Systematic Monitoring of Residues

PESTICIDES | In order to assure sufficient high-quality harvests, use of some pesticides is required in agriculture. Quantities and times of application are subject to strict legal stipulations, with the objective of having as little residues as possible on harvested goods and on food prepared with same. Maximum quantities are set out clearly. Hops have been monitored especially carefully for residues of plant protectants for a long time [1]. Hopsteiner has developed a systematic residue analysis for testing hop plants. The results of the last campaign are presented below.

HOP RAW MATERIAL was partly tested in the laboratories of hop processors that have the required know-how. As a hop plant is a relatively complex matrix in view of the high level of bitter substances and polyphenols, commonly used, widespread and recognised methods for determination of pesticide residues cannot simply be carried over to analysis of hops and associated processed products. Modified processes have to be developed for analysing residues. Based on suitable methods, Hopsteiner has drawn up a residue analysis to monitor all hop products sold completely.

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Pre-Monitoring

In addition to analyses presented in this article, a comprehensive catalogue of measures was compiled prior to start of a processing campaign in order to obtain information about the residue situation of a hop harvest as early as possible [2].

Such monitoring includes leaf samples taken at regular intervals during the vegetation period from May to September and, in particular, freshly harvested hop batches immediately upon receipt by trading companies. Results obtained generally indicate a fixed number and a specific pattern of detectable residues that can be rated as typical for a growing year. Depending on weather, stronger infestation with fungi (much rain) or mites (dry and hot weather) will occur, requiring different methods of plant treatment. These in turn will result in different spectra of pesticide residues.

In order to obtain this information about typical residues in a harvest within the shortest time possible, analyses are carried out in cooperation with external residue laboratories with the objective of analysing at least ten per cent of a harvest volume before the start of a processing campaign. This should result in the largest possible representative dataset.

For monitoring, so-called multi-residue methods are commissioned that include the highest possible number of analysis

LIMIT VALUES OF ACTIVE AGENTS APPROVED IN THE 2013 GROWING YEAR AND FREQUENCIES OF ...

... detection and application (residues detected in bold letters)

Active agent	Limit values 2013 (mg/kg)			% frequency in all individual batches	
	EU	USA	Japan	Evidence*	Application**
Abamectin	0.05	0,2	0,2	0	>90 %
Thiamethoxam	0.1	0,1	0,1	0	50 - 90 %
Dimethomorph	**50**	**60**	**80**	**93 %**	
Quinoxyfen	0.5	3	1	0	
Fosethyl	1500	45	1440	0	
Deiquat	0.1	0,2	0,04	0	
Dithianon	**100**	**100**	**100**	**7,7 %**	
Cymoxanil	2	7	2	0	
Cinidon-ethyl	0.1	-	0.1	0	
Boscalid	**60**	**35**	**35**	**88 %**	10 - 50 %
Metalaxyl	10	20	10	0	
Mandipropamid	**50**	**50**	**50**	**17 %**	
Pyraclostrobin	**10**	**23**	**15**	**60 %**	
Flonicamid	**2**	**7**	**5**	**4.1 %**	
Azoxystrobin	**30**	**20**	**30**	**21 %**	
Myclobutanil	**2**	**10**	**10**	**18 %**	
Cyhalothrin	**10**	**10**	**10**	**0.8 %**	1 - 10 %
Hexythiazox	**20**	**2**	**30**	**3.2 %**	
Imidacloprid	**10**	**6**	**7**	**1.1 %**	
MCPA	0.1	-	-	0	
Milbemectin	0.1	-	0.1	0	
Tepraloxydim	0.1	-	0.05	0	
Trifloxystrobin	**30**	**11**	**40**	**6.3 %**	
Fluazifop-p-butyl	0.1	-	0.05	0	
Pymetrozin	15	6	15	0	<1 %
Triadimenol	**10**	**-**	**5**	**0.5 %**	
Bromoxynil	0.1	-	-	0	
Pyraflufen-ethyl	0.05	-	0.05	0	
Spirodiclofen	**40**	**30**	**40**	**1.1 %**	

**determined on the basis of results of all residue analyses in the context of monitoring before the beginning of the processing campaign (about 10 % of all individual batches from the 2013 harvest were included)*

***determined on the basis of evaluation of datasheets on use of plant protectants (100 % of all individual batches from the 2013 harvest were included)*

Table 1

parameters – more than 500 active agents [3]. This ensures that even residues can be detected that are not used in hop cultivation and originate, among other things, from cross-contamination e.g. from treatment of a neighbouring culture such as cereals and fruit. But some pesticides cannot be detected by multi-residue methods and can be determined reliably only by individual methods.

