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# Brief Approach of Herbicide Resistance in Context of Crops Development Worldwide

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# 1. Introduction

The review aims to emphasize the state of art of herbicide resistance mechanisms in weeds, when ourdays realities confront us with crop productions in continuous expansion in EU and worldwide. Regarding sustainable agriculture and plant biodiversity maintenance as premise for successful development in the future, the virtual environmental threat produced by a large diversity of herbicides in use appears as entitled concern. This reality is exacerbated by another phenomenon: the development of herbicide resistant weeds reported more and more often in last four decades. In this way, even herbicides still represent the most important and effective tool in controlling weeds, in many areas, their field value decreased. The alteration produced, often as punctiform mutations, in weed genotypes in order to counteract the herbicide attacks, led to development of resistant weed biotypes that may produce huge harmful environmental effects, besides yield loss. One of the most important reasons of this phenomenon is represented by administering the same herbicide for many years to the same culture in the same cultivation field. The situation is aggravated when the herbicide has only one site of action in herbicide genome (Sigematsu et al., 1989; Kremer et al., 1999; Owen et al., 2005; Powels et al., 2010). This underlines the importance of obtaining a better understanding of the mechanism that represents the basis of resistance, in order to successful fighting against this phenomenon. It was elucidated by emphasizing the biochemical processes and genetic mechanisms that occur in plant in order to develop defending mechanisms. The genetic processes involved in weed genome react to environmental stimuli, as the attack of active principle from herbicides. Usually, the gene/genes that metabolize the active substance/substances from the herbicide are naturally multiplied of several hundred times, compared to the genotype of a plant that is not resistant. Now, gene amplification is one of the well known mechanisms of resistance against herbicides (Vila-Aiub et al., 2003; Oroian, I., 2008; Ge et al., 2010).

These mechanisms once understood can be counteracted by suitable measures taken at different levels. Some of the most important crop management strategies that could contribute to reduce the appearance and/or decrease of the frequency of this phenomenon consist in: using herbicides only when necessary, rotate crops and herbicides site of action, using combined herbicide administration system, combine mechanical weed control with chemical treatment (Paoletti et al., 1995; Berca M., 2007).

## 2. The development of crop production in EU and world

The production of the **most important cultures** according to the importance of their place in human society is presented, in order to underline the importance of the weed resistance control in these plants. The cultivated area in both EU and the world is also emphasized.



**The wheat** (Kingd. *Plantae*, Ord. *Poales*, Fam. Poaceae; *Triticum spp.*) orginary from the Near East is the main human food crop. According to FAO last updating (December 2008), the greatest production was obtained in 2008 in EU and the same orientation was reported by entire world (Fig. 1.a). The area harvested was bigger in 2008 compared to former year, but lower compared to year 2000, and 2002 when the biggest area was wheat cultivated in EU, while in 2008 was recorded the biggest area cultivated worldwide (Table 1).

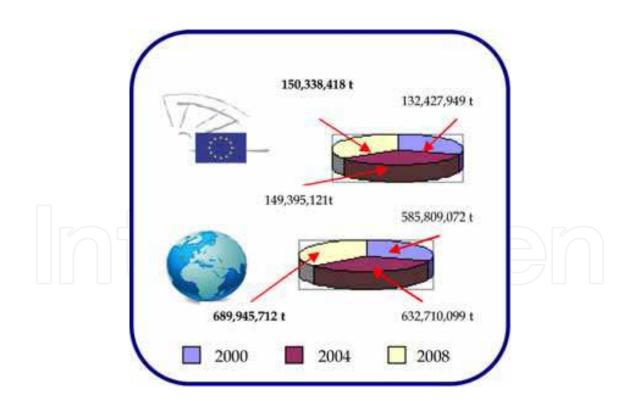


Fig. 1. a. The wheat production in EU and in the world in three reference years of the last decade



**The barley** (Kingd. *Plantae*, Ord. *Poales*, Fam. Poaceae; *Hordeum vulgare*) was cultivated from the second millennium b.Ch. in Mesopotamia. It is a cereal grain of major importance as animal fodder. According to FAO (December 2008), the greatest production was obtained in 2008 in EU and the same orientation was reported by entire world (Fig. 1.b). The area harvested was bigger in 2008 compared to 2000, while in EU increased in 2004 compared to 2000, and the same tendency was recorded worldwide, since 2004 when the biggest value was recorded (Table 1).

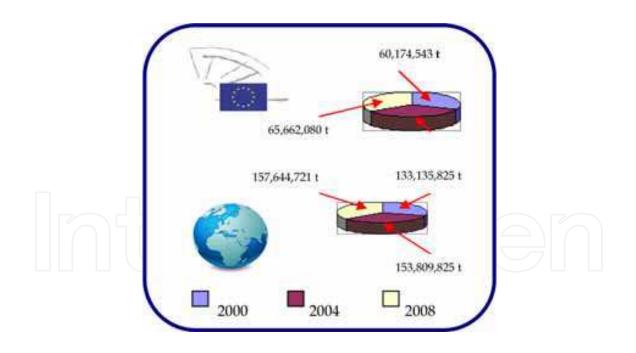


Fig. 1.b. The barley production in EU and in the world in three reference years of the last decade



**The oats** (Kingd. *Plantae*, Ord. *Poales*, Fam. Poaceae; *Avena sativa*), similarly to barley, has the most common use as livestock fodder. According to FAO last updating (December 2008), the greatest production was obtained in 2008 in EU. In 2001 was obtained the biggest barley production by entire world, while in 2008 was bigger compared to 2000, but still smaller than in 2001 (Fig. 1.c). The area harvested was bigger in 2001 compared to 2000 and 2008 worldwide, while in EU increased in 2001 compared to 2000, but in 2008 decreased by 10.64% compared to 2000 and by 13.65% compared to 2001 (Table 1).

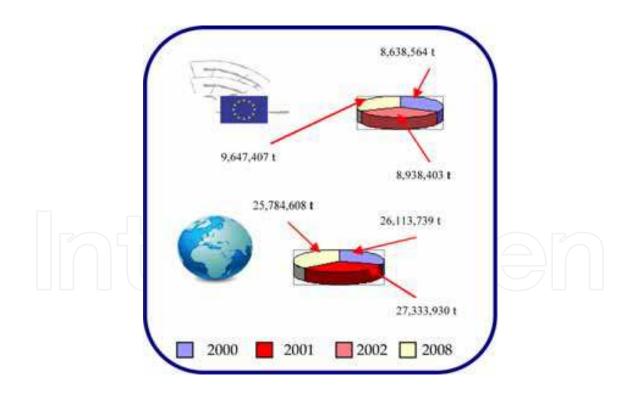


Fig. 1.c. The oats production in EU and in the world in three reference years of the last decade



**The maize** (Kingd. *Plantae*, Ord. *Poales*, Fam. Poaceae; **Zea mays**) is a known since prehistoric times, but now is spread all over the world due to its large production potential and ability to grow in diverse climates. According to FAO (December 2008), the greatest production was obtained in 2004 in EU and in 2008 worldwide (Fig. 1.d). The area harvested was 4.93% smaller in 2008 compared to 2000 in EU, while worldwide it increased by 17.53% in 2008 compared to 2000 (Table 1).

