

Herbicides carryover in systems cultivated with vegetable crops¹

Carryover de herbicidas em sistemas cultivados com olerícolas

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Abstract - The residual effect of herbicides in the soil on sensitive succeeding crops is known as carryover. Most studies on carryover in vegetable crops have been developed in other countries; however, the problems arising from this phenomenon are also a reality in Brazil. The limited information in the literature, together with the absence of alerts and periods of restriction in the instructions for use of herbicides sold in the country for sensitive vegetables grown in succession contribute to the occurrence of major damage to horticulturists. Herbicides carryover can cause injury, visibly or not, in vegetable crops, it can reduce growth and productivity, as well as compromise the quality of the product and even derail the area for cultivation for years. This review describes the dynamics of herbicides in soil and brings together several works about the residual effect of herbicides in vegetable crops. Further, it discusses the possible ways of monitoring cultivated areas through the analysis in laboratories or bioassays, and strategies to minimize the harmful effects in these cultures, which are highly sensitive. In this context, the integrated weed management is essential to reduce the need for herbicide use and accumulation these on the soil, reducing the risk of carryover, as well as legislative action for the inclusion of restriction periods of sensitive vegetables grown in the instructions for use of herbicides.

Keywords: bioassay; chromatography; crop rotation; monitoring; residual activity

Resumo - O efeito residual de herbicidas no solo sobre culturas sucessoras sensíveis é conhecido como *carryover*. A maioria dos estudos sobre *carryover* em olerícolas tem sido desenvolvida em outros países, no entanto, os problemas advindos desse fenômeno são uma realidade também no Brasil. A limitada informação presente na literatura, aliada à ausência de alertas e períodos de restrição nas bulas dos herbicidas comercializados no país para o cultivo de olerícolas sensíveis em sucessão contribuem para a ocorrência de grandes prejuízos aos olericultores. *Carryover* de herbicidas pode causar intoxicação de forma visível ou não nas olerícolas, reduzir o crescimento e a produtividade, assim como comprometer a qualidade do produto e até mesmo inviabilizar a área para o cultivo por anos. A presente revisão descreve a dinâmica dos herbicidas no solo e reúne diversos trabalhos acerca do efeito residual de herbicidas em olerícolas. Além disso, discute as possíveis formas de monitoramento das áreas cultivadas, através da análise em laboratórios ou de bioensaios, e as estratégias para minimizar os efeitos danosos nessas culturas, que são altamente

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sensíveis. Nesse contexto, o manejo integrado de plantas daninhas é essencial para redução da necessidade de utilização de herbicidas e aporte desses no solo, diminuindo os riscos de *carryover*, além de medida legislativa para inclusão dos períodos de restrição de cultivo de olerícolas sensíveis nas bulas dos herbicidas.

Palavras-chaves: bioensaio; cromatografia; rotação de culturas; monitoramento; atividade residual

Introduction

The vegetable crops have major nutritional importance in the human diet for the richness in vitamins, fiber, minerals and antioxidants, as well as relevance in the economic scenario of different producing countries. In Brazil, the South East and Southern regions stand out as the main producer, accounting for about 75% of total production, with tomatoes, potatoes, watermelon, onions, cabbage, lettuce and carrots being the most cultivated vegetables (IBGE, 2011; Camargo-Filho et al., 2013).

The vegetable crops are subjected to high germinating flows of weeds for being characterized as an intensive system of production, with plowing and harrowing of the soil, confection of beds, fertilizing at high levels and constant irrigation. Moreover, many vegetable crops have slow initial growth, like the garlic, onion and carrot, and are planted at wider spacing as tomatoes, squash and watermelon, which makes them very sensitive to interference imposed by weeds (Soares et al., 2003; Freitas et al., 2009, Silva et al., 2013). Thus, the management of weeds in crops is essential practice to avoid the damage caused to the quantity and quality of harvested products.

The high-tech and competitive level in the horticulture and in other crops on a large scale requires, in addition to other control methods, the application of herbicides on cultivated areas due to the efficiency and low cost, making it possible to cultivate relatively large areas with reduced cost of manpower.

The short production cycle of vegetable crops allows its use in crop rotation systems with other vegetables or grain. Crop rotation is commonly performed in the production areas

and it presents numerous advantages. However, the use of herbicides with long residual effect on the previous crops can impair growth and development of sensitive vegetables crops in succession (Mancuso et al., 2011), given the sensitivity of plants to these products and their residues in the soil (Felix et al., 2005; Pekarek et al., 2010; Robinson and Macnaughton, 2012). Thus, to minimize such problems it is important to monitor the inserted areas in rotation systems with vegetables and to use strategies and knowledge in an attempt to reduce the residual effect of herbicides in those areas.

