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ScienceDirect
Field Crops Research 102 (2007) 128–140
Field Crops Research
www.elsevier.com/locate/fcr

The impact of free-air CO_2 enrichment (FACE) and nitrogen supply on grain quality of rice

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Received 19 October 2006; received in revised form 24 February 2007; accepted 8 March 2007

Abstract

Because CO_2 is needed for plant photosynthesis, the increase in atmospheric CO_2 concentration ([CO_2]) has the potential to enhance the growth and yield of rice (*Oryza sativa* L.), but little is known regarding the impact of elevated [CO_2] on grain quality of rice, especially under different N availability. In order to investigate the interactive effects of [CO_2] and N supply on rice quality, we conducted a free-air CO_2 enrichment (FACE) experiment at Wuxi, Jiangsu, China, in 2001–2003. A long-duration rice japonica with large panicle (cv. Wuxiangging 14) was grown at ambient or elevated (ca. 200 μmol mol^{-1} above ambient) [CO_2] under three levels of N: low (LN, 15 g N m^2), medium (MN, 25 g N m^2) and high N (HN, 35 g N m^2 (2002, 2003)). The MN level was similar to that recommended to local farmers. FACE significant increased rough (+12.8%), brown (+13.2%) and milled rice yield (+10.7%), while markedly reducing head rice yield (−13.3%); FACE caused serious deterioration of processing suitability (milled rice percentage −2.0%; head rice percentage −23.5%) and appearance quality (chalky grain percentage +16.9%; chalkiness degree +28.3%) drastically; the nutritive value of grains was also negatively influenced by FACE due to a reduction in protein (−6.0%) and Cu content (−20.0%) in milled rice. By contrast, FACE resulted in better eating/cooking quality (amylose content −3.8%; peak viscosity +4.5%, breakdown +2.9%, setback −27.5%). These changes in grain quality revealed that hardness of grain decreased with elevated [CO_2] while cohesiveness and resilience increased when cooked. Overall, N supply had significant influence on rice yield with maximum value occurring at MN, whereas grain quality was less responsive to the N supply, showing trends of better appearance and eating/cooking quality for LN or MN-crops as compared with HN-crops. For most cases, no [CO_2] $\times$ N interaction was detected for yield and quality parameters. These data suggested that the current recommended rates of N fertilization for rice production should not be modified under projected future [CO_2] levels, at least for the similar conditions of this experiment.

Keywords: Free-air CO_2 enrichment (FACE); Global change; Quality; Rice grain; Yield

1. Introduction

Empirical records provide incontestable evidence of global changes; foremost among these changes is the increasing atmospheric carbon dioxide concentration ([CO_2]), which, as is predicted, will be double the concentration of the pre-industrial era around the mid-21st century (IPCC, 2001). Atmospheric [CO_2] enrichment must directly influences the growth and development of all terrestrial higher plants as a result of increasing the substrate availability for photosynthesis. Rice (*Oryza sativa* L.) is one of the most important plants in the world and the first staple food in Asia, providing nutrition to a large proportion of the world's population. The improvement of grain yield and quality are the two most important objectives in rice production. It is reported that, in order to assure food security in the rice-consuming countries of the world, farmers will have to produce 50% more rice with improved qualities to meet the demand of consumers in 2025 (Peng and Yang, 2003). As rice supplies increase to meet demand, and as incomes rise throughout the region, rice consumers become increasingly concerned with the chemical and physical characteristics of the rice grains that they buy; however, to date, there are far fewer

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0378-4290/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.fcr.2007.03.006

observations of the effects of elevated [CO_2] on grain quality compared to growth and grain yield mainly because of the limited number of plants that can be grown under chamber or enclosure conditions. In view of the importance of grain quality in human diet and the lack of available data on the subject, it has become increasingly necessary to evaluate how the inevitable rise in global CO_2 concentrations will affect grain quality of rice.

Grain quality of rice is a composite of several attributes, and its preference generally depends on the countries and regions people lives (Juliano, 2001). In a limited number of studies, elevated atmospheric [CO_2] at levels expected over the next century have been shown to affect grain quality in rice, though the available data was contradictory. Using short duration cultivar Jarrah as test material within a chamber experiment, Seneweera et al. (1996, 1997) reported that rice grains produced under elevated [CO_2] exhibited lower mineral (viz., N, P, Zn and Cu) and protein contents, while amylose content was higher than in those grown under ambient [CO_2], thus resulting in harder grains grown under elevated [CO_2]. In Japanese rice FACE (Free-Air CO_2 Enrichment) experiments with small panicle (average 80 spikelets per panicle) cultivar Akitakomachi, Terao et al. (2005) analyzed for protein and amylose contents as well as the starch pasting properties, finding that FACE decreased the protein content, increased maximum viscosity and breakdown of starch, but did not change amylose content and the palatability measured by sensory taste panels. During the course of the same FACE experiments, Lieffering et al. (2004) reported that only N concentration in rice grains was negatively affected by CO_2 enrichment, with other macro- (viz., P, K, Mg, S) and micronutrient contents (viz., Zn, Mn, Fe, B, Mo) remaining unaffected. These findings indicated that detailed knowledge on rice quality responses to elevated [CO_2] is still lacking to date: (1) The major determinants of rice quality are appearance, milling and cooking/eating and nutritional quality. However, CO_2 enrichment studies cited above investigated only few characteristics of grain quality. Limited measures of grain quality are hard to provide integrated responses of grain quality to CO_2-enriched atmospheres. (2) Nitrogen (N) is the most important element that not only is the biggest amount of elements that plants absorb from the soil, but also contributes to the plant growth, yield as well as quality more than other nutritional elements (Ling et al., 1994; Perez et al., 1996), and may play a important role in the response of plant to [CO_2] (Ziska et al., 1996b; Kim et al., 2003a,b). Surprisingly, no report is available to answer if and how the rice quality responses to rising [CO_2] will be moderated by N supply. (3) With respect to test materials, only cultivars with short-duration or small panicles have been investigated, with no attention given to other cultivars. As we know, the presence of large panicles of high-yielding rice cultivars ensures that a sufficient spikelets number per unit area can be obtained, leading to the increase of the grain yield potential (Ling et al., 1994; Peng et al., 1999). In addition, long-duration rice cultivars generally have higher potential of crop productivity as compared with short-duration ones (Ling et al., 1994). Based on these situations, we carried out the current FACE experiment.

The FACE system provided an opportunity to monitor seasonal trends in morphological and physiology traits of plant grown under fully open-air conditions at an agronomic scale with minimal alteration of plant microclimate, thereby without the limitations often imposed by growth chambers (McLeod and Long, 1999). In 2001 the first rice/wheat rotation FACE platform in the world, which is also the second Rice FACE system in the world, was established at Wuxi city, Jiangsu province, China, with the core objective of investigating the impact of FACE on rice/wheat growth, yield, quality and rice/wheat rotation ecosystem processes under field conditions. As in the Japanese Rice FACE project (also the first rice FACE facility in the world), rice crops were grown from transplanting to grain maturity under two levels of [CO_2] (ambient and ambient plus 200 μmol mol^{-1}) (Kim et al., 2003a,b). By contrast, however, according to the actual Chinese rice production, a cultivar with larger panicle (average 155 spikelets per panicle) that has been used in large-scale production in China was tested and three higher N levels (15, 25, 35 g N m^{-2}, compared with 8 or 9 g N m^{-2} in the Japanese Rice FACE trial) were supplied. In addition to this, the key cultivation technique (such as N application strategy and irrigation management) and environmental conditions (such as air temperature and incident solar radiation) in our experiment are also quite different from those in Japanese Rice FACE experiment. In previous articles, we investigated the effects of elevated [CO_2] and N supply on rice growth and yield formation, include phenology (Huang et al., 2005), photosynthesis (Liao et al., 2002), water relations (Liao et al., 2002; Luo et al., 2002), dry matter production and distribution (Yang et al., 2006a), nitrogen uptake and utilization (Yang et al., 2007) and yield formation (Yang et al., 2006b). As part of the long-term Chinese Rice FACE project, objectives of the present study were to determine whether and to what extent grain quality of rice, including processing suitability, appearance quality, eating/cooking quality and nutritional quality, were changed by alteration of the two important production variables, atmospheric [CO_2] and nitrogen supply using a Chinese rice cultivar with long-duration and large panicle as material. The results obtained here should provide important implications with respect to adaptation strategies of rice under future elevated CO_2 conditions.

