Influence of linseed oil ethoxylate adjuvants and rain on biological efficacy of glyphosate, evaluated using *Chenopodium album*, *Abutilon theophrasti* and *Setaria viridis*

M. Hunsche, H. Scherhag, M. Schmitz-Eiberger and **G. Noga**
Institute of Crop Science and Resource Conservation – Horticultural Sciences, University of Bonn Auf dem Hügel 6, D-53121 Bonn, Germany.

Summary

The influence of four linseed oil ethoxylate adjuvants (LSO 10, LSO 0903, LSO 30, LSO 3003) on the rain-induced wash-off and biological efficacy of glyphosate was studied using lambsquarter (*Chenopodium album* L.), velvetleaf (*Abutilon theophrasti* Medik.), and green foxtail (*Setaria viridis* L.). In addition, the adaxial leaf surface of weed species was characterized by means of scanning electron microscopy (SEM) and contact angle (CA) of solution droplets. Micro-roughness of leaf surface was quantitatively characterized by measuring the CA of water/acetone solution droplets; results show, leaves of velvetleaf (CA = 65°) were easily wetted while lambsquarter (CA = 118°) and green foxtail (CA = 118°) were difficult to wet, indicating a pronounced micromorphology. These differences arise from surface characteristics such as cell size, presence or absence of trichomes, glands or wax structures, as visualized by SEM. Evaluation of biological efficacy as a function of treatment solutions (RUM®; unformulated isopropylamine salt (glyphosate IPA) and isopropylamine salt plus adjuvants) and rain intensity (0.5, 5 and 48 mm h^{-1}) in a bi-factorial experiment for each species showed no significant interaction between the evaluated factors. In lambsquarter, heavy (5 mm h^{-1}) and torrential (48 mm h^{-1}) rain events reduced, while light rain (0.5 mm h^{-1}) raised the biological efficacy to some extent. Further, addition of LSO adjuvants to glyphosate IPA resulted in the same dry matter level as achieved with the commercial formulation RUM®. In velvetleaf, all rain intensities reduced efficacy of the herbicidal treatments significantly. Comparisons showed that all LSOs when added to glyphosate IPA achieved at least the same level as RUM® reference, whereas the best result was obtained by adding LSO 0903. In the case of green foxtail, all rain intensities significantly reduced the efficacy of treatment solutions, whereas highest reduction was observed when plants were exposed to heavy (5 mm h^{-1}) or torrential (48 mm h^{-1}) rain. Comparisons among treatments showed a significantly lower dry matter for glyphosate IPA plus LSO 30, whilst the other LSO ethoxylates had the same dry matter level as unformulated glyphosate IPA.

Introduction

Glyphosate is the largest-selling herbicide in the world with total estimated sales of about $3 billion (Knowles 2001). It has been the subject of many trials which aim to reduce drift losses and optimize deposit formation (Scherhag *et al.* 2005, Leung and Webster 1994), enhance uptake and translocation (Müller *et al.* 2001, Sharma and Singh 2000, Bariuan *et al.* 1999, Feng *et al.* 1998, Laerke and Streibig 1995, Zabkiewicz *et al.* 1993, Gaskin and Holloway 1992, Cranmer and Linscott 1991), and ultimately improve its biological efficacy (Haefs 2001, Kogan 2001, Sandbrink *et al.* 1993, Reddy and Singh 1992). Since glyphosate is highly soluble in water and therefore prone to dilution and removal from plant foliage by rainfall (Leung 1994, Reddy and Singh 1992), studies were carried out to characterize and/or enhance its rainfastness on glass slides (Leung 1994), hard surfaces (Spanoghe *et al.* 2005) and several weed species (Scherhag 2005, Monquero *et al.* 2004, Martini *et al.* 2003, Werlang *et al.* 2003, Kogan 2001, Combellack *et al.* 2001, Coble and Brumbaugh 1993, Sundaram 1991, Clay and Lawrie 1990, Wells 1989, Bryson 1987).

Adjuvants are useful tools for users to improve agrochemicals application and in this way achieve more cost-effective, better-targeted, and more environmentally acceptable pest control (Green 2001, Green 2000). In addition, the rainfastness of active ingredients can be enhanced by adjuvants (e.g. sticker-adjuvants), which form a protective water-repellent layer, preventing or reducing wash-off (Hazen 2000, Roggenbuck *et al.* 1993). When added to systemic active ingredients, adjuvants can enhance the initial penetration rate, thus limiting the wash-off potential (Roggenbuck *et al.* 1993, Field and Bishop 1988). Furthermore, penetration and rainfastness of a given active ingredient depends also on other factors such as species, surface structure, and physicochemical characteristics of the leaf surface (Leung and Webster 1994, Reddy and Singh 1992), and adjuvant properties (Kogan 2001).

Recently, several environmental and consumer friendly adjuvants have been developed to replace non-environmental friendly adjuvants such as alkyl-phenol-ethoxylates (Haefs 2001, Abribat 2001, Green 2000). In particular, oil ethoxylates derived from rapeseed were developed (Abribat 2001) and their effectiveness in enhancing biological efficacy and rainfastness of glyphosate proven (Scherhag 2005, Haefs 2001). Other ethoxylates based on seed oils such as linseed and soybean were developed and evaluated for their efficacy in enhancing the rainfastness of contact fungicides (Hunsche *et al.* 2005, Ditzer 2002), but were not evaluated with systemic herbicides. Glyphosate was chosen for our experiments because its biological efficacy greatly depends on the adjuvant type (Green 2000). In addition, an adjuvant system that would maintain the efficacy of glyphosate, avoiding the tallow amine ethoxylate surfactants and their associated plant, eye and fish toxicity would have immediate potential (Green 2001).

The objective of our study was to investigate the effect of four linseed oil ethoxylates on rain-induced wash-off and biological efficacy of glyphosate, evaluated on lambsquarter (*Chenopodium album*), velvetleaf (*Abutilon theophrasti*), and green foxtail (*Setaria viridis*).

