

# CO<sub>2</sub> effects on plant nutrient concentration depend on plant functional group and available nitrogen: a meta-analysis

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**Abstract** Elevated CO<sub>2</sub> is expected to lower plant nutrient concentrations via carbohydrate dilution and increased nutrient use efficiency. Elevated CO<sub>2</sub> consistently lowers plant foliar nitrogen, but there is no consensus on CO<sub>2</sub> effects across the range of plant nutrients. We used meta-analysis to quantify elevated CO<sub>2</sub> effects on leaf, stem, root, and seed concentrations of B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn among four plant functional groups and two levels of N fertilization. CO<sub>2</sub> effects on plant nutrient concentration depended on the nutrient, plant group, tissue, and N status. CO<sub>2</sub> reduced B, Cu, Fe, and Mg, but increased

Mn concentration in the leaves of N<sub>2</sub> fixers. Elevated CO<sub>2</sub> increased Cu, Fe, and Zn, but lowered Mn concentration in grass leaves. Tree leaf responses were strongly related to N status: CO<sub>2</sub> significantly decreased Cu, Fe, Mg, and S at high N, but only Fe at low N. Elevated CO<sub>2</sub> decreased Mg and Zn in crop leaves grown with high N, and Mn at low N. Nutrient concentrations in crop roots were not affected by CO<sub>2</sub> enrichment, but CO<sub>2</sub> decreased Ca, K, Mg and P in tree roots. Crop seeds had lower S under elevated CO<sub>2</sub>. We also tested the validity of a “dilution model.” CO<sub>2</sub> reduced the concentration of plant nutrients 6.6% across nutrients and plant groups, but the reduction is less than expected (18.4%) from carbohydrate accumulation alone. We found that elevated CO<sub>2</sub> impacts plant nutrient status differently among the nutrient elements, plant functional groups, and among plant tissues. Our synthesis suggests that differences between plant groups and plant organs, N status, and differences in nutrient chemistry in soils preclude a universal hypothesis strictly related to carbohydrate dilution regarding plant nutrient response to elevated CO<sub>2</sub>.

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## Introduction

Carbon dioxide is rising in the Earth’s atmosphere due to human activity, and plants play a major role in

modulating ecosystem response to elevated CO<sub>2</sub> (Drake et al. 1997; IPCC 2007). Decades of research suggest that elevated CO<sub>2</sub> will likely enhance plant growth in the short-term (Norby et al. 2005; Finzi et al. 2007; Seiler et al. 2009). However, nutrient limitations can be exacerbated by elevated CO<sub>2</sub>, and could constrain future C sequestration (Woodward, 2002; Luo et al. 2004; Oh and Richter, 2004).

At least 31 chemical elements are needed for life on Earth (Schlesinger 1997; Sterner and Elser 2002; Melillo et al. 2003). While the effects of elevated CO<sub>2</sub> on nitrogen concentration and allocation in plants have been extensively evaluated in elevated CO<sub>2</sub> experiments (Cotrufo et al. 1998; Taub and Wang 2008; Bloom et al. 2010), the effects of CO<sub>2</sub> on other nutrients have received far less attention. Nutrient concentrations can decline under elevated CO<sub>2</sub> as a consequence of increased photosynthesis and carbohydrate production in plant tissues (Overdieck 1993; Loladze 2002). Because carbohydrates are composed only of C, H, and O, enhanced photosynthetic activity relative to nutrient uptake will dilute the nutrient concentrations. Indeed, other meta-analyses show patterns that CO<sub>2</sub> generally reduces plant element concentrations, but these have focused on crop species (Loladze 2002; Högy and Fangmeier 2008, 2009).

Elevated CO<sub>2</sub> could reduce element concentrations even if nutrient uptake is enhanced, but dry matter accumulation outpaces uptake. Elevated CO<sub>2</sub> consistently lowers transpiration and increases water use efficiency, and therefore may reduce the nutrient uptake for elements movement from soil to plant root of which is dependent on mass flow (Jenny 1980; Kabata-Pendias 2001). Plants can also change their nutrient allocation patterns under elevated CO<sub>2</sub> and different nutrient elements might behave differently depending on their chemical properties and the specific soil type in question (Norby et al. 1986; Peñuelas et al. 2001; Finzi et al. 2007). A specific example is metal nutrients, as they generally behave similarly in soils, but iron is more soluble in acidic soils whereas molybdenum is most bio-available in slightly alkaline soils (Goldberg et al. 1996).

Other meta-analyses show that fast-growing C<sub>3</sub> herbs accumulate more biomass under elevated CO<sub>2</sub> than slow-growing C<sub>3</sub> herbs and C<sub>4</sub> plants, while CAM plants and woody plants respond moderately to CO<sub>2</sub> (Poorter and Navas 2003). In a Florida scrub-oak community, elevated CO<sub>2</sub> increased *Quercus*

*myrtifolia* aboveground biomass with +128% after 11 years but had no effect on *Q. geminata* (Seiler et al. 2009). A study comparing the effect of CO<sub>2</sub> on grasses in Britain found significant species and species by CO<sub>2</sub> treatment effects on total plant and shoot biomass among *Arrhenatherum elatius*, *Poa annua*, *Festuca ovina*, and *F. rubra* (Hunt et al. 1995). CO<sub>2</sub> enrichment of three Mediterranean trees (*Erica arborea*, *Juniperus communis*, and *Myrtus communis*) actually lowered aboveground tissue C concentrations (Peñuelas et al. 2001).

Based on the highly variable response of biomass production to elevated CO<sub>2</sub> among plant species, there is a need in the literature for a synthesis of how the nutrient status of plants under elevated CO<sub>2</sub> will vary across plant functional groups. Crops are usually grown with sufficient nutrient or water, and therefore are expected to exhibit a strong biomass response to elevated CO<sub>2</sub> (Fuhrer 2003). Under these conditions, crop species add biomass and carbohydrate to their tissues at a rate that dilutes other nutrient elements (Loladze 2002). Trees are more often nutrient limited than crops. However, enhanced root exploration for soil nutrients under elevated CO<sub>2</sub> could compensate for nutrient limitations or even result in higher nutrient concentrations. Symbiotic N<sub>2</sub>-fixing plants may become nutrient limited under elevated CO<sub>2</sub>, as evidenced by observations of long-term declines in N fixation rates (Hungate et al. 2004; van Groenigen et al. 2006). Grasses increase their root-to-shoot ratio under elevated CO<sub>2</sub> (Suter et al. 2002), which can benefit nutrient uptake capacity and perhaps lead to higher nutrient concentrations under elevated CO<sub>2</sub>.

Nutrients can be classified into three general categories based on their biochemical roles in plants (Taiz and Zeiger 2002). Phosphorus, S, and B are principally bound to C in organic molecules, which are used for providing reducing power and structural purposes. Iron, Zn, and Cu are important for electron transfer and regulate the conformational structure of enzymes. Potassium, Ca, Mg, and Mn tend to remain in ionic forms in plant tissues (Kabata-Pendias 2001; Taiz and Zeiger 2002).