2. Materials and methods

2.1. Experiment site description and meteorology

The FACE experimental system was located at the Nianyu Farm of Wuxi, Jiangsu province, China (31°37′N Latitude, 120°28′E Longitude), where the soil is classified as stagnic anthrosols (local name, huangni soil). A rice–wheat rotation system prevails in this region. The details of soil properties, climate and regional agricultural practices can be found in previous publications (Yang et al., 2007).

2.2. FACE system

The China Rice FACE system has eight rings located in different paddies having similar soils and agronomic histories.

Three replicate plots in octagon were randomly allocated for the elevated CO_2 treatments (hereinafter called FACE plots) and five for the ambient treatments (hereinafter referred to as ambient plots). More replicates for the ambient condition were set to well cover the spatial variability in soil or water management. Each replicate plot was ca. 80 m^2. In the FACE plots, crops were grown within 12.5 m diameter 'rings' which sprayed pure CO_2 both day and night throughout the growing season except for a few days during transplantation towards the plot centre from eight peripheral emission tubes (5 m long) located about 50–60 cm above the canopy. In the ambient plots, plants were grown under ambient [CO_2] without ring structures. The target [CO_2] in the FACE plots throughout the rice growth season was controlled to 200 $\mu mol\ mol^{-1}$ above that of ambient by computer system platform according to ambient CO_2 concentration variation, wind direction, wind speed, canopy height and day–night changing. Adjacent plots were buffered to avoid treatment cross-over. Details of the design, rationale, operation, and performance of the CO_2 exposure system used in this study are provided by Okada et al. (2001) and Liu et al. (2002).

2.3. Crop cultivation

A japonica cv. Wuxiangging 14 tested in the experiment was a major local cultivar with large panicle (ca. 155 spikelets per panicle) and a high-yielding potential. Standard cultivation practices as commonly performed in the area were followed in all experimental plots. Rice seeds were sown on 18 May. The seedlings for the ambient plots were grown under ambient [CO_2] conditions, while those for the FACE plots were grown under elevated [CO_2] conditions. On 13 June, the seedlings were manually transplanted at a density of three seedlings per hill into the FACE and ambient plots. Spacing of the hills was 16.7 cm × 25 cm (equivalent to 24 hills m^{-2}). Each of the eight rings (main plots) was further split into three subplots to test the effect of three different N levels, which were supplied as urea (N, 46%) and compound fertilizer ($N:P_2O_5:K_2O$ = 15:15:15, %): low (LN, 15 g N m^{-2}), medium (MN, 25 g N m^{-2}) and high N (HN, 35 g N m^{-2}). For all N levels, phosphorous (P) and potassium (K) fertilizers were applied as compound fertilizer at equal rates of 7 g P_2O_5 m^{-2} and 7 g K_2O m^{-2} in 2002 and 2003, respectively. The rates and dates of N, P and K fertilizer applications are listed in Table 1. Mixing of paddy water between N treatments was minimized by separating the LN and HN subplots from the rest of the plot (which received MN) with a 30 cm polyvinyl chloride (PVC) barrier pashed 10 cm into the soil. The paddy fields were submerged with water, about 5 cm in depth, from 13 June to 10 July, and drained dry several times from 11 July to 4 August, and flooded with intermittent irrigation from 5 August to 10 days before harvest. The plants in both FACE and ambient plots were surrounded with border plants treated the same way as the plants inside.

2.4. Determination of grain quality characters

In all 3 years (2001–2003), grains for yield and quality analyses were obtained from all the plants from a 2 m^2 (48 hills) patch (excluding plants in the borders) in each subplot at crop maturity. After harvest, the grains were threshed carefully and fertile grains were selected using an airflow separator (model NP24350, China), these fertile grains were air-dried to constant weight for rough rice (RR) yield. These samples were stored for 3–4 months at ambient temperature before processing to ensure stable grain quality. The grains were dehulled to produce brown rice (BR) using chaff-remove machine (OHYA-25, Japan), and brown rice percentage (BRP) was determined, then the appearance quality characteristics (i.e., chalky grain percentage (CGP), chalkiness area (CA) and chalkiness degree (CD)) of brown rice was measured using a C-300 Whiteness Tester (Kett Electric Laboratory, Tokyo, Japan). Then the brown rice was milled with rice polishing machine (CPC 96-3, China) until a standard degree of milling was reached for milling properties (i.e., milled rice percentage (MRP), head rice percentage (HRP)). Next, the representative milled rice samples were oven-dried at 60 °C to constant weight. The oven-dried samples were then ground with a stainless steel grinder (FW-100, China) with a 100-mesh sieve in order to further prepare them for subsequent analyses, viz., protein content (PC), amylose content (AC), gel consistency (GC), gelatinization temperature (GT), starch viscosity and elemental concentrations. Evaluation of rice quality (include MRP, HRP, CGP, CA, CD, PC, AC and GC) was conducted according to the China National Standard GB/T 17891-1999 for rice quality evaluation (issued by Ministry of Agriculture, PR China, 1999), all evaluations were conducted with two replications. Copper (Cu), iron (Fe) and

Table 1
Timing and application rates of N, P and K fertilizers in the LN, MN and HN plots over three rice cropping seasons (2001–2003)

Year	Treatment	N (g N m^{-2})/P (g P_2O_5 m^{-2})/K (g K_2O m^{-2})		
		First fertilization[a]	Second fertilization[b]	Third fertilization[c]
2001	LN	6/4.55/4.55	3/2.45/2.45	6/0/0
	MN	10/4.55/4.55	5/2.45/2.45	10/0/0
2002 and 2003	LN	9/7/7	0/0/0	6/0/0
	MN	9/7/7	6/0/0	10/0/0
	HN	9/7/7	12/0/0	14/0/0

[a] The first fertilization was applied as basal dressing on 13 June (i.e. 1 day prior to transplanting).
[b] The second fertilization was applied as tillering fertilizer on 18 June.
[c] The third fertilization was applied as ear fertilizer on 5 August, 28 July, 30 July in 2001, 2002 and 2003, respectively.

zinc (Zn) concentrations of the samples were determined with Atomic Absorption Spectrophotometer (Solaar S4 + 126 Graphite Furnace System 97, Thermo Elemental, USA) following HNO_3–$HClO_4$ (4:1) digestion procedures (Allen, 1989). Certified standard elemental (Cu, Fe and Zn) solution (GBW07605) was used to ensure precision of the analytical procedures. GT and starch viscosity was determined by Rapid Visco Analyser RVA-3D (Newport Scientific Inc., Warriewood, Australia), which was controlled by computer software, the Thermo Cycle for Windows (TCW). The experimental procedure was carried out using the AACC (1995) protocol. The major characters of the RVA profile were described as peak viscosity (PV), minimum viscosity (MV), final viscosity (FV), breakdown (BD: PV minus MV), setback (SB: FV minus PV) and consistency (CS: FV minus MV). Values for viscosity were reported in units termed ''rapid visco units'' (RVU).