Active Agents Approved in 2013

Of the 29 active agents approved for German hop cultivation in 2013, seven could be determined only by individual methods and thus they require separate analyses. All others could be jointly analysed using multi-residue methods that have meantime become established for hops.

A total of fourteen different active agents were found in hop batches analysed in the context of the monitoring process. Somewhat more than half of pesticides approved were not found in a single sample. Some pesticides were found in very isolated instances, others were present in almost all batches.

After the analysis report was available, the result was immediately verified on the basis of the so-called datasheet on use of plant protectants accompanying every hop batch and containing information from the producer about the pesticides applied at which point in time during the growing year. This makes it possible to check whether relationships are plausible and the reliability of grower data can also be checked. Table 1 lists all active agents approved and provides information about frequency of application and analytical evidence. The table is based on data from evaluations of datasheets on use of plant protectants and on residue analyses in the context of monitoring. No direct relationship between frequency of application and evidence can be derived from Table 1. The most frequently used active agent, Abamectin, was not detected in any batch. This pesticide is very efficiently broken down before harvest. However, residues of Dimethomorph, also a pesticide applied relatively frequently, were detected in almost all samples.

Based on all analyses in the context of the monitoring process before the start of the processing campaign, two important results can be summarised:

1. The following 14 active agents could be detected, all are thus typical and relevant for the 2013 hop harvest: Azoxy-

strobin, Boscalid, Cyhalothrin, Dithianon, Dimethomorph, Flonicamid, Hexythiazox, Imidacloprid, Mandipropamid, Myclobutanil, Pyraclostrobin, Pyraclostrobin, Triadimenol, Trifloxystrobin;

2. All residual values were below the allowable tolerance limits in the German Maximum Residue Limits Ordinance.

The percentage of the overall harvested quantity analysed in monitoring before the start of a processing campaign is rated as being representative but, in quantity terms, it is relatively small, about ten per cent. For that reason, all hop products produced by the Hopsteiner Group are subsequently systematically analysed for residues, corresponding to 100 per cent monitoring.

Analysis of Relevant Active Agents

In order to limit analysis time, input and expenses, active agents that were not detectable in any sample during monitoring, were rated as not being relevant and do not have to be necessarily included in the processing protocols. For the 2013 harvest, this applied, inter alia, to the active agents Milbemectin, Tepraloxydim, Deiquat, Bromoxynil, MCPA and Fosethyl that can be determined only by individual methods. However, residues of Dithianon were found in some batches, also detectable only by an individual analysis. This approved agent has been widely used for many years to combat Peronospora fungal disease. Application of same was consistently documented in the datasheets on use of plant protectants, and residues were always clearly below the relatively high maximum level of 100 mg/kg. Except for Dithianon, all other relevant active agents were covered by multi-residue methods.

A total of 491 retention samples taken during the ongoing processing campaign in the 2013/2014 season were analysed. All analyses were done in the processing plant of Hopsteiner Group in Germany. Only the relevant Dithianon active agent had to be determined by an individual method. The other thirteen relevant active agents were analysed using a multimethod developed in-house and published a short time ago [4]. It is being extended on an ongoing basis and meantime includes more than 60 parameters. Apart from approved active agents, it also includes numerous pesticides whose approval for hops has expired or whose application is admissible for other agricultural crops.

FREQUENCY OF DETECTION OF RELEVANT RESIDUES IN PER CENT RELEVANT FOR THE 2013 HARVEST ...

... in hops and pellets* relative to the respective EU limit values (2013)

Active agent	Percentage of samples without detection of a residue	Frequency of detection upon reaching a limit value of:			
		<10 %	10 - 50 %	>50 %	>100 %
Dimethomorph	8.5 %	58 %	33 %	0.5 %	0
Dithianon	89 %	6 %	5 %	0	0
Boscalid	6.5 %	62 %	31 %	0.5 %	0
Mandipropamid	16 %	60 %	24 %	0	0
Pyraclostrobin	25 %	44 %	30 %	1 %	0
Flonicamid	92 %	7.5 %	0.5 %	0	0
Azoxystrobin	28 %	69 %	3 %	0	0
Myclobutanil	59 %	17.5 %	23 %	0.5 %	0
Cyhalothrin	95 %	5 %	0	0	0
Hexythiazox	86 %	13.5 %	0.5 %	0	0
Imidacloprid	96 %	4 %	0	0	0
Trifloxystrobin	75 %	21 %	4 %	0	0
Triadimenol	98.5 %	1 %	0.5 %	0	0
Spirodiclofen	98.5 %	1.5 %	0	0	0

*in 100 % of all products of this category marketed by Hopsteiner

Table 2

FREQUENCY OF DETECTION OF RELEVANT RESIDUES IN PER CENT RELEVANT FOR THE 2013 HARVEST ...

