

Combined effects of elevated [CO₂] and high temperature on leaf mineral balance in *Coffea* spp. plants

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Abstract Modelling studies predicted that climate change will have strong impacts on the coffee crop, although no information on the effective impact of elevated CO₂ on this plant exists. Here, we aim at providing a first glimpse on the effect of the combined impact of enhanced [CO₂] and high temperature on the leaf mineral content and balance on this important tropical crop. Potted plants from two genotypes of *Coffea arabica* (cv. Icatu and IPR 108) and one from *C. canephora* (cv. Conilon Clone 153) were grown under 380 or 700 μL CO₂ L⁻¹ air, for 1 year, after which were exposed to an stepwise increase in temperature from 25/20 °C (day/night) up to 42/34 °C, over 8 weeks. Leaf macro-(N, P, K, Ca, Mg, S) and micronutrients (B, Cu, Fe, Mn, Zn) concentrations were analyzed at 25/20 °C (control), 31/25 °C, 37/30 °C and 42/34 °C. At the control temperature, the 700 μL L⁻¹ grown plants showed a moderate dilution effect (between 7 % and 25 %) in CL 153 (for N, Mg, Ca, Fe) and Icatu (for N, K and Fe), but not in IPR 108 (except for Fe) when compared to the 380 μL L⁻¹ plants. For temperatures higher than control most nutrients tended to increase, frequently presenting maximal contents at 42/34 °C (or 37/30 °C), although the relation between [CO₂] treatments did not appreciably change. Such increases offset the few dilution effects observed under high growth [CO₂] at 25/20 °C. No clear species responses were found considering [CO₂] and temperature impacts, although IPR 108 seemed less sensitive to [CO₂]. Despite the changes promoted by [CO₂] and heat, the large majority of mineral ratios were

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kept within a range considered adequate, suggesting that this plant can maintain mineral balances in a context of climate changes and global warming.

Abbreviations

A_{\max}	Photosynthetic capacity
P_n	Net photosynthetic rate
PSII	Photosystem II
RuBisCO	Ribulose-1,5-bisphosphate carboxylase/oxygenase
WUE	Water use efficiency.

1 Introduction

Over the past 800,000 years, atmospheric $[\text{CO}_2]$ changed between 180 (glacial periods) and 280 $\mu\text{L CO}_2 \text{ L}^{-1}$ (interglacial periods). Yet, from the pre-industrial period until 2013 the atmosphere $[\text{CO}_2]$ strongly increased *ca.* 43 %, from about 280 up to 400 $\mu\text{L L}^{-1}$, and, depending on future scenarios of anthropogenic emissions, further increases of $[\text{CO}_2]$ are expected, to values between 450 and 600 $\mu\text{L L}^{-1}$ by the year 2050 and between 730 and 1020 $\mu\text{L L}^{-1}$ by 2,100. That is predicted to be accompanied by a global warming between 1.4 and 5.8 °C by the end of the present century (IPCC. Climate change 2007).

The actual $[\text{CO}_2]$ in the atmosphere is below the optimal for photosynthesis of C_3 crops. Therefore leaf photosynthesis has a potential to increase in response to $[\text{CO}_2]$ enhancement (Zhu et al. 2012). In fact, the stimulation of P_n , often above 50 %, has widely reported, resulting from a simultaneous higher carboxylation rate of RuBisCO due to increased substrate availability and a competitive inhibition to O_2 , reducing the oxygenation rate and subsequently decreasing the CO_2 loss and energy costs associated with the flux of 2PG through the photorespiratory pathway (Sage 1994; Long et al. 2004; Ainsworth and Rogers 2007; Kirschbaum 2011). On the other hand, supra-optimal temperatures have impacts on plant growth and metabolism by changing the stomatal conductance and energy use, modifying the thylakoid structure and gas diffusion within the mesophyll (Lambers et al. 2008), reducing the net C-gain in C_3 species, due to a higher proportional increase in photorespiration than in photosynthesis (Long 1991), and, ultimately, impairing the Calvin cycle activity (Pastenes and Horton 1996). Therefore, by reducing photorespiration, air CO_2 enrichment is expected to increase photosynthesis more at high than at low temperatures, thus, at least partially, offsetting the effects of supra-optimal temperatures on yield (Long 1991; Polley 2002).

The impact of enhanced $[\text{CO}_2]$ on plant productivity and growth has been often explored in conjunction with alterations in photosynthesis, respiration and carbon use and allocation (Luo et al. 1999; Zhu et al. 2012), whereas the corresponding modifications in mineral composition (with the exception of nitrogen) has received much less attention (Thiec et al. 1995; Roberntz and Linder 1999; Blank et al. 2011). It was suggested that the main impacts related to the nutrient maintenance or decrease in leaf tissues under enhanced $[\text{CO}_2]$ include, among others, the regulation of the photosynthetic apparatus (e.g., with influence in N, S and Fe), the increase of enzyme activity (e.g., on K, P, Mn and Fe), changes of redox reactions (e.g., on Fe, Zn e Cu), and on the storage of energy and maintenance of structural integrity of chloroplast membranes (e.g., B) (Overdieck1993; Manderscheid et al. 1995; Fangmeier et al. 1997; Leakey et al. 2009; Blank et al. 2011). Changes in mineral contents may affect the plant development itself, but could also impact the human and animal nutrition, herbivory, litter decomposition rates, vegetation combustibility, etc. (Blank et al. 2011).