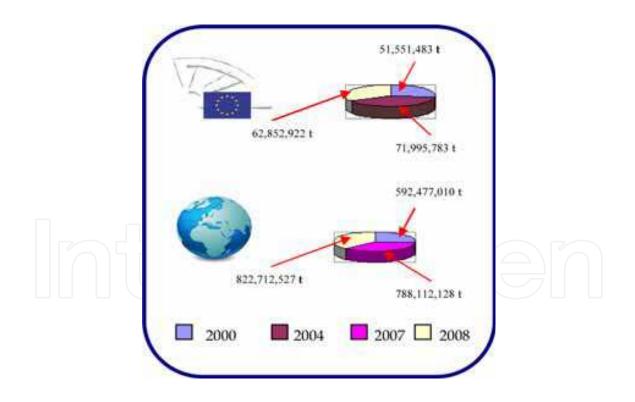


Fig. 1.d. The maize production in EU and in the world in three reference years of the last decade



**The soya bean** (Kingd. *Plantae*, Ord. *Fabales*, Fam. Fabaceae; **Glycine max**) native to Asia, is an annual species of legume, rich source of oil, carbohydrates and protein. It is also considered one of the most versatile crops. According to FAO last updating (December 2008), the greatest production was obtained in 2001 in EU, and worldwide in 2008 (Fig. 1.e). The smallest production (almost one half of that obtained in 2001) was obtained in 2008 in EU. The area harvested was 52.89% smaller in 2008 compared to 2000 in EU, while worldwide, it increased by 30.26% in 2008 compared to 2000 (Table 1).

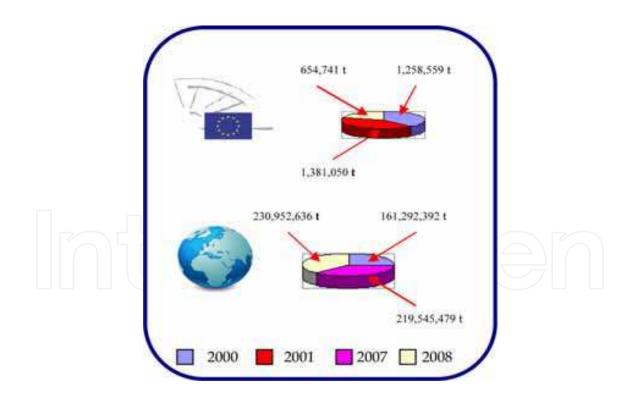


Fig. 1. e. The soya bean production in EU and in the world in three reference years of the last decade



**The sunflower** (Kingd. *Plantae*, Ord. *Asterales*, Fam. Asteraceae; *Helianthus*) is orginary from Central America. It is of great importance in food industry. According to FAO (December 2008), the greatest production was obtained in 2008 in EU and the same orientation was reported by entire world (Fig. 1.b). The area harvested was bigger in 2008 compared to 2000 worldwide. It increased by 18.47%. In EU, the area cultivated increased by 1.31% in 2008 compared to 2000, but decreased by 11.87% compared to 2003, when the biggest area was cultivated during the analyzed interval, 2000 – 2001, respectively (Table 1).

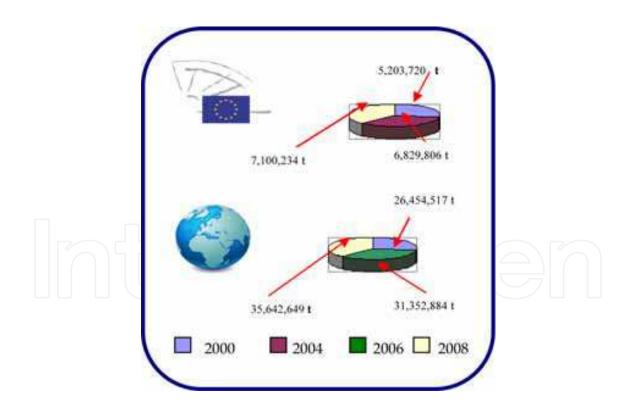


Fig. 1. f. The sunflower production in EU and in the world in three reference years of the last decade



**The rapeseed** (Kingd. *Plantae*, Ord. *Brassicales*, Fam. Brassicaceae; *Brassica napus*) is a valuable source of animal feed and vegetable oil for human consumption and biodiesel. Certain varieties of oilseed rape are commonly named canola. According to FAO last updating (December 2008), the greatest production was obtained in 2008 in EU and the same orientation was reported by entire world (Fig. 1.a). The area harvested was 17,31% bigger in 2008 compared to 2000 worldwide, while in EU it increased by 48,01% in 2008 compared to 2000 (Table 1).

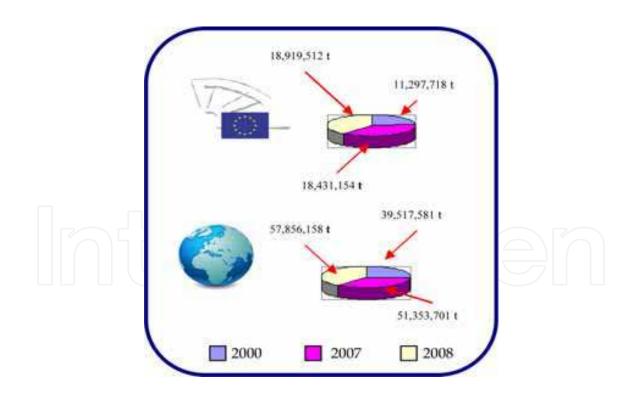


Fig. 1. g. The rapeseed production in EU and in the world in three reference years of the last decade



**Vineyard** (Kingd. *Plantae*, Ord. *Vitales*, Fam. Vitaceae; *Vitis vinifera*). The wine producing is known since millenniums b.Ch According to FAO (December 2008), the greatest production was obtained in 2008 in EU (by 36.44% compared to production obtained in 2000) and the same orientation was reported by entire world, by 34.74% bigger in 2008 compared to the production obtained in 2000, respectively (Fig. 1.b). The area harvested was 9.34% bigger in 2008 compared to 2000 in EU, while it increased by 0,91% in 2008 compared to 2000, worldwide (Table 1).

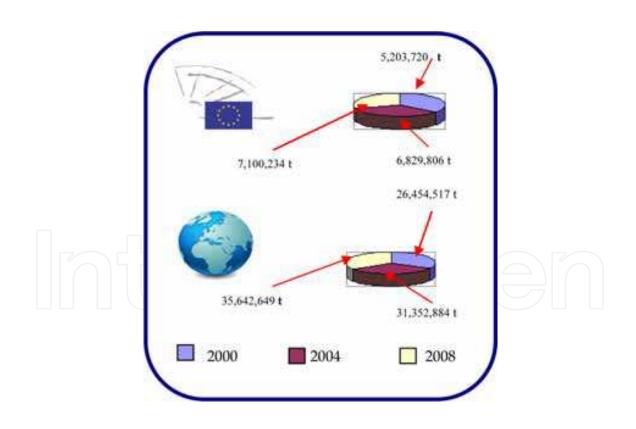


Fig. 1. h. The wheat production in EU and in the world in three reference years of the last decade



**Vegetables** include a series of plants (potatoes, eggplants, tomatoes, cucumbers, cabbages, onions, garlic, peas, cauliflowers, spinach, pumpkins, etc.) often intensively managed and with high input costs. They are important both agricultural economy of countries, food industry, and food consumption, being essential to a healthy diet. In 2005, according to FAO, there were 66 million Ha of vegetables grown in the world. This figure includes of potatoes (19 million Ha) but excludes nearly 5 million Ha of watermelons and other melons which are sometimes included with vegetables. If we include melons, the biggest production was obtained in 2005 in EU (Fig. 1.i.).