2.5. Statistical analysis

Data were analyzed with the statistical package SPSS10.0 and EXCEL'2000 for Win. The experimental was designed as a blocked split–split plot. Experimental year was treated as a fixed effect and was the whole-plot treatment. The $[CO_2]$ was the split-plot treatment, and N was the split–split plot treatment. Average values of the sampled hills from different locations in each N subplot were used in the statistical analyses. Data were statistically analyzed by the ANOVA procedures to determine the main and interactive effects of the three factors of year, $[CO_2]$ and N. If the hypothesis of equal means has been rejected by the ANOVA test, the Fisher LSD procedures were employed to distinguish among treatment means.

3. Results

3.1. Processing quality

In general, the processing quality is evaluated by three milling traits, namely, brown rice percentage (BRP), milled rice percentage (MRP) and head rice percentage (HRP).

BRP is defined as the percentage of brown rice to the weight of total rough rice, it responded positively to FACE (Fig. 1a). Though the degree of stimulation due to FACE was less overall, showing values 0.5% higher across 3 years, the effect reached significant level ($P < 0.01$, Table 2). Across both $[CO_2]$ levels, BRP increased significantly with increased amount of N fertilizer.

MRP is expressed as the percentage of milled rice to the weight of rough rice, while HRP represents the percentage of head milled rice (include whole grains and grains with four-fifths of the whole grain) to the weight of rough rice. On

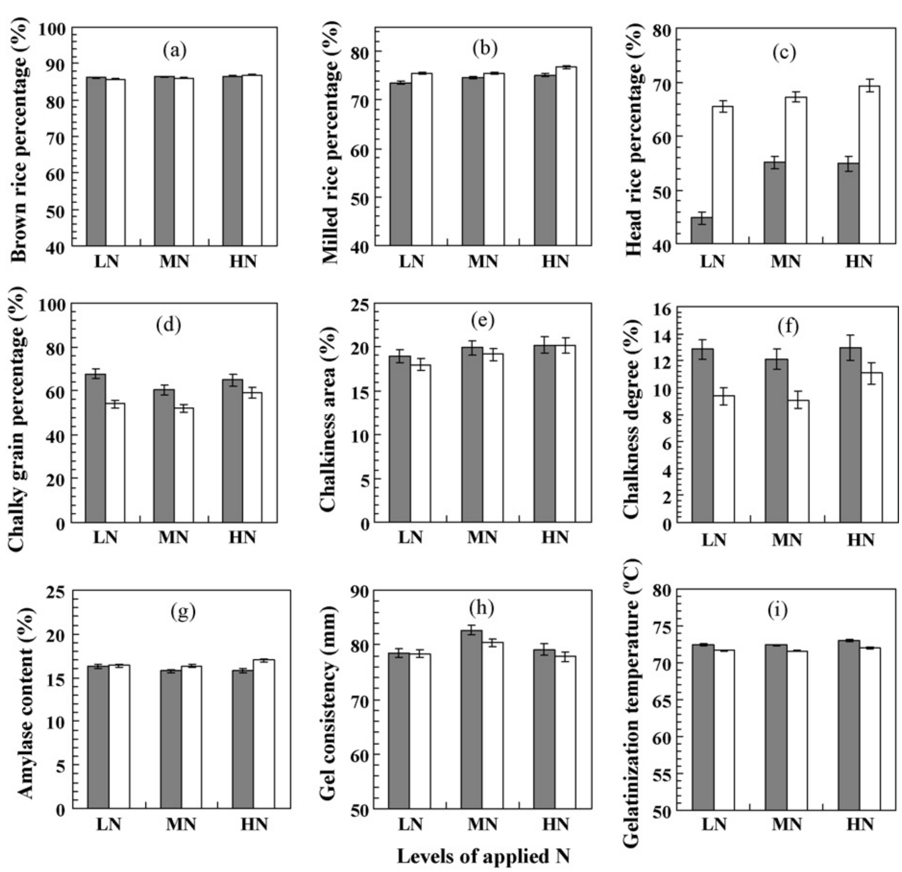

Fig. 1. Brown rice percentage (a), milling rice percentage (b) and head rice percentage (c), chalky grain percentage (d), chalkiness area (e), chalkiness degree (f), amylose content (g), gel consistency (h) and gelatinization temperature (i) of rice plants subjected to ambient CO_2 (AMB; unfilled square) and free-air CO_2 enrichment (FACE, 200 μmol mol^{-1} above AMB, filled squares) under low (LN, 15 g N m^{-2}), medium (MN, 25 g N m^{-2}) and high (HN, 35 g N m^{-2}) levels of N application over three cropping seasons (2001–2003). Data are average values across 3 years with ±1 S.E. (vertical bars).

Table 2
Significance of elevated CO_2 (C), nitrogen (N), year (Y), and their interactions on various measures of rice grain qualities from the 2001–2003 experiments

Parameters	C	N	C × N	Y	C × Y	N × Y	C × N × Y
Brown rice percentage (BRP, %)	**	**	n.s.	**	**	n.s.	*
Milled rice percentage (MRP, %)	**	**	n.s.	**	n.s.	**	n.s.
Head rice percentage (HRP, %)	**	**	**	**	n.s.	**	n.s.
Chalky grain percentage (CGP, %)	**	n.s.	n.s.	**	**	n.s.	n.s.
Chalkiness area (CA, % reflectance)	n.s.	n.s.	n.s.	**	n.s.	**	n.s.
Chalkiness degree (CD, %)	**	n.s.	n.s.	**	**	n.s.	n.s.
Amylose content (AC, %)	**	n.s.	n.s.	**	n.s.	n.s.	n.s.
Gel consistency (GC, mm)	n.s.	**	n.s.	n.s.	n.s.	n.s.	n.s.
Gelatinization temperature (GT, °C)	**	n.s.	n.s.	**	n.s.	n.s	*
Protein concentration (PC, %)	**	**	n.s.	**	n.s.	n.s.	n.s.
Zn concentration (mg kg^{-1})	n.s.	n.s.	n.s.	**	n.s.	n.s.	n.s.
Cu concentration (mg kg^{-1})	**	n.s.	n.s.	*	n.s.	n.s.	n.s.
Fe concentration (mg kg^{-1})	n.s.	n.s.	n.s.	**	*	n.s.	n.s.
Protein yield (g m^{-2})	**	**	n.s.	**	n.s.	n.s.	n.s.
Zn yield (mg m^{-2})	**	n.s.	n.s.	**	n.s.	n.s.	n.s.
Cu yield (mg m^{-2})	n.s.	n.s.	n.s.	**	n.s.	n.s.	n.s.
Fe yield (mg m^{-2})	n.s.	n.s.	n.s.	**	**	n.s.	n.s.
Peak viscosity (PV, RVU)	**	**	n.s.	**	n.s.	*	n.s.
Minimum viscosity (MV, RVU)	**	**	n.s.	**	n.s.	**	n.s.
Breakdown (BD, RVU)	**	n.s.	n.s.	**	n.s.	*	n.s.
Final viscosity (FV, RVU)	**	**	n.s.	**	n.s.	**	n.s.
Setback (SB, RVU)	*	n.s.	n.s.	**	n.s.	n.s.	n.s.
Consistency (CS, RVU)	*	n.s.	n.s.	**	*	n.s.	n.s.

