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Free-air CO₂ enrichment modifies maize quality only under drought stress

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Abstract Climate scenarios show that atmospheric CO₂ concentrations will continue to increase. As a consequence, more frequent and severe drought periods are expected. Drought will thus modify plant growth. Although maize is a major crop globally, little information is available on how atmospheric and climatic changes will change maize quality. Here, in a field experiment, maize was grown in 2007 and 2008 under ambient (380 ppm) and elevated CO₂ (550 ppm) using free-air CO₂ enrichment. In 2007, maize was grown under well-watered conditions only. In 2008, we applied a drought stress treatment in which the plants received only half the amount of water of the well-watered treatment. We measured the concentrations of minerals and quality-related traits in above-ground biomass and kernels at the end of each growing season. Results show first the absence of effect of elevated CO₂ under well-watered conditions. By contrast, drought stress modified several traits and interactions under elevated CO₂. These results support the hypothesis that the C₄ plant maize does not react to an increase in atmospheric CO₂ as long as no drought stress is prominent. This finding contrasts with the impact of elevated CO₂ on C₃ plants. Several drought stress effects found in our study will have important implications for food and feed use. However, the effects of drought

stress on the traits were less pronounced under elevated CO₂ than under ambient CO₂ level. Hence, an elevated CO₂ concentration mitigates the drought stress impacts on elemental composition and quality traits of maize.

Keywords Carbon dioxide · Climate change · FACE · Fiber fractions · Food and feed · Free-air CO₂ enrichment · Microelements · Minerals · Protein fractions · Rain shelter · Stoichiometry · Water availability · Water deficit · Zeamaize

1 Introduction

With regard to food supply, the global demand for maize is projected to exceed that for wheat and rice within the next decades (Pingali 2009), and already, today, maize is the second most important crop globally (FAO 2011). In spite of this importance of maize, only a few studies have been carried out which have addressed the combined effects of more than a single anticipated climate change factor on this relevant crop (Leakey et al. 2006; Manderscheid et al. 2014). A main driver of global climate change is the increase in atmospheric carbon dioxide (CO₂) concentration, which is expected to exceed 550 μmol mol⁻¹ by the middle of the twenty-first century (Meehl et al. 2007). Crops of the C₃ type are known to show an increased photosynthesis as well as enhanced growth and yield under elevated CO₂ (Kimball et al. 2002; Long et al. 2006). In contrast, photosynthesis of C₄ plants like maize is not influenced directly by rising CO₂ because current CO₂ concentrations are not rate-limiting to their photosynthesis. However, stomatal conductance of both C₃ and C₄ plants is reduced by CO₂ enrichment, resulting in a reduced transpiration and an improved water status (Ghannoum 2009). A few experimental results available indicate that, for C₄ crops, elevated CO₂ impacts might also result in yield increases. The underlying reason could be the reduced water

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consumption that mitigates drought stress by conserving soil moisture (Ghannoum et al. 2000; Leakey et al. 2006; Markelz et al. 2011; Manderscheid et al. 2014).

Along with an increased biomass production, C_3 plants grown under CO_2 enrichment frequently show changes of their chemical composition, e.g. diminished concentrations of minerals and other quality-related components (Loladze 2002; Wang and Frei 2011). Among the various mechanisms that are discussed as putative causes for these changes are (1) a dilution effect due to the surplus of assimilated carbon compounds and (2) a reduced plant uptake of elements from the soil due to reduced transpirational water flow through the plant (Taub and Wang 2008; McGrath and Lobell 2013). As the second mechanism may also be relevant for C_4 plants, the concentrations of minerals in these plants should also be affected by elevated CO_2 (Lindroth and Dearing 2005; Ghannoum et al. 2006). A meta-analysis by McGrath and Lobell (2013) revealed that the decrease of nutrients acquired mostly by mass flow like potassium, calcium and magnesium is more pronounced under elevated CO_2 . Overall, CO_2 -induced changes in elemental composition and quality characteristics could potentially have negative consequences for the nutritional quality of food and feed and for the element turnover of ecosystems. Both elevated CO_2 and drought stress affect plant–water relations. Hence, these two climate change factors interact in their impact on the chemical composition of plants. However, for C_4 crops and particularly for maize, there is currently no information available from field studies that have addressed this important topic. In their review, McGrath and Lobell (2013) pointed out that the relationship between plant transpiration and nutrient concentrations should be examined under realistic environmental conditions in order to gain a deeper understanding of the underlying processes.