In this light, the aim of this review is discuss aspects of the herbicide behavior in soil emphasizing the residual effect of different herbicides in vegetable crops, as well as to present forms of waste monitoring in areas of vegetables and possible strategies to reduce the residual herbicides in soil.

Herbicides Behavior in Soil

The behavior of the herbicide in the soil profile affects the weeds control period duration and the efficacy of herbicides, especially those applied in pre-emergence, directly into the soil, besides the effects on the environment (Westra et al., 2014). Therefore, the study of herbicide behavior has been accomplished through estimates of trends to which they are subject according to three main processes: retention, transport and transformation (Figure 1), which interact with each other, even though these processes are described isolated (Silva et al., 2007).

The retention of herbicides through the soil solid phase theoretically known by sorption, is measured by partition coefficients (K_d e K_{oc}) from aqueous solution. Typically, the herbicide

sorption increases with the increased content of organic carbon and mineral clay in the soil, thus increasing sorption may retard the movement of the herbicide in the soil (Mendes et al., 2014). The adsorbed molecules herbicides can return to the soil solution by desorption, or remain retained on an unavailable form, called residue linked (Christoffoleti et al., 2008).

The transport is defined as the movement of the herbicide in the soil, which may occur by leaching, runoff, volatilization and absorption by plants (Christoffoleti et al.,

2008). The herbicide transport intensity depends on several factors, such as application rate, persistence and mobility, precipitation, topography and local climate. Leaching refers to the vertical movement of the herbicide in the soil depth, the mass flow due to the gravitational force and the water pressure differences in the soil pores (Carter, 2000), while runoff regards to its lateral movement, on soil surface, both being dependent on rainfall, and the time or intensity of irrigation.

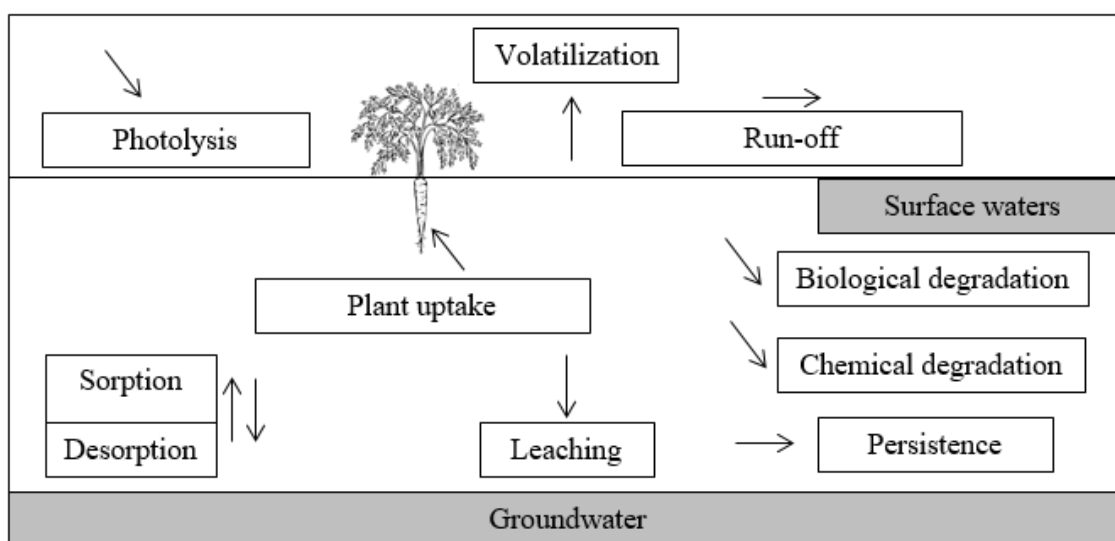


Figure 1. Diagram of the herbicide behavior in soil. Adapted of Bedmar and Gianelli (2014).

Volatilization is the process by which the herbicide is conveyed from the soil to the atmosphere due to the passage of molecules from a liquid to vapor form, depending on its vapor pressure (Silva et al., 2007). This is most significant when the residues of herbicides remain on the surface of dry or moist soil, since the incorporation of herbicides in the soil profile can significantly reduce losses caused by volatilization (Carter, 2000).