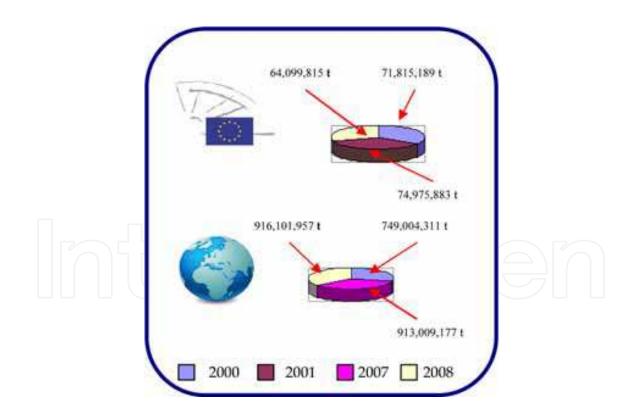


Fig. 1. i. The vegetables production in EU and in the world in three reference years of the last decade

1) Eu									
<sup>1)</sup> European Union, <sup>2)</sup> World	Issue/Yea	r	2000	2001	2002	2003	2004	2005	
an U	Wheat	1)	26560780	26412836	26888507	24329061	26597861	26441014	249
<sup>f</sup> nior		2)	215472863	214597539	213806041	207658164	216894341	219736189	211
1, 2) V	Maize	1)	9337537	9618975	9262990	9737571	10059931	8991942	85
Vorle		2)	136999105	137485945	137293647	144673388	147472375	147441686	148
<u>D</u> .	Barley	1)	14202011	14330156	14269355	14027708	13704760	13824772	137
		2)	54520176	56173845	55272435	57730908	57535566	55342779	563
	Oats	1)	3063167	3055184	3240881	3178923	2912364	2879314	29
		2)	12682536	13124757	12452273	12141204	11696607	11269443	116
	Soya beans	1)	501604	452795	354185	422878	386726	419319	48
		2)	74366760	76799819	78962290	83663393	91602610	92506171	952
	Sunflower	1)	3693610	3484659	3473261	4245848	3716073	3599920	39
		2)	21120631	17811931	19448548	23417226	21436622	23025310	237
	Rapeseed	1)	4139854	4172497	4246639	4161306	4557222	4867009	53
		2)	25835280	22560773	22914090	23468954	25316569	27693540	274
	Grapes	1)	3920220	3876898	3871812	3860016	3737869	3716264	36
		2)	7341221	7406923	7438751	7497740	7343476	7345439	73
	Vegetables	1)	3031888	2902895	2848534	2940864	2927856	2826443	26
		2)	45074440	46808658	47805184	50200877	49881448	50992160	522

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Table 1. Area Harvested (Ha) in European Union and in the world

Worldwide, the biggest production was obtained in 2008. The cultivated area decreased by 18% in 2008 compared to 2000, while worldwide it increased by 20% in 2008 compared to 2000 (Table 1).

Discrepancies are recorded in both production and cultivated areas in EU and worldwide. The production (tonnes) of some cultures dramatically decreased in EU in 2008 compared to previous years, but it considerably increased worldwide during the same time interval. The same tendency is observed concerning the area cultivated (Ha).

The oats production increased in 2008 compared to 2000 in EU, while de production decreased I worldwide during the same time interval. The maize production decreased in 2008 compared to 2004, even it is bigger compared to 2000. Worldwide, it is bigger in 2008 compared to 2000. The soy bean production dramatically decreased in 2008 compared to 2000 in EU, while it increased in 2008 compared to 2000 worldwide. The sunflower production increased in 2008 compared to 2000, but it is smaller compared to production obtained in 2004, when the biggest production of the analyzed time interval was recorded. In the same culture, the production increased in 2008 compared to 2000 worldwide. The vegetable production, including melons, decreased in 2008 compared to 2000 in EU, while it increased during the same time interval (2000 – 2008) worldwide (Fig. 1).

Differences in tendencies concerning area cultivated with analyzed crops were also recorded between EU and world during the time interval 2000 – 2008. Smaller area was cultivated with oats, maize, soya beans and vegetables in 2008 compared to 2000 in EU, while bigger field areas were cultivated with the same cultures in 2008 compared to 2000 worldwide (Table 1).

# 3. Common herbicides in use that confront weed resistance

A series of large scale used herbicides in use confront with weed herbicide resistance phenomenon (Practical Guide for Farmers, Alcedo 2010). They are commonly administered to most important crops, in fight against a large variety of annual and/or perennial dicotyledonous and monocotyledonous weeds. The resistance developed against these herbicides is based on the activity of specific enzymatic systems (Table 2).

Commercial	Active principle/s	Enzymatic	Chemical formula
name of		system	
herbicide and		developing	$(\bigcirc)(\bigcirc)(\bigcirc)$
producer		resistance/target	
		class of weeds	
		Wheat	
BUCTRIL	Bromoxynil	Photosystem II/	Br
UNIVERSAL	3,5-dibromo-4-	Annual and	OH
(bromoxynil	hydroxybenzonitrile	perennial	Br
280 g/l + acid		dicotyledonous	N
2,4-D 280 g/l)	МСРА	weeds	I 9
Bayer	(4-Chloro-o-tolyloxy-		СОСОН
Cropscience	acetic acid)		
Ag., Germany			u. –

Table 2. Herbicides in use and enzymatic system of weeds susceptible to develop resistance

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Brief Approach of Herbicide Resistance in Context of Crops Development Worldwide

Commercial	Active principle/s	Enzymatic	Chemical formula
name of		system	
herbicide and		developing	
producer		resistance/target	
		class of weeds	
		Maize	
BROMOTRIL	Bromoxynil	Photosystem II/	
40 EC	3,5-dibromo-4-	Annual	Br
(bromoxynil	hydroxybenzonitrile	dicotyledonous	ОН
400 g/l)		weeds	Br
Makhteshim			N <sup>*</sup>
Agan, Israel			
BUCTRIL UNIV	/ERSAL	· · · · · ·	
CAMBIO	Bentazone	Photosystem II/	l o
(bentazone	2,2-dioxo-3-propan-	Annual	
320 g/1 +	2-yl-1H-benzo[1,2,6]	dicotyledonous	N CH
dicamba 90	thiadiazin-4-one	weeds	o ch.
g/l) BASF SE,			
Germany	Dicamba		ОН
	3,6-dichloro-2-		OCH3
	methoxybenzoic acid		ĊI
SURDONE	Surdone,	Photosystem II/	
(metribuzin	4-amino-6- <i>tert</i> -butyl-	Annual	H <sub>2</sub> C、 / <sup>CH</sup> 3
70%)	4,5-dihydro-3-	dicotyledonous	C N N
Feinchemie	methylthio-1,2,4-	and some mono-	H <sub>3</sub> C III
Schwebda	triazin-5-one	cotyledonous	
GmbH,		weeds	ŇH <sub>2</sub>
Germany			
ZEAGRAN	Bromoxynil	Photosystem II/	Br
340 SE	3,5-dibromo-4-	Annual	
(bromoxinil	hydroxybenzonitrile	dicotyledonous	Br
90 g/1 +		weeds and	N
terbutilazine	Terbutilazine	partially	
250 g/l)	N2-tert-butyl-6-	perennial	
Nufarm	chloro-N4-ethyl-		NNN
GmbH & Co.	1,3,5-triazine-2,4-		H <sub>5</sub> C <sub>2</sub> -NH NH -C(CH <sub>3</sub> )
Kg, Austria	diamine		-16°2
		Sunflower	
FOCUS	Cicloxidim	Acetyle CoA	0 N-0C.H.
ULTRA	(5 <i>RS</i> )-2-[( <i>EZ</i> )-1-	carboxylase/	CH,CH,CH,
(cicloxidim	(ethoxyimino)butyl]-	Sorghum	
100  g/l	3-hydroxy-5-[(3 <i>RS</i> )-	halepense	S ОН
BASF Ag.,	thian-3-yl]cyclohex-		$\sim$
Germany	2-en-1-one		

