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Dynamics of herbicide degradation in cauliflower

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ABSTRACT

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The aim of this work was to compare the dynamics of the degradation of herbicides commonly used in brassica vegetables. Series of plot field experiments were carried out in planting cauliflower in 2012–2014. The amount of herbicide residues with the maximum residue level (MRL) determined by the Regulation (EC) No. 396/2005 and with requirements of non-residue production (up to 10 μg/kg of active ingredient in harvested product) was compared. Napropamide, clomazone and dimethachlor were applied before planting and pendimethalin, S-metolachlor, pyridate, ethametsulfuron, dimethenamid, metazachlor, quinmerac, picloram, clopyralid, cycloxydim, fluazifop, propaquizafop and quizalofop were applied after planting the cauliflower. Besides fluazifop and quizalofop, all tested herbicides showed a fast degradation and can be recommended for non-residue production. The amount of fluazifop residues did not fall below the MRL even 6 weeks after application. Residues of post-emergently applied quizalofop were detected in cauliflower 10–44 days after application in most of the samples at concentration 9–73 μg/kg (below the MRL).

Keywords: pesticides residues; weed control; *Brassica oleracea* var. *botrytis*; food contaminant

Vegetables are an important group of crops and they constitute a major part of the human diet. Pesticides are widely used in most sectors of agricultural production to protect crops against pest, diseases and weeds to increase the crop yield (Abdulra'uf and Tan 2013). For better and higher quality production, farmers use a large amount of pesticides during the whole growing period of vegetables (Baig et al. 2009). However, its intensive use has caused great environmental problems due to its ability to penetrate into the tissues of vegetables and then affect the food chain (Abdulra'uf and Tan 2013). Risk to human health can occur, especially when farmers ignore the recommended time period between the pesticide application and harvest (Baig et al. 2009, Wang et al. 2013). In order to ensure the supply of safe food, pesticides should be used only following good agricultural practices (GAP). In addition, even though pesticides might have been applied following GAP, the distribution of pesticide residues in individual crop parts might be very wide with some food items containing residue levels much higher than others (Prodhan et al. 2016).

Among the brassica vegetables, cauliflower has the lowest speed of residue degradation (Kocourek et al. 2017) and also can be a source of noxious toxic substances such as herbicides (Prodhan et al. 2016).

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Herbicides can remain on the soil surface due to the adsorption processes (Sondhia 2009) and potentially stable herbicides can be taken up by plant forming unwanted residues (Jaźwa et al. 2009).

Different herbicides have been registered for use in cauliflower for pre- or post-emergence weed control (Scott et al. 1995). Pendimethalin has been extensively used globally and it is a significant herbicide for the control of annual weeds in vegetable crops (Tsiropoulos and Miliadi 1998). Curvale et al. (1979) recommended napropamide for weed control. Metazachlor is highly recommended by Zinikeviciute and Baleliunas (1998) for high marketable cauliflower yield. Qasem (2007) tested the phytotoxicity of quizalofop in cauliflower. Henderson and Cairns (2002) proved that clopyralid, picloram and pyridate are able to well control weeds in cauliflower with minimal crop damage. Ethametsulfuron is the only herbicide from the group of acetolactate synthase inhibitors, to which cauliflower possessed an acceptable level of tolerance (Sikkema et al. 2006). Clomazone was used for weed management in cabbage production for over 20 years, however it may damage cauliflower (Harrison et al. 2015).

For extraction and detection of herbicide residues, Lehotay et al. (2010) recommended the most commonly used method QuEChERS (quick, easy, cheap, effective, robust and safe) with liquid chromatography and mass spectrometry. This method has detection with a practical limit of quantitation of 1 μg/kg (Farkas et al. 2014).

Non-residue production is the agricultural production, in which weed control is carried out, so that residues of used herbicides in products are below the limit of 10 μg/kg. This limit is currently set by the Czech decree No. 46/2014 Coll., which is used for products intended as infant food (Kocourek et al. 2017).

Because of specific behaviour of different pesticides in plants and environment, it can be assumed that that amounts of their residues in harvested cauliflower samples differ. The first objective of this work was to compare differences in the dynamics of selected herbicide degradation in cauliflower. The second objective was to compare herbicide residues concentrations with the maximum residue levels (MRL), to compare results with requirements of non-residue production and to develop recommendations of their use.

