Evaluation of the potency of different seed oil ethoxylates to increase herbicide efficacy in comparison to commercial adjuvants

Evaluierung der Wirkung von verschiedenen Pflanzenöl-Ethoxylaten auf die Steigerung der Wirkung von Herbiziden im Vergleich zu kommerziellen Adjuvantien

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Summary

The efficacy of many herbicides can be increased by adding adjuvants to the spray solution. Surfactants are able to increase foliar uptake of active ingredients for example, by enhancing retention of spray droplets on cuticles and penetration and absorption into leaf tissue. In this study, dose-response studies with ethoxylated seed oils (soybean, linseed, safflower and high oleic sunflower oil), in combination with the herbicides sulfosulfuron, carfentrazone-ethyl and foramsulfuron & iodosulfuron were conducted. Commercial adjuvants (polyethylated fatty alcohol, polyether siloxane and rapeseed oil methyl-ester) served as standards. The experiments were carried out under greenhouse conditions, using *Abutilon theophrasti* Medik. as test species. Dry weight of *A. theophrasti* was measured three weeks after treatment and dose-response curves were calculated by nonlinear regression analysis. Results showed that two of three herbicides did not control *A. theophrasti* sufficiently when they were applied without any adjuvant. The ethoxylated linseed oil decreased the ED_{90} of sulfosulfuron and foramsulfuron & iodosulfuron by 245- and 44-fold, respectively, whereas the ED_{90} of carfentrazone-ethyl was reduced 2-fold by the ethoxylated safflower oil. Furthermore, none of the herbicides developed its best efficiency in combination with the respective recommended commercial adjuvant. This experiment demonstrates that the potential of an herbicide can be increased adding ethoxylated seed oil adjuvants. Hence, with precise recommendations for herbicide-adjuvant-mixtures, herbicide application rates and costs could be reduced.

Keywords: Biodegradable adjuvants, dose-response studies, reduced application rates

Zusammenfassung

Die Wirkung vieler Herbizide kann durch die Zugabe von Adjuvantien zur Applikationslösung gesteigert werden. Surfactants können die Aufnahme von Wirkstoffen in die Kutikula steigern. Dies geschieht z. B. durch die Erhöhung der Retentionszeit von Applikationströpfchen und/oder durch eine Steigerung der Penetration und Aufnahme in das pflanzliche Gewebe. In dieser Studie wurden Dosis-Wirkungsversuche mit ethoxylierten Pflanzenölen (Sojabohnen-, Lein-, Färberdistel- und „High Oleic" Sonnenblumenöl) in Kombination mit den Herbiziden Sulfosulfuron, Foramsulfuron & Iodosulfuron und Carfentrazon-ethyl durchgeführt. Als Standard dienten kommerziell erhältliche Adjuvantien (polyethylierter Fettsäurealkohol, Polyether-Siloxan und Rapsöl-Methylester). Die Experimente wurden mit Hilfe der Testspezies *Abutilon theophrasti* Medik. unter Gewächshausbedingungen durchgeführt. Drei Wochen nach der Behandlung von *A. theophrasti* wurde das Trockengewicht der Pflanzen bestimmt und Dosis-Wirkungskurven mittels Regressionsanalyse generiert. Die Ergebnisse zeigten, dass zwei der drei Herbizide keine ausreichende Bekämpfung von *A. theophrasti* erzielten, wenn sie ohne Adjuvantien appliziert wurden. Das ethoxylierte Leinöl verringerte die ED_{90} von Sulfosulfuron und Foramsulfuron & Iodosulfuron um das 245- bzw. um das 44-fache. Die ED_{90} von Carfentrazon-Ethyl hingegen konnte um das Zweifache durch die Zugabe des ethoxylierten Färberdistelöls gesenkt werden. Außerdem zeigte keines der Herbizide seine maximale Wirkung durch die Zugabe der kommerziell erhältlichen Adjuvantien. Diese Studie zeigt, dass das Potential eines Herbizides durch die Zugabe eines ethoxylierten Pflanzenöls gesteigert werden kann. Durch präzise Empfehlungen für Herbizid-Adjuvant-Mischungen könnten Herbizid-Aufwandmengen und Kosten reduziert werden.