Materials and methods

Plant material and growth conditions

Experiments were conducted with the dicotyledonous weeds lambsquarter (*Chenopodium album* L.) and velvetleaf (*Abutilon theophrasti* Medik.), and the monocotyledonous weed green foxtail (*Setaria viridis* L.). Weeds were raised from seed in individual pots placed in a greenhouse, with a 12 h photoperiod, a daily temperature of 20 ± 4°C and relative humidity of 55 ± 10%.

Characterization of the adaxial leaf surface

Surface micro-roughness and contact angle of treatment solution droplets Leaf micro-roughness was characterized quantitatively by measuring the contact angle of water/acetone solution droplets (80/20 v/v), as proposed by Forster and Zabkiewicz (2001). Contact angles were measured optically with a Contact Angle Measuring System (G10; Krüss GmbH, Hamburg, Germany) by applying single 1 µL droplets with a microsyringe (Hamilton-Bonaduz, Switzerland) on the adaxial leaf surface. In order to facilitate the measurements, discs were punched from the leaf centre (first completely developed leaf from the top) and fixed on a double sided adhesive tape (Tesa® double face, Beiersdorf, Hamburg), previously mounted on a glass slide.

Tangents were measured for both visible sides of each droplet, and readings of the angles were taken on 50 droplets for each plant species.

Determination of contact angle of the spray solutions on the leaf surfaces was carried by adopting the same measuring procedure.

Surface micromorphology (SEM) Micromorphology of the adaxial leaf surface was investigated by using a scanning electron microscope (XL 30 ESEM, FEI-Phillips, Kassel; Microsoft control software, version 5.90). Leaf discs (0.8 cm^2) were punched and mounted on aluminium stubs, placed into the microscope analysis chamber, and scanned in the low vacuum mode (0.8 Torr). Wax crystalloids on the leaf surface were classified according to Barthlott *et al.* (1998) and Baker (1982).

Chemicals Glyphosate (Gly) solutions were prepared at a concentration of 43 mmol L^{-1} with isopropylamine salt 62% (Monsanto Europe S.A., Antwerp, Belgium). Linseed oil ethoxylates (LSO, Cognis® AgroSolution, Düsseldorf, Germany) with an average of 10 and 30 ethylene oxide (EO) units (LSO 10 and LSO 30, respectively) as well as LSO with ethylene oxide and propylene oxide (PO) blocs [LSO 0903 (09EO/03PO) and LSO 3003 (30EO/03PO)] in the hydrophilic chain were added to the spray solution at 1 g L^{-1}. Plants treated with the commercial glyphosate formulation Roundup® Ultra Max (RUM®, Monsanto Agrar Deutschland GmbH, Düsseldorf, Germany) as well as untreated plants served as control.

Application of treatment solutions
Treatment solutions were applied with a laboratory pesticide sprayer (B-PSA-1; Institute of Agricultural Engineering, University of Bonn, Germany), equipped with an air-induction nozzle (AI 11004 VS, Teejet Co., Germany). Treatment solutions were applied at a speed of 6 km h^{-1} and a pressure of 3×10^5 Pa, equivalent to an application rate of 190 L ha^{-1}. Five minutes after pesticide application plants were returned into the greenhouse for 2 h before onset of rainfall simulation.

Rainfall simulation
Tap water was used to simulate a natural rainfall by using a laboratory rain simulator (B-LRS-2; Institute of Agricultural Engineering, University of Bonn, Germany), as described elsewhere (Ditzer 2002, Kromer *et al.* 1996). Five millimetres of rain at three intensities were applied: light rain (0.5 mm h^{-1}), heavy rain (5 mm h^{-1}) and torrential rain (48 mm h^{-1}), with a volume medium diameter (VMD) of 377 µm, 1075 µm and 2043 µm, respectively. The applied rain intensity and quantity were programmed in the rain simulator and checked with a rain gauge. Plants were returned to the greenhouse 20 minutes after rain simulation. Not rain-exposed plants served as reference.

Biological efficacy
Dry mass was the parameter used to evaluate biological efficacy of treatment solutions and the effect of rainfall on weed control. Plants (shoots and leaves) were harvested at the soil level eight days after herbicide application, placed in paper-bags, and dried at 105°C until constant weight.

Experimental design and statistical analysis
Results were analyzed with the software SPSS 12.0 (SPSS Inc., Chicago, USA) and graphs designed with the software Sigma Plot 7.101 (Systat Software GmbH, Erkrath, Germany). Experiments on biological efficacy were conducted in a bi-factorial arrangement (treatment solutions *vs.* precipitation) for each weed species, with 12 replicates per treatment. After ascertaining normal distribution, data was subjected to analysis of variance (ANOVA). In the cases of statistical significances, results were compared by Duncan's test $P \leq 0.05$.

Results

Micro roughness
Measurements of the contact angle of acetone/water solution droplets revealed that adaxial leaf surfaces of the evaluated weed species differ significantly in their micro roughness. These differences were more evident when comparing dicotyledonous weeds: contact angle on *C. album* leaves was 118.7° while *A. theophrasti* had a contact angle of only 65° (Figure 1). The monocotyledonous *S. viridis* had a rougher surface and correspondingly potentially poor wetability, with a contact angle of 118.3°.

Contact angle of the treatment solutions
Addition of LSO-ethoxylates to the unformulated glyphosate IPA significantly influenced contact angle on the adaxial leaf surface of all weed species (Table 1). On *C. album*, contact angle of glyphosate IPA (92.5°) was reduced with addition of the more hydrophobic adjuvants LSO 10 (81.4°) and LSO 0903 (73.1°). In contrast, glyphosate IPA formulated with the more hydrophilic adjuvants LSO 30 (106°) and LSO 3003 (108.3°) had a contact angle comparable to water (109.2°) or RUM® (108.1°).

In case of *A. theophrasti*, lowest contact angles were obtained when formulating glyphosate IPA with LSO 0903 (53.1°) and LSO 3003 (51.2°). Water droplets had a contact angle of 78.6°, while droplets of RUM® had a contact angle of 57.1°. The adjuvants LSO 10 and LSO 30 reduced the contact angle of glyphosate solution to a lower extent (contact angles of 58.9° and 57.2°).

