We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Brief Approach of Herbicide Resistance in Context of Crops Development Worldwide

Ioan Gh. OROIAN
University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca
Romania

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. *Plantæ*, 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).
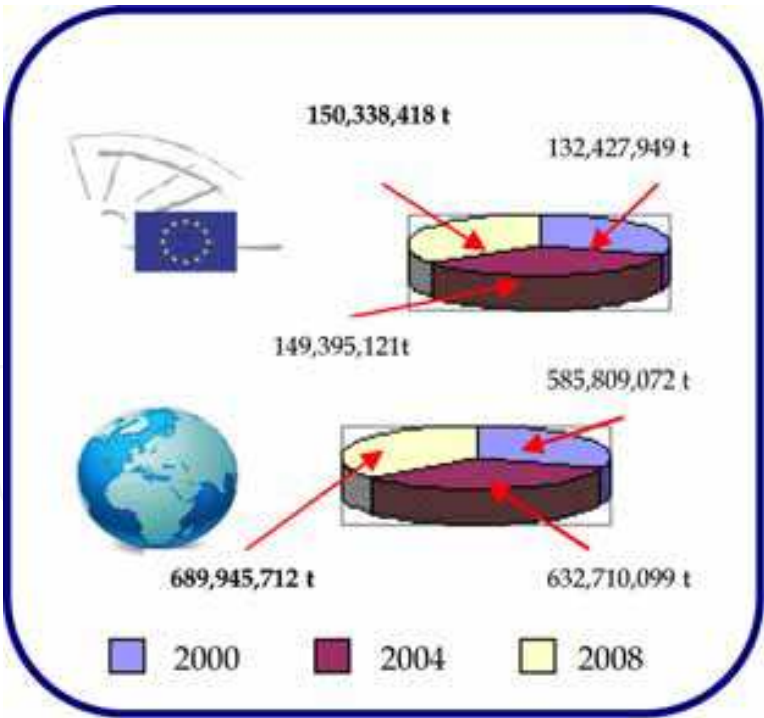

Fig. 1. a. The wheat production in EU and in the world in three reference years of the last decade

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).
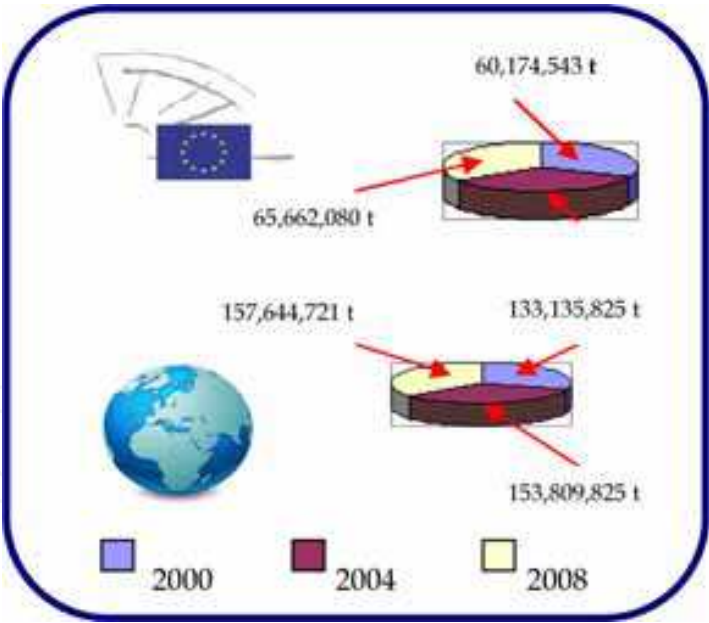

Fig. 1.b. The barley production in EU and in the world in three reference years of the last decade

The oats (Kingd. *Plantæ*, 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).
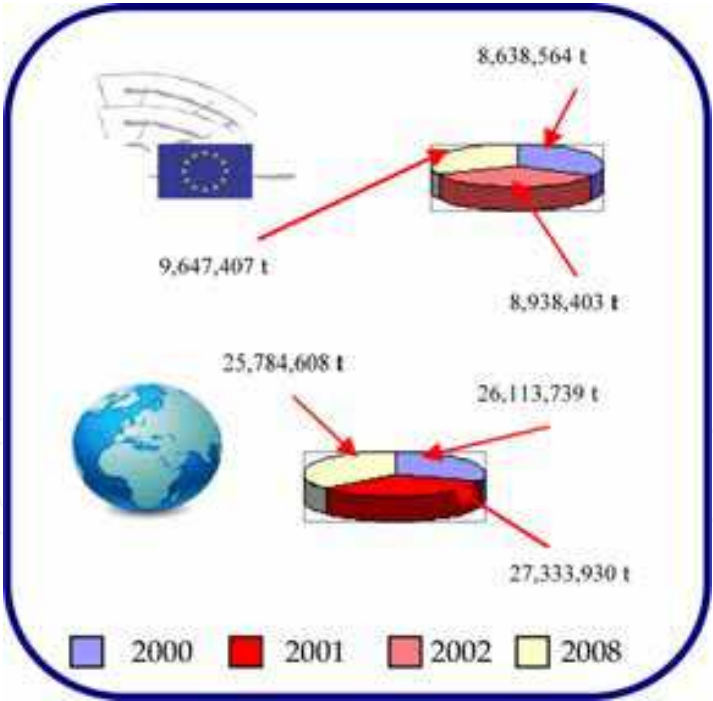

Fig. 1.c. The oats production in EU and in the world in three refrence years of the last decade

The maize (Kingd. *Plantæ*, 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).
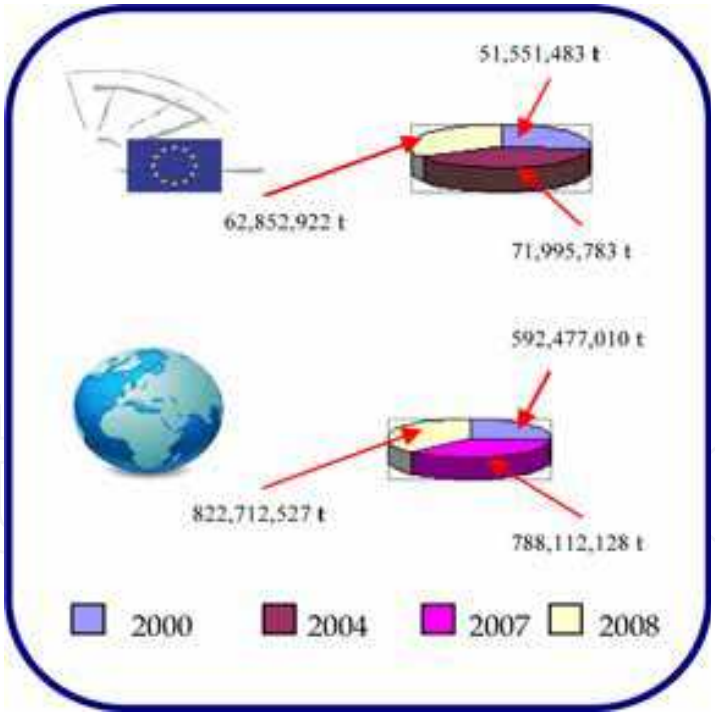

Fig. 1.d. The maize production in EU and in the world in three reference years of the last decade

The soya bean (Kingd. *Plantæ*, 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).
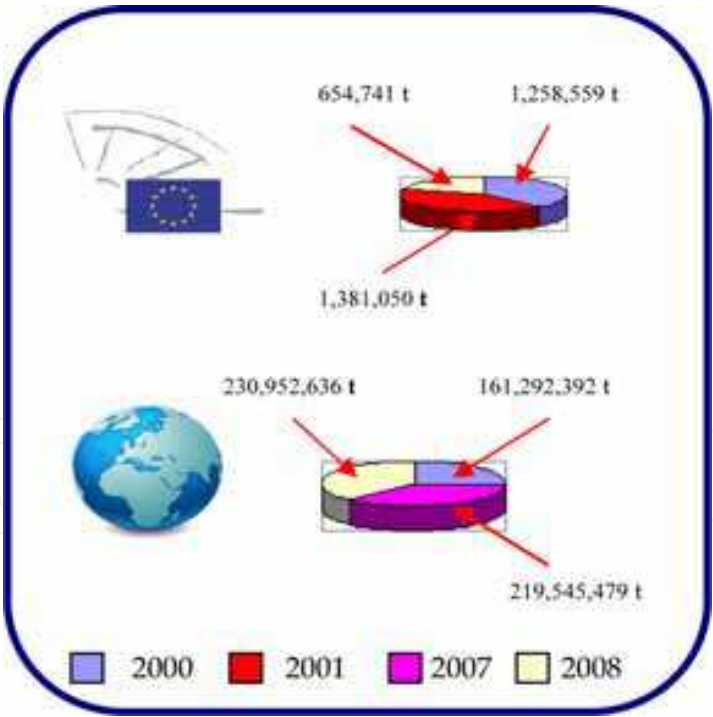