Impacts of elevated CO_2 on the quality of C_3 grain crops have been examined in several field studies using free-air CO_2 enrichment (FACE) technique (Long et al. 2006; Högy and Fangmeier 2008). In contrast, elevated CO_2 effects on elemental composition and quality characteristics of C_4 plants like maize have not been evaluated under such experimental conditions. Findings from the small number of field studies on drought stress effects on maize are contradictory. For example, Kruse et al. (2008) identified temperature and radiation as main drivers for quality changes in maize, while Crasta et al. (1997) found plant available soil water content to be the most relevant factor for maize forage quality. Currently, there is no information from field studies available on the interactions of elevated CO_2 and drought on quality characteristics of C_4 crops like maize, although the necessity for such experiments has clearly been pointed out by several authors (Leakey et al. 2006; Ghannoum et al. 2006; Ainsworth et al. 2008; Wang and Frei 2011).

Previous results which originated from the same experiment (Manderscheid et al. 2014) have shown that maize yield

did not respond to elevated CO_2 under ample water supply while, under drought stress, there was significant yield stimulation due to elevated CO_2 . In this study, a main effect of elevated CO_2 was an increase in water-use efficiency accompanied by a reduction in soil water depletion which caused a delay in the incidence of drought stress, leading to better performance of maize under drought. As these results point to reduced transpirational water flow, it was of interest to investigate whether this may result in an altered elemental composition of maize aboveground biomass and kernel tissue. In the present study, the impacts of free-air CO_2 enrichment and low water availability on elemental composition and quality traits of field-grown maize are presented. We tested the following hypotheses: (1) an increase in atmospheric CO_2 concentration reduces the transpiration of maize and thus the amount of minerals transported by the transpiration flux. In our study, it was examined whether the concentrations of minerals in aboveground biomass and kernels of maize are generally decreased under elevated CO_2 . (2) Elevated CO_2 reduces plant transpiration which leads to a slower depletion of soil water by plants which in turn leads to a later incidence of drought stress under CO_2 enrichment. In our study, we examined if an increase in CO_2 will mitigate the drought stress-induced effects on the concentrations of minerals and quality traits. To our knowledge, this is the first report on impacts of combined elevated CO_2 and controlled drought stress on elemental composition and quality traits in maize grown under real agronomic conditions.

2 Material and methods

2.1 Field conditions and experimental treatments

The experiment was carried out on a 7-ha field site of the experimental station of the Friedrich Loeffler-Institut, Braunschweig, South-East Lower Saxony, Germany (52°18'N, 10°26'E, 79 m asl). The soil at the experimental area is a luvisol of a loamy sand texture in the plough horizon with a pH of 6.5, a mean organic matter content of 1.4 % and a comparatively shallow rooting zone (0–0.6 m). The subsoil consists of a mixture of gravel and sand. The drained upper and lower limits (0.01 and 1.5 MPa soil water tension) of plant available volumetric soil water content within the 0.6 m soil profile are about 23 % and 5 %, respectively. The plant available water capacity within the rooting zone is about 100 mm. A FACE system engineered by Brookhaven National Laboratory was operated that consisted of three circular plots of 20 m in diameter with an enhanced seasonal average CO_2 concentration of 549 $\mu\text{mol mol}^{-1}$ in both years. Another three circular plots of the same size served as controls with seasonal average ambient CO_2 levels of 382 and 385 $\mu\text{mol mol}^{-1}$ in the 2 years, respectively. In 2008, all of

the six circular main plots were split into two semicircles to establish a well-watered and a drought stress subplot treatment. The drought stress subplots were equipped with tent frames of a size of 12×20 m each (Fig. 1) which were covered with transparent PVC tarpaulins during periods of forecasted rainfall of >10 mm day⁻¹ (Erbs et al. 2012). In the well-watered subplots, soil water content in the 0–0.6 m profile was kept above 50 % of maximum by drip irrigation. In the drought stress treatment, soil water content in the 0–0.6 m profile was reduced to about 20 % of the well-watered subplot content from the middle of the 2008 growing season on (Manderscheid et al. 2014).

