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Original Research Article

Characterization of the nutrient composition of German beer styles for the German nutrient database

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ABSTRACT

Scientific data of nutrient variations in different beer styles are scarce. This study focuses on characterizing German beer styles in regard to their differences in nutrient composition and aims to improve available data for the calculation of nutritional value. 25 retail beer samples of five different German beer styles (Pilsner beer, wheat beer, crystal wheat beer, export beer, dark beer) were analyzed for their nutrient content. Overall this survey revealed significant differences ($p<0.05$) in the proximate composition (ash, protein, ethanol, glucose), vitamins (thiamine, riboflavin, vitamin B_6) and elements (copper, manganese) for the chosen beer styles. The benefit of these new data is exemplified by the calculation of the nutritional supply for average beer consumption and compared with previous data. For the average beer consumer, this study gives higher values for the percentage of daily nutrient recommendation of niacin, vitamin B_6 and folate, whereas lower values are given for alcohol and elements like copper and iodine. Our findings demonstrate that these new data provide an improved basis for nutritional value calculation in future consumption studies.

1. Introduction

The consumption of beer and beer-based beverages is usually restricted to people above a certain age (e.g. at least 16 years in European countries to at least 21 years in the U.S.). Nevertheless, in many countries around the world it is considered a socially accepted stimulant for adults with increasing consumption (Barth-Haas-Group, 2018; Colen and Swinnen, 2016).

With 8.723.136 t beer produced from barley in 2014, Germany has the highest beer production in Europe (FAO, 2020). An important historical milestone in the long history of beer brewing in Germany is the German purity law of the year 1516 which states that only water, barley malt and hops may be used to brew beer. Despite this restriction, a large number of different beer styles have developed. Their differences in nutrient content can be based on the usage and conditioning of malt, the hops and yeast used, the type of alcoholic fermentation and the technical processing during brewing (Hucker et al., 2016a, 2011, 2016b).

In Germany, the classification of beer styles does not follow any legal regulation but is determined by the prevailing public understanding (Deutscher Brauer-Bund e.V., 2018; Strong, 2015). Beer is differentiated by style according to alcoholic fermentation (bottom- or top-fermented), original gravity, color, ingredients, alcohol content and taste, as can be seen for the most popular beer styles in Germany (Table 1). Original gravity is the gravity of the wort before beer fermentation and depends on the amount of fermentable sugar (Entwisle et al., 2008)

The German nutrient database "Bundeslebensmittelschluessel" (BLS) contains nutrient data of about 15,000 foods on the German market. The BLS was originally developed as a standard tool to calculate nutrient

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Table 1
Brief description of different German beer styles (Deutscher Brauer-Bund e.V., 2018; Strong, 2015).

Beer style	Original gravity [%]	ABV[a] [%]	Characteristics	Fermentation
Pilsner	>11	4.8	Gold-colored, bitter, hop aroma, use of Pilsner malt and German hop varieties	bottom-fermentation
Black beer	>11	4.6–5.6	Dark colored, malty flavor, moderate bitterness, use of roasted malts	
Export beer	≈12	5.0–6.0	Gold-colored, slightly stronger than average pale beers, malty character	
Bock beer	>16	7	Pale and dark variants, strong and very malty	
Wheat beer	11–14	5.4	Crystal-clear or opaque, fruity flavour from Weizen ale yeast, at least 50 % malted wheat, remainder is Pilsner malt	top-fermentation
Altbier	≈ 11.5	4.8	Copper-colored, slightly bitter but malty, use of German base malts	

[a] ABV: Alcohol-by-Volume.

intakes in nutritional epidemiological studies and consumption surveys in Germany. The database also forms the basis for nutritional counselling and the calculation of the nutrient content of menus in communal catering. In this context, the quality of the nutrient data available in the BLS, especially of vitamins and trace elements, has a direct impact on the nutritional assessment of foods. The nutrient data listed in the BLS also provide independent information that serves as policy advice for the Federal Ministry of Food and Agriculture and is trusted by consumers throughout Germany (Hartmann et al., 2008).

Scientific data in regard to nutrient variations in different styles of beer are scarce. To perform a nutritional assessment of alcoholic beverages, updated data of beer that reflect the broad variety in nutrients are necessary as was done for sausages in Cunningham et al. (2015).

As differences in the brewing process and the use of ingredients lead to different beer styles, we hypothesised that this might also have an impact on the nutrient content, especially in regards to the vitamin composition.

Beer is a known source of different B vitamins. They come from malt and their amount increases during the germination of barley (Vinas et al., 2003). This has been demonstrated for riboflavin (Hucker et al., 2011), folate (Mayer et al., 2001) and thiamine (Hucker et al., 2011; Priest and Stewart, 2006).

The element content (bulk elements and trace elements) in beer results from different ingredients in beer such as water, hops, malt and yeast, which all contain different amounts of elements. Industrial processing as well as containers and disturbances in the brewing process also lead to the migration of elements into the brewing product (Wyrzykowska et al., 2001).

The present study is aiming to characterize a selection of popular German beer styles by comprehensive nutrient analyses and to compare the differences in their respective composition. Proximate composition such as alcohol, protein, starch and ash content was determined. The analysis also included determination of vitamins (thiamine, riboflavin, niacin, vitamin B_6, folate) and bulk and trace elements.

The results of these determinations are interpreted and compared with existing data from literature and BLS version 3.02. The impact of the new data is then determined by using the new data points to estimate the contribution of different nutrients in beer to the calculated daily nutrient intake.

2. Materials and methods

The methods used for this study range from microbiological methods to advanced LC–MS methods (for the determination of folate) and ICP-MS (for the determination of elements).