Plants influence soil properties via litter inputs and root exudates, and the production of both can be stimulated by elevated CO<sub>2</sub> (Cheng and Johnson 1998; Finzi et al. 2001). Root exudates and CO<sub>2</sub> produced via root respiration acidify the rhizosphere, making some nutrients more available to plants and others less

available (Kabata-Pendias 2001). Plants facilitate P uptake by exuding phosphatases that can become more abundant under elevated CO<sub>2</sub> (Ebersberger et al. 2003). C<sub>3</sub> plants also use water more efficiently under CO<sub>2</sub> enrichment, which increases soil water content and influences highly soluble elements like K (Bazzaz 1990; Drake et al. 1997; Brady and Weil 2002). Furthermore, there is recent experimental evidence that elevated CO<sub>2</sub> increases the accumulation of metals in oaks (Duval et al. 2011).

Organically bound elements like P and B are prone to dilution from elevated CO<sub>2</sub> if carbohydrates increase in plant tissues and if local soils have limited pools of these nutrients. Boron is also involved in hemi-cellulose and structural protein formation, and its concentration will likely be related to how plant N concentration is affected by elevated CO<sub>2</sub> (Taiz and Zeiger 2002). Although S is also organically bound, soils generally have S in excess of plant needs (Schlesinger 1997), and luxury uptake could lead to increased S concentrations under high CO<sub>2</sub> if other essential nutrients are limited (Sterner and Elser 2002).

Effects of CO<sub>2</sub> enrichment on Ca, Cu, K, Fe, Mg, Mn, and Zn concentrations are likely influenced by rhizosphere conditions. Copper, Fe, Mn, and Zn all are redox sensitive and reduced to more mobile forms at lower pH (Adriano 2001). Metal reduction and mobilization facilitates plant uptake of these elements (Kabata-Pendias 2001), but metal transformations can also lead to increased leaching of these elements from rhizosphere soil with excess water (Brady and Weil 2002). Because K, Ca, Mg, and Mn often exist in plants as free ions instead of bound in organic compounds, the concentration of these elements may be more related to water status and vacuole size and be less sensitive to carbohydrate production under high CO<sub>2</sub>.

Nitrogen most often limits plant growth in temperate and high latitude ecosystems (Vitousek and Howarth 1991), and so the N status of plants under high CO<sub>2</sub> could influence the concentration of other elements. Plants replete with N can respond more strongly to CO<sub>2</sub>, with the consequence of greater nutrient dilution from more biomass production (Loladze 2002; Reich et al. 2006).

The convention of many CO<sub>2</sub> studies is to examine nutrient content in either foliar tissues or whole plants. However, different plant organs respond differently to

CO<sub>2</sub>. Leaves are the largest sinks for N in plants, but roots tend to have high Fe and Mg concentrations, and K is an important buffer in roots against toxic Na levels (Rubio et al. 1995; Brady and Weil 2002). Furthermore, dilution of nutrients in plants likely results from increases in structural and non-structural carbohydrates, suggesting that nutrients in stem tissues respond most strongly to elevated CO<sub>2</sub>. Therefore, we examined differences in nutrient concentration for different plant organs.

We report for the first time a synthesis of the available literature that quantifies trends of the effect of elevated CO<sub>2</sub> on plant nutrient concentration using meta-analysis. We specifically test the following hypotheses: (1) Changes of plant nutrient concentration due to elevated CO<sub>2</sub> depend on plant functional group. We expect large differences between crops and trees, as crops are generally not nutrient limited, and trees are more likely to be nutrient limited; (2) nutrient concentrations decrease the most under elevated CO<sub>2</sub> in plant organs that are strong C sinks (stems and roots); (3) nutrient concentrations decrease more when N availability is high; (4) the reduction of nutrient concentration is the greatest in CO<sub>2</sub> studies with high levels of CO<sub>2</sub> enrichment (>600 μmol mol<sup>-1</sup> CO<sub>2</sub>); and (5) reductions in nutrient concentration under elevated CO<sub>2</sub> are proportional to biomass response (i.e., the dilution hypothesis).

## Materials and methods

We created a database (references in Table 1) of CO<sub>2</sub> effects on plant nutrient concentrations beginning with a search of the ISI Web of Science, using the search terms “elevated CO<sub>2</sub>,” “plant nutrients,” “plant nutrition,” and the specific elements surveyed: boron, calcium, copper, iron, potassium, magnesium, manganese, phosphorus, sulfur, and zinc, as well as their chemical symbols, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn. We also compiled data from articles found via searches in Science Direct, Academic Search Premier, JSTOR, and Google Scholar. We compiled additional data from references listed within articles found in these searches, and by contacting authors directly when data were difficult to extract from figures or not included in published studies. When electronic versions of articles were not available, we acquired hard copies of articles from the collections and interlibrary

**Table 1** References and plant species used in meta-analysis of elevated CO<sub>2</sub> effects on plant nutrient concentrations

Plant Species	CO <sub>2</sub> enrichment (μmol mol <sup>-1</sup> )	<i>n</i>	Reference
<i>Trifolium repens</i>	350	4	Almeida et al. (1999)
<i>Raphanus sativus</i>	375	2	Barnes and Pfirrmann (1992)
<i>Agrostis capillaris</i>	340	4	Baxter et al. (1994)
<i>Festuca vivipara</i>	340	4	Baxter et al. (1994)
<i>Poa alpina</i>	340	4	Baxter et al. (1994)
<i>Poa alpina</i>	340	4	Baxter et al. (1997)
<i>Lepidium latifolia</i>	340	2	Blank and Derner (2004)
<i>Bromus tectorum</i>	150	5	Blank et al. (2006)
<i>Lupinus albus</i>	333	3	Campbell and Sage (2002)
<i>Solanum tuberosum</i>	640	3	Cao and Tibbitts (1997)
<i>Lycopersicon esculentum</i>	450	5	Cheng et al. (2009)
<i>Triticum aestivum</i>	350	2	De la Puente et al. (2000)
<i>Galactia elliottii</i>	360	6	Duval et al. (unpublished)
<i>Quercus myrtifolia</i>	360	8	Duval et al. (unpublished)
<i>Triticum aestivum</i>	160	2	Fangmeier et al. (1997)
<i>Triticum aestivum</i>	320	2	Fangmeier et al. (1997)
<i>Triticum aestivum</i>	66	2	Fangmeier et al. (1999)
<i>Triticum aestivum</i>	149	2	Fangmeier et al. (1999)
<i>Triticum aestivum</i>	109	2	Fangmeier et al. (1999)
<i>Triticum aestivum</i>	264	2	Fangmeier et al. (1999)
<i>Solanum tuberosum</i>	320	3	Fangmeier et al. (2002)
<i>Triticum aestivum</i>	264	3	Fangmeier et al. (pers comm.)
<i>Aster tripolium</i>	160	9	Geissler et al. (2009)
<i>Hordeum vulgare</i>	400	5	Haase et al. (2008)
<i>Trifolium repens</i>	160	8	Heagle et al. (1993)
<i>Trifolium repens</i>	240	8	Heagle et al. (1993)
<i>Trifolium repens</i>	350	8	Heagle et al. (1993)
<i>Triticum aestivum</i>	190	7	Högy and Fangmeier (2008)
<i>Solanum tuberosum</i>	320	2	Högy and Fangmeier (2009)
<i>Gossypium hirsutum</i>	190	4	Huluka et al. (1994)
<i>Galactia elliottii</i>	340	8	Hungate et al. (2004)
<i>Trigonella foenum-graecum</i>	240	3	Jain et al. (2007)
<i>Spinacia oleracea</i>	240	3	Jain et al. (2007)
<i>Quercus geminata</i>	360	8	Johnson et al. (2003)
<i>Quercus myrtifolia</i>	360	8	Johnson et al. (2003)
<i>Liquidambar styraciflua</i>	182	3	Johnson et al. (2004)
<i>Citrus madurensis</i>	150	5	Keutgen and Chen (2001)
<i>Citrus madurensis</i>	300	5	Keutgen and Chen (2001)
<i>Citrus madurensis</i>	450	5	Keutgen and Chen (2001)
<i>Citrus madurensis</i>	600	5	Keutgen and Chen (2001)
<i>Lactuca sativa</i>	640	20	Knecht and O'Leary (1983)
<i>Lycopersicon esculentum</i>	360	3	Li et al. (2007)
<i>Oryza sativa</i>	500	3	Li et al. (2010)
<i>Pinus sylvestris</i>	330	4	Luomala et al. (2005)
<i>Oryza sativa</i>	190	5	Ma et al. (2007)
<i>Triticum aestivum</i>	190	5	Ma et al. (2007)