Leaf mineral nutrient concentrations are frequently found to decline in the biomass in response to enhanced atmospheric [CO₂] exposure. This was largely attributed to higher growth rates, but also to increased amounts of non-structural carbohydrates (mainly starch), to lower leaf transpiration rates, or to changes in the nutrient allocation patterns (Conroy and Hocking 1993; Ceulemans and Mousseau 1994; Thiec et al. 1995; Cotrufo et al. 1998). Still, such dilution effect might represent a qualitative physiological change rather than a lack of nutrient availability (Thiec et al. 1995), as often the total absorbed mineral amounts increase with the enhanced growth under high [CO₂] (Overdieck 1993).

Studies dealing with nutrients focused mostly the N decrease and the C/N ratio rise (Conroy and Hocking 1993; Cotrufo et al. 1998; Taub and Wang 2008; Blank et al. 2011). Yet, reductions of several other minerals have also been reported, as K, Ca, Mg, Mn, Fe in herbaceous and woody species (Overdieck 1993), P, K, Ca, S, Na, Al, Cu, Fe, Mn, Zn and Sr in herbarium samples (Penuelas and Matamala 1993), in the macronutrients N, P, K, Mg, S and Ca in *Picea abies* (Roberntz and Linder 1999) and in N, P, Ca and Mn (but not in P, Mg and S) in *Quercus rubra* (Thiec et al. 1995). Thus, taking into account the importance of mineral concentrations and balance to virtually all biological processes, the understanding of mineral impact of growth [CO₂] is of crucial importance.

Coffee, a tropical crop grown in approximately 80 countries, it is one of the world's most traded agricultural products. Together, two species, *C. arabica* L. and *C. canephora* Pierre ex A. Froehner, are responsible for ca. 99 % of world coffee bean production, constituting the economic basis of many tropical developing countries (DaMatta and Ramalho 2006; Partelli et al. 2011; Davis et al. 2012). Optimal annual mean temperatures to plant development are between 18 and 23 °C for *C. arabica*, and between 22 and 26 °C (or even 30 °C) for *C. canephora* (DaMatta and Ramalho 2006; DaMatta et al. 2007). With annual mean temperature above 23 °C the development and ripening of Arabica coffee fruits are accelerated, often leading to loss of beverage quality, whereas high temperature during blossoming, especially if associated with a prolonged dry season, may cause abortion of flowers (Camargo 1985). Temperatures up to 30 °C are needed for floral bud initiation, but their development, as well as fruit growth should occur at values around 23/17 °C (Camargo 1985). Therefore, the coffee tree growth and fruit production are closely related to natural climatic conditions, with particular relevance to extreme temperatures and water availability conditions (DaMatta and Ramalho 2006; Camargo 2010; Davis et al. 2012). Not surprisingly, studies addressing global warming have predicted dramatic effects on this crop that might threaten the world's coffee supply, as it were estimated heavy losses of yield (Gay et al. 2006), suitable areas (Assad et al. 2004) and genetic variability due to extinction of *C. arabica* wild populations (Davis et al. 2012). Nevertheless, such estimates neglected possible mitigating effects of the enhanced atmospheric [CO₂] on the adverse impacts of elevated temperatures. Moreover, the recognized ability of some coffee genotypes to metabolically adjust to harsh environmental constraints of temperature, irradiance, water and nutrients (Ramalho et al. 1999; DaMatta and Ramalho 2006; Fortunato et al. 2010; Batista-Santos et al. 2011; Scotti-Campos et al. 2014) should also be taken into account, including their mineral dynamics (Ramalho et al. 2013b). For instance, in contrast to early works claiming that coffee photosynthesis is quite sensitive to temperatures above 20–25 °C, by gradually rising temperature and considering a sufficiently long acclimation time, *C. arabica* plants showed P_n increases up to 30 °C, whereas A_{max} was observed to be maintained up to 35 °C for both *C. arabica* and *C. canephora* plants (DaMatta and Ramalho 2006). Therefore, the photosynthetic apparatus seems to display some tolerance to elevated temperatures, which agrees with the high field productivity in tropical environments, where leaf temperature easily reaches values above 40 °C along the day, especially in the outer leaves of the canopy (DaMatta and Ramalho 2006).

Despite the agronomic importance of the coffee crop, only recently the effects of enhanced growth [CO_2] on the coffee physiology begun to be addressed (Ramalho et al. 2013a), but until now there is no information on the impact of the combined elevated [CO_2] and temperature, namely, on the mineral nutrient contents and dynamics. Such information is of utmost importance, namely because the maintenance of adequate mineral availability to the plant, and in the leaves, is crucial to the ongoing vegetative and reproductive development, affecting bean yield and quality (Malavolta 1993). Furthermore, fertilization has been considered as a mitigating strategy of climate changes, mostly because the higher CO_2 availability acts as a C-fertilization. This can modify the C/N ratio and the relation with other nutrients in the biomass, with implications on plant fertilizer management (Thiec et al. 1995) to better take advantage from the higher C-availability without other minerals limitation.

This work aims at giving the first insights on the interacting effect of atmospheric CO_2 and temperature on the leaf mineral dynamics and balance, on a context of predicted climate changes and global warming, using three genotypes with agronomic importance from the two main producing species, *C. arabica* and *C. canephora*.

