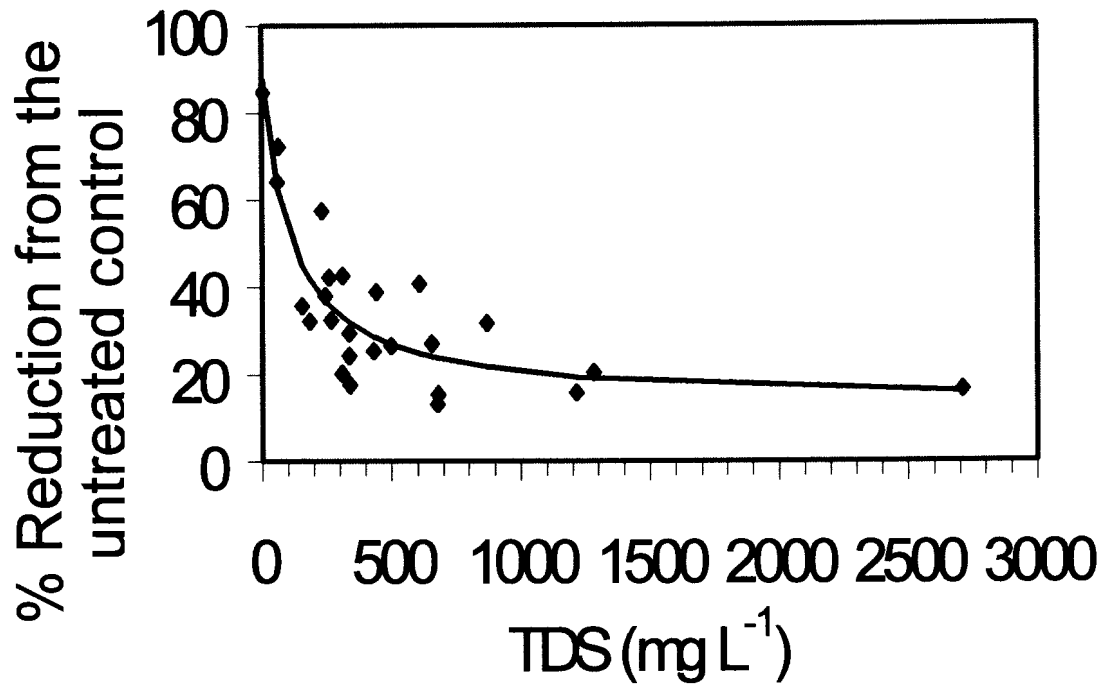


Figure 9 ($R^2 = 0.738$)

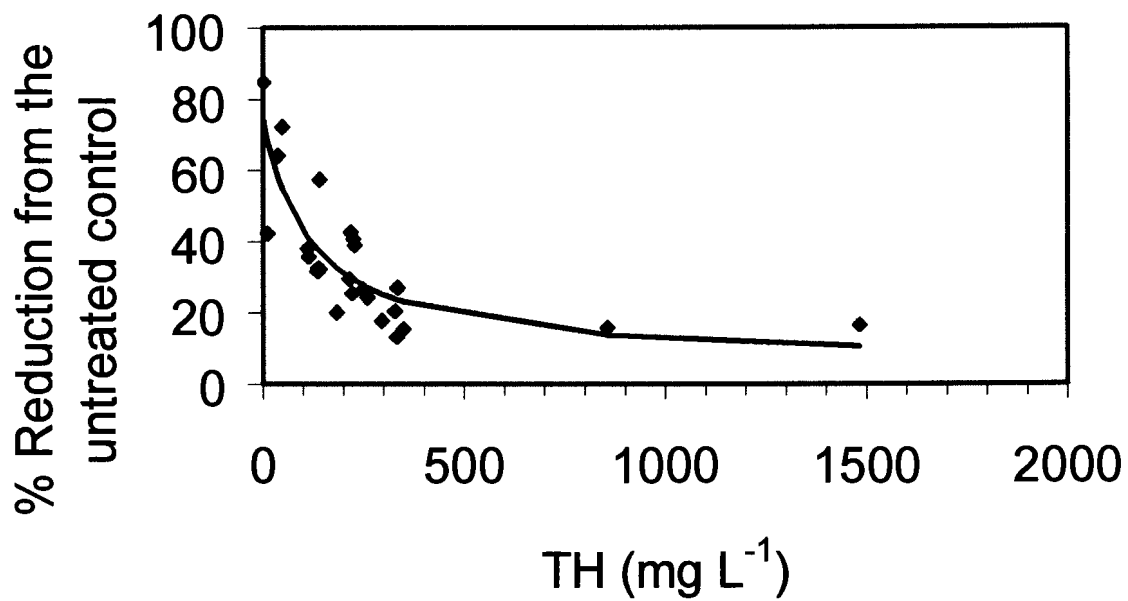


Figure 10 ($R^2 = 0.659$)

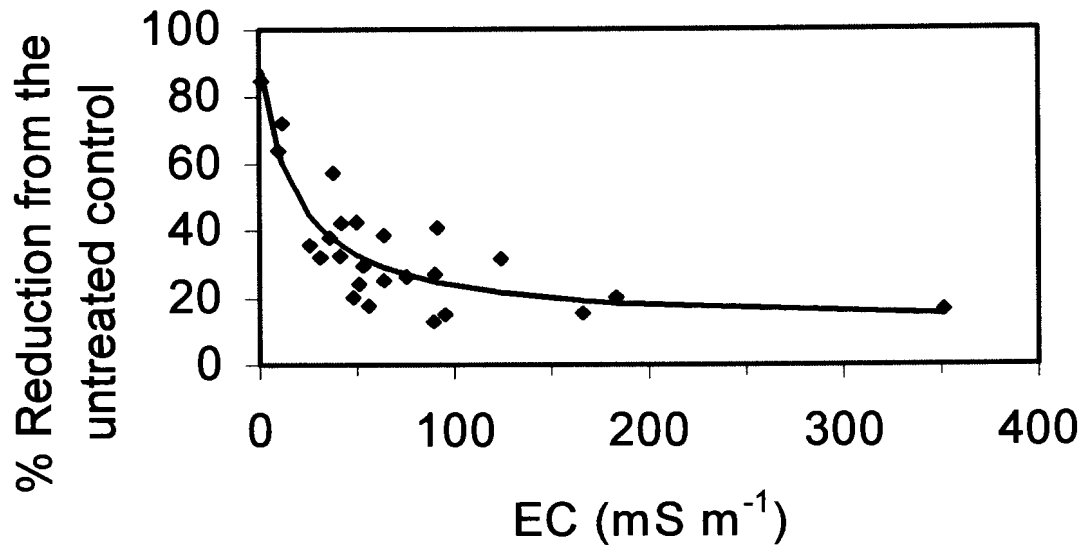


Figure 11 ($R^2 = 0.73$)

2.3.4 Correlation between individual ions and factors

The correlation coefficient is a measure of the linear relationship between two random variates (Table 3). This only indicates the extent to which two variates are linearly related and does not imply any causal relationship between them (Draper & Smith, 1981). Generally, a coefficient of about ± 0.7 or more is regarded as indicating fairly strong correlation, and in the region of ± 0.9 it indicates very strong correlation. In the region of ± 0.5 the correlation is moderate, and in the range -0.3 to $+0.3$ it is weak (Rayner, 1969).

Table 3 Correlation matrix of individual cations, anions and combination factors

Ions	Correlation										
Ca ²⁺	1.000										
Mg ²⁺	0.955	1.000									
Na ⁺	0.441	0.597	1.000								
K ⁺	0.053	0.138	0.241	1.000							
Cl ⁻	0.891	0.943	0.739	0.036	1.000						
HCO ₃ ⁻	0.360	0.511	0.792	0.374	0.485	1.000					
SO ₄ ²⁻	0.807	0.863	0.669	0.225	0.904	0.371	1.000				
NO ₃ ⁻	0.559	0.466	0.014	0.031	0.274	0.250	0.127	1.000			
TDS	0.883	0.950	0.802	0.185	0.967	0.648	0.890	0.389	1.000		
TH	0.989	0.988	0.523	0.095	0.927	0.439	0.844	0.519	0.926	1.000	
EC	0.869	0.941	0.819	0.204	0.957	0.680	0.875	0.393	0.999	0.914	1.000

Critical $r = 0.4438$ ($P < 0.05$)

$r = 0.5614$ ($P < 0.01$)

$r = 0.6788$ ($P < 0.001$)

116011004
615413433

Electrical conductivity and total dissolved solids proved to be strongly correlated with antagonistic ions such as calcium, magnesium, sodium, chloride and bicarbonate. Total hardness was obviously positively correlated with calcium, magnesium and chloride but was less strongly correlated with sodium and bicarbonate. Factors such as total dissolved solids and electrical conductivity can therefore be used with great success to determine water quality by determining a single factor.

2.4 Conclusions

Glyphosate formulated as Roundup® was antagonized by individual cations and anions, electrical conductivity, total hardness and total dissolved solids in carrier water. These findings suggest that carrier water quality is a critical consideration for producers who use glyphosate, and that a practical solution to the problem is of importance. Electrical conductivity and total dissolved solids appear to be excellent indicators of antagonistic ion concentration and can be used with great success by farmers to determine the antagonistic potential of water sources.

2.5 References

- BUHLER, D.D. & BURNSIDE, O.C., 1981. Effect of water quality, added acid and carrier volume on glyphosate toxicity. *Proc. North Central Weed Control Conference* 36, 19.
- BUHLER, D.D. & BURNSIDE, O.C., 1983a. Effect of spray components on glyphosate toxicity to annual grasses. *Weed Sci.* 31, 124-130.
- BUHLER, D.D. & BURNSIDE, O.C., 1983b. Effect of water quality, carrier volume, and acid on glyphosate toxicity. *Weed Sci.* 31, 163-169.

- DRAPER, N. & SMITH, H., 1981. *Applied Regression Analysis* (2nd Ed.). John Wiley & Sons, New York.
- GLASS, R.L., 1984. Metal complex formation by glyphosate. *J. Agric. Food Chem.* 32, 1249-1253.
- MERVOSH, T.L. BALKE, N.E., 1991. Effects of calcium, magnesium, and phosphate on glyphosate absorption by cultured plant cells. *Weed Sci.* 39, 347-353.
- NALEWAJA, J.D. & MATYSIAK, R., 1991. Salt antagonism of glyphosate. *Weed Sci.* 39, 622-628.
- NALEWAJA, J.D. & MATYSIAK, R., 1992. 2,4-D and salt combinations affect glyphosate phytotoxicity. *Weed Tech.* 6, 322-327.
- NALEWAJA, J.D., WOZNICA, Z. & MATYSIAK, R., 1991. 2,4-D amine antagonism by salts. *Weed Tech.* 5, 873-880.
- O'SULLIVAN, P.A., O'DONAVAN, J.T. & HAMMAN, W.M., 1981. Influence of non-ionic surfactants, ammonium sulphate, water quality and spray volume on the phytotoxicity of glyphosate. *Can. J. Plant Sci.* 61, 391-400.
- RAYNER, A.A., 1969. *A first course in Biometry for agriculture students.* University of Natal Press, Pietermaritzburg.
- SANDBERG, C.L., MEGGIT, W.F. & PENNER, D., 1978. Effect of diluent volume and calcium on glyphosate phytotoxicity. *Weed Sci.* 26, 476-479.
- SHEA, P.J. & TUPY, D.R., 1984. Reversal of cation-induced reduction in glyphosate activity with EDTA. *Weed Sci.* 32, 802-806.

SHILLING, D.G. & HALLER, W.T., 1989. Interactive effects of diluent pH and calcium content on glyphosate activity on *Panicum repens* L. (torpedograss). *Weed Res.* 29, 441-448.

STAHLMAN, P.W. & PHILLIPS, W.M., 1979. Effects of water quality and spray volume on glyphosate phytotoxicity. *Weed Sci.* 27, 38-41.

CHAPTER 3

CALCIUM AND MAGNESIUM IN SPRAY CARRIERS ANTAGONIZE GLYPHOSATE PERFORMANCE (*Appl. Plant Sci.* 10(1), 10-11)

3.1 Introduction

In South Africa, ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+) are often found at high levels in spray water carriers utilized by farmers for herbicide application (de Villiers & du Toit, 1993). The fact that many local farmers apply herbicides in high carrier volumes can make it a compounding factor, as there are a large amount of salts to react with the herbicide. Certain glyphosate labels in South Africa also allow for volumes between 12 and 600 L ha^{-1} . De Villiers & du Toit (1993) found that carriers containing high levels of Ca^{2+} , Mg^{2+} and Na^+ could antagonize glyphosate at 360 g ai ha^{-1} by up to 72%. This antagonism occurred at a carrier volume of 350 L ha^{-1} .

Subramaniam & Hoggard (1988) stated that glyphosate has three groups namely an amine, a carboxylate and a phosphonate group. At near to neutral pH, the carboxylate and phosphonate groups will be deprotonated and should strongly bond with cations such as calcium and magnesium. In addition, all the metabolites of glyphosate should also form strong bonds with these cations. Metal complex formation of herbicides is usually the exception, and glyphosate is in a unique class of strongly chelating herbicides. Salts such as calcium sulphate and calcium chloride however did not inhibit the absorption of glyphosate at cell membrane level (Burton & Balke, 1988) and even increased absorption in certain cases (Mervosh & Balke, 1991). This does not explain the antagonism of various salts on glyphosate activity (Nalewaja & Matysiak, 1991).

