Effect of precipitation on the dissipation, efficacy and selectivity of three chloroacetamide herbicides in sunflower

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ABSTRACT

The aim was to compare the efficacy, selectivity to sunflower and dissipation of three chloracetamide herbicides (acetochlor, metolachlor and pethoxamid) in dependence on precipitation after application. A small plot field trial was carried out with sunflower in Central Bohemia in 2010 and 2011. The remaining concentration of active ingredient in the soil of all studied herbicides was lower in the year with a higher temperature and a low level of total natural precipitation at the beginning of the growing season. Higher leaching of metolachlor and pethoxamid was recorded in irrigated plots. No leaching was found in the case of acetochlor. The highest leaching was found for metolachlor (9.2–25.5% in soil layer 5–10 cm). The highest phytotoxicity was found for acetochlor (9.8%) > pethoxamid (4.6%) > metolachlor (1.8%). The mean phytotoxicity in the irrigated plots was 6.9%, compared with 3.9% in the non-irrigated plots. The efficacy of the tested herbicide was affected by wet conditions. The highest efficacy on *Chenopodium album*, *Amaranthus retroflexus*, *Echinochloa crus-galli* and *Solanum physalifolium* was recorded after application of acetochlor and irrigation.

Keywords: acetochlor; metolachlor; pethoxamid; weed control; phytotoxicity; leaching; *Helianthus annuus*

Most of the herbicides used on sunflower are registered for pre-emergent application. The residual activity of these herbicides ensures control of weed emergence, but the environmental and crop safety risks are higher. The efficacy of pre-emergent herbicides is significantly affected by soil moisture; under dry conditions, their efficacy usually decreases. However, intense precipitation after the application of these herbicides can cause the transport of active ingredients in the soil profile, crop injury and/or leaching (Soukup et al. 2004). Sandy soils, which usually have a lower sorption capacity, have a higher risk of herbicide leaching. However, clay soils are more vulnerable to erosion and runoff (Wischmeier and Mannering 1969). According to Renaud et al. (2004), pesticide leaching is affected mainly by the preferential flow, soil sorption capacity, pesticide half-life and diffusion inside the soil aggregates.

For the pre-emergent control of dicotyledonous weeds in sunflower, active ingredients such as linuron, flurochloridone, oxyfluorfen, pendimethalin, prosulfocarb, bifenox, aclonifen, flumioxazin, chlorbromuron, fenuron, metobromuron and lenacil are used (Vischetti et al. 2002, Pannacci et al. 2007, Nádasy et al. 2008), usually in combination with acetamide herbicides (acetochlor, dimethenamid, pethoxamid, metolachlor, flufenacet, propisochlor and propachlor), which are intended mainly for the control of grass weeds (De Prado et al. 1993, Nádasy et al. 2008).

Acetochlor is still used worldwide, but full restriction of its usage is expected in the near future. The activity of acetochlor in soil decreases with increasing soil organic matter content (Vasilakoglou et al. 2001). A high level of acetochlor leaching causes crop phytotoxicity. Therefore, different safeners (e.g. dichlormid, furilazole) are formulated in ace-

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tochlor herbicides. These safeners increase the metabolisation of acetochlor only in maize cells but not in other crops, so these safeners are inefficient and their phytotoxicity may be high in sunflower.

The metolachlor adsorption in soil is quite high (Bedmar et al. 2011) and increases with soil organic carbon content. The selectivity of metolachlor in sunflower is relatively good and, therefore, may also be used for early post-emergent application (Pannacci et al. 2007), but spectrum of controlled weed is relatively narrow. According to Novak et al. (2001), metolachlor leaching in groundwater proceeds primarily by macropore flow, which is greater in clay soil than in sandy soil, and it occurs mainly during the spring/summer periods. However, Inoue et al. (2010) recorded a more intensive leaching of metolachlor in sandy soils than in clay soils. Metolachlor that has escaped degradation or binding to organic matter on the soil surface may leach into the subsurface soil, where it will dissipate slowly and be subject to transport to groundwater (Si et al. 2009).

Pethoxamid has a relatively good environmental profile and, therefore, is a prospectively useful herbicide after the full restriction of acetochlor (Guennigmann and Rohde 2002). The activity of pethoxamid in the soil depends on the decrease of its concentration in soil water with time, except under conditions of low soil moisture insufficient for seedling growth (Dhareesank et al. 2006).