MATERIAL AND METHODS

The plots experiments were carried out in Prague, Czech Republic, Central Europe (285 m a.s.l., GPS: 50°7'N, 14°22'E) in the period 2012–2014. The soil in the area was classified as Haplic Chernozem with clay content of 19%, sand content of 25%, silt content of 56%, which is specific for silt loam soil. The soil had the following chemical characteristics: pH_{KCl} 5.75; 156 mg P/kg; 275 mg K/kg; 177 mg Mg/g; and 7984 mg Ca/kg. Sorption capacity was 209 $mmol_+$/kg. Annual mean air temperature in this area is about 9°C and mean annual precipitation about 500 mm. An overview of weather conditions during the experiments is shown in Table 1.

Experimental design. Pre-plant cauliflowers (cv. Chamborg) with three true leaves were manually transplanted into the plots, in a spacing of 0.5 m between rows and 0.7 m between seedlings. Netto area of plot was 12 m^2 (2 × 6 m) spaced by 0.5 m from each other. Two central rows were considered for sampling of cauliflower. The experiment was designed in a complete randomized blocks with three replications. Cauliflowers were planted on 9. 5. 2012; 6. 5. 2013 and 5. 5. 2014.

Cultural practices commonly used in agriculture were carried out according to the requirements of the cauliflower studies. The area was irrigated by a sprinkler system depending on weather conditions. Herbicides (Table 2) were applied in two terms:

Table 1. Weather conditions during the experiments

Month	Total precipitation (mm/month)			Average monthly temperature (°C)			Long-term normal	
	2012	2013	2014	2012	2013	2014	precipitation (mm/month)	temperature (°C)
May	23.4	106.5	136.9	16	12.7	13	77.2	12.7
June	46.8	173.4	20.2	18.1	16.8	17.3	72.7	15.9
July	55.9	89.5	42.9	20	18.5	17.2	66.2	17.5

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Table 2. Description of tested herbicides

Trade name	Active ingredient (a.i.)	Concentration of a.i. (g/L (g/kg))	Formulation	Manufactured
Devrinol	napropamide	450	SC	UPL Europe Ltd.
Brasan	clomazone dimethachlor	40 500	EC EC	Syngenta Syngenta
Stomp	pendimethalin	400	SC	Syngenta
Dual Gold	S-metolachlor	960	EC	Syngenta
Lentagran	pyridate	450	WP	Belchim Crop Protection
Salsa	ethametsulfuron	750	WG	DuPont
Butisan Max	dimethenamid metazachlor quinmerac	200 200 100	SL SL SL	BAFS SE BAFS SE BAFS SE
Galera	picloram clopyralid	67 267	SL SL	Dow AgroSciences Dow AgroSciences
Stratos Ultra	cycloxydim	100	EC	BAFS SE
Fusilade Forte	fluazifop	150	EC	Syngenta
Garland Forte	propaquizafop	100	EC	ADAMA
Targa Super	quizalofop	50	EC	Nissan Chemical Ind. Ltd.

SC – soluble concentrate; SL – soluble liquid; EC – emulsifiable concentrates; WP – wettable powders; WG – water dispersible granules

before planting and after planting of cauliflower. Terms of application in all experimental years are shown in Table 3. Herbicides were applied by a nonresidue sprayer Schachtner at a spray volume of 300 L/ha and pressure of 300 kPa. All tested herbicide doses are the highest registered doses for brassica vegetables. The samples of cauliflower were collected continuously during the growing season (Table 4) from the central part of each plot. A minimum of three cauliflowers were collected from one plot at each sampling. The samples were stored in the freezer at –20°C until the extraction procedure.

Analyses. Cauliflower samples were tested in the fully certified laboratory of the Department of Food Analysis and Nutrition at the University of Chemistry and Technology Prague. Extraction of pesticide residues was based on the QuEChERS method. Pesticides were extracted from a portion of the homogenized sample (10 g) by acetonitrile. After separation of aqueous and acetonitrile layers (induced by addition of anhydrous $MgSO_4$ and NaCl salts) an aliquot of the upper organic layer was transferred into a vial for LC-MS/MS. For the final identification and quantification of pesticides residues, the U-HPLC system coupled to a triple quadrupole mass spectrometer with electrospray

