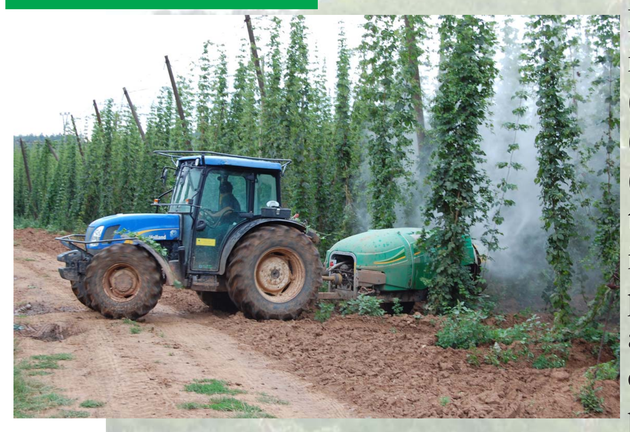
HOPS PESTICIDE SCREENING PROGRAMME BY V.F. HUMULUS

Vojtěchová D., Kroupa F. - V. F. HUMULUS Ltd., U Odborů 787, 438 01 Žatec 1, Czech Republic
e-mail: vfhumulus@seznam.cz

Introduction



Pesticides are substances used to kill insects (insecticides), weeds (herbicides), molds and fungi (fungicides) and rodents (rodenticides). Pesticide residues are the remains of pesticides contained in treated plants, crops (or their products), soil, water, etc. The amount of pesticide residue depends on their chemical stability in the particular environment, i.e. on their length of duration of decomposition. Since September 1, 2008, new unified standards of MRL (Maximum Residue Limit) have been introduced throughout the EU. The regulation covers approximately 1100 pesticides used in agriculture, either within the EU or in other countries. For treatment of hops, only authorized products may be used in the Czech Republic. In 2010, there were 26 registered active substances for the protection of hops allowed for use in Czech Republic, see Table - 1.

