# Rising atmospheric $CO_2$ and human nutrition: toward globally imbalanced plant stoichiometry?

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**Terrestrial vascular plants obtain their major constituent – carbon (C) – from atmospheric carbon dioxide ($CO_2$), but draw all other chemical elements largely from the soil. Concentrations of these elements, however, do not change in unison with steadily increasing concentrations of $CO_2$ [$CO_2$]. Thus, relative to pre-industrial times, modern plants are experiencing a global elemental imbalance. Could this imbalance affect the elemental composition of plants, the most important food source on Earth? Apart from an overall decline in nitrogen concentration, very little is known about the effects of high [$CO_2$] on other chemical elements, such as iron, iodine and zinc, which are already deficient in the diets of the half of human population. Here, I apply stoichiometric theory to argue that high [$CO_2$], as a rule, should alter the elemental composition of plants, thus affecting the quality of human nutrition. The first compilation, to my knowledge, of published data supports the claim and shows an overall decline of the (essential elements):C ratio. Therefore, high [$CO_2$] could intensify the already acute problem of micronutrient malnutrition.**

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The increasing concentration of atmospheric carbon dioxide $CO_2$ and the quality of our nutrition are two important problems that we are currently facing. A link between these two problems, however, is not apparent. Indeed, intensive and numerous studies on the effects of high [$CO_2$] on plants have covered a wide range of issues, but its effects on plant stoichiometry (i.e. elemental composition) have received very little attention. Yet, plants are the foundation of our food supply. The low concentrations of several essential micronutrients, such as iron (Fe), iodine (I) and zinc (Zn), in modern crops contribute to the problem of micronutrient malnutrition (i.e. 'hidden hunger'), which diminishes the health and economy of over the half of the world's population. Here, by using the theory of ecological stoichiometry, I can link high [$CO_2$] with plant stoichiometry and the quality of human nutrition. The tools of ecological stoichiometry are chemical elements and their ratios in organisms and the environment.

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### How can stoichiometry provide insight?

Analysing biological dynamics from a chemical element perspective has advantages in both its simplicity and rigor ([1], I. Loladze, PhD thesis, Arizona State University 2001). A cell contains thousands of complex substances, but all life requires ~32 different chemical elements [2]. Life continuously assembles and disassembles complex substances, but it can neither create nor decompose chemical elements, and it cannot convert one element into another. These elemental laws are rather self-evident, but are frequently overlooked in our perception of biological dynamics. Yet the universality and certainty of these laws, which are valid on all organizational scales, from molecules to the biosphere, provide a unified framework that helps to reveal patterns hidden on disparate organizational scales. The stoichiometric argument that I discuss here draws on multiple scales, from the structure of carbohydrates to a plant cell to an agricultural plot to globally rising [$CO_2$].

### The need for essential elements and the problem of micronutrient malnutrition

The human body needs at least 24 chemical elements. Although some of the elements, such as chromium (Cr), Fe, I, selenium (Se), or zinc (Zn), comprise <0.01% of human body weight, their absence renders our life impossible. Because the human organism cannot generate any element that is lost through excretion, we must replenish it from our food. Plants are the basis of human nutrition, providing a staggering 84% of calorie intake worldwide [3]. Almost half of this comes from two staple crops: rice and wheat [3]. Concentrations of several essential elements in modern crops are insufficient for optimal human nutrition, thus contributing to the enormous 'hidden hunger' problem [4–6]. Iron deficiency affects >3.5 billion people, mostly in the developing world, and 'impairs the cognitive development of children, causes productivity and educational losses, and increases morbidity and maternal mortality' [4]. Iodine deficiency is a public health problem in at least 130 countries, with over seven hundred million people suffering from goitre and tens of millions afflicted by brain damage and cretinism [4]. Nearly half of the world's population is at risk of inadequate Zn intake [5]. Deficiencies of other essential elements are also widespread, even in industrial countries, but often are not manifested in overt clinical syndromes.