The aim of this work was to compare the efficacy, selectivity to sunflower and dissipation of three chloracetamide herbicides dependent on precipitation after application.

MATERIAL AND METHODS

A plot field trials were carried out in sunflower (*Helianthus annuus*, hybrid Alexandra) in Central Bohemia (Prague), Central Europe (300 m a.s.l.), in 2010 and 2011. The soil was classified as Haplic Chernozem, with a clay content of 19.3%, a sand content of 24.4%, a silt content of 56.3% (silt loam soil), a soil pH_{KCl} of 7.5 and a sorption capacity of 209 $mmol_{(+)}$/kg. The nutrient content was 87 mg/kg P, 203 mg/kg K, 197 mg/kg Mg, 8073 mg/kg Ca. Winter wheat was the preceding crop in both years. Sunflower was sown on April 7, 2010 and April 4, 2011. The experimental plots were organised in randomised blocks with three replicates, with each plot size 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 *Chenopodium album* (10–80 plants/m^2) in both experimental years. Other weeds species found in the fields at a lower density (4–12 plants/m^2 for individual species) included the following: *Echinochloa crus-galli*, *Amaranthus retroflexus*, *Mercurialis annua*, and *Solanum physalifolium*.

Pre-emergent applications of the herbicides were performed shortly after sunflower sowing (the same day). The herbicides Trophy (768 g/L of acetochlor), Dual Gold 960 EC (960 g/L of S-metolachlor) and Successor 600 (600 g/L of pethoxamid) were used at the recommended rates (acetochlor 2000 g/ha a.i., S-metolachlor 1152 g/ha a.i., pethoxamid 1200 g/ha a.i.). The experiment included untreated control plots. A small-plot sprayer was used to apply the herbicides (application volume 300 L/ha, nozzle Lurmark 015 F 80, application pressure 0.3 MPa). After the emergence of sunflower (cotyledonous leaves – May 1, 2010, April 26, 2011), respectively, half of each plot (10 m^2) was irrigated by the simulator of rain (30 mm), while the other half remained untreated. A description of the meteorological characteristics from sunflower sowing to canopy closing is shown in Table 1.

Determination of the herbicide concentration in soil methanol extracts was performed using an HPLC instrument. The modified method of Kočárek et al. (2010) was used to determine the herbicide concentration in the soil methanol extracts. The detection limit was 0.06 mg/kg for acetochlor,

Table 1. Weather conditions at the beginning of the growing season

Meteorological characteristics		2010	2011
Total natural precipitation (mm)	from sowing to irrigation*	54.8	16.1
	from irrigation to canopy closure**	71.8	19.6
Mean monthly temperature (°C)	April	9.7	11.5
	May	12.2	14.2

*08.04.–01.05. 2010; 07.04.–26.04. 2011; **01.05.–02.06. 2010; 26.04.–08.06. 2011

Table 2. Important properties of the tested herbicides in the environment (source: Footprint database)

		Acetochlor	S-metolachlor	Pethoxamid
Solubility in water at 20°C (mg/L)		282	480	400
GUS leaching potential index		1.77	1.94	1.41
Soil degradation (aerobic)	field DT 50 (days)	12.1	21.0	14.2
	lab at 20°C DT50 (days)	10.6	14.5	6.1
Adsorption strength by Freundlich	K_f	4.50	1.88	1.70
	K_{fOC}	285	226	154

GUS – groundwater ubiquity score; DT 50 – pesticide half-life; K_f – Freundlich adsorption coefficient; K_{fOC} – Freundlich organic carbon adsorption coefficient

0.05 mg/kg for metolachlor and 0.015 mg/kg for pethoxamid. The amount of herbicides present in the soil extracts was expressed as the total amount of solute per mass unit (mg/kg). The total herbicide amount in soil was calculated using a soil bulk density of 1.4 g/cm^3 and 1.6 g/cm^3 in the 0–5 cm and 5–10 cm soil layers, respectively. Because of different application rates of the studied

Table 3. Sunflower injury after application of the tested herbicides and concentrations of used herbicides in two soil layers one week after irrigation dependent on the used herbicides, irrigation and experimental years

