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Mineral Nutrients and Malt Quality of Spring Barley (*Hordeum vulgare* L.)

Samples of barley grains from 10 varieties and 8 locations were analysed on 48 mineral nutrients and 13 malt quality parameters. The article presents means, ranges of variation and (expanded) measurement uncertainties. For many elements a significant influence of varieties could be found. The statistical analysis includes the calculation of coefficients of correlation between the element content and the quality parameters using a covariance analysis in order to eliminate the variety effects (partial coefficient r_p). The closest positive r_p (adjusted by varieties) to malt quality have been found for K, Pb, Mo and Na. Most of minerals correlate negatively to the malt quality index, especially Zn ($r_p = -0,67$), Mg ($r_p = -0,47$) and Fe ($r_p = -0,43$). The opposite behaviour of zinc in malt and yeast is discussed, as well as the physiological background of the minerals with relation to the malt quality and the practical relevance of the results for farming and breeding.

Descriptors: mineral elements, malt quality, mineral content, correlation, spring barley

1 Introduction

Mineral nutrients are essential for the growth of plants. While the macronutrients (nitrogen, phosphorus, potassium, magnesium, sulphur and calcium) have to be provided in larger amounts by the application of fertilizer, the micronutrients (trace elements) – mainly sodium, iron, manganese, copper, zinc, molybdenum, boron and chlorine – are also important, but play a minor role in fertilizer application because the supply of the soil is often sufficient. Further minerals of limited or unknown importance are silicium, nickel, cobalt, aluminum, selenium, fluorine, cadmium, lead, arsenic, uranium and vanadium [1]. According to Mengel [2] iodine, brome, fluorine, aluminum, nickel and selenium have a negative influence on plants, depending on their concentration.

This list does not describe the entire spectrum of all mineral nutrients present in plants. From almost every group of elements in the periodic table of elements a representative member can be found in plants due to their natural occurrence in the soil (noble metals like silver or gold) or immissions from the environment (caesium, strontium). In recent times, the lanthanides have caught interest due to positive effects in animal nutrition [3, 4, 5].

The physiological function of micro and macro nutrients has been clarified to a large extent. Except for the non-metals as important parts of organic molecules, they are either components of enzymes

or act as activators or substrates for enzymes. In addition, they are important for the phyto hormones and the water balance in plants [2, 1].

While the requirements of crops for major nutrients are known, and their environmental behaviour as well, deficits in knowledge do exist, however, regarding the classical trace elements and even more the miscellaneous elements, in particular with respect to their influence on the quality of the final product.

As far as symptoms of micronutrient deficit are visible, application of fertilizer will improve the quality. But it is not yet clear to what extent these elements are responsible – in a positive or negative way – for the quality performance of plants in a range of deficit which produces no symptoms.

An example for a still unknown interrelation of mineral nutrients and product quality is malting barley. It is well known from previous publications [6, 7, 8] that phosphorus and potassium reduce the husk content of the barley grain, improve the grain shape and therefore increase extract yield for beer production. Vice versa intensifying nitrogen (N) application increases the risk for lodging associated with inferior grain shape and increased protein content which both influence malt quality in a negative way. But few results have been published about the importance of the mineral nutrients for malt quality of barley.

Hopule [9] describes the content of K, Na, Ca, Mg, Cu, Fe, Mn and Zn in spring barley malt produced from seven varieties grown at eight locations in Germany. Contents of K, Ca, Mg and Mn are determined in a similar way, both from variety and location, whereas Na, Cu, Fe and Zn content in the malt is more influenced by location than by variety. In the same study, the influence of malting technology on the composition of the mineral nutrients was also reported. Malting conditions show only a minor influence on the micronutrients. The germination time had the largest effect. Correlations between single elements and malt quality parameters were not presented. The studies from Schippers [10] and Grau [11] about the presence of mineral nutrients in grains and

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Tables and figures see Appendix

their meaning for grain quality also do not offer any information about the context of malt quality and mineral nutrients. Neither does the research paper from *Mengel* and *Forster* [12] provide any clarification on the influence of K on malt quality of water-cultivated spring barley.

Data about the influence of Ca and Na content in malt are available for one particular trait, Hartong No. [13]. According to this study, increasing Na content enhances malt quality, while increasing amounts of Ca in the malt has a contrary effect. Both effects are significantly influenced by location and variety.

The element zinc plays a special role in the brewing process. A sufficient supply of the yeast with zinc is necessary to avoid disturbance during fermentation. Zinc ions enhance cell division and accelerate the fermentation because they improve the uptake of maltose and maltotriose by yeast. An experimental prove of the enhanced growth rate of yeast was published [14]. Zinc content in standard wort should be in a range of 0.15–0.20 mg/l [15]. These authors also point out that up to 98 % of the zinc made available by the malt is precipitated during wort boiling and remains in the draff, where it is not available for the feeding of the yeast. More recent studies by *Kühbeck* [16] confirm these findings both experimentally and through evaluation of further publications.

Nevertheless, plant breeders have shown interest for the modification of the content of mineral nutrients in wheat and barley. Differences were detected between varieties of both species regarding P, K, Ca and Mg [17]. The genetic background has been considered sufficient for the selection during breeding, in particular when performed on the basis of family means instead of individual plants.

In view of still deficient data sources, the authors of this paper have carried out an extensive analysis of the mineral content of spring barley grains. In this context, the relations between mineral nutrients and the major malt quality parameters from the produced malt have also been analysed. The results present for the first time an almost complete overview of the mineral compounds in the malting barley grain. Simultaneously, the correlations between the individual elements and malt quality have been calculated. The analyses include 48 cationic elements, but no anionic elements like P, S or Cl.

