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Soil carbon dioxide partial pressure and dissolved inorganic carbonate chemistry under elevated carbon dioxide and ozone

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Abstract Global emissions of atmospheric CO_2 and tropospheric O_3 are rising and expected to impact large areas of the Earth's forests. While CO_2 stimulates net primary production, O_3 reduces photosynthesis, altering plant C allocation and reducing ecosystem C storage. The effects of multiple air pollutants can alter below-ground C allocation, leading to changes in the partial pressure of CO_2 (pCO_2) in the soil, chemistry of dissolved inorganic carbonate (DIC) and the rate of mineral weathering. As this system represents a linkage between the long- and short-term C cycles and sequestration of atmospheric CO_2, changes in atmospheric chemistry that affect net primary production may alter the fate of C in these ecosystems. To date, little is known about the combined effects of elevated CO_2 and O_3 on the inorganic C cycle in forest systems. Free air CO_2 and O_3 enrichment (FACE) technology was used at the Aspen FACE project in Rhinelander, Wisconsin to understand how elevated atmospheric CO_2 and O_3 interact to alter pCO_2 and DIC concentrations in the soil. Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 μl l^{-1}, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1}, respectively. Measured concentrations of soil CO_2 and calculated concentrations of DIC increased over the growing season by 14 and 22%, respectively, under elevated atmospheric CO_2 and were unaffected by elevated tropospheric O_3. The increased concentration of DIC altered inorganic carbonate chemistry by increasing system total alkalinity by 210%, likely due to enhanced chemical weathering. The study also demonstrated the close coupling between the seasonal $\delta^{13}C$ of soil pCO_2 and DIC, as a mixing model showed that new atmospheric CO_2 accounted for approximately 90% of the C leaving the system as DIC. This study illustrates the potential of using stable isotopic techniques and FACE technology to examine long- and short-term ecosystem C sequestration.

Keywords Carbon-13 · Carbon sequestration · FACE · Free air carbon dioxide and ozone enrichment · Global carbonate/silicate weathering cycle

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Introduction

Physiological effects of elevated atmospheric CO_2 and tropospheric O_3

Global CO_2 emissions have risen consistently from pre-industrial levels of 275 μl l^{-1} to current levels in excess of 360 μl l^{-1}, with a concentration of 550 μl l^{-1} predicted by the middle of this century (Houghton et al. 1996). Concurrent with increasing atmospheric CO_2, tropospheric O_3 levels have risen from pre-industrial levels of 10 nl l^{-1} to current summer daytime O_3 levels of 50–70 nl l^{-1}. Estimates of increases in tropospheric O_3 of 1–2% per year may result in a tripling of O_3 concentrations within the next 30–40 years (Chameides et al. 1994; Marenco et al. 1994). Even at low concentrations plants exhibit physiological toxicity to O_3 (Karnosky et al. 1996). With 50% of the world's forests expected to experience increased exposure to both CO_2 and O_3 by 2100 (Fowler et al. 1999), the resulting balance of stimulatory/inhibitory effects on physiological processes may profoundly influence the C stocks of terrestrial ecosystems.

The interacting effects of these two atmospheric pollutants on ecosystem C dynamics are largely unknown, although their individual effects have been well studied. C3 plant photosynthesis is limited by the concentration of atmospheric CO_2, and an increase in the ratio of CO_2:O_2 will increase C assimilation (Tolbert and Zelitch 1983; Sage 1994). This increase in net photosynthesis under elevated CO_2 has consistently been found to change C cycling in forest ecosystems, including: (1) greater C inputs to soil due to increased rates of litterfall, root turnover and rhizodeposition (Pregitzer et al. 1995; DeLucia et al. 1999); (2) increased fungal and bacterial activity and enhanced substrate degradation (Phillips et al. 2002); and (3) increased partial pressure of soil CO_2 (soil pCO_2) (Andrews and Schlesinger 2001; King et al. 2001).

Whereas CO_2 stimulates photosynthesis, increased tropospheric O_3 reduces photosynthesis compared to ambient concentrations (Reich et al. 1990). The decrease in photosynthesis is caused by oxidative damage to cell membranes, light harvesting processes, C fixation, and disruption of C allocation patterns (Pell 1987; Landry and Pell 1993; Chappelka and Samuelson 1998). Oxidative damage can lead to a number of negative effects on forest productivity that ultimately decrease ecosystem C accumulation. These effects include decreased stomatal conductance and photosynthesis, premature leaf abscission, and decreased leaf size (Coleman et al. 1995). The interactive effects of elevated CO_2 and O_3 have recently been found to strongly influence ecosystem C storage. Loya et al. (2003) found that when forest plots under elevated CO_2 are also exposed to elevated O_3, they formed less new soil C than plots exposed to elevated CO_2 alone. However, virtually nothing is known about how elevated CO_2 and O_3 will interact to affect the inorganic C chemistry of soil solutions in forested ecosystems.