**Table 1** continued

Plant Species	CO <sub>2</sub> enrichment (μmol mol <sup>-1</sup> )	<i>n</i>	Reference
<i>Hordeum vulgare</i> (cv. Alexis)	358	2	Manderscheid et al. (1995)
<i>Hordeum vulgare</i> (cv. Arena)	358	2	Manderscheid et al. (1995)
<i>Triticum aestivum</i> (cv. Star)	358	2	Manderscheid et al. (1995)
<i>Triticum aestivum</i> (cv. Turbo)	358	2	Manderscheid et al. (1995)
<i>Bouteloua gracilis</i>	350	8	Morgan et al. (1994)
<i>Liquidambar styraciflua</i> (Oak Ridge FACE)	182	3	Natali et al. (2009)
<i>Liquidambar styraciflua</i> (Duke FACE)	221	3	Natali et al. (2009)
<i>Pinus taeda</i>	221	3	Natali et al. (2009)
<i>Quercus chapmanii</i>	360	8	Natali et al. (2009)
<i>Quercus geminata</i>	360	8	Natali et al. (2009)
<i>Quercus myrtifolia</i>	360	8	Natali et al. (2009)
<i>Agrostis capillaris</i>	250	3	Newbery et al. (1995)
<i>Quercus suber</i>	350	2	Niinemets et al. (1999)
<i>Betula pendula</i>	290	4	Oksanen et al. (2005)
<i>Liquidambar tulipifera</i>	332	6	O'Neill et al. (1987)
<i>Triticum aestivum</i>	240	16	Pal et al. (2003)
<i>T. alexadrium</i>	240	3	Pal et al. (2004)
<i>Cucumis sativus</i>	640	10	Peet et al. (1986)
<i>Erica arborea</i>	340	6	Peñuelas et al. (2001)
<i>Juniperus communis</i>	340	6	Peñuelas et al. (2001)
<i>Myrtus communis</i>	340	6	Peñuelas et al. (2001)
<i>Cirus aurantium</i>	300	2	Peñuelas et al. (1997)
<i>Picea abies</i>	390	2	Pfarrmann et al. (1996)
<i>Solanum tuberosum</i>	284	6	Piikki et al. (2007)
<i>Bouteloua curtipendula</i>	135	2	Polley et al. (2011)
<i>Sorghastrum nutans</i>	135	2	Polley et al. (2011)
<i>Phaseolus vulgaris</i>	840	30	Porter and Grodzinski (1984)
<i>Gossypium hirsutum</i>	190	2	Prior et al. (1998)
<i>Sorghum bicolor</i>	360	3	Prior et al. (2008)
<i>Glycine max</i>	360	3	Prior et al. (2008)
<i>Picea abies</i>	340	5	Roberntz and Stockfors (1998)
<i>Fagus sylvatica</i>	300	8	Rodenkirchen et al. (2009)
<i>Picea abies</i>	300	8	Rodenkirchen et al. (2009)
<i>Larix kaempferi</i>	340	3	Shinano et al. (2007)
<i>Picea rubens</i>	340	2	Shiple et al. (1992)
<i>Oryza sativa</i>	340	5	Seneweera and Conroy (1997)
<i>Picea abies</i>	350	4	Le Thiec et al. (1995)
<i>Quercus rubra</i>	350	4	Le Thiec et al. (1995)
<i>Apium graveolens</i>	640	27	Tremblay et al. (1988)
<i>Pinus sylvestris</i>	230	4	Utrianen et al. (2000)
<i>Calluna vulgaris</i>	100	10	Woodin et al. 1992
<i>Calluna vulgaris</i>	200	10	Woodin et al. (1992)
<i>Triticum aestivum</i>	340	3	Wu et al. (2004)
<i>Oryza sativa</i>	252	4	Yamakawa et al. (2004)

The level of CO<sub>2</sub> enrichment is given as μmol mol<sup>-1</sup> CO<sub>2</sub> above ambient levels, and *n* is the sample replication within a given study

loan service of Cline Library, Northern Arizona University, Flagstaff, Arizona, USA and the library system of the University of Illinois at Urbana-Champaign, Urbana, Illinois, USA. Because few studies considered CO<sub>2</sub> effects on nutrients other than N and P, we included all available articles irrespective of duration of CO<sub>2</sub> enrichment or sample size. Several studies also reported results for ozone (O<sub>3</sub>) enrichment and interactions with CO<sub>2</sub>. For these experiments, we only used data from control and single-factor CO<sub>2</sub> treatments. We compiled a dataset of foliar element concentrations and an additional dataset of element concentrations in non-foliar tissues (stems, roots, grain). The data we compiled from the literature are available as supplementary material to this article (Tables S1, S2).

To examine differences between plant functional groups, species were categorized as grasses, trees, crops, or N<sub>2</sub> fixers. As these categories are not mutually exclusive, we set the following parameters to delineate plant groups: grasses were classified as all non-crop grass species, trees were all woody species, crops were all non-N<sub>2</sub> fixing, non-tree cultivars, and N<sub>2</sub> fixers were all species that are known to host microbial N<sub>2</sub>-fixing symbionts.