2 Materials and methods

2.1 Plant material and experimental design

Three genotypes with agronomic importance from the two main producing species were used. The experimental design and plant growth conditions were based in Ramalho et al. (2013a). Potted plants of 1.5 years old from *C. arabica* L. (cv. Icatu and cv. Catucaí IPR 108) and *C. canephora* Pierre ex Froehner cv. Conilon Clone 153 (CL 153), grown in 12 L pots, were transferred from a greenhouse (ambient [CO_2]) into walk-in growth chambers (EHHF 10,000, ARALAB, Portugal) and placed in 26 L pots. The plants were then grown under environmental controlled conditions of temperature (25/20 °C, day/night), RH (75 %), irradiance (ca. 700–800 $\mu\text{mol m}^{-2} \text{s}^{-1}$), photoperiod (11.5 h) and two CO_2 concentrations (380 or 700 $\mu\text{L L}^{-1}$) on a long term basis (ca. one year). Each of the 10 plants per genotype and [CO_2] treatment was fed on a monthly basis with 5 g of the following fertilizer mixture: 7 % Ca (NO_3)₂, 5 % KNO_3 , 7.8 % P_2O_5 , 17 % K_2O , 1.6 % MgO , 20 % MgSO_4 , 0.02 % H_3BO_3 and 0.01 % ZnSO_4 . To reinforce the N and Ca availability, a complementary fertilization of 2 g was done every 3 months with a mixture of 27 % NH_4NO_3 and 6 % CaO . Both fertilizers were provided as solid spheres that slowly dissolved over successive watering, allowing a gradual release of minerals to the soil/plant. To improve micronutrient availability, 500 mL of a solution containing 0.02 % Fe-EDTA, 0.01 % CuSO_4 , 0.01 % MnCl_2 , and 0.005 % H_2MoO_2 , were added on a monthly basis.

After one year, the plants were exposed to a gradual temperature rise (0.5 °C per day), in order to allow the expression of acclimation capability, from 25/20 °C up to 42/35 °C (day/night), with a six/seven day permanence at 31/25, 37/30 and 42/35 °C, to allow the programmed data collection, taking ca. eight weeks until the end of the experiment. All the other environmental conditions were maintained as described above, including the two air [CO_2] (380 or 700 $\mu\text{L L}^{-1}$). The plants were grown without water, nutrient or root development restrictions, the latter as judged by visual examination by the end of the experiment when plants were removed from pots.

The experiment was set up using a 2×4×3 factorial distribution with 10 replicates (one plant per pot), being the factors: two growth [CO_2] levels (380 or 700 $\mu\text{L L}^{-1}$), four temperature levels (25/20, 31/25, 37/30 and 42/34 °C) and three coffee genotypes.

2.2 Leaf sampling

All samples were taken from recently mature leaves, fully developed under each [CO₂], from the light exposed top branches (both plagiotropic and orthotropic), after *ca.* 2 hours of illumination, from 8 to 10 plants of each treatment and genotype, by the third/fourth day of exposure to each of the studied temperature levels.

2.3 Tissue nutrient analysis

The leaf samples were dried at 65 °C, until constant weight was reached (*ca.* 48 h), and reduced to powder (using a mill CIENLAB CE-430; 8 blades, 1,725 rpm, 20 mesh size).

To quantify the P, K, Ca, Mg, S, Cu, Fe, Mn and Zn contents, *ca.* 400 mg aliquots (dry weight), were submitted to a nitric-perchloric digestion (65 % and 70 %) followed by analysis through atomic absorption spectrometry (VARIAN AA-240-FS, [Agilent Technologies](#), USA) (EMBRAPA-Empresa Brasileira De Pesquisa 1997).

Total nitrogen concentration was determined in 100 mg aliquots (dry weight), by the micro Kjeldahl method. Digestion was performed in 5 mL of H₂SO₄ (a mixture of potassium sulphate and red mercuric oxide, 1:10, w/w, was used as catalyst and salicylic acid was included to reduce nitrate) (Vogel 1961), as previously optimized for coffee (Ramalho et al. 1999).

For B quantification, *ca.* 200 mg aliquots (dry weight) were used, to which 2 mL of 40 mM ammonium acetate buffer containing 7.5 % EDTA (w/v), and 2 mL of a solution of 10 mM azomethine-H to promote the reaction were added. After agitation the samples were left for 30 min and the B quantification was performed spectrophotometrically (420 nm, a 25 °C), using a standard curve of B, following Bataglia et al. (1983).

All determinations were performed in triplicates.

2.4 Statistical analysis

The data were subjected to a two-way ANOVA ($p \leq 0.05$), considering the factors genotype and [CO₂], after which a Tukey test ($p \leq 0.05$) was applied for mean comparison, as the two-way ANOVA for macronutrients (N, P, K, Ca, Mg and S) and micronutrients (B, Cu, Fe, Mn and Zn) revealed significant interaction between all treatments.

3 Results

3.1 Impact of enhanced growth [CO₂] on leaf mineral contents irrespective of temperature

Globally, under control temperature (25/20 °C, day/night) the leaf macronutrient contents varied significantly in a genotype-dependent basis (Table 1). Under control temperature conditions, significant reductions under enhanced [CO₂] were noted for N (7.5 % in CL 153 and 16 % in Icatu), K (24 % in Icatu), and Mg and Ca (24 % and 18 %, respectively, CL 153) (Table 1), whereas IPR108 did not significantly respond to [CO₂].

With the exposure to higher temperatures, the macronutrients N and K stand out when comparing the growth [CO₂] levels. Upon 700 $\mu\text{L L}^{-1}$ leaf N content tended to lower values irrespective of temperature and genotype. Such decreases were significant for all temperatures in CL 153 (up to 11 %), in IPR 108 at 31/25 °C and 37/30 °C (*ca.* 7 %) and in Icatu at 42/34 °C (6 %). Still above 25/20 °C, K showed also significant reductions in CL 153 in all temperatures, between 14 and 18 %, in Icatu at 31/25 °C (19 %) and 37/30 °C (7 %), and in IPR108 at

Table 1 Leaf macronutrient contents (mg g⁻¹, dry weight) in *C. arabica* (Icatu and IPR 108) and *C. canephora* (Conilon CL 153) grown at either 380 or 700 μL CO₂ L⁻¹, at 25/20; 31/25; 37/30; 42/34 °C, (day/night). Each value represents the mean of ten replicates

