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Environmental contaminants in hops

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Environmental contaminants in hops include substances such as metals, radionuclides and fungal toxins. Other substances are, for example, nitrate and zinc reaching the plant from soil fertilisers. This paper deals with the levels of selected metals, Cs 137 and Cs 134 radionuclides as well as a number of mycotoxins.

Hops contributes groups of substances vital for brewing. Bitter substances, aroma substances and polyphenols make a significant contribution to the character of a beer. In addition to these three substance groups, hops contains components which are not necessarily desirable. It is well known that hops is a natural product and thus exposed to environmental influences during the vegetation phase. This may result in contaminations.

Environmental contaminants in hops include substances such as metals, radionuclides and fungal toxins. Other substances are, for example, nitrate and zinc reaching the plant from soil fertilisers.

Investigations into pesticide residues are not included in this paper as plant protectants are used purposefully for combating pests and diseases and possible residues are not due to environmental contamination. Besides, pesticide residues in hops are checked regularly.

Introduction

The "Working Group Hop Analysis" (AHA) carried out a screening to detect heavy metals in hops of the 1995 crop (1). Forster et al. reported on the presence of nitrate and radionuclides in earlier works (2, 3). Biendl published investigations into mycotoxins in hop products from the 1998 harvest (4). In order to get an overview of current levels of possible contaminants, the AHA decided to perform another screening of hops harvested in 2002. In addition to analysing the levels of various metals, the amount of Cs 137 and Cs 134 radionuclides were also analysed in order to determine residual contaminations from the Chernobyl reactor accident. To round off the picture, mycotoxins were also investigated.

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Sample material

The hops to be investigated was combined to lots from cultivation batches supplied by HVG, Barth and Steiner; these represent hop quantities of 25 – 50 t per sample. The hops originates mainly from the Hallertau growing area. Two hop lots from Tettnang and one lot each from the Elbe-Saale regions, Czechia and Slovenia were also investigated. Labor Veritas, Zurich, performed the analyses for metal levels in hops, and the Bavarian Central Testing In-

Table 1 Metal levels (mg / kg) listed individually

Growing area and variety	As	Pb	Cd	Cr	Co	Fe	Mo	Ni	Hg	Se
H Hallertauer mfr.	0.05	0.31	<0.01	0.41	0.07	164	0.12	1.4	<0.01	0.03
H Hall. Tradition	0.03	0.15	<0.01	0.18	<0.01	83	0.10	1.4	<0.01	<0.01
H Hall. Tradition	0.03	0.20	<0.01	0.22	0.07	104	0.17	2.5	<0.01	0.04
H Hall. Tradition	0.03	0.21	<0.01	0.27	0.09	96	0.16	2.4	<0.01	0.03
H Hall. Magnum	0.02	0.09	<0.01	0.21	0.09	81	0.08	2.0	<0.01	0.03
H Hall. Magnum	0.02	0.11	<0.01	0.24	0.05	91	0.12	2.1	<0.01	0.02
H Hall. Magnum	0.03	0.35	<0.01	0.19	0.08	91	0.08	2.7	<0.01	0.04
H Hall. Taurus	0.02	0.29	<0.01	0.27	0.03	104	0.17	1.7	<0.01	0.02
H Hall. Taurus	0.03	0.05	<0.01	0.26	0.07	92	0.17	3.4	<0.01	0.03
H Hall. Taurus	0.03	0.12	<0.01	0.20	0.07	114	0.08	2.8	<0.01	0.04
H Hersbrucker spät	0.03	0.17	<0.01	0.20	0.04	87	0.17	1.6	<0.01	0.03
H Hersbrucker spät	0.04	0.23	<0.01	0.19	0.06	91	0.24	1.9	<0.01	0.05
H Northern Brewer	0.03	0.20	<0.01	0.22	0.06	112	0.13	1.7	<0.01	0.01
H Northern Brewer	0.04	0.24	<0.01	0.24	0.05	134	0.26	2.4	<0.01	0.04
H Perle	0.03	0.13	<0.01	0.17	0.01	64	0.11	1.0	<0.01	0.05
H Perle	0.03	0.16	<0.01	0.20	0.06	92	0.16	1.6	<0.01	0.05
H Perle	0.02	0.12	<0.01	0.18	0.08	75	0.08	2.1	<0.01	0.04
H Spalt Select	0.07	0.16	<0.01	0.17	0.02	102	0.08	1.3	<0.01	0.01
H Spalt Select	0.03	0.20	<0.01	0.19	0.04	114	0.13	1.5	<0.01	0.05
E Hall. Magnum	0.05	0.25	<0.01	0.39	0.08	194	0.17	1.1	<0.01	<0.01
T Hallertauer mfr.	0.02	0.57	<0.01	0.14	0.03	80	0.35	2.0	0.05	0.02
T Tettnanger	0.02	0.24	<0.01	0.17	0.04	77	0.40	1.0	<0.01	0.04
SI Aurora	0.05	0.31	<0.01	0.31	0.14	148	0.21	2.1	0.02	0.03
CZ Saazer	0.07	0.40	<0.01	0.31	0.05	155	0.30	0.94	<0.01	0.03