We also evaluated the N status of soil or growth media used in experiments as a grouping variable explaining the effect of CO<sub>2</sub> on other nutrients. Nitrogen status was classified as “Low N” if soils or growth media had N concentrations or additions equivalent to less than 30 kg N ha<sup>-1</sup> year<sup>-1</sup>. Nitrogen application rates above 30 kg N ha<sup>-1</sup> year<sup>-1</sup> were classified as “High N,” similar to de Graaff et al. (2006).

We also evaluated the effect of different elevated CO<sub>2</sub> concentrations. The elevated CO<sub>2</sub> treatments from each study were classified as “high” (final CO<sub>2</sub> concentration ≥ 600 μmol mol<sup>-1</sup>) or “low” (CO<sub>2</sub> concentration between ambient and 600 μmol mol<sup>-1</sup>). Individual nutrients were evaluated using “high” or “low” elevated CO<sub>2</sub> as a grouping variable in the meta-analysis. We also used CO<sub>2</sub> enrichment as a continuous variable to determine the effect of CO<sub>2</sub> concentration on individual nutrient concentrations.

We used Meta-Win (v. 2.1, Rosenberg et al. 2000) to analyze foliar, root, grain, and stem element concentrations. We weighted studies by the inverse of the variance, calculated as

$$\text{Variance} = \left( (\text{SE}_e)^2 / (n_e) * (\mu_e)^2 \right) + \left( (\text{SE}_a)^2 / (n_a) * (\mu_a)^2 \right), \quad (1)$$

where SE<sub>e</sub> and SE<sub>a</sub> are the standard errors of the mean element concentration under elevated and ambient CO<sub>2</sub> concentration.

$$\text{SE}_{\text{mean}} = \text{SD} / \sqrt{n}, \quad (2)$$

where SD is the standard deviation for nutrient concentration under elevated CO<sub>2</sub> or ambient CO<sub>2</sub>; μ<sub>e</sub> and μ<sub>a</sub> are the mean concentrations of nutrients under elevated CO<sub>2</sub> and ambient CO<sub>2</sub>, respectively; and n<sub>e</sub> and n<sub>a</sub> are the sample sizes under elevated and ambient CO<sub>2</sub>, respectively (Hedges et al. 1999). We used the bootstrap function in Meta-Win (999 iterations) to calculate mean effect sizes and estimate 95% confidence intervals (CIs).

We used the natural log of the response ratio (lnR) as our effect size metric: ln(E/A), where E is element concentration in the elevated CO<sub>2</sub> treatment and A is element concentration in the control treatment. The metric lnR is preferable to the non-adjusted response ratio (E/A), because it provides a more normal distribution than the non-adjusted response ratio when bootstrapped (Hedges et al. 1999).

We report mean effect sizes and bootstrapped 95% CI, Q statistics, and P values (α = 0.05) generated by Meta-Win. Q statistics are a measure of variability between studies (Q<sub>b</sub>), within studies (Q<sub>w</sub>), or the total variation within an analysis (Q<sub>t</sub> = Q<sub>b</sub> + Q<sub>w</sub>). For individual nutrients within a grouping variable, we considered a CO<sub>2</sub> effect significant if the 95% CI did not overlap with 0. In some instances, we reported % CO<sub>2</sub> effect, when data from only one study was available.

A model developed by Loladze (2002) predicted that increased biomass under elevated CO<sub>2</sub> dilutes the concentration of elements other than C, H, and O, the principal constituents of carbohydrates. All subsequent use of the terms “element” and “nutrient” refer to chemical elements other than C, H, and O. The Loladze (2002) model assumes equal availability of elements in soils exposed to elevated CO<sub>2</sub>. A reduced nutrient concentration in plant tissues is often reported (Overdieck 1993; Huluka et al. 1994; Loladze, 2002); thus, we tested the ubiquity of dilution in explaining reduced nutrient concentration in response to elevated



CO<sub>2</sub>. For this test, we used the Loladze's (2002) model as a starting point to calculate an expected CO<sub>2</sub> dilution of nutrient concentrations when biomass data were available. Due to the few studies of grasses and N<sub>2</sub> fixers that reported both biomass and element concentration, we only calculated nutrient dilution ( $N_d$ , detailed below) for crop and tree species.

Loladze (2002) used the % effect of CO<sub>2</sub> on biomass to predict element dilution:

$$\% \text{ Dilution} = -\delta/(\delta + 1), \quad (3)$$

$$\delta = \% \text{ change in biomass due to elevated CO}_2, \quad (4)$$

with  $\delta$  as the % response of biomass. For example, the CO<sub>2</sub> biomass stimulation ( $\delta$ ) of 25% leads to an expected 20% dilution (concentration reduction) for a given element. Based on that idea, we calculated the expected concentrations of nutrients and the effect of elevated CO<sub>2</sub> on nutrient dilution ( $N_d$ ) in our dataset with the following formulas:

$$\frac{(\text{Amb}_{[\text{exp}]} \times \text{Amb biomass})/\text{Elev biomass}}{= \text{Elev}_{[\text{exp}]}, \quad (5)$$

$$\frac{(\text{Elev}_{[\text{obs}]} - \text{Amb}_{[\text{obs}]})/(\text{Elev}_{[\text{exp}]} - \text{Amb}_{[\text{exp}]})}{= \text{CO}_2 \text{ nutrient dilution } (N_d), \quad (6)$$

where  $\text{Amb}_{[\text{exp}]}$  and  $\text{Elev}_{[\text{exp}]}$  are the expected nutrient concentrations under ambient CO<sub>2</sub> and elevated CO<sub>2</sub> treatment, and  $\text{Amb}$  and  $\text{Elev}$  biomass are the reported biomass values, and compared this to observed dilutions. An  $N_d$  value of 1 equals an exact correspondence with the expected dilution via carbohydrate accumulation under elevated CO<sub>2</sub> (Loladze 2002). Values less than 1 are interpreted as less dilution than expected, while values greater than 1 are interpreted as more dilution than expected via carbohydrate accumulation.

We estimated publication bias by constructing a funnel plot of the inverse of the standard deviation of studies ( $x$ -axis) plotted against effect sizes ( $\ln R$ ,  $y$ -axis) (Egger et al. 1997). This metric allows a simple visual evaluation of the distribution of effect sizes. The inverse values of the standard deviation of effect sizes in our synthesis were symmetrical around 0 (no effect), and we thus assumed that publication bias was not a significant driver of our results (Fig. S1).