2.1. Samples and sample preparation

For the determination of their chemical composition, five different German beer styles were sampled. For each beer style (Pilsner beer, wheat beer, crystal wheat beer, export beer and dark beer), five (n = 5) branded products were chosen based on market share data to approximately represent the German market. Market share data were the most important selection criteria, as commercial samples lacked information on other influencing factors such as ingredients, regional differences or different manufacturing processes. The final number of samples resulted in a total of 125 bottles of 500 mL (5 beer style x 5 different brands x 5 bottles). Samples were purchased in three different local supermarkets in the region of Karlsruhe, Germany, in July 2016.

For sample preparation, beer bottles were opened, filled into a beaker and carefully degassed in an ultrasound bath for 10 min. Homogenization was achieved by constant stirring during the degassing process. In determinations where pooled samples were used, all five branded products per beer style were pooled. All analyses were conducted in degassed samples, except for the ethanol determination, which was performed in freshly opened beer. Aliquots were stored at −80 °C until analysis.

2.2. Proximate composition

Dry matter was determined gravimetrically in beer samples after mixing the sample with sea sand and drying in an air oven at 103 ± 2 °C to constant weight (AOAC 950.46 (AOAC International, 2020)). Water content was calculated by subtracting the dry matter and ethanol content from 100 (water = 100 - dry matter – ethanol).

Ash content was determined by igniting and drying the sample in a platinum dish overnight (18 h) at 550 ± 5 °C (AOAC 923.03 (AOAC International, 2020)).

The determination of nitrogen was based on AOAC 920.53 (Kjeldahl method (AOAC International, 2020)), using automated digestion and distillation units (Digestion Unit K-35, KjelFlex K360, Büchi, Essen, Germany). Titration was done with 0.05 M sulfuric acid and a conversion factor of 6.25 was used to estimate the crude protein.

Ethanol content was determined by an enzymatic kit (Ethanol UV-Test, cat. No. 10176290035, r-biopharm AG, Darmstadt, Germany) at a wavelength of 340 nm. To remove carbon dioxide in the beer sample, it was mixed with potassium hydroxide platelet and the resulting solid bicarbonate was removed. Samples were diluted 1:1000 before measurement.

Dextrins in beer were measured by means of an enzymatic kit (starch test kit, cat. No. 10207748035, r-biopharm AG, Darmstadt, Germany). Samples were degassed by stirring for 10 min and afterwards diluted 1:50. Measurement was carried out at a wavelength of 340 nm.

Soluble sugars (sucrose, fructose, glucose and maltose) were determined according to Van Den et al. (Van Den et al., 1986) using high performance liquid chromatography (HPLC) with RI-detection (Agilent 1100 series HPLC, Agilent, Waldbronn, Germany). Soluble sugar standards were purchased from Sigma-Aldrich, Chemical Co. USA.

2.2.1. Validation of sugar method

The method was tested for its suitability with respect to beer samples prior to sample measurement. The level of detection (LOD) for soluble sugars was determined by signal to noise ratios (S/N) of standard solutions and the limit of quantification (LOQ) was determined by precision measurements in low concentration ranges of each analyte in beer samples (precision-based approach (ICH, 1996; Shrivastava and Gupta,

2011; Thompson et al., 2002; Wellmitz and Michael, 2005)). LOD was based on a signal-to-noise ratio (S/N) ≥ 3. Replicate measurements of beer samples in low concentration ranges (S/N ≈ 3–9) of fructose, glucose, sucrose and maltose were then performed. Relative standard deviations were plotted against the corresponding concentrations for each sugar. To ensure accurate quantification, an upper limit for the coefficient of variation (CV%) of 15 % was chosen and the respective analyte concentration was set as LOQ for each sugar.

All analyses were performed in duplicate.

2.3. Vitamin analyses

Beer samples were analyzed in duplicates for thiamine, riboflavin, vitamin B_6, folate and niacin.

2.3.1. Thiamine and riboflavin

For the determination of thiamine and riboflavin, samples were treated with acidic (hydrochloric acid) and enzymatic (taka-diastase) hydrolysis. Quantification was done by HPLC with fluorescence detection (($\lambda_{ex} = 450$ nm and $\lambda_{em} = 525$ nm for riboflavin, $\lambda_{ex} = 365$ nm and $\lambda_{em} = 435$ nm for thiamine as thiochrome) (Oguntoyinbo et al., 2016). Thiamine and riboflavin standards (thiamine chloride hydrochloride and riboflavin) were obtained from Merck KGaA, Karlsruhe, Germany. Determination of LOD and LOQ was the same as for the analysis of soluble sugars, in which LOD was determined as a S/N-ratio ≥ 3 and LOQ by a precision-based approach (see 2.2).

2.3.2. Vitamin B_6

Vitamin B_6 as pyridoxine, pyridoxal and pyridoxamine was extracted with acid (hydrochloric acid) and enzymatic hydrolysis by means of taka-diastase and β-glucosidase. For sample extraction 40 g of liquid beer sample was weighed in a 100 mL conical flask. Ten millilitres of hydrochloric acid (1 mol/L, Merck KGaA, Karlsruhe, Germany) was added and the solution was placed in an autoclave at 120 °C for 30 min. After cooling to room temperature, the solution was diluted to 100 mL with distilled water. An aliquot of the sample solution (50 mL) was centrifuged at 3000 *g* for 4 min and subsequently filtrated. For enzymatic hydrolysis, 5 mL of the filtrate was filled in a 10 mL brown conical flask. The pH was adjusted to 4.8 with 2.5 M sodium acetate buffer and 500 µL of a mixture of taka-diastase (100 mg/mL enzyme solution, Sigma-Aldrich, Chemical Co., USA) and β-glucosidase (15 mg/mL enzyme solution, Sigma-Aldrich, Chemical Co. USA) was added. After enzyme incubation in a water bath (Haake W19, Thermo Fisher Scientific Inc., USA) at 37 °C for 18 h, the solution was cooled to room temperature. The pH was adjusted to 6.5 with potassium hydroxide solution (10 %, Merck KGaA, Karlsruhe, Germany) and the sample solution was diluted to 10 mL with potassium dihydrogen phosphate (Merck KGaA, Karlsruhe, Germany) buffer solution (pH 6.6). Before the solution could be used for HPLC, it was filtrated through a HPLC syringe filter (SPARTAN Filter unit 30/0.2 RC, Whatman plc, GE Healthcare Life Sciences, U.K.).