2 Materials and methods

2.1 Plant material

Samples from the official Bavarian variety trials from the year 2003 were used for this study. The characteristics of the eight locations where the two-rowed spring barley was grown are described in Table 1.

The variety trials are preformed with the two factors, variety and treatment. The varieties were grown with two treatment levels of fertilizer and pesticides. For the presented study only level 1 was analysed which was treated with an N level reduced by

20–30 kg N ha⁻¹ compared to the local standard level. A bulked sample from three replications of each variety was used for the analyses.

The tested varieties (*Annabell*, *Auriga*, *Barke*, *Braemar*, *Danuta*, *Margret*, *Pasadena*, *Ria*, *Scarlett* and *Ursa*) represent typical malting barley varieties with a good to very good score in the malt quality index (MQI) and a medium to very good grain quality. In contrast to the malt quality parameters, agronomic parameters like yield and disease resistance show a larger variation on the panel of varieties.

2.2 Analysis of malt quality

The N content of the grain was analysed with an Elementar analysis device according to the method DUMAS, and crude protein was calculated according to the equation “Crude Protein = N x 6,25”. The amount of mineral nutrients was also assessed, using the untreated barley grains from treatment level 1. All other quality parameters represent results from malted barley.

Micromalt of barley samples

The procedure applied for this study has been described by *ME-BAK* [18] and is a standard procedure for micromalt since 1971. The protocol was adapted for the application by the automated micromalt devices (*Phoenix Micromalt Systems Pty Ltd.*, *Edwardstown/Australia*). From each sample, 220 g grains from the grading fraction >2.5 mm were loaded into the slotted drums of 20 cm diameter. For a time course of 72 h under a constant temperature of 14 °C, steeping and air rest alternate in defined cycles. The water content of the grains is adjusted to 45 % by adding water manually up to three times during steeping.

The subsequent germination step requires 72 h at a constant temperature of 14 °C and relative humidity of 95–98 %. During 10 % of the germination time, the drums rotate with a speed of 5 rpm.

Kilning of the germinated grains takes 23 h in total. The process starts at 45 % water content and a 16 h kilning step at a temperature of 50 °C. The temperature is slowly increased by holding for one hour at 60 °C and one hour at 70 °C until the final temperature of 80 °C is reached which is held for 5 h.

After kilning, radicles are mechanically removed and after storage for 14 days, the malt is analysed in the laboratory.

Determination of malt quality

Following parameters of the malt are analysed:

Brabender (Nm): The power for milling of 15 g malt is measured by an electrodynamic device (*Brabender*). A low energy for the milling process characterizes a good cytolytic potential of the malt.

Friabilimeter (%): The friability of the malt is analysed by grinding the malt with a rubber cylinder and grading the ground material with a sieve of defined size. A high percentage of grain which is

pressed through the sieve is desired and delivers an estimation for the quality of the cytolysis.

Glassiness (%): The residue remaining in the sieve of the friabilimeter procedure represents the proportion of hardly solved malt and is required to be as low as possible for good malt quality.

Soluble nitrogen (mg N (100g)⁻¹ DM): The amount of nitrogen solved in the wort is measured by the DUMAS method and its ratio to the dry matter is determined. The soluble nitrogen should be in a range close to 700 mg (100g)⁻¹.

Kolbach index (%): The proportion of protein (N x 6.25) in the congress wort compared to the protein content of the malt should stay in a range between 40 and 42 %.

Hartong No. (%): This index describes the proportion of extract in a mash of 45 °C temperature compared to the maximal extract content in a 70 °C congress mash. This parameter mirrors the gelatinization of the starch and should reach a high level [13].

Malt extract (%): All compounds which are solved during mashing are summarized by the measure of the density of the wort. A high level of malt extract is preferred.

Apparent attenuation (%): This parameter characterizes the degradation of starch in the wort and is determined by measurement of fermentable extract. A good malt shows an apparent attenuation >80 %.

Viscosity (mPa*s): With a Brookfield laboratory viscometer the torque of the wort at 20 °C is measured. A low value (<1,5 mPa*s) represents a good degradation of hemi cellulose to fragments of low molecular size.

Colour of wort (EBC units): Colour and transparency of the wort are determined photometrically according to the protocol of the European Brewing Convention. A low value is desired.

pH-value: To ensure optimum efficiency of all enzymes, the pH-value of the congress wort at 20 °C should not differ considerably from 5.9.

Malt quality index (MQI): This index summarizes characteristic malt parameters, Hartong No., friabilimeter, malt extract and apparent attenuation. The biased sum of these parameters is the basis for a simplified classification into quality categories for breeders and farmers.

2.3 Analytically of the mineral nutrients

Chemical pulping of samples

The standard method using aqua regia for a chemical pulping of the samples does not allow one to determine the total content of the full range of elements. Considering the diversity and the very low concentration of the analysed elements, chemical pulping under pressure with azotic acid was necessary. This is a well-established

method at the Bavarian State Institute of Forestry for determining the element content of plants.

Samples were dried at 105 °C and ground to grain size <0.5 mm with a mill, avoiding contamination. The ground samples were pulped in a pressure ashing device (Seif Aufschlusstechnik, Germany). In a quartz tube 120–180 mg of sample were incubated for 6 h under pressure at 168 °C in 1.0 ml distilled azotic acid. After the reaction, water is added to the chilled mixture to a volume of 15 ml and the solution is analysed directly.