Soil pCO_2-dissolved inorganic carbonate interactions

CO_2 and O_3 alter leaf-level plant dynamics, affecting the allocation of photosynthate to root systems, quality of litter inputs, and soil respiration. As CO_2 accumulates in the soil due to the respiration of plant roots and associated soil microorganisms, concentrations of up to 100x atmospheric levels can result (Berthelin 1988). Soil CO_2 reacts with soil water to form dissolved inorganic carbonate (DIC) through the following reaction:

$$\text{Soil } CO_2 + H_2O = H_2CO_3^* \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \tag{1}$$

Thus, changes in belowground C allocation driven by leaf-level dynamics can significantly control DIC production.

In our free air CO_2 and O_3 enrichment (FACE) experiment (see below) the application of a two-member mixing model to DIC chemistry can illustrate the source of increased DIC concentrations in soils. By utilizing the distinct isotopic signal of the highly depleted fumigation CO_2, the measured $\delta^{13}C$ of soil pCO_2, and the measured $\delta^{13}C$ of DIC, we can show the proportion of DIC-C that is attributable to the fumigation gas. Also, by understanding isotopic fractionation, the seasonal $\delta^{13}C$ of DIC can be used to provide evidence for altered belowground chemistry due to changes in soil CO_2 concentrations. Total system DIC, i.e. [DIC], is equal to the summed concentrations of the four inorganic carbonate species:

$$[DIC] = [CO_{2(aq)}] + [H_2CO_3^o] + [HCO_3^-] + [CO_3^{2-}] \tag{2}$$

Though by convention, dissolved CO_2 is expressed in its hydrated form as carbonic acid where:

$$[H_2CO_3^*] = [H_2CO_3^o] + [CO_{2(aq)}] \tag{3}$$

The speciation of Eq. 2 is determined by soil solution pH. At a soil pH lower than approximately 6.4 (depending upon temperature and soil pCO_2), $H_2CO_3^*$ dominates DIC, with HCO_3^- dominating at pH from 6.4 to 10.3. Significant isotopic fractionation occurs during the pH-mediated speciation of DIC. Soil CO_2 undergoes a 1.1‰ depletion as it forms $H_2CO_3^*$, and then a 9.0‰ enrichment as it forms HCO_3^- (Clark and Fritz 1997). Presumably, changes in the $\delta^{13}C$ ratio of DIC correlate with changes in inorganic chemistry: as soil alkalinity rises, increasing the abundance of HCO_3^-, the $\delta^{13}C$ signature of DIC should become increasingly enriched relative to that of soil pCO_2.

Field studies have shown that elevated atmospheric CO_2 increases the concentration of soil CO_2 (Andrews and Schlesinger 2001; King et al. 2001). Henry's Law (i.e., the amount of gas that dissolves in a liquid is proportional to the partial pressure of the gas over the liquid) dictates that an increase in CO_2 concentration alone will increase the equilibrium concentration of $H_2CO_3^*$ by a factor of $10^{-1.5}$ (Pankow 1991). Thus, not only does elevated soil pCO_2 potentially increase the rate of mineral weathering in soil, it can be expected that elevated atmospheric CO_2 increases the rate of amount of mineral weathering by increasing the formation of $H_2CO_3^*$ (Berner 1997; Bormann et al. 1998; Berg and Banwart 2000). $H_2CO_3^*$ then readily weathers carbonates to form free Ca^{2+} and HCO_3^- :

$$CaCO_3 + H_2CO_3^* \Rightarrow Ca^{2+} + 2HCO_3^- \tag{4}$$

Through this reaction, weathering neutralizes acidic CO_2 that is in the form of $H_2CO_3^*$, and keeps it in solution as HCO_3^-. Silicate weathering meanwhile, extracts alkalinity from silicate minerals, as exhibited by the weathering of olivine by $H_2CO_3^*$:

$$Mg_2SiO_4 + 4H_2CO_3^* \Rightarrow 2Mg^{2+} + H_4SiO_4 + 4HCO_3^-; \tag{5}$$

and/or the hydrolysis of orthoclase feldspar by H^+:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \Rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+. \quad (6)$$

The combined processes of weathering, riverine export, and deposition of marine carbonates is a transfer and sequestration of atmospheric CO_2, representing a long-term negative feedback to global warming (Drever 1994; Lackner 2002). However, the extent to which this feedback mechanism has been fully explored under experimental conditions of elevated atmospheric CO_2 is limited and confounded by gaps in understanding the ecosystem-level effects of elevated atmospheric O_3.