In certain parts of the world the problem of antagonistic salts in carrier water is partially overcome by applying glyphosate in water volumes of 50 L ha^{-1} or less

(Nalewaja & Matysiak, 1991; Buhler & Burnside, 1983a; Buhler & Burnside, 1983b). In South Africa this is however not the case with ground tractor-driven applications and relatively high carrier volumes, and therefore other avenues will also have to be implemented to resolve this antagonism. The aim of this research was to determine at what levels, and to what extent, glyphosate was antagonized by salts, with the ultimate goal of possible herbicidal optimization with a suitable and affordable adjuvant.

3.2 Materials and Methods

3.2.1 General procedures

The study was conducted in a glasshouse utilizing oats (*Avena sativa* cv. Witteberg) as a bioassay indicator for glyphosate phytotoxicity. Twenty seeds were seeded 2 cm deep in a sandy-loam soil, contained in 2-L plastic pots. Plants were thinned out to fifteen uniform plants per pot one week after emergence, and were watered by hand and fertilized for optimal plant growth. The temperature varied between 15°C (night) and 25°C (day).

3.2.2 Application information

All herbicide treatments were applied with a moving nozzle pot sprayer with a delivering capacity of 310 L ha⁻¹ at 200 kPa from two 8001 Teejet flat-fan nozzles. Herbicide treatments were applied at the 3-leaf stage and the oats were harvested 14 days after herbicide application and fresh shoot mass determined.

Spray carriers were produced by adding salts to deionized water at various concentrations. The salts were analytical grade (>95% pure, Merck, Germany) calcium chloride (CaCl₂), calcium nitrate (Ca(NO₃)₂), calcium sulphate (CaSO₄), potassium chloride (KCl), potassium bicarbonate (KHCO₃), magnesium chloride (MgCl₂), magnesium sulphate (MgSO₄), sodium sulphate (Na₂SO₄), sodium chloride (NaCl) and sodium bicarbonate (NaHCO₃). The concentrations of these

salts ([] cation) were, 1 mM, 2 mM, 3 mM, 4 mM, 5 mM, 6 mM, 7 mM, 8 mM and 30 mM. Glyphosate isopropylamine (Roundup®, Monsanto, USA) at 360 g ai ha⁻¹ was added to the carriers just prior to application of treatments.

Data are expressed as a percentage reduction from the untreated control. The experiment had a completely randomized design with four replications per treatment. Analysis of variance was conducted on the data and the least significant differences at the 95% probability level were calculated using the Tukey method.

3.3 Results and Discussion

CaCl₂, Ca(NO₃)₂, CaSO₄ and MgCl₂ were all antagonistic to glyphosate activity (Figure 1). This confirmed the findings of Nalewaja & Matysiak (1991) who found these salts to be antagonistic. These scientists further reported that Na₂SO₄, NaHCO₃, NaCl and MgSO₄ were antagonistic to glyphosate, but this was not confirmed in this study. A possible explanation for this lack of antagonism of these salts on glyphosate activity could be the higher rate of glyphosate, the test species or the concentration of salts used in this study. The lack of antagonism by sodium bicarbonate was particularly surprising as it had indicated to be an important antagonist of glyphosate in the previous study and was more antagonistic than calcium sulphate in the research by Nalewaja & Matysiak (1991). Detectable CaCl₂ antagonism commenced at 3 mM and reached a maximum at 30 mM where glyphosate efficacy decreased by 48%. Ca(NO₃)₂ was equally antagonistic at 30 mM (51%) but antagonism was only detected at a higher concentration (4 mM) of the salt. MgCl₂ antagonism was first detected at 6 mM and reached a maximum of 35% at 30 mM. CaSO₄ only antagonized glyphosate activity at 30 mM (solubility exceeded) by 27% and was thus the least antagonistic of these four salts. None of the other salts tested resulted in any antagonism of glyphosate. Nalewaja & Matysiak (1991) also found CaCl₂ and Ca(NO₃)₂ to be the principle antagonists of glyphosate.

The fact that antagonism of glyphosate was induced at low levels of salts is problematic because antagonism from ions in spray carrier water tends to be

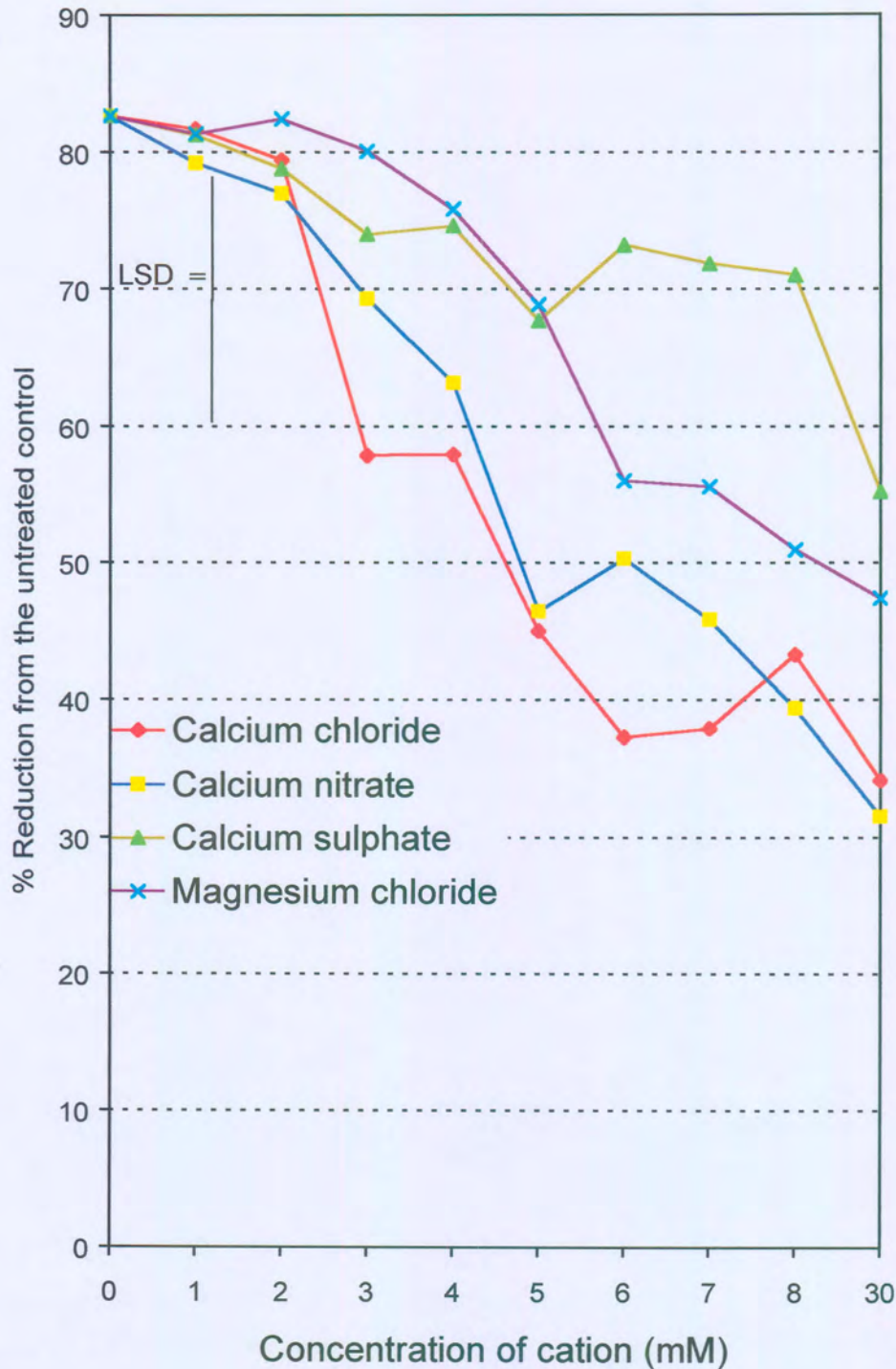


Figure 1 Influence of salt concentration on glyphosate activity

additive (Nalewaja & Matysiak, 1993). This additive effect explains the considerable antagonism of glyphosate by natural carrier water (de Villiers & du Toit, 1993) which was relatively low in individual ions.

3.4 Conclusions

Certain salts antagonized glyphosate at relatively low levels and this antagonism increased with salt concentration. Various adjuvants should be tested with glyphosate to stabilize and promote the activity of this herbicide.

3.5 References

- BUHLER, D.D. & BURNSIDE, O.C., 1983a. Effect of spray components on glyphosate toxicity to annual grasses. *Weed Sci.* 31, 124-130.
- BUHLER, D.D. & BURNSIDE, O.C., 1983b. Effect of water quality, carrier volume, and acid on glyphosate phytotoxicity. *Weed Sci.* 31, 163-169.
- BURTON, J.D. & BALKE, N.E., 1988. Glyphosate uptake by suspension-cultured potato (*Solanum tuberosum* and *S. brevidens*) cells. *Weed Sci.* 36, 146-153.
- DE VILLIERS, B.L. & DU TOIT, D., 1993. Chemical composition of carrier water influences glyphosate efficacy. *S. Afr. J. Plant Soil* 10(4), 178-182.
- MERVOSH, T.L. & BALKE, N.E., 1991. Effects of calcium, magnesium, and phosphate on glyphosate absorption by cultured plant cells. *Weed Sci.* 39, 347-353.
- NALEWAJA, J.D. & MATYSIAK, R., 1991. Salt antagonism of glyphosate. *Weed Sci.* 39, 622-628.

NALEWAJA, J.D. & MATYSIAK, R., 1993. Optimizing adjuvants to overcome glyphosate antagonistic salts. *Weed Tech.* 7, 337-342.

SUBRAMANIAM, V. & HOGGARD, P.E., 1988. Metal complexes of glyphosate. *J. Agric. Food Chem.* 36, 1326-1329.

CHAPTER 4

SURFACTANTS, SALTS AND FORMULATION AFFECT GLYPHOSATE RETENTION AND ABSORPTION (*Weed Res.* 36, 241- 247)

4.1 Introduction

Glyphosate activity is influenced by salts in South African water carriers (de Villiers & du Toit, 1993), especially calcium and magnesium salts (de Villiers, Lindeque & Knobel, 1996). The actual reasons for this antagonism have however not been proven. The effective performance of higher HLB (hydrophilic/ lipophilic balance) surfactants with glyphosate (Nalewaja, Koziara, Matysiak & Manthey, 1995) also needs to be clarified.

Glyphosate absorption by wheat was generally found to increase as the ethylene oxide (EO) content of 1-alkanol surfactant increased from 6 to 14 moles (*c.* HLB 11 to 15) with no further increase from 18 EO moles (*c.* HLB 16) (Gaskin & Holloway, 1992). The high HLB value surfactants generally caused high glyphosate absorption even though these high HLB surfactants gave poor herbicide solution spreading on leaf surfaces (Stock & Holloway, 1993).

The increase in glyphosate absorption when applied with high HLB surfactants may be from either the polar surfactant promoting glyphosate penetration into the leaf, or through the non-spreading high EO surfactant leaving a more concentrated herbicide deposit on the leaf surface (Cranmer & Linscott, 1991; Gaskin & Holloway, 1992). Spray carriers with high surface tension have a high contact angle (Stevens & Bucovac, 1987) and droplets could bounce from the leaf on contact, thus reducing spray retained on the leaf. The greater glyphosate phytotoxicity and absorption with high HLB surfactants indicates that if any

reduced spray retention with high HLB surfactants occurs, it is probably compensated for by other factors.

Calcium chloride in the spray solution lowered the optimum surfactant HLB for glyphosate efficacy on *Kochia scoparia* (Nalewaja *et al.*, 1995). However, the reduction did not occur when ammonium sulphate was present in the solution. The first aim of the present studies was to determine the influence of HLB of nonylphenol surfactants, calcium, and ammonium sulphate on both spray retention and glyphosate absorption by wheat and *K. scoparia*.

Ammonium sulphate is often added to glyphosate spray solutions. Although it enhances glyphosate phytotoxicity (Suwunnamek & Parker, 1975; O'Sullivan O'Donovan & Hamman, 1981) many cations are antagonistic (Wanamarta & Penner, 1989; Nalewaja & Matysiak, 1991). Ammonium sulphate, in addition to directly enhancing glyphosate phytotoxicity in certain species, overcomes antagonism from various cations (Nalewaja & Matysiak, 1993). It is assumed that ammonium sulphate overcomes salt antagonism of glyphosate by preventing the formation of glyphosate salts that are less effective than the commercially formulated isopropylamine. However, no reports were found comparing the efficacy or absorption of various glyphosate salts that might be formed from a common cation in spray water. Thus, series of experiments were conducted to determine phytotoxicity and absorption of various glyphosate salt formulations in wheat.

4.2 Materials and Methods

4.2.1 General procedures

K. scoparia and spring wheat (*Triticum aestivum* cv. Marshall) were grown in the glasshouse during the summer. Wheat seeds were placed 2 cm and *K. scoparia* seed 0.5 cm deep in a glasshouse potting mixture of one part sandy loam soil and one part commercial peat-based potting material, contained in 0.5 L plastic pots.

Plants were thinned to seven per pot one week after emergence for the phytotoxicity and spray retention experiments and three per pot for the [^{14}C]glyphosate experiments. Metal halide lamps providing $450 \mu \text{E m}^{-2} \text{s}^{-1}$ PAR at the plant level were used to supplement the natural light in the morning and evening of a 16h light period. Temperature varied from 20 to 30°C and humidity was high due to the use of evaporative cooler.