Analytical measurements

The majority of the samples was analysed by mass spectrometry (ICP-MS) using the Agilent 7500i spectrometer (Agilent Technologies). This device allows online dosage of the internal standard (50 µg l⁻¹ In-115) and direct calibration using matrix-adjusted mixed standards. The method permits the detection of the following isotopes in ng g⁻¹ DM above the detection limit (3σ of the blank value; see bracketed values):

Ag-107 (5), Al-27 (300), As-75 (4), Au-197 (0.3), B-11 (100), Ba-137 (60), Be-9 (0.3), Bi-207 (0.3), Cd-111 (1), Ce-140 (0.7), Co-59 (2), Cr-52 (90), Cu-63 (100), Dy-163 (0.07), Er-166 (0.04), Eu-153 (0.02), Fe-57 (1000), Ga-69 (4), Gd-157 (0.06), Ge-72 (4), Hf-178 (2), Ho-165 (0.01), Ir-193 (0.7), La-139 (0.7), Li-7 (1), Lu-175 (0.01), Mo-95 (6), Na-23 (300), Nb-93 (0.5), Nd-146 (0.3), Ni-60 (300), Os-189 (0.5), Pb-208/209 (10), Pd-105 (1), Pr-141 (0.08), Pt-195 (0.1), Rb-85 (6), Re-185 (0.07), Rh-103 (0.06), Ru-101 (0.06), Sb-121 (0.4), Sc-45 (4), Se-82 (20), Si-28 (24000), Sm-147 (0.1), Sn-118 (2), Sr-88 (3), Ta-181 (50), Tb-159 (0.02), Te-125 (1), Th-232 (1), Ti-47 (300), Tl-205 (0.1), Tm-169 (0.007), U-238 (0.3), V-51 (1), W-182 (500), Yb-172 (0.08), Zn-66 (400) und Zr-90 (8).

Because of their higher level, for the analysis of Ca, Mg, and Mn an optical emission spectrometry measurement using the OPTIMA 3000 (Perkin Elmer) was a more appropriate tool.

The following elements were analysed, but could not be quantified in a sufficient accuracy in the samples and were therefore excluded from testing: Bi, Hf, Ir, Li, Ni, Pd, Ru, Se, Sm, Sn, Ta, Te, Ti, Tl, W und Zr.

In total, the 80 malt samples [10 varieties, 8 locations) could be analysed for 48 elements (duplicate analyses) and 13 quality parameters (single analysis).

2.4 Statistical analyses

Analysis of variance (ANOVA) was performed for the content of mineral elements based on a two factorial design with two replications. The factor location was defined as random and the factor varieties as fixed. Because no replications of field samples were available, both factors were tested against the interactions location x variety using the F statistic. Measurement error (measurement uncertainty) and coefficient of variation (standard deviation in % of mean) result from the residual variance (laboratory sample error). In Table 3 the doubled value of measurement error ("ex-

panded measurement uncertainty”) is displayed in order to assure a significance level of ca. 5 %.

The calculation of a measurement error for the malt quality parameters was omitted due to the single analysis.

For the calculation of correlations inhomogeneity of data caused by the significant varietal effects could be avoided by using a covariance analysis and partial correlation coefficients to eliminate the varietal effects.

All statistical calculations were performed using the Statistical Analysis System (SAS) version 9.1 [19].

3 Results

3.1 Element content

One main objective of the study was the determination of the entire spectrum of mineral elements stored in the barley grain. As displayed in Table 2 a total of 48 elements could be quantified. The specification of the range of variation and the expanded measurement uncertainty (doubled standard deviation) is presented and characterizes the means and their quality respectively depending on location and variety. The last column of Table 2 displays the result of the F test for the fixed factor variety.

The contents of *alkaline and alkaline earth metals* in the grain except beryllium (Be) show a large range of variation which has a high significance for the influence of the variety. Potassium (K) and magnesium (Mg) show the smallest range of variation, but are also highly significant determined by the variety.

Also the elements of the *3rd–5th main group* have a large dispersion (CV 10–50 %). Only silicon (Si) and arsenic (As) do not reach the 5 % significance level for varieties.

The elements of the *B group excluding noble metals* from cadmium (Cd) to zinc (Zn) show also a coefficient of variation (CV) over 10 %. Cobalt (Co), chrome (Cr), niob (Nb), scandium (Sc) and vanadium (V) are not significantly influenced by the variety. Due to their rareness, the values of these elements show a relative high measurement error.

The general content of *noble metals* is also at a very low level. They show variation between locations, but no differences between varieties except gold (Au).

From the 15 members in the groups of the *lanthanides and actinides* which are present in traces, only thulium (Tm) has a variety specific variation.

In general, this survey shows that the origin of the sample causes a relative large range of variation of micro elements in the barley grain. But also in many cases, in particular for the classical micro and macro nutrients (K, Na, Mg, Cu, Fe, Mn, Mo, Zn), a strong influence of the variety is responsible for the variation of their content in the grain. Therefore solitary results (origin or variety)

have only a limited informative value. Considering the presented remarkable range of variation, reliable interrelations with other parameters characterizing quality can be assumed.

3.2 Malt quality parameters

Table 3 summarizes the statistics of malt quality parameters of varieties and locations. An important observation is the remarkable range of variation in all parameters, even though all tested barley varieties have a very high level of malt quality. These observations are confirmed by the results of the ANOVA which shows high significant effects of the variety except for the parameter glassiness.