## Results

### Plant functional groups

When considering individual elements, there was a significant difference in CO<sub>2</sub> effects for P between the four plant groups ( $Q_b = 55.39$ ,  $df = 3$ ,  $P = 0.001$ ), likely driven by a lack of a CO<sub>2</sub> effect on crop P, and the negative CO<sub>2</sub> effect on grass, trees, and N<sub>2</sub>-fixer P (Table 2; Fig. 1). We also observed a trend for Cu concentrations to vary between plant groups ( $Q_b = 6.74$ ,  $df = 3$ ,  $P = 0.07$ , Table 2). This result is driven by the significantly positive effect of CO<sub>2</sub> on grass Cu concentration, but significantly lower Cu in tree and N<sub>2</sub>-fixer leaves (Fig. 1b, c). Elevated CO<sub>2</sub> significantly lowered the foliar concentration of Mg in crops (Fig. 1a) and decreased foliar concentrations of Cu and Fe in trees (Fig. 1b). Symbiotic N<sub>2</sub>-fixing plants had lower foliar concentrations of B, Cu, Fe, and Mg, but higher Mn concentrations under elevated CO<sub>2</sub> (Fig. 1c). There was a significant, positive effect of elevated CO<sub>2</sub> on Cu, Fe, and Zn concentrations in grasses, but a negative CO<sub>2</sub> effect on Mn concentration (Fig. 1d).

### Plant organs

Elevated CO<sub>2</sub> increased the concentration of Cu in plant stems across plant groups, but CO<sub>2</sub> reduced stem Ca, S, and Zn (Fig. 2). The response of nutrient concentration in tree and crop roots was not significantly affected by elevated CO<sub>2</sub>. However, when plant groups were considered collectively, roots exposed to high CO<sub>2</sub> had lower concentrations of B and P, but higher Zn concentrations (Fig. 3). CO<sub>2</sub> decreased overall grain nutrient concentration ( $\ln R -0.12$ ; 95% CIs  $-0.19$  to  $-0.08$ ). However, only grain S was significantly reduced under elevated CO<sub>2</sub> (Fig. 4).

### Interactions between CO<sub>2</sub> and N availability

Crops grown with low N availability had significantly lower foliar Mn concentrations under elevated CO<sub>2</sub> compared to controls, while, when grown with high N, Mg, and Zn concentrations were reduced by CO<sub>2</sub> (Table 4). CO<sub>2</sub> reduced grass P concentration, and this effect was more pronounced under low N (four studies) compared to high N (seven studies)

**Table 2** Model results (random effects model) from meta-analysis of elevated CO<sub>2</sub> effects (ln*R*; natural log of the response ratio elevated CO<sub>2</sub>/ambient CO<sub>2</sub>) on plant nutrient concentration between plant functional groups

Element	Model	df	<i>Q</i>	Probability ( $\chi^2$ )	Probability (random)
Boron	Between	2	2.72	0.26	0.20
	Within	17	14.62	0.62	
	Total	19	17.34	0.58	
Calcium	Between	3	1.11	0.78	0.66
	Within	68	73.26	0.31	
	Total	71	74.36	0.37	
Copper	Between	3	6.74	0.08	0.07
	Within	31	33.16	0.36	
	Total	34	39.90	0.22	
Iron	Between	3	1.03	0.79	0.76
	Within	51	35.63	0.95	
	Total	54	36.66	0.97	
Potassium	Between	3	0.51	0.92	0.95
	Within	70	110.41	0.001	
	Total	73	110.91	0.003	
Magnesium	Between	3	0.16	0.98	0.47
	Within	62	3.65	1.00	
	Total	65	3.81	1.00	
Manganese	Between	3	4.25	0.24	0.21
	Within	52	39.31	0.90	
	Total	55	43.56	0.87	
Phosphorus	Between	3	55.39	0.00	0.01
	Within	78	106.66	0.02	
	Total	81	162.06	0.00	
Sulfur	Between	2	2.27	0.32	0.32
	Within	36	25.94	0.89	
	Total	38	28.21	0.88	
Zinc	Between	3	3.87	0.28	0.31
	Within	43	69.68	0.006	
	Total	46	73.55	0.006	

( $Q_b = 3.73$ ,  $df = 1$ ,  $P = 0.05$ ). Only one study in our dataset measured nutrients in grass roots (Baxter et al. 1997). CO<sub>2</sub> enrichment with high N resulted in roots with 15% lower Ca concentrations and 3% lower Mg, while grass roots in the low N treatment had a 129.4 and 50.0% higher Ca and Mg concentrations, respectively, under elevated CO<sub>2</sub>.

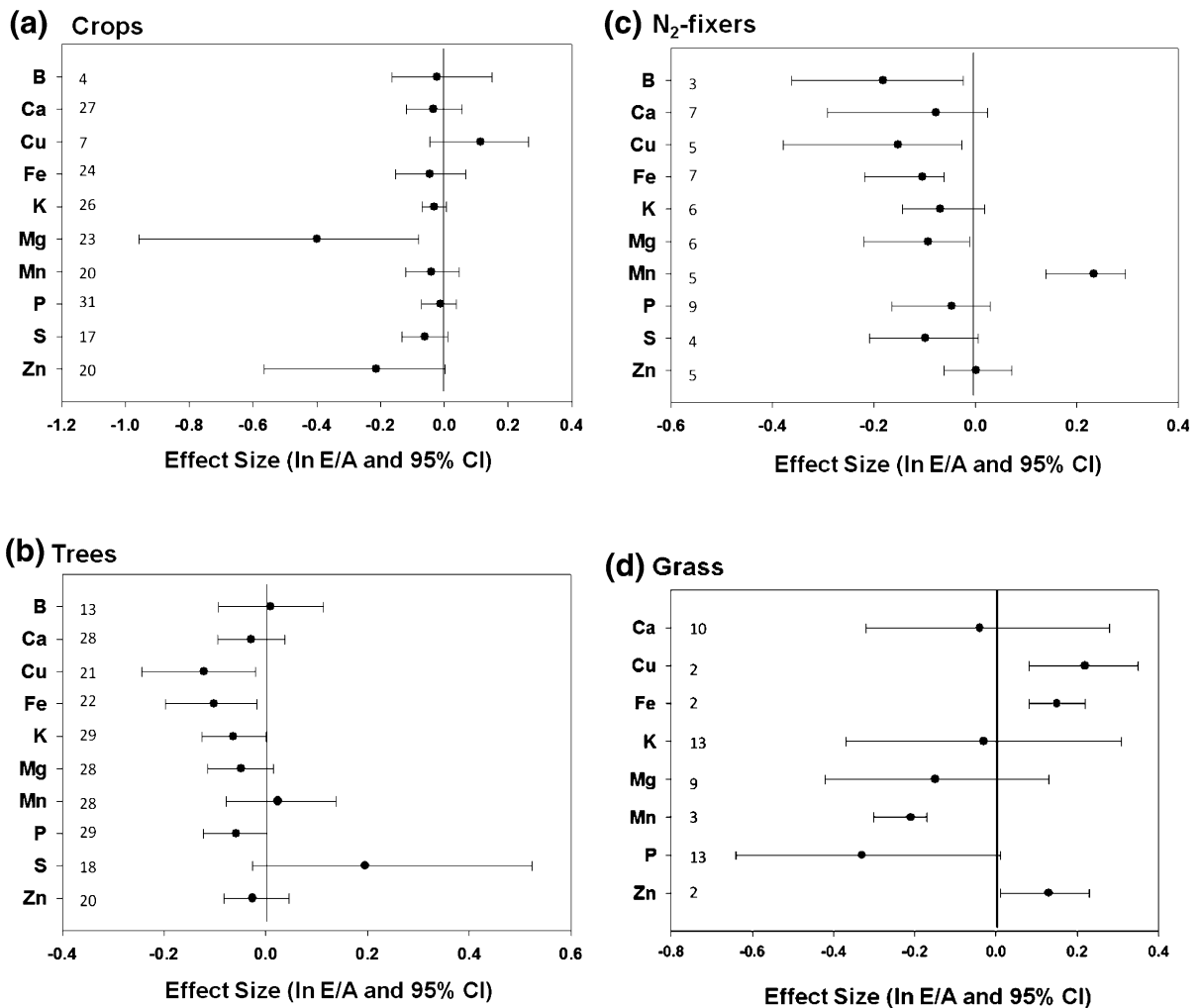
We found significant differences in CO<sub>2</sub> effects in tree leaves between high and low N levels on Cu ( $P = 0.02$ ), K ( $P = 0.03$ ) and Mg concentrations ( $P = 0.01$ ). CO<sub>2</sub> lowered the concentrations of tree Cu, Fe, Mg, and S at high N (Table 3), but reduced Fe