Genotypes [CO ₂]	CL 153		Icatu		IPR 108	
	380 μL L ⁻¹	700 μL L ⁻¹	380 μL L ⁻¹	700 μL L ⁻¹	380 μL L ⁻¹	700 μL L ⁻¹
25/20 °C						
N (mg g ⁻¹)	34.28 aA	31.72 bB	37.13 aA	31.13 bB	36.45 aA	36.22 aA
P (mg g ⁻¹)	1.35 aA	1.46 aA	1.29 aA	1.04 aA	1.74 aA	1.64 aA
K (mg g ⁻¹)	18.98 aA	17.53 aAB	18.54 aA	14.08 bB	18.49 aA	19.25 aA
Ca (mg g ⁻¹)	13.52 aA	11.07 bA	9.75 aB	10.42 aA	8.05 aB	8.60 aA
Mg (mg g ⁻¹)	2.22 aA	1.68 bA	1.83 aA	1.53 aA	1.94 aA	1.77 aA
S (mg g ⁻¹)	1.99 aA	1.86 aA	2.19 aA	1.83 aA	2.14 aA	2.12 aA
31/25 °C						
N (mg g ⁻¹)	38.51 aA	34.29 bA	36.86 aA	34.68 aA	36.73 aA	34.19 bA
P (mg g ⁻¹)	1.35 aA	1.38 aA	1.27 aA	1.22 aA	1.71 aA	1.59 aA
K (mg g ⁻¹)	21.85 aA	17.97 bA	20.65 aA	16.78 bB	18.35 aA	19.07 aA
Ca (mg g ⁻¹)	10.78 bA	13.22 aA	10.74 aA	11.2 aAB	10.62 aA	9.55 aB
Mg (mg g ⁻¹)	2.22 aA	1.79 aA	2.17 aA	2.03 aA	2.40 aA	1.95 aA
S (mg g ⁻¹)	2.27 aA	2.01 aA	2.17 aA	2.04 aA	2.15 aA	2.07 aA
37/30 °C						
N (mg g ⁻¹)	39.61 aA	35.12 bA	38.41 aA	37.29 aA	38.56 aA	35.76 bA
P (mg g ⁻¹)	1.26 aA	1.18 aA	1.51 aA	1.21 aA	1.71 aA	1.24 aA
K (mg g ⁻¹)	24.92 aA	21.43 bA	23.57 aA	21.97 bA	22.03 aA	16.80 bB
Ca (mg g ⁻¹)	11.03 aA	12.26 aA	11.12 aA	12.19 aA	10.01 aA	10.26 aA
Mg (mg g ⁻¹)	2.48 aA	2.25 aA	2.94 aA	2.69 aA	2.80 aA	2.36 bA
S (mg g ⁻¹)	2.32 aA	2.06 aA	2.25 aA	2.20 aA	2.25 aA	2.10 aA
42/34 °C						
N (mg g ⁻¹)	40.84 aA	37.80 bA	41.32 aA	38.75 bA	41.69 aA	39.49 aA
P (mg g ⁻¹)	1.15 aA	1.01 aA	1.52 aA	1.26 aA	1.78 aA	1.43 aA
K (mg g ⁻¹)	24.72 aA	20.88 bB	25.23 aA	24.88 aA	26.39 aA	21.12 bB
Ca (mg g ⁻¹)	11.67 aA	10.54 aA	12.31 aA	12.97 aA	11.65 aA	10.84 aA
Mg (mg g ⁻¹)	2.85 aA	2.80 aA	3.18 aA	3.16 aA	3.31 aA	3.07 aA
S (mg g ⁻¹)	2.41 aA	2.23 aA	2.42 aA	2.30 aA	2.44 aA	2.32 aA

Different letters express significant differences between CO₂ treatments within the same genotype (a, b), or between genotypes within the same CO₂ treatment (A, B, C), after a mean comparison using a Tukey test at 5 % of probability.

the two highest ones (*ca.* 20–24 %). For the remaining macronutrients, only a few modifications were detected, with an Mg reduction at 37/30 °C in IPR 108, and a Ca increase at 31/25 °C in CL 153 (Table 1).

With regard to the leaf micronutrients, under control temperature B, Mn and Zn contents did not change significantly due to the enhanced [CO₂] in either genotype (Table 2). In contrast, Cu increased in CL 153 (7 %) and Icatu (12 %) and decreased in IPR 108 (16 %), whereas, Fe content diminished in all genotypes upon high [CO₂], ranging from 10 % (Icatu) to 25 % (CL 153). Notably, the contents of both Cu and Fe changed significantly under other temperatures. Under the moderate high temperature of 31/25 °C, Cu and Fe decreased in all

genotypes, but at 42/34 °C Cu was higher in the plants at 700 $\mu\text{L L}^{-1}$ in IPR 108 (12 %) and increased as much as 56 % in CL 153. Fe tended to decrease at 31/25 °C and 37/30 °C in all genotypes under enhanced $[\text{CO}_2]$. These differences were absent at 42/34 °C, mostly, because Fe content in the plants grown at 380 $\mu\text{L L}^{-1}$ tend to lower values, approaching those of the plants grown at 700 $\mu\text{L L}^{-1}$. Regarding other micronutrients, B content was lower under high $[\text{CO}_2]$ conditions in all increased temperatures in CL 153 (ca. 9–14 %), 37/30 °C for IPR 108 and 42/34 °C for Icatu. Mn tended to higher values in enhanced $[\text{CO}_2]$ at the two highest temperatures, particularly at 37/30 °C in the *C. arabica* genotypes, Icatu (21 %) and IPR 108 (30 %), which was mostly related to an effective rise in leaf Mn content in the 700 $\mu\text{L L}^{-1}$ plants. Zn contents differed minimally, if any, in each genotype (Table 2).