### Global imbalance of essential elements and plant stoichiometry

Human activities profoundly alter the global cycles of several essential elements [1,7]. The pursuit of higher agricultural yields, rather than crop quality, fertilizes soil disproportionately with N, phosphorus (P), and potassium (K). Fossil-fuel burning adds N and sulphur (S) via atmospheric deposition and, together with changes in land use, increases [$CO_2$]. Thus, human activities have been altering the pool of a few essential elements in severe

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disproportion to others. Relative to pre-industrial times, we have been rapidly creating a global elemental imbalance. Can this imbalance, in turn, affect us by altering the stoichiometry of our fundamental food source – plants? To answer this question, I concentrate here on the role of rising [$CO_2$] for the following three reasons.

First, unlike the controversy surrounding the effects of [$CO_2$] on climate change, the increase in [$CO_2$] itself is confirmed by several independent sources [8]. Currently, every terrestrial plant is exposed to ~30% higher [$CO_2$] relative to pre-industrial times; during this century [$CO_2$] levels could double or triple over pre-industrial levels [8]. This increase is instantaneous on a geological timescale and is unprecedented in the history of the human species. Because a modern tree might experience the doubling of [$CO_2$] over its lifetime, such an increase is also very fast on evolutionary and even ontogenetic timescales. Second, plants build the bulk of their dry weight by fixing C from $CO_2$. Third, because of the gaseous properties of $CO_2$ and high mixing rates in the atmosphere, no other human impact compares to rising [$CO_2$] in its uniformity. Plants worldwide, both agricultural and wild, are exposed to very similar [$CO_2$] concentrations. For these reasons, global patterns in the changes of plant stoichiometry can prevail in spite of local environmental heterogeneity (temperature, humidity, fertilizers, etc.).

#### Plants in enriched $CO_2$ atmospheres

The effects of high [$CO_2$] on plant stoichiometry have received little attention, but its effects on other plant characteristics have been thoroughly studied. Free-Air $CO_2$ Enrichment (FACE) experiments have been running at 32 locations worldwide and >2700 studies have been published in the past decade alone [9]. Doubling ambient [$CO_2$] generally stimulates photosynthesis, enhances plant growth and increases agricultural yields, on average, by 41% [10–13]. These benefits, however, become questionable if enriched [$CO_2$] alters crop stoichiometry. That chemical composition of plants can change under increased [$CO_2$] has been suggested [e.g. 1,7,10], but much of the experimental work has ignored chemical elements and has instead focused on complex compounds, many of which show little consistency in their response to high [$CO_2$] [14,15]. A clear pattern, however, exists for N, the only element whose concentrations in plants under conditions of high [$CO_2$] have been studied extensively. The meta-analysis of the concentrations of N in aboveground plant tissues revealed, on average, a 14% decline in its concentrations under high [$CO_2$] levels [16]. Microelements, such as Fe, I, and Zn, in plants are vital for human health, but little is known about their response to high [$CO_2$]. Not a single study, to my knowledge, analyses the effects of high [$CO_2$] on the concentrations of Se, which is an important antioxidant, or Cr, which is extremely important in the regulation of blood-sugar levels and which is probably deficient in human nutrition [17]. The obscurity of data might explain why no comprehensive review exists about the effects of high [$CO_2$] on plant stoichiometry and why its role in micronutrient malnutrition has not been addressed. As Sterner and Elser [1] point out ‘the limited and diffuse data on elemental composition…result in little awareness and little ability to perceive patterns of interest’, which in turn ‘result in little new data being generated and little effort at compiling those already available’. In lieu of real experiments on plant stoichiometry under increased [$CO_2$], I have run a ‘thought experiment’ (see below). Such ‘experiments’ are conventionally reserved for inherently simpler physical rather than biological systems, but the reliance on stoichiometry simplifies the biology and provides sufficient rigor to gain an insight into the effect of increased [$CO_2$] on plant stoichiometry.

