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Scientific paper

Thermodynamic Characterisation of Early Phytotoxic Effects of Sulfonylurea Herbicides to Maize Lines

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SUMMARY

Variations in susceptibility of maize lines to herbicides depend on different factors. Visible signs of phytotoxicity do not occur in the first few days after application when plants are tolerant to some herbicides. The aim of our experiment was to study susceptibility of 16 ZP lines to nicosulfuron and foramsulfuron 48 hours after application in the 2006-2009 period. The alterations in dry matter content, as well as thermodynamic parameters of free energy and enthalpy, were analyzed. The examined parameters show that season had a significant influence on phytotoxicity expression, with high EWRC values obtained together with high values of free energy and dry matter during the cold season with lower precipitation level (period after herbicide application). In susceptible lines, the phytotoxic effect induced an increase in dry matter and free energy. Phytotoxic effects of nicosulfuron and foramsulfuron have basically different impact on system energetic properties: the effects of nicosulfuron could be connected to greater energy consumption, and the effects of foramsulfuron to increasing potential energy, mainly from metabolism, which could be associated with a "metabolic burst". From that point of view, the examined parameters can be successfully used as indicators of herbicide stress immediately after application.

Keywords: Nicosulfuron; Herbicides; Phytotoxicity; Thermodynamics; Energy

INTRODUCTION

The application of herbicides in maize seed crops is difficult due to a reduced tolerance of some maize lines to different herbicides. On the other side, lagging in growth of different lines is connected to their lower competitiveness under high weed infestation. According to Ostojić et al. (1995), maize lines are susceptible to different herbicides as a result of their low vigor, slower growth and smaller habitus. Seed crop susceptibility depends highly on environmental conditions. Bonis et al. (2006) have pointed at a greater phytotoxic damage under cool and wet weather, which retarded the metabolic processes of maize. The intensity of phytotoxic response can be strong in sensitive lines, leading to their drying and dying, while lines of slighter sensitivity have been observed to recover after some time (Stefanović and Simić, 2008). It is important to test the reaction of every line to new herbicides, which will improve the technological process of seed production.

Weed control became more efficient when sulfonylurea herbicides were introduced (Foy and Witt, 1990). Efficient and safe application of sulfonylurea herbicides has lately been reduced in some maize lines because of their different responses (Stefanović et al., 2000). Tolerance to sulfonylurea herbicides is not always beneficial for plant metabolism, but other factors can also contribute to different degrees of selectivity expression.

According to de Carvalho et al. (2009), energy disposal in a susceptible plant treated with a herbicide with partial selectivity occurs through processes of rapid metabolization of a part of herbicide molecules and a recovery from damages caused by molecules that reached the herbicide site of action. Even considering that the energy used in metabolic processes of detoxification is naturally available and does not cause loss to crop yield, the energy for recovering the damaged structures (phytotoxicity) may not be considered as a natural physiological response in a way that plant recovery can result in a larger or smaller yield loss. Nemeny (2009) has emphasized that stress in an agro-ecological system (maximum energy input) can be calculated and quantified by thermodynamics.

Living systems transform energy and matter during metabolism, which can be described as a controlled capacity to transform energy under the First Law of Thermodynamics. Nevertheless, energy transformation includes a loss of some free energy as heat under the Second Law of Thermodynamics (Dragicevic and Sredojevic, 2011). The energy concept of growth processes could be applied to water in plant tissues. Boyer (1969), Manz et al. (2005) and Kikuchi et al. (2006) have quantified water transport into plant as energy input. In living systems, the largest energy flow by water has been enabled through the soil-plant-atmosphere continuum (Yeo and Flowers, 2007). Recently, Sun (2002) recognized free energy input by water as a presumable factor of plant growth. According to the Hess Law, free energy is cumulative, irrespective of its origin; hence, all the potential energy present in a plant system is given as the sum of individual energy states resulting from a double-phase shifting of water and that released from metabolic reactions.

Opposite to free energy, enthalpy is a measure of total energy of a system. From that point of view, enthalpy represents a thermodynamic potential. Total enthalpy of a system cannot be measured directly, it is estimated by a change in enthalpy, which is a more useful quantity than its absolute value. The change of enthalpy is positive in endothermic reactions, and negative in heat-releasing exothermic processes. It is important to emphasize that the domination of exothermic reactions (Davies, 1961; Sun, 2002) is important for realisation of the energy necessary for all biological processes, and the more intensive they are, the greater is the growth potential of the system.