3.2 Changes in leaf mineral contents due to temperature increase on both growth $[\text{CO}_2]$

Overall, there were no significant differences in the macronutrients contents among the genotypes grown at 380 $\mu\text{L L}^{-1}$ at 25/20 °C, with the exception for Ca that displayed a higher content in CL 153. This pattern was closely followed for all the genotypes grown at high $[\text{CO}_2]$, with the exceptions of N (higher in IPR 108) and K (lower in Icatu).

The above described pattern was similar for 31/25, 37/30 and 42/34 °C given that no differences could be found among genotypes for all macronutrients at 380 $\mu\text{L L}^{-1}$. In the plants grown under enhanced $[\text{CO}_2]$, little differences were found, mostly restricted to K, but Icatu evolved from the lowest (25/20 °C) to the highest (42/34 °C) content among genotypes due to a considerable (76 %) gradual K rise.

The coffee genotypes globally revealed a tendency for increased macronutrients contents with the increasing temperature. In fact, irrespective of growth $[\text{CO}_2]$, macronutrient values generally peaked at the highest temperature treatments (Table 1). This pattern was clear in the *C. arabica* genotypes (Icatu and IPR 108) in which only the P content in IPR 108, grown under 700 $\mu\text{L L}^{-1}$, did not show a maximal value at 42/34 °C. The CL 153 displayed the highest K contents (at both $[\text{CO}_2]$) at 37/30 °C, although close to those observed at 42/34 °C. The other exceptions were noted in CL 153 that peaked at control for P for both growth $[\text{CO}_2]$ and for Ca that showed the highest contents at control (380 $\mu\text{L CO}_2 \text{ L}^{-1}$) or 31/25 °C (700 $\mu\text{L CO}_2 \text{ L}^{-1}$) (Table 1).

Concerning the micronutrients, under control temperature and ambient $[\text{CO}_2]$, CL 153 and IPR 108 displayed the highest contents of B, Cu and Fe (except for Cu in IPR 108) and Icatu the lowest ones. Under high $[\text{CO}_2]$ conditions CL 153 and IPR 108 still showed higher mineral contents, except for Cu in IPR 108 and Fe (for which all genotypes displayed similar contents). The Mn and Zn contents did not differ significantly among genotypes, irrespective of $[\text{CO}_2]$.

As for the case of macronutrients, almost all maximal absolute micronutrient contents peaked at the two highest temperatures, irrespective of growth $[\text{CO}_2]$. Indeed, at temperatures higher than control and for ambient CO_2 , the highest contents of B, Cu, and Fe gradually shifted from CL 153 and IPR 108 to Icatu that showed the maximum contents of those minerals at 42/34 °C (except for Fe). For the plants grown under enhanced $[\text{CO}_2]$ the changes of these minerals with temperature rise were not so clear. Yet, maximal values for B, Cu, and Fe were found at 37/30 or 42/34 °C (except Cu in IPR 108). The more obvious example was observed in Icatu plants grown under 700 $\mu\text{L CO}_2 \text{ L}^{-1}$, which showed maximal contents of all micronutrient at 42/34 °C, although with similar or lower levels than those observed under 380 $\mu\text{L CO}_2 \text{ L}^{-1}$ (Table 2).

In what concerns Mn and Zn, only at the extreme temperature of 42/34 °C some differences between genotypes arise. Mn tended to be higher in CL 153 in both growth $[\text{CO}_2]$, whereas Zn was particularly high in Icatu at 380 $\mu\text{L CO}_2 \text{ L}^{-1}$.

Table 2 Leaf micronutrient contents ($\mu\text{g g}^{-1}$, dry weight) in *C. arabica* (Icatu and IPR 108) and *C. canephora* (Comilon CL 153) grown at 380 or 700 $\mu\text{L CO}_2 \text{ L}^{-1}$, at 25/20; 31/25; 37/30; 42/34 $^{\circ}\text{C}$, (day/night). Each value represents the mean of ten replicates.

Genotypes	CL 153		Icatu		IPR 108	
	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$
[CO ₂]						
	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$
	25/20 $^{\circ}\text{C}$					
B ($\mu\text{g g}^{-1}$)	59.55 aA	58.59 aA	54.70 aB	53.61 aB	59.63 aA	58.30 aA
Cu ($\mu\text{g g}^{-1}$)	18.74 bA	20.14 aA	14.56 bB	16.31 aB	13.73 aB	11.47 bC
Fe ($\mu\text{g g}^{-1}$)	23.34 aA	17.39 bA	19.73 aB	17.64 bA	24.15 aA	19.25 bA
Mn ($\mu\text{g g}^{-1}$)	253 aA	216 aA	288 aA	298 aA	208 aA	220 aA
Zn ($\mu\text{g g}^{-1}$)	9.18 aA	9.00 aA	8.52 aA	8.24 aA	9.07 aA	9.02 aA
	31/25 $^{\circ}\text{C}$					
B ($\mu\text{g g}^{-1}$)	67.86 aA	58.92 bA	55.44 aB	54.76 aB	55.97 bB	59.73 aA
Cu ($\mu\text{g g}^{-1}$)	19.17 aB	14.55 bB	14.95 aC	12.78 bB	30.4 aA	24.07 bA
Fe ($\mu\text{g g}^{-1}$)	22.52 aA	12.76 bC	24.61 aA	17.27 bB	25.06 aA	21.85 bA
Mn ($\mu\text{g g}^{-1}$)	286 aA	248 aA	291 aA	283 aA	214 aA	211 aA
Zn ($\mu\text{g g}^{-1}$)	10.58 aA	9.07 bA	8.68 aA	8.43 aA	8.64 aA	9.17 aA
	37/30 $^{\circ}\text{C}$					
B ($\mu\text{g g}^{-1}$)	73.69 aA	62.97 bA	57.97 aB	57.93 aB	60.65 bB	66.86 aA
Cu ($\mu\text{g g}^{-1}$)	16.77 bB	19.96 aA	14.05 aB	13.70 aB	23.69 aA	14.52 bB
Fe ($\mu\text{g g}^{-1}$)	21.98 aB	19.93 aA	24.69 aA	20.07 bA	25.38 aA	22.76 bA
Mn ($\mu\text{g g}^{-1}$)	314 aA	295 aA	253 bA	306 aA	220 bA	288 aA
Zn ($\mu\text{g g}^{-1}$)	11.03 aA	9.68 aA	9.07 aA	8.90 aA	9.28 aA	10.28 aA
	42/34 $^{\circ}\text{C}$					
B ($\mu\text{g g}^{-1}$)	69.80 aB	63.71 bB	76.57 aA	59.00 bB	59.49 bC	71.79 aA
Cu ($\mu\text{g g}^{-1}$)	19.74 bB	30.92 aA	23.96 aA	22.73 aB	13.31 bC	14.86 aC
Fe ($\mu\text{g g}^{-1}$)	18.38 aB	18.36 aB	21.78 aAB	21.01 aAB	25.01 aA	24.02 aA
Mn ($\mu\text{g g}^{-1}$)	355 aA	371 aA	272 aAB	307 aAB	234 aB	276 aB
Zn ($\mu\text{g g}^{-1}$)	10.84 aB	9.75 aAB	16.34 aA	9.06 bB	9.14 bB	11.07 aA