#### A FACE ‘thought experiment’

Two underpinnings of ecological stoichiometry are useful when running a FACE ‘experiment’: (1) a self-evident but important fact that organisms cannot create or convert elements; and (2) the proportions of elements in a plant cell can vary widely, largely because of the presence of a large central vacuole, which is unique to plant cells [1]; for example, Fe or Zn content can vary tenfold or more in grass forage [18].

Suppose that a terrestrial vascular plant, for example wheat, has been grown on two plots, A and B, in identical conditions, except that [CO2] is ambient in A but is doubled in B. If the dry weight of the standing stock in B is $\delta$% higher than in A, are the stoichiometries of A plants and B plants different? Even though the amounts of each individual element in the soil were the same in the two plots, the higher biomass in plot B is the result of stimulated photosynthesis that increased carbohydrate production. If the increase in carbohydrates, the chief constituent of plants, had been the only difference between the two plots, then the C, oxygen (O) and hydrogen (H) content in B plants would differ very little from that in A plants (Box 1, Eqn II). But every other element would have decreased by $\frac{\delta}{1+\delta}$% (Box 1, Eqn III), which provides a baseline estimate of the potential shift in the plant stoichiometry. This underlines the dichotomy between C, O, H (which constitute >90% of the dry weight of plants) and other elements. Hence, patterns in the changes of plant chemical composition should be more evident on the chemical scale of elements rather than on the coarser scales of complex compounds, many of which contain C, O, H and other elements simultaneously.

**Box 1. Elemental vectors: the shift in the stoichiometry of B plants because of carbohydrate dilution**

In ecological stoichiometry, elemental vectors are very useful because they provide a simple means with which to apply the power of mass balance laws to every element.

Let $(a_1,a_2,\ldots,a_n),(b_1,b_2,\ldots b_n)$ and $(c_1,c_2,c_3,0\ldots,0)$ denote elemental vectors for dry A plants, dry B plants and carbohydrates respectively, where the first three terms represents carbon (C), oxygen (O) and hydrogen (H) concentrations and other terms represent concentrations of every other element. Then $\sum_1^n a_i = \sum_1^n b_i = \sum_1^n c_i = 1$ .

Let $M$ denote the total dry weight of A plants. If the $\delta$% increase in biomass of B plants is solely because of the increase in carbohydrates, then mass balance yields (Eqn I):

$$M\cdot(a_1,a_2,\ldots,a_n)+\delta\cdot M\cdot(c_1,c_2,c_3,0\ldots,0)=(1+\delta)\cdot M\cdot(b_1,b_2,\ldots,b_n) \quad \text{[Eqn I]}$$

Thus, $b_i = \dfrac{a_i+\delta c_i}{1+\delta}, i=1,2,3$ and $b_j = \dfrac{a_j}{1+\delta}, j=4,\ldots,n$.. The percentage change in concentrations of C, O and H is $\dfrac{b_i}{a_i}-1=\dfrac{\delta}{1+\delta}\dfrac{a_i-c_i}{a_i}, i=1,2,3$ but because the content of these three elements in plants and carbohydrates is similar, (i.e. $a_i \approx c_i$), it follows that (Eqn II)

$$a_i \approx b_i,\ i=1,2,3 \quad \text{[Eqn II]}$$

For the rest of the elements, the percentage change equals to (Eqn III)

$$\frac{b_j}{a_j}-1=-\frac{\delta}{1+\delta},\ j=4,\ldots,n. \quad \text{[Eqn III]}.$$

The dilution by carbohydrates, however, is unlikely to be the only difference between A and B plants. B plants might adapt to doubled [$CO_2$] by changing their transpiration, root:shoot ratio, root morphology, root activity or symbiotic association with mycorrhizae. Could these adaptations equalize the stoichiometries of A and B plants by increasing the net uptake of every element by the same percentage as the net increase in C? I argue here that these adaptations could alter the $\frac{\delta}{1+\delta}$% decline caused by carbohydrate dilution, but will not neutralize it.