2.2 Crop management and environmental conditions

Agricultural management of the field site and the experimental plots was carried out according to local farm practice. Maize (*Zea mays* L., cv. 'Romario') was sown with a row distance of 0.75 m and a seeding density of 10 plants m⁻². Weed control was done by application of herbicides in May and manual weeding in the experimental plots. Mineral nutrients were added according to local fertilising practice based on soil analysis in early springtime. The following amounts of fertilisers were applied per hectare in 2007: 171 kg nitrogen (ammonium and urea), 92 kg phosphorous (P₂O₅), 200 kg potassium (K₂O) and 36 kg sulfur. In 2008, the following amounts of fertilisers were applied per hectare: 198 kg nitrogen (ammonium and urea), 92 kg phosphorous (P₂O₅), 25 kg magnesium (MgO) and 20 kg sulfur. The anthesis stage was reached at 18th and 25th of July in 2007 and 2008, respectively, and did not differ between the treatments. For the years 1971–2000, mean air temperature was 8.8 °C; mean air temperature of July (warmest month) was 17.0 °C; sum of precipitation amounted to 618 mm (half of it deposited between

Fig. 1 The experimental maize field showing the plots with the frames of the rain shelter tents without tarpaulins installed. At the plot in the front the free-air CO₂ enrichment (FACE) area is denoted by the *white dashed circle*. The surrounding black tubes are vertical vent pipes for CO₂ release. At each of the circular plots, one half is covered by the tent (drought stress treatment), and the other half is equipped with drip irrigation (well-watered treatment)

May and September), and 1,514 h of sunshine were recorded. The two growing seasons largely differed from each other. While the later 2007 growing season was very rainy, the 2008 growing season was rather dry, with sums of precipitation between June and September of 386 and 209 mm, respectively. A more detailed description of the climatic conditions, soil moisture measurements and respective data is given in Erbs et al. (2012) and Manderscheid et al. (2014).

2.3 Plant sampling

All plant samples for the analyses were taken at final harvest in both of the growing seasons. For the final harvests, the plants of an area of 2 m² in all plots of the treatments were cropped resulting in 12 samples (2×3 plots for both CO₂ treatments with each of them divided into two water treatments). From each sample, ten representative plants were chaffed on the whole and used for the evaluation of traits in aboveground biomass. The other plants of a sample were separated into leaves, stems and cobs. Kernels from these cobs were used in the present study.

2.4 Measurements of elemental composition

Elemental composition was determined directly from ground sample material of aboveground biomass and kernels for nitrogen and sulphur using an element analyser (TruSpec CNS, Leco). For the analyses of the mineral concentrations of phosphorus, potassium, calcium, magnesium, iron and zinc, sample material was prepared with incineration followed by disintegration with nitric acid. Except for phosphorus, all other elements were analysed by atomic absorption spectrometry (AA-200, Varian) referring to a poplar leaf standard (NCS DC73350, Breitländer) at the following wavelengths: potassium 766.5 nm, calcium 422.7 nm, magnesium 285.2 nm, iron 248.3 nm and zinc 213.9 nm. Sample phosphorus concentration was assessed photometrically as acidic ammonium molybdate complex at 880 nm (Segmented Flow Analyzer, Skalar Analytic).

2.5 Measurements of quality characteristics

The crude nutrient contents were analysed according to the methods of the Association of German Agricultural Analytic and Research Institutes (VDLUFA 2006). Crude fiber was investigated according to method number 6.1.1 of VDLUFA (2006), and acid detergent fiber analysis was carried out by using method number 6.5.2. Neutral detergent fiber and lignin were determined as described by van Soest et al. (1991). All fiber fractions were expressed without residual ash. Fat content was determined by the Soxhlet extraction method after acid digestion (method number 5.1.1). Sucrose was analysed according to the method of Luff-Schoorl (method number

7.1.1) and starch by using the polarimetric method (method number 7.2.1). Protein fractions were analysed only for the 2008 plant material. The extraction was carried out according to a modified Osborne fractionation developed for wheat flour (Wieser et al. 1998). Separation and quantitation of fractions were performed by reversed-phase high-performance liquid chromatography using a Beckman instrument (solvent module 126). Filtered extracts were injected into a Nucleosil column (Macherey-Nagel, Dueren), and a linear gradient was applied for protein elution. The quantitation of glutelins and prolamins was based on UV absorbance at 210 nm, which is highly correlated with the amount of eluted proteins (Wieser et al. 1998).