Different letters express significant differences between CO₂ treatments within the same genotype (a, b), or between genotypes within the same CO₂ treatment (A, B, C), after a mean comparison using a Tukey test at 5 % of probability.

The exceptions for these overall patterns were observed for Fe in CL 153 ($380 \mu\text{L CO}_2 \text{ L}^{-1}$) that showed maximal Fe contents at control temperature with a slow decrease with the increasing temperature, for Mn in Icatu ($380 \mu\text{L CO}_2 \text{ L}^{-1}$) and Cu for IPR 108 (both $[\text{CO}_2]$) that presented, respectively, the highest Mn and Cu contents at $31/25 \text{ }^\circ\text{C}$.

3.3 Elevation of $[\text{CO}_2]$ and temperature promote changes in the relationships between leaf minerals

The modifications in the individual minerals, due to either growth $[\text{CO}_2]$ or temperature, showed a moderate impact on the balance between nutrients for the coffee crop, as highlighted in Table 3 for the control and the highest temperature regimens ($42/34 \text{ }^\circ\text{C}$). Under control temperature, the genotypes showed values for N/P (only for CL 153), N/S, N/Cu, P/Zn and B/Zn ratios close to those considered as adequate for this crop, whereas N/P (*C. arabica* genotypes), K/Mg and Cu/Zn ratios showed slightly higher values and Ca/Mn below what could be expected.

The impact of high temperature in some nutrient ratios differed among genotypes. The N/P increased in CL 153 and IPR 108 but not in Icatu. The N/S, P/Zn and B/Zn showed some changes but were maintained within adequate values. On the other hand, K/Mg was reduced irrespective of genotype and $[\text{CO}_2]$ (except in CL 153, $380 \mu\text{L CO}_2 \text{ L}^{-1}$) but was still at values higher than adequate. Also, the N/Cu ratio increased in CL 153 and IPR 108 at $380 \mu\text{L CO}_2 \text{ L}^{-1}$, but decreased at $700 \mu\text{L CO}_2 \text{ L}^{-1}$, similarly to Icatu on both $[\text{CO}_2]$.

The impact of growth $[\text{CO}_2]$ was also diverse. Some ratios (as N/S and B/Zn) were not affected at both temperatures and others were not affected only at control (Ca/Mn), whereas N/P tended to higher ratio values with enhanced growth $[\text{CO}_2]$.

4 Discussion

Foliage mineral content and specific ratios (balance) between some of them are often used to assess the nutritional status of plants or to explain visual symptoms, namely in coffee (Malavolta 1993; Bragança et al. 2007). Taking into account that our experiment took about 13.5 months under pot conditions, it seems crucial to evaluate the mineral plant availability through leaf contents. Considering the values at control temperature ($25/20 \text{ }^\circ\text{C}$), the macronutrient (N, P, K, Ca, Mg, S) levels were within a good range for this crop, although N on one side and P and Mg on the other were rather above and below of adequate, respectively. In what regards the micronutrients (B, Cu, Fe, Mn and Zn), only Fe might be considered below adequate levels (Malavolta 1993; Ramalho et al. 1995; Bragança et al. 2007; Guimarães and Reis 2010; Ramalho et al. 2013b). Therefore, as evaluated through visual observation and confirmed by leaf mineral contents, the plants had a suitable nutrient availability along the experimental period.

4.1 Impact of enhanced growth $[\text{CO}_2]$ on leaf mineral contents irrespective of temperature

Both herbaceous and woody species commonly present mineral nutrients changes overtime (e.g., in N, P, K, Mg, S, Ca) in response to enhanced atmospheric $[\text{CO}_2]$ (Overdieck 1993; Roberntz and Linder 1999; Blank et al. 2011). The recently mature leaves of the studied coffee genotypes, presented only moderate dilution effects under high $[\text{CO}_2]$ conditions at $25/20 \text{ }^\circ\text{C}$ on some macro- and micronutrients, notably, without changing its level of availability, what agrees with the good physiological performance under temperature control conditions observed in these plants (Ramalho et al. 2013a). Even the observed nutrient dilution may reflect qualitative physiological changes rather than a lack of nutrients (Thiec et al. 1995). In fact, CL

Table 3 Ratios between some leaf minerals in *C. arabica* (Icatu and IPR 108) and *C. canephora* (Conilon CL 153) grown either at 380 or 700 $\mu\text{L CO}_2 \text{ L}^{-1}$, at control (25/20 °C) and the highest (42/34 °C) temperatures. Values obtained directly from the mean values from tables 1 and 2.