On *S. viridis* leaves, the more hydrophobic adjuvants LSO 10 and LSO 0903 reduced the contact angle of glyphosate IPA (100.9°) to 95° and 80.2° respectively. Water droplets and RUM® droplets had a higher contact angle, 118.3° and 105.7°

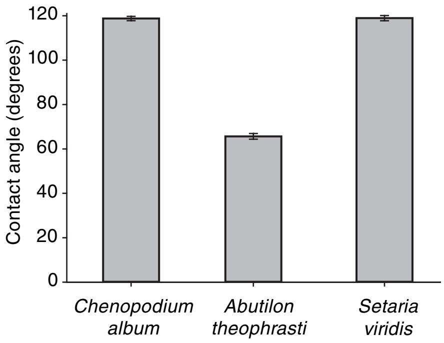

Figure 1. Micro-roughness of adaxial leaf surface of *C. album*, *A. theophrasti* and *S. viridis*, as characterized by measuring the contact angle of water/acetone (80/20 v/v) solution droplets (1 µL). Vertical bars represent the standard error.

Table 1. Contact angle of glyphosate solutions on adaxial leaf surfaces of *C. album*, *A. theophrasti* and *S. viridis*. Water was used as reference.

	Contact angle (degrees; Mean ± SE)[A]		
Spray solution	*Chenopodium album*	*Abutilon theophrasti*	*Setaria viridis*
Water	109.2 ± 1.7 a	78.6 ± 1.5 a	118.3 ± 2.0 a
RUM®[B]	108.1 ± 1.9 a	57.1 ± 2.7 c	105.7 ± 1.7 b
Glyphosate IPA[C]	92.5 ± 2.2 b	67.9 ± 4.9 b	100.9 ± 4.6 bc
Glyphosate IPA + LSO 10	81.4 ± 0.9 c	58.9 ± 2.6 c	95.0 ± 3.1 c
Glyphosate IPA + LSO 0903	73.1 ± 2.3 d	53.1 ± 0.9 d	80.2 ± 4.1 d
Glyphosate IPA + LSO 30	106.0 ± 3.9 a	57.2 ± 2.5 c	103.8 ± 3.9 b
Glyphosate IPA + LSO 3003	108.3 ± 4.1 a	51.2 ± 1.3 d	108.0 ± 2.3 b

[A] Means in the column followed by the same letter are not different by Duncan $P \leq 0.05$.
[B] Roundup® Ultra Max.
[C] Glyphosate isopropylamine salt.

respectively. Addition of the more hydrophilic adjuvants LSO 30 and LSO 3003 to the spray solution did not reduce the contact angle in comparison to the other glyphosate treatments.

SEM investigations

Epidermal layer of the adaxial leaf surface of *C. album* presented little polygonal cells and numerous glands varying in size and forming a three-dimensional structure (Figure 2A). Cell surfaces were completely covered with little, almost imperceptible wax structures (Figure 2B), which became apparent as vertical platelets at higher magnification (Figure 2C). The platelets were generally arranged in localized groups of 4–5 (Figure 2D).

The *A. theophrasti* leaf surface was characterized with little polygonal cells with many glandular trichomes on the surface (Figure 3A). These soft trichomes were simple or complex, some of them with globular appendices on the top (Figure 3B). Cell surfaces had no detectable wax structures (Figure 3C), but there was a rudimental indication of a thin amorphous wax layer covering the epidermal cell layer (Figure 3D).

Setaria viridis exhibited longitudinal cells arranged in parallel, with many little stomata in the cell lines along the veins; cell lines over the veins had trichomes resembling thorns (Figure 4A). Cell surface presented a densely arranged wax structure (Figure 4B), e.g. little vertical platelets (Figure 4C) organized as rosettes (Figure 4D).

Influence of treatment solutions and rain intensity on biological efficacy

Statistical evaluations showed no significant interactions between treatment solutions and precipitations over all evaluated weed species (Table 2); hence only data for the main effects (precipitations and treatment solutions) are presented.

In *C. album*, simulation of 5 mm of torrential rain 2 h after application of treatment solutions significantly reduced the biological efficacy of glyphosate (Figure 5a). Heavy rain showed no influence, while light rain slightly enhanced biological efficacy when compared to non-rained plants. As expected, plants sprayed with water had higher dry matter than plants treated with glyphosate solutions (Figure 5b). Addition of LSO adjuvants to glyphosate IPA resulted in the same dry matter level as plants treated with the commercial formulation RUM® (Figure 5b).

Irrespective of rain intensity, rainfall significantly reduced the efficacy of herbicidal treatments in *A. theophrasti* (Figure 6a). Comparisons on the efficacy of treatment solutions revealed that all combinations of glyphosate IPA plus LSOs achieved at least the same level as RUM® reference, whereas the best result was obtained by adding LSO 0903 (Figure 6b).

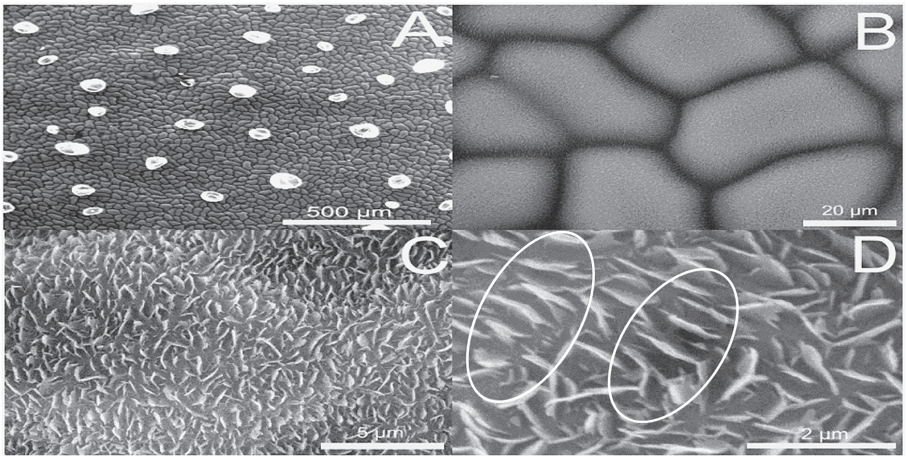

Figure 2. Adaxial leaf surface of *C. album*: (A) little polygonal cells and numerous glands varying in size and forming a three-dimensional structure; (B) leaf surface completely covered with little, almost imperceptible wax structures; (C) wax crystalloids organized as vertical platelets become apparent at higher magnification; (D) organization pattern of the wax crystalloids: 4–5 locally parallel grouped platelets (encircled).