The objective of this study was to investigate variations in dry matter and thermodynamic parameters (free energy and enthalpy) 48 hours after application of two sulfonylurea herbicides and to correlate signs of phytotoxic effects (EWRC evaluation, 21 days after herbicide application) with alterations in dry matter and thermodynamic parameters in 16 ZP lines in order to determine the sensitivity of individual lines and potential tolerance patterns.

MATERIAL AND METHODS

An experiment was conducted in the field of the Maize Research Institute at Zemun Polje during 2006-2009 on a slightly calcareous chernozem type of soil under rain-fed conditions. The effect of nicosulfuron and foramsulfuron on 16 ZP lines 48 hours after application was estimated. The experiment was conducted as a randomised block complete design with four replications: the main plots included 4 rows for each line, while subplots included the two herbicide treatments and control (no herbicide application).

Sowing was performed on April 29, 2006, April 18, 2007 and April 12, 2008, while the herbicides were applied at the 4-6 leaf stage: nicosulfuron (Motivell) at a rate of 50 g ha^{-1}a.i., and foramsulfuron (Equip) at a rate of 50.0 g ha^{-1}a.i. Fourty-eight hours after herbicide application, plant shoots were collected (4x5), weighted and dried at 105°C for dry matter (DM) determination. The difference between dry and fresh matter included contents of free and bulk water, which was used for calculating thermodynamic parameters by using the sorption isotherm (Davies,1961; Sun, 2002):

$$\Delta H = \frac{RT_1T_2}{T2-T1}\ln\left(\frac{a_{w1}}{a_{w2}}\right) \qquad [1]$$

$$\Delta G = RT\ln(a_w) \qquad [2]$$

where, at a given tissue water content:

a_{w1} and a_{w2} are the relative water contents at the lower and higher temperatures,

T_1 and T_2, respectively,

ΔH is the differential enthalpy of hydration,

ΔG is the differential free energy,

R is the gas constant (8.3145 J mol^{-1} K^{-1}).

Table 1. Average monthly temperatures and precipitation during April and May of 2006, 2007, 2008 and 2009

	Temperature (°C)					Precipitation (mm)				
Month	2006	2007	2008	2009	Aver.	2006	2007	2008	2009	Aver.
April	13.4	13.8	14.1	15.8	14.3	19.4	11.0	27.3	7.3	16.3
May	16.9	18.9	19.3	19.8	18.7	15.2	52.6	39.7	27.4	33.7
Mean/Sum.	15.2	16.4	16.7	17.8		34.6	63.6	67.0	34.7	

Phytotoxicity evaluation of maize plants was conducted 21 days after herbicide application, as recommended by the European Weed Research Council (EWRC) (Feldfersuche, 1975).

The experimental data were statistically processed by the ANOVA, the LSD-test (5 %) and regression analysis.

Meteorological conditions. The study was performed during the starting period of maize vegetation, i.e. April-May (Table 1). The average temperature had an increasing trend in April and May of 2006 through 2009 (13.4-15.8 and 16.9-19.8 °C, respectively). On the other hand, precipitation was higher in 2007 and 2008 (almost double against 2006 and 2009).

RESULTS AND DISCUSSION

The obtained results show that significant differences in average DM contents of maize shoots existed only at annual level, and in the interaction between year, herbicide and line (Table 2). Significantly higher DM values were noticed mainly under the influence of

Table 2. Average dry matter content in maize shoots (48 h after application of herbicides) and EWRC values (20 days after application of herbicides)

	Dry matter (%)				Phytotoxicity (2006-2008)		
	Control	Nicosulfuron	Foramsulfuron	Mean	Nicosulfuron	Foramsulfuron	Mean
Line	Average for examined years						
L1	13.99	14.33	15.53	14.62	4.11	5.94	5.03
L2	14.36	13.97	14.19	14.17	1.56	1.83	1.69
L3	14.08	13.38	14.60	14.02	1.28	1.94	1.61
L4	14.75	16.53	14.72	15.33	1.28	1.78	1.53
L5	15.10	17.34	14.55	15.66	1.44	1.78	1.61
L6	13.52	15.92	13.39	14.28	2.06	2.39	2.22
L7	13.42	10.77	13.62	12.60	1.67	1.78	1.72
L8	12.90	12.80	16.27	13.99	1.94	1.78	1.86
L9	14.40	13.40	12.28	13.36	1.78	2.17	1.97
L10	14.66	14.28	14.89	14.61	1.33	1.72	1.53
L11	14.42	14.38	15.47	14.76	1.61	1.72	1.67
L12	14.77	14.54	14.38	14.56	2.06	2.28	2.17
L13	12.96	13.72	14.07	13.58	1.89	1.94	1.92
L14	13.44	12.90	13.53	13.29	1.56	1.78	1.67
L15	13.29	15.05	14.01	14.12	2.22	2.22	2.22
L16	14.71	13.05	13.11	13.62	1.56	2.06	1.81
Year	Average for examined lines						
2006	18.20	20.57	20.78	19.85	2.35	2.46	2.41
2007	11.46	11.65	11.84	11.65	1.75	1.83	1.79
2008	13.37	12.30	13.00	12.89	1.40	2.29	1.84
2009	13.17	12.07	11.54	12.26	–	–	–
Mean	14.05	14.15	14.29		1.83	2.19	
LSD 0.05	Genotype		4.59			0.75	
	Herbicide		4.47			1.06	
	Year		2.62			1.04	
	Genotype X Herbicide		5.12			0.77	
	Year X Herbicide		2.57			1.02	