at low N. A summary of the within and between group variability for nutrients in trees and crops is in Table 4.

#### Level of CO<sub>2</sub> enrichment

Across plant groups, K concentration was lower in experiments with low CO<sub>2</sub> increases compared to experiments with high CO<sub>2</sub> increases (73 studies,  $Q_b = 10.58$ ,  $df = 1$ ,  $P = 0.009$ ). The level of CO<sub>2</sub> enrichment (Table 1) as a continuous variable was significantly related to the foliar concentrations of all elements other than Cu (Table 5).





**Fig. 1** Mean effects of elevated CO<sub>2</sub> on foliar nutrient concentration determined via meta-analysis. Values are mean lnR (log of the response ratio (concentration under elevated

CO<sub>2</sub>/concentration under ambient CO<sub>2</sub>)). The 95% CIs were determined from bootstrap analysis, 999 iterations. **a** CO<sub>2</sub> effects on crops, **b** trees, **c** symbiotic N<sub>2</sub> fixers%, **d** grasses

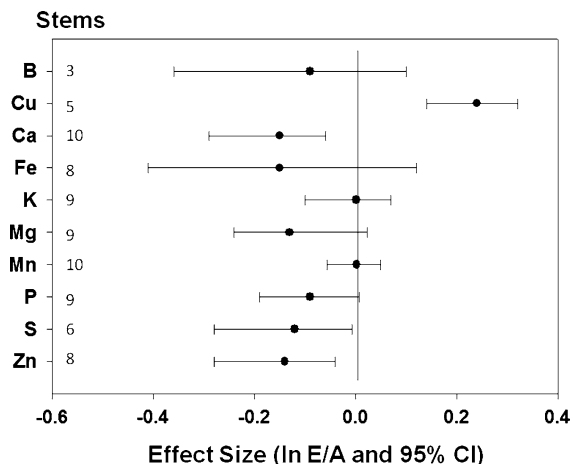
**Testing the dilution hypothesis**

Plant biomass increased under elevated CO<sub>2</sub> (lnR = 0.33; 95% CI 0.15–0.43). Crop biomass response to elevated CO<sub>2</sub> (lnR = 0.38; 95% CI 0.17–0.49) was similar to that in grasses (lnR = 0.36; 95% CI 0.23–0.68). The effect of CO<sub>2</sub> on tree biomass was not significantly different from zero (lnR = 0.21; 95% CI –0.11 to 0.50). Using the Loladze (2002) model as an expectation for nutrient dilution, we calculated an expected CO<sub>2</sub> dilution effect on nutrient concentrations of 18.4%. However, the actual dilution effect of elevated CO<sub>2</sub> was only 6.6%.

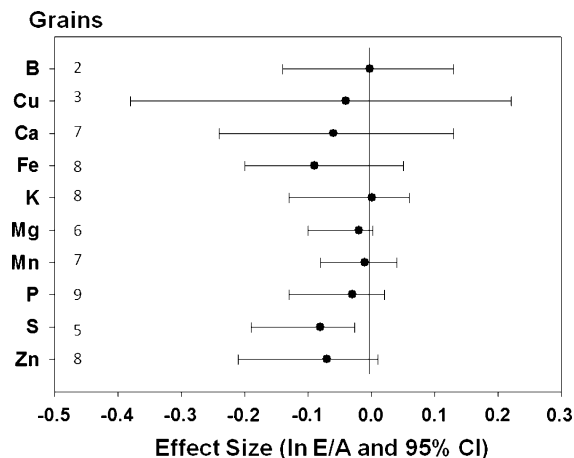
For crops, B, Fe, and Mn had CI overlapping 1 (not significantly different from expected dilution), while Ca, K, Mg, P, S, and Zn were diluted more than expected, and Cu was diluted less than expected (Fig. 5a). Tree foliar tissue B, Cu, Fe, Mn, and Zn concentrations were diluted more than expected by elevated CO<sub>2</sub>, while Ca, K, Mg, and P were diluted less than expected (Fig. 5b).

**Discussion**

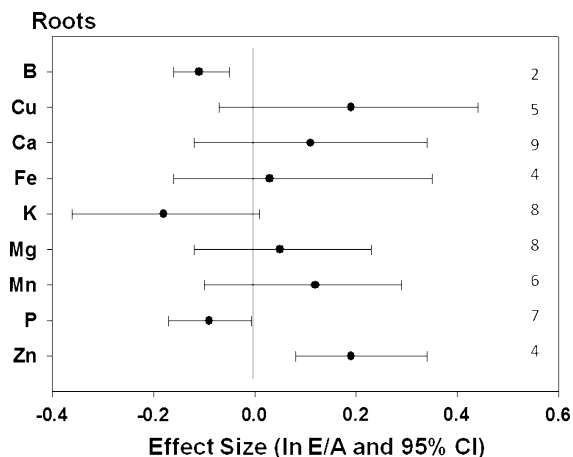
Our meta-analysis showed that while elevated CO<sub>2</sub> tends to lower the concentration of nutrients in plants,



**Fig. 2** Mean effects of elevated CO<sub>2</sub> on stem nutrient concentration. Values are mean lnR (log of the response ratio (concentration under elevated CO<sub>2</sub>/concentration under ambient CO<sub>2</sub>)). The 95% CIs were determined from bootstrap analysis, 999 iterations



**Fig. 4** Mean effects of elevated CO<sub>2</sub> on crop-grain nutrient concentration determined via meta-analysis. Values are mean lnR (log of the response ratio (concentration under elevated CO<sub>2</sub>/concentration under ambient CO<sub>2</sub>)). 95% CIs were determined from bootstrap analysis, 999 iterations



**Fig. 3** Mean effects of elevated CO<sub>2</sub> on root nutrient concentration determined via meta-analysis. Values are mean lnR (log of the response ratio (concentration under elevated CO<sub>2</sub>/concentration under ambient CO<sub>2</sub>)). 95% CIs were determined from bootstrap analysis, 999 iterations

we also observed increased nutrient concentrations. The effects of elevated CO<sub>2</sub> on mineral nutrition depend on the specific element, plant functional group, plant organ, N availability, and, in some cases the level of CO<sub>2</sub> enrichment. These results challenge the assumption that plant nutrient concentrations are generally lowered by elevated CO<sub>2</sub> strictly on the basis carbohydrate dilution (Loladze 2002).