2.6 Statistical analysis

Data were analysed with the R statistical software (R 2.14.0, The R Foundation for Statistical Computing). Shapiro-Wilks tests for normal distribution were applied to all data, and in cases of $p > 0.10$, data were log-transformed for the analyses of variance. Analyses of variance were carried out including only data of the well-watered treatments of both growing seasons with the factors CO₂ and year. Additionally, for the 2008 data, split-plot analyses of variance were calculated based on the averages of the semicircles with CO₂ as main factor and water supply as split-plot factor.

3 Results and discussion

As a result of previous research of the present experiment, Manderscheid et al. (2014) have shown that maize yield did not respond to elevated CO₂ under ample water supply while, under drought stress conditions, there was significant yield stimulation due to CO₂ enrichment. A main effect of elevated CO₂ in the study of Manderscheid et al. (2014) was an enhanced water use efficiency of the maize canopies accompanied by a reduction in soil water depletion, which resulted in a better growth performance. Thus, clear interactions between the CO₂ and water treatment were found. In the present study, no significant impacts of elevated CO₂ were observed in the data of the well-watered treatment from both growing seasons. However, in several traits, impacts of the growing season (factor year) became obvious, but no interactions with the CO₂ treatment were found. It is assumed that the underlying reason was the difference in precipitation and hence water supply between the two growing seasons (Erbs et al. 2012; Manderscheid et al. 2014). Effects of CO₂ were only significant in the split-plot analyses of the 2008 data in which interactions with the drought stress treatment were also observed (Table 1). In the subsequent discussion, all treatment-induced significant percentage changes in the traits refer to the

respective results of the ambient CO₂, well-watered treatment used as reference.

3.1 Elemental composition of maize aboveground biomass

For maize, aboveground biomass of the well-watered treatment effects of the growing seasons was found for nitrogen, phosphorous, calcium, iron and zinc (Table 1). In 2008, the nitrogen concentration was increased by CO₂ enrichment by 2 % (Table 2, Fig. 2). Drought increased the nitrogen concentration by 25 % and 4 % under ambient and elevated CO₂, respectively. These higher nitrogen levels will be advantageous for the nutritive value of maize (Johnson et al. 1999). Drought-induced increases in nitrogen concentrations have also been found in several studies on C₃ crops (Wang and Frei 2011; McGrath and Lobell 2013). Biomass calcium concentration was reduced under drought by 24 % in ambient and 20 % in elevated CO₂. The magnesium concentration was increased under drought stress by 15 % and 3 % under ambient and elevated CO₂, respectively. Magnesium is mostly transported passively by transpirational water flow (Mota Oliveira et al. 2010), and thus, the magnesium concentration should be reduced under drought. This is in contrast to our results on both aboveground biomass and kernels. In their review, McGrath and Lobell (2013) summarised that concentrations of nutrients acquired mostly by mass flow like potassium, calcium and magnesium decrease under elevated CO₂. This is only confirmed for calcium by our results. Rastija et al. (2010) found drought stress to increase zinc concentration in maize, and a positive correlation was found between zinc and phosphorous concentration. However, our data on maize biomass do not support these findings, whereas in kernels a drought-induced increase in zinc concentrations was observed. Significant interactions between the CO₂ and water treatment were found for concentrations of nitrogen in which elevated CO₂ attenuated the respective drought stress impacts.