The plots A and B are monocultures, as are most staple crop fields; thus, by employing any of the adaptations listed above, an individual B plant is unlikely to gain any advantage relative to its almost identical neighbours. Moreover, none of the adaptations *per se* can change the total mass of any element in the plot (except C, O and H), but they do alter conditions in the soil, including the stoichiometry of soil near roots and soil moisture. Because elements differ in their diffusion rates and uptake kinetics, the net uptake of each element cannot increase by the same percentage. For example, at higher concentrations, [$CO_2$] diffuses into leaves more easily, thus enabling plants to narrow stomatal apertures and consequently to lose less water, that is to decreases transpiration. This effect has been well documented in experiments with doubled [$CO_2$] on both C3 (e.g. rice and wheat) and C4 (e.g. maize and sugarcane) plants with an average 23% reduction of transpiration [11–13]. Reduced transpiration leads to reduced mass flow in the soil and it can also increase soil moisture [19]. Thus, the two primary mechanisms that transport elements to the vicinity of roots, mass flow and diffusion, are altered in plot B. Mass flow is generally more important for mobile elements, such as N, and diffusion is more important for immobile elements, such as P. Hence, the change in uptake rates should be different among elements in plot B. Furthermore, increased photosynthesis puts differential internal demands on elements. For example, under high [$CO_2$], plant demand can increase for P but decrease for N [20,21]. To summarize, B plants have higher C fixation rates, altered internal elemental demands and changed availability of elements near roots. Therefore, A and B plants should differ not only in C:(other elements) ratios but also in the ratios among other elements (e.g. C:N, N:P and P:Zn should also be different). In other words, the change in the stoichiometry of B plants should be nonuniform across elements. Hence, A plants having the same stoichiometry as B plants should be an exception. (If plant biomass decreases in high [$CO_2$], then a similar argument can again show that plant stoichiometry changes.) Therefore, the conclusion is that high [$CO_2$], as a rule, alters plant stoichiometry.

### Are overall patterns possible?

The above argument suggests that the change in the concentration of elements (except C, O and H) moves in an opposite direction to the change in biomass, but it does not exclude the possibility that levels of some elements can increase or remain unchanged with an increase in biomass under high [$CO_2$]. For human nutrition, however, it is important to know whether overall patterns would exist in high [$CO_2$] world. Terrestrial vascular plants worldwide share what is fundamentally the same physiology and are exposed to essentially the same [$CO_2$], suggesting that overall patterns in the changes of plant stoichiometry are possible. A particularly disturbing, but plausible pattern is one in which the concentrations of essential elements, including those that are already deficient in the diets of the half of the world's population, decrease in plants. As suggested above, both increased carbohydrate accumulation and reduced mass flow can lead to this pattern. All else being equal, this pattern would mean lower (nutritional value):(caloric value) of crops and the aggravation of the micronutrient malnutrition problem. It would also increase the imperative to breed rice, wheat and other staple crops with superior ability to concentrate essential elements such as Fe, Zn, I and Se [6].

### What do the scant published data reveal?

Motivated by the conclusion of the 'thought experiment', I searched extensively for published data on the effects of high [$CO_2$] on the elemental