Table 2. Herbicides in use and enzymatic system of weeds susceptible to develop resistance – continued

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Commercial name of herbicide and producerActive principle/sEnzymatic system developing resistance/larget class of weedsChemical formulaSURDONEBROMOTRIL 40 ECSoganPhotosystem II/ Annual dicotyledonous weedsImage: Chemical formulaBASAGRAN FORTEBentazon sisopropyl-(IH)- (bentazon 480 g/1 + Wettol 150 g/l) 2,2-dioxidePhotosystem II/ Annual dicotyledonous weedsImage: Chemical formulaBASF Ag., GermanyWettol weetorPhotosystem II/ Annual dicotyledonous weedsImage: Chemical formulaSENCOR 70 WG (Intribuzin 3'(methylthio)1, 2, 4- triazin-5(41)-onePhotosystem II/ Annual dicotyledonous weedsImage: Chemical formulaSELECT SUPER (letodim 120 g/l) g/l) proyt]-5-[2- enoneChemical formulaImage: Chemical formulaSELECT SUPER (letodim 120 g/l) g/l) g/l) g/l) g/l) g/l) g/l) g/l) g/l) hydroxycyclohex-2- enoneAcetyle CoA carboxylase/ Annual dicotyledonous weedsImage: Chemical formulaFOCUS ULTRA VegetablesImage: Chemical formulaImage: Chemical formulaFOCUS ULTRA USAN FORTE bydroxycyclohex-2- enoneSet Set COR 70 WG (potato, tomato)Image: Chemical formulaFOCUS ULTRA UCUS ULTRA (tomato, beans)Set Set COR 70 WG (potato, tomato)Image: Chemical formulaFOCUS ULTRA (tomato, beans)Set Set COR 70 WG (potato, tomato)Set Set COR 70 WG (potato, tomato)Set COR formal Set COR 70 WG (potato, tomato)Set Set COR 70 WG (potato, tomato)Set COR 7		Γ	1	
herbicide and producer class of weeds SURDONE BROMOTRIL 40 EC Soya bean BASAGRAN Josepropyl-(IH)- (bentazon 480 g/1 + Wettol Maret dispersible granules of liquid pesticides SENCOR 70 WG Germany Wettol Water dispersible granules of liquid pesticides SENCOR 70 WG (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one Bayer CropScience Ag., Germany SELECT SUPER (cletodim 120 g/1) g/1) g/1) model g/1) proy1]-5-[2- chloroallyloxyimino] g/1) g/1) g/1) g/1) g/1) Germany SELECT SUPER (cletodim 120 g/1) g/1) g/1) g/1) g/1) g/1) g/1) G/1 Cletodim SELECT SUPER (cletodim 120 g/1) g/1) g/1) g/1) g/1) G/1 SELECT SUPER (cletodim 120 g/1) g/1) g/1) g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1 SELECT SUPER (cletodim 120 g/1) g/1 SELECT SUPER (cletodim 120 g/1 SELECT SUPER (cletodim 120 g/1 SELECT SUPER (cletodim 120 g/1 SAT SUPER (cletodim 120 g/1 SAT SUPER (potato, tomato) SELECT SUPER (potato, beans) SUPONE SUPON SUPO		Active principle/s	5	Chemical formula
producer    resistance/target class of weeds      SURDONE    E      BROMOTRIL 40 EC    Soya bean      BASAGRAN    Bentazon 3-isopropyl-(IH)- (bentazon 480    Photosystem II/ Annual dicotyledonous weeds      Germany    Wettol      Water dispersible granules of liquid pesticides    Photosystem II/ Annual dicotyledonous weeds      SENCOR 70    Metribuzuin (I, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(411)-one    Photosystem II/ Annual dicotyledonous weeds      SELECT    Cletodim granules of liquid pesticides    Photosystem II/ Annual dicotyledonous weeds      SELECT    Cletodim (RS)-2-[(F)-1-[(F)-3- (cletodim 120 g/l) propyl]-5-[2- corporation    Acetyle CoA carboxylase/ Annual dicotyledonous weeds and Sorghum halepense      FOCUS ULTRA    Vegetables      SELECT SUPER (potato, tomato)    SELECT SUPER (potato, tomato)      SELECT SUPER (potato, beans)    ULTRA (tomato, beans)			5	
SURDONE      BROMOTRIL 40 EC      Soya bean      BASAGRAN      FORTE      (benzon 480      g/1 + Wettol      150 g/1)      22-dioxide      BASF Ag.,      Germany      Wettol      Water dispersible granules of liquid pesticides      SENCOR 70      Mctribuzuin      70%)      Bayer      CropScience      Ag., Germany      SELECT      SUPER      (letvilthio)propyl]-5[-2]      chloroallyloxyiminol g/1)      propylic      propylic      SELECT      Cletodim      (letvilthio)propyl]-5[-2]      enne      Vegetables      FOCUS ULTRA      Vegetables      SELECT SUPER (potato, tomato)      SELECT SUPER (potato, beans)      SURDONE (potato)				
SURDONEBROMOTRIL 40 FCSoya beanBASAGRAN FORTE (bentazon 480 g/1 + Wettol 150 g/1) BASF Ag., GermanyBentazon -2,1,3- thiadiazine-4-Retone- 2,2-dioxidePhotosystem II/ Annual dicotyledonous weedsSENCOR 70 WG (I,1-dimethylethyl)- netribuzin 70%) Bayer CropScience Ag., GermanyWettol Wettol Water dispersible granules of liquid pesticidesPhotosystem II/ Annual dicotyledonous weedsSENCOR 70 WG (I,1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one Bayer (cletodim 120 g/1) propyl]-5-[2- (cletodim 120 g/l) propyl]-5-[2- (ethylthio)propyl]-3- Lifescience CorporationAcetyle CoA carboxylasc/ Annual dicotyledonous weeds and Sorghum halepenseFOCUS ULTRA Vegetables SELECT SUPER (cletodim 120 g/1)Cletodim propyl]-5-[2- enoneAcetyle CoA carboxylasc/ Annual Sorghum halepenseFOCUS ULTRA Vegetables SURDONE (potato, tomato)FOCUS ULTRAUSA	producer			
BROMOTRIL 40 EC      Soya bean      BASAGRAN FORTE      Bentazon 480 benzo-2,1,3- thiadiazine-4-Retone- 2,2-dioxide      BASF Ag., Germany      Wettol Water dispersible granules of liquid pesticides      SENCOR 70 WG (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one      WG (2, 1)      SELECT SUPER (cletodim 120 g/l)      SELECT SUPER (cletodim 120 g/l)      Cletodim (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one      Acetyle CoA carboxylase/ Ag., Germany      SELECT SUPER (cletodim 120 g/l)      Cletodim (S)-2-[(E)-1-[(E)-3- chloroallyloxyimino] propyl]-5-[2- enone      Arvesta Lifescience Corporation USA      FOCUS ULTRA      Vegetables      SENCOR 70 WG (potato, tomato)      SELECT SUPER (potato, beans)			class of weeds	
Soya bean      BASAGRAN FORTE    Bentazon      Germany    Bentazon      Wettol    thiadiazine-4-Retone- 2,2-dioxide    Photosystem II/ Annual dicotyledonous weeds      BASF Ag., Germany    Wettol    Water dispersible granules of liquid pesticides    Photosystem II/ Annual dicotyledonous      SENCOR 70 WG (netribuzin 70%)    Metribuzuin (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one    Photosystem II/ Annual dicotyledonous      SELECT CorpoScience Ag., Germany    Cletodim (RS)-2-[(E)-1-[(E)-3- chloroallyloxyimino] propyl]-5-[2- enone    Acetyle CoA carboxylase/ Annual dicotyledonous weeds and Sorghum holepense      FOCUS ULTRA    Vegetables      FOCUS ULTRA    Vegetables      SENCOR 70 WG (potato, tomato) SELECT SUPER (potato, beans)    Suppose				
BASAGRAN FORTE    Bentazon      Germany    Bentazon 480      g/1 + Wettol    thiadiazine-4-Retone- 150 g/l)    2,2-dioxide      BASF Ag.,    Wettol      Germany    Wettol      Water dispersible granules of liquid pesticides    Photosystem II/ Annual      SENCOR 70    Metribuzuin (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one    Photosystem II/ Annual      Bayer    CropScience Ag., Germany    Metribuzuin (RS)-2-[(E)-1-[(E)-3- chloroallyloxyimino] propyl]-5-[2- enone    Acetyle CoA carboxylase/ Annual dicotyledonous weeds and Sorghum halepense      FOCUS ULTRA    Vegetables      FOCUS ULTRA    SELECT SUPFR (potato, beans)    SURDONE (potato), beans)		0 EC		
FORTE (bentazon 480 g/1 + Wettol 150 g/1) BASF Ag., Germany    3-isopropyl-(IH)- benzo-2,1,3- thiadiazine-4-Retone- 2,2-dioxide    Annual dicotyledonous weeds      Wettol Water dispersible granules of liquid pesticides    Metribuzuin (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one    Photosystem II/ Annual dicotyledonous weeds      SENCOR 70 WG (metribuzin 70%) Bayer CropScience Ag., Germany    Metribuzuin (1, 1-dimethylethyl)- 3-(methylthio)-1, 2, 4- triazin-5(4H)-one    Photosystem II/ Annual dicotyledonous weeds      SELECT SUPER (cletodim 120 g/1) Arvesta Lifescience Corporation USA    Cletodim (RS)-2-[(E)-1-[(E)-3- chloroallyloxyimino] propyl]-5-[2- enone    Acetyle CoA carboxylase/ Annual dicotyledonous weeds and Sorghum halepense      FOCUS ULITRA    Vegetables    Sorghum halepense    Acetyle CoA carboxylase/ Annual dicotyledonous weeds and Sorghum halepense      FOCUS ULITRA    Vegetables    Surdon (potato, tomato)    Surdon (potato, tomato)				
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Table 2. Herbicides in use and enzymatic system of weeds susceptible to develop resistance – continued