Objectives and hypothesis

The objectives of this study were to determine the effects of elevated CO_2 and O_3 on DIC and soil inorganic chemistry in north temperate forest ecosystems, and comment upon their role in the silicate weathering cycle in soil. This was done by quantifying DIC, tracking the $\delta^{13}C$ signature of the ecosystem, and examining DIC speciation and $\delta^{13}C$ fractionation. Our first hypothesis was that elevated atmospheric CO_2 increases soil pCO_2 and DIC concentrations, while elevated O_3 results in a decrease in soil pCO_2 and DIC. We further hypothesized that soil pH would decrease under elevated CO_2 due to an increase in the activity of H^+ and $H_2CO_3^*$.

Materials and methods

Study site

This study was conducted at the 32-ha FACTS-II Aspen FACE Project, a CO_2 and O_3 enrichment experiment located near Rhinelander, Wisconsin (latitude 45.6°, longitude 89.5°). The soil is a Pandus sandy loam (mixed, frigid, coarse loamy Alfic Haplorthod) derived from non-calcareous sandy to loamy glacial till. These soils were deposited over lower Proterozoic system mafic to felsic and tonalitic to granodioritic rocks. The field experiment consists of a randomized complete block design: three blocks of four treatments (control, elevated CO_2, elevated O_3, and elevated CO_2+O_3). The experimental rings are 30 m in diameter and each treatment is replicated 3 times. The rings were planted in June 1997 with trees at a 1×1 m spacing: half of the ring was planted with *Populus tremuloides* var. Michaux (trembling aspen) clones of differing sensitivity to CO_2 and O_3, a quarter was planted with a 1:1 mix of *P. tremuloides* and *Betula papyrifera* var. Marsh (paper birch), and the final quarter was planted with a mix of *P. tremuloides* and *A. saccharum* var. Marsh (sugar maple). Only the aspen and aspen-birch sections of the ring were measured in this study.

CO_2 is stored and transferred to ambient-air heat exchangers that vaporize the liquefied CO_2 before it is routed as a gas to individual rings. Liquefied O_2 is transferred as needed to an ozone generator before it is routed as O_3 to each ring. At each ring, pipes spaced uniformly around each plot release the fumigation gases in proportions dictated by real-time computer algorithms. For the 2002 growing season the CO_2 fumigation period lasted from 28 May to 11 October for an exposure period of 138 days. Ambient CO_2 levels averaged 360 ± 16 μl l^{-1} while the concentration of elevated CO_2 plots averaged 542 ± 81 μl l^{-1} (J. Sober, personal communication). The O_3 fumigation period lasted from 29 May to 11 October for an exposure period of 137 days. Ambient O_3 levels averaged 33 ± 14 nl l^{-1} while the concentration of elevated O_3 plots averaged 49 ± 24 nl l^{-1} (J. Sober, personal communication). A complete description of the project design, justification, hardware, and performance data can be found in Dickson et al. (2000).

Field sampling

Bi-weekly samples were collected from 1 May to 28 October 2002 using belowground collection equipment installed in 1998 and methodology as described by King et al. (2001). Soil pCO_2 was withdrawn from soil gas wells at depths of 15, 30, and 125 cm in each species section and injected into serum vials sealed with butyl rubber septa. Samples were analyzed at the USDA Forestry Sciences Laboratory (Houghton, Mich.) with a Varian CP-3800 gas chromatograph equipped with a thermal conductivity detector; certified NIST-traceable gas was used to develop standard curves. Soil solution was collected using tension lysimeters installed adjacent to each soil gas well. Soil solution was withdrawn, and volume, temperature, pH, and conductivity were measured using a portable pH meter. Water samples were collected in acid-washed HDPE bottles and transported under refrigeration to the laboratory where they were acidified to pH≈2.0 with HCl, filtered (0.45 μm), and stored at 4°C. The speciation and concentration of DIC was calculated for each sampling date according to well-established carbonate equilibria reactions (Garrels and Christ 1965) using field measured soil pCO_2, solution pH, and temperature. Field measured pH was corrected for degassing following the method of Suarez (1987) and used to calculate DIC.

