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Reduction of Nitrosamines in Beer - Review of a Success Story

Due to their carcinogenic properties the occurrence of nitrosamines in beer raised major concerns in the 1980s. Since then, the production technologies were changed, especially to minimize nitrosamine formation during malt kilning. In this study, our systematic results of nitrosamine analysis between 1992 and 2006 as well as results of a computer-assisted literature review about nitrosamines in beer are reported.
The technical threshold value of 0.5 µg/kg NDMA in beer was exceeded by 70 % of all samples in 1978. The incidence was lower in 1980 (23 %) and 1982 (6 %). Our results show that the incidence was 5 % in the 1990s, whereas it was only 1 % since 2000 (only 6 of 418 samples had concentrations above the threshold value between 2000 and 2006).
It may be concluded that nowadays beer is nearly negligible compared to other sources of NDMA intake in human nutrition. This almost complete prevention of NDMA in beer can be seen as a success story of the brewing industry. However, our literature review shows that nitrosamines may still be a problem in beers brewed in developing countries.

Descriptors: nitrosamines, *N*-nitrosodimethylamine, beer, review, malt

1 Introduction

The chemical class of nitrosamines includes the IARC Group 2A carcinogen *N*-nitrosodimethylamine (NDMA) [1,2]. The occurrence and formation of *N*-nitroso compounds in food and beverages have been reviewed [3,4].

In alcoholic beverages, NDMA was first found in German beers in 1978 [5]. Concentrations of up to 68 µg/L caused worldwide concern. Subsequent research has shown that NDMA was a contaminant of malt, which had been kilned by direct firing, the predominant production method at that time. Once the source and the mechanism of its formation had been elucidated, reduction of NDMA in beer was achieved by switching to indirect firing of the malt kiln. As an interim measure, kiln flame temperatures were reduced or sulfur was introduced to release sulfur dioxide which scavenges oxides of nitrogen that would otherwise nitrosate the free amines [6]. The possibilities for minimizing nitrosamine formation during malt kilning were reviewed [7,8].

In this article, the trends of nitrosamine content in beer during the last 30 years is systematically studied using data from the literature as well as data from our own survey of nitrosamines in the German Federal state of Baden-Württemberg.

2 Materials and Methods

Our own analyses for nitrosamines in beer and malt samples were conducted according to the German official method L36.00-6 and L00.00-17, respectively. The limit of detection was 0.2 µg/kg for beer and malt. The sampling was done in the German Federal State of Baden-Württemberg. However, products from other Federal States and European countries available in Baden-Württemberg were included in the samplings, so that the results are interpreted as representative for the German situation.

The review about nitrosamines in beer was compiled by a computer-assisted literature search in the following databases: PubMed (U.S. National Library of Medicine, Bethesda, MD), Web of Science (Thomson Scientific, Philadelphia, PA), Food Science and Technology Abstracts (International Food Information Service, Shinfield, UK), and Scopus (Elsevier B.V., Amsterdam, Netherlands). The references including abstracts were imported into Reference Manager V.11 (Thomson ISI Research Soft, Carlsbad, CA) and the relevant articles were manually identified and purchased in full text. The reference lists of all articles were checked for relevant studies not included in the databases.

3 Results and discussion

3.1 Occurrence of NDMA in German Beer

As effect of the improvements in malt quality, a technical threshold value of 0.5 µg/kg NDMA in beer was established as recommendation for the brewing industry. In 1978, this value was exceeded by 70 % of all samples, in 1980 by 23 % and in 1982 by 6 % [9]. In 1988, this value was exceeded by only 21 of 514 analysed German beer samples (4 %) [10].

Our analysis results of NDMA in beer and malt from the years 1992-2006 are presented in Table 1. In this time frame, NDMA was detectable in 29 malt samples (43 %) and it was detectable in 81 beer samples (7 %). The technical threshold value was exceeded by 49 of 1242 German beers (4 %).

In the 1990s, we had an incidence of 5 % (42 samples out of 824 above the threshold). If we examine only the time frame between 2000 and 2006, we had a significantly lower incidence with only 6 samples of 418 samples above the threshold value (1 %).

Therefore, we can confirm that the NDMA levels in German beers decreased further since the last studies in the 1980s (see also Fig. 1). Today in the vast majority of beer samples on the German market, NDMA is not detectable anymore.

