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Effect of adjuvants on the dissipation, efficacy and selectivity of three different pre-emergent sunflower herbicides

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ABSTRACT

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The aim of this work was to compare the efficacy, selectivity to sunflower and dissipation of three pre-emergent herbicides. Flurochloridone, linuron and oxyfluorfen were applied individually and each herbicide was also applied in a tank mix with two different adjuvants (a silicon-based adjuvant and paraffin oil). Small-plot field trials were carried out with sunflower in Central Bohemia in 2012 and 2015. Around 25–35% of the active ingredients in the applied herbicides were detected in soil 60 days after application in both years, except for oxyfluorfen in 2012, whose residual concentration was 60%. The tested soil adjuvants did not affect the dissipation of any of the tested herbicide in soil in either experimental year. Oxyfluorfen exhibited the highest mobility and caused the greatest degree of sunflower injury (18%), especially in the year with high rainfall shortly after application. None of the tested adjuvants significantly affected sunflower injury by any tested herbicide. The efficacy of flurochloridone and linuron on *Fallopia convolvulus* was strongly affected by weather conditions shortly after application. The efficacy of oxyfluorfen was around 85% and was not affected by weather conditions. The effect of adjuvant on herbicide efficacy was positive only in dry conditions, where the efficacy of flurochloridone on *F. convolvulus* was positively affected by the silicon-based adjuvant.

Keywords: *Helianthu annuus*; herbicide persistence in soil; weed control; phytotoxicity

Sunflower is relatively sensitive to most post-emergent (POST) herbicides and therefore pre-emergent (PRE) herbicides are usually used in this crop. The efficacy and selectivity of PRE herbicides in sunflower are strongly affected by weather conditions, especially soil moisture at the time shortly after application (Kudsk 2002, Jursík et al. 2015). Under dry conditions, the efficacy of PRE herbicides decreases; in contrast, intense precipitation after the application of these herbicides can cause the transport of active ingredients into the soil profile and resulting crop injury (Jursík et al. 2013). PRE herbicides exhibit longer residual activity and can be used also in herbicide tolerant (HT) crops to reduce the risk of herbicide resistance to glyphosate (Elezovic et al. 2012, Knezevic et al. 2013).

For pre-emergent control of dicot weeds in sunflower, linuron, flurochloridone, oxyfluorfen, pendimethalin, prosulfocarb, bifenox, aclonifen, flumioxazin and lenacil are often used, usually in combination with acetamide herbicides (acetochlor, dimethenamid, pethoxamid, metolachlor, flufenacet and propisochlor), which are intended for grass weed control (Pannacci et al. 2007, Nadasy et al. 2008, Kilinc et al. 2011, Jursík et al. 2015);

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however, tank mix combinations of some of these herbicides can decrease the selectivity to sunflower (Erasmo et al. 2010).

The behaviour of the active ingredients of herbicides in soil can be affected by the formulation of the particular pesticide (Hall et al. 1998, Keifer et al. 2008) and the addition of different adjuvants (Swarcewicz et al. 1998, Hall et al. 1998, Locke et al. 2002). Additive compounds affect the dispersion of active ingredients on the soil surface, their sorption in soil, and their vaporization and photodegradation, while the effect of different adjuvants on a specific herbicide can vary (Locke et al. 2002). The aim of this work was to compare the efficacy, selectivity to sunflower, and dissipation of three pre-emergent herbicides (flurochloridone, linuron and oxyfluorfen) applied singly as well as in tank-mix combinations with two different adjuvants.

MATERIAL AND METHODS

Small-plot field trials were carried out in sunflower (cv. Biba) in Central Bohemia (Kolín), Central Europe (250 m a.s.l.) in 2012 and 2015. The soil was classified as Arenic Chernozem, with a clay content of 11.6%, a sand content of 62.3%, a silt content of 26.1% (silt loam soil), a soil pH_{KCl} of 7.1, and a sorption capacity of 148.3 $mmol_+$/kg. Winter wheat was the previous crop in both years. Sunflower was sown on the 6th April 2012 and 23th March 2015. The experimental plots were organised in randomised blocks with three replicates, with plot area of 24.5 m^2 (3.5 × 7 m). The row spacing was 0.7 m, with an in-row plant spacing of 0.16 m. The dominant weed species was *Fallopia convolvulus* (20–40 plants/m^2) in both experimental years. Other weed species found in the fields were at a lower density (4–12 plants/m^2 for individual species) and included the following: *Echinochloa crus-galli* (2012), *Viola arvensis* (2012), *Chenopodium album* (2015) and volunteer oilseed rape (2015).