Detailed attention was drawn to the parameter malt quality index (MQI) which includes the single parameters Hartong No., friabilimeter, malt extract and apparent attenuation. The mean of 8.50, a coefficient of variation of 16.4 % and a range of 5.5–11.3 include high significant varietal effects ($P > F < 0.01$ %); effects of locations are not presented. These results represent a sufficient basis of data for the analysis of interrelations between malt quality and mineral content.

3.3 Correlation between element content and malt quality

The statistical model includes the random variables “location” and “replications of measurement” and the fixed variable “variety”. Valid correlations depend on random variables. In order to avoid biased data caused by varietal influence, analysis of covariance was applied to generate partial coefficients of correlation.

Table 4 displays the partial correlations (r_p) of the 12 single parameters of malt quality with the micro elements as far as $|r_p|$ reaches a level ≥ 0.40 . The coefficient of determination (r_p^2) at this limit amounts 16 %.

Several malt quality parameters are highly significant correlated to the content of mineral nutrients, with exception of Kolbach index, glassiness and wort colour, having a correlation between $r_p = 0,40$ (Sc) and $r_p = -0,63$ (Zn, Pb)).

The “mass element” potassium (K) is negatively correlated with crude protein content and also with brabender – hence malt quality is increased by this element.

Among the other elements, iron (Fe) and lead (Pb) show on five quality parameters a high r_p . Fe increases crude protein, brabender and viscosity, and decreases the values for Hartong No. and apparent attenuation and therefore decrease malt quality. Unexpectedly, lead content (Pb) has only positive effects, proven by the positive correlations to friabilimeter, Hartong No. and apparent attenuation as well as by the negative correlations to brabender and viscosity.

Zn and Sb show a $|r_p| \geq 0.40$ for four quality parameters. Zn increases protein content and brabender, but reduces friability and extract; this element causes a general loss of quality. For Sb a contrary effect can be observed. The element is correlated with improvement of brabender, friability, apparent attenuation and viscosity.

Significant correlations with $|r_p| \geq 0.40$ to only two malt quality parameters are provided by Mn, Mo, Cd and gallium (Ga), identifying Mn (crude protein, soluble N), Cd (brabender, viscosity) and Ga (extract, pH) as depleting factors and Mo (brabender, apparent attenuation) as a increasing element regarding malt quality.

For only one quality parameter negative correlations are to be ascertained for As with soluble N, Ge and Mg with extract and Cu with viscosity. On the contrary positive correlations exist for Na with extract, Sc with apparent attention and Ba, Eu, Sr with pH-value. The positive r_p with pH must be rated negatively because strong variation of this parameter is undesirable.

Very important information is provided by the analysis of the interrelation of the malt quality index (MQI) and the mineral nutrients. Table 5 comprises an overview over all 48 analysed elements.

The criterion $|r_p| \geq 0.40$ for the MQI is only performed by Fe ($r_p = -0.43$), Mg ($r_p = -0.47$) and Zn ($r_p = -0.67$). Not only Mg, but also the heavy metals Fe and Zn show negative effects on malt quality. The element Zn has an extraordinary influence on MQI; 45 % ($r_p = -0.67$) of MQI is controlled by this metal. As shown in Figure 1 all varieties show a negative reaction against increasing Zn uptake independent of their total Zn level.

The last chart in Figure 1 illustrates the regression of the means of the locations expressed by the equation

$$\text{MQI} = 16,439 - 0,2906 * \text{Zn}$$

The coefficient of determination is $r^2 = 0.676$. The coefficient of regression and r^2 are biased by the influence of the variety. The unbiased results adjusted by analysis of covariance are $b_p = -0.2411$ and $r_p^2 = 0.45$. One additional μg of Zn reduces the MQI by 0.24 points.

Between Mg and Zn there is a varietal adjusted correlation of $r_p = 0.68$ and between Zn and Fe of $r_p = 0.22$. If the influence of Mg and Fe, respectively, is eliminated, the following coefficients for the relation between Zn and MQI can be calculated:

$$b_{p,\text{Mg}} = -0.2314 \text{ (h.s.)}; r_{p,\text{Mg}} = -0.53; r_{p,\text{Mg}}^2 = 0.28$$

$$b_{p,\text{Fe}} = -0.2170 \text{ (h.s.)}; r_{p,\text{Fe}} = -0.65; r_{p,\text{Fe}}^2 = 0.42$$

This means that Fe does not influence at all the interrelation between Zn and MQI, whereas Mg only reduces the coefficient of determination, which is an expression for the dispersion of the values around the regression line. Due to the negative correlations of Mg and Fe to the character MQI, a low content of Zn, Fe and Mg is desirable with respect to malt quality.

Regarding further high significant but $|r_p| < 0,40$ correlations ($P > F \leq 0,01$) as shown in Table 5, the following elements also have relevance for the specification of the MQI (r_p in brackets):

Al (-0.23), Au (-0.29), Ba (-0.33), Ca (-0.33), Cd (-0.22), Eu (-0.25), Ga (-0.34), Ge (-0.26), K (0.38), Mn (-0.24), Mo (0.35),

Na (0.31), Os (0.26), Pb (0.37), Rb (-0.32), Re (-0.21), Sb (0.31), V (-0.23).

The results give evidence that members of all groups of the periodic table of the elements have a highly significant influence on malt quality. Only K, Mo, Na, Os, Pb and Sb improve MQI, all other elements have a reducing effect on malt quality. A striking observation is that among the lanthanides only europium (Eu) has a low, but significant negative influence on MQI.