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Figures see Appendix

Besides NDMA, other nitrosamines were detected only in single cases. In the time period between 2004 and 2006, *N*-nitrosopiperidine was detected in one case in barley malt (0.55 μg/kg), *N*-nitrosopyrrolidine was detected in a lager beer (3.0 μg/kg), and *N*-nitrosodiethylamine was detected in six different barley or caramel malts (2.0-4.8 μg/kg).

3.2 Worldwide surveys for NDMA in beer and other alcoholic beverages

The concentrations of NDMA in beer determined in different countries are summarized in Table 2. Österdahl analysed NDMA in beers and other beverages on the Swedish market [11]. A NDMA mean level of 0.3 μg/kg in beer (258 samples), 1.2 μg/kg in whisky (15 samples) and 0.1 μg/kg in other spirits (13 samples) was determined. In none of 60 wine samples NDMA could be detected.

In a survey of 194 US and Canadian beers, Scanlan *et al.* noted that the average levels of NDMA had dropped to 0.074 μg/kg, about 1-5 % of the amounts found a decade previously [12]. Sen *et al.* also showed that levels of NDMA in both Canadian and imported beers had decreased significantly since 1978 [13]. Of 162 Canadian beers analysed during 1982-89, the average level of NDMA was 0.098 μg/kg compared with average levels of 1.4 and 0.7 μg/kg determined in two earlier surveys (1978 and 1989, respectively). In two surveys of beers imported to Canada carried out during 1991-92 and 1994, the respective averages were 0.71 μg/kg (106 samples) and 0.15 μg/kg (36 samples). Glória *et al.* analysed NDMA in 166 Brazilian, US domestic and US imported beers and similarly found significantly reduced levels, with an overall mean level of 0.07 μg/kg [14]. The results reflect the successful efforts of the malting and brewing industries to reduce the formation of NDMA [12].

Shin *et al.* analysed nitrosamines in a range of alcoholic beverages in the Republic of Korea in two surveys in 1995 and 2002, including first reports about the traditional Korean beverages chungju (fermented rice alcohol), takju (fermented cereal alcohol) and soju (distilled from fermented cereal alcohol). NDMA was detected in the 1995 survey in chungju (< 0.1 μg/kg) and soju (mean, 0.2 μg/kg) but in none of the samples in the 2002 survey. For domestic Korean beers, an average of 0.8 μg/kg and 0.3 μg/kg were reported for 1995 and 2002, respectively. In whisky and liqueurs an average of less than 0.1 μg/kg was found in both surveys [15].

In general, the worldwide studies show the same decrease of nitrosamines in alcoholic beverages as in our own study. However, Sen *et al.* (1996) noted that higher levels of NDMA in beers might be present in developing countries than in North America or Europe [13]. The malt-drying techniques in various countries are unknown, so that a continuous monitoring and control of imported beers might be necessary. As an example, high levels were found in a survey of 120 Indian beers with an average of 3.2 μg/kg and a maximum of 24.7 μg/kg [16]. However, there is a general lack of data on nitrosamine contents of beer in developing countries.

4 Conclusion

Tricker and Preussmann [17] reviewed food surveys on NDMA. Dietary intake of NDMA was approximately 0.5 μg/day or less in most countries which is about one third of the intake in 1979–80. Previously, beer was the major source of NDMA in human nutrition (65 % contribution). The average daily intake of NDMA in 1988 was calculated as approximately 10 % of the value in 1979 [10]. In 1990, beer was estimated to contribute to about 31 % of total NDMA intake [17].

From the large number of negative samples in our survey, we conclude that nowadays beer may be nearly neglected compared to other sources of NDMA intake in human nutrition. This almost complete prevention of NDMA in beer can be seen as a success story of the brewing industry. Due to our risk-oriented sampling approach [18], we have therefore reduced the numbers of beer samples intended for nitrosamine analysis during the last years and increased the numbers of higher nitrosamine-risk product groups (i.e. mascaras, hand soaps and recently drinking water).

However, a control of malt and beer for NDMA is still needed, especially due to the fact that a significant amount of malt is imported into Germany every year (e.g. according to the Deutscher Mälzerbund e.V. 238 702 t of malt were imported in 2005, which is 13 % of the total malt usage of 1 778 678 t). Imported malt might partly have been produced by direct kilning in a developing country. We therefore conclude that the control of imported malt should be done with higher priority to prevent the return of nitrosamines due to the globalisation of the food market.