Factor	Phytotoxicity (%) sunflower		Concentration of herbicides in soil (mg/kg) soil depth	
	BBCH 14	BBCH 32	0–5 cm	5–10 cm
Effect of used herbicides				
Acetochlor	5.7^b	9.8^b	1.157^c	0.000^a
Metolachlor	1.3^a	1.8^a	0.893^b	0.118^b
Pethoxamid	0.0^a	4.6^a	0.461^a	0.020^a
$LSD_{0.05}$	2.3	3.1	0.194	0.052
F	14.00	14.77	27.29	12.15
P	0.0000	0.0000	0.0000	0.0001
Effect of irrigation				
Non-irrigated	1.0^a	3.9^a	0.966^b	0.025^a
30 mm of irrigation	3.6^b	6.9^b	0.709^a	0.066^a
$LSD_{0.05}$	1.9	2.5	0.158	0.042
F	8.08	6.26	10.92	3.87
P	0.0079	0.0178	0.0024	0.0582
Effect of years				
2010	2.8^a	8.4^b	0.998^b	0.072^b
2011	1.8^a	2.4^a	0.677^a	0.020^a
$LSD_{0.05}$	1.9	2.5	0.158	0.043
F	1.06	24.58	17.10	6.18
P	0.3119	0.0000	0.0003	0.0185

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

herbicides, the percentage of remaining pesticide (related to the application rate) in the soil layers was used to compare pesticide leaching. Important environmental characteristics of the tested herbicides are described in Table 2.

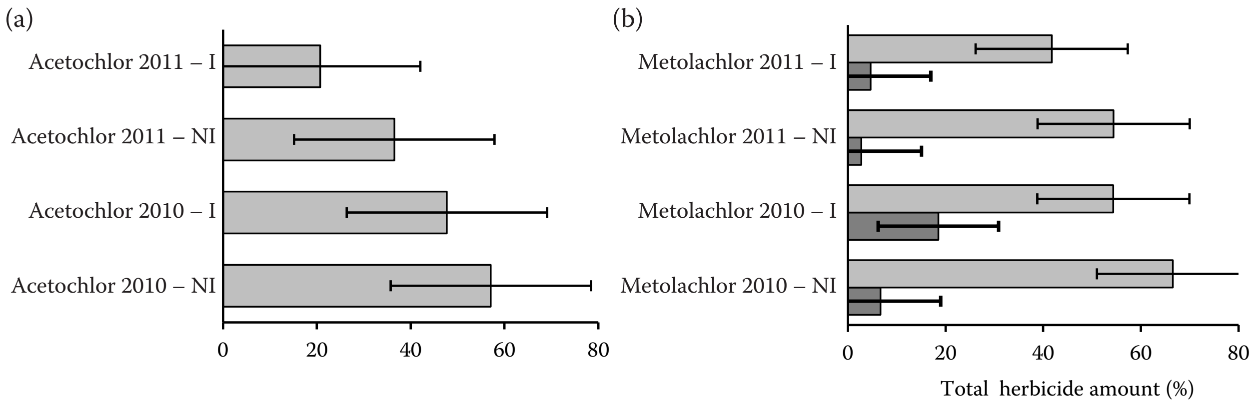
The herbicide efficacy was assessed by the estimation method using a percentage scale from 0% to 100% (0% = untreated, 100% = full control) according to the European and Mediterranean Plant Protection Organisation (EPPO) 1/63 (3) guidelines. The first assessment was performed shortly after weed emergence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

The experimental data were evaluated using the software package Statgraphics Plus 4.0. (Statpoint, Inc., Herndon, USA) A one-way ANOVA was used. The contrasts between treatments were verified by the *LSD* test ($P < 0.05$).

RESULTS AND DISCUSSION

Herbicide dissipation from soil. The dissipation of herbicides was affected by all tested factors – used herbicide, irrigation and experimental years (Table 3). The remaining concentration of active ingredient of all studied herbicides detected in the soil samples was lower in 2011 than in 2010. The irrigated plots had a lower amount of remaining active ingredients compared with the non-irrigated plots, except for metolachlor in 2010 (the metolachlor amount in both 0–5 cm layers was similar, but the higher in layer 5–10 cm in the irrigated plots) and by higher leaching (except for non-leached acetochlor). The irrigated plots also had higher amounts of active ingredients in the 5–10 cm soil layer compared with the non-irrigated plots (except for acetochlor).