Quantification of the vitamin B_6 vitamers was concluded by HPLC on an Agilent 1100 binary system, using a Discovery RP-Amide-C16 column (5 µm, 250 × 4.6 mm i.d.). Analyte detection was performed by a fluorescence detector set at $\lambda_{ex} = 330$ nm and $\lambda_{em} = 390$ nm. Vitamin B_6 standards (pyridoxal hydrochloride, pyridoxamine dihydrochloride, pyridoxine hydrochloride) were purchased from Sigma-Aldrich, Chemical Col, USA. The mobile phase consisted of potassium dihydrogen phosphate and was pumped at a flow rate of 1.0 ml/min. The column temperature was 30 °C and the injection volume was 50 µL. The LOD was based on a signal-to-noise ratio (S/N) ≥ 3. The criteria for the determination of the LOQ were a S/N-ratio ≥ 9 and a maximum CV% of 20 %.

2.3.3. Niacin

The determination of niacin in the samples was performed in an accredited laboratory which was audited by Deutsche Akkreditierungsstelle (DAkks). Quality-assurance and quality-control measurements were in place. The method of determination was an in-house reversed-phase HPLC-method for niacin and previous sample digestion with sodium thiosulphate solution and glacial acetic acid.

2.3.4. Folate

The determination of the total folate content and folate derivatives (folic acid (PteGlu), tetrahydrofolate (H_4folate), 5-methyltetrahydrofolate (5-CH_3-H_4folate), 5-formyltetrahydrofolate (5-CHO-H_4folate), and 10-formylfolic acid (10-CHO-PteGlu)) was performed according to the recently published method by Striegel et al. (Striegel et al., 2018) using LC–MS/MS and stable isotope dilution assay with slight modifications. Briefly, 500 mg degassed beer sample was weighed into Pyrex bottles. After addition of buffer for extraction and an equilibration step, samples were spiked with internal standards ([$^{13}C_5$]-PteGlu, [$^{13}C_5$]-H_4folate, [$^{13}C_5$]-5-CH_3-H_4folate, and [$^{13}C_5$]-5-CHO-H_4folate) in amounts adjusted to the expected contents of the respective analytes to fall in the given calibration range (11–250 µmol). After further equilibration (15 min), samples were boiled for 10 min and cooled on ice. 2 mL of chicken pancreas and 500 µL of rat serum were added to the samples and incubated overnight (12 h). The amounts of enzymes needed for complete deconjugation was verified before using LC–MS/MS. Further details on extraction as well as LC–MS/MS measurements and validation parameters were previously published (Striegel et al., 2018).

2.4. Element analyses

Elements (sodium, magnesium, potassium, calcium, phosphorus, manganese, copper, zinc, iron, selenium and iodine) were determined by inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion according to §64 LFGB L 00.00 19/1 (BVL).

For analysis of sodium, magnesium, potassium, calcium, phosphorus, manganese, copper, zinc, iron and selenium, 5 g of each beer sample was digested in duplicate with 5 mL of nitric acid (suprapur, Merck, Darmstadt, Germany; purified by a sub-boiling distillation system (DST-1000, Savillex, Minnetonka, USA)) and 1 mL of hydrochloric acid (suprapur, Merck, Darmstadt, Germany) at 180 °C for 20 min using a microwave device (Start 1500, MLS GmbH, Leutkirch, Germany). After digestion, the samples were made up to a final volume of 25 mL with ultrapure water (18.2 MΩ cm, Synergy 185, Merck Millipore, Darmstadt, Germany) and were analyzed without further dilution. Analysis was performed by ICP-MS (Agilent 7800, Agilent Technologies, Waldbronn, Germany) using Argon 4.6 as sample introduction, plasma and aerosol dilution gas. Helium and hydrogen were used as collision and reaction gas, respectively. Multielement calibration standards were prepared from single element standards (sodium, magnesium, potassium, calcium, phosphorus (Labkings, Hilversum, Netherlands), selenium (UltraScientific, Kingstown, USA)) and a multielement standard (manganese, copper, zinc, iron (Sigma-Aldrich, Steinheim, Germany)) in six concentrations (32 µg/L–100 mg/L sodium, phosphorus, potassium, calcium; 16 µg/L–50 mg/L magnesium; 0.32–1000 µg/L iron, copper, zinc, manganese; 0.016–50 µg/L selenium). The acid matrix of the standards was matched to the matrix in the digested beer samples. An internal standard solution containing scandium (Ultra-Scientific, Kingstown, USA), germanium (Agilent Technologies, Santa Clara, USA) and rhodium (Ultra-Scientific, Kingstown, USA) was continuously added to the sample flow. Reagent blank solutions were taken through the same preparation steps as the beer samples and were used for determination of the LOQ. Certified reference material Corn Bran (NIST RM 8433) was used for quality control. Analyses were performed in duplicate or quadruplicate.