H = Hallertau E = Elbe-Saale T = Tettnang SI = Slovenia CZ = Czechia

Table 2 Comparison of metal levels from the 1995 and 2002 screenings (analytical results in mg / kg)

Harvest	As	Pb	Cd	Cr	Co	Fe	Mo	Ni	Hg	Se
2002 Ø	0.034	0.219	<0.01	0.230	0.060	106	0.168	1.861	0.035	0.033
2002 Minimum	0.02	0.05	<0.01	0.14	<0.01	64	0.08	0.94	<0.01	<0.01
2002 Maximum	0.07	0.57	<0.01	0.41	0.14	194	0.40	3.40	0.05	0.05
2002 "sR"	0.01	0.11	*)	0.07	0.03	31.74	0.09	0.63	0.02	0.01
2002 "vkR"	42.2%	51.8%	*)	29.6%	46.6%	29.9%	51.7%	33.9%	60.6%	36.5%
1995 Ø	0.070	0.340	0.014	0.350	<0.1	n.a.	n.a.	1.620	0.050	<0.05
1995 Minimum	0.03	0.17	0.01	0.16	<0.1	n.a.	n.a.	1.01	<0.02	<0.05
1995 Maximum	0.22	0.52	0.031	0.84	<0.1	n.a.	n.a.	2.49	0.07	<0.05
1995 "sR2"	0.04	0.08	0.01	0.12	*)	*)	*)	0.41	0.01	*)
1995 "vkR"	61.4%	24.7%	38.4%	34.9%	*)	*)	*)	25.3%	25.9%	*)

*n.a. = not analysed *) = cannot be evaluated*

Table 4 Results of Swiss monitoring for salads published in 2000 (values in mg / kg dry matter)

	Pb (mg/kg)	Cd (mg/kg)
Minimum	0.1	0.2
Maximum	4.8	1.7
Avg. open air production	1.5	0.7
Average greenhouse	0.7	0.8

Table 5 Mycotoxin and radionuclide levels listed individually

Growing area and variety	Ochratoxin A mg/kg	Aflatoxins (B1, B2, G1, G2) mg/kg	Caesium 137 Bq/kg	Caesium 134 Bq/kg
Hallertau Hall. Tradition	<0.0005	<0.0003	<3	<3
Hallertau Northern Brewer	<0.0005	<0.0003	<3	<3
Hallertau Hall. Magnum	<0.0005	<0.0003	<3	<3
Hallertau Hall. Taurus	<0.0005	<0.0003	<3	<3
Hallertau Perle	<0.0005	<0.0003	<3	<3
Tettnang Tettnanger	<0.0005	<0.0003	<3	<3

Table 3 Potential contributions from hops to beer compared to limit values laid down in the German Drinking Water Regulation (values in mg / l)

A	As	Pb	Cd	Cr	Co	Fe	Mo	Ni	Hg	Se
B	0.000034	0.000219	<0.00001	0.000234	0.000058	0.106	0.000168	0.00186	0.00001	0.000031
C	0.01	0.01	0.005	0.005	*)	0.2	*)	0.02	0.001	0.01
D	294.1	45.7	>500	21.4	–	1.9	–	10.8	100	322,6

A = metal investigated B = introduction in mg/l dosage with hop addition of 100 g/hl beer
C = Drinking Water Regulation D = ratio Drinking Water Regulation : hop introduction
**) no limit value in Drinking Water Regulation*

stitute, Weihenstephan checked for mycotoxins. Nateco$_2$ GmbH & Co. KG, Wolnzach, analysed radionuclide levels.

Heavy metals

Brewers' specifications for hops and hop products frequently contain the term "heavy metals", giving their maximum tolerable levels. But not all heavy metals are harmful, and the term "heavy metals" is not defined in food law under existing legislation. Limit values for individual chemical substances are laid down in the Drinking Water Regulation which also includes heavy metals but no overall limit value has been specified for the sum of heavy metals.