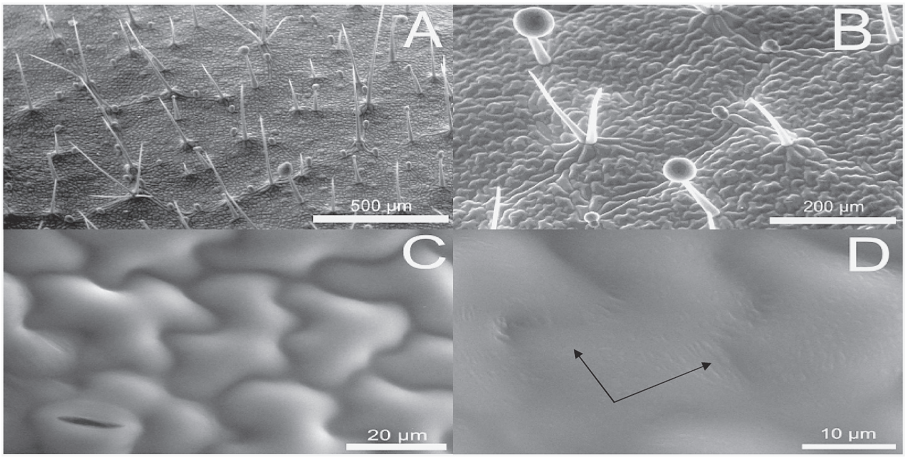

Figure 3. Adaxial leaf surface of *A. theophrasti*: (A) little polygonal cells with numerous glandular trichomes on the surface; (B) simple and complex soft trichomes, some of them with globular appendices on the top; (C) absence of detectable wax structures, but presence of stomata; (D) indications for an amorphous wax film covering the cell surface.

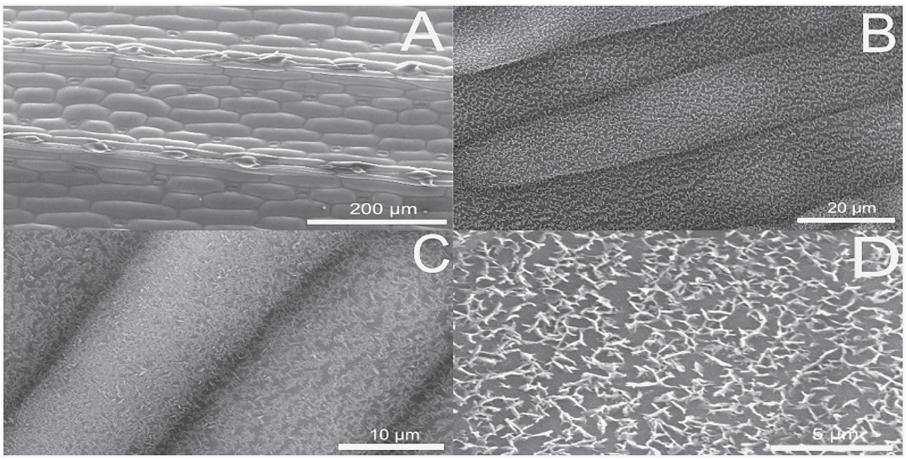

Figure 4. Adaxial leaf surface of *S. viridis*: (A) longitudinal cells arranged in parallel, with many little stomata in the cell lines along the veins; cell lines over the veins had trichomes resembling thorns; (B) cell surface presented a densely arranged wax structure; (C) wax structure as little platelets; (D) platelets organized as rosettes.

In the case of *S. viridis*, all rain intensities significantly reduced efficacy of the treatment solutions (Figure 7A). Highest reduction was observed when the plants were exposed to heavy or torrential rain events. Comparisons among treatment solutions revealed the lowest dry matter due to addition of LSO 30 (Figure 7B). However, the observed differences in dry matter were small.

Discussion

Micro roughness and contact angle of treatment solutions

SEM evaluations revealed significant differences among adaxial surfaces of the examined weed species (Figure 2–4). Leaf surfaces are very diverse and range from simple and smooth to very complex and rough surfaces (Green 2001). This diversity may be responsible for the established differences in micro-roughness (Figure 1). Roughness is determined by factors such as leaf surface topography, wax crystal structure and chemical composition (Forster and Zabkiewicz 2001) as well as cell surface contours, leaf venation and presence of trichomes (Chachalis *et al.* 2001, Kirkwood 1999, Barthlott and Neinhuis 1997, Brewer *et al.* 1991, Holloway 1970). Surfaces presenting contact angles greater than 110° (measured with water droplets) are usually characterized both by hydrophobic properties originating from the wax deposits and pronounced roughness (Holloway 1970). Contact angle measurements of water/acetone solution droplets provide a quantitative estimate for the roughness factor (Forster and Zabkiewicz 2001).

Roughness primarily affects formation of the pesticide deposit (Chachalis *et al.* 2001, Green 2001) and its distribution on the leaf surface (Hess and Falk 1990). In our studies, enhanced contact between solution droplets and leaf surface was accomplished by glyphosate IPA formulated with LSO ethoxylates; however, the effect of the added adjuvants differed among weed species (Table 1). In case of the difficult-to-wet leaves (*C. album* and *S. viridis*), lower contact angles were achieved with the more hydrophobic adjuvants LSO 10 and LSO 0903. In the case of *A. theophrasti*, all LSOs reduced contact angle in comparison to unformulated glyphosate IPA. An even lower contact angle was achieved when three propylene oxide units (PO) were included in the hydrophilic chain of the adjuvant molecule.

The contact angle of liquids on plant surfaces reflect their spreading behaviour and wetability (Foy and Smith 1965), which is governed mainly by the nature of the exposed chemical groups, surface roughness and leaf orientation (Juniper and Jeffree 1983). Fortunately, the use of adjuvants can diminish adverse effects of leaf topography, epicuticular wax, and trichomes (Hess and Falk 1990), mainly by reducing surface tension of the spray solution (Hess and Foy 2000). An enhanced surface wetability may contribute to an increased uptake rate of active ingredients into the plant tissue (Sun 1996, Leung and Webster 1994) and thereby also improve rainfastness of some pesticides (Green and Hazen 1998, Reddy and Singh 1992).