... in carbon dioxide extracts* relative to the respective EU limit values (2013)

Active agent	Percentage of samples without detection of a residue	Frequency of detection upon reaching a limit value of:			
		<10 %	10 - 50 %	>50 %	>100 %
Dimethomorph	0	86 %	14 %	0	0
Dithianon	100 %	0	0	0	0
Boscalid	0	52 %	48 %	0	0
Mandipropamid	4 %	69 %	27 %	0	0
Pyraclostrobin	2 %	68 %	30 %	0	0
Flonicamid	80 %	20 %	0	0	0
Azoxystrobin	12 %	88 %	0	0	0
Myclobutanil	17 %	53 %	30 %	0	0
Cyhalothrin	100 %	0	0	0	0
Hexythiazox	78 %	22 %	0	0	0
Imidacloprid	100 %	0	0	0	0
Trifloxystrobin	63 %	31 %	6 %	0	0
Triadimenol	73 %	24 %	3 %	0	0
Spirodiclofen	100 %	0	0	0	0

*in 100 % of all products of this category marketed by Hopsteiner

Table 3

FREQUENCY OF DETECTION OF RELEVANT RESIDUES IN PER CENT RELEVANT FOR THE 2013 HARVEST ...

... in ethanol extracts* relative to the respective EU limit values (2013)

Active agent	Percentage of samples without detection of a residue	Frequency of detection upon reaching a limit value of:			
		<10 %	10 - 50 %	>50 %	>100 %
Dimethomorph	0	65 %	35 %	0	0
Dithianon	100 %	0	0	0	0
Boscalid	0	58 %	42 %	0	0
Mandipropamid	0	71 %	29 %	0	0
Pyraclostrobin	0	75 %	25 %	0	0
Flonicamid	93 %	7 %	0	0	0
Azoxystrobin	8 %	92 %	0	0	0
Myclobutanil	33 %	39 %	29 %	0	0
Cyhalothrin	100 %	0	0	0	0
Hexythiazox	100 %	0	0	0	0
Imidacloprid	100 %	0	0	0	0
Trifloxystrobin	43 %	54 %	3 %	0	0
Triadimenol	82 %	18 %	0	0	0
Spirodiclofen	97 %	3 %	0	0	0

*in 100 % of all products of this category marketed by Hopsteiner

Table 4

Costly Analysis Methods

Both the individual as well as the multi-method start with wet chemical sample preparation, i.e. extraction of hops and/or hop products using organic solvents in order to isolate the highest quantity of analytes possible from the sample matrix. This is followed by chromatographic steps (solid phase extraction) for cleaning the sample extract. Gas chromatographic (GC) or liquid chromatographic (LC) methods, in order to clean the sample extract obtained. For final measurement of analytes, gas chromatography (GC) or liquid chromatographic (LC) processes, coupled with mass spectrometry, are used for measuring the analytes. Sample preparation of analytes and evaluation of results is time-consuming. In addition, modern equipment and highly qualified staff are required to assure detection limits and analysis accuracies required. Regular participation in pesticide ring analyses guarantees analytical competence.

Evaluation

All active agents, rated typical and relevant beforehand, were found in the almost 500 samples analysed during the 2013/2014 processing campaign. As in monitoring, some pesticide residues were found in very individual instances whereas others were detected very frequently. As shown in Tables 2 to 4, most of the residue values found were below ten per cent of the admissible EU maximum value for the particular active agent. In very few instances, more than fifty per cent of the tolerance limit was analysed for Dimethomorph, Boscalid, Myclobutanil and Pyraclostrobin only, but limit values were never exceeded.

When comparing the different hop products, no really conspicuous differences in terms of the residue situation were found. Active agents determined in rare cases as well as frequently were below the limit values in hops and pellets sold (Table 2), similar to those in the extracts. Neither carbon dioxide extraction (Table 3) nor ethanol extraction (Table 4) led to major changes in distribution though it is known that both methods do not give rise to quantitative transfer of residues [4].

The reduction factor is a function of polarity of the active agent in the pesticide and the extraction medium. The only aspect worth mentioning would be the fact that no sample contained even 50 per cent of the allowable limit value of an active agent, though this was the case for hops or pellets in individual instances.

Based on this comprehensive and end-to-end processing monitoring, all hop products sold by the company could be proven to be marketable. ■

Literature

1. "Rückstandskontrollen bei Hopfen und Hopfenprodukten", in: Hopfenrundschau International 1995/1996, pp. 58-64.
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