Other sources such as the German and European pharmacopoeia do not contain a definition at present. The Römpp Chemical Dictionary (5) defines heavy metals exclusively by mass density, independently of potential toxicity which has to be considered in any event when evaluating heavy metals. Important heavy metals that are regarded as harmful metals are those which have a clearly toxic effect. They include lead, cadmium and mercury. Arsenic is regarded as a metalloid and must be included in evaluations.

Consequently, the relevant heavy metals lead, cadmium and mercury as well as arsenic must be regarded as harmful metals. Copper is left out here because copper is specified in the Regulation on Maximum Residue Limits and is checked regularly in the context of pesticide analyses.

In the screening referred to, hop lots were investigated for levels of the following metals: the harmful metals arsenic (As), lead (Pb), cadmium (Cd) and mercury (Hg), the metals chromium (Cr), cobalt (Co), iron (Fe), molybdenum (Mo), nickel (Ni) and the metalloid selenium (Se).

Table 1 shows results of the current metal analyses for individual hop lots, Table 2 gives average values, as well as maxima and minima from the 2002 harvest compared to the values of the 1995 harvest screening. A comparison of the two screening values shows that levels decreased meantime compared to those from the 1995 crop.

Assessment of results

In order to be able to assess results, two comparisons are used: presence of metals in hops compared with maximum values laid down in the Drinking Water Regulation and with amounts present in non-processed food for immediate consumption.

Comparison with Drinking Water Regulation

The 1995 harvest screening already showed for metals investigated that entry into beer via the hop route was lower by at least an order of magnitude compared to admissible maximum levels in drinking water. Table 3 shows the current comparison.

Comparison with non-processed food for immediate consumption

In the context of a monitoring program in Switzerland, salads were analysed for lead, cadmium, copper and zinc (6). The salads originated from different regions in Switzerland. Table 4 lists the results. It can be seen that salads have even higher levels of lead and cadmium than hops, based on dry matter. As salads are consumed without being processed, the impact on humans must certainly be regarded as being more significant than that of hops or beer.

When comparing metal levels in the salads with data for a Provisional Tolerable Weekly Intake (PTWI) published by the WHO/FAO, lead and copper intake through salad is less than 2% of this PTWI level. In hops, the percentage is clearly more favourable, on the one hand due to dilution through to the final beer and, on the other hand, due to filtration and drop-out processes in beer production.

Mycotoxins

The Bavarian Central Testing Institute for Agriculture at the Technical University of Munich screened six hop samples to determine mycotoxin levels. In all instances, no aflatoxin (B1, B2, G1, G2) levels were above the detection limit of 0.0003 mg/kg. Likewise, it was not possible to detect ochratoxin A in samples (at a detection limit of 0.0005 mg/kg). Table 5 shows the individual results.

Radionuclides

The same six hop samples analysed for mycotoxins were also subjected to radioactivity analysis. A measurement system, supplied by Nateco$_2$ GmbH & Co. KG equipped with a sodium iodide detector, was used to check for presence of Cs 134 and Cs 137 nuclides released in the wake of the Chernobyl accident in 1986. None of the six samples had levels above the detection limit of three Bq/kg (see Table 5). This result could be confirmed in analyses carried out by the Bavarian Land Institute for Soil Culture and Plant Cultivation (LBP), Hüll/Germany (7). An average of 0.69 Bq/kg (maximum 1.13 Bq/kg) of Cs 137 and 0.13 Bq/kg of Cs 134 was found in fifteen Bavarian hop samples from the 2001 harvest. It can be concluded from both test series that German hops is contaminated to an insignificant extent, if at all.

Summary

The presence of undesirable environmental contaminants in hops such as metals, mycotoxins and radionuclides was investigated in the context of a screening of hop samples from the 2002 harvest. Heavy metals are defined by their mass density. Among heavy metals, only lead, cadmium and mercury are classified as being toxic for humans. They are classified as harmful metals together with the harmful metalloid arsenic. To round off the picture, other metals were also included in the investigations. The metal levels found do not affect the beer as the resulting concentrations are lower by some orders of magnitude than limit values laid down in the Drinking Water Regulation. Moreover, hops contains lower quantities of lead and cadmium than salads. In no instance could aflatoxins or ochratoxin A be detected in hops. The Cs 137 and Cs 134 radionuclides could be determined in a series of measurements but their levels were very low. The results show that entry of harmful metals, mycotoxins and radionuclides into beer via hops is far below limit values that might be harmful for human health.

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