Iodine was measured in diluted beer samples based on a modified extraction method for iodine in animal feeds (Leiterer et al., 2011). 25 g of the beer sample were added to 20 g of 1.25 % suprapur ammonia and 5 g of 10 % semiconductor grade 2-propanol. The mixture was shaken

overnight and filtered first through 1.2 µm GL microfiber filters (neoLab, Heidelberg, Germany) and then through 0.45 µm cellulose acetate filters (Sartorius Minisart NML, Goettingen, Germany). ^{127}Iodine in the obtained solution was measured undiluted by ICP-MS (iCAP Q, Thermo Scientific, Waltham, Massachussetts, United States) in standard mode with a dwell time of 10 ms and using Argon 5.0 (Linde AG, Dortmund, Germany) as plasma gas and ^{103}Rhodium as internal standard. Standard addition was used for calibration (1−10 µg/L iodine). Certified reference material skimmed milk powder (ERM-BD 150) was used to check accuracy and precision of the extraction method. Analyses were performed in triplicate.

For elemental analyses, a hidden comparison control sample (identical to another sample in the sample series but with a different sample code) served as a quality control. Precision was measured by quintuple measurement of a beer sample.

2.5. Calculations, statistics and data presentation

Results are given as mean ± standard deviation (n = 5) per 100 g of liquid and degassed beer sample. The density of each beer (additional experiment; see supplementary material, Table S1 for density values) style was used to convert results from "per 100 mL" to "per 100 g" for the nutrients dextrins and ethanol. Conversion factors for back-calculating vitamin standards to vitamins were 1.012 for pyridoxal and 1.006 for pyridoxamine to calculate vitamin B_6 as pyridoxine; 1.00 for back-calculating nicotinic acid to nicotinamide, respectively. The standard deviation describes the variation within the different brands. All analyses of single samples were performed at least in duplicate. The comparison of nutrient content for five different beer styles was performed using IBM SPSS Statistics Version 20 (IBM Corp., Armonk, NY, USA). To perform a one-way ANOVA, substitute values were assigned for concentrations below the limits of detection and quantification: concentrations < LOQ (but > LOD) were replaced with a value of LOQ/2 for the respective analytes; for concentrations < LOD, a substitute value of 0 was assigned. Significances were calculated by one-way analysis of variances (ANOVA) with Tukey post-hoc test. A normal distribution was assumed. For analytes with results below the LOD or LOQ, this information is provided for each sample in the detailed results tables (Supplementary material, Tables S2 and S3). Mean values were calculated with substitute values as was done for the one-way ANOVA: concentrations < LOQ (but > LOD) were replaced with a value of LOQ/2 for the respective analytes; for concentrations < LOD, a substitute value of 0 was assigned.

3. Results

Results of proximate composition, vitamin and element content of analysed samples of five important German beer styles are shown in Tables 2–4, respectively.

3.1. Proximate composition

The sum of proximates (moisture content including water and ethanol, ash, protein, sum of soluble sugars and dextrins, see Table 2) for beer overall was 99.1 ± 0.2 g/100 g and, therefore, within the acceptable range (97−103 g/100 g) set for food composition databases (Greenfield and Southgate, 2003). The water content was ~ 92 g/100 g in all analyzed styles of beer. The amount of dry matter varied from 3.7 g/100 g in Pilsner beer to 4.3 g/100 g in dark beer (see Table 2).

Significant differences for proximate composition could be found for ash content (p = 0.009), where Pilsner beer was significantly lower than export beer. Protein content varied from 0.42 g/100 g (Pilsner beer) to 0.61 g/100 g (wheat beer). Protein content in wheat beer was significantly (p < 0.001) higher than in the four other beer styles. Ethanol ranged from 3.9 g/100 g in Pilsner beer to 4.4 g/100 g in export beer. There was a significant difference between the lowest ethanol content in Pilsner beer and the highest in export beer (p = 0.009).

Table 2
Proximate composition, data mean ± SD, n = 5.

Nutrient	Pilsner beer	Wheat beer	Crystal wheat beer	Export beer	Black beer	*p-values*
Water [g]	92.5 ± 0.1	91.6 ± 0.4	91.9 ± 0.4	91.7 ± 0.2	91.6 ± 0.7	0.050
Dry matter [g]	3.7 ± 0.2	4.2 ± 0.3	4.0 ± 0.4	4.0 ± 0.3	4.3 ± 0.5	0.050
Ash [g]	0.14 ± 0.01 ^{a}	0.17 ± 0.01 ^{a,b}	0.15 ± 0.02 ^{a,b}	0.18 ± 0.01 ^{b}	0.17 ± 0.02 ^{a,b}	0.009
Protein[1] [g]	0.42 ± 0.02 ^{a}	0.61 ± 0.06 ^{b}	0.50 ± 0.06 ^{a}	0.49 ± 0.03 ^{a}	0.50 ± 0.04 ^{a}	<0.001
Ethanol [g]	3.9 ± 0.1 ^{a}	4.2 ± 0.2 ^{a,b}	4.1 ± 0.1 ^{a,b}	4.4 ± 0.2 ^{b}	4.0 ± 0.4 ^{a,b}	0.009
Dextrins[2] [g]	2.1 ± 0.2	2.4 ± 0.3	2.4 ± 0.3	2.1 ± 0.2	2.1 ± 0.1	0.158
Fructose [mg]	25 ± 11	11 ± 7	12 ± 2	17 ± 5	20 ± 9	0.047
Glucose [mg]	53 ± 7 ^{a}	21 ± 0 ^{b}	21 ± 0 ^{b}	56 ± 4 ^{a}	52 ± 20 ^{a}	<0.001
Maltose [mg]	21 ± 16 *	27 ± 37 *	11 ± 0*	87 ± 92	71 ± 136*	0.433

Composition given per 100 g liquid beer sample, standard deviation describes variations within the different styles, one-way ANOVA, different letters in superscript indicate significant differences between beer styles with Tukey post-hoc-test (p<0.05).
[1] Conversion of total nitrogen to protein by Nx6.25.
[2] Calculated as starch.
* At least 3 out of 5 of the single values were below LOD or LOQ (see Supplemental material Table S2); all calculations (mean, standard deviation, one-way ANOVA and Tukey post-hoc test) were carried out with substitute values (see 2.6).