The $\delta^{13}C$ of the CO_2 in the fumigation tank was sampled by withdrawing a 50-ml sample from the supply line with a syringe, flushing a 10-ml Exetainer vial (Labco no. 438B) with 40 ml of the gas, and then injecting the final 10 ml. The vial was then subsampled and diluted with He prior to isotopic analysis. Soil pCO_2 for $\delta^{13}C$ analysis was subsampled concurrently with soil pCO_2. A set of 10-ml Exetainer vials (Labco no. 438B) that had been previously flushed with high purity He was brought into the field. Immediately before sampling, 4 ml He was withdrawn with a syringe from the vial, and 4 ml soil CO_2 for $\delta^{13}C$ analysis was injected to maintain a constant pressure. DIC for $\delta^{13}C$ analysis was sampled from lysimeters using a modified gas evolution technique (Atekwana and Krishnamurthy 1998; Andrews and Schlesinger 2001). Using this technique, 0.25 μl of 85% phosphoric acid was added to a Labco Exetainer vial (no. 738 W) that was subsequently evacuated. Immediately upon removal of water from the tension lysimeter, 1.5 ml of the soil solution was injected into the sealed Exetainer vial with a syringe for the $\delta^{13}C$ analysis of DIC. All samples were analyzed within the 9-day precision estimates provided by Tu et al. (2001). The $\delta^{13}C$ analyses were performed at the Forest Ecology Stable Isotope Ratio Mass Spectrometry Laboratory in the School of Forest Resources and Environmental Science at Michigan Technological University.

C stable isotope analysis and stable C tracer

The gas isotopic analysis was performed using a ThermoFinnigan GasBench II coupled to a DELTA^{plus} continuous flow-stable isotope ratio mass spectrometer (Bremen, Germany). IAEA-, USGS-, and NIST-certified isotopic standards were used to calibrate standard gas with a $\delta^{13}C$ value of −49.6‰, relative to V-PDB dolomite, where δ is defined as $[(\text{ratio}_{\text{sample}}/\text{ratio}_{\text{standard}})-1]\times 1{,}000$. Overall analytical precision was ±0.3‰ for $\delta^{13}C$. The proportion of C in DIC attributable to biogenic pCO_2 (f_{bio}) was calculated using the equation: $f_{\text{bio}} = (\delta_1 - \delta_o)/(\delta_2 - \delta_o)$, where δ_1 and δ_2 are the measured $\delta^{13}C$ values of DIC and soil pCO_2, respectively, and δ_o the $\delta^{13}C$ value of soil carbonate. The $\delta^{13}C$ value of soil carbonate was assumed to be −1.7‰, halfway between the reported range of −5.3 to +1.9 as reported by Middleton et al. (1990) for southern Ontario and Taylor and Sibley (1986) for the Michigan basin, respectively. A sensitivity analysis revealed that the range of values had no impact on the results of the mixing model (results not shown). The $\delta^{13}C$ values of $H_2CO_3^*$ and HCO_3^- were calculated from fractionation measurements provided by Clark and Fritz (1997). The experimental fumigation CO_2 is derived from fossil fuel and had a cumulative 4-year $\delta^{13}C$ mean (SD) of −42.1‰ (1.85) from 1999 to 2002. The treatment-level $\delta^{13}C$ of atmospheric CO_2 means (SD) in the forest canopy in 2002 were: control, −7.6‰ (0.46); $+CO_2$, −18.5‰ (0.94); $+O_3$, −7.2‰ (0.22); $+CO_2\times O_3$, −19.0‰ (2.25). These values represent the $\delta^{13}C$ of atmospheric CO_2 after the fumigation gas was mixed with the ambient atmosphere.