Spray treatments were applied with a moving nozzle sprayer using only the 10 cm centre area of the 50 cm fan produced by a 650067 nozzle (Spray Systems Co., USA) delivering 160 L ha^{-1} at 270 kPa. Treatments were to 2.5-leaf wheat and 10 cm tall *K. scoparia* plants. Spray delivered to the treatment area was determined by weighing of the spray collected in six replicate 9 cm diameter petri dishes.

4.2.2 Phytotoxicity experiments

Phytotoxicity of glyphosate salt formulations was tested using formulations prepared by mixing technical glyphosate acid on a molar basis of 1:1 and 1:2 with sodium hydroxide, ammonium hydroxide, and isopropylamine and at 1:0.5, 1:1, and 1:2 with calcium hydroxide. These glyphosate formulations were applied at 30 g ai ha^{-1} with surfactant MON-0818 (Monsanto, USA), Tween 20 (ICI Surfactants, USA), or X-77 (Loveland Industries, USA) at 1% V/V. A non-surfactant treatment was not included because surfactants are required for commercial glyphosate use. Treatment was made at only 30 g ai ha^{-1} because of the known high activity, under humid conditions, in the glasshouse when using evaporative coolers in the summer.

Plants were harvested 12 days after treatment, weighed and data expressed as percentage fresh weight reduction compared with untreated plants. The experiment was carried out as a randomized complete block with a factorial arrangement of treatments replicated four times. Means were separated using Fischer's protected LSD at 0.05 probability.

4.2.3 *Spray retention experiments*

Glyphosate spray retained by wheat and *K. scoparia* plants was determined for nonylphenoxy poly(ethyleneoxide) ethanol surfactants (Rhone-Poulenc, USA), Igepal CO-530, CO-610, CO-660, CO-730, and CO-887 having HLB values of 10.8, 12.2, 13.2, 15.0 and 17.2, respectively. Glyphosate isopropylamine formulated without surfactant (Honcho[®], Monsanto, USA) was used at 200 g ai ha⁻¹ and the surfactants at 1% V/V in distilled water only or with distilled water containing 500 µg g⁻¹ calcium (calcium chloride) or with 500 µg g⁻¹ calcium and 1% w/v ammonium sulphate. The 200 g ai ha⁻¹ rate was chosen for the retention experiments to match those in previous experiments (Nalewaja *et al.*, 1995) conducted during the winter. The amount of spray retained by wheat plants was determined by including Chicago Blue Sky dye (Sigma Chemical Co., USA) at 7.5 g L⁻¹ in the spray solution.

Plants were cut at soil level after the spray droplets had dried, placed in a test tube containing 10 ml distilled water and 0.1% polyoxyethylene sorbitan monolaurate (Tween 20, ICI Surfactants Inc., USA) and 0.01% commercial antifoam (Foambuster, Ostlund Chemical, USA) and shaken for 20 seconds. Plants were then washed for 20 seconds in a second test tube with 4 ml of distilled water. The two solutions were combined and brought up to 15 ml with distilled water. The amount of glyphosate retained per gram of plant tissue was calculated by reference to spectrophotometric absorption measurements at 620 nm of the dye in the wash solution.

4.2.4 [¹⁴C]glyphosate absorption experiments

The effect of surfactants and glyphosate salt formulation on absorption of [¹⁴C]glyphosate was investigated by determining ¹⁴C label washed off the treated plant material. Prior to treatment, plants were thinned to 1 plant per pot. Six individual plants were treated as six replicates. The experiment was a completely randomized design with a factorial arrangement of treatments. The applied ¹⁴C

label not recovered from the treated plant material was assumed to have been absorbed. Plants were placed 24h before treatment in a growth chamber at 20 °C and 75% relative humidity under a 16h light period at 250 $\mu\text{Em}^{-2} \text{ s}^{-1}$ PAR.

In the HLB experiment, treatment consisted of first applying formulated isopropylamine glyphosate (Honcho[®])(which contains no surfactant) with the various surfactants and salts in two 1 μL droplets placed 1 cm apart, one-third of the distance from the tips of the second wheat leaf and on the upper most fully expanded *K. scoparia* leaf. The surfactants were at 0.075%, calcium at 500 $\mu\text{g g}^{-1}$ supplied as calcium chloride, and ammonium sulphate at 0.5% (w/v). A second 1.5 μL droplet containing 17,000 dpm 51 mCi-mM^{-1} [¹⁴C]glyphosate acid (Amersham Corporation, USA) was applied to each partly dried 1 μL droplet. The total glyphosate applied was at 200 g ai ha^{-1} assuming the two droplets represented 1 cm^2 , of which 10% was [¹⁴C]glyphosate acid. After treatment, plants were returned to the growth chamber for 48 hours. Treated leaf area was excised and washed by shaking for 20 seconds in 3 ml distilled water containing 0.1% Tergitol 15-S-9 (Union Carbide Corp, USA). The ¹⁴C in the wash water was assayed by scintillation spectrometry (Delta 300, TM Analytic Inc., USA) with an external standard ratio quench correction using ScintiSafe Plus 50% cocktail (Fisher Scientific, USA). Treatments were replicated six times and data expressed as [¹⁴C]glyphosate absorbed as a percentage of that applied. [¹⁴C]glyphosate absorption by wheat plants as influenced by salt formulation was determined using methods similar to the phytotoxicity experiment. [¹⁴C]glyphosate acid with a specific activity of 8.08 mCi mM^{-1} (Monsanto, USA) was mixed with technical glyphosate and reacted with sodium hydroxide at 1:1 and 1:2 molar equivalents, ammonium hydroxide at 1:2, isopropylamine at 1:2, calcium hydroxide at 1:1, or left as the acid. [¹⁴C]glyphosate and technical glyphosate were in amounts for 100 g ai ha^{-1} at 17,000 dpm, assuming that treatment area represented 1 cm^2 . Treatment solution contained 0.01% MON 0818 surfactant (Monsanto, USA). Treatment was a single application of four separate 1 μL droplets in the laboratory and plants were kept at 85% relative humidity in the growth chamber.

4.3 Results and Discussion

Glyphosate spray retained by wheat and *K. scoparia* plants was greater when the spray contained nonylphenoxy surfactants with HLB values of 15.0 and 17.2 than 10.8 or 12.2 (Table 1). Spray retained by *K. scoparia*, but not by wheat, was greater for the surfactant with HLB of 17.2 than 15.0. These results indicate that the increase in glyphosate phytotoxicity in *K. scoparia*, and maximal effect in wheat at the surfactant HLB of 15-17, (Nalewaja *et al.*, 1995) was due, at least in part, from greater spray retention. Calcium chloride or calcium chloride plus ammonium sulphate in the spray solution did not change spray retention by wheat or *K. scoparia* (data not shown), even though calcium generally reduced the optimum surfactant HLB value for glyphosate phytotoxicity in *K. scoparia* (Nalewaja *et al.*, 1995).

Glyphosate spray retained per gram of plant tissue was greater for *K. scoparia* than for wheat. This probably reflects the fact that the weed has more horizontally oriented leaves than wheat, thus intercepting more spray. The more vertical leaf orientation of wheat leaves might cause some droplets to bounce away upon contact or the leaf-air boundary area cause droplets to bypass the leaf. The lack of increase of spray retention by wheat with an increase of the surfactant HLB from 15.0 to 17.2 may be from an interaction between high surface tension of the spray solution and vertically oriented leaves which could cause droplets to roll or bounce off the leaves.

The general increase in spray retention with increasing HLB values of surfactant suggests that a very low surface tension is not necessary for a spray to be retained by plants. The increase in retention by *K. scoparia* as HLB value increased from 10.8 to 17.2, but only from 10.8 to 15.0 for wheat, indicates that specific leaf characteristics influence spray retention response to HLB of surfactants.

Table 1 Retention of glyphosate with different surfactants on wheat and *Kochia scoparia*

Surfactants	Wheat			Kochia	
	HLB value	Glyphosate on plant tissue ($\mu\text{g g}^{-1}$)	Average retention relative to IgepalCO 530 (%)	Glyphosate on Plant tissue ($\mu\text{g g}^{-1}$)	Average retention relative to Igepal CO 530 (%)
Igepal CO 530	10.8	9.3	100	31.8	100
Igepal CO 610	12.2	9.3	100	33.4	103
Igepal CO 660	13.2	10.3	110	34.7	109
Igepal CO 730	15.0	12.9	139	38.4	119
Igepal CO 887	17.2	12.7	138	42.4	131
LSD ($P=0.05$)		0.6		3.0	

Surface tension of the solution increased with the surfactant HLB and was not influenced by the presence of calcium chloride or ammonium sulphate (data not presented). All spray treatments were applied at 160 L ha^{-1} , which did not appear to cause spray to run off the leaf of either species due to excessive wetting. The surface tension of a herbicide-surfactant solution could influence the rate at which spray solution passes through the nozzle orifice and/or the spray distribution and thus confound spray retention results. Low HLB surfactants generally have a low water solubility and give a cloudy solution, which may resist the passage of

solution through the nozzle and reduce the amount of spray delivered. Furthermore, low surface tension solutions may affect the spray distribution pattern.

The spray solution delivered to the area under the spray fan used for plant treatment increased by 12% with the highest compared with the lowest HLB surfactants whether in distilled water alone or with calcium chloride or calcium chloride plus ammonium sulphate. The averaged amount of spray solution collected per 9 cm petri-dish was 60.9, 62.4, 63.2, 64.4, and 68.4 mg for the nonylphenoxy surfactants with HLB of 10.8, 12.2, 13.2, 15.0, and 17.2, respectively. Spray delivery from the nozzle was not determined, but the spray pattern appeared to become narrower for sprays with the high HLB surfactants, which would increase delivery to the centre of the spray fan used for the treatment.

The increased spray delivery to the target area may explain in part the greater glyphosate phytotoxicity in *K. scoparia* as previously reported (Nalewaja *et al.*, 1995) for high HLB nonylphenoxy surfactants. However, spray delivery response to surfactants cannot explain the differences between wheat and *K. scoparia* in the amount of spray retained (Table 1) or in the difference in phytotoxic response between weed and wheat plants to surfactants of increasing HLB (Nalewaja *et al.*, 1995).

The amount of [¹⁴C]glyphosate absorbed by wheat and *K. scoparia* increased with surfactant HLB value when in distilled water without salts, was maximal at a surfactant HLB of 13.2 for distilled water, with calcium chloride plus ammonium sulphate, but was not affected by surfactant HLB for distilled water with calcium chloride (Table 2). The increase in glyphosate absorbed by wheat and *K. scoparia* in response to increasing nonylphenoxy surfactant HLB generally

Table 2 Percentage [^{14}C]glyphosate absorbed by wheat and *Kochia scoparia* as influenced by surfactants and salts

Surfactants	HLB value	Salts					
		Wheat			<i>Kochia</i>		
		None	CaCl_2	$\text{CaCl}_2 +$ $(\text{NH}_4)_2\text{SO}_4$	None	CaCl_2	$\text{CaCl}_2 +$ $(\text{NH}_4)_2\text{SO}_4$
% of applied							
Igepal CO 530	10.8	12	9	35	8	8	23
Igepal CO 610	12.2	11	11	25	11	10	15
Igepal CO 660	13.2	16	12	47	13	10	50
Igepal CO 730	15.0	25	9	51	25	9	38
Igepal CO 887	17.2	33	9	52	30	5	37
LSD ($P=0.05$)		4			6		

agrees with the increased glyphosate found to be absorbed by wheat and field bean (*Vicia faba* L.) plants (Gaskin & Holloway, 1992) with high EO content aliphatic alcohol, nonylphenol and aliphatic amine surfactants in distilled water. The increase in absorption accounts for the previously reported increase in glyphosate phytotoxicity to *K. scoparia* with increasing surfactant HLB, but not for wheat, where phytotoxicity was maximal with a surfactant HLB of 15 (Nalewaja *et al.*, 1995). The increased absorption trend in wheat to increasing surfactant HLB with greatest phytotoxicity at surfactant HLB 15 (Nalewaja *et al.*, 1995), may be due to the presence of smaller droplets in the spray used in the phytotoxicity experiment and the larger droplets in the absorption experiment. Large droplets with high HLB surfactants did not spread on leaf surfaces and remained wet much longer than the droplets with low HLB surfactants (Stevens & Bukovac, 1987).

These large moist deposits would allow for greater absorption of water-soluble glyphosate (Stock & Holloway, 1993).

Glyphosate in solutions containing ammonium sulphate and calcium chloride had the greatest absorption with an intermediate surfactant HLB value. Both ammonium sulphate and surfactants reduced the formation of glyphosate crystals and increased absorption by Tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.) (Maclsaac, Paul & Devine, 1991). Spray droplet residual may be particularly important for *K. scoparia* which has leaves covered with highly crystalline waxes that are difficult to wet (Nalewaja, Matysiak & Freeman, 1992). The textured leaf surface of *K. scoparia* may reduce droplet spread so that similar response to HLB occurred for efficacy and absorption. The low absorption of glyphosate in the presence of calcium chloride is probably due to the formation of glyphosate-calcium (Nalewaja & Matysiak, 1993).

The effectiveness of various salt formulations of glyphosate in reducing wheat fresh weight was affected by surfactant (Table 3). All the glyphosate formulations were less effective when applied with X-77 than MON 0818 or Tween 20 at 1% in the spray solution. Glyphosate-isopropylamine generally was the most active form regardless of surfactant. The presence of sodium or calcium at twice molar excess of glyphosate further reduced activity below that of sodium or calcium molar equivalence, with Tween 20 or X-77 but not with MON 0818 (Table 3). The ratio of glyphosate to ammonium or isopropylamine did not influence phytotoxicity on wheat.