[CO ₂]	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$	380 $\mu\text{L L}^{-1}$	700 $\mu\text{L L}^{-1}$
Temperature								
25/20 °C								
CL 153	N/P 25.4	21.7	N/S 17.2	17.1	N/Cu 1829.2	1,575	P/Zn 1.47.1	162.2
Icatu	28.8	29.9	17	17	2550.1	1908.6	151.4	126.2
IPR 108	20.9	22.1	17	17.1	2654.8	3157.8	191.8	181.8
42/34 °C								
CL 153	35.5	37.4	16.9	17	2068.9	1222.5	106.1	103.6
Icatu	27.2	30.8	17.1	16.8	1724.5	1704.8	93	139.1
IPR 108	23.4	27.6	17.1	17	3132.2	2657.5	194.7	129.2
25/20 °C	K/Mg		Ca/Mn		B/Zn		Cu/Zn	
CL 153	8.5	10.4	53.4	51.3	6.5	6.5	2	2.2
Icatu	10.1	9.2	33.9	35.0	6.4	6.5	1.7	2
IPR 108	9.5	10.9	38.7	39.1	6.5	6.5	1.85	1.3
42/34 °C								
CL 153	8.7	7.5	32.8	28.4	6.4	6.5	1.8	3.2
Icatu	7.9	7.9	45.2	42.2	4.6	6.5	1.5	2.5
IPR 108	8	6.9	49.7	39.3	6.5	6.5	1.65	1.3

Values considered adequate to coffee crop *C. arabica* / *C. canephora* cv. Conilon: N/P: 16–18/18–26; N/S: 16–18/12–16; N/Cu: 2,000–3,375/1,450–3,200; P/Zn: 125–187/80–160; K/Mg: 6.1–6.6/5–7; Ca/Mn: 66–75/12.5–25; B/Zn: 5.0–7.3/3.3–6; Cu/Zn: 1/0.7–2 (Malavolta 1993; Bragança et al. 2007).

153 showed decreases in N, Mg, Ca, Fe (between 7.5 % and 25 %), Icatu in N, K and Fe (between 10 and 24 %), whereas IPR 108 showed no significant changes for all macronutrients and reductions on Cu and Fe regarding micronutrients. Fe was the only nutrient that was significantly reduced in all coffee genotypes (between 10 % in Icatu and 25 % in CL 153). These results partially agree with those reports that noted an impact of high growth [CO₂] on micronutrients, with reductions between 10 and 30 %. Still, only a few minerals were modified in coffee plants, revealing a much lower extent than in other species, where reductions included a wider number of nutrients as Mn, Fe and Zn (Overdieck 1993; Manderscheid et al. 1995), Al, Cu, Sr, Fe, Mn, Na and Zn (Penuelas and Matamala 1993), Fe and Zn (Fangmeier et al. 1997) and Mn (Thiec et al. 1995).

The relatively low change extent of mineral contents might also be related to the unrestricted roots volume, water and nutrient supply conditions in the present experiment. The maintenance of root functioning would in turn allow to keep the sink strength for the enhanced photosynthate synthesis (which did not increase), coming from a higher photosynthetic functioning capacity (Ramalho et al. 2013a). Moreover, such enhanced photosynthetic functioning observed at 25/20 °C, together with the moderately lower (CL 153 and Icatu) or similar (IPR 108) N content would increase the photosynthetic nitrogen use efficiency (Leakey et al. 2009).

For the temperatures higher than control, 31/25 °C and 37/30 °C, N, K, Fe and Cu tended to lower values in all genotypes at 700 relatively to 380 μL L⁻¹. Still, upon the extreme 42/34 °C, almost all macronutrients (except N and K) showed close contents amongst [CO₂] levels. Notably, Mn tended to higher values in enhanced [CO₂] at the two highest temperatures in the *C. arabica* genotypes (Icatu and IPR 108), mostly, related to a rise in leaf Mn content in the 700 μL L⁻¹ plants. Due to the crucial role of Mn on PSII functioning, such increased levels might have contributed to the maintenance of higher levels of PSII activity at temperatures higher than control (data not shown) as observed in coffee leaves under cold conditions (Ramalho et al. 2013b).

Also, the increase in the growth [CO₂] and temperature did not modify the content order of macronutrients, as most cases maintained the order N>K>Ca>Mg>S>P (Table 1) and are close to those recommended for this crop (Malavolta 1993).

4.2 Changes in leaf mineral contents due to temperature increase on both growth [CO₂]

For temperatures higher than control an absence of differences between genotypes within each [CO₂] level was observed for almost all macronutrients. Ca (at 31/25 °C) and K (at all temperatures) were the exceptions, with Icatu starting the lowest K content at 25/20 °C and reaching the highest at 42/34 °C, related to a gradual K rise that paralleled the temperature enhancement. The changes in each *Coffea* spp. genotype along a gradual temperature increase, revealed a global tendency for macronutrient accumulation in the leaf tissues at higher temperatures when compared to control for almost all macronutrients (Table 1). In fact, irrespective of growth [CO₂], almost all absolute maximal macronutrient contents were found in the highest temperature, although some of them did not clearly differ from other temperatures (Table 1). That denotes a strong mineral dynamics/mobility in recently mature leaves in response to the temperature increase, with particular relevance to N. In fact, an increase in N content might have positive consequences, as coffee plants are highly N-demanding and an adequate content with N availability is decisive for development and yield (Carelli et al. 2006), as well as for the triggering of stress acclimation mechanisms, namely, to high irradiance (Ramalho et al. 1998; 2000).