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Received 02 May, 2007, accepted 18 June, 2007

Appendix

Table 1 Levels of *N*-nitrosodimethylamine (NDMA) in beer, beer-like beverages and malt collected from the market of Baden-Württemberg

Commodity	Year	No. of samples	NDMA-positive (%)	NDMA (µg/kg)			
				Individual values	Median	Mean	Range
Beer and beer-like beverages	1992	46	48	2x 0.6, 2x 0.7, 5x 0.9, 3x 1.0, 3x 1.1, 4x 1.2, 2x 1.3, 1x 1.4, 24x n.d.	1.0	1.0	n.d.–1.4
	1993	17	6	1x 1.2, 16x n.d.	1.2	1.2	n.d.–1.2
	1994	2	0	2x n.d.	-	-	n.d.–0.0
	1995	134	0	134x n.d.	-	-	n.d.–0.0
	1996	127	6	1x 0.26, 1x 0.36, 1x 0.5, 1x 0.52, 1x 0.6, 1x 0.65, 1x 1.2, 1x 1.6, 119x n.d.	0.56	0.71	n.d.–1.4
	1997	412	5	1x 0.15, 7x 0.3, 1x 0.4, 1x 0.45, 3x 0.5, 1x 0.6, 1x 0.75, 1x 0.78, 1x 0.8, 1x 0.85, 1x 1.2, 1x 1.8, 1x 2.4, 391x n.d.	0.50	0.66	n.d.–2.4
	1998	67	8	1x 0.2, 1x 0.22, 1x 0.4, 2x 0.7, 62x n.d.	0.40	0.40	n.d.–2.2
	1999	19	0	19x n.d.	-	-	-
	2000	39	8	1x 0.73, 1x 1.3, 1x 1.7, 36x n.d.	1.3	1.2	n.d.–1.7
	2001	156	5	6x 0.2, 1x 0.3, 1x 0.4, 148x n.d.	0.20	0.24	n.d.–0.40
	2002	89	1	1x 0.4, 88x n.d.	0.40	0.40	n.d.–0.40
	2003	60	13	2x 0.2, 2x 0.3, 4x 0.4, 52x n.d.	0.35	0.33	n.d.–0.40
	2004	20	0	20x n.d.	-	-	-
	2005	37	11	1x 0.5, 1x 0.53, 1x 0.6, 1x 0.66, 33x n.d.	0.57	0.57	n.d.–0.66
	2006	17	0	17x n.d.	-	-	-
Malt	1992	6	33	1x 0.5, 1x 1.4, 4 x n.d.	1.0	1.0	n.d.–1.4
	1993	3	67	1x 1.0, 1x 1.8, 1x n.d.	1.4	1.4	n.d.–1.8
	1994	8	13	1x 1.5, 7x n.d.	1.5	1.5	n.d.–1.5
	1995	5	60	1x 0.5, 1x 1.2, 1x 1.9, 2x n.d.	1.2	1.2	n.d.–1.9
	1996	12	50	1x 0.7, 1x 0.9, 1x 3.2, 1x 5.5, 1x 16, 1x 20, 6x n.d.	4.4	7.7	n.d.–20
	1997	4	75	1x 0.2, 1x 5.2, 1x 6.3, 1x n.d.	5.2	3.9	n.d.–6.3
	1998	1	100	1x 2.2	2.2	2.2	-
	2004	6	50	1x 1.3, 1x 1.4, 1x 3.0, 3x n.d.	1.4	1.9	n.d.–3.0
	2005	18	33	2x 0.7, 1x 0.96, 1x 1.2, 1x 1.7, 1x 2.9, 12x n.d.	1.1	1.4	n.d.–2.9
	2006	4	50	1x 0.7, 1x 0.9, 2x n.d.	0.80	0.80	n.d.–0.90

n.d.= not detectable; median = median of positive samples; mean = mean of positive samples