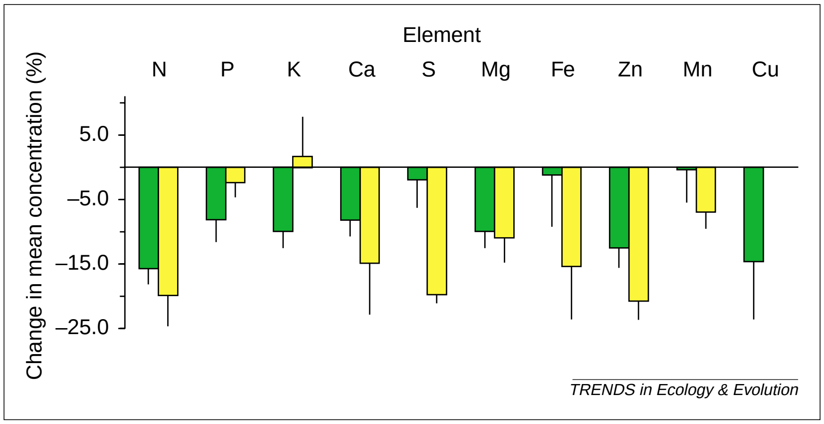


Fig. 1. Changes (%) in the mean concentration of essential elements in plants grown in twice-ambient atmospheric [$CO_2$] relative to those grown at ambient levels [all plants (foliar), green; wheat (grains), yellow]. The figure is based on 25 studies covering 19 herbaceous and 11 woody plant species, and five wheat cultivars [21,24–47], in which multiple elements were measured under increased concentrations of atmospheric carbon dioxide [$CO_2$]. If several [$CO_2$] levels were reported, the data for the levels closest to the ambient and twice-ambient were used. The studies with superenriched or naturally high [$CO_2$] were excluded. Multiple data for a single species or a cultivar were averaged before calculating means. Error bars indicate the standard error of the mean; for foliar data, $n = 30$ for nitrogen (N), phosphorous (P), and potassium (K), 29 for calcium (Ca), 26 for magnesium (Mg), 14 for iron (Fe) and manganese (Mn), 12 for zinc (Zn), 9 for sulphur (S) and copper (Cu); for wheat grains, $n = 5$ for N, P, K, Ca, Mg, Fe and Zn, and 3 for S and Mn. Upon request, I will gladly provide a detailed table with all the data on which this figure is based.

composition of plants. The data are surprisingly scant. I hope that the scarcity and importance of the data will encourage the generation of new data on the changes in plant stoichiometry caused by a globally altered environment. It is startling that, among thousands of publications on doubled [$CO_2$], only one investigated its effects on the grain stoichiometry of rice, the world's most important crop [22]. This study found decreased concentrations of four out of five measured elements in brown rice grains (N, on average, dropped by 14%, P by 5%, Fe by 17%, Zn by 28%, but calcium (Ca) increased by 32%). One can only hope that subsequent studies will not show such a disturbing drop in the levels of Fe and Zn. If high [$CO_2$] does decrease Fe or Zn content in various rice cultivars, even by a few percent, the consequences for the economy and health of regions with strong dietary dependence on rice, such as southeast Asia, could be drastic. For example, rice provides 76% of all calorie intakes for Bangladesh [3], the world's eighth most populous country, where micronutrient deficiency already lowers by 5% its gross domestic product [23].

For the world's second most important crop, wheat, data are also very limited, but exist for at least five cultivars. All three studies show statistically significant changes in grain stoichiometry [24–26] (Fig. 1). On average, the concentration of every measured element except K declined. No similar data, to my knowledge, has been published on other important crops such as maize or rye. Ironically, relatively more data exist on nonstaple crops [27–35] and other terrestrial vascular plants [21,36–47], particularly on their foliar content. All studies found statistically significant changes in the stoichiometry of plant tissues. Although the levels of a few elements increased in some studies, the concentration of every element, on average, decreased (Fig. 1). (Note that the decrease in foliar N is close to the 14% decrease seen for N in aboveground parts, as reported in a meta-analysis by Cotrufo *et al.* [16].) I will not contemplate here on the consequences of these changes to human nutrition and health, but I hope that it is clear that further research on the effects of high [$CO_2$] on plant stoichiometry is vital.

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### Further questions

Are there positive aspects of high [$CO_2$] for human nutrition, other than the expected increases in agricultural yields? Some vitamins, such as A or C, are based entirely on the elements C, O and H; hence, an increase in the levels of those vitamins is not constrained stoichiometrically. For example, vitamin C increased by 5% in orange juice harvested from optimally fertilized trees grown under twice-ambient [$CO_2$] [15]. If the overall content of elements (except C, O and H) decreases, then it is possible that levels of harmful heavy metals, such as lead (Pb) or mercury (Hg), would follow the same trend. If high [$CO_2$], however, aggravates the dietary deficiency of essential elements then none of the above mentioned or any other benefits could induce human bodies to make up the deficit.