Influence of rain intensity

It is known that rainfall soon after agrochemical application results in partial or complete loss of glyphosate activity (Reddy and Singh 1992), because the active ingredient needs at least a 6 h rain-free period for penetration and effective weed control (Martini *et al.* 2003, Werlang *et al.* 2003, Chow 1993; Sundaram 1991, Wells

Table 2. Dry matter of *C. album*, *A. theophrasti* and *S. viridis* as influenced by treatment solutions and precipitation (factorial analysis).

Weed species	Source of variation	Significance level (Dry matter)
Chenopodium album L.	Precipitation	0.000
	Treatment solutions	0.000
	Precipitation *vs.* Treatment solutions	0.217
Abutilon theophrasti Medik.	Precipitation	0.001
	Treatment solutions	0.000
	Precipitation *vs.* Treatment solutions	0.361
Setaria viridis L.	Precipitation	0.000
	Treatment solutions	0.002
	Precipitation *vs.* Treatment solutions	0.229

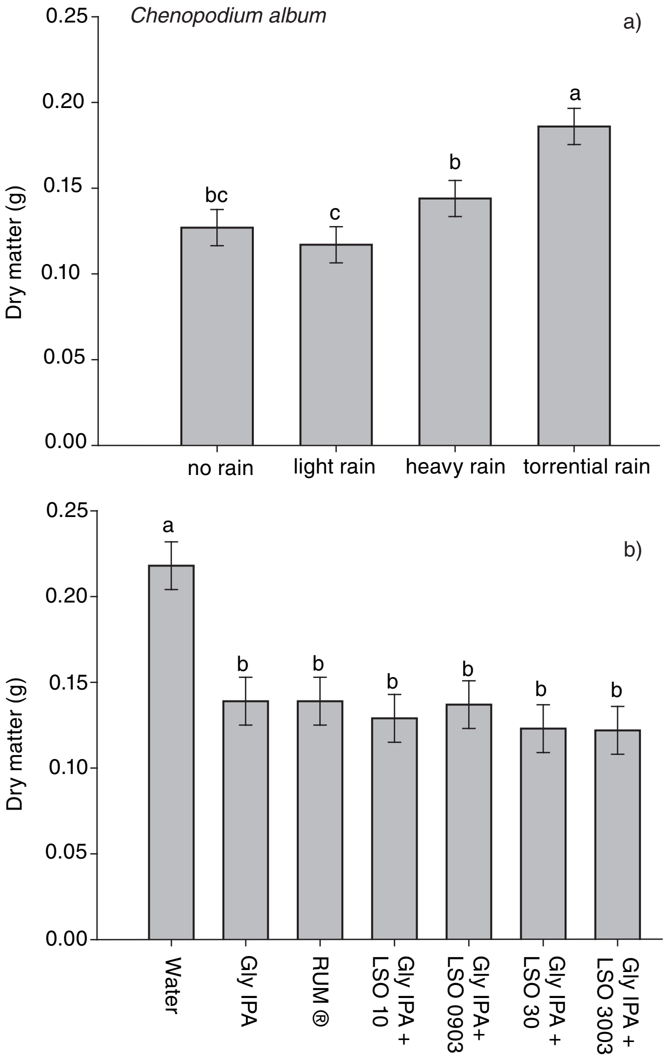

Figure 5. Influence of rainfall and rain intensity (A) and treatment solutions (B) on dry matter of *C. album*. Vertical bars represent the standard error. Means of dry mass followed by the same letter are not different by Duncan's test P ≤0.05.

1989). Enhancement of rainfastness and reduction of rain-induced wash-off can be reached in two ways, namely by water-repellency of the deposit and/or by enhanced penetration rate (Green 2001, Leung and Webster 1994, Roggenbuck *et al.* 1993). Therefore, adjuvants preferentially designed to enhance rainfastness of the deposits of systemic compounds can better show their beneficial influence when it rains shortly after application. For these reasons we chose a rain-free period of only two hours.

Our results clearly demonstrate that occurrence of a light rain was sufficient to remove the greatest part of the active ingredient deposit from adaxial leaves of *A. theophrasti* while no increase in wash-off was observed by increasing rain intensity. In *S. viridis*, a light rain significantly reduced deposit of active ingredient. However, when leaves were exposed to heavy or torrential rain, respectively, higher herbicide losses occurred.

In *C. album* lowest dry matter was measured for no rain or when light rainfall (0.5 mm h^{-1}) impacted 2 h after glyphosate application. Scherhag (2005) evaluated the effect of rapeseed oil ethoxylates on rainfastness and biological activity of glyphosate and also observed that light rain increased efficacy of the active ingredient in *C. album*. Kirkwood (1999) noted that penetration of hydrophilic compounds may be enhanced by hydration of the leaf cuticle. Other authors (Schönherr 2000, 2002, Schönherr and Baur 1994) showed that an environment with high relative humidity may cause a swelling of the cuticle, induce formation of water pores, and solubilize the isopropylamine salt. The above-mentioned events, associated with the fact that low-intensity rain is characterized by droplets with a low VMD, which probably do not have the necessary kinetic force to remove herbicide deposits from the surface, may have contributed indirectly for a greater active ingredient penetration into the leaves.

In contrast, torrential rain (48 mm h^{-1}) washed-off a great part of the active ingredient as demonstrated by a high level of dry matter. It is assumed that rain event with this intensity removes the major part of the herbicide deposit on the leaves.

Our results show that glyphosate efficacy on weeds with rough surfaces (*C. album* and *S. viridis*) was not negatively affected due to light rain as compared to the weed species with a relative smooth surface (*A. theophrasti*). Considering *A. theophrasti* as a unique species that did not have crystalline wax structures on its surface, we therefore hypothesize that the wax fine structure must have played an important role in preventing glyphosate wash-off, especially under light rain conditions. Leung (1994) showed that a film of cuticular wax reconstituted on a glass slide could not protect glyphosate deposits against rain-washing. However, the author did not give any information on the presence of wax fine structure elements.