Fig. 1. e. The soya bean production in EU and in the world in three reference years of the last decade

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).
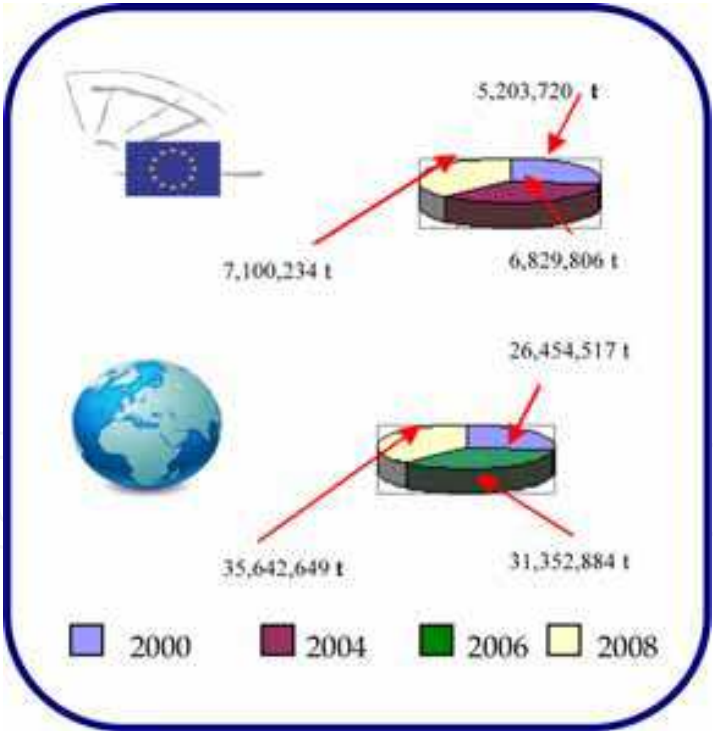

Fig. 1. f. The sunflower production in EU and in the world in three reference years of the last decade

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).
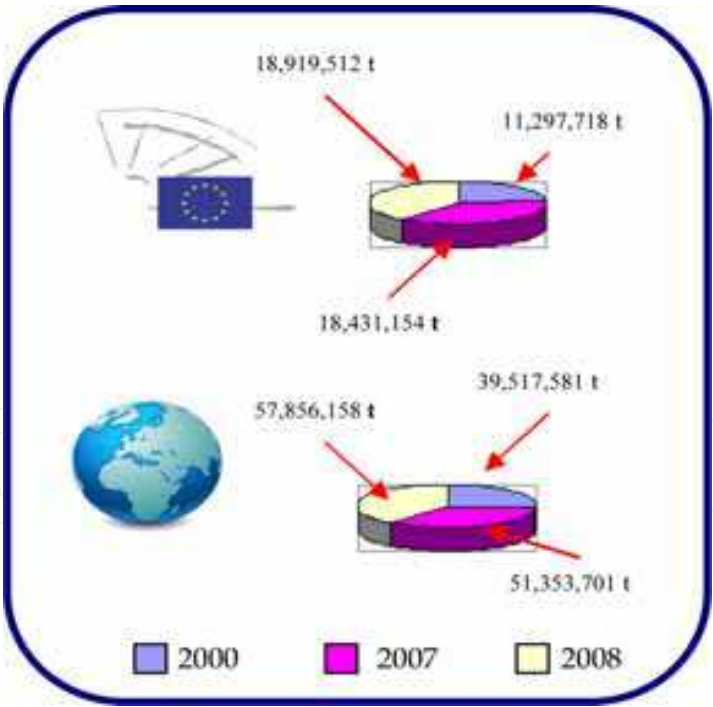

Fig. 1. g. The rapeseed production in EU and in the world in three reference years of the last decade

Vineyard (Kingd. *Plantæ*, 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).
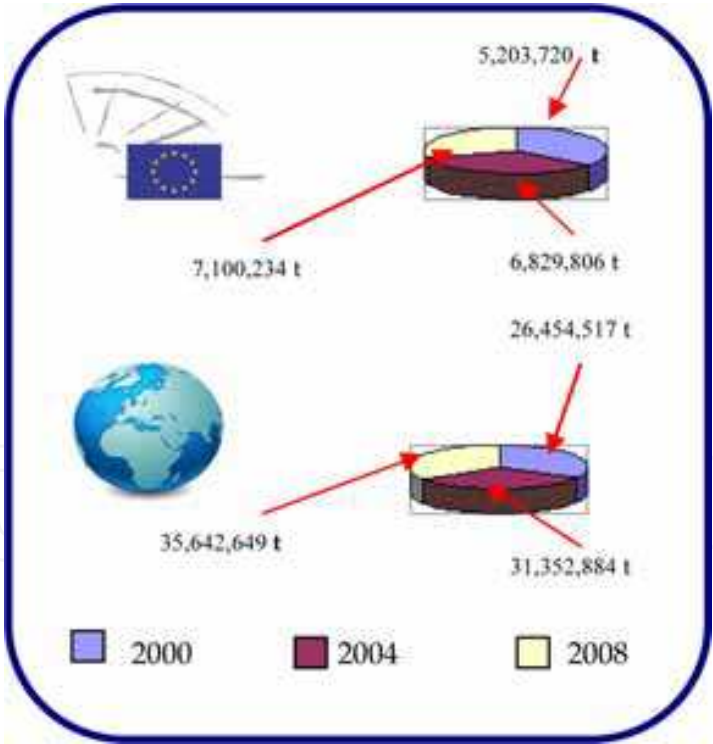
Fig. 1. h. The wheat production in EU and in the world in three reference years of the last decade

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.).
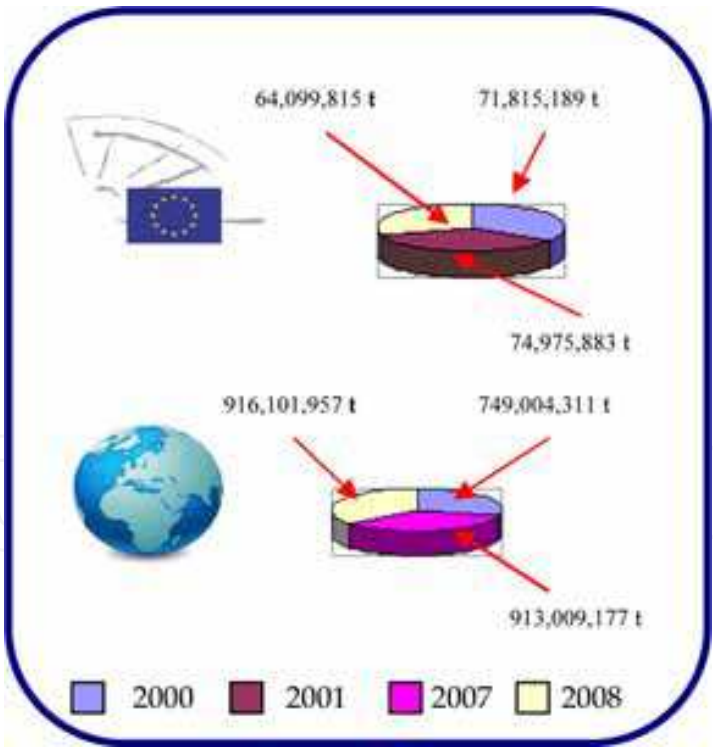

Fig. 1. i. The vegetables production in EU and in the world in three reference years of the last decade

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

Issue/Year		2000	2001	2002	2003	2004	2005	
Wheat	1)	26560780	26412836	26888507	24329061	26597861	26441014	249
	2)	215472863	214597539	213806041	207658164	216894341	219736189	211
Maize	1)	9337537	9618975	9262990	9737571	10059931	8991942	85
	2)	136999105	137485945	137293647	144673388	147472375	147441686	148
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

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 name of herbicide and producer	Active principle/s	Enzymatic system developing resistance/target class of weeds	Chemical formula
Wheat			
BUCTRIL UNIVERSAL (bromoxynil 280 g/l + acid 2,4-D 280 g/l) Bayer Cropscience Ag., Germany	Bromoxynil 3,5-dibromo-4-hydroxybenzonitrile MCPA (4-Chloro-*o*-tolyloxy-acetic acid)	Photosystem II/ Annual and perennial dicotyledonous weeds	