Do changes in plant stoichiometry themselves persist over years? Because staple crops have a life span of only a few months, this question is more suited for perennials. In leaves of orange trees, declines in the concentrations of several elements that had been monitored after 30 months of exposure to twice-ambient [$CO_2$], gradually diminished over the subsequent five years [33]. These trees, however, were always well watered and optimally fertilized, and therefore an elemental imbalance in their surroundings was subsided. In Norway spruce, however, the changes in stoichiometry of needles persisted even in fertilized trees over the four years exposure to twice-ambient levels of [$CO_2$] (the experiment used 'branch bag' $CO_2$ exposure technique) [42]. Only one study compared modern plants with those growing at historically lower ambient [$CO_2$]. Herbarium specimens of 13 plant species were analysed for 12 elements [48], including Fe, Zn and Ca. All elements are currently at lower levels than at any time in the past three centuries; notably, stomatal density has also decreased. (The differences in other environmental conditions, however, might also have contributed to these changes.) This raises an important question of whether the current higher [$CO_2$] has already contributed to the existing 'hidden hunger' problem. Over longer timescales, have historic fluctuations of [$CO_2$] affected herbivores by changing the stoichiometry of their resource? It is known that changes in plant quality in twice-ambient [$CO_2$] can strongly affect herbivorous insects [49,50]. From a stoichiometric perspective, all herbivores are similar, thus such effects should not be confined only to insects. Ruminants, including livestock, and other grazers could also be affected. Therefore, it is imperative to recognize and quantify at the early stage how the changing environment shifts the stoichiometry of plants – the foundation of human nutrition and the base of virtually all food webs in nature.