Statistical analysis

Analysis required repeated measures ANOVA since the same experimental units were measured repeatedly over time. Data were analyzed with a repeated measures ANOVA model for a randomized complete block design using SAS 8.02 (Cary, N.C.) after King et al. (2001). Experimental block is a fixed effect (Dickson et al. 2000) accounting for soil differences across the site. To control for heterogeneity of variance, soil pCO_2, total alkalinity, [DIC], [H_2CO_3*], [HCO_3^-], [CO_3^{2-}], [OH^-] and [H^+] normal probability plots were inspected. Data were square root transformed prior to analysis, as this transformation best satisfied model assumptions. Hypothesis tests were conducted at the $P \le 0.05$ level of confidence, and trends were reported when $P < 0.10$. Displayed values represent the plot means averaged across the two species split plots (aspen and aspen-birch), three depths (15, 30, and 125 cm), and $n=3$ replicates. To simplify display, the $+O_3$ and control treatments and the $+CO_2$ and $+CO_2\times O_3$ treatments were combined in Figs. 1 and 2. The tabular data remain unchanged.

Results

Soil pCO_2

CO_2 concentrations in the soil atmosphere were positively related to changes in soil temperature. Seasonal patterns in soil pCO_2 appeared to be related to increases in mean daytime soil temperature, with peak soil pCO_2 concentrations occurring with peak soil temperature in July and August (Fig. 1). This gave rise to a highly significant seasonal effect ($P < 0.001$). The soil pCO_2 level in the elevated CO_2 treatments was higher on all sampling dates than in the ambient CO_2 treatments, with this difference being marginal from early May until late June, and most pronounced from July to September, when the soils were warmer. Soil pCO_2 concentrations in the ambient CO_2 plots ranged from 7,000 μl l^{-1} in early May to a peak of 24,000 μl l^{-1} in mid July. Soil pCO_2 concentrations in the elevated CO_2 plots followed the same temporal pattern with a 7,500 μl l^{-1} baseline in early May and a mid July peak of 32,500 μl l^{-1}. Exposure to elevated atmospheric CO_2 significantly increased soil pCO_2 concentrations ($P = 0.0239$), though there were no other significant interactions. Although no other interaction was significant, there was a trend in the data toward a $+O_3\times$Time interaction ($P = 0.0599$). This effect, however, did not appear to be distinct from the other treatments (data not shown).

Dissolved inorganic carbonate

DIC concentrations followed very similar patterns to soil pCO_2 across the growing season, giving rise to a highly significant seasonal effect ($P < 0.001$). Soil DIC concentration was greater in the elevated CO_2 treatment on all sampling dates ($P = 0.0189$), and this difference was consistent through the growing season (Fig. 1c).