Stichwörter: Biologisch abbaubare Adjuvantien, Dosis-Wirkungsversuche, reduzierte Aufwandmengen

1. Introduction

Almost all herbicide formulations contain adjuvants. They act as important tools to improve physical aspects of herbicide application and/or to enhance biological efficacy (GREEN and FOY, 2000). Adjuvants are "substances added to a pesticide formulation or to the spray tank to modify pesticide activity or application characteristics" (STEPHENSON et al., 2006). There are two main adjuvant types: (1) Utility adjuvants or tank-mix modifiers which, for example, are able to adjust or buffer pH or reduce spray drift, and (2) activator adjuvants which enhance herbicide activity for example by wetting the leaf surface or softening cuticular waxes (HAZEN, 2000). Seed or vegetable oil derivates can be classified as surfactants which again can be counted to the type of activator adjuvants. Modified vegetable oils represent a group of biodegradable adjuvants (CORNISH et al., 1993) which are proposed to be as effective as petroleum oils (ROBINSON and NELSON, 1975). Due to the fact that this group of adjuvants is not phytotoxic, environmental friendly and enhances herbicide efficacy, it is interesting for pesticide formulations (HAEFS et al., 2002). Though various research on seed oil adjuvants for herbicides was conducted, their mode of action is still not completely clear. However, it is known that seed oils are poor solvents for epicuticular waxes, but are able to impregnate the wax (GAUVRIT and CABANNE, 1993). This might lead to modifications of the physical properties of the epicuticular waxes and to an increased fluidity (GAUVRIT and CABANNE, 1993). In an earlier study, MANTHEY and NALEWAJA (1992) claimed that a solubilization of epicuticular waxes might also be a reason for an enhanced uptake of active ingredients (a.i.). Furthermore, oils possess the ability to penetrate into the cuticle and, hence, this could be related to a transfer of a.i. into plants (GAUVRIT and CABANNE, 1993). For agriculture, the enhancement of herbicide action by the addition of adjuvants could reduce herbicide application rates. Although the usage of herbicides is adopted by most farmers, the interest in reduced application rates constantly grows (BLACKSHAW et al., 2006). Reducing herbicide amounts while still maintaining an adequate efficacy against weeds has a great importance in plant protection to decrease costs, environmental impacts of chemical plant protection and losses in crop yield caused by herbicide damages. However, long time studies proved that a constant reduction of the application rate by 50 % leads to a gradual increase of weed infestation and selection of weed species which are difficult to control (PALLUTT and MOLL, 2008). Furthermore, the risk of selecting herbicide resistant weeds increases due to a reproduction of species which were not completely controlled. Hence, the population density can grow over the years, leading to an increased gene pool in which resistant species will be more likely (BLACKSHAW et al., 2006). In the present study, we investigated the potency of several ethoxylated seed oil adjuvants, based on soybean (ESBO), linseed (ELO), high oleic sunflower (EHOSO) and safflower oil (ESO). For this purpose, dose response studies were conducted with formulated herbicides [Monitor®, Monsanto (800 g/kg sulfosulfuron); Oratio® 40 WG, Syngenta (400 g/kg carfentrazon-ethyl); MaisTer®, Bayer CropScience (300 g/kg foramsulfuron, 10 g/kg iodosulfuron-methyl-sodium)]. Adjuvants, which were recommended for those herbicides served as standards. In this study, *Abutilon theophrasti* Medik. (velvetleaf), a difficult to control annual weed, served as test species. Velvetleaf belongs to the family of *Malvaceae* and reduces crop yields by competing for water and nutrient supply, shading of the cultivar and release of allelopathic compounds (HAENSEL, 2005). In the USA, *A. theophrasti* causes huge problems in soybean, cotton, and maize, whereas in Germany difficulties occur mainly in sugar beet because there the herbicides mostly are ineffective against this weed (MEINLSCHMIDT, 2006). The aim of the present study was to compare the potency of the ethoxylated seed oils with the standard adjuvant formulations on the efficacy of herbicides.