No leaching was found in the case of acetochlor (Figure 1a). Acetochlor (the herbicide with the lowest water solubility of the studied herbicides – Table 2) was detected only in the upper soil layer in both experimental years and in both irrigated and non-irrigated treatments. A significant difference ($P = 0.0136$) was found in the total amount of acetochlor in the upper soil layer (0–5 cm) between the irrigated and non-irrigated treatments in 2011; that year it was a very dry condition (Table 2). A similar low leaching of acetochlor in sandy loam soil and its strong adsorption in the upper soil layer was described by Ma et al. (2000).



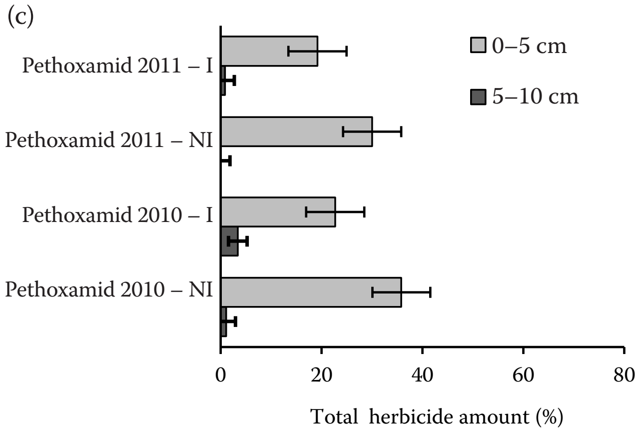


Figure 1. Percentage of (a) total acetochlor amount in the 0–5 cm; (b) metolachlor amount in the 0–5 cm and 5–10 cm, and (c) pethoxamid amount in the 0–5 cm and 5–10 cm soil layer one week after herbicide application in both irrigated (I) and non-irrigated (NI) treatments, error bars indicate significant differences ($LSD_{0.05}$)

Table 4. Efficacy (%) of the tested herbicides shortly before the sunflower canopy closed the rows dependent on used herbicides, irrigation and experimental years

	Echinochloa crus-galli	*Amaranthus retroflexus*	*Chenopodium album*	*Mercurialis annua*	*Solanum physalifolium*
Effect of used herbicides					
Acetochlor	97^{b}	99^{b}	79^{b}	34^{a}	95^{b}
Metolachlor	94^{ab}	95^{ab}	41^{a}	24^{a}	60^{a}
Pethoxamid	91^{a}	94^{a}	59^{a}	23^{a}	73^{a}
$LSD_{0.05}$	5	4	19	22	14
F	2.66	3.22	8.11	0.62	12.70
P	0.0857	0.0535	0.0015	0.5462	0.0001
Effect of irrigation					
Non-irrigated	93^{a}	95^{a}	51^{a}	13^{a}	66^{a}
30 mm of irrigation	95^{a}	97^{a}	68^{a}	41^{b}	86^{b}
$LSD_{0.05}$	4	4	16	18	12
F	1.21	2.72	5.51	9.88	12.48
P	0.2806	0.1093	0.0254	0.0037	0.0013
Effect of years					
2010	98^{b}	99^{b}	74^{b}	28^{a}	91^{b}
2011	90^{a}	93^{a}	46^{a}	26^{a}	61^{a}
$LSD_{0.05}$	4	4	16	18	12
F	14.11	11.72	12.79	0.08	28.07
P	0.0007	0.0018	0.0012	0.7813	0.0000

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

The highest leaching was found for metolachlor (Figure 1b). Metolachlor was detected in the 5–10 cm soil layer in both years and in both the irrigated and non-irrigated treatment. In 2010, the total metolachlor amount in tested soil layers was quite similar (73%). However, 25.5% of the metolachlor was found in the 5–10 cm soil layer in the irrigated plots, and 9.2% of the metolachlor was found in the 5–10 cm soil layer in the non-irrigated plots. In 2011, the total metolachlor amount in tested soil layers was lower (46% in irrigated and 57% in non-irrigated plots). These results are in agreement with other authors, who describe metolachlor as more persistent than other acetamide herbicides in the environment and as having a greater potential to leach into groundwater (Mueller et al. 1999, Si et al. 2009). The leaching of metolachlor in the soil is relatively high compared with other acetamides (Vasilakoglou et al. 2001).

From the studied herbicides, pethoxamid has a medium level of leaching (Figure 1c). No leaching was found in the non-irrigated plots in 2011. The highest leaching was observed in the irrigated plots in 2010, where 13% of the pethoxamid was found in the 5–10 cm soil layer. The highest total differences in pethoxamid amount (P = 0.0007) were recorded between irrigated and non-irrigated treatments. These results are in contrast to the results of Dhareesank et al. (2006). They found a similar pethoxamid concentration decrease in both the liquid and solid soil phases under different soil moisture conditions.

