

Contents of pesticide residues in hops



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Introduction

Application of pesticides against pests and diseases represents worldwide one of the most important factors of agricultural production intensification. Elimination or eradication of harmful organisms like insects, mites, fungal diseases or weeds enables to reach good yields, reduce the losses during transport and improve quality of the product. On the contrary residues of pesticide active ingredients (a.i.) can persist in the crop for a long time and can potentially endanger consumers health. Hops belong to the crops with intensive chemical protection. In spite of not being used for direct consumption, limit levels of residues in hops have to be established.

Material and methods

In the period 2004-2006 decline curves of several zoocide active ingredients were determined. Selected aphicides (imidacloprid, acetamiprid) and miticides (fenpyroximate, hexythiazox) were applied at the stage of hop flowering, cones forming and maturation according to approved methodology. Application amounts of tested pesticides are summarized in Table 1. Samples of leaves and later cones as well were taken in regular intervals since treatment to harvest. Samples were dried and kept in refrigerator until analysis. Determination of residues in leaves is more accurate because the development of leaves is practically finished in the time of inflorescence and cones formation. On the contrary development of inflorescence and hop cones still goes on. Their growth has a considerable effect on residue contents. Solvent extraction, liquid-liquid extraction, column chromatography and solid phase extraction (SPE) were used for purification of plant samples. Analytical determination of residues was performed by gas and liquid chromatography (GC/NPD/MS, HPLC/DAD), see Table 2.

Results and discussion

Dynamics of fenpyroximate decomposition was determined in the years 2004 and 2005. The results are summarized in Table 3. Fenpyroximate decline on hop leaves is very slow. Almost 20 ppm of active substance remains on leaves three weeks after treatment. Determination of fenpyroximate in cones at the time of crop harvest proved trace amounts of active substance. If biological admixtures were manually removed, cones were free of fenpyroximate residues. Maximal residue level of fenpyroximate at the range of 10-15 ppm (see Table 4) are high enough in order that MRL in cones was not exceeded. Potential risk of persistent pesticides findings in hops may threaten from biological admixtures (leaves, stems, bine fragments) that are always a part of harvested hops.

Table 1: Application amounts of tested pesticides

Pesticide	Active substance (a.i.)	Content in product	Amount a. i. (mg/kg)
Confidor 70 WG	imidacloprid	70%	115 g
Mospilan 20 SP	acetamiprid	20%	32 g
Ortus 5 SP	fenpyroximate	20 g/l	105 g/l
Nissorun 10 WP	hexythiazox	10%	100 g

Table 2: Principles of pesticide residues determination in hop leaves and cones

Analytical step	Fenpyroximate	imidacloprid	acetamiprid	hexythiazox
Extraction (leaves, cones)	hexane	hexane	hexane	hexane
Purification steps	gel chromatography (Bio-Salts SXC)	column chromatography (Florisil)	SPE	liquid-liquid ext. SPE
Analytical determination	GC/NPD/MS	HPLC/DAD	HPLC/DAD	HPLC/DAD

Table 3: Fenpyroximate residues on hop leaves (2004 a 2005) and in cones (2005)

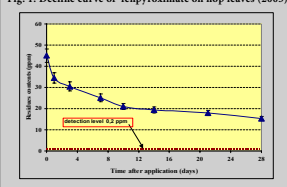
Sampling date	Time after treatment (days)	Residue level (mg/kg)	Fenpyroximate (ppm)	Time after treatment (days)	Residue level (mg/kg)
13.7.2004	Control leaves	< 0.05	< 0.05	Control leaves	< 0.05
22.7	1	61.1 ± 4.3	2.8	4 hours	45.2 ± 2.1
23.7	2	52.2 ± 3.9	2.5	1 day	34.5 ± 1.4
28.7	5	34.2 ± 2.7	1.6	3	30.5 ± 1.4
2.8	12	30.1 ± 1.9	1.4	7	25.1 ± 1.6
7.8	19	30.2 ± 1.9	1.4	10	23.5 ± 1.5
-	-	38.3	1.8	14	19.2 ± 1.1
-	-	32.4	1.5	21	18.1 ± 0.9
-	-	30.8	1.4	28	15.5 ± 0.7
-	-	25.8	1.2	-	-
-	-	20.8	1.0	-	-
-	-	15.8	0.8	-	-
-	-	10.8	0.5	-	-
-	-	5.8	0.3	-	-
-	-	0.8	0.04	-	-