Moreover, most nutrients exhibited dilution under elevated CO<sub>2</sub> that was less than expected (Fig. 5), suggesting that mechanisms related to soil/root interactions under elevated CO<sub>2</sub> perhaps increase nutrient uptake and mask effects of carbohydrate production.

We hypothesized there would be differences across plant functional groups, especially between crops and trees. We based this hypothesis on the observation that crops are usually not nutrient limited, but trees in temperate regions more often grow in nutrient-limited ecosystems. It is also possible that differences in C allocation and C–N interactions within trees and crops exposed to elevated CO<sub>2</sub> may compensate for nutrient limitations. Atmospheric CO<sub>2</sub> exerts a strong control over photosynthesis while sink size and activity determine where carbohydrates are utilized (Farrar and Jones 2000). Increases in carbohydrate production can serve as a negative feedback to photosynthesis and induce C storage in tissues (Koch 1996). Under elevated CO<sub>2</sub> and sufficient N, plants have high photosynthetic rates and high C sink activity, preventing the long-term build-up of carbohydrates in leaves, in contrast to situations where sink activity is N limited (Stitt and Krapp 1999).

Low available N and elevated CO<sub>2</sub> could cause N limitation to photosynthesis, and existing C reserves would be more quickly redistributed to sinks within a plant (Farrar and Jones 2000). Increased nutrient uptake due to a CO<sub>2</sub>-enhanced growth rate, and luxury

**Table 3** Meta-analysis results for CO<sub>2</sub> effects on element concentration attributable to N fertilization level (low = <30 kg N ha<sup>-1</sup> year<sup>-1</sup>, high = >30 kg N ha<sup>-1</sup> year<sup>-1</sup> fertilizer) for crops and trees

	High N			Low N		
	Number of studies	Effect size (lnR)	95% CI	Number of studies	Effect size (lnR)	95% CI
<i>Crops</i>						
B	3	-0.02	-0.21 to 0.22	1	-0.04	(Var) 0.008 <sup>a</sup>
Ca	22	-0.04	-0.15 to 0.07	5	-0.02	-0.06 to 0.05
Cu	7	0.11	-0.03 to 0.27	N/A		
Fe	20	-0.05	-0.19 to 0.07	4	-0.004	-0.05 to 0.04
K	20	-0.02	-0.07 to 0.02	6	-0.07	-0.09 to 0.01
Mg	22	-0.41	-0.97 to -0.08	1	-0.11	(Var) 0.01
Mn	16	-0.02	-0.12 to 0.10	4	-0.13	-0.19 to -0.07
P	25	-0.03	-0.09 to 0.03	6	-0.03	-0.06 to 0.10
S	13	-0.07	-0.16 to 0.02	4	-0.02	-0.09 to 0.04
Zn	16	-0.26	-0.69 to -0.003	4	-0.007	-0.03 to 0.02
<i>Trees</i>						
B	1	0.09	(Var) 0.92	12	0.003	-0.12 to 0.11
Ca	8	-0.003	-0.05 to 0.05	20	-0.04	-0.13 to 0.05
Cu	2	-0.97	-1.45 to -0.73	19	-0.07	-0.16 to 0.01
Fe	3	-0.07	-0.15 to -0.04	19	-0.10	-0.21 to -0.008
K	9	-0.008	-0.21 to 0.03	20	-0.04	-0.11 to 0.05
Mg	8	-0.16	-0.22 to -0.09	20	-0.004	-0.08 to 0.07
Mn	3	0.02	-0.13 to 0.11	25	0.03	-0.09 to 0.16
P	9	-0.08	-0.22 to 0.004	20	-0.05	-0.13 to 0.03
S	2	-0.08	-0.10 to -0.04	16	0.23	-0.03 to 0.53
Zn	1	-0.008	(Var) 1.01	19	-0.03	-0.09 to 0.04

Differences are considered significant if the bootstrap 95% CI (999 iterations) does not overlap zero. Effect of CO<sub>2</sub> is reported as lnR. *Q* statistics, and *P* values from meta-analysis are provided in Table S4

<sup>a</sup> For *n* = 1, we report the reported variance instead of a bootstrap CI

N/A designates that no studies were available

uptake in the face of other nutrient limitations, could result in higher foliar concentrations for some elements if the total amount of nutrients remains constant but sugars are more efficiently allocated to stems or roots. While CO<sub>2</sub> did reduce foliar Mn concentrations in crops at low N application, and Mg and Zn at high N (Table 3), the absence of significant effects across N regimes could be due to sufficient soil nutrients in those studies. Trees under high N availability had reduced concentrations of Cu, Fe, Mg, and S, but those elements are usually in abundance in most soils (Kabata-Pendias 2001). Based on those results, we need to reject our hypothesis that greater N availability induces a greater reduction in element concentration.

Carbon allocation to roots could also be a mechanism explaining the differences between N

availability and nutrient concentration in trees. Plants often invest C in root production under nutrient stress (Lynch and Brown 2001; Taiz and Zeiger 2002). Since the available tree's root nutrient data were from low N studies (Table S2), greater allocation of C to root growth would increase the available surface area for nutrient uptake. This could explain lower nutrient concentration at high CO<sub>2</sub> in tree root Ca, K, Mg, and P concentration if there is more C in roots (Table S2). However, as increased uptake of nutrients could also be occurring, increased C allocation to roots might also be a mechanism masking overall CO<sub>2</sub> effects and highlights the importance of parsing CO<sub>2</sub> effects on different plant organs.

A major finding of this synthesis is the lack of effect of CO<sub>2</sub> on crop grains nutrient concentration (Fig. 4).