Regarding the micronutrients contents, a comparison between genotypes showed that Icatu presented the lowest contents of B, Cu and Fe at 380 μL L⁻¹ and for B and Cu at 700 μL L⁻¹, whereas Mn and Zn contents did not differ between genotypes, at control temperature. Still, some changes occurred at higher temperatures for ambient CO₂ as the higher contents of B,

Cu, and Fe gradually shifted from CL 153 and IPR 108 to Icatu, which at 42/34 °C showed globally the highest values of those minerals (Table 2). For the plants grown under enhanced [CO₂] conditions, the trends showed by these minerals were not so clear. Still, as for macronutrients, with a few exceptions the maximal absolute values were also found when the plants were submitted to the two highest temperatures, irrespective of growth [CO₂]. Such increase in response to the rising temperature totally overcame the dilution of some minerals observed at 25/20 °C under high growth [CO₂] conditions, as most mineral concentrations reached values close (or above) those registered at control conditions (of temperature and CO₂). This effect of global mineral content rise at higher temperatures in the coffee plant follows the same dynamics referred above for macronutrients, and is in opposition with other studies that point to a decrease of mineral contents on leaf tissue justified by decreases of biomass and leaf area, as well as loss of photosynthetic functioning (Chen et al. 1982; Lambers et al. 2008; Waraich et al. 2012). However, several studies with coffee reported that temperatures somewhat above optimal might not implicate limitations on the photosynthetic metabolism, stomatal conductance, branch growth, leaf area persistence (Camargo 1985; DaMatta and Ramalho 2006; Amaral et al. 2006) and in bean production (Teixeira et al. 2013). Also, it was reported that the coffee plant might present higher rates of growth in periods of high temperature and rainfall (thus with large water availability), concomitantly with an enhancement of mineral absorption (Silva et al. 2004; Bragança et al. 2008). Furthermore, it should be taken into account that, in order to counteract the increased air temperature the coffee plants strongly increased their transpiration rates between 4 and 6 fold, to promote leaf cooling. Such higher transpiration flow might have in turn supported a higher mineral capture and translocation, linked also to an almost absence of limitations at the photosynthetic metabolism level until 37/30 °C (data not shown).

Notably, the maintenance of such a mineral dynamics under environmental conditions outside the optimal temperature range was earlier observed in coffee plants and was suggested to have an important role in the cold acclimation ability. That would be related to the minerals roles in the cell metabolism, with implications in the maintenance of photosynthetic performance and the reinforcement of the defense mechanisms against oxidative stress (e.g., Cu, Zn, Fe, Mn) generated under cold conditions, as well as due to a global plant vigor strengthening (e.g., N) (Ramalho et al. 2013b).

4.3 Elevation of [CO₂] and temperature promote changes in the leaf minerals relationships

The modifications in the individual mineral dynamic and its presence in leaf tissues, promoted both by growth [CO₂] and increased temperatures, had impact in some important balance between nutrients for coffee (Table 3), although no clear picture was depicted amongst genotypes. It is noteworthy that most of the ratios were in the range considered as adequate (N/P for CL 153, N/S, N/Cu, P/Zn and B/Zn) or close (K/Mg and Cu, Zn), for both species (Malavolta 1993; Bragança et al. 2007). Also, despite the above reported mineral drifts, the large majority of contents and ratios did not suffer a change in the level of adequacy relative to what was observed at 25/20 °C and 380 μL L⁻¹, and it seems acceptable to state that these ratios were globally irresponsive to temperature and growth [CO₂].

Therefore, knowing that most nutrient balances were kept and that the coffee plant would benefit from the increases of most minerals in leaf tissues under higher temperatures, it seems likely that the coffee plant could be suited to cope with the climatic changes and global warming conditions.

5 Conclusions

Globally, under adequate temperature (25/20 °C) the enhanced growth [CO₂] moderately changed the mineral accumulation pattern of a few minerals and their balance in the coffee leaves, with a dilution effect between 7 and 25 % (depending on the mineral) in *C. canephora* cv. Conilon CL 153 (reductions of N, Mg, Ca, Fe) and *C. arabica* cv. Icatu (reductions of N, K and Fe), but not in IPR 108 (except for Fe) plants. Despite those [CO₂]-promoted modifications, the nutrient levels were maintained within a range considered adequate for this crop (except for Fe), similar to that of 380 μL L⁻¹ plants.

With temperatures higher than control the relation between [CO₂] treatments did not appreciably change, but almost all macro and micronutrient tended to rise, presenting their maxima at 37/30 °C or 42/34 °C (particularly in the latter), what reveals a strong mineral dynamics in the recently mature leaves. Noteworthy, such increases observed at higher temperatures offset the dilution effect showed for some minerals under high growth [CO₂], as compared to the values at 380 μL L⁻¹ and 25/20 °C, considered as control. These changes implicated some adjustments in some mineral ratios (e.g., N/P increased) although not in others (e.g., N/S, B/Zn), but the large majority of contents and ratios was maintained in the same range observed at 25/20 °C and 380 μL CO₂ L⁻¹, considered adequate for the coffee plant, suggesting that the coffee plant could cope in some extent with the climatic changes and global warming.

Despite the reported modifications on mineral contents, no clear species dependent responses were found considering a long-term exposure to enhanced growth [CO₂] and temperature impacts, although IPR 108 seemed less sensitive to [CO₂].

Although field studies are required, the presented data, obtained without nutrient, water supply and root development restrictions, provide the first glimpse ever on the effect of the combined impact of enhanced [CO₂] and temperature on mineral leaf content and dynamics, raising questions with possible implications to fertilizer management for this important tropical crop, on a context of predicted climate changes and global warming.

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