4 Discussion

The results confirm that a large spectrum of mineral nutrients can be detected by the use of modern methods of analyses. In general, remarkable effects on the content of micro elements caused by the variety have been observed, excepting noble metals, lanthanides and actinides. The varietal effects have additional influence on the variability in the accumulation of elements caused by environmental factors. Due to the dispersion of the field trials over the most important agricultural areas in Bavaria, covering diverse geographic and climatic environments, the values documented in Table 1 have a high informative value.

The view on single malt quality parameters already indicates the positive (K, Pb, Sb, Mo, As, Na, Sc, Cu) or negative effects (Fe, Zn, Mn, Ga, Cd, Ge, Mg, Ba, Eu, Sr) of a group of elements on quality. The summarizing parameter MQI, based on the single traits Hartong No., friabilimeter, malt extract and apparent attenuation is mainly influenced by Zn, followed by Mg and Fe all decreasing the MQI. K, Mo, Na, Pb and Sb have a positive effect on MQI, but on a lower level (in all cases $r_p > 0,30$). A few more elements also have a certain influence, mostly negative for MQI.

The results confirm that the correlations are independent of varietal influence, and therefore, the location-specific uptake of elements is of general importance. This leads to the conclusion that malt quality of barley can be increased by an optimised supply of potassium (and sodium) in the soil [20], whereas fertilisation with micronutrients should be omitted, as long as no symptoms of deficiency are visible. In addition, the use of secondary organic fertilizer like sludge or compost has to be considered critically, because of a certain contamination with heavy metals (Zn, Fe, Mn, Cd) in many cases.

On the other hand, the correlations between Zn/Mg/Fe/K and MQI offer a realistic chance to select locations with a higher content of these metals in the soil, with successful results for malt quality. In that regard, the findings from Rasmusson [17] can be extended to this aspect. But there still remains some doubt whether a breeding program that includes the analyses of micronutrients is feasible, considering the high costs involved.

To a certain extent, the correlations can be explained by the physiological background. Potassium plays an important role for the water balance in the plant, is involved in the activation of numerous enzymes, and enhances the production of carbohydrates in the grain [2]. Sodium, as a second alkali metal, is able to replace partially the effects of potassium, considering barley as a

species with a high affinity to sodium. The reason for the negative correlation of Rb and MQI may be that Rb cannot take over the specific functions of K and – at higher soil concentrations – has a toxic effect on the plant.

The positive effect of molybdenum might be caused by its participation in the structure of some metallo enzymes (nitrate reductase, hydrogenase) [1]. A surprise is the positive correlation between lead and MQI ($r_p = 0.37$), because no physiological function in plants is known until now. The same is valid for the noble metal Osmium (Os, $r_p = 0.26$).

In the group of mineral elements with a negative effect on malt quality, in particular MQI, the elements Zn, Mg, and Fe are of special interest. Like Mo, Zn is a component of metallo enzymes, but this element is also responsible for the activity of other enzymes like alkaline and acidic phosphatase, enolase and polyphenole oxidase [1]. It is also well known that Zn is part of the protein biosynthesis, interrelated with peptidases [2], which might explain the positive correlation to crude protein content and the negative correlation to malt extract.

Although the negative influence of zinc on the malt quality has become obvious, the positive effect of this element for the process of fermentation due to a better yeast growth is also an established fact. But this seemingly contradictory behaviour of zinc is only of minor practical importance, because yeast is not able to utilize zinc from the malt. Only with decreasing pH-value of mash and changing further mash conditions the availability of zinc increases marginally [15]. Therefore, the zinc supply of yeast must be considered independently from the zinc content of malt.

Not fully coherent is the negative correlation of Mg and MQI. On the one hand, Mg is important for the phosphorylation processes in the plant and therefore also for starch synthesis. But the protein fractions also increase with increasing Mg concentration, which could explain the negative correlation to malt extract.

In contrast, the negative correlation of Fe can be explained convincingly. Fe is also involved in metallo enzymes and enhances the protein synthesis, but reduces two components of MQI, Hartong No. and apparent attenuation.

One might speculate about the physiological background of the elements showing a lower degree of correlation to malt quality, but in any case it needs to be considered that there are also correlations between the mineral elements which can partially simulate weak correlations to single quality parameters. Therefore, this study focuses on the most prominent correlations of micro elements to single parameters of malt quality and the summarizing parameter MQI, respectively. However, it must be taken into account that the content of mineral elements in the barley grain is to a large extent negatively related to both single and summarizing parameters of malt quality.

Comparable results have rarely been published. *Keßler* [13] analysed the influence of Ca and Na in the malt on the Hartong No. The results delivered high level correlations (Na: $r = 0.81^{**}$, Ca: $r = -0.64^{**}$). But the results are based on analyses of only

24 samples without eliminating the effects of the varieties which can disturb the calculation of the correlations. The direct comparison of the present study and the results from *Keßler* [13] show the same trend resulting in $r = 0.11$ (Na; n.s.) bzw. $r = -0.268^{**}$ (Ca). Rather more important appear the antagonistic effects of Ca and Na with MQI (for Na $r_p = 0.31^{**}$ for Ca $r_p = -0.33^{**}$) which have been found in the presented study.

5 Summary

Samples of barley grains from 10 varieties originating from 8 locations were subjected to an extensive analysis of the cationic elements using ICP-OES and ICP-MS. In parallel procedures, the samples were micromalted and 13 common parameters describing malt quality were determined. This extensive data set is considered to be suitable for the calculation of correlations between elements and malt quality. Statistical analysis of the 48 elements included the calculation of the range, the coefficient of variation and the error of measurement. The results show that with the exception of the groups of the noble metals, lanthanides and actinides, high significant varietal effects can be found in general.