Probability levels are indicated by n.s., * and ** for 'not significant', 0.05, and 0.01, respectively.

average, FACE significantly reduced MRP by 2.0% across the three seasons, with averages of 1.1%, 2.4% and 2.2% in 2001, 2002, and 2003, respectively (Table 2; Fig. 1b). For HRP, the FACE plants were dramatically reduced by 23.4% across the 3 years, averaging 22.1%, 23.7% and 25.0% in 2001, 2002 and 2003, respectively (Fig. 1c). Across both [CO_2] levels, both MRP and HRP increased apparently with increasing N supply: averaged across two [CO_2] levels and 3 years, the integrated MRP was 74.5%, 75.0% and 75.9% for LN, MN and HN-crops, respectively (Fig. 1b); and the integrated HRP was 55.1%, 61.1% and 62.1% for LN, MN and HN-crops, respectively (Fig. 1c).

Brown rice (BR) yield, milled rice (MR) yield and head rice (HR) yield are determined by multiplying rough rice (RR) yield by BRP, MRP and HRP, respectively. Compared to ambient [CO_2], FACE significantly increased yield of RR, BR and MR regardless of N application levels, averaging 12.8%, 13.2% and 10.7% across the 3 years, respectively (Table 3). Overall, the average response showed a tendency to be greater under a high N application than under a low N application, but [CO_2] × N interaction was not statistically significant due to the high variability between sampling replicate plants and seasons. As for HR yield, a sharp decline of 13.3% due to FACE was recorded across the 3 years. Across [CO_2] levels, the yield of RR, BR, MR and HR increased significantly with N supply from 15 to 25 g N m^2, but further increases in N supply to 35 g N m^{-2} resulted in significant decline. Hence, as in ambient plots, maximum yield in the FACE plots was reached by MN-crops.

The ANOVA results showed that the year effects were all significant for BRP, MRP, HRP, and yield of RR, BR, MR and HR (Table 3); however, for the most part, interactions between all treatments variables (CO_2 × N, CO_2 × year, N × year, CO_2 × N × year) were not detected for these parameters.

3.2. Appearance quality

Fig. 1d–f summarize three main appearance quality properties, including of chalky grain percentage (CGP), chalkiness area (CA), chalkiness degree (CD) of brown rice. CGP is expressed as the percentage of number of chalky brown rice to number of total brown rice, while CA is expressed as the ratio of the area of chalkiness to the area of the whole brown rice. CD was calculated as the product of CGP and CA. CGP was consistently higher at the elevated relative to the ambient [CO_2] regardless of the N treatment ($P < 0.01$), showing an average increase of 16.9% across 3 years (Table 2; Fig. 1d). With respect to CA, it was enhanced due to FACE by 3.1% on average (Fig. 1e). Concerning CD, FACE treatment showed a substantial increase, averaging 28.3% larger compared to ambient [CO_2] (Fig. 1f). By contrast to [CO_2], N had relatively minor effects on appearance quality properties. Although N effects were not statistically, the trends were for lower N application (15, 25 g N m^{-2}) to reduce the chalkiness of grains (Fig. 1d–f).

The year-to-year differences were all significant at a 1% level for CGP, CA and CD (Table 2), whereas, for the most part, we did not detect interactions between all treatments variables for these three parameters.

3.3. Eating/cooking quality

The cooking/eating quality of rice is largely determined by three primary physical and chemical characteristics of the starch in the endosperm: amylose content (AC), gel consistency

Table 3
Effect of elevated [CO_2] on yield of paddy rice (PR), brown rice (BR), milled rice (MR) and head rice (HR) under three levels of nitrogen (N) application [LN, 15 g N m^{-2}; MN, 25 g N m^{-2}; HN, 35 g N m^{-2}] over three cropping seasons (2001–2003)

Year	N	CO_2	PR yield (g m^{-2})	BR yield (g m^{-2})	MR yield (g m^{-2})	HR yield (g m^{-2})
2001	LN	FACE	1149.0	996.3	845.7	537.7
		AMB	1039.8	882.6	774.4	687.7
		%change	10.5	12.9	9.2	−21.8
	MN	FACE	1216.8	1047.8	889.7	672.7
		AMB	1095.0	935.6	808.0	696.6
		%change	11.1	12.0	10.1	−3.4
2002	LN	FACE	1063.7	907.0	777.4	461.9
		AMB	979.8	845.5	743.0	662.9
		%change	8.6	7.3	4.6	−30.3
	MN	FACE	1167.2	1007.5	884.8	712.9
		AMB	991.7	856.4	759.2	721.9
		%change	17.7	17.6	16.5	−1.2
	HN	FACE	1080.7	928.2	812.9	642.3
		AMB	931.8	806.8	718.7	691.5
		%change	16.0	15.0	13.1	−7.1
2003	LN	FACE	1003.2	867.8	742.8	441.4
		AMB	880.3	758.3	670.2	554.0
		%change	14.0	14.4	10.8	−20.3
	MN	FACE	975.7	846.3	728.4	475.8
		AMB	902.7	780.1	687.9	574.0
		%change	8.1	8.5	5.9	−17.1
	HN	FACE	936.3	817.2	702.2	471.8
		AMB	783.0	681.9	598.2	504.8
		%change	19.6	19.8	17.4	−6.5
ANOVA results						
CO_2 (C)			**	**	**	**
N			**	**	**	**
C × N			n.s.	n.s.	n.s.	**
Year (Y)			**	**	**	**
C × Y			n.s.	n.s.	n.s.	n.s.
N × Y			n.s.	n.s.	n.s.	**
C × N × Y			n.s.	n.s.	n.s.	n.s.

n.s., * and ** indicating no significance, $P < 0.05$ and $P < 0.01$, respectively.

(GC) and gelatinization temperature (GT), together with starch-pasting properties.

The AC was expressed as a percentage of amylose to the weigh of milled rice. In general, the varieties with low or intermediate AC are generally most preferred because they cook dry and fluffy retaining their soft texture even after cooling. When averaged over all N levels and years, FACE significantly decreased AC in milled rice by 3.8%, with average decreases of 0.5%, 3.7% and 4.8% in 2001, 2002 and 2003, respectively (Table 2; Fig. 1g). Though no significant response of AC to N supplies was detected, AC showed a decreasing trend with decreasing N application rate.

GC is measured by the length of cold milled rice paste in a test tube in horizontal position. A higher number indicates a softer consistency. GC showed only a weak increase (2%, $P > 0.05$) in FACE grains compared to ambient ones (Table 2; Fig. 1h). Across [CO_2] levels, varying the supply of N significantly influenced GC with greatest GC occurring at MN (25 g N m^{-2}) rather than LN or HN.

GT was measured by temperature at which about 90% of the starch granules have swelled irreversibly in hot water. The FACE plants showed an average increase of 0.8 °C (relative increases 1.2%) across 3 years (0.8, 0.7 and 1.0 °C in 2001, 2002 and 2003, respectively; Table 2; Fig. 1i) in GT, however, no significant impact of N fertilization was observed on GT.