The reduced glyphosate phytotoxicity by the higher amounts of sodium and calcium with Tween 20 and X-77 indicates the possible involvement of two of the three reactive sites on the glyphosate molecule (Wouchope, 1976). Increasing the calcium to a 1:2 molar ratio apparently was not adequate to involve the third glyphosate site as phytotoxicity was not reduced below that of the 1:1 ratio.

Table 3 Percentage wheat shoot fresh weight reduction 12 days after application of 30 g ai ha⁻¹ glyphosate from different formulations applied with surfactants at 1% (V/V)

Formulation	Molar equiv.	Surfactant		
		MON 0818	Tween 20	X-77
Glyphosate acid		56	57	37
Glyphosate sodium	(1:1)	56	41	23
Glyphosate sodium	(1:2)	54	30	18
Glyphosate ammonium	(1:1)	53	54	33
Glyphosate ammonium	(1:2)	54	55	33
Glyphosate isopropylamine	(1:1)	60	58	38
Glyphosate isopropylamine	(1:2)	57	59	39
Glyphosate calcium	(1:0.5)	29	27	19
Glyphosate calcium	(1:1)	28	17	11
Glyphosate calcium	(1:2)	27	15	11
LSD (<i>P</i> =0.05)		5		

Glyphosate:sodium or glyphosate:calcium ratios did not influence phytotoxicity with MON 0818. The greater glyphosate effectiveness and lack of response to sodium and calcium concentration in the presence of MON 0818 may relate to its amine cation property or its chemical and physical characteristics that allow for absorption. The amine may have reduced the formation of glyphosate sodium or glyphosate calcium. The Roundup® formulation (Monsanto, USA) containing MON 0818 is antagonized by salts in the spray solution (Stahlman & Phillips, 1979). In the present studies Mon 0818 was at 1% and glyphosate only at 30 g ai ha⁻¹ which

probably provides more MON 0818 relative to glyphosate than that in the commercial formulation.

Wheat absorbed most glyphosate when formulated as an isopropylamine, followed by ammonium and sodium, and least as a calcium salt (Table 4). Absorption of glyphosate acid was intermediate to the isopropylamine and ammonium formulations.

Table 4 Percentage [^{14}C]glyphosate absorbed by wheat plants as influenced by salt formulation containing 0.01% MON 0818 surfactant

Formulation	Molar equiv.	^{14}C absorbed (% of applied)
Glyphosate acid		49
Glyphosate sodium	(1:1)	18
Glyphosate sodium	(1:2)	21
Glyphosate ammonium	(1:2)	44
Glyphosate isopropylamine	(1:2)	59
Glyphosate calcium	(1:1)	1
LSD ($P=0.05$)		5

These results support previous assumptions that sodium and calcium antagonism of glyphosate phytotoxicity was from formation of the less absorptive glyphosate salt during spray droplets drying on the leaf surface (Nalewaja & Matysiak, 1993). Glyphosate absorption was reduced by sodium in the presence of 0.01% MON 0818, even though phytotoxicity was not reduced by sodium in the presence of 1%

MON 0818. The low concentration of MON 0818 may have been inadequate to overcome antagonism, but sufficient to prevent expression of a significant response to sodium concentrations. Glyphosate formulated as a calcium salt severely reduced absorption by wheat which accounts for the frequently reported antagonism from calcium cations in spray solutions (Stahlman & Phillips, 1979; O'Sullivan *et al.*, 1981).

4.4 Conclusions

These experiments indicate that the effects on glyphosate phytotoxicity by nonylphenoxy surfactants previously reported for *K. scoparia* and wheat was in part due to effects on the amount of spray delivered and retained by plants, but mainly from the influence of the surfactant HLB on glyphosate absorption. Furthermore the absorption of glyphosate sodium and calcium salts was less than for isopropylamine or ammonium salts which accounts for the antagonism of glyphosate phytotoxicity by the presence of these salts in spray solutions.

4.5 References

- CRANMER, J.R. & LINSKOTT, D.L., 1991. Effects of droplet composition on glyphosate absorption and translocation in velvetleaf (*Abutilon theophrasti*). *Weed Sci.* 39, 251-254.
- DE VILLIERS, B.L. & DU TOIT, D., 1993. Chemical composition of carrier water influences glyphosate efficacy. *S. Afr. J. Plant Soil* 10(4), 178-182.
- DE VILLIERS, B.L., LINDEQUE, R.C. & KNOBEL, H.H., 1996. Calcium and magnesium in spray carriers antagonize glyphosate performance. *Appl. Plant. Sci.* 10(1), 10-11.
- GASKIN, R.E. & HOLLOWAY, P.J., 1992. Some physicochemical factors influencing foliar uptake enhancement of glyphosate-

- mono(isopropylammonium) by polyoxyethylene surfactants. *Pestic. Sci.* 34, 195-206.
- MACISAAC, S.A., PAUL, R.N. & DEVINE, M.D., 1991. A scanning electron microscope study of glyphosate deposits in relation to foliar uptake. *Pestic. Sci.* 31, 53-64.
- NALEWAJA, J.D. & MATYSIAK, R., 1991. Salt antagonism of glyphosate. *Weed Sci.* 39, 622-628.
- NALEWAJA, J.D., MATYSIAK, R. & FREEMAN, T.P., 1992. Spray droplet residual of glyphosate in various carriers. *Weed Sci.* 40, 576-589.
- NALEWAJA, J.D. & MATYSIAK, R., 1993. Influence of diammonium sulfate and other salts on glyphosate phytotoxicity. *Pestic. Sci.* 38, 77-84.
- NALEWAJA, J.D., KOZIARA, W., MATYSIAK, R. & MANTHEY, F.A., 1995. Relationship of surfactant HLB to glyphosate phytotoxicity. in *Pesticide Formulation and Application Systems* 14, 269-277, ASTM STP 1234 Philadelphia PA.
- O'SULLIVAN, P.A., O'DONOVAN, J.T. & HAMMAN, 1981. Influence of nonionic surfactants, ammonium sulfate, water quality and spray volume on the phytotoxicity of glyphosate. *Can. J. Pl. Sci.* 61, 391-400.
- STAHLMAN, P.W. & PHILLIPS, 1979. Effects of water quality and spray volume on glyphosate phytotoxicity. *Weed Sci.* 27, 38-41.
- STEVENS, P.J.G. & BUKOVAC, M.J., 1987. Studies on octylphenoxy surfactants. Part 1: Effects of oxyethylene content on properties of potential relevance to foliar absorption. *Pestic. Sci.* 20, 19-35.

STOCK, D. & HOLLOWAY, P.J., 1993. Possible mechanisms for surfactant - induced foliar uptake of agrochemicals. *Pestic. Sci.* 38, 165-177.

SUWUNNAMEK, U. & PARKER, C., 1975. Control of *Cyperus rotundus* with glyphosate: the influence of ammonium sulphate and other additives. *Weed Res.* 15, 13-19.

WANAMARTA, G. & PENNER, D., 1989. Foliar absorption of herbicide. *Weed Sci.* 4, 214-231.

WAUCHOPE, D., 1976. Acid dissociation constants of arsenic acid, methylarsenic acid (MAA), dimethylarsenic acid (cacodylic acid), and N-(phosphonomethyl)glycine (glyphosate). *J. Agric. Food Chem.* 24, 717-721.

CHAPTER 5

OPTIMIZING GLYPHOSATE PERFORMANCE WITH ADJUVANTS

(*S. Afr. J. Plant Soil*, 14 (4), 146-148)

5.1 Introduction

De Villiers & du Toit (1993) found that South African carrier waters in the Free State and Northern Cape Provinces could antagonize glyphosate activity. This antagonism occurred especially with hard waters (de Villiers, Lindeque & Knobel, 1996). Nalewaja, de Villiers & Matysiak (1996) found that calcium chloride antagonism and the overcoming thereof with ammonium sulphate was as a result of glyphosate absorption. Nalewaja *et al.* (1996) reported that the absorption of glyphosate-calcium and glyphosate-sodium is much lower than glyphosate-isopropylamine, glyphosate-ammonium and glyphosate-acid. Glyphosate antagonism therefore occurs as a result of the formation of glyphosate compounds that are not readily absorbed by plants. When calcium is present in the carrier water, glyphosate-calcium is formed during droplet drying. Glyphosate-calcium has a solubility of 30 g L⁻¹ whereas glyphosate-isopropylamine has a water solubility of 500 g L⁻¹. During droplet drying the least soluble salt namely glyphosate-calcium precipitates first. This glyphosate-calcium does not penetrate through the plant cuticle (Nalewaja *et al.*, 1996). In the presence of ammonium sulphate, calcium sulphate is precipitated first during droplet drying because of low solubility namely 2 g L⁻¹. Thus the calcium ions are removed from solution preventing the formation of glyphosate-calcium. The ammonium from the ammonium sulphate would in part produce glyphosate-ammonium (300 g L⁻¹) as concentration increases during droplet drying (Nalewaja & Matysiak, 1993a). Glyphosate-ammonium enters into the plant more readily than glyphosate-calcium (Nalewaja *et al.*, 1996).

Nalewaja & Matysiak (1993b) found that optimization of glyphosate activity can be achieved with suitable adjuvants to overcome salt antagonism and to increase

glyphosate activity. Glyphosate activity is greatly influenced by the type of surfactant and the presence of salts in the spray solution (Hatzios & Penner, 1985). Most surfactants increase glyphosate phytotoxicity, but ethoxylated amine surfactants enhance phytotoxicity more than nonionic surfactants (Wyrill & Burnside, 1977). Nalewaja, Koziara, Matysiak & Manthey (1995) found that within the group of nonionic surfactants, ethoxylated nonylphenoxys are more effective than octylphenoxys. Nonyl- and octyl-phenoxy surfactants increased glyphosate phytotoxicity to *Kochia scoparia* L. with increasing HLB value, but for wheat (*Triticum aestivum* L.) the optimum HLB value was about 15.

The aim of this study was to identify suitable South African adjuvants with the dual purpose of eliminating calcium antagonism of glyphosate while adding additional surfactant for increased absorption.

5.2 Materials and Methods

5.2.1 General procedures

Treatment solutions were prepared by first adding the calcium, followed by the 360 g ai L⁻¹ glyphosate isopropylamine (Roundup®, Monsanto, USA) and adjuvants except in the case of Bladbuff 5 (Plaaskem, South Africa) that was added prior to the glyphosate.

5.2.2 Glasshouse study

Twelve oat (*Avena sativa* cv. Witteberg) seeds were planted 2 cm deep per 2-L pot filled with sandy-loam soil with a 20% clay content. Each pot represented one replication of a treatment and there were four replications per treatment. The soil was fertilized and watered adequately for healthy plant growth. At the one leaf stage, the plants were thinned to eight uniform plants per pot. Treatments were applied with a moving nozzle pot sprayer consisting of two 8001 flat-fan nozzles. A constant pressure of 200 kPa was maintained by regulated compressed air and for spray delivery of 310 L ha⁻¹. Glyphosate at 65 g ai ha⁻¹ was applied to four-leaf

oats. Adjuvants applied with glyphosate are indicated in Table 1, and the water sources in Table 2. Adjuvant rates were zero, half the registered rate, registered rate and double the registered rate in South Africa.

Table 1 Description of adjuvants used in glasshouse and field experiments

Trade name	Chemistry of ingredients	Rates
Armoblen 650 (Akzo, Netherlands)	Tallow amine ethoxylate and sugar based surfactant (buffer pH 4-6)	0
		0.075 %
		0.15 % *
		0.3 %
Frigate (ISK Biosciences)	Tallow amine ethoxylate (800 g L ⁻¹)	0
		0.5 L ha ⁻¹
		1 L ha ⁻¹ *
		2 L ha ⁻¹
Bladbuff 5 (Plaaskem, South Africa)	Acid, surfactant and colour indicator (colour change at pH 4.5, buffer pH 3)	0
		0.0625 %
		0.125 % * (pink)
		0.25 %
EXP94KG1 (present trade name: Power-Up)	Coded Small Grain Institute surfactant and ammonium sulphate	0
		1 L ha ⁻¹
		2 L ha ⁻¹ *
		4 L ha ⁻¹
Beef-up AS (GAP Chemicals, South Africa)	Ammonium sulphate solution (500 g L ⁻¹)	0
		1 %
		2 % *
		4 %

* Recommended rate envisaged for EXP94KG1 and registered rates of the other adjuvants with glyphosate

Table 2 Water carriers applied in glasshouse and field experiments, with the cation concentration expressed in mg L⁻¹ (mM in parenthesis)

Cations	Carrier 1 (Glasshouse & field)	Carrier 2 (Glasshouse)
Calcium	93.0 (2.32)	393.0 (9.81)
Sodium	24.5 (1.07)	24.5 (1.07)
Magnesium	12.2 (0.50)	12.2 (0.50)
Potassium	5.2 (0.13)	5.2 (0.13)

The experiment was arranged as a completely randomized design. Treatments were evaluated 14 days after application by determination of fresh shoot mass. Data were expressed as a percentage reduction from the untreated control. Data was subjected to analysis of variance and least significant differences were calculated using the Tukey test at a 95% probability level.