nicosulfuron in L4, L5 and L6 shoots. The highest DM values were obtained in 2006, as a result of lower temperature and precipitation at the time of herbicide application. Sacala et al (2003) also reported that lower rates of rimsulfuron induced DM increase, while stress induced by simultaneous herbicide effect and salinity decreased DM equally to the simultaneous influence of herbicide and meteorological conditions. The highest difference in DM values between control and herbicide treatment present in the L1 foramsulfuron treatment and L15 nicosulfuron treatment could indicate desiccation induced by herbicide stress (Stefanović and Simić, 2008). Moreover, the high DM average in the L1 plot identified it as the most sensitive line, according to the highest average phytotoxicity values present during the period 2006-2008. Besides L1, significantly higher average phytotoxicity (EWRC) values were noticed in L12 and L15 plots under the effect of both herbicides than they were in all other examined lines. Year also had significant influence on phytotoxicity expression, its values were significantly higher in 2006 than in the other years. In 2009, signs of herbicide phytotoxicity were not present in the experimental field. Regardless of the low precipitation during the April-May period of that year, May can be considered as a month of moderate precipitation, which could have resulted in a higher stress tolerance of the examined inbreds.

According to the results shown in Table 3, positive values of free energy and negative values of enthalpy indicate that the resultant of all chemical reactions in maize lines were endergonic (not spontaneous) and exothermic. Moreover, only L1 expressed significantly higher averages of free energy, compared to all other lines, while the interaction between genotype and herbicide highlighted L10 and L12 as the genotypes with significantly higher values of free energy in control and both herbicide treatments.

Table 3. Average free energy (ΔG) and enthalpy (ΔH) in maize shoots (48 h after application of herbicides)

	ΔG ($J\ mol^{-1}$)				ΔH ($J\ mol^{-1}$)			
	Control	Nicosulf.	Foramsulf.	Mean	Control	Nicosulf.	Foramsulf.	Mean
Line	Average for examined years							
L1	0.38	0.42	0.45	0.42	-6.00	-6.51	-6.31	-6.27
L2	0.40	0.41	0.38	0.39	-5.49	-7.18	-6.52	-6.40
L3	0.40	0.39	0.42	0.40	-6.28	-6.63	-6.42	-6.44
L4	0.37	0.44	0.38	0.40	-5.42	-5.87	-8.38	-6.56
L5	0.36	0.45	0.37	0.39	-5.15	-5.86	-5.24	-5.42
L6	0.35	0.39	0.37	0.37	-5.82	-5.55	-5.63	-5.67
L7	0.36	0.33	0.39	0.36	-5.93	-7.17	-6.66	-6.58
L8	0.38	0.35	0.43	0.39	-6.51	-5.52	-5.94	-5.99
L9	0.36	0.39	0.36	0.37	-5.59	-6.99	-6.29	-6.29
L10	0.42	0.40	0.42	0.41	-5.86	-6.24	-5.97	-6.02
L11	0.37	0.38	0.42	0.39	-4.74	-5.18	-5.25	-5.06
L12	0.41	0.41	0.41	0.41	-5.38	-6.17	-5.66	-5.74
L13	0.39	0.39	0.39	0.39	-6.77	-6.25	-5.92	-6.31
L14	0.40	0.36	0.38	0.38	-6.26	-6.09	-6.43	-6.26
L15	0.39	0.39	0.39	0.39	-6.76	-5.48	-6.26	-6.17
L16	0.44	0.38	0.40	0.41	-6.31	-6.62	-7.64	-6.85
Year	Average for examined lines							
2006	0.39	0.46	0.46	0.44	-2.71	-2.71	-2.59	-2.67
2007	0.36	0.36	0.37	0.36	-7.79	-7.85	-8.14	-7.92
2008	0.42	0.38	0.40	0.40	-7.55	-7.40	-7.19	-7.38
2009	0.38	0.37	0.35	0.37	-5.52	-6.88	-7.20	-6.53
Mean	0.39	0.39	0.40		-5.89	-6.21	-6.28	
LSD 0.05		Genotype		0.06				2.78
		Herbicide		0.06				2.68
		Year		0.06				1.22
		Genotype X Herbicide		0.07				3.12
		Year X Herbicide		0.05				1.24