The Rapid Visco Analyser (RVA) is the most useful tool available for rapidly and reproducibly assessing eating/cooking quality of rice. Fig. 2 shows the starch-pasting properties, including perk viscosity (PV), minimum viscosity (MV), final viscosity (FV), breakdown (BD), setback (SB), and consistency (CS) in RVA-profile. The starch-pasting properties influence texture and stickiness of cooked rice. FACE significantly increased PV independently of N fertilization, showing an average increase of 4.5% (+11.4 RVU) across 3 years (Table 2; Fig. 2a). Similar patterns of responses to FACE were also observed for MV (Fig. 2b), FV (Fig. 2c), as well as BD (Fig. 2d), with average responses of 6.5% (+8.5 RVU), 1.9% (+4.5 RVU) and 2.9% (+4.0 RVU), respectively. In contrast,

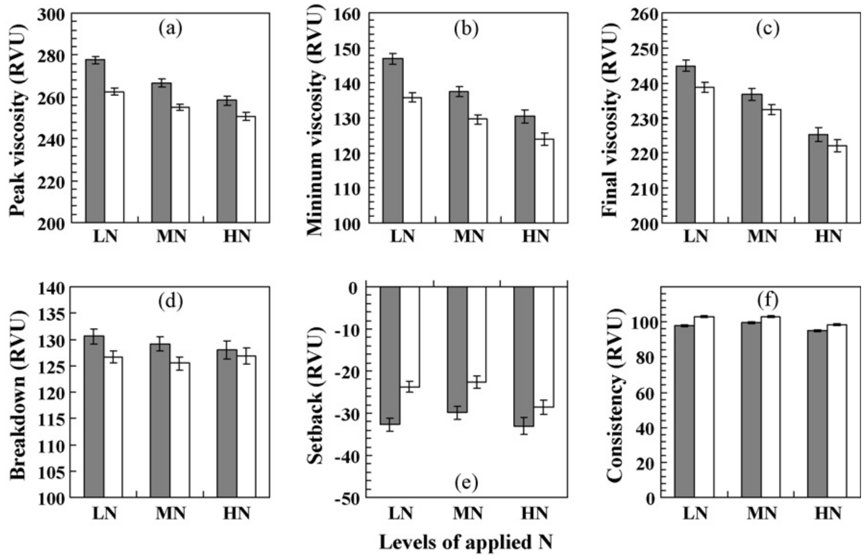

Fig. 2. The values of peak viscosity (a), minimum viscosity (b), final viscosity (c), breakdown (d), setback (e) and consistency (f) in the RVA profile of rice plants subjected to ambient CO_2 (AMB; unfilled square) and free-air CO_2 enrichment (FACE, 200 μmol mol^{-1} above AMB, filled squares) under low (LN, 15 g N m^{-2}), medium (MN, 25 g N m^{-2}) and high (HN, 35 g N m^{-2}) levels of N application over three cropping seasons (2001–2003). Data are average values across 3 years with ±1 S.E. (vertical bars).

FACE substantially reduced the values of SB and CS by 27.5% (−6.9 RVU; Fig. 2e) and 3.9% (−3.9 RVU; Fig. 2f), respectively. Across [CO_2] levels, PV, MV and FV all decreased significantly with increasing N level (Table 2), while no effect of N was noted on BD and SB.

There was obvious variation between different years with regards to AC, GT and starch-pasting properties (Table 2); however, interactions between all treatments variables were generally, but not always, nonsignificant for these parameters across the season.

3.4. Nutritional quality

Regardless of N application rate, FACE significantly reduced protein content (PC) in milled rice, while protein yield (PY) per square meter exhibited an opposite trend ($P < 0.01$; Table 2; Fig. 3a and e): averaged across two [CO_2] levels and 3 years, PC in milled rice was lower under FACE by 6.2%, while a significant increase of 6.0% was found for PY. Across [CO_2] levels, PC increased apparently with increasing N supply: averaged across all N levels and years, the integrated PC was 69.5, 73.6 and 77.1 mg g^{-1} for LN, MN and HN-crops, respectively. Unlike PC, PY increased with increasing N supply, but luxury N application (35 g N m^{-2}) resulted in a significant reduction: averaged across all N levels and years, integrated PY was 60.5, 67.4 and 61.9 g m^{-2}, for LN, MN and HN-crops, respectively (Fig. 3e). Interactions between all treatments variables were not detected for the two parameters although there was obvious variation between different years.

Of the three elements analysed in this study, only Cu showed a significant decrease (−20%) in concentration in FACE versus ambient plants across the 3 years (Table 2; Fig. 3b). The concentrations of the other two elements (i.e., Fe, and Zn) showed no significant change under FACE though for Fe there was a tendency to decrease (Fig. 3c and d). Multiplying this by the average grain elemental concentration in these 3 years (Table 3), the total amounts of the three elements removed by harvesting the grains can be calculated (Fig. 3f–h). Compared to ambient CO_2, similar amounts of Cu and Fe were contained in rice grains under FACE; in contrast, substantially more Zn (+10%). N fertilization had no influence on all the three elements. The year effects were all significant for these parameters; however, with the exception of $CO_2 \times$ year interaction for Fe concentration and amount, interactions between all treatments variables were not observed for these parameters.

4. Discussion

4.1. Effects of elevated [CO_2] on processing quality of rice

Processing quality of rice is one of the most important traits in rice as it is directly related to market value and thus influences income of both rice producers and processor. To date, however, little is known regarding the impact of elevated [CO_2] on processing quality of rice. A prominent phenomenon observed in this study was the significant decreases due to FACE in milling traits, viz., MRP and HRP (Fig. 2b and c), indicating a higher fraction of removed outer layer (i.e., pericarp and aleurone) and broken (or damaged) rice during milling. Because the milling conditions were identical for the FACE and ambient plants, the grains in the FACE plots were supposed to be lower hardness or more easily ground than those in the ambient plots. The dramatic 23.5% reduction in HRP due to FACE needs requisite attention in future research because most rice is consumed in the whole grain form.

The CO_2-induced changes in BRP, MRP and HRP directly influence the final yield of BR, MR and HR on the basis of unit