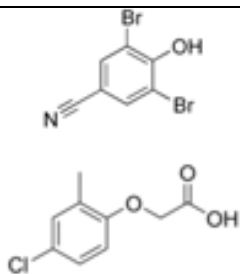Table 2. Herbicides in use and enzymatic system of weeds susceptible to develop resistance
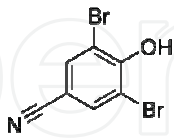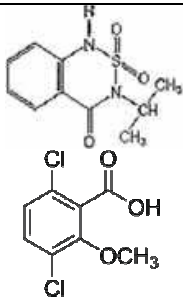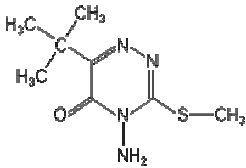
Commercial name of herbicide and producer	Active principle/s	Enzymatic system developing resistance/target class of weeds	Chemical formula
Maize			
BROMOTRIL 40 EC (bromoxynil 400 g/l) Makhteshim Agan, Israel	Bromoxynil 3,5-dibromo-4-hydroxybenzonitrile	Photosystem II/ Annual dicotyledonous weeds	
BUCTRIL UNIVERSAL			
CAMBIO (bentazone 320 g/l + dicamba 90 g/l) BASF SE, Germany	Bentazone 2,2-dioxo-3-propan-2-yl-1H-benzo[1,2,6] thiadiazin-4-one Dicamba 3,6-dichloro-2-methoxybenzoic acid	Photosystem II/ Annual dicotyledonous weeds	
SURDONE (metribuzin 70%) Feinchemie Schwebda GmbH, Germany	Surdone, 4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one	Photosystem II/ Annual dicotyledonous and some mono-cotyledonous weeds	
ZEAGRAN 340 SE (bromoxinil 90 g/l + terbutilazine 250 g/l) Nufarm GmbH & Co. Kg, Austria	Bromoxynil 3,5-dibromo-4-hydroxybenzonitrile Terbutilazine *N*2-tert-butyl-6-chloro-*N*4-ethyl-1,3,5-triazine-2,4-diamine	Photosystem II/ Annual dicotyledonous weeds and partially perennial	
Sunflower			
FOCUS ULTRA (cicloxidim 100 g/l) BASF Ag., Germany	Cicloxidim (5*RS*)-2-[(*EZ*)-1-(ethoxyimino)butyl]-3-hydroxy-5-[(3*RS*)-thian-3-yl]cyclohex-2-en-1-one	Acetyle CoA carboxylase/ *Sorghum halepense*	

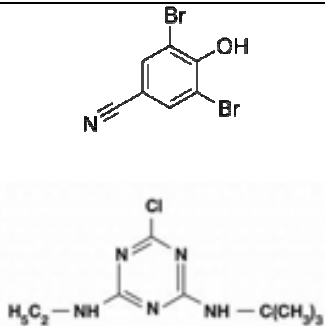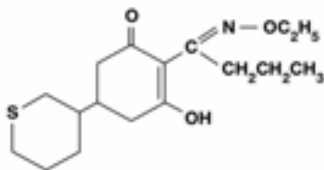Table 2. Herbicides in use and enzymatic system of weeds susceptible to develop resistance – continued

Commercial name of herbicide and producer	Active principle/s	Enzymatic system developing resistance/target class of weeds	Chemical formula
SURDONE			
BROMOTRIL 40 EC			
Soya bean			
BASAGRAN FORTE (bentazon 480 g/l + Wettol 150 g/l) BASF Ag., Germany	Bentazon 3-isopropyl-(IH)-benzo-2,1,3-thiadiazine-4-Retone-2,2-dioxide Wettol Water dispersible granules of liquid pesticides	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/l) Arvesta Lifescience Corporation USA	Cletodim (RS)-2-[(E)-1-[(E)-3-chloroallyloxyimino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxycyclohex-2-enone	Acetyle CoA carboxylase/ Annual dicotyledonous weeds and *Sorghum halepense*	
FOCUS ULTRA			
Vegetables			
SENCOR 70 WG (potato, tomato)			
SELECT SUPER (potato, beans)			
SURDONE (potato)			
FOCUS ULTRA (tomato, beans)			
BASAGRAN FORTE (beans)			

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. Herbicide-resistant 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)
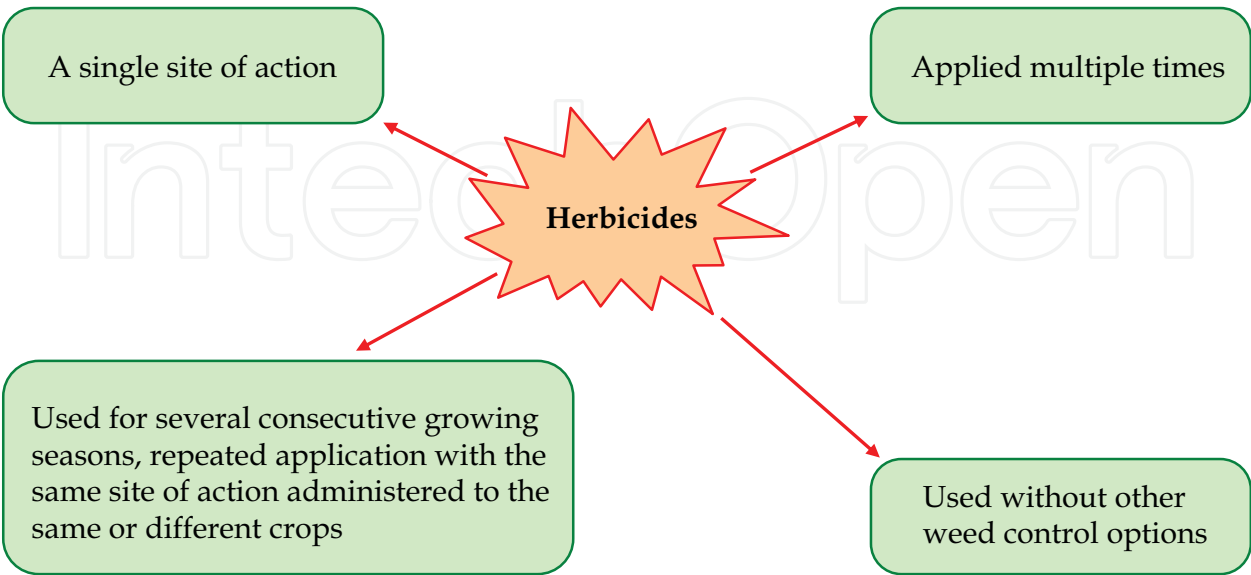

Fig. 2. The herbicide administration practices and/or intrinsic traits that contribute to herbicide resistance

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.