**Table 4** Effects of elevated CO<sub>2</sub> on plant nutrient concentration in crops and trees as a function of nitrogen application rates (low = <30 kg N ha<sup>-1</sup> year<sup>-1</sup>, and high = >30 kg N ha<sup>-1</sup> year<sup>-1</sup> fertilizer)

Model	df	<i>Q</i>	Probability ( $\chi^2$ )	Probability (random)
<i>Crops, high N</i>				
Between	9	1.13	0.99	0.41
Within	154	15.57	1	
Total	163	16.7	1	
<i>Crops, low N</i>				
Between	6	1.47	0.96	0.27
Within	26	3.3	1	
Total	32	4.77	1	
<i>Trees, high N</i>				
Between	7	24.75	0.001	0.02
Within	36	24.62	0.92	
Total	43	49.37	0.23	
<i>Trees, low N</i>				
Between	9	16.75	0.05	0.1
Within	180	167.34	0.74	
Total	189	184.09	0.59	

Results are from random effects models and represent the between and within variability across a suite of 10 nutrient elements

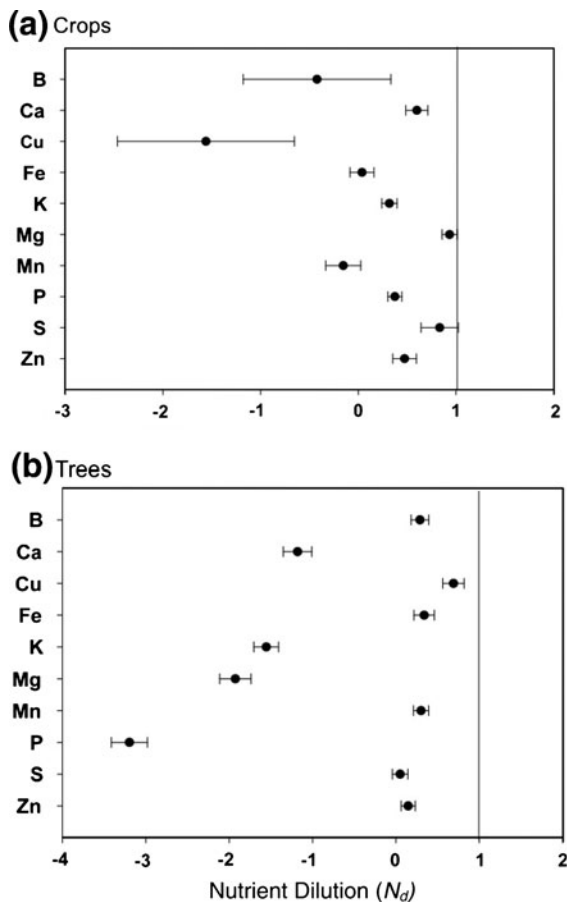
**Table 5** Meta-analysis results using the level of CO<sub>2</sub> enrichment above ambient as a continuous predictor for plant foliar nutrient concentration

Element	Number of studies	Intercept	Slope	<i>Q</i> <sub>t</sub>	<i>P</i>
Boron	20	-0.38	0.001	409.48	<0.001
Calcium	64	-0.13	0.001	490.35	<0.001
Copper	33	0.17	-0.005	34.31	0.27
Iron	53	-0.10	0.001	1701.54	<0.001
Potassium	73	0.01	-0.006	1952.37	<0.001
Magnesium	66	0.42	-0.002	106.97	<0.001
Manganese	54	-0.16	0.001	2466.43	<0.001
Phosphorus	82	0.51	-0.002	823.72	<0.001
Sulfur	38	-0.38	0.001	123.72	<0.001
Zinc	45	-0.30	0.001	1943.25	<0.001

The range of CO<sub>2</sub> concentrations for each experiment used as predictor variables is reported in Table 1, while *n* for each test = number of studies in the second column of Table 1

There was a reduction in grain S under elevated CO<sub>2</sub>, but our analysis showed no other significant changes in grain nutrient concentration. The prospect that elevated CO<sub>2</sub> will reduce element concentrations and result in “hidden hunger” (Loladze 2002) is an intriguing idea; however, we did not find significant support for this notion in our synthesis of the available literature (Fig. 4).

Elevated CO<sub>2</sub> improves the transport of labile C from plants to symbiotic bacteria and can stimulate the energetically expensive process of N<sub>2</sub> fixation. Not surprisingly, many studies report that CO<sub>2</sub> increases fixation rates in the short term (Thomas et al. 1991; Hungate et al. 1999). However, N<sub>2</sub> fixation can also become nutrient limited (Silvester 1989; Vitousek and Howarth 1991; Hungate et al. 2004), as evidenced in a



**Fig. 5** Mean nutrient dilution ( $N_d$ ) under elevated  $\text{CO}_2$ . Values with 95% CI not overlapping 1 are considered significantly different from the expected dilution. An  $N_d$  value of 1 equals an exact correspondence with the expected dilution via carbohydrate accumulation under elevated  $\text{CO}_2$  (Loladze 2002). Values less than 1 are interpreted as with less dilution than expected, while values greater than 1 are interpreted as with more dilution than expected via carbohydrate accumulation

recent review showing that elevated  $\text{CO}_2$  only increases  $\text{N}_2$ -fixation rates when fertilizers containing K and molybdenum are added (van Groenigen et al. 2006). Our study shows that elevated  $\text{CO}_2$  lowered Fe and Mg concentrations in  $\text{N}_2$  fixers (Fig. 1c), and both of those elements are vital components of the nitrogenase enzyme (Williams and Frausto da Silva 2002). Nutrient deficiency could be a mechanism that deserves consideration in longer-term  $\text{CO}_2$  studies that show declines in  $\text{N}_2$  fixation.

Our synthesis demonstrates that reductions in nutrient concentrations are not completely explained by biomass stimulation (Fig. 5a, b). This is likely

because plants under elevated  $\text{CO}_2$  do not experience the same nutrient availability compared with plants at ambient  $\text{CO}_2$  (Manderscheid et al. 1995). Plants have mechanisms to facilitate nutrient uptake, such as increasing root growth and producing root exudates that can increase the turnover of older soil organic matter and liberate nutrients (Ebersberger et al. 2003; Langley et al. 2009). Furthermore, nutrient availability can be changed by shifts in soil microbial communities (Carney et al. 2007) or  $\text{CO}_2$ -induced acidification of the rhizosphere (Oh and Richter 2004).

There is also growing evidence that elevated  $\text{CO}_2$  induces a priming effect on soil microbial activity that is important for element cycling (Carney et al. 2007; Langley et al. 2009). While most research has focused on N mineralization, we hypothesize that increased soil microbial activity, initiated by an input of labile carbon from elevated  $\text{CO}_2$ , will facilitate the mobilization of other nutrient elements, via accelerated microbial activity. While there are not sufficient data to parse the microbial/soil interaction component of the overall effect of elevated  $\text{CO}_2$  on plant nutrient uptake, this is a promising area for future research.

Our synthesis shows that the nutrient concentration of plants under elevated  $\text{CO}_2$  is not uniformly reduced, but is affected by plant functional group, plant organs,  $\text{CO}_2$  concentration, and N availability, and differs by element. We observed significant differences in the effects of elevated  $\text{CO}_2$  on nutrient concentrations between crops and trees in foliar, stem, and roots, and across the suite of nutrient elements surveyed. From an ecological standpoint, these changes will have an impact on litter quality and influence microbial communities and recycling of nutrients within ecosystems. Therefore, we suggest that future research on  $\text{CO}_2$  effects and global change studies in general should take an expanded view of the periodic table and include soil element data. Multiple elements are necessary for plant growth, enzyme function, and our analysis suggests that nutrients clearly differ in their response to global change (Sterner and Elser 2002; Hungate et al. 2003).

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