Depending on the single element, the results of the analysis of correlation to the 13 malt quality parameters show a wide range. The utmost influence on malt quality is caused by zinc (Zn). Zn is correlated to malt quality index (MQI) with $r_p = -0.67$ (partial correlation adjusted by variety). One $\mu\text{g Zn g}^{-1}$ DM reduces MQI by 0.24 points. Magnesium (Mg) and iron (Fe) have also a negative correlation to malt quality of $r_p = -0.47$ and $r_p = -0.43$, respectively. The closest positive relations to MQI have been found for K ($r_p = 0.38$), Pb ($r_p = 0.37$), Mo ($r_p = 0.35$) and Na ($r_p = 0.31$).

A remarkable number of correlations between elements and single parameters for malt quality were found with $|r_p| \geq 0.40$. But the majority of the micro nutrients show only a weak and mainly negative interrelation to malt quality. For elements from the group of lanthanides no appreciable interaction with malt quality could be detected at all.

An explanation based on physiological effects is in part possible. The majority of the micro elements act as components (metalloenzymes) or activators of enzymes and is therefore involved in a large number of processes regarding synthesis and degradation of metabolites in the plant. For brewing process the negative correlation between zinc content of malt and malt quality is not important although yeast growth provides a good zinc supply. It is well known that malt zinc cannot be utilized by yeast.

A practical aspect for farming and breeding is given by the conclusion that fertilization with potassium has a positive influence on quality, while fertilization with trace elements should be applied with care due to their predominantly negative effect on quality. In the same way, the use of secondary organic fertilizer like sludge or compost has to be considered critically because of the potential contamination with heavy metals. The improvement of malt quality by a breeding program using analyses of element content is considered to be promising, but costly.

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Appendix

Table 1 Description of the growing areas for the analysed barley samples

Location	Geological description	Altitude (m)	Type of soil		Content of nutrient in soil (mg (100g) ⁻¹)		Soil pH	Preceding crop
					P ₂ O ₅	K ₂ O		
Arnstein	Shell limestone	280	TL	65	19	28	6,9	Wheat
Bieswang	Jura mountains	530	L	66	9	25	6,9	Wheat
Brunn	Northern Bavarian uplands	480	L	41	18	26	6,0	Rape seed
Grafenreuth	Primary rocks	530	sL	40	11	27	6,1	Rape seed
Günzburg	Morainial area	470	UL	64	8	20	5,9	Wheat
Haar	Brash plains	537	sL	37	23	28	6,9	Wheat
Osterseeon	Tertiary uplands	560	sL	46	21	18	6,8	Rape seed
Schmidhausen	Morainial uplands	438	L	65	8	18	6,8	Rape seed

Table 2 Statistical key data of the analysed elements

Group/ Element	No. of analyses	Mean $\mu\text{g g}^{-1}$ DM	Statistics of the mean			F test variety ²⁾ P > F
			CV (%)	Variation	Measuram. error % ¹⁾	
Alkali metal						
K	160	5873	9.2	4586-7110	5.0	<0.0001
Na	160	27.8	38.3	10.1-56.0	12.4	<0.0001
Rb	160	1.23	50.5	0.9-2.92	5.1	<0.0001
Alkaline earth metal						
Ba	160	2.64	35.1	1.21-6.19	5.2	<0.0001
Be	160	0.0058	2.0	0.0056-0.0063	3.4	0.2230
Ca	160	440.8	11.3	335.6-552.4	5.0	<0.0001
Mg	160	1351	7.0	1122-1589	5.2	0.0008
Sr	160	1.00	28.0	0.36-1.68	4.4	<0.0001
3rd Main group						
B	160	0.657	10.0	0.553-0.883	6.0	0.0188
Al	159	5.88	22.7	3.08-11.03	19.2	0.0381
Ga	159	0.068	33.8	0.031-0.151	5.5	<0.0001
4th and 5th Main group						
As	159	0.0073	33.6	0.0019-0.0134	19.0	0.0594
Ge	160	0.018	33.1	0.011-0.031	9.4	0.0318
Pb	159	0.121	50.2	0.007-0.247	19.7	0.0101
Sb	159	0.0085	75.5	0.0004-0.0223	17.3	0.0004
Si	160	99.8	13.1	67.1-129.0	18.8	0.7859
B-group (without noble metals)						
Cd	158	0.0068	65.6	0.0006-0.0247	13.4	<0.0001
Co	156	0.0056	27.2	0.0034-0.0132	36.8	0.4853
Cr	159	0.280	27.3	0.150-0.608	40.6	0.5632
Cu	157	3.25	17.6	1.98-5.14	21.0	<0.0001
Fe	160	31.7	13.5	21.9-46.5	6.8	<0.0001
Mn	160	13.3	14.5	8.9-16.8	4.9	<0.0001
Mo	160	0.435	62.6	0.039-1.220	5.1	0.0001
Nb	157	0.0010	61.1	0.0003-0.0047	116.4	0.4534
Sc	160	0.023	12.9	0.015-0.028	17.6	0.8142
V	158	0.0095	19.1	0.0052-0.0183	24.8	0.1970
Zn	160	27.3	13.0	20.3-35.5	7.6	<0.0001

Table 2 continued ...

Table 2 continued ...