2. Materials and methods

2.1 Plant material

Seeds of velvetleaf (*Abutilon theophrasti*; Herbiseed, UK) were pre-germinated in plastic pots (11 x 11 x 6 cm) filled with vermiculite (2-3 mm) in a greenhouse (25/20 °C, additional light (~ 122 µmol/m^2/s for 12h) for 5-6 days until cotyledons were developed. Pre-cultivated seedlings were transferred into paper pots (8 x 8 cm) filled with a compost soil-sand mixture (2:1 v/v) and cultivated under the described conditions. Plants were watered daily with tap water. No water was applied to plants for at least 24 hours after application of herbicides. All plants were completely randomized with four replicates.

2.2 Herbicide and adjuvant application

The seed oil adjuvants investigated in this study contained ten ethylene oxide units and belong to the class of non-ionic surfactants. Their chemical structure is based on an ethoxylated triacylglycerid with a varying composition of fatty acids which have different saturation degrees (Tab. 1).

Tab. 1 Fatty acid composition of the ethoxylated seed oil adjuvants according to BOCKISCH (1993).

Tab. 1 *Fettsäurezusammensetzung der ethoxylierten Pflanzenöl-Adjuvantien nach BOCKISCH (1993).*

Adjuvant	Fatty acid distribution (only C18) % Stearic acid (C18:0)	% Oleic acid (C18:1)	% Linolic acid (C18:2)	% Linolenic acid (C18:3)
Ethoxylated soybean oil **(ESBO)**	~ 4	~ 21	~ 56	~ 8
Ethoxylated high oleic sunflower oil (**EHOSO**)	< 5	>80	<5	traces
Ethoxylated safflower oil (**ESO**)	~ 2-3	~ 15	> 75	traces
Ethoxylated linseed oil (**ELO**)	~ 4	~ 22	~ 16	~ 52

ESBO, EHOSO, ESO and ELO were tested in combination with the formulated herbicides displayed in Table 2. Therefore, they were doted in a concentration of 1 l/ha to nine concentrations of each herbicide solution (dose ranges are given in Tab. 2). As reference, herbicide solutions were applied alone and in combination with their recommended adjuvants. Application rate of recommended adjuvants was used as displayed in Table 2. Untreated velvetleaf plants served as control. Every treatment was replicated four times. Plants were treated when the second true leaf was completely developed. Application was done with a track sprayer (Aro, Langenthal, Switzerland), which simulated a water volume of 400 l/ha (nozzle: 8004 EVS, Teejet® Spraying Systems Co., Wheaton, IL, USA).

Tab. 2 Table of herbicides and their recommended commercial adjuvants.

Tab. 2 *Tabelle der Herbizide mit denen jeweils empfohlenen kommerziellen Adjuvantien.*

Herbicide trade name (recommended adjuvant)	Active ingredient (a.i.)	Mode of action	Herbicide dose-range (g a.i. ha^{-1})	Adjuvant type	Adjuvant short form	Adjuvant dose (l ha^{-1})
Monitor® (Monfast®)	Sulfosulfuron	ALS-inhibitor	0.078 - 20	Polyoxylated fatty alcohols, propylenglycol	EFA	0.8
Oratio® 40 WG (Break-Thru® S 240)	Carfentrazone-ethyl	PPO-inhibitor	0.078 - 20	Organomodified (Polyether) siloxane	PS	0.1
MaisTer® (Mero®)	Foramsulfuron + iodosulfuron	ALS-inhibitor	0.182 - 46.5	Rapeseed oil methyl-ester	ROME	2.0