# 3. Mechanism of herbicide resistance

The herbicide resistance is a concept, which could regard both, culture plants and weeds. According to AgBiosafety – University of Nebraska "Herbicide resistance is when plants become resistant to the negative effects of a particular herbicide formulation or are genetically engineered in order to have resistance to a particular herbicide. Herbicideresistant crops can be sprayed with a particular herbicide, killing weeds growing in and around the crop plants, without being damaged."

Concerning weeds, the Illinois Agricultural Pest Management Handbook (2008) adopts the following definition **"Resistance is the inherited ability of a plant to survive and reproduce following exposure to a dose of herbicide normally lethal to the wild type."** 

Resistance of weeds to herbicides is not a unique phenomenon. In fact, resistance to herbicides is a worldwide problem that became more and more acute in last 20 years, due to increased production capacity.

According to Prather et al. (2000), resistance may appear in weeds as consequence of random punctiform mutation occurred in plant genome. If we deal with a herbicide selection pressure the resistant plants will survive, while susceptible plant will disappear.

The first report concerning resistance against pest, fungi, herbicide, etc. was reported in 1908, when insects resistant to insecticides were identified. Plant pathogens resistant to fungicides were emphasized for the first time in 1940, and weeds resistant to herbicides beginning with 1950s, when dandelion and wild carrot biotypes were reported to be resistant to 2,4-D (MCPA or 4-Chloro-*o*-tolyloxy-acetic acid), and then groundsel resistant to triazines was reported in 1968 (Kremer et al., 1999; Oroian, I., 2008).

By 2008,183 weed biotypes that were resistant to triazine herbicides and 15 other herbicide families were reported and well documented. Results of a 1992 North Central Weed Science Society survey of the north central United States and Canada reflect a world wide trend of increasing appearance of herbicide resistance (Yamasue et al., 1992; Oroian, I., 2008).

Besides intrinsic weed traits, a series of culture practices may favourize the installation of herbicide resistance phenomenon (Fig. 2)

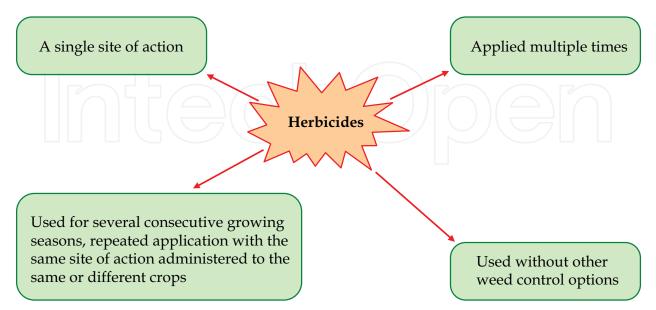


Fig. 2. The herbicide administration practices and/or intrinsic traits that contribute to herbicide resistance

Two mechanisms are at the origin of the herbicide resistance. One is the so-called "exclusionary resistance" and the other, "the site action resistance" (Cummins et al., 2010).

#### 3.1 The exclusionary resistance

The mechanism consists in the exclusion of the herbicide molecule from the specific site located in target plant where it induces the characteristic toxic response (Fig. 3).

Several well known mechanisms, elucidated by now, can explain the processes involved in resistance developed by weeds against herbicides. Among them, we can enumerate: differential herbicide uptake, differential translocation, compartmentation in different specific regions of the weed, and metabolic detoxification (Oroian, I., 2008; Cummins et al., 2010).

Differential herbicide uptake. Some groups of weeds develop morphological particularities (e.g. reduced leaf area) that determine specific new conformation, due to tissue mass or/and shape alteration. The direct consequence consists in differences recorded in uptaking the herbicides. **Differential translocation.** In resistant weed biotypes, the transport mechanism of the active principles from herbicide is modified (reduced). The alterations are observed at both apoplastic (cell wall, xylem) and symplastic (plasma lemma, phloem) levels. Mechanisms **Compartmentation.** Herbicides can be stopped, by specific mechanisms, in a certain location (function of their structure) before reaching the targeted site. In this way they are immobilized and unable to produce the aimed effect. Metabolic detoxification. Weeds can develop internal defense mechanisms than will detoxify the herbicide before it reaches the site of action at a rate sufficiently rapid that the plant is not killed. The biochemical pathways that represent the mechanisms of detoxifying herbicides can be grouped into four major categories of reactions: oxidation, reduction, hydrolysis, and conjugation.

Fig. 3. The exclusionary resistance mechanisms

The metabolic detoxification involves three enzyme systems (Hakala et al., 2006; Kurth et al., 2009; McCourt et al., 2006) that catalyze the specific reactions that represent the basis of herbicide resistance in weeds (table 3).