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.
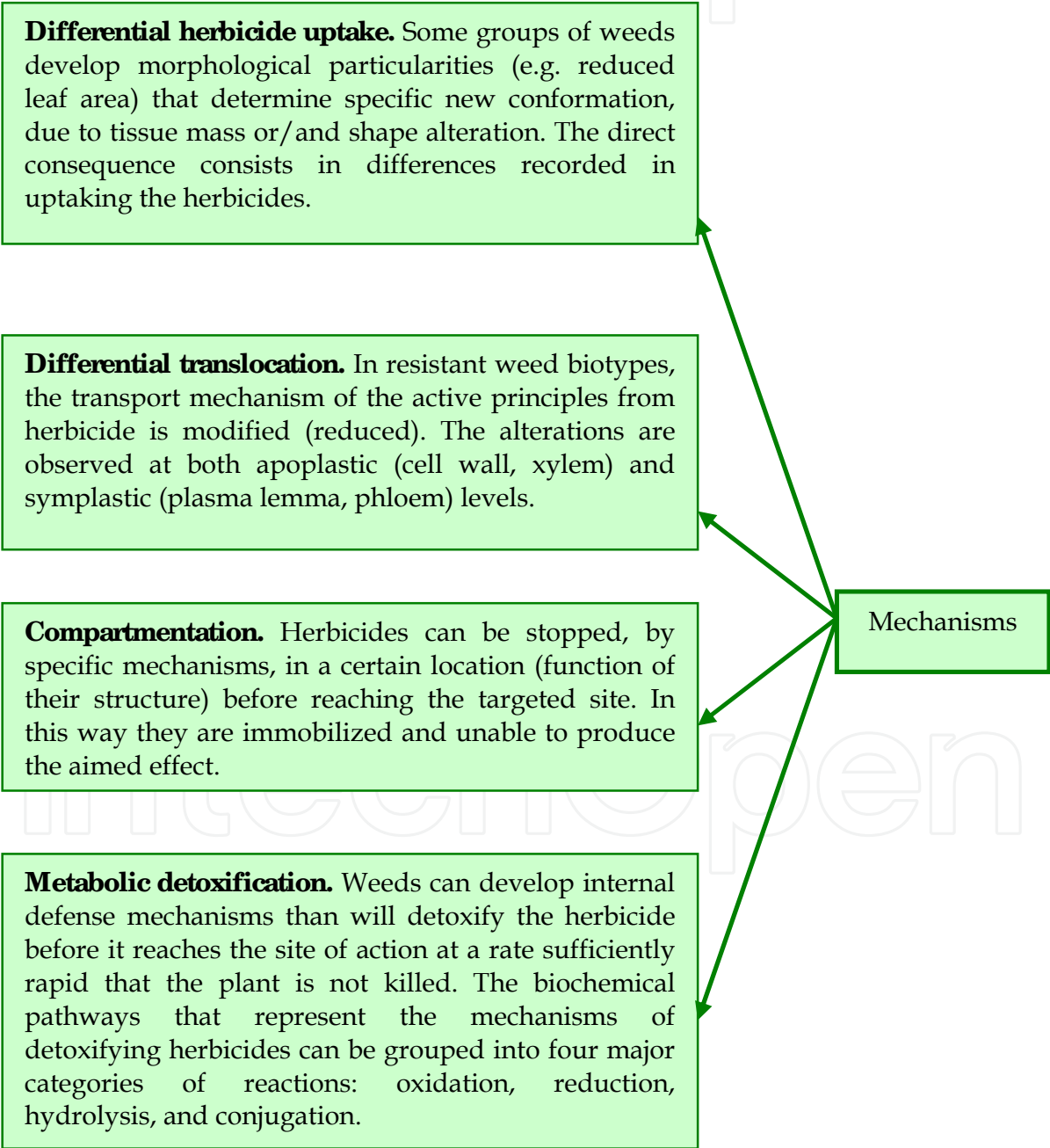
Mechanisms

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.
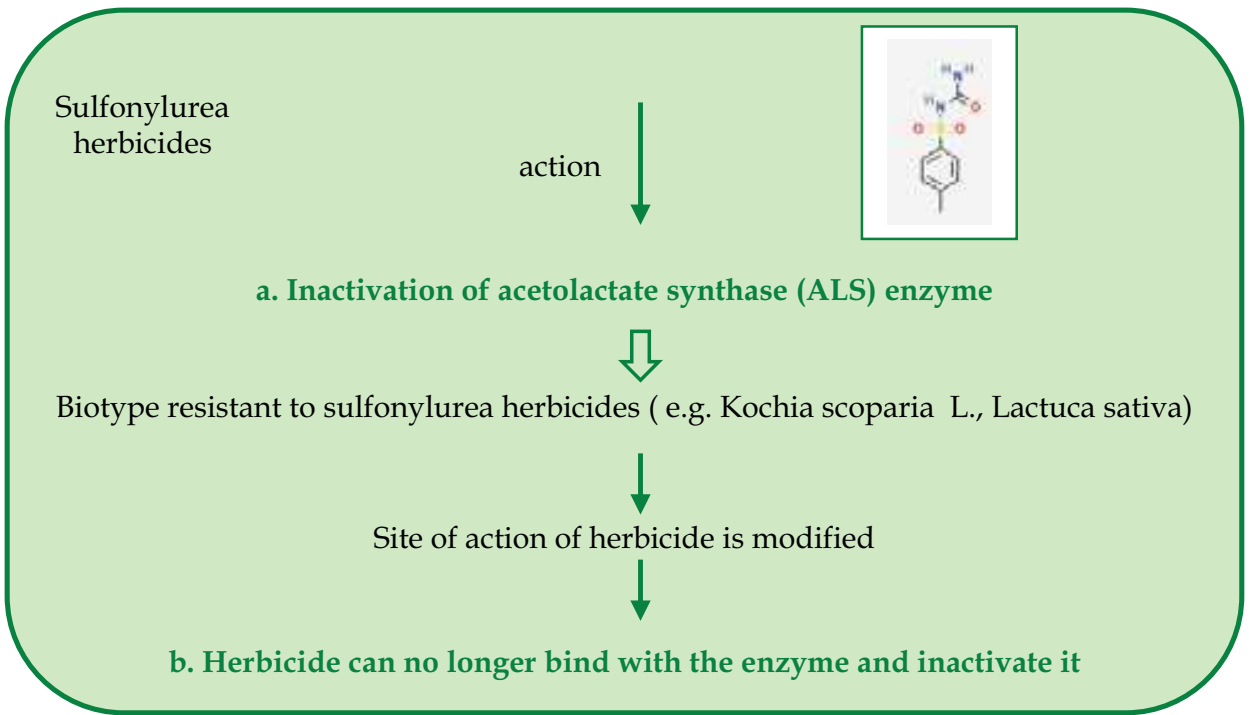

Fig. 4. Mechanism of herbicide action (a) and resistance (b) in biotypes resistant to sulfonylurea herbicides (e.g. *Kochia scoparia* L., *Lactuca sativa*)
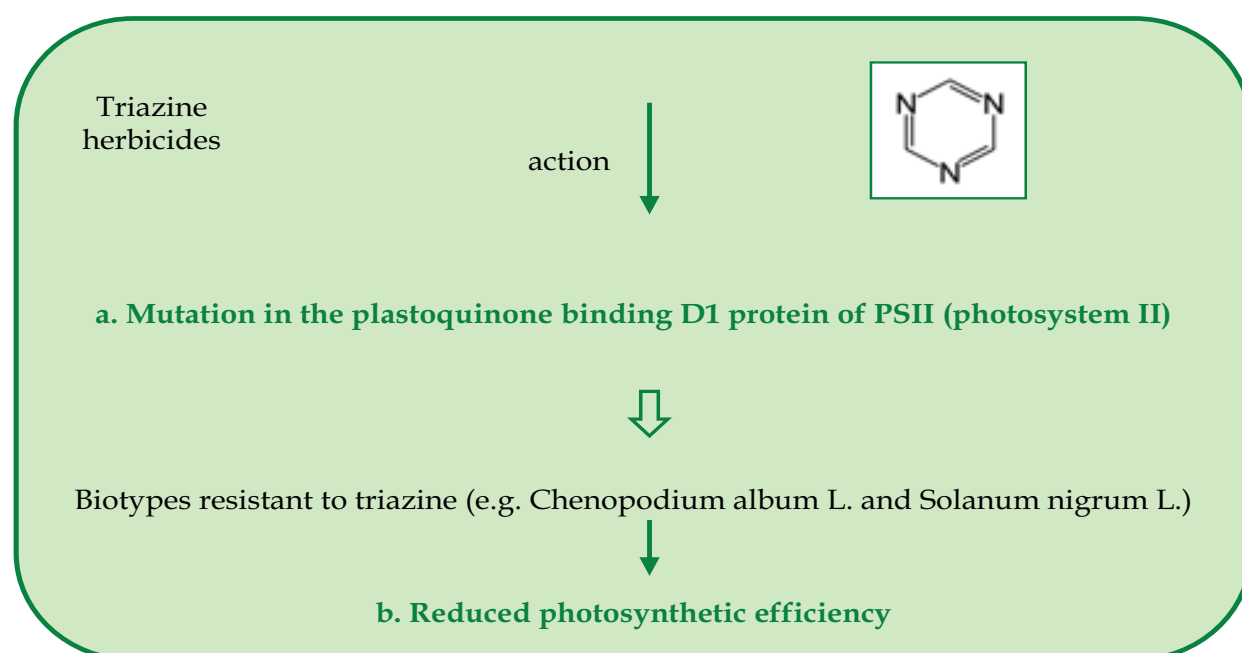
Fig. 5. Mechanism of herbicide action (a) and resistance (b) in biotypes resistant to triazine herbicides (e.g. *Chenopodium album* L. and *Solanum nigrum* L.)