Data measuring and data analysis

The study was conducted from March to May 2010 with four different experiments, where each herbicide represented one separate experiment. The above ground biomass of plants was harvested three weeks after application, dried at 80 °C for 48 hours and weighed. Biomass data was analyzed with the four-parameter log-logistic model (STREIBIG et al., 1993) (equation 1) using the software package drc of the statistical program R.

$$(1) \qquad y = C + \frac{D - C}{1 + e^{b(\ln(x) - \ln(ED50))}}$$

D and *C* denote the upper and lower limits, respectively, and ED_{50} is the dose where a response half-way between the upper and lower limit is reached. *B* denotes the slope around the ED_{50} value. When the lower limit of curves was 0, the model was reduced to a three-parameter model (C=0). To compare different curves, generated from biomass data of each treatment, the residual sum of squares of the regression analysis was compared and assessed by an F-test for lack-of-fit. In weed control studies response levels at ED_{90}, the dose causing 90 % weed control, might be of higher interest (KNEZEVIC et al., 2007) compared to the ED_{50} value. According to equation 3 (RITZ and STREIBIG, 2005, modified), ED_{90} values were calculated

$$(2) \qquad ED\,x = ED_{50}\,[x/(100-x)]^{1/b}.$$

To compare the different efficacies of herbicide-adjuvant combinations, relative potencies (*r*) were calculated for parallel curves according to equation 4 (RITZ et al., 2006):

$$(3) \qquad r_A = \frac{x_B}{x_A}$$

X is the herbicide dose, *B* the reference spray solution, i.e. the herbicide without adjuvant, and *A* the herbicide-adjuvant-mixture. As *r*A is not constant across response levels in case of non-parallel curves, *rA*-values were only evaluated for pre-set response levels (ED_{50} and ED_{90}; CABANNE et al., 1998)

3. Results

3.1 Sulfosulfuron

The test for lack-of-fit for the sulfosulfuron data yielded a p-value of 0.33 which is not significant at 5 % and hence, the nonlinear regression model provided an acceptable description of observed data (Fig. 1). All additives decreased the amount of sulfosulfuron required to achieve a 50 % reduction in dry weight compared to sulfosulfuron alone. However, the differences were not significant. The recommended adjuvant EFA showed the best effect on sulfosulfuron performance compared to the other adjuvants and decreased the ED_{50} of the herbicide by 19-fold. For the adjuvants ELO, EHOSO and ESBO, the efficacy enhancing effect was less pronounced with an average reduction of the ED_{50} of sulfosulfuron by 6.7-fold (± 0.7). ESO decreased the ED_{50} by 3.5-fold and, hence, was the least effective adjuvant. Regarding the ED_{90} values, all adjuvants reduced the necessary amount of sulfosulfuron. Sulfosulfuron mixed with ELO showed the best efficacy on velvetleaf biomass compared to all other treatments. It was 9.0-fold more effective than EFA and on average 4.4-fold (± 0.9) more effective than ESO, EHOSO and ESBO. With an application rate of 91 g a.i./ha for a 90 % control of velvetleaf, sulfosulfuron mixed with EFA was the weakest herbicide-adjuvant combination.

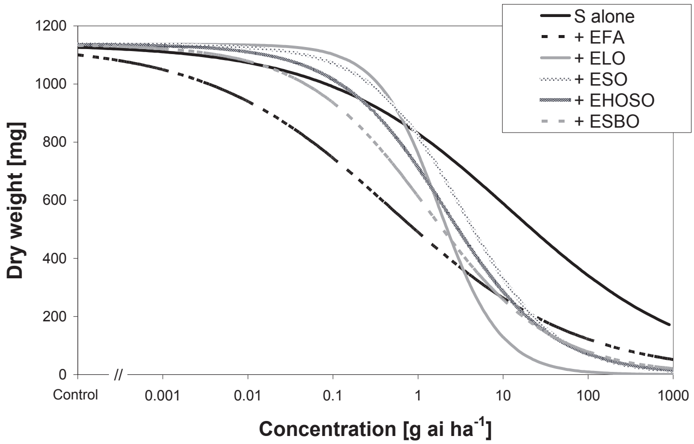

Fig. 1 Modelled dose-response curves of sulfosulfuron (S) applied with and without adjuvant to *Abutilon theophrasti*. Recommended field rate for sulfosulfuron: 20 g a.i./ha.