Group/ Element	No. of analyses	Mean $\mu\text{g g}^{-1}$ DM	Statistics of the mean			F test variety ²⁾ P > F
			CV (%)	Variation	Measur. error % ¹⁾	
Noble metals						
Ag	159	0.020	34.5	0.003-0.037	50.4	0.7265
Au	160	0.00071	37.1	0.00030-0.00193	62.9	0.0240
Os	160	0.0019	9.5	0.0015-0.0025	15.9	0.1740
Pt	159	0.00074	5.2	0.00066-0.00086	9.5	0.2809
Re	160	0.00040	3.5	0.00037-0.00044	6.3	0.9567
Rh	160	0.00023	12.1	0.00017-0.00036	21.0	0.5260
Lanthanides						
Ce	159	0.0084	47.2	0.0040-0.0309	77.6	0.0976
Dy	159	0.00092	22.1	0.00061-0.00216	35.6	0.3939
Er	159	0.00099	9.4	0.00084-0.00162	17.0	0.4337
Eu	160	0.0012	7.4	0.0011-0.0015	8.2	0.2487
Gd	160	0.0014	17.0	0.0011-0.0021	25.0	0.0718
Ho	158	0.00035	10.4	0.00029-0.00054	16.0	0.2730
La	159	0.0052	41.3	0.0026-0.0159	68.1	0.1243
Lu	160	0.00051	3.8	0.00048-0.00065	17.0	0.1813
Nd	159	0.0036	44.7	0.0017-0.0135	74.8	0.1107
Pr	159	0.0016	28.3	0.0011-0.0043	47.9	0.0670
Tb	160	0.00041	7.3	0.00037-0.00054	11.4	0.1478
Tm	158	0.000094	15.9	0.00068-0.00177	28.1	0.0419
Yb	157	0.00065	11.0	0.00050-0.00095	16.7	0.5003
Actinides						
Th	160	0.0031	25.0	0.0020-0.0070	40.2	0.3850
U	159	0.0011	12.3	0.0008-0.0017	19.2	0.0614

¹⁾ Expanded error of measurement: Standard deviation x 2 ($\alpha = 5\%$); ²⁾ ANOVA: location = random; variety = fixed

Table 3 Statistical key data of malt quality parameters

Quality parameter	Unit	No. of analyses	Mean	Key values of mean		P > F _{Variety}
				CV (%)	Variation	
Crude protein	%	80	10.4	5.6	8.8-11.5	<0.0001
Brabender	Nm	80	109.9	14.7	84-164	<0.0001
Friabilimeter	%	80	81.8	12.8	44.5-99.5	<0.0001
Glassiness	%	80	1.2	117.3	0-11.1	0.1178
Soluble N	mg N 100g ⁻¹	80	698.8	9.5	503-874	<0.0001
Kolbach index	%	80	41.4	10.3	24.3-51.0	0.0007
Hartong No.	%	80	43.9	9.8	33.3-53.7	<0.0001
Malt extract	%	80	82.7	1.47	79.8-85.8	<0.0001
App. attenuation	%	80	83.8	2.2	79.4-87.6	<0.0001
Viscosity	mPa*s	80	1.48	4.9	1.40-1.73	<0.0001
Colour	EBC	80	3.2	20.9	2.1-5.0	<0.0001
pH	pH	80	6.0	---*)	5.88-6.15	<0.0001
MQI	Index	80	8.5	16.4	5.5-11.3	<0.0001

*) Interval scale, designation impossible

Table 4 Partial correlation (r_p) between elements and malt quality parameters (except MQI) after elimination of varietal effects; only $|r_p| \geq 0.40$ ($P < 0.0001$)

Crude protein			Brabender			Friabilimeter			Glassiness			Soluble N			Kolbach index		
El.	r_p	DF	El.	r_p	DF	El.	r_p	DF	El.	r_p	DF	El.	r_p	DF	El.	r_p	DF
Fe:	0.47	150	Cd:	0.41	148	Pb:	0.55	149	-----	As:	-0.41	149	-----				
K:	-0.47	150	Fe:	0.51	150	Sb:	0.62	149		Mn:	0.51	150					
Mn:	0.50	150	K:	-0.44	150	Zn:	-0.47	150									
Zn:	0.54	150	Mo:	-0.45	150												
			Pb:	-0.63	149												
			Sb:	-0.58	149												
			Zn:	0.45	150												
Hartong No.			Extract			App. Atten.			Viscosity			Colour			pH-value		
El.	r_p	DF	El.	r_p	DF	El.	r_p	DF	E.	r_p	DF	El.	r_p	DF	El.	r_p	DF
Fe:	-0.48	150	Ga:	-0.41	150	Fe:	-0.42	150	Cd:	0.41	148	-----	Ba:	0.50	150		
Pb:	0.43	149	Ge:	-0.60	150	Mo:	0.50	150	Cu:	-0.46	147		Eu:	0.41	150		
			Mg:	-0.58	150	Pb:	0.56	149	Fe:	0.47	150		Ga:	0.50	150		
			Na:	0.58	150	Sb:	0.51	149	Pb:	-0.57	149		Sr:	0.60	150		
			Zn:	-0.63	150	Sc:	0.40	150	Sb:	-0.54	149						

Table 5 Partial correlation (r_p) between elements and malt quality index (MQI) after elimination of varietal effects