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

Single site of action
Active point on enzyme

Multiple site of action
Active points on enzyme

Herbicide

1 site of action

Herbicides

Sites

Herbicide activity

site 1   sites 2 … n - 1   site n

Herbicide activity

Herbicide

1 site of action = blocked

No herbicide activity

Herbicides

1 site of action blocked
n – 1 active sites of action

site 1   sites 2 … n - 1   site n

Herbicide activity (les effective)

Herbicides

n sites of action blocked

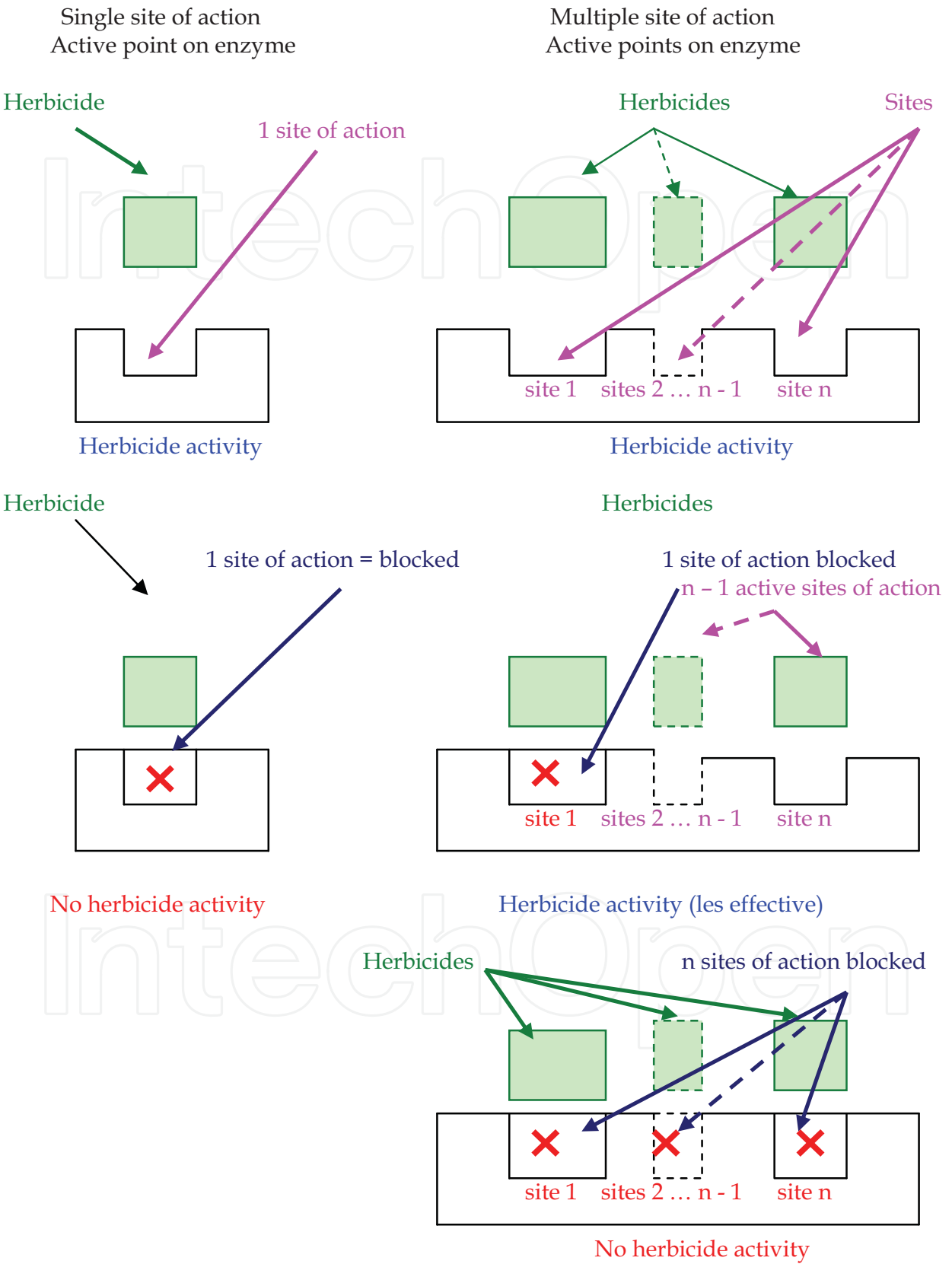site 1   sites 2 … n - 1   site n

No herbicide activity

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_6f complex, lipids, pigments (chlorophylls and β-carotene and cofactors (early electron acceptors vitamin K_1 phylloquinone in electron transport chain, Q_K A and B, Ferredoxin-NADP$^+$ oxidoreductase enzyme, FNR respectively, Mg$^+$ and Ca$^+$).
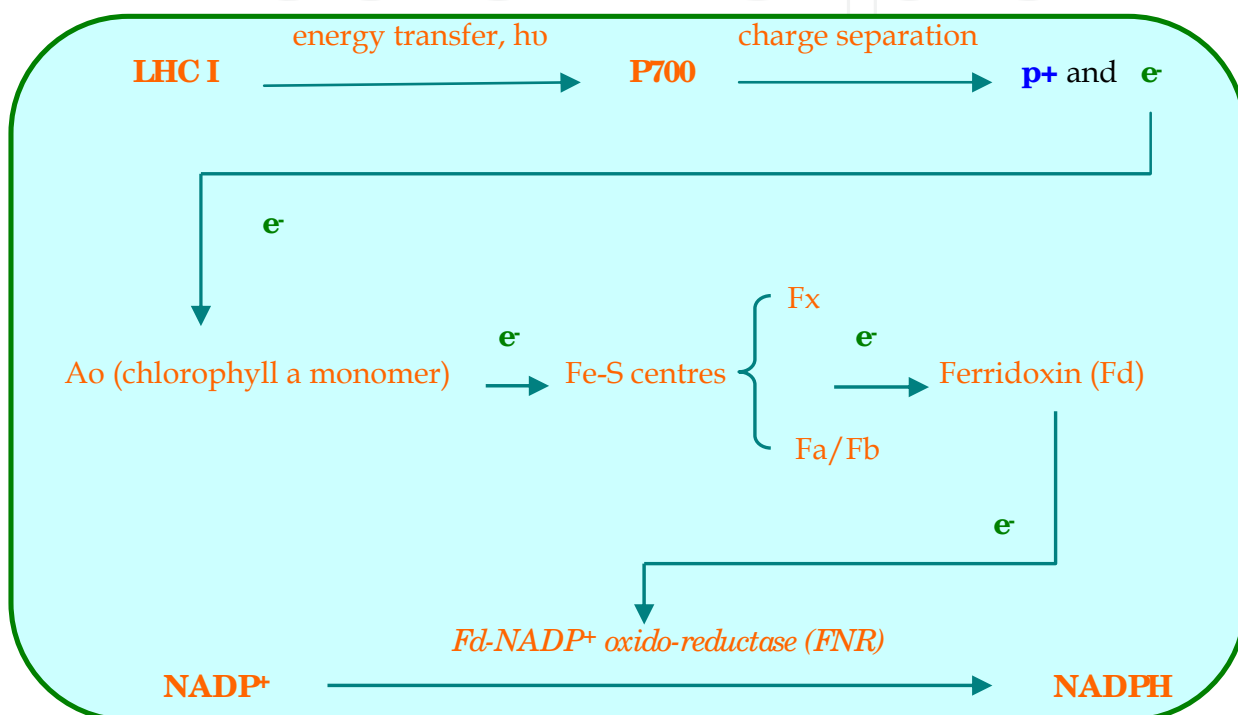

Fig. 7. The mechanism of PSI function in driving energy

The main inhibitors of photosystem I belong to post-emergence non-selective contact herbicides. They are represented by the chemical family Bipyridillum with herbicides Paraquat 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_2O into

Mechanism of resistance

Detoxification of the toxic products formed. The herbicide treatment produces superoxide and hydroxide radicals, hydrogen peroxide, and singlet oxygen. This resistance mechanism involves the action of the protective enzymes, which detoxifies the above mentioned radicals before they could initiate lipid peroxidation. The detoxifying enzymes are: superoxide dismutase, ascorbate peroxidase, glutathione reductase, dehydroascorbate reductase, catalase and peroxidase.