Overall, wheat and crystal wheat beer samples are lowest in their amount of soluble sugars such as glucose, sucrose and maltose with values below LOD and LOQ, respectively. This results in a significant difference between (crystal) wheat beer samples and barley-based beers like Pilsner, export and dark beer. Sucrose could only be quantified (> LOQ; LOQ: 14 mg/100 g) in three out of 25 beer samples (two export beers and one dark beer) while its presence could not be detected in the remaining samples (x < LOD), so mean values for sucrose content in beer samples are not available. Similar results were obtained for maltose, where a mean value could only be given for export beer.

3.2. Vitamin content

Table 3 shows the content of water-soluble vitamins thiamine, riboflavin, vitamin B_6 (with vitamers pyridoxamine and pyridoxine), niacin and different vitamers of the water-soluble vitamin folate. Thiamine content could only be quantified (x > LOQ) in 7 out of 25 beer samples (for single values see supplementary material, Table S4) so mean values (including substitute values LOQ/2 and 0 for concentrations < LOQ and < LOD, respectively) are only available for (crystal) wheat beer samples. In order to carry out a one-way ANOVA for thiamine, substitute values for values below limits of detection and quantification were assigned as stated above (see 2.6). The thiamine content in wheat beer was significantly higher than in Pilsner, export and dark beer (p = 0.007).

A significant difference in riboflavin content was revealed between wheat beer and crystal wheat beer (p = 0.026). Vitamin B_6 content differed significantly between crystal wheat beer (46.9 ± 15.7 µg/100 g) and export beer (69.7 ± 11.6 µg/100 g; p = 0.039) whereas no significant differences could be found for vitamers pyridoxine and pyridoxamine of vitamin B_6 while pyridoxal could not be detected. For the determination of folates in beer, three naturally occurring vitamers, namely 5-methyl-H_4-folate, 5-formyl-H_4-folate and 10-formylfolic acid, could be detected and quantified, whereas H_4-folate and folic acid were

Table 3
Content of thiamine, riboflavin, vitamin B_6 and niacin, data mean ± SD, n = 5.

Nutrient	Pilsner beer	Wheat beer	Crystal wheat beer	Export beer	Black beer	*p-values*
Thiamine[1] [µg]	0 ± 0 [a]*	10 ± 7 [b]	5 ± 3 [a,b]	1 ± 1 [a]*	2 ± 3 [a]*	0.006
Riboflavin [µg]	34 ± 2 [a,b]	38 ± 4 [a]	32 ± 2 [b]	36 ± 2 [a,b]	36 ± 3 [a,b]	0.026
Pyridoxamine [µg]	13.0 ± 2.8	9.44 ± 6.15	8.41 ± 2.81	14.9 ± 2.2	11.5 ± 4.9	0.121
Pyridoxine [µg]	48.3 ± 8.7	40.4 ± 10.3	38.4 ± 6.0	54.7 ± 10.5	47.9 ± 9.1	0.065
Vitamin B_6[2] [µg]	61.3 ± 9.8 [a,b]	49.9 ± 15.7 [a,b]	46.9 ± 7.82 [a]	69.7 ± 11.6[b]	59.4 ± 11.9 [a,b]	0.039
Niacin[3] [mg]	1.36 ± 1.21	2.13 ± 1.13	1.63 ± 0.93	1.16 ± 0.53	1.00 ± 0.14	0.318
5-CH_3-H_4folate[4] [µg]	4.1 ± 0.9 [a,b]	4.4 ± 0.5 [a]	3.6 ± 0.9 [a,b]	2.4 ± 1.6 [b]	3.9 ± 0.8 [a,b]	0.047
5-CHO-H_4folate[4] [µg]	1.8 ± 0.3	1.8 ± 0.3	1.5 ± 0.2	1.6 ± 0.5	2.0 ± 0.3	0.197
10-CHO-PteGlu[4] [µg]	2.7 ± 0.2	2.7 ± 0.3	2.5 ± 0.3	2.5 ± 0.5	2.5 ± 0.3	0.864
Total Folate[5] [µg]	8.4 ± 1.2	8.8 ± 0.8	7.6 ± 0.9	6.4 ± 2.6	8.4 ± 1.0	0.109

Contents given per 100 g liquid beer sample, one-way ANOVA, different letters for significant differences between beer styles with Tukey post-hoc-test ($p < 0.05$).

[1] Calculated as thiamine chloride hydrochloride; one-way ANOVA and Tukey post-hoc test were carried out with substitute values (see 2.7).

[2] Calculated as pyridoxine.

[3] Calculated as nicotinamide.

[4] Folates all calculated as PteGlu.

[5] Total folate as sum parameter of the three folate vitamers.

* At least 3 out of 5 of the single values were below LOD or LOQ (see Supplemental material Table S3); all calculations (mean, standard deviation, one-way ANOVA and Tukey post-hoc test) were carried out with substitute values (see 2.6).

Table 4
Content of different elements in German beer styles, data mean ± SD, n = 5.