Table 3. Application rates, terms and dates

Active ingredient	Dose (g/ha)	Application term	Days after planting		
			2012	2013	2014
Napropamide	1800	BP	0	0	0
Clomazone	80	BP	0	0	0
Dimethachlor	1000	BP	0	0	0
Pendimethalin	1200	AP	6; 33	7; 37	4
S-metolachlor	1152	AP	6; 33	7; 37	4
Pyridate	450	AP	21; 33	23; 37	19; 32
Ethametsulfuron	22	AP	6; 21	7; 23	4; 19
Dimethenamid	500	AP	6; 21	7; 23	4; 19
Metazachlor	500	AP	6; 21	7; 23	4; 19
Quinmerac	250	AP	6; 21	7; 23	4; 19
Picloram	80	AP	21; 33	23; 37	19; 32
Clopyralid	20	AP	21; 33	23; 37	19; 32
Cycloxydim	200	AP	41; 49	49; 62	39; 53
Fluazifop	300	AP	41; 49	49; 62	39; 53
Propaquizafop	150	AP	41; 49	49; 62	39; 53
Quizalofop	125	AP	41; 49	49; 62	39; 53

BP – before planting; AP – after planting

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Table 4. Periods between herbicide application and cauliflower sampling (harvest)

Herbicide	Sampling after application (days)		
	2012	2013	2014
Napropamide	69	72	74
Clomazone	63; 69	72	
Dimethachlor	69	72	
Pendimethalin	48	35; 47; 65	32; 70
S-metolachlor	48	35; 65	32; 70
Pyridate	20; 28; 48	35; 49	32; 45
Ethametsulfuron		49; 65	50; 75
Dimethenamid	48	35; 65	32; 70
Metazachlor	48; 63	65	45; 70
Quinmerac	48	65	45; 70
Picloram	20; 28; 48	35; 49	32; 45
Clopyralid	20; 28; 48	35; 49	32; 45
Cycloxydim	20; 28; 36	10	
Fluazifop	20; 28; 36; 44	10; 22; 23; 35	11; 16; 25; 30
Propaquizafop	20; 28; 36	10	
Quizalofop	20; 28; 36; 44	10; 22; 23; 35	11; 16; 25; 30

ionization in positive ion mode (ESI+) was used. The generated data were processed by MassLynx software version 4.1 (Milford, USA).

Analysis of target herbicides was a part of a multiresidue analytical method that had been fully validated by ISO 17025 (2005). The individual samples were assayed for residues of herbicides in μg/kg. The measured values were compared with the MRL established by the Regulation (EC) No. 396/2005 and with requirements of non-residue (up to 10 μg/kg of active ingredient in harvested product) production. MRL for clomazone, ethametsulfuron, dimethenamid, picloram and fluazifop was 10 μg/kg; for dimethachlor it was 20 μg/kg; for metazachlor 40 μg/kg; for pendimethalin, S-metolachlor and pyridate 50 μg/kg; for napropamide and quinmerac 100 μg/kg; for propaquizafop 300 μg/kg; for quizalofop 400 μg/kg; for clopyralid 3000 μg/kg and for cycloxydim it was 5000 μg/kg, respectively.

Data evaluation. The obtained data were processed in the XLSTAT 2009 (New York, USA). Non-linear models of degradation of individual herbicides in cauliflower were created after the evaluation. Models of degradation are calculated according to the equation:

$$y = a \times (\exp(-x/b))$$

Where: y – amount of active ingredient (μg/kg); x – number of days after application. Parameters of models (a; b) were estimated as a = 2531; b = 147.266 for fluazifop and a = 18.135; b = 14.15 for quizalofop.

RESULTS AND DISCUSSION

Measured concentrations of herbicides residues confirmed that there are differences in the rate of metabolization of herbicides in cauliflower. After evaluating the data, it was found out, that the residues of herbicides applied before planting (napropamide, clomazone and dimethachlor) were not detected in samples of harvested cauliflower during the whole harvesting seasons. Post-emergently applied S-metolachlor, pyridate, ethametsulfuron, dimethenamid, metazachlor, quinmerac, picloram, clopyralid, cycloxydim and propaquizafop were not detected in any cauliflower samples, either. These active ingredients can be rapidly metabolized in cauliflower or their uptake by roots and xylem transport in cauliflower is low. As published by EFSA (2016), it is possible that residues of propaquizafop can quickly degrade in plants to other ester metabolite. Stachniuk et al. (2017) evaluated a pesticide residue contamination of brassica vegetables from Polish farmers and herbicide metazachlor, S-metolachlor, linuron or pendimethalin were not detected. Similar results were found by Łozowicka et al. (2012) who did not detected metribuzin, napropamide or propyzamide in the tested samples of brassica vegetables.