Rapid sequestration of the herbicide mechanisms. This mechanism was exemplified in *E.canadensis* and *E.sumatrensis*, (Yamasue et al., 1992) for Paraquat. The mobility of Paraquat is restricted in resistant biotypes since it is being rapidly sequestered. Autoradiogram studies confirm this mechanism.
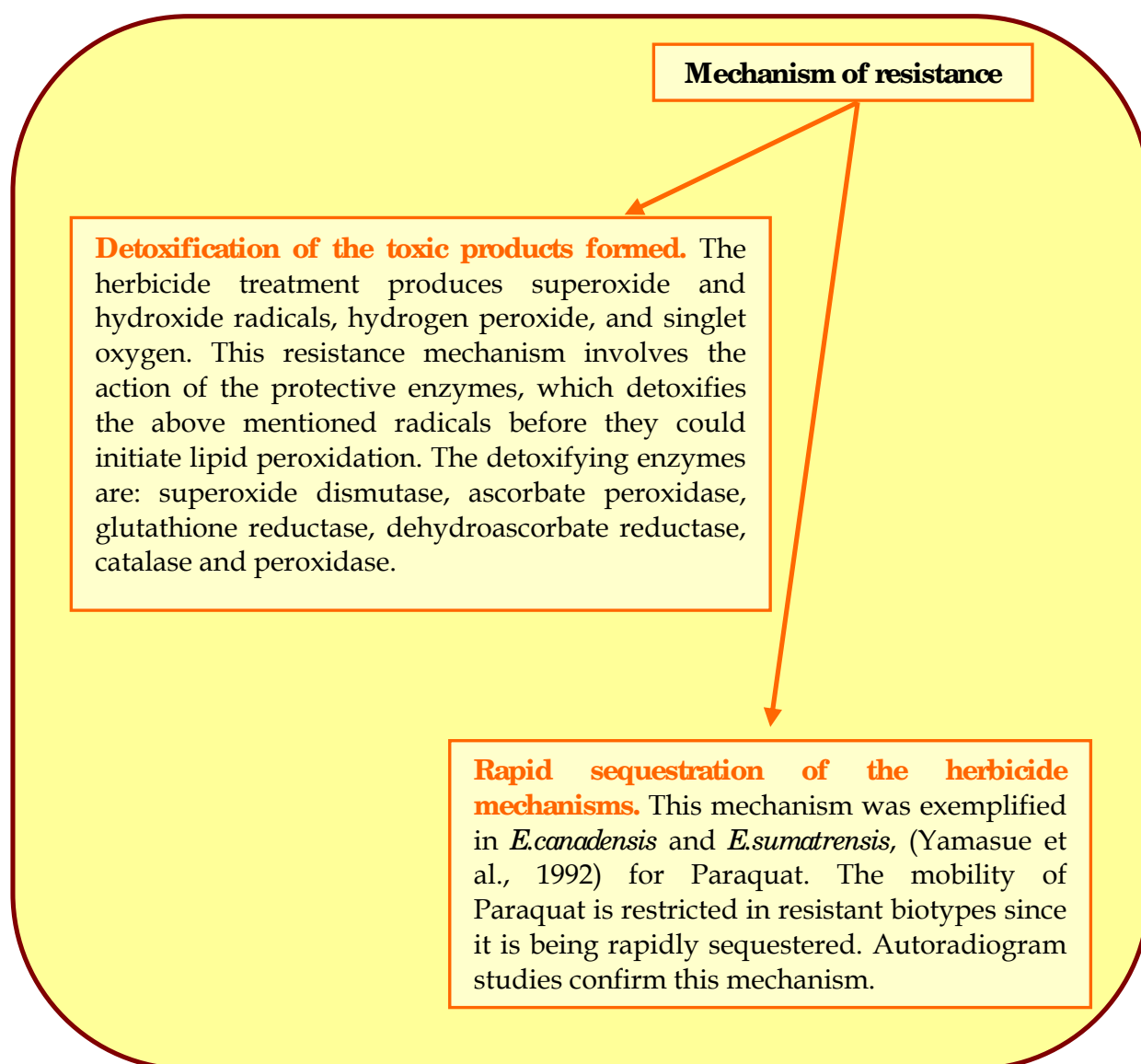
Fig. 8. The mechanisms involved in weed resistance against PSI inhibitors

O_2, 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,
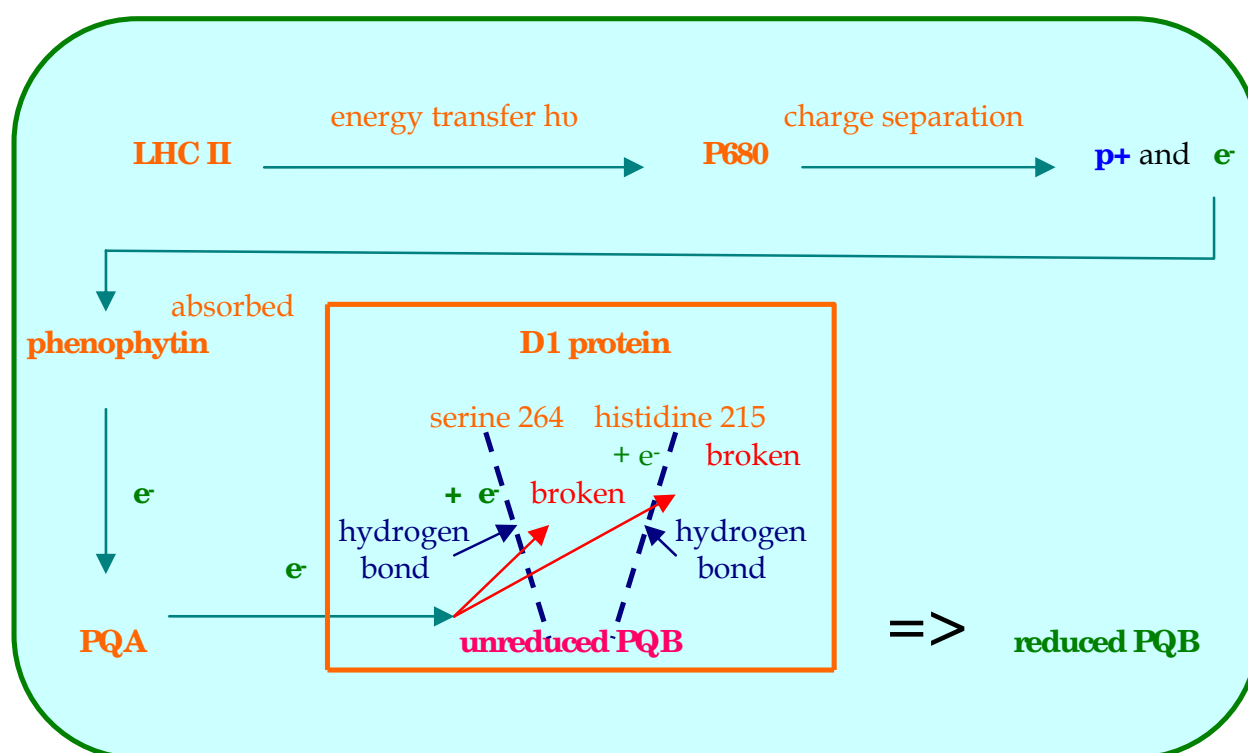- managanese centre (Guskov et al., 2009).