The transformation and degradation of the herbicide concerns to changing its molecular structure by biotic and abiotic factors being measured by half-life ($t_{1/2}$) - time when 50% of the herbicide initially applied is dissipated in soil. The biological degradation, usually carried out by microorganisms and chemical degradation

by hydrolysis and oxidation-reduction reactions can be completed, resulting in CO_2 , H_2O and minerals (mineralization), or partial, resulting in the formation of metabolites (Christoffoleti et al., 2008). The photodecomposition or photolysis is the transformation of the herbicide by sunlight in topsoil.

The period during which an herbicide remains intact and biologically active in the soil is called persistence (Bedmar and Gianelli, 2014). Herbicides with greater persistence can result in the phenomenon known as residual or *carryover* effect, which can be defined as herbicide toxic waste used in the previous crops that remain in the soil, which can affect sensitive crops grown in succession or rotation.

Several factors influence the carryover of herbicides in the soil, which fall into three categories that are strongly interrelated: soil (microorganisms, humidity, texture, structure, porosity, organic carbon content and pH), environmental conditions (temperature, management, rainfall and cultivated plant species) and physico-chemical properties of the herbicide (degree of retention, half-life, ionization constant, dose, vapor pressure and solubility) (Bedmar and Gianelli, 2014).

Herbicides Carryover in Vegetable Crops

The permanence of residual activity of herbicides in the soil is important aiming to expand the weed control period. However, the residue of herbicides in the soil can lead to contamination of surface and groundwater (Marchesan et al., 2010; Otto et al., 2012; Santos et al., 2015), besides causing intoxication and harm the growth and development of crops in succession (Artuzi and Contiero, 2006; Dan et al., 2010; Mancuso et al., 2011). This toxicity may or may not be visible and result in reduction of growth, the quality and productivity of the culture, even in the presence of low concentrations of herbicide in the soil (Robinson, 2008).

Symptoms of carryover in the cultures are related to herbicide dose, the plant developmental stage and planted cultivars (Thornton and Eberlein, 2001). Damage to high-value crops, as in the case with many vegetable crops, can result in substantial economic losses. In potato plants, for example, the effects may appear on the leaves, with injuries in various patterns, depending on the herbicide. In the tuber, one can observe a reduction in growth, yield and physiological disorders such as: multiple and deep cracks, tubers folding, spiral tubers, numerous side tubers connected to a single tuber or tuber in chain (Eberlein et al., 1997; Thornton and Eberlein, 2001).

The crop succession/rotation in vegetables cultivated areas is a practice widely

used, since it allows effective covering of soil, income diversification and nutrient cycling as well as it favors the breaking of pathogens cycles of pests and weeds. Vegetable crops are planted commonly in rotation with grains such as corn, soybeans and wheat and other vegetables. The use of persistent molecules in such crops is common, being soil herbicide persistence an important characteristic to be considered in agricultural production systems, since the waste herbicides can harm sensitive crops in rotation.

In agriculture, genetic improvement afforded the shorter cycle cultivars development; however, the residual period of herbicides, over the years, has not changed. Thus, the use of persistent products in fields with early maturing cultivars may be more damaging to sensitive succeeding crops, since the area is released quickly for growing species in succession/rotation and if the risks are not known and a safety period respected, the problems with sensitive species injury can be even sharper. A similar situation is the cultivation of corn for silage, in which there is the anticipation of removal of plant material concerning the maize for grain (Brighenti et al., 2002).

Although cases of carryover in vegetable crops are not rare in the major producing regions, causing losses and even invalidating areas for cultivation research are scarce in Brazilian literature on the residual effect of herbicides on this group of plants. Moreover, the instructions for use of the products sold in Brazil do not include cultivation restriction periods for most vegetable crops, not even suggest conducting bioassays before potentially sensitive species cultivation, unlike what happens in the instructions for use of herbicides registered in other countries.

Thus, it highlights the importance of conventional studies in the field, evaluating the carryover effect of herbicides applied in preceding crop, as well as studies that simulate the carryover effect of herbicides through the

application and immediate cultivation of susceptible species (Table 1).

Suspensions of carryover effect in garlic crops were raised in the Upper Paranaíba region by the use of ethoxysulfuron one year before planting this Alliaceae. Preliminary studies have

confirmed that herbicide residues in soil are responsible for causing malformation and cranny of outer leaf of garlic seed-bulb compromising the quality for trade (personal communication).