5.2.3 Field study

Strips of oats (cv. Witteberg) at the six leaf stage were treated with glyphosate at 61, 104, 190 and 360 g ai ha⁻¹. A CO₂ pressurized knapsack sprayer with five 8001 Teejet flat-fan nozzles delivering 177 L ha⁻¹ with a swath width of 2,25 m was utilized to apply the treatments. Plots were 10 m² with 5 m² untreated control plots adjacent to each treatment. Humidity at application was 51% and the difference between wet and dry bulb temperatures was 5.5°C.

Adjuvant treatments in the field were identical to the glasshouse experiment but only Carrier 1 was used and the recommended or registered adjuvant rates. Bladbuff 5 attained the desired pink colour change at this rate. Only the 61 g ai ha⁻¹ rate will be discussed as differences between adjuvants treatments were most pronounced here at 28 days after application. Data was visible percentage reduction in oat growth compared with untreated oats.

The experiment was arranged as a randomized block design with four replicates per treatment. Data were subjected to analysis of variance and least significant differences were calculated using the Tukey test at a 95 % probability level.

5.3 Results

5.3.1 *Glasshouse study*

EXP94KG1 was the most efficacious adjuvant with glyphosate for both water sources used in the glasshouse (Figure 1). Frigate and Armoblen 650 were less effective than the other adjuvants in carriers with high calcium concentration. The efficacy of the treatment containing Frigate decreased drastically as calcium content was increased. EXP94KG1 was significantly more effective than all the other adjuvants in Carrier 1 with lower calcium content. The other four adjuvants were equally as effective in Carrier 1. With the higher calcium content of Carrier 2 however, Frigate and Armoblen 650 were less effective with glyphosate than the other adjuvants in overcoming calcium antagonism. EXP94KG1 again was the most effective adjuvant in the high calcium spray carrier. Beef-up As and Bladbuff 5 efficacy were similar to when they were sprayed with Carrier 1. EXP94KG1 was significantly more effective than the other adjuvants even when applied at half the recommended rate, determined over both water sources (Figure 2).

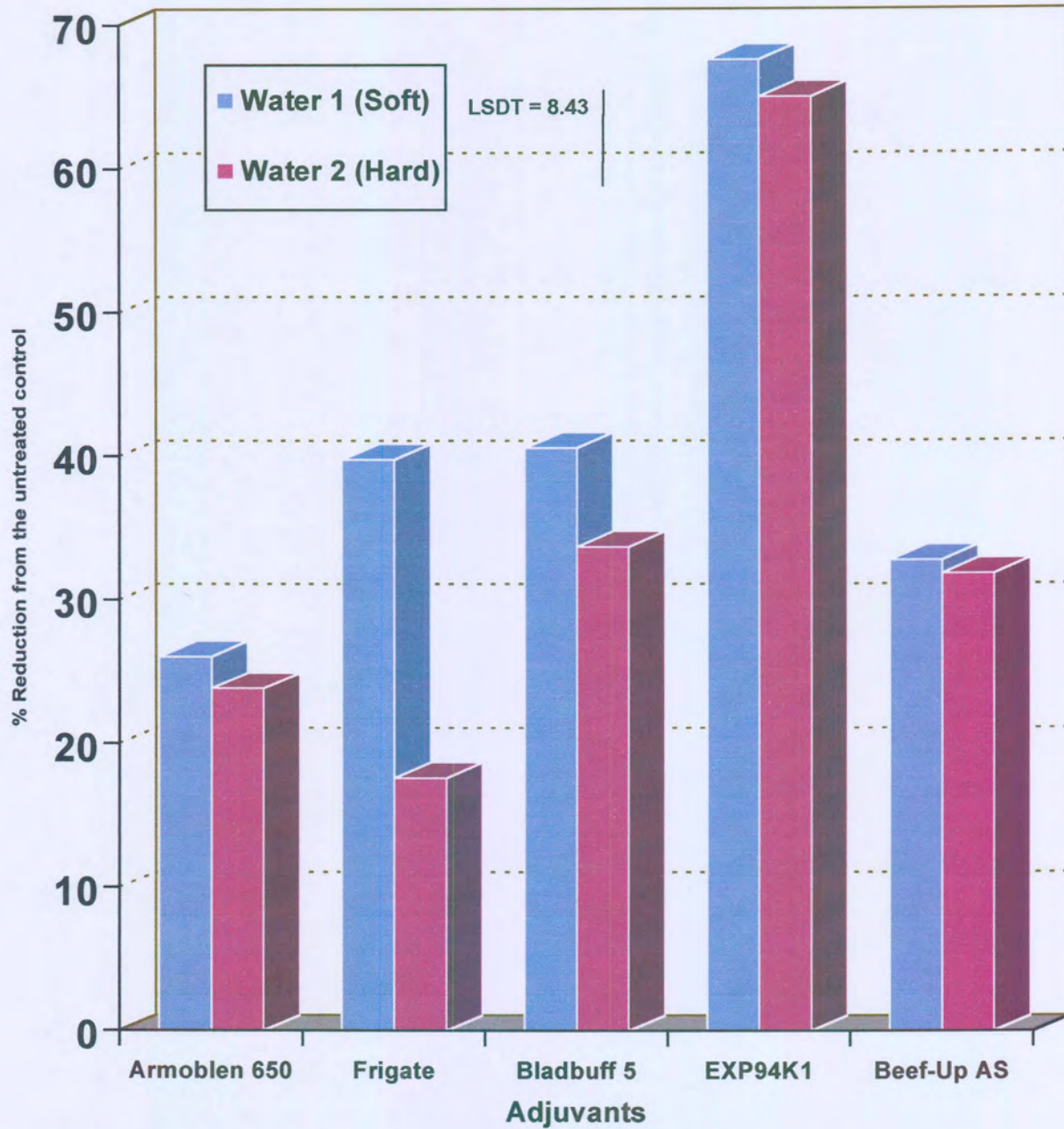


Figure 1 The influence of adjuvants with two carrier sources on the efficacy of glyphosate in the glasshouse

5.3.2 Field study

In the field, Frigate and EXP94KG1 were the most effective adjuvants. Armoblen 650, Bladbuff 5 and Beef-up As were equally effective with glyphosate, but significantly less effective than EXP94KG1 and Frigate (Figure 3).

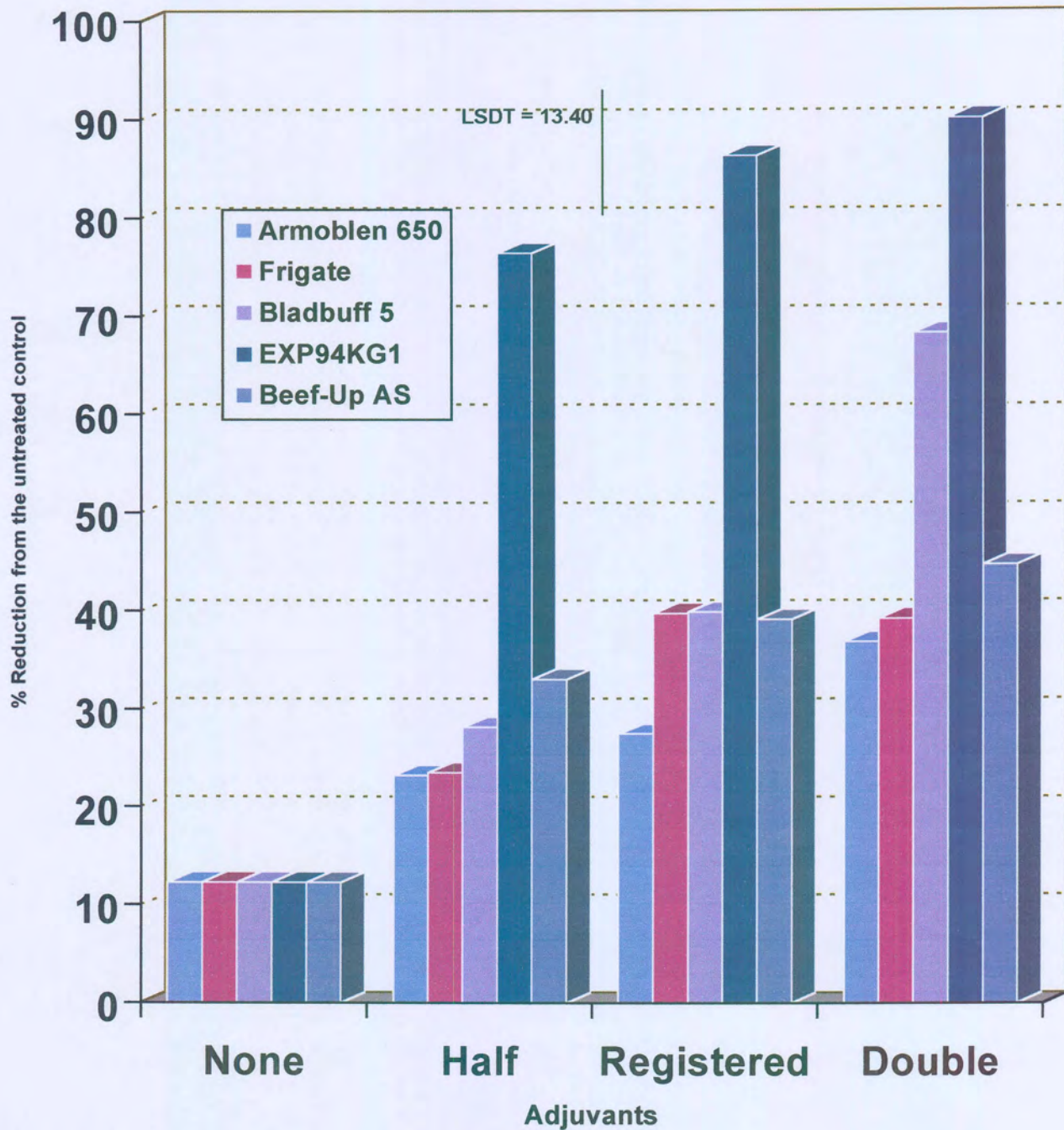


Figure 2 The influence of adjuvant type and adjuvant rate on the efficacy of glyphosate averaged over both water sources in the glasshouse

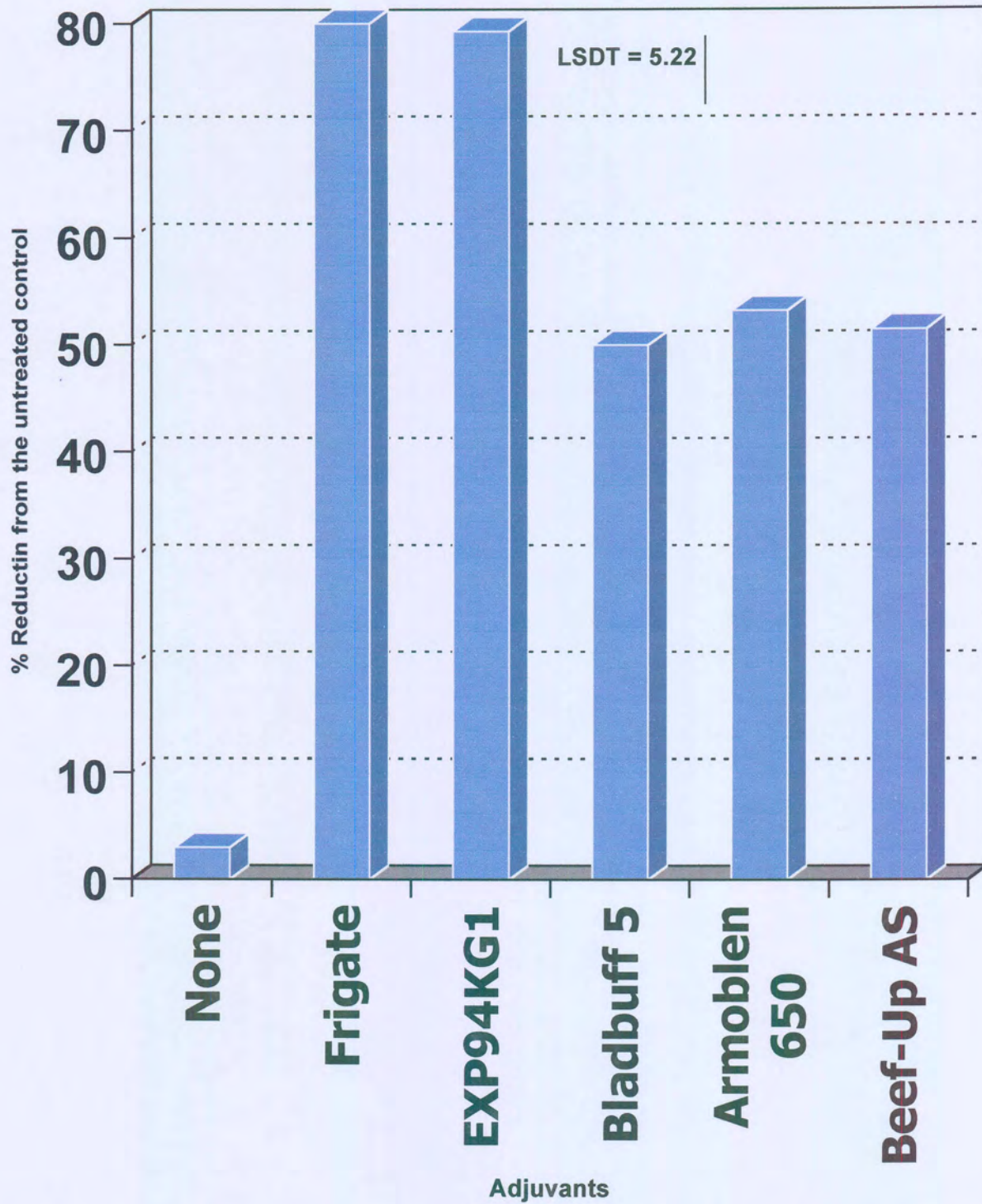


Figure 3 The influence of adjuvants on the efficacy of glyphosate under field conditions

5.4 Discussion

The results further confirm that glyphosate is antagonized by various salts in the spray carrier (Buhler & Burnside, 1983a; Buhler & Burnside, 1983b; de Villiers & du Toit, 1993). Additional calcium also increased the antagonism in the absence of an effective adjuvant. Adjuvants with the dual purpose of rectifying salt antagonism and supplementing surfactant are of importance when optimizing the performance of glyphosate at low rates and high carrier volumes. This is the reason for the stable activity of glyphosate mixed with EXP94KG1.