Abb. 1 *Modellierte Dosis-Wirkungskurven für Sulfosulfuron (S) mit und ohne Adjuvant appliziert auf Abutilon theophrasti. Empfohlene Aufwandmenge für Sulfosulfuron: 20 g a.i./ha.*

3.2 Carfentrazone-ethyl

With a p-value of 0.86, the nonlinear regression model for carfentrazone-ethyl described the observed data quite well (Fig. 2). The ED_{50} of carfentrazone-ethyl could be reduced by the addition of adjuvants, whereas PS, EHOSO and ESBO showed the best efficacy on carfentrazone-ethyl reducing the ED_{50} *by* 5-fold (± 0). ELO and ESO decreased the amount of carfentrazone-ethyl required to achieve the ED_{50} by 1.4- and 1.8-fold, respectively, compared with carfentrazone-ethyl alone and, thus, were less effective than the other adjuvants. Comparing ED_{90} values showed that at this response level only ESO distinctly enhanced the efficacy of carfentrazone-ethyl (rED_{90} = 2.0). Moreover, the addition of PS and ELO even increased the amount of carfentrazone-ethyl needed to achieve a 90 % response by 1.7- and 2.9-fold, respectively.

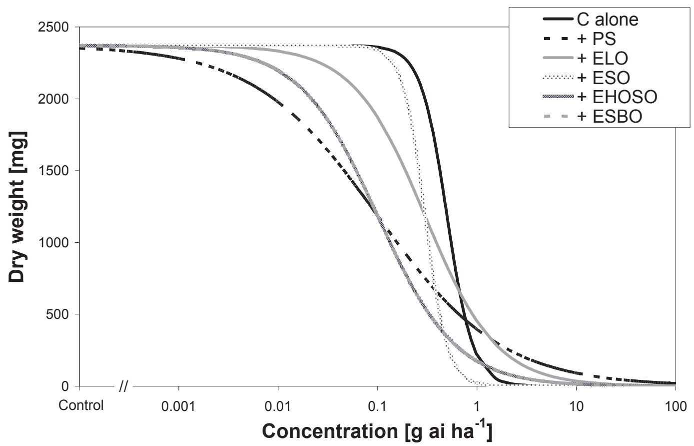

Fig. 2 Modelled dose-response curves of carfentrazone-ethyl (C) applied with and without adjuvant to *Abutilon theophrasti*. Recommended field rate for carfentrazone-ethyl: 20 g a.i./ha.

Abb. 2 *Modellierte Dosis-Wirkungskurven für Carfentrazon-ethyl (C) mit und ohne Adjuvant appliziert auf Abutilon theophrasti. Empfohlene Aufwandmenge für Carfentrazon-ethyl: 20 g a.i./ha.*

3.3 Foramsulfuron & iodosulfuron (FI)

Plotted FI data showed, that the nonlinear regression model fitted the data (p = 0.07; Fig. 3). It was observed, that all adjuvants significantly decreased the amount of FI needed to get a 50 % reduce of biomass by 5-fold (±1.5). Furthermore, ELO was even more effective than the recommended ROME (rED_{50} = 1.3). Regarding the ED_{90}, all adjuvants reduced biomass by 96 % (± 1.7) compared with FI applied alone. However, this reduction was not significant. ELO was also the most effective adjuvant (rED_{90} = 44.2), followed by ESBO (rED_{90} = 38.1) and ESO (rED_{90} = 32.1). EHOSO represented the least effective seed oil (rED_{50} and rED_{90} = 2.6 and 16.7) in combination with FI.