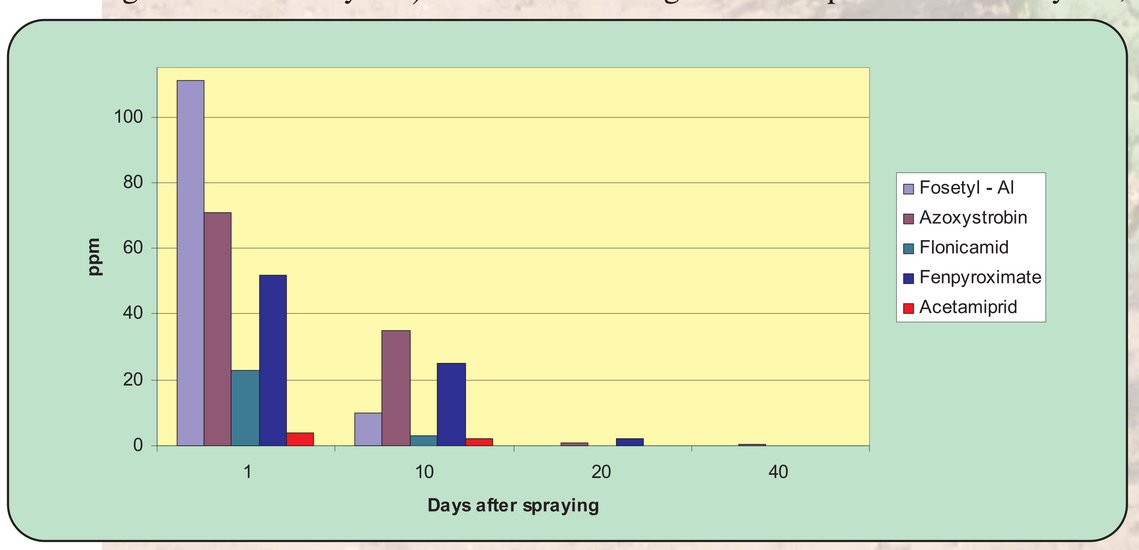
Pesticide active substance	Trade Name	Application purpose
Azoxystrobin	Ortiva	**fungicide -** downy mildew
Cymoxanil	Curzate K	**fungicide** - downy mildew
Folpet	Ridomil Gold Combi Pepite	**fungicide** - downy mildew
Fosetyl-Al	Aliette 80 WP, Aliette Bordeaux	**fungicide** - downy mildew
Metalaxyl-M	Ridomil Gold Combi Pepite	**fungicide** - downy mildew
Quinoxyfen	IQ-Crystal	**fungicide** - powdery mildew
Sulfur	Kuprikol 50, Kuprikol 250 SC, Cuproxat SC, Funguran…	**fungicide** - powdery mildew
Copper compounds	Sulikol K,Kumulus WG	**fungicide** - powdery mildew
Tebuconazol	Horizon 250 EW	**fungicide** - powdery mildew
Triadimenol	Bay idan 250 EC	**fungicide** - powdery mildew
Abamectin	Vertimec 1,8 EC	**miticide** - red spider mite
Acetamiprid	Mospilan 20 SP	**insekticide** - hop aphids
Alpha-cypermethrin	Vaztak 10 EC, 10 SC, Alfametrin	**insekticide** - hop aphids, alfalfa snout beetle,flea beetle
Bifenthrin	Talstar 10 EC	**insekticide** - hop aphids , **miticide** - red spider mite
Fenpyroximate	Ortus 5 SC	**miticide** - red spider mite
Flonicamid	Teppeki	**miticide** - red spider mite
Hexythiazox	Nissorun 10 WP	**miticide** - red spider mite
Imidacloprid	Confidor 70 WG,Kohinor 70WG, Warrant 700 WG	**insekticide** - hop aphids
Lambda – cyhalothrin	Karate Zeon 050 CS	**insekticide** - hop aphids, alfalfa snout beetle, flea beetle, bugs
Propargite	Omite 30 W	**miticide** - red spider mite
Pymetrozine	Chess 25 WP,Chess 50 WG	**insekticide** - hop aphids
Cyanamid	Alzodef	**herbicide** - chemical scraping hop garden
Fluazifop-P-butyl	Fusilade Forte 150 EC	**herbicide** - liquidation of grass and weeds monogerm
Glyphosate	Roundup Biaktiv	**herbicide** -disposal of idle hop
Linuron	Afalon 45 SC	**herbicide** - dicotyledonous weeds
MCPA	Aminex, Agritox	**herbicide** - dicotyledonous weeds

Table - 1 : List of registered pesticides used to protect hop in CZ for the year 2010

On the basis of brewers' increasing requirements for health safety of hop products (such as regulations valid in Japan - Positive List System for Agricultural Chemical Residues in Foods (May 2006)), we have decided to extend our research and business activity and begin an assessment of pesticide residue in hops.

Sampling and screening of hops

During the growing season, we monitored content and decomposition curves of active substances (eg. Fosetyl-Al, Azoxystrobin, Fenpyroximate, Flonicamid) for selected pesticides. Chemical treatment usually starts in May, when protection against primary infection of downy mildew is being applied (most commonly used active ingredient is Fosetyl-Al). When monitoring the decomposition of Fosetyl-Al, we analyzed the hop leaves collected before spraying and after spraying. Accordingly, we proceeded with the residues of active substances Azoxystrobin, Flonicamid, Fenpyroximat, Acetamiprid, etc.



Graph – 1: Decomposition curves of selected pesticides

Compound/ Pesticide	Limit of detection	Analyte concentration	Units	Analytical method
Azoxystrobin	0,05	0,23	mg/kg	LC/MS
Fosetyl-Al	2	n.d.	mg/kg	LC/MS
Fenpyroximate	0,1	1,31	mg/kg	LC/MS
Flonicamid	0,5	n.d.	mg/kg	LC/MS
Folpet	10	n.d.	mg/kg	GC/MS
Hexythiazox	2	n.d.	mg/kg	LC/MS
Imidacloprid	0,1	n.d.	mg/kg	LC/MS
Lambda-cyhalothrin	1	n.d.	mg/kg	GC/MS
Metalaxyl-M	0,05	n.d.	mg/kg	LC/MS
Propargite	0,1	1,08	mg/kg	LC/MS
Pymetrozine	1	n.d.	mg/kg	LC/MS

Table - 2: Analyzing rezidues pesticidec - SAAZ harvest 2010

After hops harvest in 2010, we randomly selected samples from several hops producers. These samples of hops cones were tested for all active substances that had been used during the growing period, see Table - 2. We analyzed a total of 22 types of pesticides.