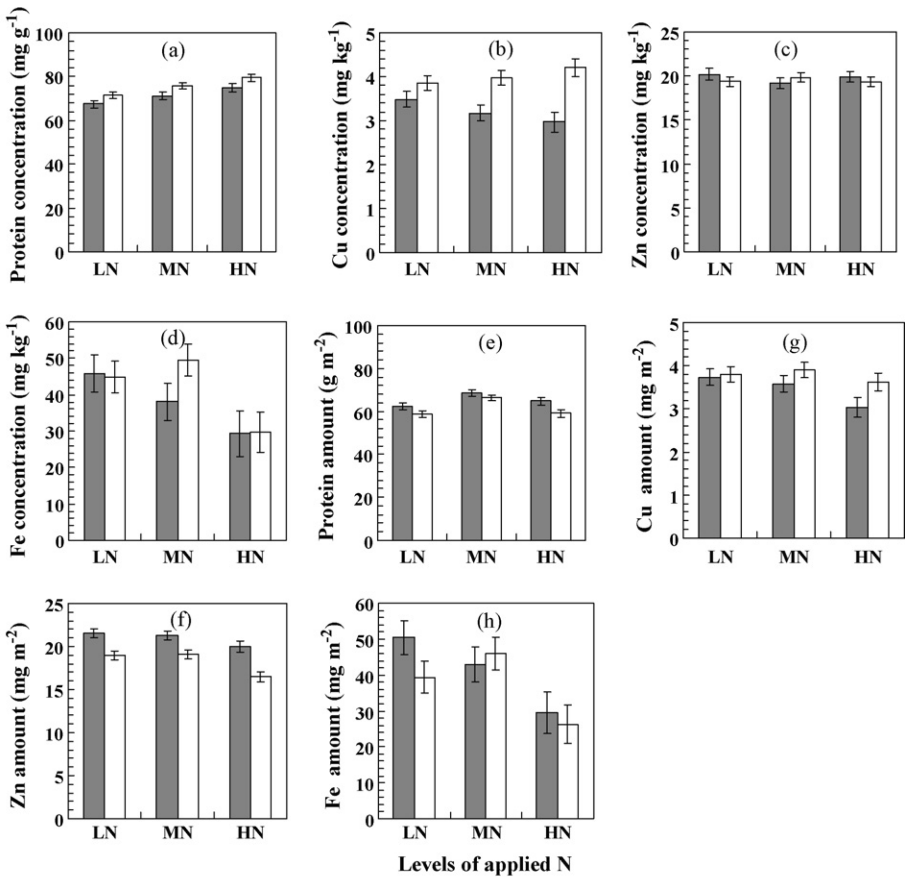

Fig. 3. Protein concentration (a), Cu concentration (b), Zn concentration (c), Fe concentration (d), protein yield (e), Cu yield (f), Zn yield (g), Fe yield (h) in milled rice supplied LN (15 g N m^{-2}), MN (25 g N m^{-2}) and HN (35 g N m^{-2}) levels of N application under ambient CO_2 (AMB, unfilled square) and free-air CO_2 enrichment (FACE, 200 μmol mol^{-1} above AMB, filled squares) over three cropping seasons (2001–2003). Data are average values across 3 years with ±1 S.E. (vertical bars).

area. As an important economic parameter, there have been numerous observations over the last two decades of the effects of elevated [CO_2] on RR yield (i.e., grain yield) of rice crops under various conditions (Seneweera et al., 1996; Ziska et al., 1997; Moya et al., 1998; Kim et al., 2003a; Yang et al., 2006b). However, there is no information on the effect of elevated [CO_2] on rice yield of BR, MR and HR. Because the magnitude of the CO_2-induced changes in both BRP (+0.3%) and MRP (+2%) were small, so the enhancement of BR yield (+13.2%) and MR yield (+10.7%) by FACE is close to that of RR yield (+12.8%) (Table 3). Nevertheless, as the significant 23.5% decline in HRP was more than compensated for by RR yield increase of 12.8%, the overall HR yield was greatly reduced (−13.3%). It must be noted that, unlike the result for RR yield by Kim et al. (2003a) under low N application (4–15 g N m^{-2}), no significant [CO_2] × N interaction on yield of RR, BR, MR and HR (Table 3) was detected, suggesting that the positive effects of N availability on rice yield responses to elevated [CO_2] will reduced or even disappear under higher levels of fertilizer N (as in this trial). Regardless of CO_2 treatment, the absolute values of yield increased significantly with N supply from 15 to 25 g N m^2, but further increases in N supply to 35 g N m^{-2} resulted in significant reduction, which were also different from the published results by Kim et al. (2003a) under low N availabilities, suggesting that, as under ambient condition, the absolute yield of RR, BR, MR and HR under elevated [CO_2] will also approach a ceiling at a given N level.

4.2. Effects of elevated [CO_2] on appearance quality of rice

Chalkiness, an opaque area in the grains, is an undesirable characteristic in all markets except the arborio market. Our results for the first time indicated FACE increased CA (+3.1%, Fig. 1e), CGP (+16.9%, Fig. 1d) and CD (+28.3%, Fig. 1f), the latter two parameters all reaching the significant level. The higher extent of chalkiness implies that rice grains grown under higher [CO_2] condition have a lower density of starch granules and are therefore more prone to breakage during milling, as also indicated by a close negative correlation in this study between CGP ($r = -0.757$**, Fig. 4a), CA ($r = -0.393$**, Fig. 4b), CD ($r = -0.544$**, Fig. 4c) and HRP when plotted for each combination of years, CO_2, N and blocks. Similar intrinsic relationship between chalkiness and milling quality has also been reported in the literatures (Nakatat and Jackson, 1973). In contrast, the relationships between chalkiness and eating (or sensory) properties of rice grains are highly variable, showing positive (Chen et al., 1997), negative (Lisle et al., 2000; Sui

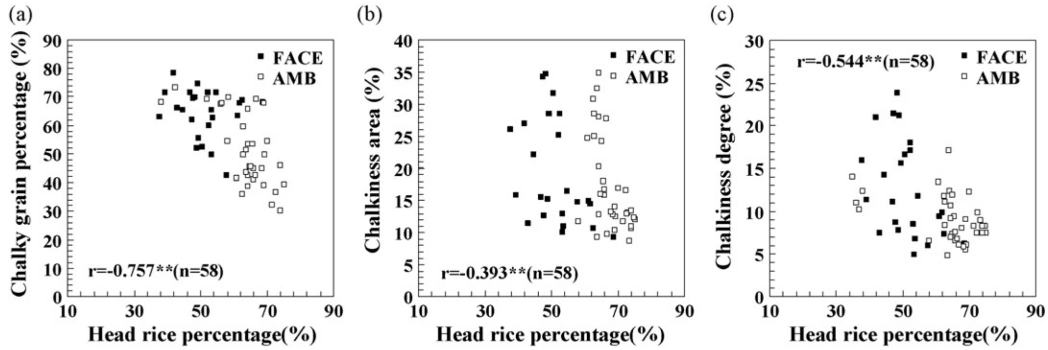

Fig. 4. Relationship between chalky grain percentage (a), chalkiness area (b), chalkiness degree (c) and head rice percentage for each combination of year × CO_2 × N × block (in 2001–2003). The ambient daytime CO_2 levels were about 370 μmol mol^{-1} (open squares), while CO_2 levels were controlled at 200 μmol mol^{-1} above ambient in the FACE plots (closed squares). N application rates were 15, 25, 35 g N m^{-2}, respectively. First degree polynomial fitted for all treatments combined; *r* is shown.

et al., 2005) or poor correlations (Cheng et al., 2002) in different experiments. So in this experiment, it is hard to evaluate the possible effect of increased chalky grain percentage and chalkiness degree on the taste (palatability) of cooked rice.