Enzyme	Global process	Action	Target substance
Glutathione-s-transferase	Resistance to herbicides	Detoxifies	Atrazine
Aryl-acylamidase	Resistance to herbicides	Detoxifies	Propanil
Cytochrome P450 monoxygenase	Resistance to herbicides	Increased herbicide metabolism	Inhibitors of ACCase, ALS and PSII

Table 3. The enzymes and their role in herbicide resistance of weeds

#### 3.2 Resistance due to the site of action

From this point of view, two types of resistance are known: due to the altered site of action and site of action overproduction (Cummins et al., 2010).

**Altered site of action.** The site of action is modified in such a way that it cannot be affected by the herbicide action. The molecular mechanisms of resistance are mainly based on impossibility of herbicide binding to the target protein from weed specific tissue. This is the consequence of a mutation, usually punctiform (resulted form a single nucleotide change) in the gene encoding the protein to which the herbicide normally binds.

The direct consequence is the change produced in the amino acid sequence of the target protein. And this is the process that represents the basis of destroying the possibility of the herbicide to interact with the specific protein.

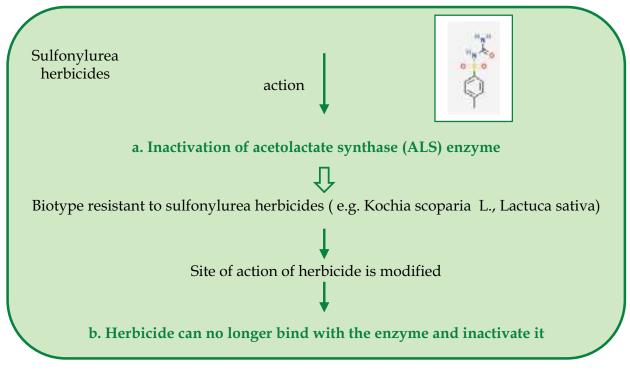


Fig. 4. Mechanism of herbicide action (a) and resistance (b) in biotypes resistant to sulfonylurea herbicides (e.g. *Kochia scoparia* L., *Lactuca sativa*)

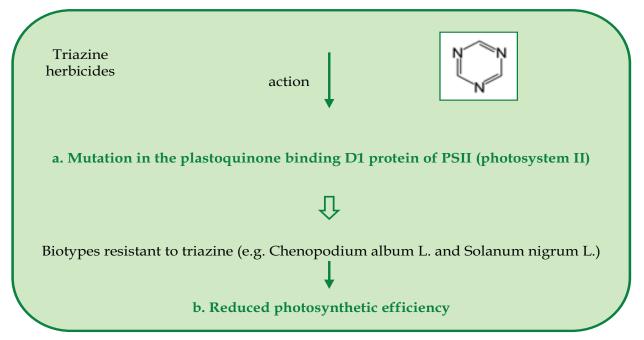


Fig. 5. Mechanism of herbicide action (a) and resistance (b) in biotypes resistant to triazine herbicides (e.g. *Chenopodium album* L. and *Solanum nigrum* L.)

**Site of action overproduction.** The first consequence of this overproduction will be a decreased intensity of the herbicide effect. An overproduction of the herbicide action site being recorded, the active principle of the weed control product will be less effective and finally it will not be able to inactivate the entire enzyme produced.

### 3.2.1 Herbicides and site of action

Whatever the resistance site directed mechanism (altered site or overproduction), herbicides are organized into groups based on their site of action. Herbicides in the same group all kill plants the same way. Weed populations may be resistant to herbicides in different chemical families if those families share the same site of action. Resistance to herbicides with different sites of action can also occur (Oroian, I., 2008; Cummins et al., 2010).

One herbicide may action on a single site and/or on multiple sites (Fig. 6).

**Single Site of Action**. A mutation reported in a specific site within analyzed weed, will lead to resistance to a particular herbicide with action on the site with mutation. The mutation may or may not determine resistance to other herbicides that have in common the action on the same site. The reason for this is there can be many different binding sites at a particular site of action (e.g. an enzyme) and those binding sites can be very herbicide specific. Therefore, several different herbicides may bind to the same enzyme but at different sites on the enzyme.

**Multiple Site of Action**. It can occur that one herbicide has multiple action sites. It makes more difficult for host organism to develop mutations at all of the sites of action that confer resistance, and develop resistance for herbicides with multiple action sites.

# 3.3 The main enzymatic systems involved in resistance mechanism against some important herbicide groups

# 3.3.1 Photosystem I (PSI)

**Photosystem I** (plastocyanin: ferredoxin oxidoreductase) is characteristic for the photosynthetic light reactions of algae, plants, and some bacteria, being part of photosynthetic

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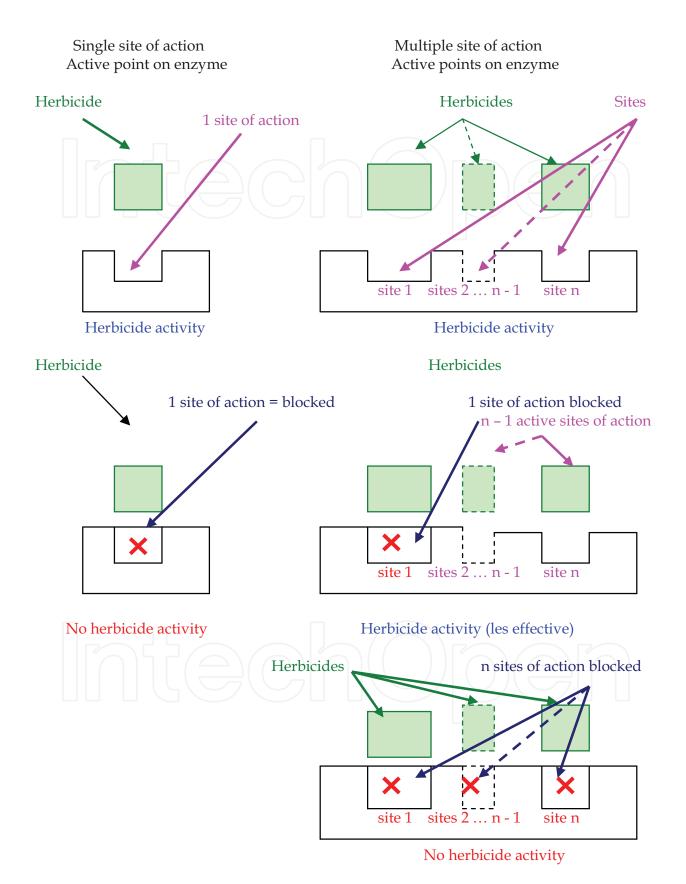


Fig. 6. Herbicide activity on one ore more sites

electron transport located in thylakoid membranes and an iron-sulfur type (Fe-S) reaction centre (Fig. 7).

It is involved in electron flow in the chloroplast thylakoid membrane of plants and in cyanobacteria, using light energy. It is excited best by light at about 700 nm, and is thus sometimes called P700 (Stockel et al., 2004; Hakala et al., 2006; Sharon et al., 2009). It contains eleven protein subunits, the cytochrome b<sub>6</sub>f complex, lipids, pigments (chlorophylls and  $\beta$ -carotene and cofactors (early electron acceptors vitamin K<sub>1</sub> phylloquinone in electron transport chain, Q<sub>K</sub> A and B, Ferredoxin-NADP<sup>+</sup> oxidoreductase enzyme, FNR respectively, Mg<sup>+</sup> and Ca<sup>+</sup>).