Nutrient	Pilsner beer	Wheat beer	Crystal wheat beer	Export beer	Black beer	*p-values*
Sodium [mg]	1.50 ± 0.08	1.33 ± 0.97	1.27 ± 0.59	1.45 ± 0.37	1.64 ± 0.43	0.852
Magnesium [mg]	8.60 ± 0.86	9.32 ± 1.22	8.68 ± 1.32	9.93 ± 0.69	9.82 ± 0.63	0.132
Phosphorus [mg]	21.2 ± 2.82	26.5 ± 4.85	25.9 ± 3.84	26.4 ± 5.08	27.1 ± 4.87	0.244
Potassium [mg]	53.6 ± 11.1	54.7 ± 3.66	52.0 ± 2.95	55.2 ± 3.18	56.2 ± 6.06	0.851
Calcium [mg]	5.16 ± 1.58	5.66 ± 1.97	6.60 ± 2.70	7.01 ± 1.05	4.61 ± 1.05	0.225
Manganese [µg]	11.1 ± 1.92 [a]	20.5 ± 4.15 [b]	21.1 ± 7.97 [b]	11.7 ± 3.42 [a]	14.2 ± 1.91 [a,b]	0.003
Iron [µg]	4.50 ± 2.35*	12.9 ± 10.7	10.0 ± 5.44	4.54 ± 2.45*	12.2 ± 3.87	0.083
Copper [µg]	5.47 ± 0.98 [a,b]	4.18 ± 0.43 [a]	4.23 ± 0.59 [a]	5.34 ± 1.30 [a,b]	6.33 ± 1.54 [b]	0.020
Selenium [µg]	0.10 ± 0.03	0.08 ± 0.01	0.09 ± 0.02	0.11 ± 0.03	0.09 ± 0.01	0.530
Iodine [µg]	0.30 ± 0.07	0.54 ± 0.57	0.59 ± 0.54	0.26 ± 0.08	0.23 ± 0.08	0.377

Contents given per 100 g liquid beer sample, one-way ANOVA, different letters for significant differences between beer styles with Tukey post-hoc-test ($p < 0.05$).

* At least 3 out of 5 of the single values were below LOD or LOQ; all calculations (mean, standard deviation, one-way ANOVA and Tukey post-hoc test) were carried out with substitute values (see 2.6).

not detectable in any of the beer samples (LOQ being 0.76 µg/100 g and 0.96 µg/100 g, respectively).

Significant differences for folates could only be found between the highest content in wheat beer (4.4 ± 0.5 µg/100 g) and the lowest content in export beer (2.4 ± 1.6 µg/100 g; $p = 0.047$) for 5-CH_3-H_4folate. Contents of 5-CHO-H_4-folate ranged from 1.5 ± 0.2 µg/100 g in crystal wheat beer to 2.0 ± 0.8 µg/100 g in dark beer. In terms of 10-CHO-PteGlu, the values for the five beer styles were very similar (2.5–2.7 µg/100 g). Final folate content (given as PteGlu) is given as the sum of all quantified vitamers and ranged from 6.4 ± 2.6 µg/100 g in export beer to 8.8 ± 0.8 µg/100 g in wheat beer.

3.3. Element content

The elemental composition across the five beer styles was very similar (Table 4). Only for manganese and copper, significant differences between the beer styles could be detected. In wheat and crystal wheat beer, manganese content was significantly higher than in Pilsner and export beer ($p = 0.003$). Additionally, copper content was significantly lower in wheat and crystal wheat beer than in dark beer ($p = 0.020$).

Highest concentrations were found for potassium and phosphorus, with mean contents of 54.3 and 25.4 mg/100 g, respectively. Bulk elements magnesium, calcium and sodium had mean contents of 9.27, 5.81 and 1.44 mg/100 g, respectively. For Pilsner beer and export beer, no mean iron values could be given as most of the single values were below LOQ of 6.9 µg/100 g. All single values for zinc were below the LOQ of 20.2 µg/100 g. Due to the high standard deviation for (crystal) wheat beer samples, there was no significant difference in iodine concentrations between beer styles ($p = 0.377$).

4. Discussion

4.1. Nutrient content

Overall, this survey showed that German beer styles differ significantly with respect to some nutrients, as numerous differences were observed in proximate composition, vitamins and elements.

The results for water content, ash, protein, ethanol and dextrins for Pilsner beer agreed very well with values for Pilsner beer from literature, where water content is reported as 91.9 g/100 g, protein content as 0.5 g/100 g, ethanol as 4.00 g/100 g and ash as 0.2 g/100 g, respectively (Piendl, 1990). These values can also be found in another German nutrient database (Souci et al., 2016).

The significantly higher protein content in wheat beer compared to the other four beer styles could be due to the fact that, unlike the other four styles, this beer style is not deprived of yeast. Also, the protein content in beer comes primarily from the malt, which can lead to variations in the protein content of the beer depending on whether barley malt or wheat malt was used. Differences in the amount of alcohol formed during fermentation can be attributed to the original gravity, which is particularly different when comparing Pilsner beer (11 % original gravity) and export beer (12 % original gravity) (Deutscher Brauer-Bund e.V., 2018).

In general, the concentration and presence of soluble sugars in beer strongly depend on sugar production by amylase activity from germinated barley or wheat and sugar utilization during yeast-induced fermentation (Gotsick and Benson, 1991). Although we expected variations in dextrin content due to different yeast and mashing processes, no significant differences were found between beer styles in this study. We assume that this is due to other influencing factors dependent on the producers (e.g. different mash temperatures and durations, use of different yeast strains), which also contribute to the variation of different brands within a beer style.