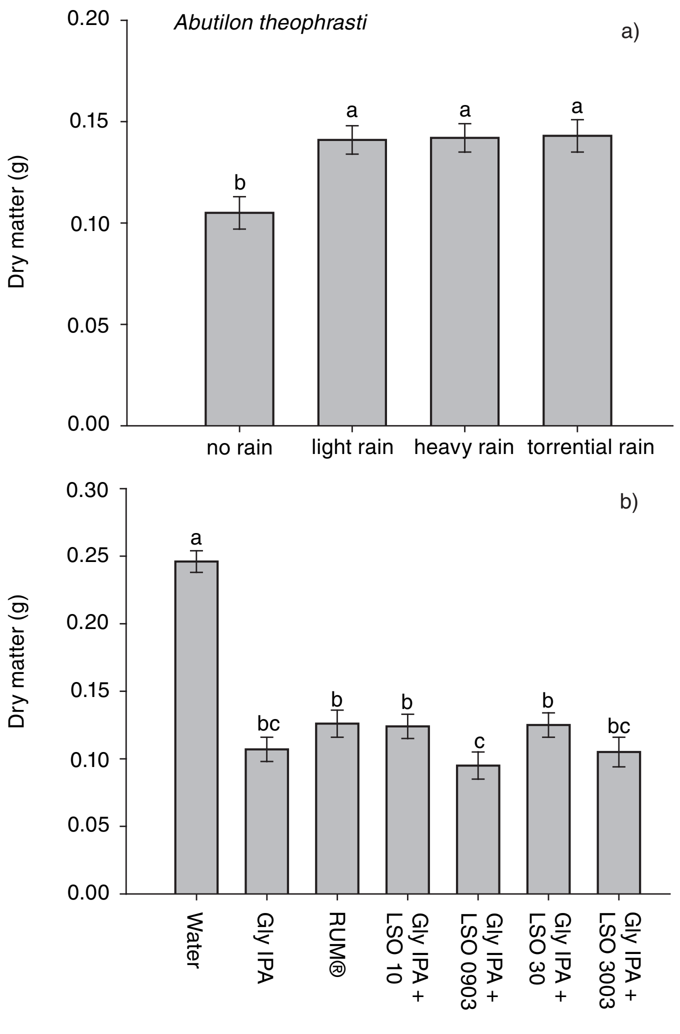

Figure 6. Influence of rainfall and rain intensity (A) and treatment solutions (B) on dry matter of *A. theophrasti*. Vertical bars represent the standard error. Means of dry matter followed by the same letter are not different by Duncan's test P ≤0.05.

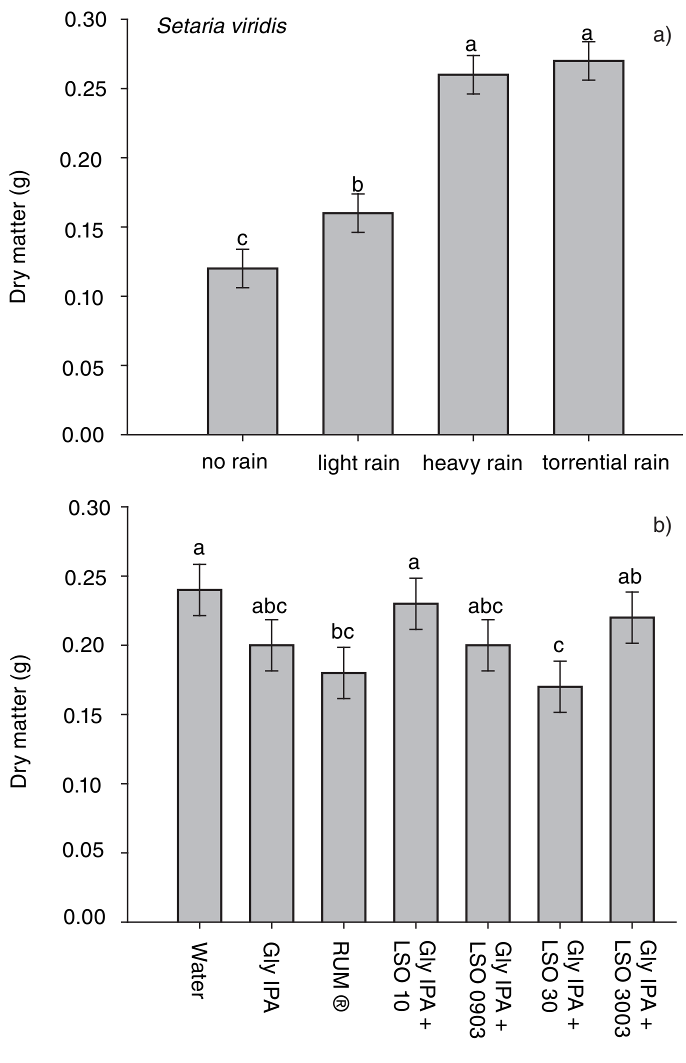

Figure 7. Influence of rainfall and rain intensity (A) and treatment solutions (B) on dry matter of *S. viridis*. Vertical bars represent the standard error. Means of dry mass followed by the same letter are not different by Duncan's test P ≤0.05.

Influence of treatment solutions

Because of the obvious differences in physical characteristics of the leaf surfaces (Figure 1–4), different responses to treatment solutions for the evaluated weed species were expected. While in *C. album* addition of LSO ethoxylates to unformulated glyphosate IPA yielded about the same dry matter level as with RUM®, in *A. theophrasti* and *S. viridis* better results were obtained when formulating glyphosate IPA with LSO 0903 or LSO 30, respectively. A clear relation between biological efficacy, roughness, contact angle of spray solution droplets, and EO units in the hydrophilic chain of the adjuvant could not be established. A critical factor which may have influenced our results is the mass and composition of surface waxes. Studies have shown that hydrophilic herbicides have lower efficacy in weeds with more lipophilic compounds in the epicuticular wax (Monquero *et al.* 2004, Chachalis *et al.* 2001).