Pre-emergent applications of the herbicides were performed shortly after sunflower sowing (second day). The herbicides Racer 250 EC (250 g/L of flurochloridone), Afalon 45 SC (450 g/L of linuron), and Galigan 240 EC (240 g/L of oxyfluorfen) were used at the recommended rates (flurochloridone 750 g/ha a.i. (active ingredient), linuron 675 g/ha a.i., oxyfluorfen 240 g/ha a.i.). The adjuvants BreakThru (832 g/L polymethylsiloxane-copolymer) and Grounded (732 g/L of refined paraffin oil, aliphatic hydrocarbons, hexahydric alcohol ethoxylates, and C18–C20 fatty acids) were used at the recommended application rates (BreakThru 0.25 L/ha, Grounded 0.40 L/ha). The important environmental characteristics of the tested herbicides are described in Table 1.

The experiment included untreated control plots. A small-plot sprayer was used to apply the herbicides. The water volume applied was 200 L/ha. Lurmark 015F110 nozzles were used, with an application pressure of 0.25 MPa. A description of the meteorological characteristics from sunflower sowing to canopy closure is shown in Table 2.

Soil samples for the measurement of final herbicide concentrations in soil were collected 60 days after herbicide application using soil cylinders (0.0001 m^3) from soil layers of depth 0–5 cm

Table 1. Important properties of the tested herbicides in the environment (source: Footprint database)

		Flurochloridone	Linuron	Oxyfluorfen
Solubility in water at 20°C (mg/L)		21.9	63.8	0.12
Molecular mass (g/mol)		312.12	249.09	361.70
GUS leaching potential index		1.99	2.21	0.26
Soil degradation (aerobic)	field DT_{50} (days)	40.6	48.0	73.0
	lab at 20°C DT_{50} (days)	53.0	57.6	138
Adsorption strength by Freundlich	K_f	9.4	10.43	99.37
	K_{fOC}	700	559	7.566

GUS – groundwater ubiquity score (Gustafson 1989); DT_{50} – pesticide half-life; K_f – Freundlich adsorption coefficient; K_{fOC} – Freundlich organic carbon adsorption coefficient

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Table 2. Weather conditions during the monitored sunflower growing season and long-term normal

Meteorological characteristics		2012	2015	Long-term normal
Total natural precipitation (mm)	April	44	26	34
	May	17	29	71
	June	47	39	72
Mean monthly temperature (°C)	April	9.6	9.1	8.0
	May	16.0	13.7	13.0
	June	18.0	16.8	16.1

and 5–10 cm. The determination of herbicide concentrations in soil methanol extracts was performed using an HPLC instrument, according to the modified method devised by Kočárek et al. (2010). The detection limit was 0.016 μg/g for fluorochloridone, 0.015 μg/g for linuron, and 0.022 μg/g for oxyfluorfen. The amount of herbicide present in soil extracts was expressed as the total amount of solute per mass unit (μg/g). Because of the different application rates of the studied herbicides, the percentage of residual pesticide (related to the application rate) in soil layers was used to compare pesticide mobility. The pesticide degradation rate constant (*k*) was calculated using the following first order equation (Hurle and Walker 1980):

$$C = C_0 e^{-kt} \quad (1)$$

Pesticide half-life (DT_{50}) was then calculated using the following equation (Hurle and Walker 1980):

$$DT_{50} = \frac{\ln 2}{k} \quad (2)$$

Herbicide efficacy was assessed by the estimation method using a percentage scale from 0% to 100% (0% = untreated, 100% = full control) according to the European and Mediterranean Plant Protection Organisation (EPPO) 1/63 (3) guidelines. The first assessment was performed shortly after weed emergence (four true sunflower leaves), while the second was performed shortly before canopy closure. Selectivity was assessed according to the EPPO 1/135 (3) guideline and at the same time efficacy was assessed.