The occurrence and content of water-soluble vitamins depend to a large extent on the original gravity of the beer. The significant difference

in riboflavin content between wheat beer and crystal wheat beer can be related to the fact that the yeast is not filtered out of the wheat beer products. Crystal wheat beer and export beer differ significantly in vitamin B_6 content, which may be due to the higher original gravity in export beer samples and the higher amount of malt containing vitamin B_6. In the literature, values for the content of water-soluble vitamins in bottom-fermented beer are reported (thiamine as 35.7 µg/L and riboflavin as 307 µg/L in lager beer (Hucker et al., 2011), niacin (as nicotinamide) as 0.77 mg/100 g and vitamin B_6 as 62 µg/100 g, respectively (Souci et al., 2016)), which agree well with the mean values of Pilsner beer samples. Since B group vitamins can be traced to the germinated barley in malt and are relatively stable during roasting, Vinas et al. (Vinas et al., 2003) determined the thiamine content not only in beer samples but also in raw products like malt, hops and brewer's yeast. The latter study found that thiamine content was highest in malt (650 µg/100 g) and brewer's yeast (510 µg/100 g) in contrast to hops (34 µg/100 g) and the raw barley grain (66 µg/100 g). Our results confirm the assumptions about differences in water-soluble vitamins in different German beer styles, such as higher levels of vitamins in beers with higher original gravity or residual yeast. Due to large variations between brands within a beer style, no other significant difference were found.

The element content in beer has a clear influence on quality of the beer, its stability, its taste and its nutritional value. The concentrations found in the present study for the bulk elements potassium, phosphorus, magnesium, calcium and sodium are of the same order of magnitude as in the literature (Alcázar et al., 2002; Montanari et al., 2009; Rodrigo et al., 2017). For trace elements, a large variation in concentrations is found in the literature. In his review article, Pohl (Pohl, 2008) found differences of one to two orders of magnitude for manganese, iron and copper in German beers. The analytical values of our study are in this range.

Different raw materials such as water, malt, hops or yeast are regarded as sources of elements in beer. For Pilsner beer, Wietstock et al. (2015) found the highest contribution of calcium, magnesium, iron and copper coming from hops, and the highest contribution of zinc from yeast. However, when considering the amount of the different raw materials used for brewing, malt was found to be the main source of element content in beer (Montanari et al., 2009; Wietstock et al., 2015). Another important source of elements is brewing water, which has even led to the development of different beer styles in different regions, for example the Dortmunder Export or the Münchener Helles (Montanari et al., 2009).

In studying stout, ale, lager and wheat beer, Bellido-Milla et al. (Bellido-Milla et al., 2000) found that it was possible to classify beer samples with respect to the usage of barley or wheat malt based on the element content. This is consistent with our results, as we found significantly different levels of manganese in wheat and crystal wheat beer compared to Pilsner and export beer, and of copper compared to Dark beer. In the BLS nutrient database (Max Rubner-Institut, 2014), manganese content in unprocessed wheat is more than twice that in unprocessed barley, and copper content is 13 % lower in wheat than in barley. When analyzing beer samples from 10 different countries in different containers and packagings, Rodrigo et al. (Rodrigo et al., 2017) found that the element content in beer is generally determined more by beer style than by geographical origin or type of container. However, the geographical origin can also have a significant impact on some elements, such as selenium, which was found in higher concentrations in beer from the USA in comparison to Europe. This has been attributed to higher selenium content in grain in the USA (Rodrigo et al., 2015).

According to Hampel et al. (Hampel et al., 2009), beer from the northern part of Germany has a higher concentration of iodine than beer samples from the south (e.g. Bavaria) of Germany. This observation could not be confirmed in the present study, especially since one brand of Bavarian (crystal) wheat beer exceeds the iodine content of the other brand samples. This brand is also the main reason for the large variation of iodine content in wheat beer and crystal wheat beer samples.

Our results support the assumption that there are significant differences in the nutrient composition of different beer styles and that our revised data represent a good contribution to improving the quality of nutrient data of beers. However, we are aware that there are other factors that influence the nutrient content in beer that could not be considered in this study. These include e.g. the method and duration of storage or the technological processes of bottling, mashing techniques or the brewing water profile. For example, it has been shown that storage time can have an impact on folic acid content in fruit juices (Frommherz et al., 2014). Although beers can be classified in different styles, the manufacturer still has enough options to influence the final product in terms of its nutrient profile, so that individual brands within a beer style can also deviate from other brands, as we have seen especially for iodine concentrations.

Further research should look at changes in soluble sugar and vitamin composition during storage and beer maturation as well as new and emerging beer styles with increasing consumption, such as (India) Pale Ales or stouts.

4.2. Comparison to existing BLS data for German beer styles

Since, as described above, only limited information is available on the nutrient content of individual beer styles, only Pilsner beer, wheat beer and export beer could be compared to existing entries in BLS version 3.02 from 2014 (Max Rubner-Institut, 2014) (Table 5). Since the BLS only publishes mean values, statistical mean comparisons could not be made. In general, many of the updated data points investigated in this study are higher than those reported in BLS version 3.02. This is true for carbohydrate contents of fructose, glucose and dextrins, and for the vitamins niacin and folate. In contrast to carbohydrate concentrations,

Table 5
Comparison of selected nutrients of German beer styles from this survey (mean of n = 5 individual samples) and from BLS version 3.02 (published in 2014).