3.2 Elemental composition of maize kernels

The mineral concentrations of maize kernels (Table 2) were in the same order of magnitude as found in other studies (Nuss and Tanumihardjo 2010). The data of the well-watered treatment from both growing seasons did not reveal a similar influence of the factor year as was observed in elemental composition of aboveground biomass, and only results on nitrogen and calcium were affected. In 2008 (Tables 1 and 2, Fig. 2), the nitrogen concentration was decreased due to CO₂ enrichment by 1 %, while drought-induced increases of 38 % and 8 % were observed under ambient and elevated CO₂, respectively. In terms of nutritive value, the drought stress-induced increase in nitrogen concentration would be advantageous, which is partly diluted by elevated CO₂. Drought reduced the potassium concentration by 8 % and 13 % in

Table 1 Results of the two statistical evaluations of the elemental composition (Minerals) and quality characteristics (Quality) of maize aboveground biomass and kernels

Minerals		Aboveground biomass								Kernels							
	<i>p</i> level	N	P	K	Ca	Mg	S	Fe	Zn	N	P	K	Ca	Mg	S	Fe	Zn
WW	CO ₂	0.641	0.941	0.164	0.842	0.243	0.485	0.345	0.295	0.576	0.645	0.141	0.751	0.212	0.054	0.622	0.798
	Year	> 0.001	> 0.001	0.955	0.041	0.342	0.276	0.038	0.004	> 0.001	0.117	0.830	0.020	0.206	0.108	0.486	0.699
	CO ₂ ×Year	0.366	0.835	0.369	0.359	0.787	0.996	0.896	0.971	0.312	0.279	0.671	0.165	0.270	0.256	0.304	0.733
2008	CO ₂	0.013	0.435	0.117	0.481	0.053	0.778	0.510	0.732	0.012	0.102	0.479	0.937	0.049	0.300	0.616	0.181
	H ₂ O	0.007	0.880	0.180	0.009	0.031	0.201	0.961	0.710	0.010	0.205	0.001	0.068	0.002	0.127	0.235	0.004
	CO ₂ ×H ₂ O	0.011	0.064	0.926	0.435	0.170	0.251	0.723	0.454	0.046	0.156	0.036	0.164	0.017	0.110	0.399	0.010
Quality																	
	<i>p</i> level	Fat	CF		Lignin	ADF	NDF		Starch	Glut		Prol	Fat		Starch	Sucrose	
WW	CO ₂	0.361	0.666		0.065	0.533	0.959		0.658	0.753		0.760	0.289		0.172	0.058	
	Year	0.093	0.090		0.178	0.366	> 0.001		0.008	n.a.		n.a.	0.018		0.018	> 0.001	
	CO ₂ ×year	0.954	0.829		0.729	0.833	0.848		0.644	n.a.		n.a.	0.442		0.668	0.589	
2008	CO ₂	0.123	0.633		0.421	0.316	0.298		0.089	0.004		0.010	0.961		0.013	0.142	
	H ₂ O	0.148	0.040		0.092	0.010	0.004		0.035	0.006		0.011	0.053		0.082	0.172	
	CO ₂ ×H ₂ O	0.306	0.325		0.095	0.086	0.099		0.069	0.055		0.108	0.534		0.104	0.430	

WW refers to the results of analyses of variance including only the data of plants grown under well-watered conditions and two CO₂ treatments (ambient and elevated CO₂) from both growing seasons (2007 and 2008), 2008 refers to the results of split-plot analyses of variance including the data of the plants from the 2008 growing season grown under two CO₂ treatments (ambient and elevated CO₂) and two water treatments (well-watered and drought stressed-factor H₂O), *N* nitrogen, *P* phosphorous, *K* potassium, *Ca* calcium, *Mg* magnesium, *S* sulphur, *Fe* iron, *Zn* zinc, *CF* crude fiber, *ADF* acid detergent fiber, *NDF* neutral detergent fiber, *Glut* glutelin, *Prol* prolamin, *n.a.* not assessed

Significant results ($p < 0.05$) are shown in bold

ambient and elevated CO₂, respectively. CO₂ enrichment reduced the magnesium concentration by 1 %, while drought stress resulted in increases of 23 % under ambient and 6 % under elevated CO₂. For zinc, drought stress caused an increase in the concentrations of 29 % and 3 % in ambient and elevated CO₂, respectively. Oktem (2008) showed that maize kernel concentrations of iron and zinc were reduced under low water supply in the field, while protein concentration was increased. In our study, nitrogen concentration was affected by drought stress in a similar manner (assuming nitrogen and protein concentration to be correlated), whereas for zinc opposite results were observed. This discrepancy might be caused by the different levels and the timing of drought stress applied. While in our study the drought stress treatment was started before the maize plants reached their full height, in the study of Oktem (2008), drought stress was applied in a much earlier developmental stage of the maize after an initial irrigation. The occurrence of drought in different developmental stages between the two studies might be the reason for the difference in its effect on elemental composition. Ge et al. (2010) examined elemental composition in kernels of maize grown under severe drought stress and found increased concentrations of calcium, magnesium and zinc, while concentrations of phosphorous and potassium were decreased. Drought stress impacts found in our study largely confirm the findings of Ge et al. (2010) with the exception of phosphorous which