Table 1. Residual effect of herbicides in different vegetable crops.

Vegetable crops	Herbicides	Doses (g ha ⁻¹ a.i.)	Time after application	Negative Effects	Local	References
Beet, alfalfa and pea	imazapyr + imazapic and imazapyr + imazethapyr	39.9 + 119.7 39.9 + 119.7	140 days	Reduction of yield and fresh weight	Santiago, Chile	Alister and Kogan (2005)
Beet, pea and cucumber	mesotrione	70 to 560	One year	Injury; reduction of dry matter and yield	Ontario, Canada	Riddle et al. (2013)
Beet, pea and cucumber	mesotrione	7 to 56	Planting immediately after application	Injury; reduction of dry matter and yield	Ontario, Canada	Riddle et al. (2013)
Cabbage	flumetsulam	70; 140	One, two and three years	Injury; yield reduction	Ontario, Canada	O' Sullivan et al. (1999)
Cabbage and pumpkin	flumetsulam + metolachlor	224 + 8,400	One year	Injury; yield reduction	North Dakota, EUA	Greenland (2003)
Cabbage and beet	isoxaflutole isoxaflutole + atrazine	105; 210 105 + 1,063; 210 + 2,126	One year	Reduction of shoot dry matter and yield	Ontario, Canada	Soltani et al. (2005)
Cabbage and onion	nicosulfuron	140	One year	Injury. Onion yield reduction	North Dakota, EUA	Greenlad (2003)
Cabbage, onion and tomato	imazethapyr	280	One year	Injury. Tomato yield reduction	North Dakota, EUA	Greenlad (2003)
Carrot, broccoli, cucumber and onion	mesotrione; atrazine; mesotrione + atrazine	140 560 140 + 560	One year	Injury; reduction of shoot dry matter and yield	Ontario, Canada	Robinson (2008)
Carrot, cabbage, cucumber, onion, pepper and sugar beet	saflufenacil	100; 200	One year	Reduction of growth, yield and quality	Ontario, Canada	Robinson and Mcnaughton (2012)
Cucumber	nicosulfuron nicosulfuron + atrazine	60 30 + 1,500	7, 15 and 30 days	Injury; reduction plant height at flowering	Mato Grosso do Sul, Brazil	Carvalho et al. (2010)
Garlic	metribuzin	6 to 480	Planting immediately after application	Injury	Minas Gerais, Brazil	Walperes et al. (2015)

Table 1. Residual effect of herbicides in different vegetable crops ... (Continuation).

Vegetable crops	Herbicides	Doses (g ha ⁻¹ a.i.)	Time after application	Negative Effects	Local	References
Green onion, beet, lettuce, spinach, carrots and broccoli	imazosulfuron	224 to 450	Two years	Injury; reduction of stand and fresh weight	California, EUA	Felix et al. (2012)
Onion	metribuzin	240 to 480	Planting immediately after application	Injury; reduction of shoot dry matter and yield; and death plants	Minas Gerais, Brazil	Walperes et al. (2015)
Onion, beet and lettuce	imazosulfuron	224; 450	Two years	Yield reduction	Oregon, EUA	Felix et al. (2012)
Onion, peppers, tomato, watermelon and pumpkin	sulfentrazone	840	One year	Injury	North Caroline, EUA	Pekarek et al. (2010)
Pepper	isoxaflutole	210	One year	Yield reduction	Ohio, EUA	Felix and Doohan (2005)
Pepper, tomato and melon	imazapyr + imazapic; imazapyr + imazethapyr	39.9 + 119.7 39.9 + 119.7	300 days	Reduction of yield and fresh weight	Santiago, Chile	Alister and Kogan (2005)
Potato	cloransulam-methyl imazethapyr	44; 88; 176 140	One year	Injury; yield reduction	Ohio, EUA	Felix et al. (2002)
Potato	imazamethabenz	260; 520; 1050	One and two years	Injury	Idaho, EUA	Joo et al. (2001)
Potato	flumetsulam + clopyralid; clopyralid	39 + 105; 155 + 420 210	329 to 337 days	Injury; yield reduction	Minnesota, Ohio and Wisconsin, EUA	Felix et al. (2005)
Potato	flumetsulam	140	One year	Injury; yield reduction	Ontario, Canada	O' Sullivan et al. (1999)
Potato	aminopyralid	8 to 123	One month	Fresh mass of tubers reduction	Alaska, EUA	Seefeldt et al. (2013)
Potato	sulfometuron	240; 480; 960 ng kg ⁻¹	Planting immediately after application	Injury; yield reduction; deformation cracks and folds	Idaho, EUA	Hutchinson et al. (2007)
Potato	clopyralid and dicamba	35 to 560	One month	Injury	Alaska, EUA	Seefeldt et al. (2014)
Potato	quinclorac	150 to 300	One year	Injury	Alberta, Canada	Moyer et al. (1999)