### References


1 Sterner, R.W. and Elser, J.J. (2002) *Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere*, Princeton University Press
2 Williams, R.J.P. and Frausto da Silva, J.R.R. (1996) *The Natural Selection of the Chemical Elements: The Environment and Life's Chemistry*, Clarendon Press
3 Food and Agriculture Organization of the United Nations (2000) *Food Balance Sheets FAOSTAT Database*, available at http://apps.fao.org
4 ACC/SCN (Administrative Committee on Coordination, Subcommittee on Nutrition) and International Food Policy Research Institute (2000) *Fourth Report on the World Nutrition Situation*, United Nations
5 Brown, K.H. and Wuehler, S.E., eds (2000) *Zinc and Human Health: The Results of Recent Trials and Implications for Program Interventions and Research*, Micronutrient Initiative
6 Graham, R.D. *et al.* (2001) Addressing micronutrient malnutrition through enhancing the nutritional quality of staple foods: Principles, perspectives and knowledge gaps. *Adv. Agronom.* 70, 77–142
7 Vitousek, P.M. (1994) Beyond global warming – ecology and global change. *Ecology* 75, 1861–1876
8 Houghton, J.T. and Intergovernmental Panel on Climate Change. Working Group I. (2001) *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Chang*e, Cambridge University Press
9 Jones, M.H. and Curtis, P.S. (2000) *Bibliography on $CO_2$ Effects on Vegetation and Ecosystems: 1990–1999 Literature*, ORNL/CDIAC-129, available at http://cdiac.esd.ornl.gov/epubs/cdiac/cdiac129/cdiac129.html
10 Lemon, E.R. and American Association for the Advancement of Science (1983) *$CO_2$ and Plants: The Response of Plants to Rising Levels of Atmospheric Carbon Dioxide*, Westview Press for the American Association for the Advancement of Science
11 Kimball, B.A. *et al.* (2002) Responses of agricultural crops to fee-air $CO_2$ enrichment. *Adv. Agronom.* 77, 293–368
12 Cure, J.D. and Acock, B. (1986) Crop responses to carbon dioxide doubling - a literature survey. *Agric. Forest Meteorol.* 38, 127–145
13 Rogers, H.H. and Dahlman, R.C. (1993) Crop responses to $CO_2$ enrichment. *Vegetatio* 104, 117–131
14 Hartley, S.E. *et al.* (2000) Biosynthesis of plant phenolic compounds in elevated atmospheric $CO_2$. *Glob. Change Biol.* 6, 497–506
15 Idso, S.B. and Idso, K.E. (2001) Effects of atmospheric $CO_2$ enrichment on plant constituents related to animal and human health. *Environ. Exp. Bot.* 45, 179–199
16 Cotrufo, M.F. *et al.* (1998) Elevated $CO_2$ reduces the nitrogen concentration of plant tissues. *Glob. Change Biol.* 4, 43–54
17 Anderson, R.A. (1998) Recent advances in the clinical and biochemical manifestation of chromium deficiency in human and animal nutrition. *J. Trace Elem. Exp. Med.* 11, 241–250
18 Adams, R.S. (1975) Variability in mineral and trace-element content of dairy-cattle feeds. *J. Dairy Sci.* 58, 1538–1548
19 Hungate, B.A. *et al.* (2002) Evapotranspiration and soil water content in a scrub-oak woodland under carbon dioxide enrichment. *Glob. Change Biol.* 8, 289–298
20 Conroy, J.P. (1992) Influence of elevated atmospheric $CO_2$ concentrations on plant nutrition. *Aust. J. Bot.* 40, 445–456
21 Niinemets, U. *et al.* (1999) Interactive effects of nitrogen and phosphorus on the acclimation potential of foliage photosynthetic properties of cork oak, *Quercus suber*, to elevated atmospheric $CO_2$ concentrations. *Glob. Change Biol.* 5, 455–470
22 Seneweera, S.P. and Conroy, J.P. (1997) Growth, grain yield and quality of rice (*Oryza sativa L.*) in response to elevated $CO_2$ and phosphorus nutrition. *Soil Sci. Plant Nutr.* 43, 1131–1136
23 World Bank (1994) *Enriching Lives: Overcoming Vitamin and Mineral Malnutrition in Developing Countries*, Development in Practice Series, World Bank
24 De la Puente, L.S. *et al.* (2000) Action of elevated $CO_2$ and high temperatures on the mineral chemical composition of two varieties of wheat. *Agrochimica* 44, 221–230
25 Fangmeier, A. *et al.* (1999) Effects on nutrients and on grain quality in spring wheat crops grown under elevated $CO_2$ concentrations and stress conditions in the European, multiple-site experiment 'ESPACE-wheat'. *Eur. J. Agron.* 10, 215–229