was not affected. In our study, interactions between the CO₂ and the water treatment were observed for the concentrations of nitrogen, potassium, magnesium and zinc. The drought stress impacts were less pronounced under elevated CO₂ for the concentrations of nitrogen, magnesium and zinc. As an exception, there were more prominent drought-induced impacts on the potassium concentration under elevated than under ambient CO₂.

3.3 Quality characteristics of maize aboveground biomass

In the current study, the concentrations of lignin, acid and neutral detergent fiber (Table 2) were in the same order of magnitude as found in other studies on maize (Wiersma et al. 1993; Cox et al. 1994; Tolera and Sundstol 1999). Neutral detergent fiber and starch concentration of maize aboveground biomass in the well-watered treatment were affected by the factor year and thus by the differences between both growing seasons (Table 1). In 2008, drought stress increased the concentrations of crude fiber, acid and neutral detergent fiber in a comparable magnitude by 16 % and 9 %, 19 % and 9 %, as well as 16 % and 8 % under ambient and elevated CO₂, respectively (Fig. 3). In contrast, Kruse et al. (2008) detected changes in soil water availability to have only minor impact on maize cell wall fractions in a modeling approach. Wiersma et al. (1993) reported drought-induced decreases in

Table 2 Elemental composition (Minerals) and quality characteristics (Quality) of maize aboveground biomass and kernels presented as concentration per dry matter (glutelin and prolamin: absorption units per milligram flour (AU mg⁻¹)) grown under two CO₂ treatments (AMB: ambient air, 380 μmol mol⁻¹, FACE: free-air CO₂ enrichment, 550 μmol mol⁻¹) and two water treatments (WW: well-watered, DS: drought stress)±standard errors

Aboveground biomass														Kernels									
Minerals		N	P	K	Ca	Mg	S	Fe	Zn	N	P	K	Ca	Mg	S	Fe	Zn						
CO ₂	H ₂ O	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	μg g ⁻¹	mg g ⁻¹	μg g ⁻¹	μg g ⁻¹	μg g ⁻¹	mg g ⁻¹	mg g ⁻¹	mg g ⁻¹	μg g ⁻¹	mg g ⁻¹	μg g ⁻¹	μg g ⁻¹	μg g ⁻¹						
2007	AMB	WW	10.39±0.10	2.30±0.07	10.39±0.41	1.79±0.05	1.17±0.02	535±9	111±6	26.0±2.3	14.3±0.4	3.10±0.09	3.37±0.10	50.2±5.4	1.12±0.03	547±12	28.9±1.3	16.7±1.5					
	FACE	WW	10.32±0.22	2.29±0.07	10.60±0.27	1.82±0.02	1.15±0.02	560±35	102±10	29.2±2.5	14.7±0.1	3.22±0.04	3.54±0.11	56.0±4.8	1.04±0.06	564±12	37.8±9.6	17.4±1.5					
2008	AMB	WW	8.86±0.13	1.88±0.05	10.06±0.40	1.96±0.08	1.15±0.00	575±43	90±9	14.7±2.8	12.9±0.2	3.06±0.03	3.39±0.04	44.2±5.8	1.04±0.01	495±9	36.5±1.3	16.6±0.6					
	DS	WW	11.08±0.30	1.97±0.06	9.10±0.49	1.48±0.08	1.33±0.05	570±12	87±6	15.8±1.3	17.8±0.9	3.36±0.14	3.12±0.05	47.5±10.5	1.27±0.04	656±38	37.3±1.0	21.4±0.5					
FACE	WW	9.06±0.13	1.90±0.07	10.98±0.38	1.90±0.03	1.13±0.01	600±39	84±6	17.7±3.5	12.8±0.0	3.01±0.10	3.48±0.05	36.5±0.4	1.03±0.02	554±28	33.9±1.2	16.5±1.2						
	DS	WW	9.21±0.24	1.80±0.08	9.89±0.79	1.57±0.05	1.18±0.04	524±17	86±7	14.6±1.9	14.0±0.6	2.99±0.08	2.95±0.03	53.7±7.1	1.10±0.03	549±42	37.6±3.1	17.1±1.5					
Quality			Fat	CF	Lignin	ADF	NDF		Starch	Glut	Prol	Fat			Starch	Sucrose							
CO ₂	H ₂ O	%	%	%	%	%	%		%	AU mg ⁻¹	AU mg ⁻¹	%		%	%	%							
2007	AMB	WW	3.21±0.16	20.2±0.5		2.73±0.13	22.6±0.9	50.8±1.1		31.2±0.9	n.a.		5.93±0.19		72.8±0.4	4.77±0.14							
	FACE	WW	3.02±0.08	20.3±0.3		2.90±0.01	22.9±0.4	50.6±0.9		31.2±1.3	n.a.		5.65±0.15		72.1±0.1	5.43±0.11							
2008	AMB	WW	3.56±0.32	19.0±0.9		2.84±0.10	21.9±0.6	43.1±1.4		36.2±1.9	36.4±0.5		56.9±0.8	6.25±0.15	73.6±0.4	2.13±0.08							
	DS	WW	2.68±0.26	21.9±0.6		3.15±0.04	25.9±0.5	50.0±0.7		23.8±3.5	29.5±0.6		64.3±0.6	5.97±0.01	70.6±0.5	1.95±0.05							
FACE	WW	3.39±0.09	19.3±0.5		3.07±0.08	22.4±0.5	43.4±0.6		35.0±0.7	36.7±0.6		56.5±1.0	6.20±0.08		73.3±0.3	2.70±0.42							
	DS	WW	3.21±0.12	20.7±1.1		3.07±0.08	23.8±0.9	46.6±1.5		33.6±1.1	34.2±1.0		59.2±1.1	6.04±0.12	73.1±0.7	2.12±0.04							