This means that much of the system potential energy was metabolically consumed (Dragicevic and Sredojevic, 2011). Concerning the factor of year, we should mention that environmental factors increased the average ΔG values only in 2006, while the interaction between year and herbicide treatment pointed at higher average ΔG values in control and foramsulfuron treatment in 2008, and particularly in both herbicide treatments in 2006. Opposite to free energy, the values of enthalpy, as a measure of total energy in a system, did not vary significantly between treatments and lines. The only difference was observed under the influence of environmental factors, the highest significant values being recorded in 2006 (indicating a domination of endothermic processes) and the lowest significant values in 2007 (indicating a domination of exothermic processes). The interaction between year and applied herbicide introduced significantly lower ΔH values under the influence of nicosulfuron in 2007- 2009, and under the influence of foramsulfuron in the same years.

Regardless of generally insignificant variations in DM, ΔG and ΔH values for shoots of the examined lines and both herbicide treatments, a significant correlation was found between these three factors and phytotoxicity values (Figure 1). In nicosulfuron treatment, a significant and positive correlation was

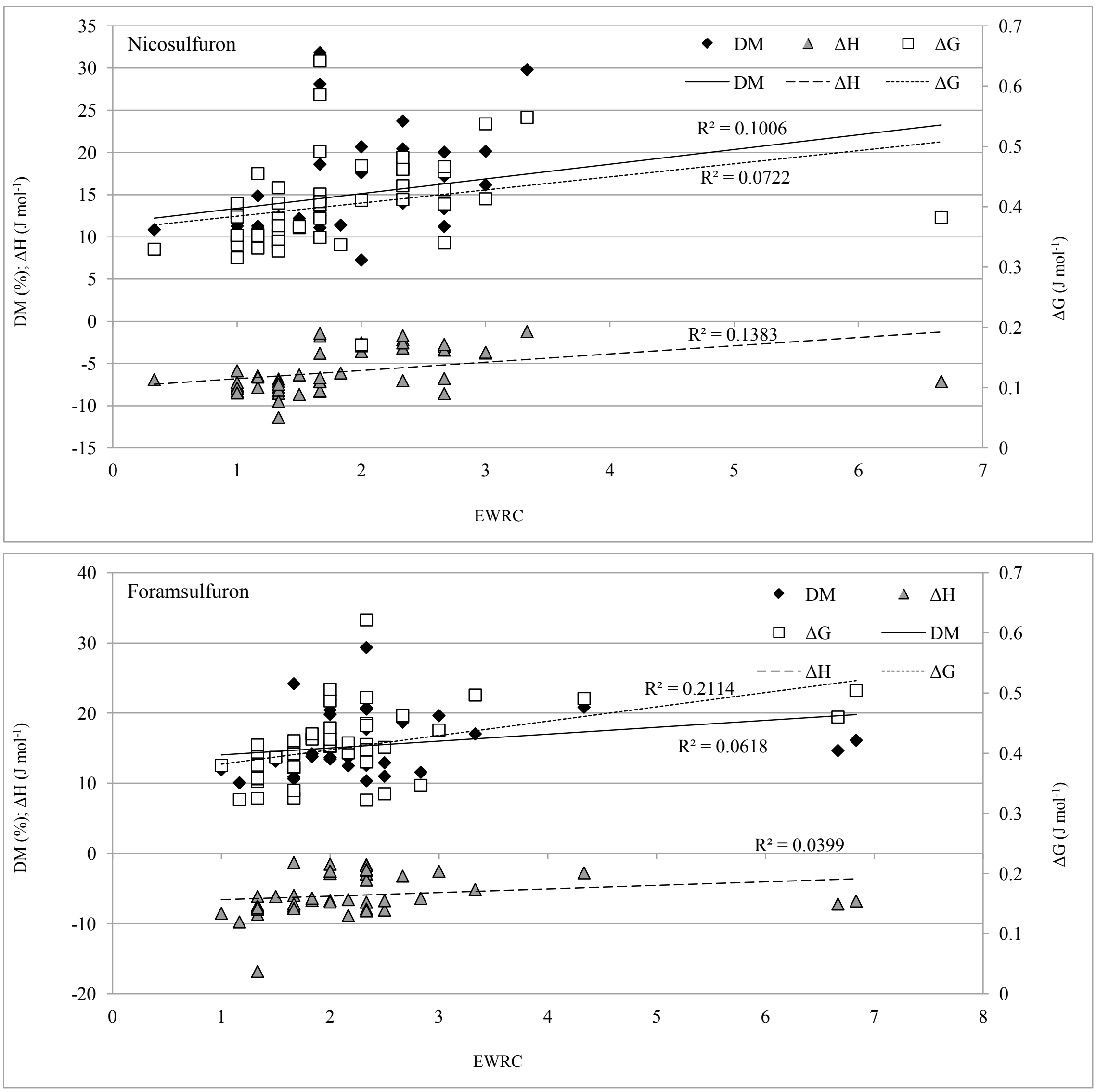

Figure 1. Correlation between phytotoxicity values, dry matter content (DM), free energy (ΔG) and enthalpy (ΔH), influenced by nicosulfuron and foramsulfuron

observed between phytotoxicity and DM increase, as well as ΔH, indicating desiccation combined with a domination of endothermic reaction (Davies 1961; Sun, 2002) as a possible impact of this herbicide. On the other hand, a significant and positive correlation was observed in foramsulfuron treatment between phytotoxicity and ΔG, indicating an increase in potential energy, which is necessary for growth. Such energy shift may be the result of higher water inputs, known as a "water induced growth" (Boyer, 1969) or domination of exothermic reactions (Davies, 1961; Sun, 2002) giving greater potential to a system's growth. But, considering also the increase in DM values (Table 2), the mentioned ΔG increase becomes mainly connected to changes in metabolism intensity and rate, and to a lesser extent to additional water input, which was particularly evident during 2006, the year of the lowest precipitation (Table 1).