Table 2 Levels of *N*-nitrosodimethylamine (NDMA) in beer

Country	Year	No. of samples	NDMA-positive	NDMA (µg/kg)		References
				Mean	Range	
USA	1979	6	100%	3.1	0.9–7	[19]
	1980	42	No data	3.4	n.d.–7.7	[20]
	1980	25	92%	5.9	n.d.–14	[21]
	1988	10	100%	0.26	0.03–0.99	[22]
	1989	148	55%	0.067	n.d.–0.58	[12]
	1997	28	50%	0.07	n.d.–0.50	[14]
Canada	1978	13	100%	1.4	0.60–4.9	[23]
	1980	55	100%	0.73	0.36–1.52	[23]
	1982	24	No data	0.31	n.d.–1.9	[23]
	1989	46	59%	0.095	n.d.–0.58	[12]
Germany	1977–78	158	70%	2.7	n.d.–68	[5]
	1979	92	63%	No data	n.d.–32.5	[24]
	1980	401	No data	0.28	n.d.–9.2	[9]
	1981	454	24%	0.44	n.d.–7.0	[25]
	1982	228	No data	0.075	n.d.–1.8	[9]
	1989	514	41.2%	0.16	n.d.–1.7	[10]
	1990	14	No data	0.17	n.d.–0.6	[17]
United Kingdom	1988–89	171	34%	0.18	0.1–1.2	[26]
Netherlands	1978	32	No data	1.4	n.d.–3.9	[27]
	1979	108	No data	2.0	n.d.–7.4	[27]
	1980	86	No data	0.2	n.d.–1.2	[27]
Italy	1982	6	67%	0.4	n.d.–0.79	[28]
	1986	15	87%	0.3	n.d.–0.71	[29]
Spain	1996	21	52%	0.11	n.d.–0.55	[30]
	2002	44	25%	0.16	n.d.–1.05	[31]
Sweden	1988	258	59%	0.3	n.d.–6.5	[11]
Poland	1989	12	83%	0.2	n.d.–0.3	[32]
China	1981	26	77%	2.7	n.d.–6.5	[33]
	1987	176	83%	0.5	n.d.–6	[34]
Japan	1980	29	93%	5.1	Tr–13.8	[35]
	1982	12	0%	0	–	[36]
Korea	1995	29	79%	0.8	0.2–4.2	[15]
	2002	18	56%	0.3	0.1–0.7	[15]
India	1994	120	84%	3.6	n.d.–24.7	[16]
Brazil	1997	60	43%	0.09	n.d.–0.55	[14]
Former USSR	1980	165	53%	No data	n.d.–56	[37]
Estonia	2003–04	158	No data	0.20	n.d.–1.31	[38]

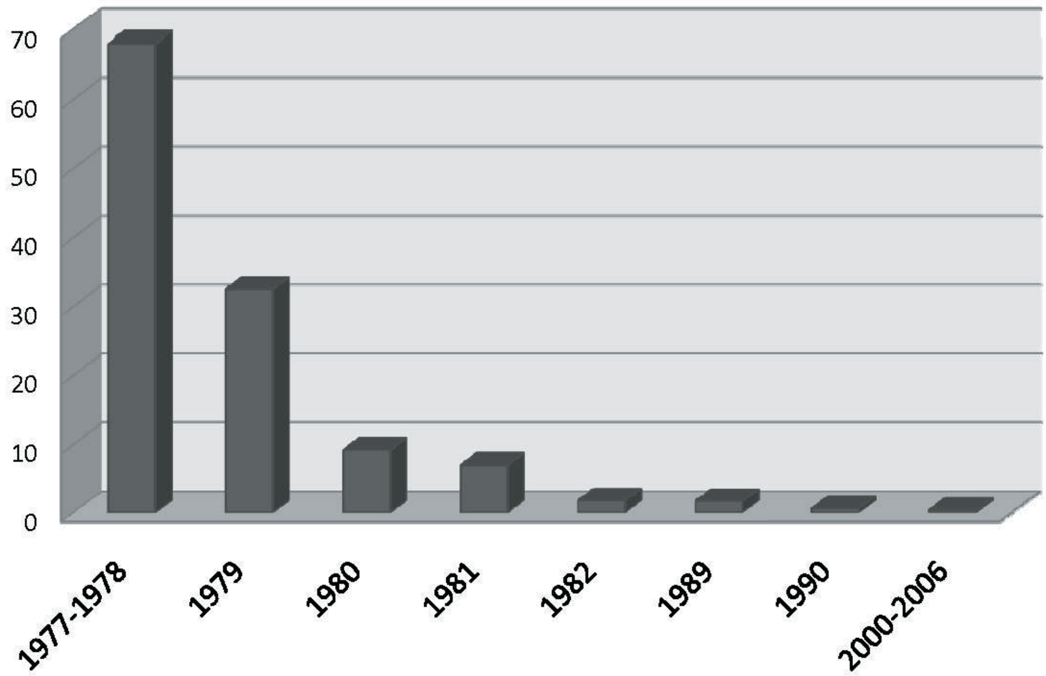

Fig. 1. Development of maximum NDMA concentration (µg/kg) in German beer (data from Table 1 (2000-2006) and Table 2 (1977-1990))