The performance of EXP94KG1 cannot be attributed only to the water conditioning agent contained in the adjuvant formulation. The non-ionic surfactant contained in the adjuvant also could have contributed to enhanced efficacy, especially at the low rates applied in this study. This confirmed the research of Ivany (1988) who reported enhanced efficacy of glyphosate with non-ionic surfactants and proved that surfactants other than ethoxylated amines could be used effectively.

The greater efficacy of Frigate relative to other adjuvants in the field than in the glasshouse may be attributed to lower water volume (177 L ha⁻¹) and consequently, lower salt to glyphosate ratio, resulting in reduced salt antagonism. This confirmed the findings of Stahlman & Phillips (1979) who found that salt antagonism was reduced when applying lower carrier volumes. However when these lower carrier volumes were applied, the increase in efficacy due to the other adjuvants was not as great as with Frigate.

5.5 Conclusions

Maximizing glyphosate phytotoxicity apparently requires specific surfactants and salts to overcome salt antagonism. EXP94KG1 met these requirements adequately. This indicates that surfactants other than the cationic ethoxylated amine surfactants could also be highly effective as glyphosate adjuvants. Glyphosate rates can be minimized by the use of proper adjuvants in conjunction

with low water volumes. These adjuvants would have the ability to overcome salt antagonism while adding additional beneficial surfactant. This will optimize the efficiency of glyphosate and also stabilize its performance over various environments and with different water sources.

5.6 References

- BUHLER, D.D. & BURNSIDE, O.C., 1983a. Effect of water quality, carrier volume, and acid on glyphosate phytotoxicity. *Weed Sci.* 31, 163-169.
- BUHLER, D.D. & BURNSIDE, O.C., 1983b. Effect of spray components on glyphosate toxicity to annual grasses. *Weed Sci.* 31, 124-130.
- DE VILLIERS, B.L. & DU TOIT, D., 1993. Chemical composition of carrier water influences glyphosate efficacy. *S. Afr. J. Plant Soil*, 10 (4), 178-82.
- DE VILLIERS, B.L., LINDEQUE, R.C. & KNOBEL, H.H., 1996. Calcium and magnesium in spray carriers antagonize glyphosate performance. *Appl. Plant. Sci.* 10(1), 10-11.
- HATZIOS, K.K. & PENNER, D., 1985. *Rev. Weed Sci.* 1, 1-63.
- IVANY, J.A., 1988. Control of quackgrass with glyphosate and additives. *Can. J. Plant Sci.* 68, 1095-1101.
- NALEWAJA, J.D., DE VILLIERS, B.L. & MATYSIAK, R., 1996. Surfactant and salt affect glyphosate retention and absorption. *Weed Res.* 36, 241-247.
- NALEWAJA, J.D., KOZIARA, W., MATYSIAK, R. & MANTHEY, F.A., 1995. Relationship of surfactant HLB to glyphosate phytotoxicity. in *Pesticide Formulation and Application Systems* 14, 269-277, ASTM STP 1234 Philadelphia PA.

NALEWAJA, J.D. & MATYSIAK, R., 1993a. Influence of diammonium sulphate and other salts on glyphosate phytotoxicity. *Pestic. Sci.* 38, 77-84.

NALEWAJA, J.D. & MATYSIAK, R., 1993b. Optimizing adjuvants to overcome glyphosate antagonistic salts. *Weed Tech.* 7, 337-342.

STAHLMAN, P.W. & PHILLIPS, W.M., 1979. Effects of water quality and spray volume on glyphosate phytotoxicity. *Weed Sci.* 27, 38-41.

WYRILL, J.B. & BURNSIDE, O.C., 1977. Glyphosate toxicity to common milkweed and hemp dogbane as influenced by surfactants. *Weed Sci.* 25, 275-287.

CHAPTER 6

SPRAY DROPLET RESIDUALS OF GLYPHOSATE WITH SOUTH AFRICAN ADJUVANTS IN CALCIUM SPRAY CARRIERS

6.1 Introduction

A possible reason for the glyphosate response to antagonistic (Buhler & Burnside, 1983) and beneficial salts (Nalewaja & Matysiak, 1991) and surfactants, may be the formation of glyphosate salts with differential absorption into plants (Nalewaja, de Villiers & Matysiak, 1996). This probably contributed to the differential efficacy of glyphosate with various South African adjuvants (de Villiers, Lindeque & Smit, 1997).

Another possible contributing factor to glyphosate performance with surfactants and salts could be the physical characteristics of the spray droplet residual (Nalewaja, Matysiak & Freeman, 1992). Spray droplet residual appearance could be an indicator of herbicide activity. Factors such as structure of the deposit, crystal formation, moisture and adherence to the leaf surface could have an influence on final absorption of glyphosate (Nalewaja *et al.*, 1992).

Hess & Folk (1990) found that spray droplet retention and absorption of the herbicide are essential for herbicide efficacy. Surfactants, when applied with glyphosate, increase droplet spread and contact with the leaf epidermal surface. Herbicide formulations that dry as solids could limit the contact with the epidermal surface. Adherence of spray deposits to this surface is influenced both by plant species as well surfactants and salts in the spray solution. Close contact between the spray deposit and the leaf surface is essential for absorption. Salts and surfactants in spray solutions could alter spray droplet residual and influence the contact with the leaf surface. This could influence the final activity of the herbicide (Nalewaja *et al.*, 1992). Experiments were therefore conducted to determine

characteristics of various spray deposits of glyphosate applied with South African registered adjuvants in distilled water and in calcium chloride containing carriers.

6.2 Materials and Methods

6.2.1 General procedures

Three oat (*Avena sativa* cv. Witteberg) seeds were planted 2 cm deep in each two litre pot filled with sandy loam soil. Plants were thinned to one uniform plant per pot, one week after emergence. The oats were grown in a glasshouse at a temperature that varied between 15°C during the night and 25°C during the day. Plants were watered and fertilized for optimal plant growth.

6.2.2 Application information and SEM technique

The oats was treated at the three-leaf stage with a 360 g ai L⁻¹ glyphosate isopropylamine (Roundup®, Monsanto, USA) formulation. Glyphosate at 180 g ai ha⁻¹ was applied with a knapsack sprayer fitted with a single 8001 Teejet flat-fan nozzle that delivered 100 L ha⁻¹ at a constant pressure of 200 kPa. The top third of the oldest leaf was used for assessment of treatment effects. Thirty minutes after treatment these fully hydrated leaf sections were transferred to the scanning electron microscope (SEM). Specimens were examined and photographed using accelerating voltages of 5 kilovolts. Typical residuals were photographed at various enlargements but for the aim of this study, only the 500x and 1200x enlargements are presented and discussed. Photographs were chosen based on clarity and had to be representative of that particular treatment.

The following adjuvants were applied: None, Armoblen 650 (Akzo, Netherlands) at 0.15%, Frigate (ISK Biosciences) at 1 L ha⁻¹, Bladbuff 5 (Plaaskem, South Africa) at 0.125% (pink colour change achieved), Beef-Up AS (GAP Chemicals, South Africa) at 2% and Power-Up (Ag-Chem Africa, South Africa) at 1%. All treatments were applied in distilled water and in water containing 300 mg L⁻¹

calcium as calcium chloride. Armoblen 650 and Frigate are tallow amine ethoxylates, whilst Power-Up and Beef-Up AS are ammonium sulphate solutions, and Bladbuff 5 contains an undisclosed acid, surfactant and colour indicator. Power-Up also contains a certain amount of nonionic surfactant.

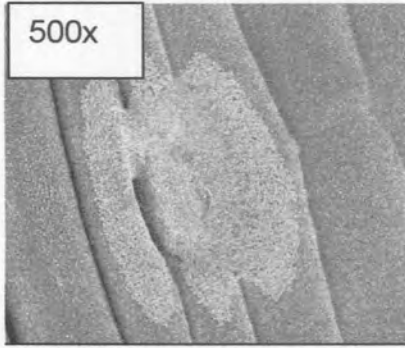
6.3 Results and Discussion

Spray droplet residuals contacted the leaf surface more closely when applied with than without an adjuvant. This is because the adjuvants consisted totally, or partially of surfactants. This coincides with the findings of Nalewaja *et al.* (1992) where oxysorbic 20 was used as surfactant. The exception in this study was Beef-Up AS that is an ammonium sulphate solution containing no surfactant (Figures I). Calcium chloride in the glyphosate treatment without adjuvant, induced an uneven, amorphous deposit (Figures B). This was also the case in the presence of Armoblen 650 and Frigate where lumps were observed in the deposits that were absent in the carriers without calcium chloride (Figures D & F). This was similar to the findings of Nalewaja *et al.* (1992) with glyphosate.

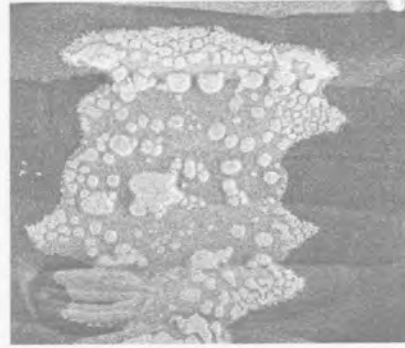
The contact of glyphosate plus calcium spray residuals with the anticlinal walls of the oat leaves appeared to be closer when applied with surfactants (Figures D & F). This contact was however poor when compared with the treatments applied in distilled water (Figures C & E). Both Power-Up and Beef-Up AS formed large crystals above the deposit when applied in distilled water (Figures G & I). These crystals are thought to be ammonium sulphate contained in both these adjuvants. These crystals apparently do not have any influence on glyphosate activity. When these two adjuvants were applied in the calcium-containing carrier, star shaped crystals, probably calcium sulphate were formed and were similar to what Nalewaja *et al.* (1992) observed (Figures H & J). These crystals were more apparent in the Beef-Up AS treatment. This could indicate a more moist deposit in the case of Power-Up and be another explanation for the higher efficacy of glyphosate with Power-Up (Nalewaja *et al.*, 1992). The effects of the moist deposit could have negated the negative effect of the poor contact with Power-Up

in certain cases. Ammonium sulphate probably decreased antagonism by calcium in this way and therefore increased absorption as was proved by Nalewaja *et al.* (1996). Bladbuff 5 also formed crystals when applied in the calcium-containing carrier (Figures L). The deposit however appeared to be more powdery than was the case with the ammonium sulphate-containing adjuvants. This could be as a result of too little acid at this rate and that not all the calcium was complexed during droplet drying. The powdery appearance of this deposit could also be calcium phosphate (assuming Bladbuff 5 contains phosphoric acid) that is very insoluble and would precipitate first from the spray solution as a powder.

It appears as if the droplet characteristics of glyphosate in amorphous residues was changed by the ammonium sulphate-based adjuvants and Bladbuff 5 in that crystals containing calcium namely calcium sulphate (2 g L^{-1}) or calcium phosphate (0 g L^{-1}) were formed. In so doing, the calcium antagonism was negated by the formation of these insoluble salts. This coincides with the research of Nalewaja *et al.* (1992) that concluded that the appearance of the deposit was an indication of glyphosate efficacy.