Experimental data were evaluated using the software package Statistica ver. 12 software package (StatSoft, Inc., 2013). A one-way analysis of variance was used. Contrasts between treatments were verified by the *LSD* (least significant difference) test (α = 0.05).

RESULTS AND DISCUSSION

Herbicide dissipation from soil. Around 25–35% of the active ingredients in the applied herbicides were detected in soil 60 days after application in 2012 and 2015, except for oxyfluorfen in 2012, whose residual concentration was 60%. The tested soil adjuvants did not affect the degradation of any tested herbicide in soil in either experimental year. Different results were presented by Kucharski and Sadowski (2011), who tested the effects of different adjuvants on the rate of degradation of metazachlor in soil. Oil and surfactant adjuvants slowed down the degradation of metazachlor in soil.

Because different herbicide doses were applied in the experiment, the residual pesticide concentra-

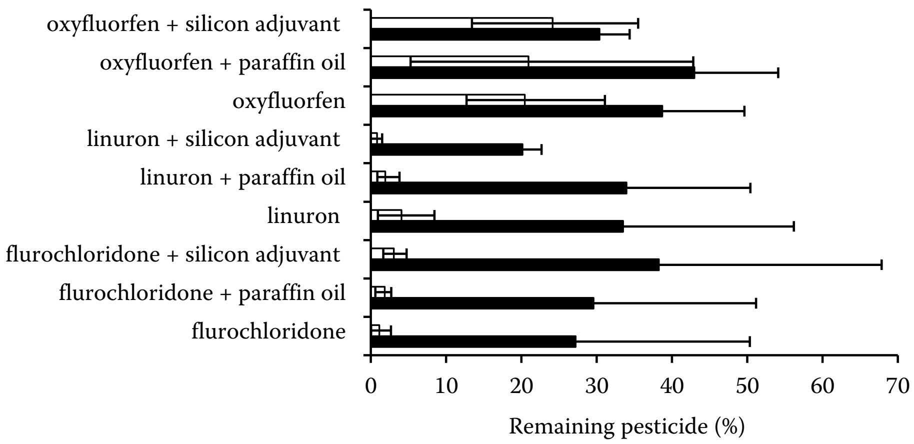

Figure 1. Percentage of residual pesticide in both tested soil layers (grey column, 0–5 cm; white column, 5–10 cm) 60 days after herbicide application in 2012 (error bars indicate maximum and minimum values)

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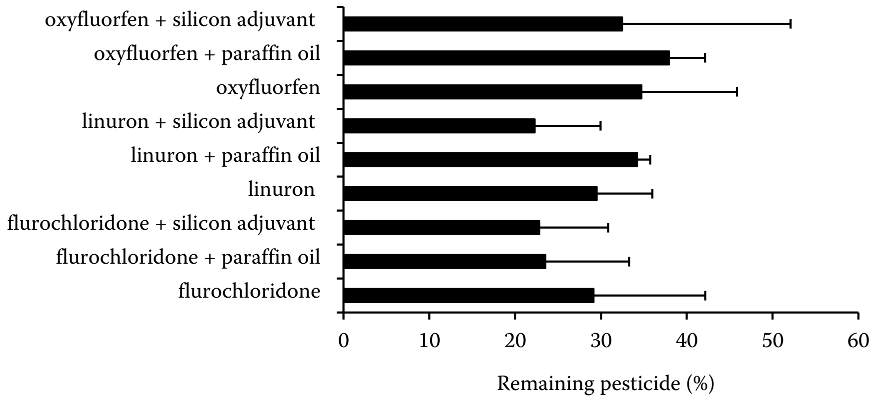

Figure 2. Percentage of residual pesticide in the 0–5 cm soil layer (no herbicide residues were detected in the 5–10 cm soil layer) 60 days after herbicide application in 2015 (error bars indicate maximum and minimum values)

tions in soil layers were expressed in percentages (Figures 1 and 2) and evaluated using ANOVA. Pesticide mobility was affected by the weather conditions (P-value = 0.0077). No pesticide was observed in the 5–10 cm soil layer in 2015 (Table 3), where very dry conditions occurred after application (April). In 2012, the percentages of flurochloridone, linuron and oxyfluorfen in the 5–10 cm soil layer were 2, 2.3, and 21.8%, respectively. In 2012, oxyfluorfen dissipation was significantly higher (P-value = 0.0113) than the dissipation of flurochloridone and linuron. Also in 2012, oxy-