It is known that adjuvant oils act mainly by enhancing penetration of herbicides, but the precise mechanisms involved are poorly understood (Sharma and Singh 2000, Gauvrit and Cabanne 1993). It was also postulated that hydrophilic herbicides often work better with hydrophilic adjuvants, because they contribute to hydration of the cuticle and in this way enhance permeation of the active ingredient (Hess and Foy 2000, Green and Hazen 1998). According to Abribat (2001), rapeseed oil ethoxylates have solvency properties that can increase cuticle permeability, enhancing penetration rate and rainfastness of hydrophilic compounds. Sharma and Singh (2000) showed that methylated seed oils enhance glyphosate efficacy in *Bidens pilosa* and *Panicum maximum* due to its solubilizing and humectant nature. We suppose that LSO ethoxylates influence glyphosate efficacy in a similar way; however, further research on this topic is needed.

References

Abribat, B. (2001). A new environmentally friendly class of pesticide potentiators: the alcoxylated triglycerides. Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals, ed. H. de Ruiter, pp. 381-9. (ISAA 2001 Foundation Amsterdam, The Netherlands).

Baker, E.A. (1982). Chemistry and morphology of plant epicuticular waxes. *In* 'The plant cuticle', ed. D.F. Cutler, K.L. Alvin, C.E. Price, p. 139-66. (Academic Press, London).

Bariuan, J.V., Reddy, K.N. and Wills, G.D. (1999). Glyphosate injury, rainfastness, absorption and translocation in purple nutsedge (*Cyperus rotundus*). *Weed Technology* 13, 112-19.

Barthlott, W. and Neinhuis, C. (1997). Characterisation and distribution of water-repellent, self-cleaning plant surfaces. *Annals of Botany* 79(6), 667-77.

Barthlott, W., Neinhuis, C., Cutler, D., Ditsch, F., Meusel, I., Theisen, I. and Wilhelmi, H. (1998). Classification and terminology of plant epicuticular waxes. *Botanical Journal of the Linnean Society* 126, 237-60.

Brewer, C.A., Smith, W.K. and Vogelmann, T.C. (1991). Functional interaction between leaf trichomes, leaf wetability and the optical properties of water droplets. *Plant, Cell and Environment* 14(9), 955-62.

Bryson, C.T. (1987). Effects of rainfall on foliar herbicides applied to rhizome Johnsongrass. *Weed Science* 35, 115-19.

Chachalis, D., Reddy, K.N. and Elmore, C.D. (2001). Characterization of leaf surface, wax composition, and control of redvine and trumpetcreeper with glyphosate. *Weed Science* 49, 156-63.

Chow, P.N.P. (1993). Adjuvants in spray formulation in relation to foliar application of herbicides. *In* 'Application technology for crop protection', eds G.A. Matthews and E.C. Hislop, p. 291-304. (CAB International).

Clay, D.V. and Lawrie, J. (1990). Effects of spray additives on the activity and rainfastness of glyphosate on perennial grass weeds of forestry. Proceedings Crop Protection in Northern Britain, pp. 181-6.

Coble, H. and Brumbaugh, E.H. (1993). Effect of nonionic surfactants on the rainfastness of glyphosate. *Pesticide Science* 38, 247-50.

Combellack, H., Pritchard, G. and Illingworth, J. (2001). Effect of simulated rainfall and selected adjuvants on the herbicidal performance of glyphosate. Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals, ed. H. de Ruiter. pp. 525-30. (ISAA 2001 Foundation, Amsterdam, The Netherlands).

Cranmer, J.R. and Linscott, D.L. (1991). Effects of droplet composition on glyphosate absorption and translocation in velvetleaf (*Abutilon theophrasti*). *Weed Science* 39, 251-4.

Ditzer, S. (2002). 'Grundlegende Faktoren der Regenfestigkeit, untersucht am Beispiel ausgewählter Kontaktfungizide bei 'Golden Delicious''. Ph.D. thesis, Rheinische Friedrich-Wilhelms Universität Bonn, 114 p. (Shaker Verlag, Aachen, Bericht aus der Agrarwissenschaft).

Feng, P.C.C., Ryerse, J.S. and Sammons, R.D. (1998). Correlation of leaf damage with uptake and translocation of glyphosate in velvetleaf (*Abutilon theophrasti*). *Weed Technology* 12, 300-7.

Field, R.J. and Bishop, N.G. (1988). Promotion of stomatal infiltration of glyphosate by an organosilicone reduces the critical rainfall period. *Pesticide Science* 24, 55-62.

Forster, W.A. and Zabkiewicz, J.A. (2001). Improved method for leaf surface roughness characterisation. Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals, ed. H. de Ruiter, pp. 113-18. (ISAA 2001 Foundation, Amsterdam, The Netherlands).

Foy, C.L. and Smith, L.W. (1965). Surface tension lowering, wetability of paraffin and corn leaf surfaces, and herbicidal enhancement of dalapon by seven surfactants. *Weeds* 13, 15-19.

Gaskin, R.E. and Holloway, P.J. (1992). Some physiochemical factors influencing foliar uptake enhancement of glyphosate-mono(isopropylammonium) by polyoxyethylene surfactants. *Pesticide Science* 34, 195-206.

Gauvrit, C. and Cabanne, F. (1993). Oils for weed control: uses and mode of action. *Pesticide Science* 37, 147-53.

Green, J.M. (2000). Adjuvant outlook for pesticides. *Pesticide Outlook* 11(5), 196-9.

Green, J.M. (2001). Factors that influence adjuvant performance. Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals, ed. H. de Ruiter, pp. 179-90, (ISAA 2001 Foundation, Amsterdam, The Netherlands).

Green, J.M. and Hazen, J.L. (1998). Understanding and using adjuvant properties to enhance pesticide activity. Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, ed. P. McMullan, pp. 25-36, (Chemical Producers and Distributor Association, Memphis, Tennessee).

Haefs, R. (2001). 'Rapeseed oil ethoxylate surfactants and their effects on retention, penetration, rainfastness and biological efficacy of selected agrochemicals'. Ph.D. thesis, Rheinische Friedrich-Wilhelms Universität Bonn, 112 p. (Cuvillier Verlag, Göttingen).

Hazen, J.L. (2000). Adjuvants – terminology, classification, and chemistry. *Weed Technology* 14, 773-84.