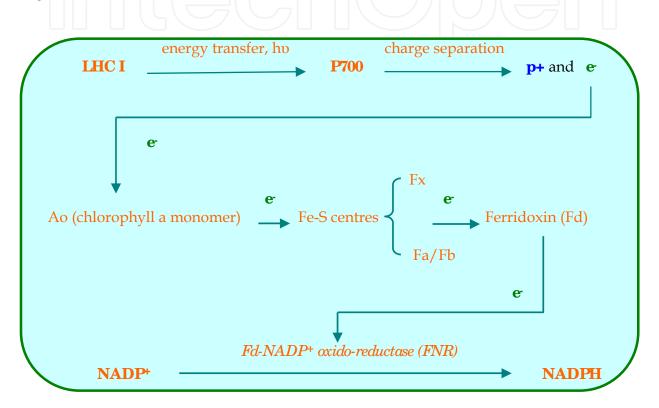


Fig. 7. The mechanism of PSI function in driving energy

The main inhibitors of photosystem I belong to post-emergence non-selective contact herbicides. They are represented by the chemical family Bipyridillum with herbicides Paraguat and Diquat.

According to Oroian I. (2008) herbicide resistance which involves the enzymatic PSI has been reported in weed species like: Amaranthus lividus, Bidens pilosa, Conyza spp., Eleusine indica, Solanum nigrum.

Mechanism of resistance to PSI inhibitors. The strategies against inhibitors of PSI may be grouped in two classes, detoxification of the toxic products formed and rapid sequestration of the herbicide mechanisms, respectively (fig. 8).

#### 3.2.2 Photosystem II (PSII)

PSII (water-plastoquinone oxidoreductase) is a protein complex located in chloroplast thylakoid membrane (Guskov et al., 2009; Watanabe et al., 2009). It is characteristic for photosynthetic organisms and has important role in driving light energy to split H<sub>2</sub>O into

Brief Approach of Herbicide Resistance in Context of Crops Development Worldwide

	Mechanism of resistance	
<b>Detoxification of the toxic</b> herbicide treatment prod hydroxide radicals, hydroge oxygen. This resistance m action of the protective enz the above mentioned radii initiate lipid peroxidation. T are: superoxide dismutase, glutathione reductase, dehy catalase and peroxidase.	aces superoxide and a peroxide, and singlet a peroxide, and singlet a peroxide, and singlet a peroxide, and singlet a peroxides the peroxides a peroxide a peroxidase, a p	
	<b>Rapid sequestration of the herbi</b> <b>mechanisms.</b> This mechanism was exempli- in <i>E.canadensis</i> and <i>E.sumatrensis</i> , (Yamasu al., 1992) for Paraquat. The mobility Paraquat is restricted in resistant biotypes s it is being rapidly sequestered. Autoradiog	fied e et of

Fig. 8. The mechanisms involved in weed resistance against PSI inhibitors

O<sub>2</sub>, protons and electrons (Fig. 9). It consist of 20 subunits and light-harvesting proteins and more than 99 cofactors. Among subunits, we can enumerate:

- light harvesting complex LHC -,
- P680 reaction centre,
- protein D1 reaction centre protein, quinone and manganese centre, binds Chlorophyll P 680 and beta-carotene,
- protein D2 reaction centre protein -,
- PsbO managnsese stabilizing protein etc.

The cofactors are represented by:

- chlorophyll a, which absorbs light,
- beta-carotene with function in quenching excess photoexcitation energy,
- plastoquinones as intra-thylakoid membrane mobile electron carriers two mobile electron carriers-plastoquinone-A (PQA), and plastoquinone-B (PQB),
- pheophytin as primary electron acceptor,

- heme,
- bicarbonate,
- n-dodecyl-beta-D-maltoside detergent molecules,
- managanese centre (Guskov et al., 2009).

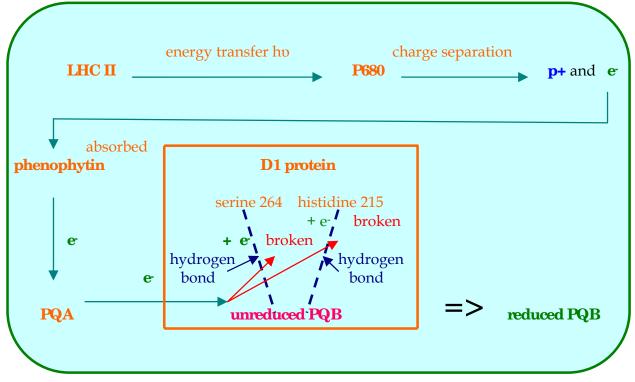


Fig. 9. The mechanism of PSII function in driving energy

The chemical herbicides that inhibit photosystem II are (Saari et al, 1990; Oroian, I., 2008): Atrazine, Cynazine, Simazine, Propazine (chemical family of Triazines), Metribuzin (chemical family of Triazinones), Bromacil and Terbacil (chemical family of Uracils), Bromoxinil (chemical family of Nitriles), Diuron and Fenuron (chemical family of Phenylureas), Pyrazon (chemical family of Pyridazinones), and Bentazon (chemical family of Benzothiadiazole).

According to Oroian I. (2008) herbicide resistance which involves the enzymatic PSI has been reported in weed species like: *Amaranthus hybridius, Solanum nigrum, Chenopodium album, Phalaris paradoxa*.

**Mechanism of resistance to PSII inhibitors.** Three ways are known to explain the weed internal defence strategies against characteristic inhibitors (fig. 10).

#### 3.2.3 Acetyle CoA carboxylase (ACCase)

ACCase is a multifunctional, biotinylated protein located in stroma of plastids. It catalyzes the ATP dependent carboxylation of Acetyl CoA to form malonyl CoA, which is the precursor of fatty acids (Sellwood et al., 2000).

It is present in prokaryotes, chloroplasts of most plants and algae, endoplasmic reticulum of most eukariotes, and even mycobacteria (Kurth et al., 2009). ACCase catalyses two partial reaction occurring at two different sites (Fig. 11).