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).
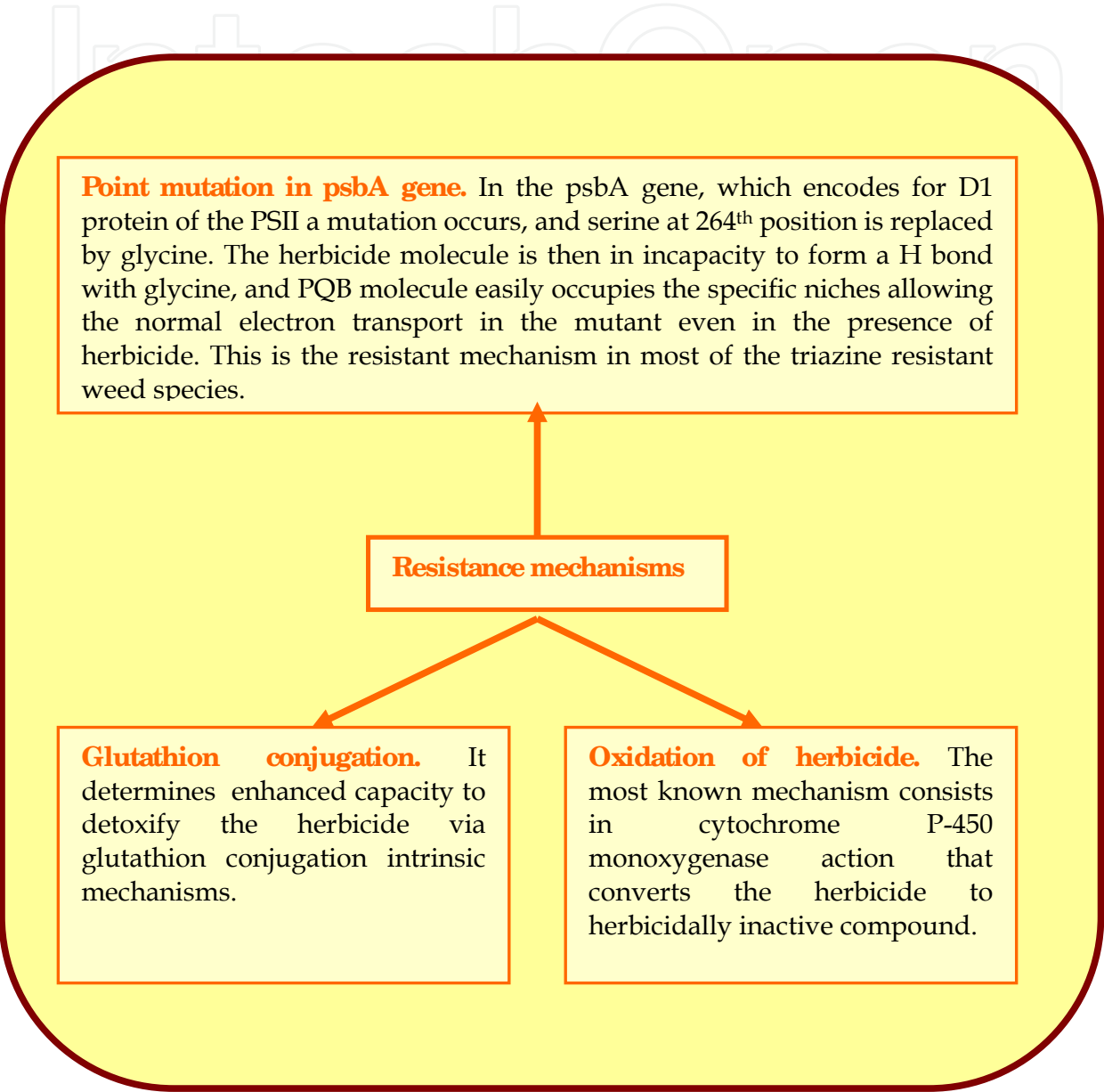
Point mutation in psbA gene. In the psbA gene, which encodes for D1 protein of the PSII a mutation occurs, and serine at 264th position is replaced by glycine. The herbicide molecule is then in incapacity to form a H bond with glycine, and PQB molecule easily occupies the specific niches allowing the normal electron transport in the mutant even in the presence of herbicide. This is the resistant mechanism in most of the triazine resistant weed species.

Resistance mechanisms

Glutathion conjugation. It determines enhanced capacity to detoxify the herbicide via glutathion conjugation intrinsic mechanisms.

Oxidation of herbicide. The most known mechanism consists in cytochrome P-450 monoxygenase action that converts the herbicide to herbicidally inactive compound.

Fig. 10. The mechanisms involved in weed resistance against PSII inhibitors
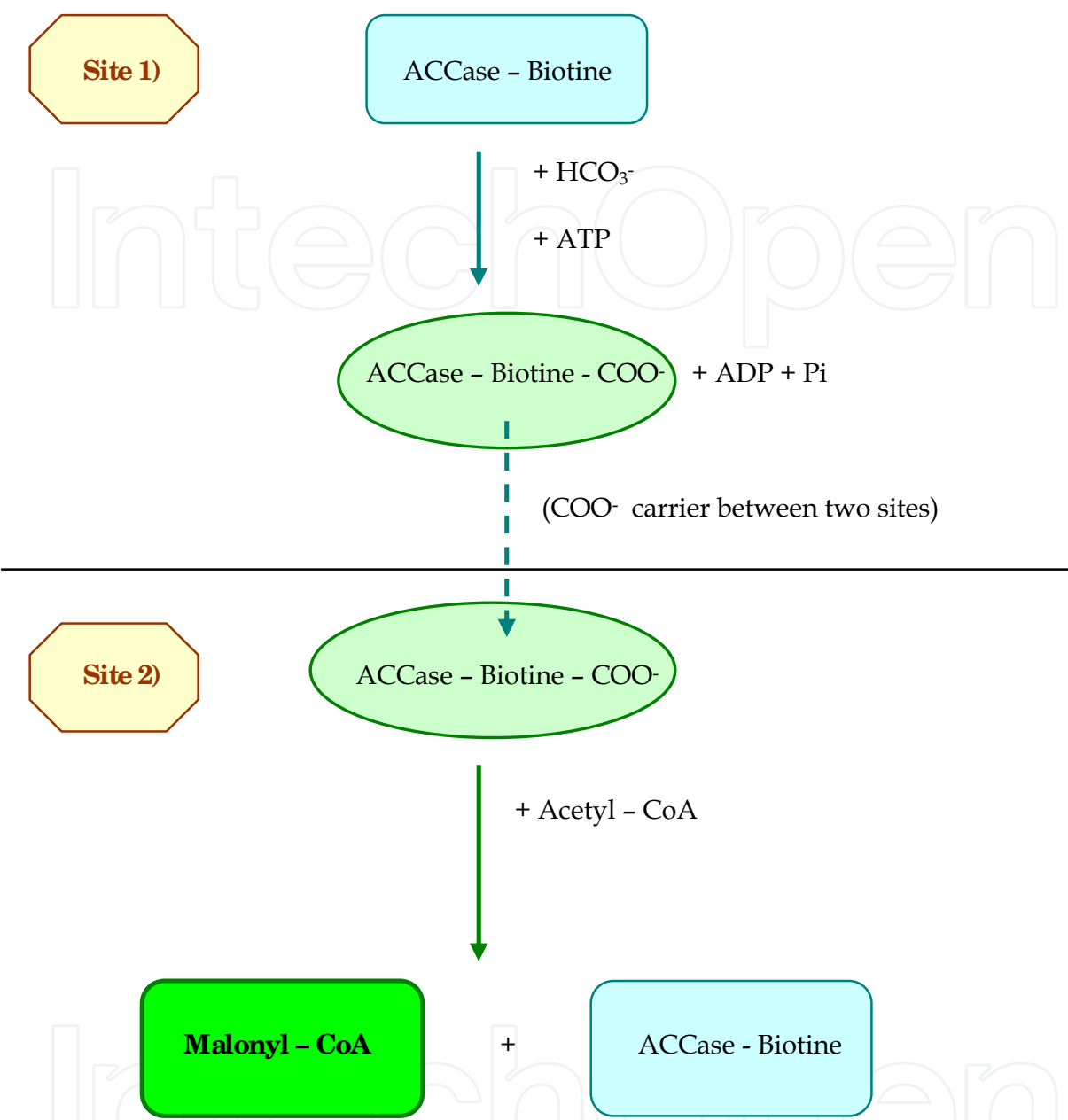
Fig. 11. The mechanism of ACCase activity

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).

Presence of tolerant form of ACCase. In majority of weed biotypes, resistance to ACCase is produced by a punctual mutation of the nuclear gene encoding the ACCase I isoform.

Resistance mechanisms

Detoxification mechanism. In resistant biotypes P450 monoxygenase is involved

Overproduction of ACCase. Usually, in resistant biotypes the ACCase levels are 2 or even 3 times greater compared to biotypes susceptible to herbicide action.