Efficacy. Efficacy on the tested weeds was affected by the used herbicide (except *M. annua*), irrigation (only *M. annua* and *S. physalifolium*) and the weather conditions in both experimental years (except *M. annua*) (Table 4). The highest efficacy on all tested weeds was recorded after the application of acetochlor on irrigated plots. This efficacy was evident especially in the dry spring of 2011, when total natural precipitation at the beginning of the growing season (from sowing to canopy closure) was only 35.7 mm, i.e., 28% of the 2010 season (Table 1). Therefore, the dif-

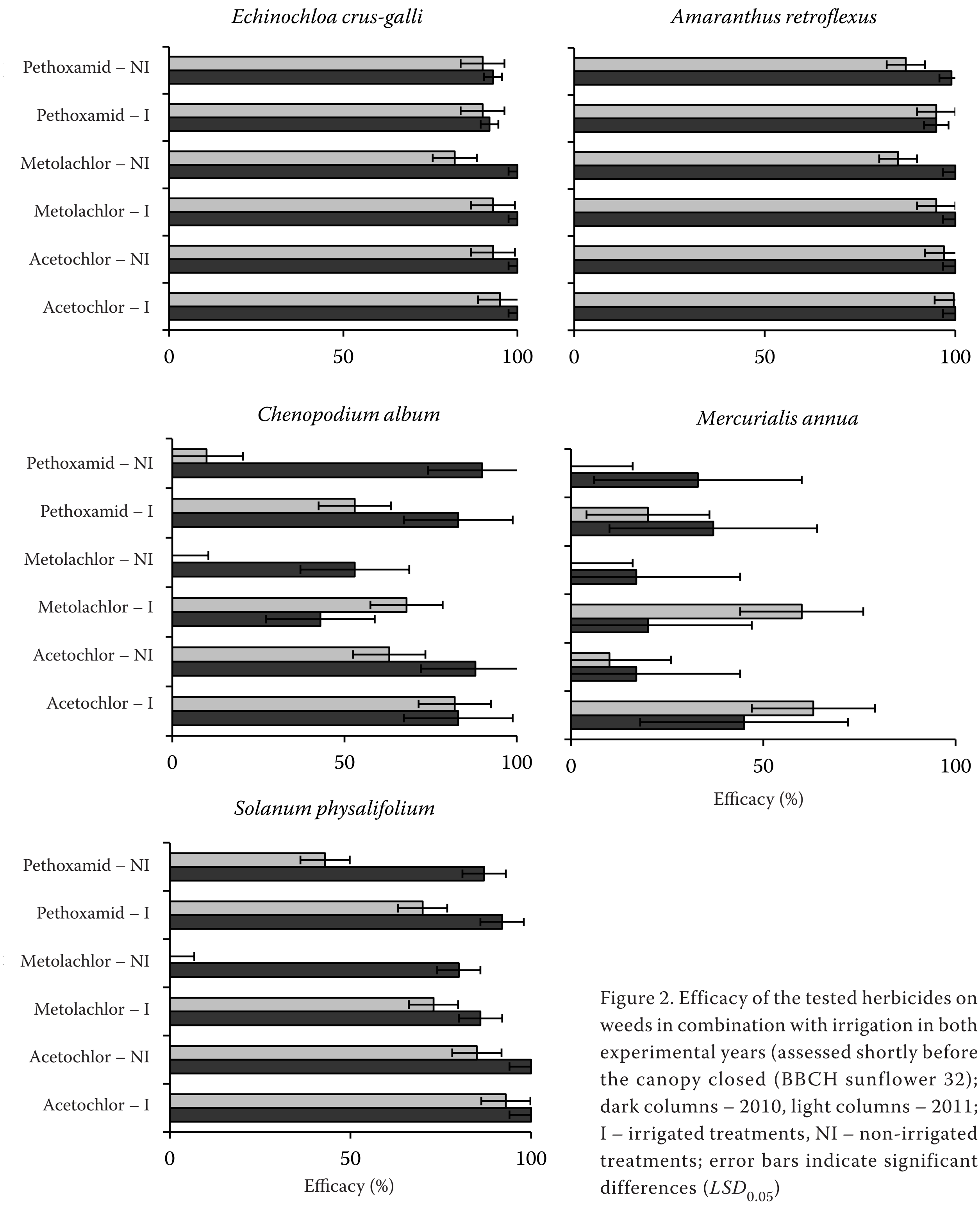


Figure 2. Efficacy of the tested herbicides on weeds in combination with irrigation in both experimental years (assessed shortly before the canopy closed (BBCH sunflower 32); dark columns – 2010, light columns – 2011; I – irrigated treatments, NI – non-irrigated treatments; error bars indicate significant differences ($LSD_{0.05}$)