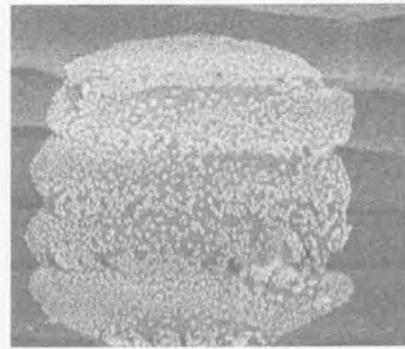
(A) Glyphosate alone



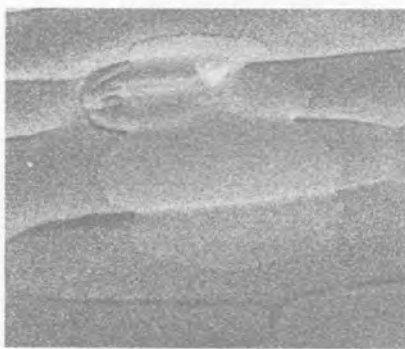
(B) Glyphosate + CaCl₂



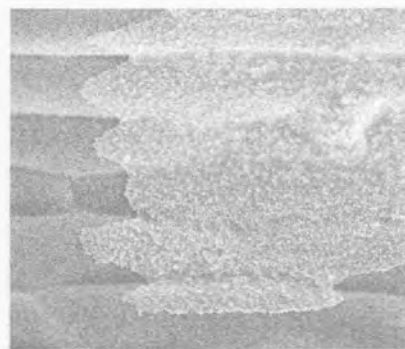
(C) Glyphosate + Armoblen 650



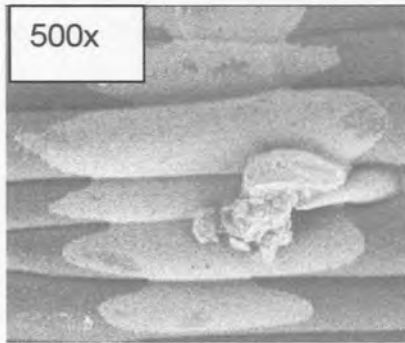
(D) Glyphosate + Armoblen 650 + CaCl₂



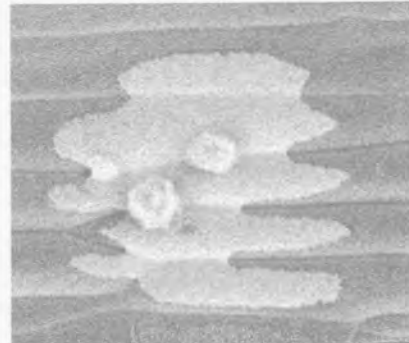
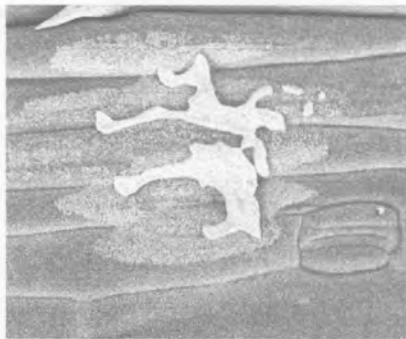
(E) Glyphosate + Frigate



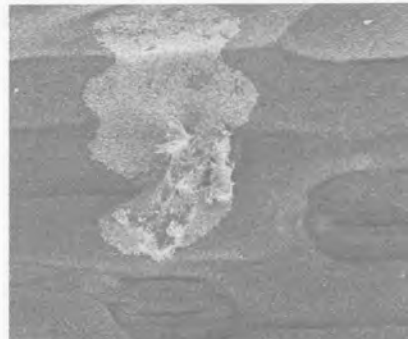
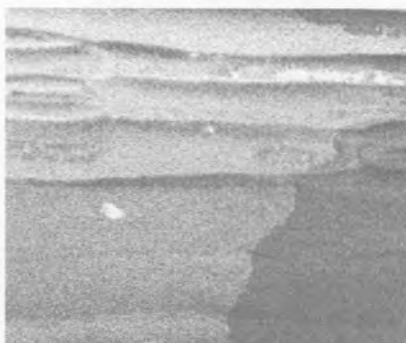
(F) Glyphosate + Frigate + CaCl₂



(G) Glyphosate + Power-Up

(H) Glyphosate + Power-Up + CaCl_2 

(I) Glyphosate + Beef-Up AS

(J) Glyphosate + Beef-Up AS + CaCl_2 

(K) Glyphosate + Bladbuff 5

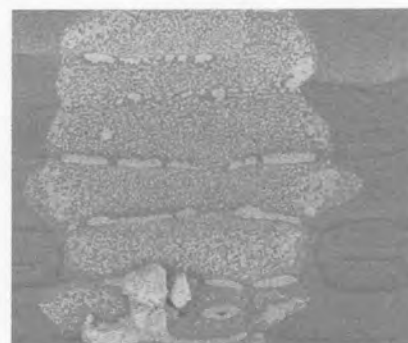
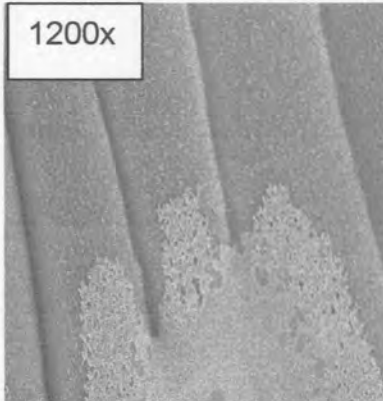
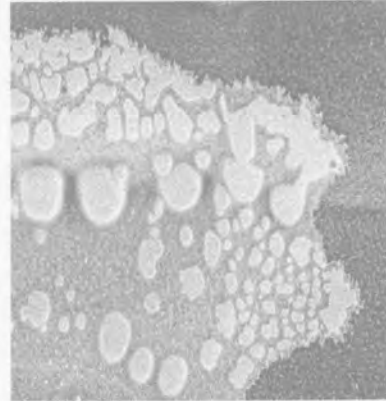
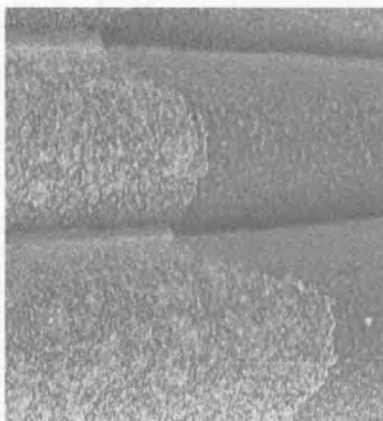
(L) Glyphosate + Bladbuff 5 + CaCl_2

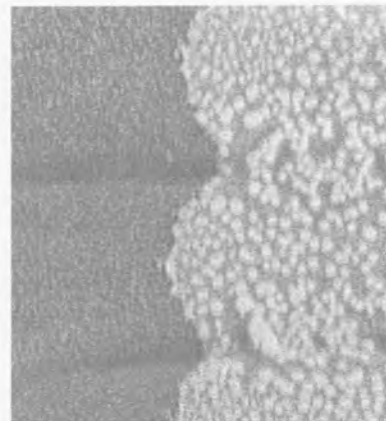
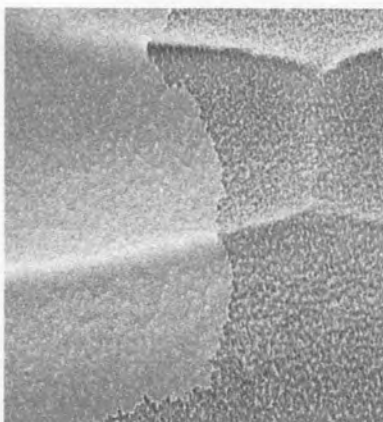
Figure 1 The influence of adjuvants on glyphosate spray droplet residuals when applied in two water carriers with various adjuvants (500X)



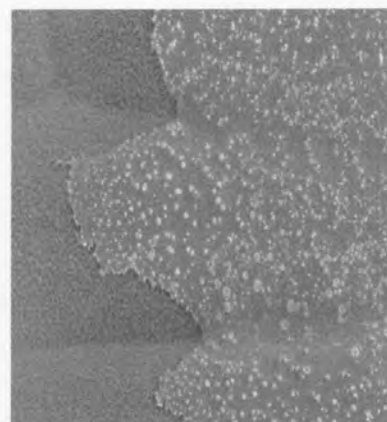
(A) Glyphosate alone

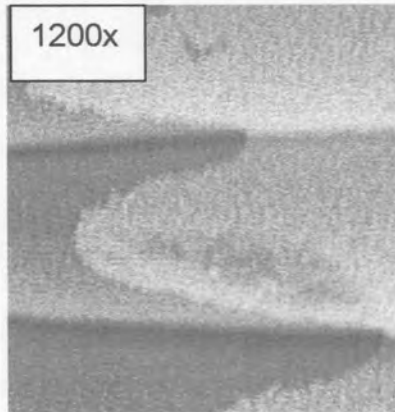
(B) Glyphosate + CaCl_2 

(C) Glyphosate + Armoblen 650

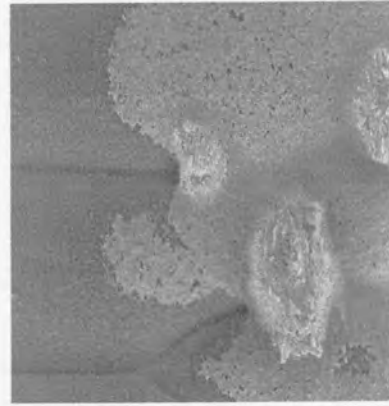
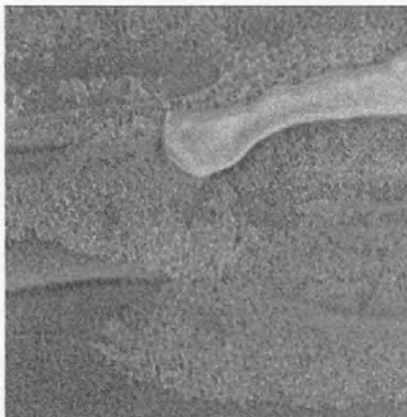
(D) Glyphosate + Armoblen 650 + CaCl_2 

(E) Glyphosate + Frigate

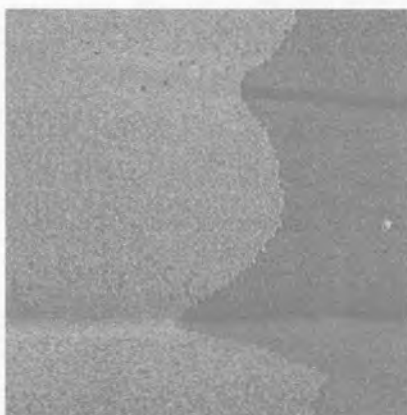
(F) Glyphosate + Frigate + CaCl_2



(G) Glyphosate + Power-Up

(H) Glyphosate + Power-Up + CaCl₂

(I) Glyphosate + Beef-Up AS

(J) Glyphosate + Beef-Up AS + CaCl₂

(K) Glyphosate + Bladbuff 5

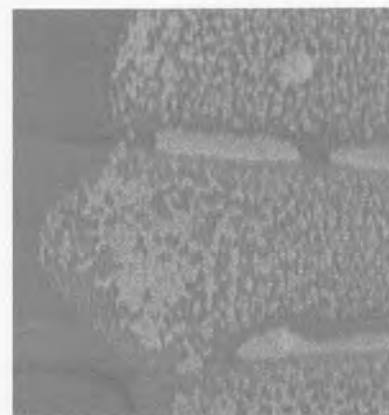
(L) Glyphosate + Bladbuff 5 + CaCl₂

Figure 2 The influence of adjuvants on glyphosate spray droplet residuals when applied in two water carriers with various adjuvants (1200X)

6.4 Conclusions

Spray droplet residuals could serve as indicators for glyphosate efficacy and absorption. Adjuvants containing a beneficial acid or ammonium sulphate can precipitate calcium as calcium sulphate or calcium phosphate. The addition of a tank mix surfactant will also benefit glyphosate, at low rates, as this will increase the contact with the leaf surface. Both Bladbuff 5 and Power-Up contain a salt or acid and a surfactant and this could explain their activity in previous studies. The fact that Power-Up contains ammonium sulphate in relatively large amounts, makes it a very useful adjuvant for glyphosate in hard water. Power-Up also induced moist deposits that may be beneficial to glyphosate activity.

6.5 References

- BUHLER, D.D. & BURNSIDE, O.C., 1983. Effect of water quality, carrier volume, and acid on glyphosate phytotoxicity. *Weed Sci.* 31, 163-169.
- DE VILLIERS, B.L., LINDEQUE, R.C. & SMIT, H.A., 1997. Optimizing glyphosate performance with adjuvants. *S. Afr. J. Plant Soil*, 14 (4), 146-148.
- HESS, D.F. & FOLK, R.H., 1990. Herbicide deposition on leaf surfaces. *Weed Sci.* 38, 280-288.
- NALEWAJA, J.D., DE VILLIERS, B.L. & MATYSIAK, R., 1996. Surfactant and salt affect glyphosate retention and absorption. *Weed Res.* 36 (3), 241-247.
- NALEWAJA, J.D. & MATYSIAK, R., 1991. Salt antagonism of glyphosate. *Weed Sci.* 39, 622-628.
- NALEWAJA, J.D., MATYSIAK, R. & FREEMAN, T.P., 1992. Spray droplet residual of glyphosate in various carriers. *Weed Sci.* 40, 576-589.

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

Glyphosate activity was adversely affected by natural South African water carriers, by water to which salts were added, and probably also by the high carrier volumes used in this research. This however relates well to practice as glyphosate is often applied in high carrier volumes. Most adjuvants registered with glyphosate in South Africa are not designed to overcome salt antagonism and some glyphosate formulations, such as Roundup® CT even prohibit the use of tank-mixed adjuvants. Salt antagonism must be overcome to stabilize glyphosate activity.

There is such a big variation in the absorption of glyphosate salts and this indicates that glyphosate is antagonized by forming complexes with salts in carrier water. These glyphosate salts are relatively insoluble and would precipitate first from spray solutions and would not be available for absorption into the leaf. The reason for poor absorption of antagonistic salts of glyphosate is largely unknown but spray droplet residuals indicated that thick, amorphous deposits with a grainy texture related to poor efficacy of glyphosate. The true reason for poor absorption could thus be due to both physical constraints and chemical constraints. The ammonium sulphate containing products namely Power-Up and Beef-Up AS induced deposits that indicated that the ammonium sulphate probably tied up the calcium by forming calcium sulphate. Calcium sulphate is very insoluble and would precipitate first from the spray solution, thereby freeing the glyphosate, probably ammonium-glyphosate to be absorbed more readily. Both Power-Up and Beef-Up AS also formed crystals in deionized water indicating that these specific crystals were not antagonistic to glyphosate and could, in certain cases, even increase herbicide efficacy. Surfactants improved the spreading of the residuals but the appearance of the deposit was similar to glyphosate without adjuvants indicating a possible reason why Armoblen 650 and Frigate did not fair well with glyphosate in hard water. Bladbuff 5 formed a powdery deposit, possibly indicating the formation of calcium phosphate that would have precipitated from

the spray solution early upon droplet drying. Surfactant optimization of glyphosate activity, especially with the higher HLB value surfactants, could partly be due to increased absorption and/or retention.