The obtained results indicate that phytotoxic effects of nicosulfuron and foramsulfuron basically have different impact on system energetic properties: the effects of nicosulfuron can be mainly associated with greater consumption of energy present in the system, while the effects of foramsulfuron are related to increased potential energy, primarily by water input and mainly from metabolism that could be connected to "metabolic burst". From this point of view, thermodynamic parameters could be a useful tool in early determination of injuries induced by herbicide stress. The expression of the observed phytotoxic effects depends mainly on meteorological factors present during the period of herbicide application and the following few weeks.

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Termodinamička karakterizacija ranih efekata fitotoksičnosti sulfonilurea herbicida kod linija kukuruza

REZIME

Variranja osetljivosti linija kukuruza na herbicide zavise od različitih faktora. Prvi znaci fitotoksičnosti, odnosno tolerantnosti na neke herbicide mogu biti prisutni već tokom prvih dana nakon primene herbicida, dok još nisu ispoljeni vidljivi znaci. Cilj rada je bio da se ispita osetljivost 16 ZP linija kukuruza na nikosulfuron i foramsulfuron, 48 sati nakon njihove primene tokom 2006-2009. godine. Analizirane su promene sadržaja suve materije, kao i termodinamičkih parametara tj. slobodne energije i entalpije. Ispitivani parametri su pokazali da sezona ima značajan uticaj na ispoljavanje fitotoksičnosti. Visoke vrednosti fitotoksičnosti su dobijene paralelno sa visokim vrednostima slobodne energije i suve materije tokom hladne sezone sa nižim nivoom padavina u periodu nakon primene herbicida. Fitotoksični efekti su kod osetljivih linija doveli do povećanja suve materije i slobodne energije. Fitotoksični efekti nikosulfurona i foramsulfurona su se suštinski drugačije ispoljili na energetske karakteristike sistema: efekti nikosulfurona bi mogli biti vezani za veću potrošnju energije, dok bi efekti foramsulfurona mogli biti vezani za povećanje energetskog potencijala, uglavnom preko metabolizma, što bi moglo da ukazuje na „metaboličku eksploziju". Sa te tačke gledišta, ispitivani parametri bi mogli uspešno da se koriste kao indikatori stresa izazvanog herbicidima, neposredno nakon njihove primene.

Ključne reči: Nikosulfuron; herbicidi; fitotoksičnost; termodinamika; energija