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).
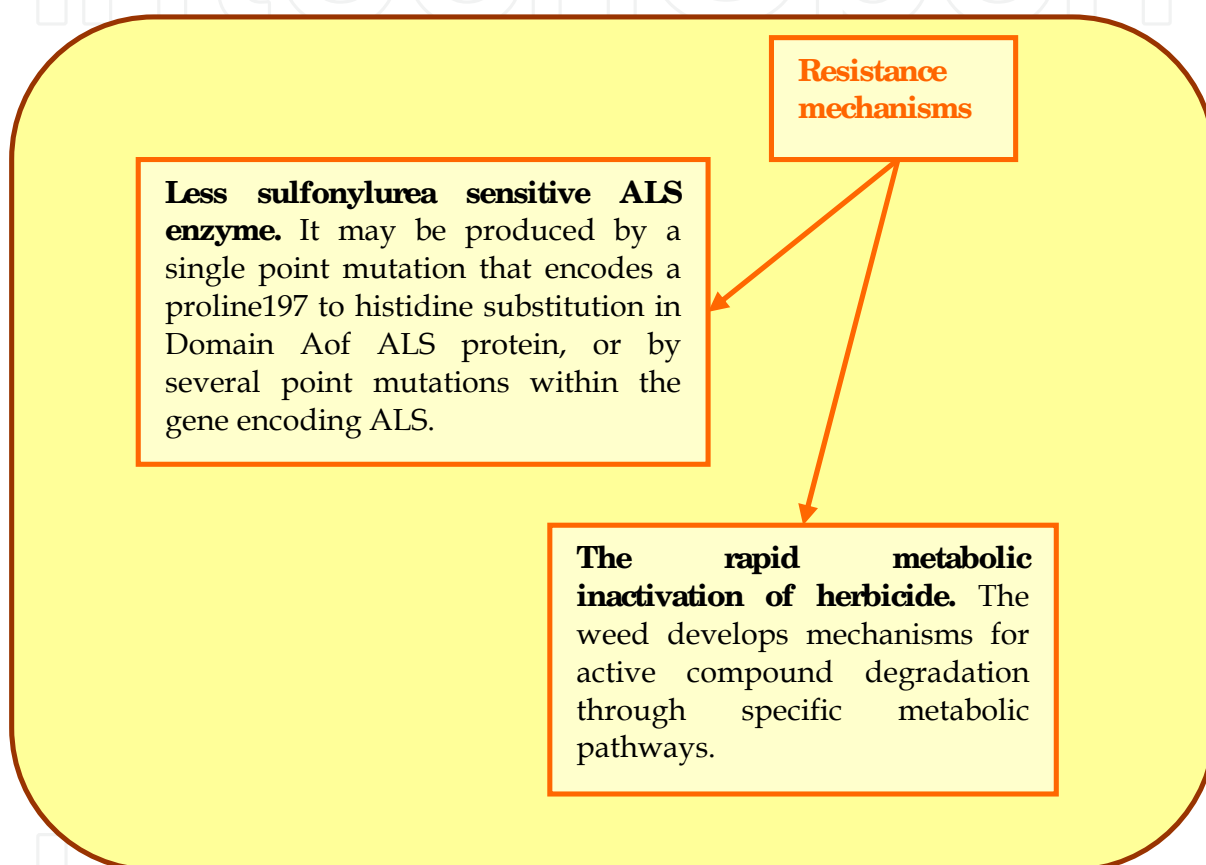
Fig. 13. The mechanisms involved in weed resistance against ALS inhibitors

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.

5. References

Berca, M. (2007). Fungicide Resistance in Agricultural Cultures from European Perimeter, *ProEnvironment*, Pilot number, pp. 8 - 20

Chipman, D., Barak,, Z., Schloss, J.V. (1998). Biosynthesis of 2-aceto-2-hydroxy acids: acetolactate synthases and acetohydroxyacid synthases, *Biochim Biophys Acta.*, 1385 (2), pp 401-419

Cummins, I., Edwards, R. (2010). The Biochemistry of Herbicide Resistance in Weeds, *Outlooks on Pest Management*, Vol. 21, No.2, pp. 73-77

Ge., X., d'Avignon, D.A., Ackerman, J.J.H., Sammons, R.D. (2010). Rapid vacuolar sequestration: the horseweed glyphosate resistance mechanism, Pest Management Science, *Vol. 66, Issue 4*, pp 345–348

Guskov, A., Kern, J., Gabdulkhakov, A., Broser, M., Zouni, A., Saenger, W. (2009). Cyanobacterial photosystem II at 2.9-A resolution and the role of quinones, lipids, channels and chloride, *Nature Structural & Molecular Biology*, 16(3), pp 334-42.

Hakala, M., Rantamaki, S., Puputti, E.-M., Tyystjarvi, T., Tyystjarvi, E. (2006). Photoinhibition of manganese enzymes: insights into the mechanism of photosystem II photoinhibition, *Journal of Experimental Botany*, Vol. 57, No. 8, pp. 1809–1816

Kremer, E. & Kropff, M.J. (1999). Comparative Growth of Triazine-susceptible and -resistant Biotypes of *Solanumnigrum* at Different Light Levels, *Annals of Botany*, 83, pp. 637-644

Kurth, D.G., Gago, G.M., de la Iglesia, A., Lyonnet, B.B., Lin, T.W., Morbidoni, H.R., Tsai, S.-C., Gramajo, H. (2009). ACCase 6 is the essential acetyl-CoA carboxylase involved in fatty acid and mycolic acid biosynthesis in mycobacteria, *Microbiology*, 155, pp 2664-2673

McCourt, J. A. & Duggleby, R. G. (2006). Acetohydroxyacid synthase and its role in the biosynthetic pathway for branched-chain amino acids, *Amino Acids*, Vol. 31, No. 2, pp 173-210

Oroian, I. (2008). Plant protection and environment, 325 pg., Todesco Cluj – Napoca, ISBN 978-973-7695-47-5 [In Romanian]

Owen, M.D.K.& Zelaya, I.A. (2005). Herbicide-resistant crops and weed resistance to herbicides, *Pest Management Science*, 61, pp. 301 - 311

Paoletti, M.G. & Pimentel, D. (1995). The environmental and economic costs of herbicide resistance and host-plant resistance to plant pathogens and insects, *Technological Forecasting and Social Change*, Vol. 50, Issue 1, pp 9-23

Powles, S.B. & Yu, Q. (2010). Evolution in Action: Plants Resistant to Herbicides, *Annual Review of Plant Biology*, Vol. 61, pp. 317-347

Prather, S.T., Ditomaso, J.M., Holt, J.S. (2000). Herbicide resistance: Definition and Management strategies, Division of Agriculture and Natural Resources, University of California, http://anrcatalog.ucdavis.edu

Preston, C. & Powles, S.B. (2002). Evolution of herbicide resistance in weeds: initial frequency of target site-based resistance to acetolactate synthase-inhibiting herbicides in *Lolium rigidum, Heredity*, 88, pp. 8 - 13

Saari, L.L., Cotterman, J.C., Primiani M.M. (1990). Mechanism of Sulfonylurea Herbicide Resistance in the Broadleaf Weed, *Kochia scoparia, Plant Physiology*, 93, 55 -61

Scarabel, L., Carraro, N., Sattin, M., Varotto, S. (2004).Molecular basis and genetic characterisation of evolved resistance to ALS-inhibitors in *Papaver rhoeas, Plant Science*, Vol., 166, Issue 3, pp. 703 - 709

Sellwood, C., Slabas, A.R., Rawsthorne S. (2000). Effects of manipulating expression of acetyl-CoA carboxylase I in *Brassica napus* L. embryos, *Biochemical Society Transactions*, Vol. 28, part 6598, pp. 600 - 615

Sharon, I., Alperovitch, A., Rohwer, F., Haynes, M., Glaser, F., Atamna-Ismaeel, N., Pinter, R.Y., Partensky, F., Koonin, E.V., Wolf, Y.I., Nelson, N., Béjà, O. (2009). Photosystem I gene cassettes are present in marine virus genomes, *Nature*, 461, pp 258-262

Sigematsu, Y., Sato, F., Yamada, Y. (1989). The Mechanism of Herbicide Resistance in Tobacco Cells with a New Mutation in the QB Protein, *Plant Physiology*, 89, pp. 986-992

Stockel, J.& Oelmuller, R. (2004). Novel Protein for Photosystem I Biogenesis, *The Journal of Biological Chemistry*, Vol. 279, No. 11, pp. 10243–10251

Vila-Aiub, M. M., Martinez-Ghersa, M.A., Ghersa, C. M. (2003). Evolution of herbicide resistance in weeds: vertically transmitted fungal endophytes as genetic entities, *Evolutionary Ecology*, Vol. 17, Nos 5 – 6, pp. 441-456

Watanabe, M., Iwai, M., Narikawa, R., Ikeuchi, M. (2009). Is the Photosystem II Complex a Monomer or a Dimer ?,*Plant Cell Physiology*, 50 (9), pp. 1674–1680

Yamasue, Y., Kamiyama, K., Haniokaand, Y., Kusanagi, T. (1992). Paraquat resistance and its inheritance in seed germination of the foliar-resistant biotypes of *Erigeron canadensis* L. and *E. sumatrensis* Retz, *Pesticide Biochemistry and Physiology*, Vol. 44, Issue 1,pp 21 - 27

*** (2008). Illinois Agricultural Pest Management Handbook, http://ipm.illinois.edu/pubs /iapmh/12chapter.pdf, pp. 272 – 276

*** (2010). Practical Guide for Farmers, Alcedo 2010, pp. 3 – 142, ISBN 978-973-7982-31-5 [In Romanian]

*** (2010). FAOSTAT, http://faostat.fao.org/site/567/default.aspx#ancor

*** (2010). http://agbiosafety.unl.edu/

Herbicides and Environment

Edited by Dr Andreas Kortekamp

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.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

INTECH
open science | open minds