Power-Up proved to be the most effective adjuvant for glyphosate for a couple of reasons. Firstly Power-Up contains ammonium sulphate. Ammonium sulphate can negate the effect of antagonistic cations in carrier water. The fact that Power-Up contains approximately 400 g L^{-1} ammonium sulphate is beneficial as it can overcome large amounts of antagonistic ions. This is a distinct advantage above Bladbuff 5. Bladbuff 5 is added in small amounts to the desired pH. This could be a problem in hard waters as too little acid could be added in these cases to complex antagonistic ions. Power-Up has the advantage over Beef-Up AS in that it contains a small amount of nonionic surfactant. This is particularly beneficial when glyphosate is applied at low rates when too little surfactant is present in the glyphosate formulation.

This proves that the specific requirements of glyphosate can be addressed by adjuvants.

CHAPTER 8

SUMMARY

Glyphosate activity was assessed with different sources of natural water carriers to establish to what extent ions in these carriers antagonize glyphosate activity. Glyphosate activity with the most antagonistic carrier was 72% less than with deionized water. Antagonistic cations were calcium, sodium and magnesium. Antagonistic anions were bicarbonate, chloride and sulphate. Combinations of ionic factors such as total dissolved solids and electrical conductivity were excellent indicators of the antagonistic capability of carriers and were strongly correlated to the most antagonistic cations and anions, namely calcium, magnesium, sodium, bicarbonate and chloride. Calcium and magnesium and the anion bicarbonate were the most antagonistic ions in combination.

Subsequently various salts were added to deionized water that were used in various carriers to establish at which salt concentration the antagonism commenced. Glyphosate was antagonized by calcium chloride at 30 mM to the extent of 48%. Calcium nitrate antagonized glyphosate by up to 51%. Magnesium chloride and calcium sulphate also antagonized glyphosate but not to the intensity of calcium chloride and calcium nitrate. Sodium bicarbonate did not antagonize glyphosate, probably as a result of the relatively high rate of glyphosate used.

Reasons for glyphosate efficacy in certain carriers and with certain surfactants was researched. The influence of nonylphenol ethoxylate surfactants and glyphosate salt formulation on spray retention, phytotoxicity, and [¹⁴C]glyphosate absorption was investigated in wheat (*Triticum aestivum* L.) and *Kochia scoparia* L. The amount of spray retained, and absorption of [¹⁴C]glyphosate increased with increasing HLB value of surfactants. The volume of spray delivered to the plant treatment area and retained by wheat and *K. scoparia* plants increased with increasing surfactant HLB values but this only partly accounted for the higher

spray retention. Spray retention by leaves of plants was not affected by calcium chloride, either alone or with ammonium sulphate in the glyphosate spray solution. [¹⁴C]glyphosate absorption by wheat and *K. scoparia* was reduced by calcium chloride alone, but not in mixtures with ammonium sulphate, regardless of surfactant. Phytotoxicity and absorption of glyphosate salt formulations for wheat was: isopropylamine > ammonium > sodium > calcium; these results indicate that the surfactant selected is important to maintain glyphosate efficacy and that sodium and calcium cations antagonize glyphosate by forming salts that are absorbed less than commercial isopropylamine formulations.

With the above-mentioned findings in mind, various adjuvants were evaluated with glyphosate with the aim of developing a South African adjuvant tailored to the specific requirements of glyphosate. In the glasshouse, EXP94KG1 (trade name: Power-Up) was the most effective adjuvant in water carriers with low and high calcium chloride content. In the field, EXP94KG1 and Frigate were both more effective than Armoblen 650, Bladbuff 5 and Beef-up AS. Frigate performance was similar to that of EXP94KG1 in the field probably as a result of the lower carrier volume used in the field.

Finally, adjuvants were applied with glyphosate in distilled water and water that contained 300 mg L⁻¹ calcium as calcium chloride. Scanning electron micrographs revealed the physical appearance of the spray droplet residuals. Calcium chloride in spray carriers resulted in thick amorphous and lumpy residuals with a grainy appearance. Beef-Up AS, Power-Up and Bladbuff 5 appeared to form crystals in this hard water, thereby freeing the glyphosate to penetrate the leaf surface. Armoblen 650 and Frigate did improve the contact between the spray residuals and the leaf surface. Power-Up and Bladbuff 5 appeared to also improve this contact. Power-Up and Beef-Up AS formed huge crystals, probably ammonium sulphate when applied in distilled water carriers. This appeared not to have an influence on glyphosate efficacy. Spray droplet residual appears to give a good indication as to reasons for lower efficacy and absorption of glyphosate.

OPSOMMING

Glifosaat effektiwiteit is bepaal met verskillende natuurlike waterbronne om vas te stel tot watter mate ione in die water die aktiwiteit kan beïnvloed. Glifosaat effektiwiteit met die mees antagonistiese draer was 72% laer as toe met gedeioniseerde water toegedien is. Antagonistiese katione was kalsium, natrium en magnesium. Antagonistiese anione was bikarbonaat, chloriede en sulfaat. Kombinasies van ioniese faktore soos totale opgeloste soute en elektriese geleidingsvermoë was uitstekende indikatore van die antagonistiese vermoë van die draers en was sterk gekorreleer met die mees antagonistiese katione en anione soos kalsium, magnesium, natrium, bikarbonaat en chloried. Kalsium en magnesium en bikarbonaat was die mees antagonistiese ione in kombinasie.

Na aanleiding hiervan is verskeie soute in gedeioniseerde water opgelos om te bepaal by watter konsentrasie antagonisme voorgekom het. Glifosaat aktiwiteit is 48 % verlaag deur kalsiumchloried by 30 mM. Kalsiumnitraat het glifosaateffektiwiteit met 51 % laat daal. Magnesiumchloried en kalsiumsulfaat was ook antagonisties maar nie tot dieselfde mate as die twee kalsiumsoute nie. Natriumbikarbonaat was nie antagonisties nie, waarskynlik as gevolg van die relatiewe hoë glifosaatdosis.

Redes vir verskille in effektiwiteit met sekere draers en met sekere benatters, is ondersoek. Die invloed van nonielfeniel-etoksilaat benatters en glifosaat soutformulasie is ondersoek op behoud, fitotoksisiteit, en [¹⁴C]glifosaatopname op koring (*Triticum aestivum* L.) en *Kochia scoparia* L. Die behoud van glifosaat sowel as die opname van [¹⁴C]glifosaat is beide verhoog met verhoogde HLB waardes van benatters. Die volume water wat toegedien is by die plantbehandelingsarea sowel as wat behou is deur koring en *K. scoparia* plante het toegeneem met verhoogde HLB waardes. Dit het egter net gedeeltelik die verhoogde behoud verklaar. Spuitbehoud deur blare van plante is nie geaffekteer deur kalsiumchloried nie, of alleen, of gemeng met ammoniumsulfaat in die spuitoplossing nie. [¹⁴C]glifosaatopname van koring en *K. scoparia* is met alle

benatters verlaag deur kalsiumchloried alleen, maar nie in mengsels met ammoniumsulfaat nie. Fitotoksisiteit en opname van glifosaat soutformulasies vir koring was: isopropielamien > ammonium > natrium > kalsium. Hierdie resultate dui aan dat die benatter belangrik is om glifosaataktiwiteit te handhaaf en dat natrium- en kalsiumkatione antagonisties is teenoor glifosaat deur soute te vorm wat minder opgeneem word as die kommersiële isopropielamien formulasies.

Met bogenoemde bevindinge in aanmerking geneem is verskeie hulpmiddels getoets met glifosaat met die doel om 'n Suid-Afrikaanse hulpmiddel te ontwerp wat pasgemaak is om aan die spesifieke behoeftes van glifosaat te voldoen. In die glashuis was EXP94KG1 (later Power-Up) die effektiëste hulpmiddel in waterdraers met beide lae en hoë kalsiumchloriedinhoud. Onder veldtoestande was EXP94KG1 en Frigate beide meer effektië as Armoblen 650, Bladbuff 5 en Beef-up AS. Frigate aktiwiteit was soortgelyk aan Power-Up, waarskynlik as gevolg van die laer watervolume wat in die veld gebruik is.

Laastens is glifosaat toegedien in gedistilleerde water en waters wat 300 mg L^{-1} kalsium in die vorm van kalsiumchloried bevat het. Skandeer elektron mikrograwe het die fisiese voorkoms van die druppel residu aangedui. Kalsiumchloried in die spuitoplossing het 'n duk amorfe residu met 'n growwe voorkoms veroorsaak. Beef-Up AS, Power-Up en Bladbuff 5 het geblyk om kristalle in hierdie harde water te vorm en sodoende die glifosaat losgemaak om vrylik die blaaroppervlakte te penetreer. Armoblen 650 en Frigate het die kontak tussen die residu en die blaaroppervlakte verbeter. Power-Up en Bladbuff 5 het ook geblyk om hierdie kontak tussen residu en blaaroppervlakte te verbeter. In gedistilleerde water het Power-Up en Beef-Up AS groot kristalle gevorm wat heelwaarskynlik ammoniumsulfaat is. Dit het blykbaar geen invloed op glifosaat effektiwiteit gehad nie. Spuitdruppel residu voorkoms blyk om 'n goeie aanduiding te wees vir effektiwiteit en opname van glifosaat.

ACKNOWLEDGEMENTS

The author would like to thank the following people and institutions that made this research possible:

- My Lord and Saviour, without who's help I can't do anything.
- Professor C.F. Reinhardt for his leadership and support.
- The University of Pretoria for the use of their facilities.
- ARC-Small Grain Institute for the use of their facilities.
- Research was made possible by the financial support of the Winter Cereal Trust and the ARC
- North Dakota State University for the use of their facilities and data generated there. Thanks especially to Drs Nalewaja and Matysiak.
- My wife Gail and my daughter Colleen for their continued support and love.

APPENDIX

POWER-UP

A LIQUID AMMONIUM SULPHATE BASED ADJUVANT FOR USE WITH GLYPHOSATE AND SULPHOSATE HERBICIDES

Complexing of Salts

ACTIVE INGREDIENTS

Acidifying System • Ammonium Sulphate
Humectant • Wetter/Spreader

Total active ingredients 562g/l

Reg. No. LG-163 Act36/1947

Contents

Humectant

Acidifying system

Manufactured and Distributed by
AC-CHEM AFRICA (Pty) Ltd
 P.O. Box 31344, Tlokweng, 0134, Rep. of SA
 Tel: (027) (12) 8042542 Fax: (027) (12) 8042903
 Reg. No. 98/13411/07

Penetration

Wetting/Spreading

Translocation

DIRECTIONS FOR USE: USE ONLY AS INDICATED.

Mix **POWER-UP** with the spray tank water before adding the herbicide. Always add the herbicide last. Do not add any other adjuvants or surfactants to the spray tank mix.

WATER QUALITY			APPLICATION RATE	
Good	PH 6-7	EC 0-500	1%	(1 litre per 100 litre water)
Average	PH 7-8	EC 500-1000	1,5%	(1,5 litre per 100 litre water)
Poor	pH >8	EC >1000	2%	(2 litre per 100 litre water)

POWER-UP contains an electrolyte tolerant wetting agent to improve the wetting, spreading and contact of the remedy with plant foliage.

POWER-UP contains an organic acidifying system that when applied correctly will acidify the majority of spray solutions to between a pH of 4-5 depending on the water quality.

POWER-UP helps prevent alkaline hydrolyses of pH sensitive herbicides.

WARNINGS:

Observe any warnings that apply to the product or products with which **POWER-UP** is to be used.

Observe caution when using **POWER-UP** with any herbicide other than glyphosate and sulfosate. **POWER-UP** may improve the efficacy of selective herbicides to such an extent that it may lose its selectivity and cause damage to the crop.

Do not use **POWER-UP** with herbicides that require an alkaline environment (pH > 7).

Store away from food and feeds.

Keep out of reach of children and animals.

PRECAUTIONS:

Avoid prolonged contact with concentrated product.

In the case of contact, wash affected area with soap and water.

In case of contact with eyes flush immediately with water for at least 10 minutes.

Rinse empty container three times with a volume of water equal to at least 10% that of the container and add the rinsings to the contents of the spray tank before disposing of the container in the prescribed manner. Destroy empty container by perforation and flattening and never use for any other purpose.

Prevent contamination of food, feeds, drinking water and eating utensils.

Although this remedy has been extensively tested under a large variety of conditions the registration holder does not warrant that it will be efficacious under all conditions because the action and effect thereof may be affected by factors such as abnormal climatic and storage conditions, quality of dilution water, compatibility with other substances not indicated on the label and the occurrence of resistance of the pest or disease against the pesticide used as well as by the method, time and accuracy of application. The registration holder furthermore does not accept responsibility for damage to crops, vegetation, the environment or harm to man or animals or for lack of performance of the remedy concerned due to failure of the user to follow the label instructions or to the occurrence of conditions which could not have been foreseen in terms of registration. Consult the supplier in the event of any uncertainty.

Power-Up label