However, residues of clomazone, metazachlor, dimethenamid and quinmerac were not detected in cauliflower, if their treatment was done at least 50 days before harvest (common use of these herbicides). Pyridate, clopyralid and picloram were not detected even if their application was carried out three weeks before harvest.

Pendimethalin applied post-emergently after planting was detected only in one sample (47 days after application) in 2013 at trace level (3 μg/kg). In this year, high precipitation shortly before harvest occurred (Table 1) and pendimethalin could be leached into deeper soil layers, where it was more easily absorbed by cauliflower roots. Not

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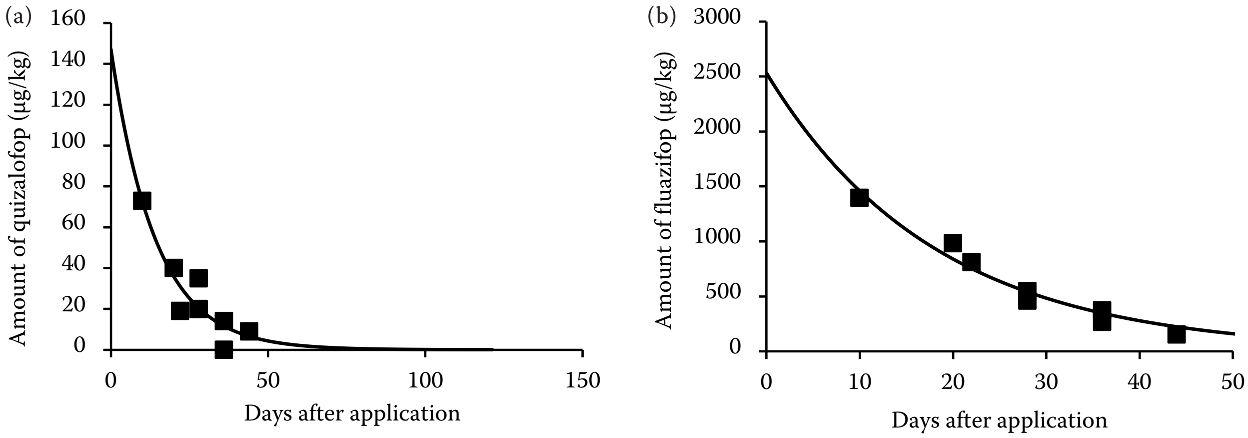

Figure 1. The course of degradation of (a) quizalofop and (b) fluazifop in cauliflower at time scale (data from 2012–2014)

just the concentration of pendimethalin residue in cauliflower but also the efficacy and phytotoxicity of pendimethalin can be affected by weather conditions in the growing season (Jursík et al. 2016). Sondhia (2013) also detected a very low concentration of pendimethalin residues (2 μg/kg) in cauliflower samples harvested 70 days after application. As published by Sondhia (2009) the most commonly detected value of pendimethalin in crop samples was on the limit of detection (1 μg/kg).

The concentration of residues of the above-mentioned herbicides in harvested product did not exceed the MRL if the recommended time between application and harvest was kept. All of these herbicides can also be recommended for non-residue production for products intended as infant food.

Residues of post-emergently applied quizalofop were detected in cauliflower after application in almost all of the samples but always below the threshold of MRL (400 μg/kg). The highest quizalofop concentration (73 μg/kg) was detected 10 days after application in 2013. However, the small residue amount (2% MRL) was still detected 6 weeks after application. It is appropriate to apply herbicide only if there is more than 50 days till harvest. Yet, the limit of non-residue production (10 μg/kg) can be easily exceeded in case of this herbicide. The course of degradation of quizalofop in cauliflower at time is shown in the Figure 1a.

The highest concentration of residues and the longest persistence were recorded in cauliflower treated by the fluazifop. Fluazifop is not even registered for cauliflower, but is registered for kale (also brassica vegetable). High fluazifop concentrations (from 490 to 2500 μg/kg) in cauliflower samples were detected between the 10^{th} and 30^{th} day after application (Figure 1b). These values are several times higher than MRL (10 μg/kg). The MRL was still exceeded 6 weeks after application (153 μg/kg). For these reasons, it is not possible to recommend fluazifop for weed control in cauliflower crops, especially for non-residue production.

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