26 Manderscheid, R. *et al.* (1995) Effects of season long $CO_2$ enrichment on cereals. 2. Nutrient concentrations and grain quality. *Agric. Ecosyst. Environ.* 54, 175–185
27 Barnes, J.D. and Pfirrmann, T. (1992) The influence of $CO_2$ and $O_3$, singly and in combination, on gas-exchange, growth and nutrient status of radish (*Raphanus sativus L*). *New Phytol.* 121, 403–412
28 Cao, W.X. and Tibbitts, T.W. (1997) Starch concentration and impact on specific leaf weight and element concentrations in potato leaves under varied carbon dioxide and temperature. *J. Plant Nutr.* 20, 871–881
29 Chagvardieff, P. *et al.* (1994) Specific effects of irradiance and $CO_2$ concentration doublings on productivity and mineral content in lettuce. *Life Sci. Space Res.* 14, 269–275
30 Huluka, G. *et al.* (1994) Effects of elevated $CO_2$ and water stress on mineral concentration of cotton. *Agri. Forest Meteorol.* 70, 141–152
31 McKeehen, J.D. *et al.* (1995) Effect of $CO_2$ levels on nutrient content of lettuce and radish. *Naur. Artif. Ecosyst.* 18, 85–92
32 Mjwara, J.M. *et al.* (1996) Photosynthesis, growth and nutrient changes in non-nodulated *Phaseolus vulgaris* grown under atmospheric and elevated carbon dioxide conditions. *Physiol. Plant.* 97, 754–763
33 Penuelas, J. *et al.* (1997) Effects of long-term atmospheric $CO_2$ enrichment on the mineral concentration of *Citrus aurantium* leaves. *New Phytol.* 135, 439–444
34 Prior, S.A. *et al.* (1998) Effects of carbon dioxide enrichment on cotton nutrient dynamics. *J. Plant Nutr.* 21, 1407–1426
35 Schaffer, B. *et al.* (1997) Leaf gas exchange, dry matter partitioning, and mineral element concentrations in mango as influenced by elevated atmospheric carbon dioxide and root restriction. *J. Am. Soc. Horticult. Sci.* 122, 849–855
36 Baxter, R. *et al.* (1994) Effects of elevated carbon-dioxide on three grass species from montane pasture. 2. Nutrient uptake, allocation and efficiency of use. *J. Exp. Bot.* 45, 1267–1278
37 Heagle, A.S. *et al.* (1993) Effects of ozone and carbon dioxide mixtures on two clones of white clover. *New Phytol.* 123, 751–762
38 Kanowski, J. (2001) Effects of elevated $CO_2$ on the foliar chemistry of seedlings of two rainforest trees from north-east Australia: implications for folivorous marsupials. *Aust. Ecol.* 26, 165–172
39 Kuehny, J.S. *et al.* (1991) Nutrient dilution by starch in $CO_2$-enriched chrysanthemum. *J. Exp. Bot.* 42, 711–716
40 Overdieck, D. (1993) Elevated $CO_2$ and the mineral content of herbaceous and woody plants. *Vegetatio* 104, 403–411
41 Pfirrmann, T. *et al.* (1996) Effects of elevated $CO_2$, $O_3$ and K deficiency on Norway spruce (*Picea abies*): nutrient supply, content and leaching. *New Phytol.* 134, 267–278
42 Roberntz, P. and Linder, S. (1999) Effects of long-term $CO_2$ enrichment and nutrient availability in Norway spruce. II. Foliar chemistry. *Trees Struct. Funct.* 14, 17–27
43 Schenk, U. *et al.* (1997) The response of perennial ryegrass white clover mini-swards to elevated atmospheric $CO_2$ concentrations: effects on yield and fodder quality. *Grass Forage Sci.* 52, 232–241
44 Shipley, B. *et al.* (1992) Interacting effects of nutrients, ph-Al and elevated $CO_2$ on the growth of red spruce (*Picea rubens sarg*) seedlings. *Water Air Soil Pollut.* 64, 585–600
45 Walker, R.F. *et al.* (2000) Growth, nutrition, and water relations of ponderosa pine in a field soil as influenced by long-term exposure to elevated atmospheric $CO_2$. *Forest Ecol. Manage.* 137, 1–11
46 Woodin, S. *et al.* (1992) Nutrient limitation of the long-term response of heather (*Calluna vulgaris (L.)* Hull) to $CO_2$ enrichment. *New Phytol.* 122, 635–642
47 Utriainen, J. *et al.* (2000) Biomass allocation, needle structural characteristics and nutrient composition in Scots pine seedlings exposed to elevated $CO_2$ and $O_3$ concentrations. *Trees Struct. Funct.* 14, 475–484
48 Penuelas, J. and Matamala, R. (1993) Variations in the mineral composition of herbarium plant species collected during the last three centuries. *J. Exp. Bot.* 44, 1523–1525
49 Fajer, E.D. *et al.* (1989) The effects of enriched carbon dioxide atmospheres on plant – insect herbivore interactions. *Science* 243, 1198–1200
50 Whittaker, J.B. (2001) Insects and plants in a changing atmosphere. *J. Ecol.* 89, 507–518