These are two possible reasons for the observed deleterious effects of elevated [CO_2] on chalkiness and milling quality. First, such results appeared to be associated with the changes in grain-filling characteristics (include rate and duration of grain filling) due to FACE. As for grain-filling rate, the FACE plants showed a significant increase during early grain filling stage (EGFS), whereas an adverse trend displayed during late grain-filling stage (LGFS): the former resulted from increased starch accumulation in stems and sheaths at heading and enhanced shoot dry matter (DM) production during EGFS (the two major contributors to grain filling) (Yang et al., 2006a), while the latter was due to clear premature senescence, as indicated by the sharp decline in N uptake, green leaf area index, net assimilation rate and subsequent DM production under FACE during LGFS (Yang et al., 2006a, 2007). Many prior studies on rice grain quality indicated that excessive grain-filling rate during EGFS and incomplete filling during LGFS will lead to chalky appearance and poor milling quality (Ling et al., 1994). In addition, our data of this study also demonstrated that, the FACE plants matured and senesced about 6–9 days earlier than the ambient plants (Huang et al., 2005). Because of the acceleration of senescence, there was a shortening of grain-filling duration, and consequently influencing final physical qualities of grains. Second, in term of external causes, previous studies show that high temperatures during grain-filling tend to increase the occurrence of chalk in rice grains (Resurreccion et al., 1977; Lisle et al., 2000). Using the same FACE platform, Luo et al. (2002) found that FACE significantly increased daytime canopy temperature and inside canopy air temperature during the ripening stage: the average daytime canopy temperature difference between FACE and ambient from flowering to maturing stage was about 0.43 °C with difference being larger at EGFS than that at LGFS, and the maximum daytime air temperature difference varied between 0.37–0.80 °C and 0.47–1.20 °C at canopy height and middle of canopy height, respectively. We speculate that this temperature rise also contributed to the increased grain-filling rate at EGFS and the earlier maturity, which resulted in incomplete filling of the grains, thereby leading to an increase in chalky appearance but a decrease in milling rate. The influence of [CO_2] on grain-filling is likely to have resulted from changes in the number of cells in the endosperm, which, in turn, is influenced by the duration and rate of cell division in the endosperm during the ripening phase. Therefore, an understanding of these parameters in response to CO_2 enrichment could be important in predicting how physical quality may change under future CO_2 scenarios.

4.3. Effects of elevated [CO_2] on eating/cooking quality of rice

Rice is usually consumed daily after preparation by boiling without the addition of seasonings. For this reason, the cooking/eating quality is a very important aspect of the grain quality and largely determines the economic value of rice.

AC is considered to be the key factor that contributes to the eating/cooking quality of rice. In general, higher contents of amylose relative to amylopectin increase the hardness of the cooked grains (Juliano, 1992; Mohapatra and Bal, 2006). In this study, AC in starch was significantly reduced by FACE, suggesting that [CO_2] enrichment is likely to reduce the hardness of the cooked grains. Our observation is in contrast to the results of Seneweera et al. (1996) and Terao et al. (2005). From a growth chamber experiment with rice, Seneweera et al. (1996) reported significant increase in AC of rice grains with elevated [CO_2], while in Japanese rice FACE experiment no change in AC was detected (Terao et al., 2005). The explanation for this inconsistency probably resides in differences in test varieties and/or environmental settings. In addition to the differences in growth duration and panicle size of the test variety as mentioned in the Introduction of this paper, difference in AC in milled grains may lead to such inconsistency: Seneweera et al. (1996) used a high-AC variety (ca. 300 mg g^{-1} or higher), and Terao et al. (2005) used an intermediate-AC rice (ca. 200 mg g^{-1}), whereas we selected a cultivar with AC of ca. 150 mg g^{-1}. In addition to varietal difference, environmental settings, especially temperature, may also lead to such inconsistency: statistics showed that the mean daily temperature in period from heading to mid-ripening stage was 25.2 and 22.5 °C for China and Japan FACE across the 3 years of experimentation, respectively. It is well known that the higher temperature during grain formation decreases the expression of granule-bound starch synthase, the enzyme responsible in amylose synthesis, thus resulting in less amylose in the grains of mainly japonica rices (Larkin and Park, 1999; Lisle et al., 2000). However, from this it is not possible to define whether the differences in AC response to rising [CO_2] between China and Japan FACE could be explained by differential temperature. Further investigations are required to determine the [CO_2] × temperature interaction on AC in milled rice.

AC in milled rice drastically affects the viscosity of starch. In particular, in many reports, it has been noted that lower AC is associated with higher values of PV and BD and lower value of SB in RVA profile (Larkin et al., 2003; Allahgholipour et al., 2006). Our measurements of viscosity properties indicated that, corresponding to the change in AC, the FACE grown plants showed a significant increase in PV and BD, but a significant decrease in SB, all these effects on the three RVA pasting properties being considered to be a favorable change for enhancing the sensory acceptability of cooked rice (Chrastil, 1994; Shu et al., 1998; Okadome et al., 1999; Allahgholipour et al., 2006). In addition, FACE significantly increased MV and FV, but significantly decreased CS. Overall, our results of changes in paste viscosity parameters were similar to the findings of Terao et al. (2005), but contradicted the results of Seneweera et al. (1996).

It has been reported that PC other than AC of grains affects starch pasting properties of cooked rice: lower PC is generally associated with higher values of PV and BD (Yanase et al., 1984; Shen et al., 2003), thus leading to increased viscosity and elasticity of cooked rice (Yamashita and Fujimoto, 1974). In the present study, we also observed a close inverse relationship between PV, BD and PC in milled rice when plotted for each combination of year, CO_2, N and block (Fig. 5). Perhaps this is because the glass transition (T_g) of protein is slightly lower than that of starch (Matveev et al., 2000) so when cooked with limited water, for example in a rice cooker, the lower the PC, the less water would be bound by proteins, leaving more water for the swelling of starch granules and leaching of amylose.

Based on above results, we assume that, in this study, the increased starch viscosity of rice grains resulting from elevated [CO_2] could be attributed to the declines in both AC and PC.

4.4. Effects of elevated [CO_2] on nutritional quality of rice

Rice is a major source of dietary protein for most of the Asian rice-growing countries. Our results indicated that, although the FACE treatment caused decreases in grain PC (Fig. 3a), the significant increase in yield due to FACE (Table 2) resulted in greater harvests of protein (Fig. 3e). This result is basically in agreement with previous results reported in the literature (Seneweera et al., 1996; Terao et al., 2005). In the same FACE experiment, Pang et al. (2006) reported that increased plant N loss and decreased root N uptake efficiency at elevated [CO_2] may play major roles in N concentration decrease in tissues of rice.

The observed decrease in PC under FACE directly reduced the nutritional value of rice, but at the same time, increased the palatability of cooked rice: generally, low PC in the grains is closely associated with the improvement of taste properties (Juliano et al., 1965; Ishima et al., 1974; Yamashita and Fujimoto, 1974; Matsue et al., 1997). Based on PC response to FACE, together with responses of AC (Fig. 1g) and three RVA pasting properties (i.e. PV, BD and SB, Fig. 2a, d and e) mentioned above which are also involved in the sensory acceptability of cooked rice, we could therefore assume that the palatability should be improved in rice grown under elevated [CO_2]. Such a hypothesis needs to be confirmed by sensory taste panel evaluation.