El.	r_p	DF ¹⁾	P ²⁾	El.	r_p	DF ¹⁾	P ²⁾	El.	r_p	DF ¹⁾	P ²⁾	El.	r_p	DF ¹⁾	P ²⁾
Ag	-0.10	149	0.21	Cu	-0.15	147	0.07	Mg	-0.47	150	<0.00	Rh	-0.17	150	0.10
Al	-0.23	149	0.00	Dy	-0.05	149	0.52	Mn	-0.24	150	0.00	Sb	0.31	149	0.00
As	-0.06	149	0.48	Er	0.00	149	0.98	Mo	0.35	150	<0.00	Sc	-0.19	150	0.02
Au	-0.29	150	<0.00	Eu	-0.25	150	0.00	Na	0.31	150	0.00	Si	-0.15	150	0.06
B	0.08	150	0.36	Fe	-0.43	150	<0.00	Nb	-0.18	147	0.03	Sr	-0.11	150	0.17
Ba	-0.33	150	<0.00	Ga	-0.34	150	<0.00	Nd	-0.08	149	0.31	Tb	-0.06	150	0.48
Be	-0.09	150	0.27	Gd	-0.11	150	0.19	Os	0.26	150	0.00	Th	-0.11	150	0.18
Ca	-0.33	150	<0.00	Ge	-0.26	150	0.00	Pb	0.37	150	<0.00	Tm	0.07	148	0.40
Cd	-0.22	148	0.01	Ho	-0.04	148	0.63	Pr	-0.09	149	0.25	U	-0.17	149	0.03
Ce	-0.11	149	0.18	K	0.38	150	<0.00	Pt	-0.15	149	0.08	V	-0.23	148	0.01
Co	0.01	146	0.90	La	-0.11	149	0.20	Rb	-0.32	150	<0.00	Yb	0.04	147	0.66
Cr	-0.10	149	0.21	Lu	-0.04	150	0.61	Re	-0.21	150	0.01	Zn	-0.67	150	<0.00

¹⁾ Degree of freedom; ²⁾ Significance probability

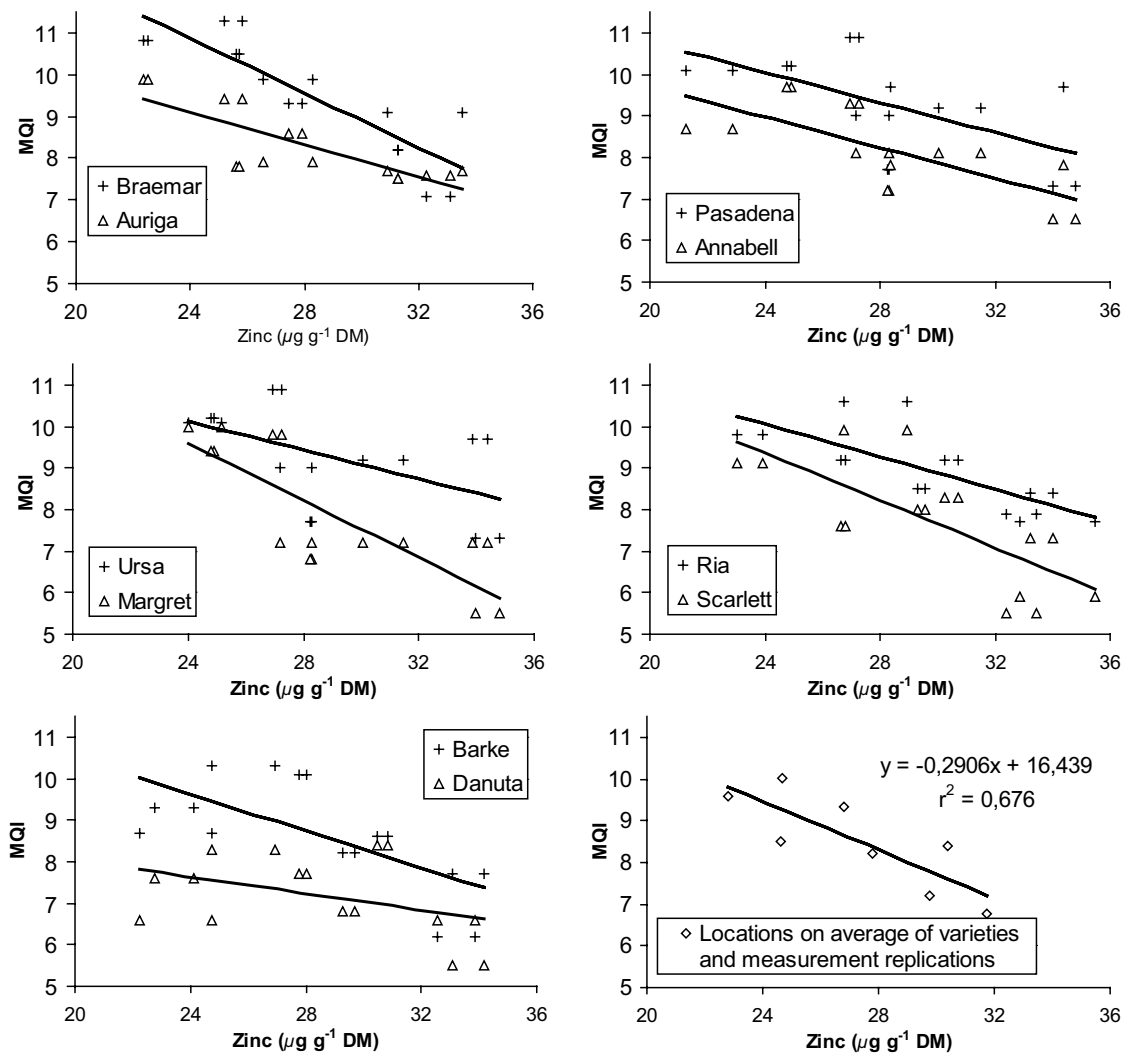


Fig. 1 Regression between zinc content in barley kernels and malt quality index (MQI) by variety and locations, respectively