Nutrient	Pilsner beer		Wheat beer		Export beer	
	BLS 3.02	this study	BLS 3.02	this study	BLS 3.02	this study
Water [g]	92.2	92.5	92.9	91.6	90.6	91.7
Ash [g]	0.20	0.14	0.14	0.17	0.20	0.18
Protein [g]	0.50	0.42	0.30	0.61	0.50	0.49
Ethanol [g]	3.96	3.9	3.53	4.2	5.5	4.4
Dextrins[a] [g]	0	2.1	0	2.4	0	2.1
Fructose [mg]	6	25	6	11	6	17
Glucose [mg]	20	53	19	21	20	56
Maltose [mg]	140	21	216	27	227	56
Thiamine[b] [µg]	3	0	1	10	6	1
Riboflavin [µg]	33	34	40	38	19	36
Vitamin B_6[c] [µg]	62	61.3	40	49.9	45	69.7
Niacin[d] [mg]	0.77	1.36	0.83	2.13	0.649	1.16
Folate[e] [µg]	6	8.4	4	8.8	5	6.4
Sodium [mg]	4	1.50	4	1.33	4	1.45
Magnesium [mg]	10	8.60	10	9.32	8	9.93
Phosphorus [mg]	32	21.2	20	26.5	22	26.4
Potassium [mg]	55	53.6	35	54.7	42	55.2
Calcium [mg]	4	5.16	2	5.66	5	7.01
Manganese [µg]	16	11.1	30	20.5	12	11.7
Iron [µg]	12	4.50	1	12.85	12	4.54
Copper [µg]	10	5.47	40	4.18	6	5.34
Iodine [µg]	1.5	0.30	1	0.54	1.5	0.26

Given per 100 g liquid beer sample.
[a] BLS entry is declared as starch.
[b] Calculated as thiamine chloride hydrochloride.
[c] Calculated as pyridoxine.
[d] Calculated as nicotinamide.
[e] Calculated as folic acid.

Table 6
Percentage of recommended intake of selected nutrients by consumption of beer; comparison of selected nutrients with notable differences between this study and BLS version 3.02 (published in 2014).

Nutrient	Recommended daily intake (DGE), male	Percentage of recommended intake, male, average consumption		Percentage of recommended intake, male, high consumption	
		BLS 3.02	this study	BLS 3.02	this study
Ethanol [g][a]	20	65 %	62 %	217 %	208 %
Niacin [mg]	15	15 %	31 %	50 %	103 %
Vitamin B_6 [µg]	1500	10 %	12 %	33 %	40 %
Folate [µg]	300	5 %	8 %	17 %	26 %
Copper [µg]	1250	4 %	1 %	15 %	4 %
Iodine [µg]	190	2 %	1 %	7 %	2 %

[a] DGE gives guideline values for alcohol intake (upper intake level) of 20 g per day, which are not to be confused with consumption recommendations.

element contents from this survey for sodium, copper, manganese and iodine are slightly lower than in the BLS version 3.02.

As analytical methods – especially for vitamins and element content – have improved over the years, there is a need to continually evaluate and update the available nutrient data. For example, the apparent increase in folate content in the three beer styles compared can be explained by advances in analytical method development (e.g. deconjugation, trienzyme treatment) in recent years. The most striking challenges in the analytical determination of folates were the inadequate deconjugation of polyglutamates in sample preparation and the fact that in microbiological methods individual vitamins react differently to the test organism, so that basic calibration with folic acid as standard reagent in the presence of other folate vitamers is not effective and sometimes led to overestimations of folate content compared to results obtained with HPLC methods (Monch and Rychlik, 2012; Ringling and Rychlik, 2017). However, differences to preexisting data could also be due to changes in raw material (especially seasonal differences in malt), brewing recipe, or the use of new manufacturing technologies in beer production.

Subsequently, the new data points were used to update the BLS and their impact on the daily nutrient intake via beer was examined. The daily intakes of beer for average (given as mean) and so-called heavy consumers (given as 90th percentile) of beer (male and female) were taken from the evaluations of the German National Nutrition Survey II (NVSII) were used as a basis (Krems et al., 2013). For the average beer consumer, a daily consumption of 299 g (male) and 47 g (female) were used for calculation, while for the so-called heavy consumers of beer, 1000 g (male) and 165 g (female) of beer consumption were assumed. Results were also compared with reference values for nutrient intake from the German Nutrition society (DGE (Deutsche Gesellschaft für Ernährung et al., 2015)). This resulted in estimates of the contribution of various nutrients in beer to the daily nutrient intake, differentiating existing BLS 3.02 data entries and those of the current study as the data basis (Table 6). In this comparison, only the reference values for men were considered, since beer consumption by women is very low.

For the average beer consumer, usage of our new nutrient data provides higher values for the percentage of daily nutrient recommendation of niacin, vitamin B_6 and folate, while providing lower values for alcohol (DGE gives guideline values for upper intake level of alcohol, which are not to be confused with consumption recommendations) and elements like copper and iodine compared to using nutrient data from BLS 3.02.These observations are even more distinct for the so-called male heavy consumers of beer (1000 g per day). At a daily consumption of 1000 g beer, 103 % of the recommended intake for niacin is achieved (compared to 50 % based on BLS version 3.02), although it should be noted that the alcohol consumed simultaneously accounts for 208 % of the DGE guideline value. When evaluating the overall contribution of beer to a healthy diet, the alcohol content has to be considered as well and therefore, in future studies, priority should be given to the analysis of the nutrient content of alcohol-free beer, as its consumption is increasing and nutrient data are even scarcer.

5. Conclusions

This survey has shown that different German beer styles differ significantly in terms of proximate composition, vitamins and elements. In general, many of the new data points investigated in this study are slightly higher than given in BLS version 3.02. For the male beer consumer, this study gives higher values for the percentage of the recommended daily intake of niacin, vitamin B_6 and folate, while giving lower values for alcohol and elements like copper and iodine. The new nutrient data obtained in this study will be used to update the BLS and to better evaluate consumption studies and nutrition consultation.

Author statement

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Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

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