Hess, D.F. and Falk, R.H. (1990). Herbicide deposition on leaf surfaces. *Weed Science* 38, 280-8.

Hess, D.F. and Foy, C.L. (2000). Interaction of surfactants with plant cuticles. *Weed Technology* 14, 807-13.

Holloway, P.J. (1970). Surface factors affecting the wetting of leaves. *Pesticide Science* 1, 156-63.

Hunsche, M., Schmitz-Eiberger, M. and Noga, G. (2005). Enhancing rainfastness of contact fungicides with adjuvants. Proceedings of the Crop Science and Technology 2005 – Congress, pp. 503-6. (British Crop Protection Council, Glasgow).

Juniper, B.E. and Jeffree, C.E. (1983). 'Plant surfaces'. (Edward Arnold Publishers, London).

Kirkwood, R.C. (1999). Recent developments in our understanding of the plant cuticle as a barrier to the foliar uptake of pesticides. *Pesticide Science* 55, 69-77.

Knowles, A. (2001). Adjuvants for agrochemicals. *Pesticide Outlook* 12(5), 183-4.

Kogan, M. (2001). Uso de adjuvantes para disminuir el efecto del lavado del glifosato desde el foliaje de *Cyperus rotundus* L. *Ciência e Investigación Agrária* 28(3), 151-6.

Kromer, K.-H., Pohen, F. and Botschek, J. (1996). Bonner Regensimulatoren, Systeme zur Messung der Bodenerosion. *Landtechnik* 51, 18-19.

Laerke, P.E. and Streibig, J.C. (1995). Foliar absorption of some glyphosate formulations and their efficacy on plants. *Pesticide Science* 44, 107-16.

Leung, J.W. (1994). A fluorometric method to determine rainfastness, volatilization and photostability of glyphosate from glass slides, after application of Vision with two adjuvants. *Journal of Environmental Science and Health, B* 29(2), 341-63.

Leung, J.W. and Webster, B.G.R. (1994). Effect of adjuvants on rainfastness and herbicidal activity of glyphosate deposits on trembling aspen foliage. *Journal of Environmental Science and Health, B* 29(6), 1169-1201.

Martini, G., Junior, A.F.F.P. and Durigan, J.C. (2003). Eficácia do herbicida glifosato-potássico submetido á chuva simulada após aplicação. *Bragantia* 62(1), 39-45.

Monquero, P.A., Christoffoleti, P.J., Matas, J.A. and Heredia, A. (2004). Caracterização da superfície foliar e das ceras epicuticulares em *Commelina benghalensis*, *Ipomoea grandifolia* e *Amaranthus hybridus*. *Planta Daninha* 22(2), 203-10.

Müller, T., Brancq, B., Milius, A., Okori, N., Vaille, C. and Gauvrit, C. (2001). Self-emulsifying ethoxylates of rapeseed oil and methylated rapeseed oil as novel adjuvants for herbicides. Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals, ed. H. de Ruiter, pp. 68-74. (ISAA 2001 Foundation, Amsterdam, The Netherlands).

Reddy, K.N. and Singh, M. (1992). Organosilicone adjuvant effects on glyphosate efficacy and rainfastness. *Weed Technology* 6, 361-5.

Roggenbuck, F.C., Penner, D., Burow, R.F. and Thomas, B. (1993). Study of the enhancement of herbicide activity and rainfastness by an organosilicone adjuvant utilizing radiolabelled herbicide and adjuvant. *Pesticide Science* 37, 121-5.

Sandbrink, J.J., Dayawon, M.M. and Kassebaum, J.W. (1993). Non-silicone-based surfactants as glyphosate rainfastness adjuvants. *Pesticide Science - Extended Summaries: Pesticide Group Symposium* 38, 272-3.

Scherhag, H. (2005). 'Rapeseed oil ethoxylate surfactants and their effects on spray application parameters and their impact on performance of selected agrochemicals'. Ph.D. thesis, Rheinische Friedrich-Wilhelms Universität Bonn, 78 p. (Logos Verlag, Berlin).

Scherhag, H., Schmitz-Eiberger, M., Downer, R. and Noga, G. (2005). Influence of rapeseed oil ethoxylates surfactants on retention and biological efficacy of glyphosate spray solutions in selected weeds. *Journal of Applied Botany and Food Quality* 79, 17-23.

Schönherr, J. (2000). Calcium chloride penetrates plant cuticles via aqueous pores. *Planta* 212, 112-18.

Schönherr, J. (2002). A mechanistic analysis of penetration of glyphosate salts across astomatous cuticular membranes. *Pest Management Science* 58(4), 343-51.

Schönherr, J. and Baur, P. (1994). Modelling penetration of plant cuticles by crop protection agents and effects of adjuvants on their rates of penetrations. *Pesticide Science* 42, 185-208.

Sharma, S.D. and Singh, M. (2000). Optimizing foliar activity of glyphosate on *Bidens frondosa* and *Panicum maximum* with different adjuvant types. *Weed Research* 40(6), 523-33.

Spanoghe, P., Claeys, J., Pinoy, L. and Steurbaut, W. (2005). Rainfastness and adsorption of herbicides on hard surfaces. *Pest Management Science* 61(8), 793-8.

Sun, J. (1996). 'Characterization of organosilicone surfactants and their effects on sulfonylurea herbicide activity'. Ph.D. thesis, Faculty of Virginia, 120 p. (Internet Publication).

Sundaram, A. (1991). Effect of adjuvants on glyphosate wash-off from white birch foliage by simulated rainfall. *Journal of Environmental Science and Health, B* 26(1), 37-67.

Wells, A.J. (1989). Adjuvants, glyphosate efficacy and post-spraying rainfall. *Plant Protection Quarterly* 4(4), 158-63.

Werlang, R.C., Silva, A.A., Ferreira, L.R. and Miranda, G.V. (2003). Efeitos da chuva na eficiência de formulações e doses de glyphosate no controle de *Brachiaria decumbens*. *Planta Daninha* 21(1), 121-130.

Zabkiewicz, J.A., Stevens, P.J.G., Forster, W.A. and Steele, K. (1993). Foliar uptake of organosilicone surfactant oligomers into bean leaf in the presence and absence of glyphosate. *Pesticide Science* 38, 135-143.