Table 3. Sunflower injury after application of the tested herbicides and the concentrations of the used herbicides in two soil layers 60 days after application, according to the used herbicide, adjuvant and experimental year

	Phytotoxicity (%)		Concentration of herbicide in soil (μg/g)	
	BBCH 14	BBCH 32	soil depth 0–5 cm	soil depth 4–10 cm
Effect of used herbicide				
Flurochloridone	8.9^{a}	8.3^{b}	0.4265^{b}	0.0150^{a}
Linuron	15.4^{b}	2.2^{a}	0.3907^{b}	0.0158^{a}
Oxyfluorfen	17.5^{b}	13.9^{c}	0.1907^{a}	0.0524^{b}
F-ratio	8.90	28.47	10.02	6.89
P-value	0.0005	> 0.0001	0.0002	0.0024
Effect of used adjuvant				
Silicon adjuvant	14.9^{a}	8.7^{a}	0.2985^{a}	0.0292^{a}
Paraffin oil	13.4^{a}	7.9^{a}	0.3678^{a}	0.0256^{a}
Without adjuvant	13.5^{a}	7.9^{a}	0.3414^{a}	0.0283^{a}
F-ratio	0.31	0.17	0.76	0.05
P-value	0.7359	0.8454	0.4739	0.9487
Effect of year				
2012	20.7^{b}	15.2^{b}	0.3496^{a}	0.0555^{b}
2015	7.1^{a}	1.1^{a}	0.3222^{a}	0^{a}
F-ratio	61.56	124.19	0.35	34.77
P-value	> 0.0001	> 0.0001	0.5577	> 0.0001

Means followed by the same letter within the column are not significantly different at $P < 0.05$

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fluorfen mobility was significantly higher (*P*-value = 0.0174) than the mobility of both flurochloridone and linuron (Figure 1, Table 3). No effect of the tested adjuvants on herbicide mobility was observed (*P*-value = 0.9860), but in studies by Hall et al. (1998) and Kucharski and Sadowski (2011), the tested adjuvants slowed down the leaching of S-metolachlor and metazachlor.

Because of pesticide transport into the 5–10 cm soil layer in 2012, pesticide concentrations in the 0–5 cm and 5–10 cm soil layers were expressed in percentages and summarized and compared with pesticide concentrations (also expressed in percentages) in the 0–5 cm soil layer in 2015 in order to evaluate pesticide dissipation. ANOVA showed no effect of adjuvants (*P*-value = 0.1852) on pesticide dissipation and no significant difference between residual pesticide concentrations at the end of the experiment (*P*-value = 0.3119). The dissipation of the tested pesticides was significantly higher in 2012 (*P*-value = 0.0049) than in 2015.

Sunflower injury. The highest level of sunflower injury was recorded on plots treated by oxyfluorfen (18%). The injury caused by oxyfluorfen on sunflower was mainly caused by raindrops bouncing from the soil surface, which contaminated leaves and caused necrosis and leaf deformation. Sunflower regeneration was very slow because each rain caused further necrosis (phytotoxicity of 14% shortly before canopy closure). Pannacci et al. (2007) and Jursík et al. (2015) demonstrated similar results in different soil conditions. Sunflower injury caused by flurochloridone was significantly lower (9%) than that caused by oxyfluorfen (Table 3). The main symptom of flurochloridone phytotoxicity was leaf bleaching. The phytotoxicity of linuron was relatively high (15%) at the four true leaves growth stage but sunflower regeneration was fast. Shortly before sunflower canopy closure, the phytotoxicity caused by linuron was significantly lower (2%) compared to that caused by the other tested herbicides. Also Grichar et al. (2015) showed high phytotoxicity in *Ricinus communis* after the pre-emergent application of linuron when rainfall occurred soon after application and the application dose was higher than 1.12 kg/ha.

None of the tested adjuvants significantly affected sunflower injury by any tested herbicide (Table 3). Sunflower injury was significantly higher in 2012, when higher precipitation was recorded during April (Table 1) and the herbicide was transported to young roots of the emerging sunflower. Also, temperature can affect the selectivity of some herbicides. Harrison and Peterson (1999) showed that broccoli (*Brassica oleracea*) was less sensitive to oxyfluorfen at temperatures between 20°C and 25°C, compared to temperatures from 10°C to 15°C.