N nitrogen, P phosphorous, K potassium, Ca calcium, Mg magnesium, S sulphur, Fe iron, Zn zinc, CF crude fiber, ADF acid detergent fiber, NDF neutral detergent fiber, Glut glutelin, Prol prolamin, n.a. not assessed

Fig. 2 Change ratio of mineral concentrations of maize aboveground biomass and kernels grown under drought stress (DS), elevated CO₂ concentration (FACE: free-air CO₂ enrichment to 550 $\mu\text{mol mol}^{-1}$) and the combination of both treatments (DS+FACE) in the 2008 growing season. Results are given relative to the respective data of the AMB WW treatment used as reference. Only significant results are shown ($***p<0.001$; $**0.001\leq p<0.01$; $*0.01\leq p<0.05$). Abbreviations: see Tables 1 and 2

maize crude fiber, acid and neutral detergent fiber, which is not in agreement with our results. Again, the reason for this discrepancy might be the different levels and the timing of drought stress applied compared with our study. Wiersma et al. (1993) compared growing seasons with different levels of ambient precipitation, which resulted in a dry growing season in one year. In our study, drought stress was experimentally imposed on the plants starting in the middle of the growing season. The different developmental stages at which drought occurred could be the reason for the different results between the studies. According to Kruse et al. (2008), drought stress induced increases in fiber concentrations as also found

in our study will reduce the usability of maize for silage and bioenergy production, because an altered cell wall composition may limit digestibility, feed intake of ruminants and reduce methane output in biogas plants. Lohölter et al. (2012) and Wroblewitz et al. (2013) examined the in vivo digestibility of maize from the present experiment but came to differing results. A potential reason for these differing results might be that the plants used in these analyses were harvested about 3 weeks later than the ones analysed in the present study. According to Lindroth and Dearing (2005), elevated CO₂ increases concentrations of carbon-based plant compounds. Our results on the C₄ plant maize do not agree with