Potato	tembotrione	8.4 to 50.4	One day	Reduction of growth, yield and tubers quality	Minas Gerais, Brazil	Dias et al. (2015a, 2015b)
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Table 1. Residual effect of herbicides in different vegetable crops ... (Continuation).

Vegetable crops	Herbicides	Doses (g ha ⁻¹ a.i.)	Time after application	Negative Effects	Local	References
Potato, tomato and cabbage	imazethapyr	100; 200	One and two years	Injury; yield reduction	Ontario, Canada	O' Sullivan et al. (1998)
Sweet potato and cabbage	sulfentrazone	840	One year	Injury; yield reduction	North Caroline, EUA	Pekarek et al. (2010)
Tomato	2,4-D and dicamba	1.14; 2.28	90 days	Epinasty; reduction of plant vigor and yield	Florida, EUA	Gilreath et al. (2006)
Tomato and radish	imazethapyr + imazapic	100; 200	1,100 days	Reduction of height, shoot dry matter and root dry matter	Rio Grande do Sul, Brazil	Sousa et al. (2012)
Tomato, pepper and cucumber	mesotrione	210; 420; 840	One year	Injury; yield reduction	Ohio, EUA	Felix et al. (2007)

Given the sensitivity of cultures to herbicide residues in the soil, precautions must be taken with the use of products based on its physical and chemical characteristics and rotation programs established for each area.

Herbicides Residue Monitoring Program in Vegetable Areas

Facing the complexity of the herbicides dynamics in soil, Brazilian horticulturists, mostly, ignore the carryover, either by ignorance of the presence of herbicides in soil or for not having seen the damage in their crops. However, some farmers watch out for the possible harmful effects on subsequent crops, however, they show difficulty on monitor the areas to safely planting.

The herbicide residue monitoring program in the soil for planning property planting areas is not reality yet. However, it is necessary to have a tool to at least provide a warning on the area involved, though there are not techniques and methods that ensure high

probabilities that the growing sensitive plants in that area is not adversely affected. This lack of warranty comes from the lack of information on the relationship between the amount of residues of herbicides in soil and injury in sensitive vegetables at different stages of farming, ie, from sowing to harvest. Some herbicides in plants do not cause injuries measured visually, and injuries are only checked at harvest, following the example of tembotrione residues affecting the productivity and causing cracks in potato tubers (Dias et al., 2015a).

The chromatographic and bioassay methods are tools that can be used in monitoring programs for detection and direct or indirect quantification of herbicide residues in the soil, respectively. Prior to detection a very important step is the soil sampling of the area involved.

According to Prata et al. (2003) for herbicide residue analysis, in order to clarify injury symptoms, soil samples should be collected between depths ranging from 0-20 cm, in the area that shows plants with symptoms, taking at least 20 single samples to form a

compound. Samples should not be dried at all; they must be packed in hermetically sealed plastic bags with string and immediately sent to the laboratory within 24 hours. During transport, samples should be kept refrigerated, which can be done in styrofoam containers with ice. In the case of a possible storage before shipment, the soil samples should be packed in plastic bags of high density, new and frozen at a temperature of - 20°C.

However, for horticulture, sampling to a depth of 20 cm, especially in production systems which commercial part takes place below the soil surface - bulbs, tubers, roots and rhizomes, is not appropriate and representative. For these crops there is soil disturbance in the layer 0-40 cm. Thus, if a persistent herbicide applied to a crop presents mobility in the soil profile, a 0-20 cm sampling may not contain residues of this product, and, when performing the inversion of layers, it may become available to the next crop in rotation causing damage. Thus, for horticulture it is recommended that soil samples be collected at least up to 40 cm.

The herbicidal residue analysis consists in chromatographic determinations providing, as a result, the presence or absence of a particular molecule (one or more) in the analyzed matrix as well as its/theirs concentration. In fact, the residue analyzes are individual because they are different for each herbicide, due to its physical and chemical properties. Therefore, a key point is to determine what herbicide or herbicides to analyze in the matrix, being water, soil or plant. However, in certain cases, there is the possibility of more than one molecule in the same checking analysis. This procedure is known as multiresidue analysis (Prata et al., 2003).