Efficacy. The efficacy of flurochloridone and linuron on *F. convolvulus* was strongly affected by weather conditions during April of each year. The efficacy of these two herbicides was higher in 2012 (95–99%), when the total natural precipita-

Table 4. Efficacy (%) of the tested herbicides shortly before sunflower canopy closure in 2012

Herbicide	Adjuvant	*Fallopia convolvulus*	*Echinochloa crus-galli*	*Viola arvensis*
Flurochloridone	–	99.0^{c}	90.0^{a}	98.7^{a}
	paraffin oil	99.0^{c}	90.0^{a}	99.3^{a}
	silicon adjuvant	97.7^{bc}	90.0^{a}	99.7^{a}
Linuron	–	95.0^{abc}	86.7^{a}	96.3^{a}
	paraffin oil	94.7^{abc}	83.3^{a}	96.3^{a}
	silicon adjuvant	86.7^{a}	80.0^{a}	96.7^{a}
Oxyfluorfen	–	86.7^{a}	76.7^{a}	99.3^{a}
	paraffin oil	88.3^{ab}	75.0^{a}	100.0^{a}
	silicon adjuvant	88.3^{ab}	73.3^{a}	100.0^{a}
F-ratio		6.94	2.70	3.03
P-value		0.0003	0.0382	0.0243

Means followed by the same letter within the column are not significantly different at $P < 0.05$

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Table 5. Efficacy (%) of the tested herbicides shortly before sunflower canopy closure in 2015

Herbicide	Adjuvant	*Fallopia convolvulus*	*Chenopodium album*	Volunteer of oilseed rape
Flurochloridone	–	40.0[bc]	76.7[d]	70.0[b]
	paraffin oil	56.7[cd]	78.3[d]	80.0[b]
	silicon adjuvant	73.3[de]	73.3[cd]	73.3[b]
Linuron	–	26.7[ab]	60.0[bcd]	16.7[a]
	paraffin oil	36.7[b]	71.7[cd]	26.7[a]
	silicon adjuvant	16.7[a]	50.0[b]	30.0[a]
Oxyfluorfen	–	80.0[e]	0.0[a]	20.0[a]
	paraffin oil	86.7[e]	53.3[bc]	36.7[a]
	silicon adjuvant	85.0[e]	43.3[b]	30.0[a]
F-ratio		48.05	32.58	18.15
P-value		> 0.0001	> 0.0001	> 0.0001

Means followed by the same letter within the column are not significantly different at $P < 0.05$

tion during April was about 69% higher than the precipitation during April 2015 (Table 1), where the efficacy was less than 75%. Bell et al. (2000) found the efficacy of linuron on *F. convolvulus* to be high in sandy soil with regular irrigation. The efficacy of oxyfluorfen on *F. convolvulus* was not affected by weather conditions and ranged around 85% (Tables 4 and 5). Melo et al. (2010) showed oxyfluorfen to have a greater residual effect in sandy soil compared to clayey soil. In our study, the efficacy of oxyfluorfen was relatively high and stable in both experimental years. Other tested weeds occurred in the experimental field only in one experimental year; therefore, the comparison of herbicide efficacy on these weeds between experimental years was impossible.

Soil adjuvants increased the efficacy of flurochloridone and oxyfluorfen only in the dry conditions observed in April 2015. The efficacy of linuron was not affected by the tested adjuvants in any experimental year. The efficacy of flurochloridone on *F. convolvulus* was significantly improved (by 23%) only by the silicon-based adjuvant (Table 5). The efficacy of flurochloridone on other weeds was not significantly affected by the tested adjuvants. Both the silicon-based and paraffin oil-based adjuvants significantly increased the efficacy of oxyfluorfen on *C. album* only (by 43% and 53%, respectively).

In conclusion, no effect of either tested adjuvant on herbicide leaching or sunflower injury was revealed. The effect of adjuvant on herbicide efficacy was positive only in dry conditions, when the efficacy of flurochloridone on *F. convolvulus* was positively affected by the silicon-based adjuvant. Oxyfluorfen exhibited the highest mobility and lowest dissipation, especially in the year with intensive rainfall after herbicide application.

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