Fig. 3 Change ratio of quality characteristic concentrations of maize aboveground biomass and kernels grown under drought stress (DS), elevated CO₂ concentration (FACE: free-air CO₂ enrichment to 550 $\mu\text{mol mol}^{-1}$) and the combination of both treatments (DS+FACE) in the 2008 growing season. Results are given relative to the respective data of the AMB WW treatment used as reference. Only significant results are shown ($***p<0.001$; $**0.001\leq p<0.01$; $*0.01\leq p<0.05$). Abbreviations: see Tables 1 and 2

this finding because no respective changes were found in the carbon-based compounds investigated (crude fiber, lignin, acid and neutral detergent fiber, starch and sucrose). However, drought stress-induced increases were observed in crude fiber and acid and neutral detergent fiber. Starch concentrations were decreased due to drought stress by 34 % and 7 % in ambient and elevated CO₂, respectively. In a growth chamber experiment with maize and sorghum, Kakani et al. (2011) found drought stress to decrease starch concentration, which is confirmed by our results.

3.4 Quality characteristics of maize kernels

Kernels of common maize varieties consist of about 70 % starch, 10 % protein and 4 % fat (Nuss and Tanumihardjo 2010) which is consistent with our findings (Table 2). In the data of the well-watered treatment, concentrations of fat, starch and sucrose were affected by the growing season (Table 1). In 2008 (Table 2, Fig. 3), CO₂ enrichment increased the concentration of the protein fraction glutelin by 1 %, while drought stress resulted in decreases of 19 % in ambient and 6 % in elevated CO₂. The concentration of the protein fraction prolamin was reduced under ample water supply and elevated CO₂ by 1 %, while under drought stress increases of 13 % and 4 % in ambient and elevated CO₂ were observed, respectively. These results are in contrast to those for the concentrations of protein fractions of winter wheat which were reduced by CO₂ enrichment (Wieser et al. 2008; Högy et al. 2009). Wang and Frei (2011) identified common stress responses of environmental impacts, including drought stress on maize quality characteristics such as increased protein concentration and a loss in starch and fat concentration. The results of our study confirm these findings for the protein fraction prolamin. In C₃ crops, elevated CO₂ is known to decrease grain nitrogen and protein concentrations (Weigel and Manderscheid 2005; Taub et al. 2008; Högy and Fangmeier 2008; Erbs et al. 2010; McGrath and Lobell 2013). According to our results, a reduction of kernel quality under elevated CO₂ due to lower nitrogen and protein concentrations in maize seems not to be relevant. In the present study, the concentration of starch was decreased by 1 % under elevated CO₂, which is the only trait that shows a CO₂ effect that is not accompanied with a drought stress effect.

The results obtained in the present study only partly confirm our hypotheses. Elevated CO₂ did not generally reduce mineral concentrations of maize aboveground biomass and kernels under ample water supply. Hence hypothesis (1) was not confirmed. In contrast, hypothesis (2) was found to be confirmed for nearly all traits because the dimensions of the drought stress effects were smaller under elevated CO₂ (exception: kernel potassium concentration). The C₄ plant maize was not affected by elevated CO₂ alone and thus reacted different than C₃ plants. Our results clearly demonstrate the

impacts of drought stress on maize elemental composition and quality characteristics. However, the increase in atmospheric CO₂ concentration will mostly mitigate the effects of drought. To our knowledge, this is the first report on the effects of elevated CO₂ and controlled drought stress on elemental composition and quality traits in maize grown under real field conditions.

4 Conclusions

The current results obtained under realistic agronomic conditions clearly show that drought stress will alter the elemental composition and quality characteristics of maize aboveground biomass and kernels. No significant influence of elevated CO₂ was observed under adequate water supply in both growing seasons. Effects of elevated CO₂ were only significant when drought stress effects were significant, too. Food and feed quality of aboveground biomass was modified by drought stress due to increases in concentrations of nitrogen, magnesium, crude fiber and acid and neutral detergent fiber, as well as by lower concentrations of calcium and starch. In maize kernels, drought stress modified the food and feed quality by increasing the concentrations of nitrogen, magnesium, zinc and prolamin and by reducing concentrations of potassium and glutelin. In all of these traits, the impacts of drought were considerably smaller in the combined treatment including also CO₂ enrichment. Thus, elevated CO₂ partially mitigated the drought stress impacts on maize. The results of the present study point out the necessity that, in projections on maize elemental composition and quality traits, the interactive effects of drought stress and elevated CO₂ concentration, two important elements of future climatic conditions, have to be included.

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