Table 4: Maximal residue levels of pesticides (MRL) for Czech, Germany, USA and Japan

Active substance	Maximal residue level (MRL) (mg/kg, ppm)			
	Czech	Germany	USA	Japan
fenpyroximate (Ortus 5 SP)	10	10	10	15
imidacloprid (Confidor 70 WG)	2	2	2	10
acetamiprid (Mospilan 20 SP)	2	2	-	-
hexythiazox (Nissorun 10 WG)	3	3	3	30



Fig. 1: Decline curve of fenpyroximate on hop leaves (2005)



The results of imidacloprid and acetamiprid field trial application in 2005 are shown on Fig. 2. Analytical determination of the same pesticides on hop leaves and cones in 2006 trial are summarized in Table 4. Residues of imidacloprid were detectable 12 days after treatment, residues of acetamiprid 8 days after application. Hop cones taken at the time of crop harvest proved trace amounts of active substance. If biological admixtures were manually removed, cones were free of imidacloprid and acetamiprid residues. Active substances of both pesticides decompose relatively very quickly. There is minimal danger to exceed MRL of imidacloprid and acetamiprid in hops if applied according to recommendation.

Fig. 2: Decline curves of imidacloprid and acetamiprid on hop leaves (2005)

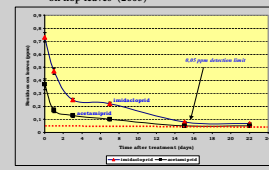


Table 4: Contents of imidacloprid and acetamiprid residues on hop leaves and cones (2006)

Sampling date	Time after treatment (days)	Imidacloprid (mg/kg)	Acetamiprid (mg/kg)
13.7.2006	Control leaves	< 0.05	< 0.05
13.7	2 hours	0.92 ± 0.05	0.11 ± 0.02
14.7	1	0.87 ± 0.05	0.09 ± 0.02
17.7	4	0.89 ± 0.05	0.09 ± 0.02
21.7	8	0.13 ± 0.02	< 0.05
25.7	12	0.04 ± 0.02	< 0.05
31.7	18	< 0.05	< 0.05
30.8.2006	Cones	< 0.10	< 0.10

In Table 5 there are summarized the results of hexythiazox residues determination on hop leaves and cones in 2006. Contents of hexythiazox residues on hop leaves immediately after application are at the level of 2 mg/kg. Decomposition of active substance during subsequent period is very slow. Residues of hexythiazox are detectable even two months after application. In spite of slow decline no residues of hexythiazox were found in hop cones at harvest (detection limit 0,25 ppm). There is no real danger to exceed MRL of hexythiazox in hops if applied according to recommendation.

Table 5: Contents of hexythiazox residues on hop leaves and cones (2006)

Sampling date	Time after treatment (days)	Residue contents (mg/kg)
3.7.2006	Control leaves	< 0.10
4.7	1 hour	1.92 ± 0.11
5.7	2 hours	1.69 ± 0.17
6.7	4	1.78 ± 0.15
7.7	8	1.76 ± 0.15
12.7	12	1.53 ± 0.13
15.7	15	1.02 ± 0.09
20.7	18	1.38 ± 0.15
25.7	21	0.79 ± 0.08
27.7	24	0.89 ± 0.08
28.7	25	0.85 ± 0.08
21.8	48	0.52 ± 0.03
22.8	49	0.12 ± 0.02
11.9.2006	Cones	< 0.25

Conclusions

The aphicides belonging to nitromethylene group, imidacloprid and acetamiprid, decline very rapidly in hop leaves. Owing to low application concentrations residue levels of imidacloprid and acetamiprid were far below MRL (Maximum Residue Level) immediately after treatment. Detectable residue levels were under limit values within 14 days after treatment. On the contrary acaricides fenpyroximate and hexythiazox were reliably detectable on hop leaves even one month after application. Nevertheless, no residues of all the tested zoocides were found in hop cones at the time of harvest. Potential risk of persistent pesticides findings in hops may threaten from biological admixtures (leaves, stems, bine fragments) that are always a part of harvested hops.

Acknowledgement

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