ferences in herbicide efficacy between irrigated and non-irrigated treatments were higher in 2011. Nagy (2008) found that at least 14 mm of rainfall is required during the first two weeks after application for the optimal activation of acetochlor.

The weeds most sensitive to the tested herbicides were *E. crus-galli* and *A. retroflexus*. The efficacy of all the tested herbicides on these weeds was higher than 90% (Figure 2). In 2010, acetochlor and metolachlor fully controlled these weeds (total amount

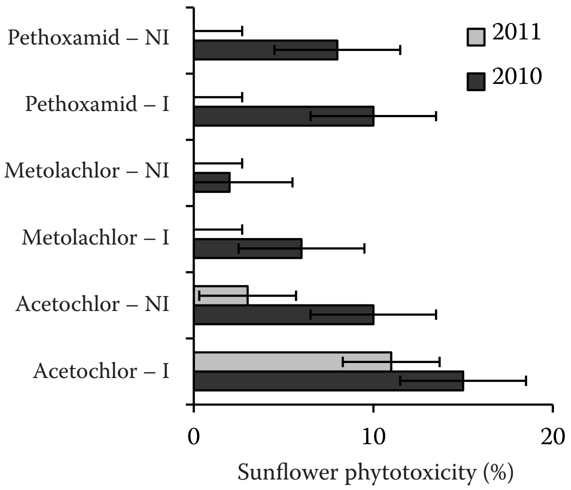


Figure 3. Sunflower injury in both experimental years, assessed shortly before canopy closed; I – irrigated treatments, NI – non-irrigated treatments; error bars indicate significant differences ($LSD_{0.05}$)

of both active ingredients in tested soil layer was nearly 30% higher than in 2011). *M. annua* was not satisfactorily controlled by any herbicide and irrigation treatment (Table 4). Similar efficacy of acetochlor and metolachlor was found by Mueller and Steckel (2011). *S. physalifolium* was satisfactory controlled (efficacy 95%) only by acetochlor. *C. album* was satisfactory controlled (efficacy above 85%) only by acetochlor and pethoxamid with a high level of precipitation (Figure 2).

Sunflower injury. Sunflower injury caused by herbicide phytotoxicity was influenced by all tested factors: the herbicides, irrigation and experimental years (Table 3). Sunflower very slowly regenerated and sunflower injury was recorded shortly before canopy closure, especially in the irrigated plots. Higher sunflower injury was recorded in 2010 when a high level of total natural precipitation was recorded and when a higher total amount of acetochlor and metolachlor was detected in tested soil layers. The main symptom of phytotoxicity was growth retardation, and, in case of acetochlor, stem shortening of first two internodes was recorded. The highest phytotoxicity was found for acetochlor (9.8%) > pethoxamid (4.6%) > metolachlor (1.8%). Sunflower was injured by metolachlor and pethoxamid only in 2010, when a high level of total natural precipitation was recorded at the beginning of the growing season (Table 1, Figure 3). The mean phytotoxicity in the irrigated plots was 3.6%, resp. 6.9% (first, resp. second assessment), compared with 1.0%, resp. 3.9%, in the non-irrigated plots (Table 3). The effect of irrigation on sunflower phytotoxicity was significant only for acetochlor in 2011 (Figure 3).

In conclusion, efficacy of acetochlor was not significantly affected by soil moisture and can be recommended for arid and semiarid crop areas. In humid area, acetochlor can cause injury of sunflower, especially in cases when intensive precipitation and/or irrigation are often at the beginning of growing season. On the contrary, efficacy of pethoxamid was strongly affected by soil moisture, and in dry conditions, the efficacy of these herbicides was insufficient. The pethoxamid showed good selectivity to sunflower and acceptable dissipation in soil and therefore can be recommended for areas with intensive precipitation or irrigation at the beginning of growing season.

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