The methods of herbicides chromatographic analysis are costly, since they depend on high-tech equipment and skilled labor. However, they show high efficiency in the quantification of multiple residues of herbicides by means of liquid or gas chromatography coupled to mass spectrometry,

LC-MS/MS and GC-MS/MS, respectively (Walorczyk et al., 2013). Jointly, to optimize its effectiveness, the official QuEChERS method as multiresidue analysis is used in the preparation of the samples. This method shows high recovery rates, greater than 80% for various herbicides with different properties, in addition to accuracy and precision, which permits corrections for the internal standard. The main disadvantage is related to the small final volume of the extract that contains the sample (Queiroz et al., 2012).

Chemical methods present low correlation limitation between the amount of some herbicides residues and intoxication of sensitive crops, however, it contributes much towards subsidizing the visual assessment of intoxication symptoms caused by remaining residues in the applications soil in previous harvests (Prata et al., 2003). Although these methods are high sensitive, some herbicides applied in low doses, cannot be detected or when detected are not exactly quantified. An alternative is the monitoring of such herbicides by the bioassay method.

The bioassay method consists in the cultivation of plants susceptible to very low amounts of herbicide residues in the soil, in the order of ppb or ppt or parts per billion or trillion, respectively (Hutchinson et al., 2007). As an auxiliary tool, the farmer can use this method to monitor herbicide residues as long as he has the history of use of these products in the area and select the appropriate bioindicators by running it a few months earlier to allow time to adapt to the property dynamics. Through the intoxication symptoms and the dry matter mass accumulation of these species there has been an indication of the contaminants presence in the soil, which may be related to the area history, and the mechanisms of action of herbicides.

The quantification of herbicide residues in the soil by this method is not exact, it is determined indirectly with the use of dose-response curves. Ideal and standardized growth conditions of bio-indicator species such as temperature, light, water in the soil and

humidity are important for increased reliability of results. Despite the lower accuracy and precision, the method is relatively simple and inexpensive, requiring knowledge on plant physiology and symptomology of herbicides. Some herbicides in low doses are detected only by this method, for example, metsulfuron-methyl (2 to 4 g ha⁻¹ a.i.) used in wheat crop.

Strategies for Reducing Herbicides Carryover in Vegetable Crops

The reduction of the residual effect of herbicides in areas cultivated with vegetables will only be possible with the use of the Integrated Weed Management (IWM). Correct identification of weeds and awareness of tools available to manage them are essential. In addition, IWM programs of crops must be in synchrony with the crop succession/rotation planning established for each area.

In this sense, for chemical weed control it is important choose less persistent products, reduced doses and less sensitive crops for the succession/rotation. Another option is the use exclusion of some action mechanisms or soil high persistence products from the dynamics of properties with a primary focus on vegetable crops. In the Alto Paranaíba-MG region some producers are excluding wheat from the rotation due to the problems caused by residues from metsulfuron-methyl (ALS inhibitor) in vegetables in succession, such as garlic and carrot (personal communication).

The use of plastic mulching in tomato production, for example, is already a reality in Brazil. This technique, in addition to controlling various weeds, is being implemented to avoid injury by metribuzin in tomato and, consequently, the carryover in succeeding crops is excluded. The use of haystack in onion beds has been tested by the Polo Regional Alta Sorocabana - APTA, in an attempt to reduce the incidence of weeds throughout the crop cycle (Hirata et al., 2014), diminishing the need for herbicide application and accumulation these on

the soil, and minimizing the potential problems of carryover.

Another strategy of great importance is legislative, in which the MAPA - Ministry of Agriculture, Livestock and Food Supply, request that the leaflet of the herbicide contains the cultivating restriction period of sensitive crops, mainly of vegetable crops of higher added value and more cultivated in the country as potato, tomato, carrot, onion and garlic.

Final Remarks

The vegetable crops in general are very sensitive to herbicide residues in the soil. The small number of research in tropical conditions on herbicides carryover in these cultures highlights the need for studies to identify the problems and quantify damages related to the cultures, as well as the importance of holding information in instructions for use of commercial products about the restriction periods of vegetable sensitive crops. It is prudent that the monitoring of vegetable areas is routinely done through the analysis in laboratories or bioassays, combined with the use of strategies to minimize the effects of carryover in vegetables cultivated in succession/rotation.

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