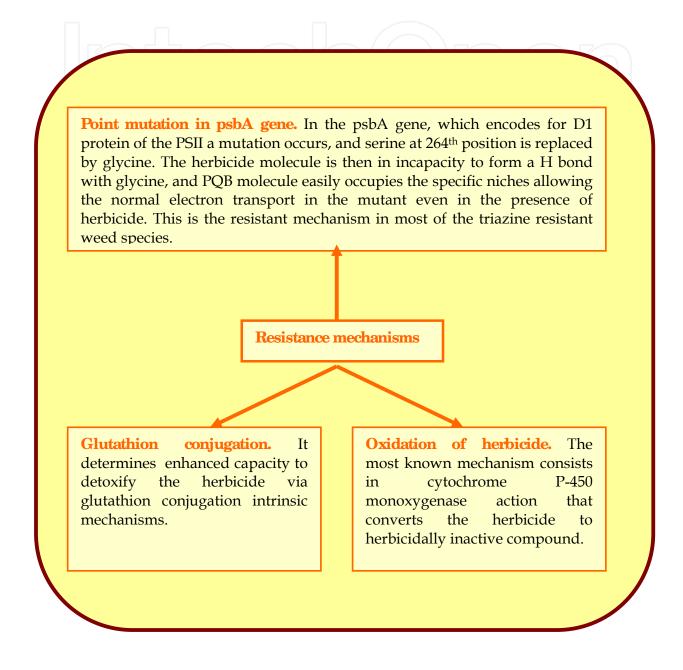
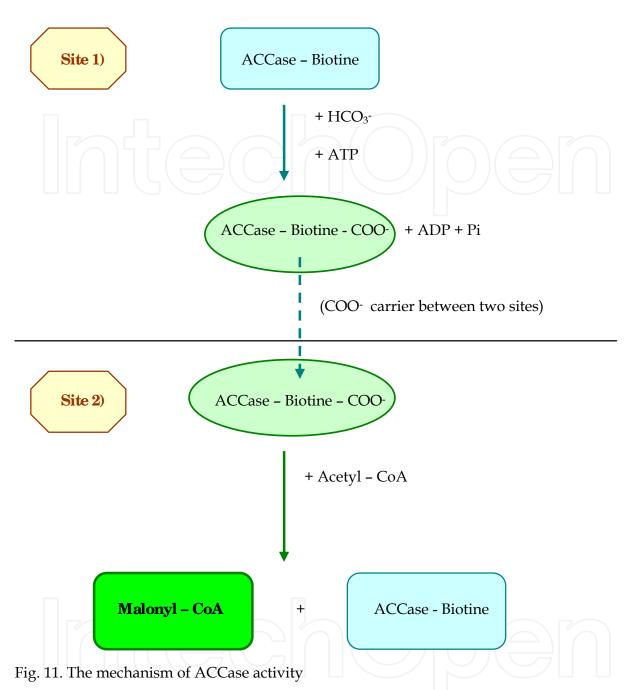


Fig. 10. The mechanisms involved in weed resistance against PSII inhibitors



The chemical herbicides that inhibit ACCase activity are (Oroian, I., 2008): Clodinafop, Diclofop, Fenoxaprop (chemical family of Aryloxyphenoxypropionates), Sethoxydim, Cycloxidim, and Clethodim (chemical family of Cyclohexanediones).

According to Oroian I. (2008) herbicide resistance which involves the enzymatic ACCase activity have been reported in weed species like: *Avena fatua*, *Digitaria sangunalis*, *Echinochloa crusgali*, *Echinochloa colona*, *Lolium* spp.

**Mechanism of resistance to ACCase inhibitors.** Up to date, three mechanisms of herbicide resistance, in which ACCase activity is involved, are described. They are: Presence of tolerant form of ACCase (alteration of target site enzyme), detoxification mechanism, and overproduction of ACCase (fig. 12).

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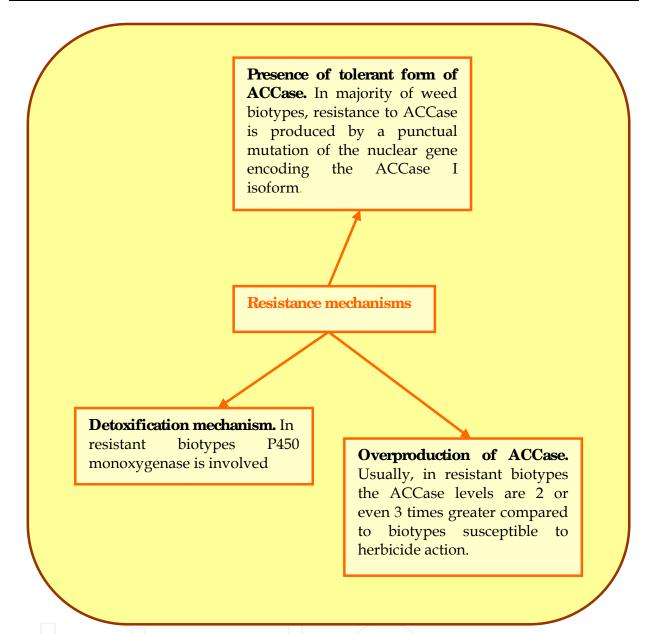


Fig. 12. The mechanisms involved in weed resistance against ACCase inhibitors

## 3.2.4 Acetolactate synthase

Two groups of enzymes are referred as Acetolactate synthase: Acetohydroxyacid synthase (AHAS), and Acetolactosynthase (ALS), respectively. It is a protein consisting of 590 residues. These residues are classified into three separate subunits: d1yhya1, d1yhya2 and 1yhya3 (Chipman et al., 1998; Preston et al., 2002; Scarabel et al., 2004). AHAS/ALS is the first enzyme common to biosynthesis of branched chain amino acids leucin, valine and isoleucine (McCourt et al., 2006) It is found in plants and micro-organisms.

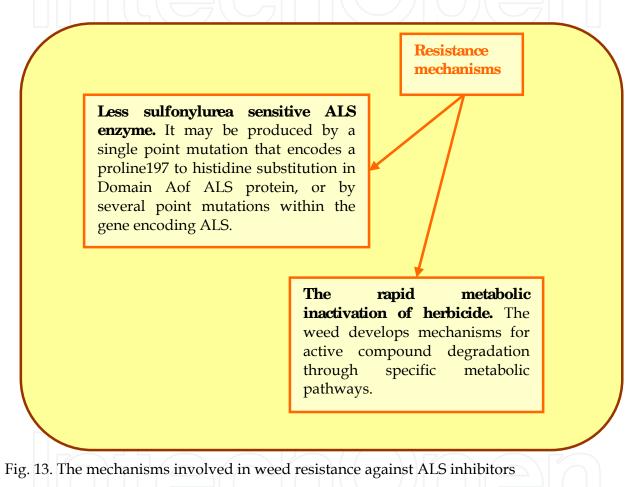
It is involved in the reaction of ketobutyrate conjugation with pyruvate to form acetohydroxybutyrate, which develops in parallel with reaction of conjugation of 2 molecules of pyruvate to form acetolactate, reaction also catalyzed by this enzyme.

The chemical herbicides that inhibit the enzyme activity are (Oroian, I., 2008): Chlorosulfuron, Sulfosulfuron (chemical family of Sulfonylureas), Imazapyr (chemical

family of Imidazolinones), Diclosulam, Flumetsulam, Metosulam (chemical family of Triazolopyrimidines), Pyriminobac-methyl, Bispyribac, Pyriftalid (chemical family of Pyrimidinyl-thio-benzoate Imidazolinones).

According to Oroian I. (2008) herbicide resistance which involves the enzymatic acetolactosynthase activity have been reported in weed species like: *Amaranthus* sp. *Avena fatua, Conyza* sp., *Eleusine indica, Lolium* spp.

**Mechanism of resistance to ALS inhibitors.** Two mechanisms of herbicide resistance are known: less sulfonylurea sensitive ALS enzyme and rapid metabolic inactivation of herbicide (fig. 13).



# 4. Conclusion

Even the concern of weed resistance against herbicides appeared a few decades ago, it still remains a serious concern and a continuous challenge for both farmers and producing industry.

To date, the most valuable information concerning the weed resistance against herbicides came from weed genetics. This capacity of auto defence is the result of the plant ability to auto generates gene variability. Studying the plant intrinsic molecular processes, valuable answers were obtained.

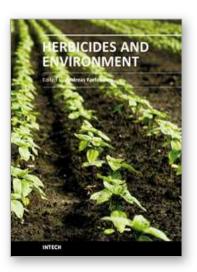
Understanding herbicide mechanisms of action in context of permanent evolution of weed resistance represents the main way of fighting against this phenomenon, and this approach delivers the most valuable tool for research, development and practice.

Mastering the state of art in the field will supply the appropriate basis to efficient fight against new and more and more developed herbicide resistance mechanisms.

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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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