The method of determination

Dried samples of leaves and hop cones (or pellets) were ground by the ultra-centrifugal mill. Samples were extracted by a modified multi-residue method QuEChERS. The retrieved share of acetonitrile phase was further purified by adding sorbent PSA, GCB or C18, depending on the chemical characteristics of pesticide residues sought. The filtered sample was analyzed by liquid or gas chromatography with a mass spectroscopy (LC-MS or GC-MS).

Results and Conclusion

Methodologies for determining the most active chemical substances used for hop protection have been elaborate. Until now, the performed analyses of hop products have not shown any which exceed MRL standards.
For some pesticides, we are trying to reduce the value of the limit of detection (LOD) by modifying the QuEChERS method and instrumentation. The list of analyzed pesticides will be updated as per customer requirements. In 2011, we have newly begun to assess residues to Cymoxanil, Mandipropamid, Spirotetramat and Thiamethoxam.

Pesticide active substance	Trade Name	MRL in ppm		LOD in hops	Analytical method
		CZ (EU)	JAPAN	ppm	
Acetamiprid	Mospilan 20 SP	0,10	0,01	**0,01**	**LC/MS**
Azoxystrobin	Ortiva	30	30	**0,05**	**LC/MS**
Hexythiazox	Nissorun 10 WP	20	30	**2**	**LC/MS**
Imidacloprid	Confidor 70 WG, Warrant 700 WG	10	7	**0,1**	**LC/MS**
Lambda – cyhalothrin	Karate Zeon 050 CS	10	10	**1**	**GC/MS**
Propargite	Omite 30 W	100	100	**0,1**	**LC/MS**
Fenpyroximate	Ortus 5 SC	10	15	**0,1**	**LC/MS**
Metalaxyl	Ridomil Gold Combi Pepite	10	10	**0,05**	**LC/MS**
Quinoxyfen	IQ-Crystal	0,5	1	**0,1**	**LC/MS**
Dimethomorph	Acrobat	50	50	**5**	**LC/MS**
Pymetrozine	Chess 25 WP, Chess 50 WP	15	6	**1**	**LC/MS**
Tolylfluanid	Euparen	50	50	**1**	**LC/MS**
Tebuconazole	Horizon 250 EW, Lynx, Ornament	30	30	**1**	**LC/MS**
Fosethyl - Al	Aliette 80 WP, Aliette Bordeaux	1500	1440	**2**	**LC/MS**
Folpet	Ridomil Gold Pepite	150	120	**10**	**GC/MS**
Bifenthrin	Talstar 10 EC	10	10	**1**	**GC/MS**
Spirodiclofen	Envidor	40	_	**1**	**LC/MS**
Flonicamid	Teppeki	2	5	**0,5**	**LC/MS**
Abamectin	Vertimec 1,8 EC	0,05	0,1	**0,05**	**LC/MS**
Triadimenol	Bayfidan	10	5	**1**	**LC/MS**
Alpha-cypermethrin	Vaztak 10 EC, Alfametrin	30	20	**3**	**GC/MS**
Linuron	Afalon 45 SC	0,1	0,02	**0,1**	**LC/MS**
Cymoxanil	Curzate K	2	2	**0,2**	**LC/MS**
Mandipropamid	Pergado F	50		**0,1**	**LC/MS**
Spirotetramat	Movento 150 OD	15	15	**1**	**LC/MS**
Thiamethoxam	Actara	0,1		**0,5**	**LC/MS**
Fluopicolide	Infinito, Profiler	0,02		**0,5**	**LC/MS**

Table - 3 : List pesticides analyzed by V.F.HUMULUS in 2011

Literature:

1.) EU Pesticides database 2011
2.) U.S.Hop industry comitee
3.) European standard EN 15662
4.) Metodika ochrany chmele 2010, Chmelařský institut Žatec s.r.o.