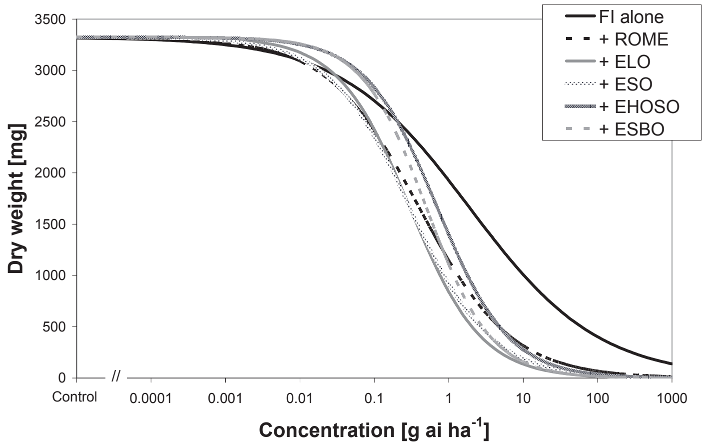

Fig. 3 Modelled dose-response curves of foramsulfuron & iodosulfuron (FI) applied with and without adjuvant to *Abutilon theophrasti*. Recommended field rate for sulfosulfuron: 46.5 g a.i./ha.

Abb. 3 *Modellierte Dosis-Wirkungskurven für Foramsulfuron & Iodosulfuron (FI) mit und ohne Adjuvant appliziert auf Abutilon theophrasti. Empfohlene Aufwandmenge für FI: 46.5 g a.i./ha.*

4. Discussion

4.1 Improving herbicide efficacy with seed oil adjuvants

Generally, in this study the efficacy of every herbicide was improved after adding one of the seed oil adjuvants. The fact that modified seed oils improve herbicide efficacy is already known and was reviewed over 20 years ago by GAUVRIT and CABANNE (1993). An increased spreading of spray droplets on target plants and an enhanced penetration of active ingredients into leaves seem to be the reasons for the herbicide enhancing action of seed oils (LIU, 2004). Since many oil-based adjuvants act well as penetration enhancers, it can be assumed, that the herbicide enhancing effect of seed oil adjuvants can be attributed mainly to this mechanism (STOCK and BRIGGS, 2000).

4.2 ELO, ESO, EHOSO and ESBO and their potential on reducing herbicide application rates

In this study, ELO demonstrated the best efficacy in combination with the sulfonylureas, whereas ESO was most effective with carfentrazone-ethyl. Since it is known that the efficacy of sulfonylureas can be reduced by precipitation within a few hours after application (RUSSELL et al., 2002), an increased rainfastness of those herbicides might have been achieved by the addition of the ethoxylated linseed oil in this study. In an experiment conducted by HUNSCHE and NOGA (2008), it was proved that ethoxylated linseed oils showed a better effect on rainfastness of the fungicide mancozeb compared to ethoxylated soybean oils. ESBO acted 2-fold (± 0.5) better compared to the recommended adjuvants. Thus, ESBO could present an alternative adjuvant for a widespread use. However, EHOSO demonstrated the least pronounced effect in combination with all herbicides and hence, might not be suitable as adjuvant for herbicides. Furthermore, it can be concluded, that a higher content of unsaturated fatty acids affected the herbicidal efficacy in a positive way. Those results imply that an addition of ethoxylated seed oils could be an approach to reduce herbicide application rates while still maintaining a sufficient weed control. However, the problem is that reducing the application rate, which is recommended by chemical companies, would result in a loss of the companies guarantee. Moreover, results of an experiment conducted by ZHANG et al. (2000), demonstrated that the addition of adjuvants to below-labeled herbicide rates did not show any improvement of herbicide efficacy. Thus, the general concept of increasing the uptake of reduced herbicide rates with the help of adjuvants to achieve an adequate weed control might be refuted.

4.3 Conclusion

Only with an appropriate adjuvant, herbicides can develop their maximum efficacy – even at lower than recommended doses. Ethoxylated seed oils contain a high potential as biodegradable adjuvants for herbicides, whereas further investigations on additional weeds and field trials have to be conducted.

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