Cu, Zn, Fe concentrations in rice grains are extremely important, particularly for the populations of Asian countries because rice is a major staple in their diet. However, the available data on these element responses to high [CO_2] for rice are rather limited and contradictory. In the report of Seneweera and Conroy (1997), rice plants were grown in a very low P status soil and different rates of P fertiliser were applied, the concentration of Zn in BR decreased on average about 15% while that of Fe decreased over 60%, the effects being more pronounced at low to medium P addition for Zn and higher P addition for Fe. However, In a FACE study conducted under

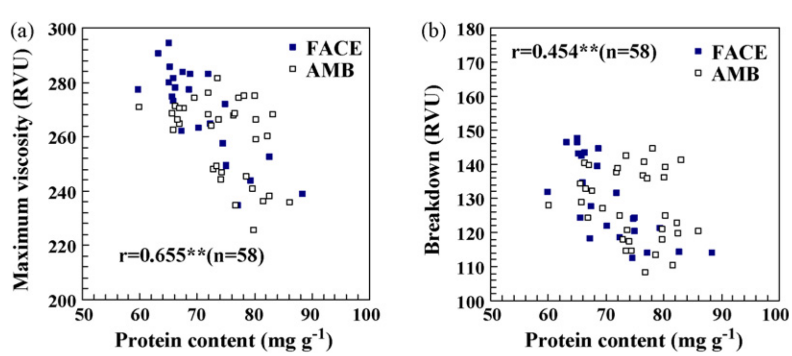

Fig. 5. The relationships between (a) maximum viscosity or (b) breakdown in RVA profile and protein concentration in milled rice for each combination of year × CO_2 × N × block (in 2001–2003). The ambient daytime CO_2 levels were about 370 μmol mol^{-1} (open squares), while CO_2 levels were controlled at 200 μmol mol^{-1} above ambient in the FACE plots (closed squares). N application rates were 15, 25, 35 g N m^{-2}, respectively. First degree polynomial fitted for all treatments combined; r is shown.

very high P application rates (30 or 48 g P_2O_5 m^2 was applied), Lieffering et al. (2004) reported that Zn and Fe concentrations in rice grains showed strong tendency to increase by elevated [CO_2] with a significant CO_2 effect on Fe recorded in one season. Our field FACE experiments, conducted under relatively low P availabilities (3.5 or 7 g P_2O_5 m^2 was applied), indicated that both of them showed no significant change with a decreasing trend for Fe (Table 2, Fig. 3c and d). As for Cu concentration, Lieffering et al. (2004) reported a clear increasing trend under FACE, though no significant response was detected. However, in the present investigation, we not only detected a marked decrease in brown rice (Table 2, Fig. 3b), but also in other parts of plants (data not shown), with the relative degree of reduction consistent over three growing seasons. We hypothesize that, these inconsistencies noted above showed the potentially complex nature of the CO_2 effect on elemental concentrations, which could be attributed to complex interactions between the uptake elements at different availability and mobility under varied experimental conditions (include varieties, soil type and weather). Further studies are needed to investigate these interactions to encourage selection of cultivars with enhanced uptake efficiency of desirable elements in elevated-CO_2 environments.

4.5. Interactive effects of [CO_2] and N on grain yield and quality

Limited studies on rice growth and yield (Ziska et al., 1996b; Kim et al., 2003a,b) have shown that the effect of [CO_2] is significantly influenced by N supply under relatively low N addition rates (0–20 g N m^{-2}, or 4–15 g N m^{-2}); however, in a same FACE experiment as reported herein, we previously reported that (Yang et al., 2006b, 2007), for the most part, no interactive effects of [CO_2] and N supply was detected for rice growth and yield under relatively high N addition rate (15–35 g N m^{-2}). Consistent with these results, the present study demonstrated that, with exception of HRP, no synergistic effect was detected between [CO_2] and N with respect to all other grain quality traits measured (Table 2), as well as yield of BR, MR and HR (Table 3), reinforcing that, under higher soil N availability (15–35 g N m^{-2}), the interactive effect between elevated [CO_2] and N supply is not important as compared with the first order main effects of the CO_2 itself.

5. Conclusions

Using a long-duration rice japonica with large panicle, we conducted the comprehensive investigation on grain quality response to elevated [CO_2] at a range of N availabilities in what we believe to be the first such report for rice crops. Overall, the results presented here indicate that FACE has a consistent and substantial impact on both grain yield and quality across the three growth seasons (2001–2003). FACE significantly increased yield of PR, BR and MR while decreasing HR yield. Measurements of physical quality attributes indicated that rice grains from high-CO_2-grown plants would be characterized by lower hardness which could make the rice more prone to breakage during milling, as suggested by a significant decrease in MRP, HRP, and a significant increase in CGP and CD. Measurements of cooking/eating quality suggests the starch in rice grown under elevated [CO_2] gelatinizes more easily and exhibits higher viscosity and elasticity, as indicated by the significant decreases in AC and SB, and increases in PV and BD in RVA profile, which are favorable changes for enhancing the palatability of rice. However, the nutritive value of grains was negatively influenced by FACE due to a reduction in PC and Cu concentration in milled rice. With respect to rice responses to N supply, overall, N had pronounced influence on yield of RR, BR, MR and HR with maximum value occurring at medium N application, whereas grain quality was less responsive to N, showing trends of higher chalkiness and worse eating/cooking quality at HN compared with MN and LN. Surprisingly, however, all CO_2 responses (except for HRP response) were all independent of N fertilization.

These data presented here in conjunction with pervious relevant studies have important implications for both N management and variety selection in a future high CO_2 environment.

With respect to N strategies, in order to achieve maximum productivity while maintaining desirable quality characteristics, the current recommended rates of N fertilization (ca. 25 g N m^2 in China) for rice production systems should not be modified as the [CO_2] rise, at least for the similar conditions of this experiment. Excessive N supply would not only reduce the rice yield (Table 3) and quality (Figs. 2 and 3) (Ling et al., 1994; Matsue et al., 1997), but also induce bad environmental pollution (Ling et al., 1994). However, in order to take full advantage of strong N uptake capacity during the early growth stage and facilitate N uptake during the middle and late growth stages, the proportion of N application should be altered: the proportion of N applied after panicle initiation (i.e., the ratio of ear-grain fertilizer to base-tillering fertilizer) may need to be higher than current recommendations (Yang et al., 2007). Under relatively higher N availability, proper increase in N fertilizer proportion after panicle initiation is not only beneficial to grain yield formation (Ling et al., 1994; Perez et al., 1996), but also to some aspects of grain quality (e.g., milling quality, appearance quality and protein content) (Ling et al., 1994).

Both experiments cited here (Seneweera et al., 1996; Seneweera and Conroy, 1997; Terao et al., 2005) and our experiment exhibited obvious inconsistency in responses to increasing [CO_2] with respect to some aspects of grain quality (e.g., AC, starch-pasting properties and elemental concentrations), probably reflecting strong interactions between [CO_2] and varieties on rice quality. Preliminary results from a 4-variety experiment conducted currently using Chinese rice FACE platform further confirmed such hypothesis (Y. Wang, unpublished data). With respect to yield responses to elevated [CO_2], sufficient intraspecific variation among cultivars have been clearly demonstrated in glasshouses by Ziska et al. (1996a), who showed that the response to high [CO_2] of 17 different rice cultivars varied between 30% and 400%. Experiments with different rice cultivars in chambers (Moya et al., 1998; Baker, 2004) also presented clear genotype-dependent effects of elevated [CO_2] on grain yield. Integrating these findings, we consider that not only is more field work required to investigate the iterative effect between elevated [CO_2] and fertilizer management (such as N, P and K), but research aimed at selecting desirable cultivars which show optimal responses of both grain yield and quality under realistic field conditions should be a top priority, in order to get the full benefit of expected future increases in atmospheric [CO_2].

Acknowledgements

This work was funded jointly by the National Natural Science Foundation of China (Grants Nos. 30671226, 30270777, 30471013, 40231003), and the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KZCX3-SW-440). Authors express their appreciation to Yuhua Shan, Jian Hu and Juan Zhou for their fruitful technical assistance and field observation. Thanks are also owed to the Japan National Institute for Agro-Environmental Sciences (NIAES) and the Japan Agricultural Research Centre for Tohoku Region (NARCT) for establishing the FACE facilities.

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