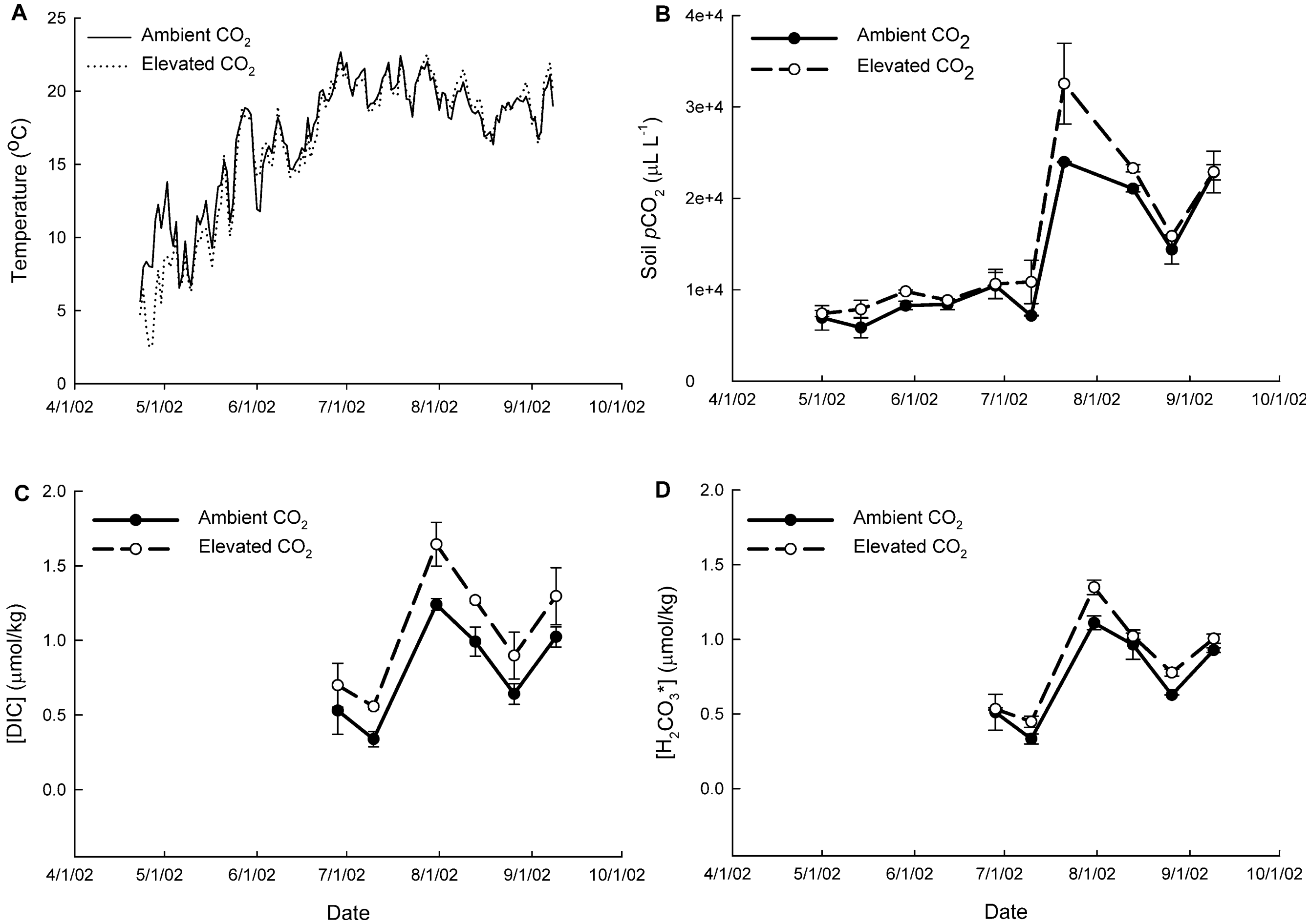

Fig. 1 Seasonal 2002 soil temperature at 10 cm (**a**), soil partial pressure of CO_2 (pCO_2) (**b**), soil solution dissolved inorganic carbonate concentration (*[DIC]*) (**c**), and soil solution carbonic acid concentration (*[$H_2CO_3^*$]*) (**d**) at the FACTS II Aspen free air CO_2 and O_3 enrichment (FACE) experiment located near Rhinelander, Wisconsin. Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 µl l^{-1}, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1}, respectively. For display purposes, the $+O_3$ and control treatments and the $+CO_2$ and $+CO_2 \times O_3$ treatments were combined, respectively. Displayed values are plot means averaged across two species subplots, three depths, and $n = 6$ replicates; *bars* represent SEs

DIC concentrations in the ambient CO_2 plots ranged from 0.33 to 1.24 µmol kg^{-1}, while concentrations in the elevated CO_2 plots ranged from 0.56 to 1.65 µmol kg^{-1}. Depth was also significant ($P < 0.001$), with concentrations increasing with increasing soil depth. Although there was a trend in the $+CO_2 \times O_3$ treatment towards higher DIC concentrations ($P = 0.0829$) (Table 1); there were no other Species×Time or Species×Depth interactions.

To ensure that the pH correction was not affecting the calculated differences in DIC concentrations, DIC was also calculated using the uncorrected pH measurements. The results were similar to those obtained using the corrected pH (data not shown). Seasonal patterns were very similar to soil pCO_2, with DIC concentrations in the elevated CO_2 treatments consistently higher than those in the ambient treatments ($P = 0.1141$). However, the use of uncorrected pH measurements in the DIC calculation overstated DIC concentrations by 6–24% compared to the use of corrected pH measurements.

Inorganic carbonate chemistry

The concentrations of H_2CO_3*, HCO_3^-, CO_3^{2-}, OH^- and total alkalinity (A_T) followed seasonal patterns similar to that of soil pCO_2 (Fig. 1d, results only shown for H_2CO_3*). Exposure to elevated CO_2 consistently increased ion concentrations and A_T (Table 1). The opposite effect, however, was observed for [H^+], where exposure to elevated CO_2 reduced the concentration. Though these changes were significant for [$H_2CO_3^*$] ($P = 0.0281$), they were not statistically significant for any other ionic species. All ionic species other than [$H_2CO_3^*$] exhibited a highly significant depth effect (Table 2): the concentration of $H_2CO_3^*$ and H^+ increased with soil depth, while the concentration of HCO_3^-, CO_3^{2-}, OH^- and A_T decreased with soil depth. Time was also highly significant for A_T and all ionic species, except [H^+] and [OH^-], with peak concentrations occurring in August. These results were driven by changes in soil pCO_2 with depth, time of year, and treatment.

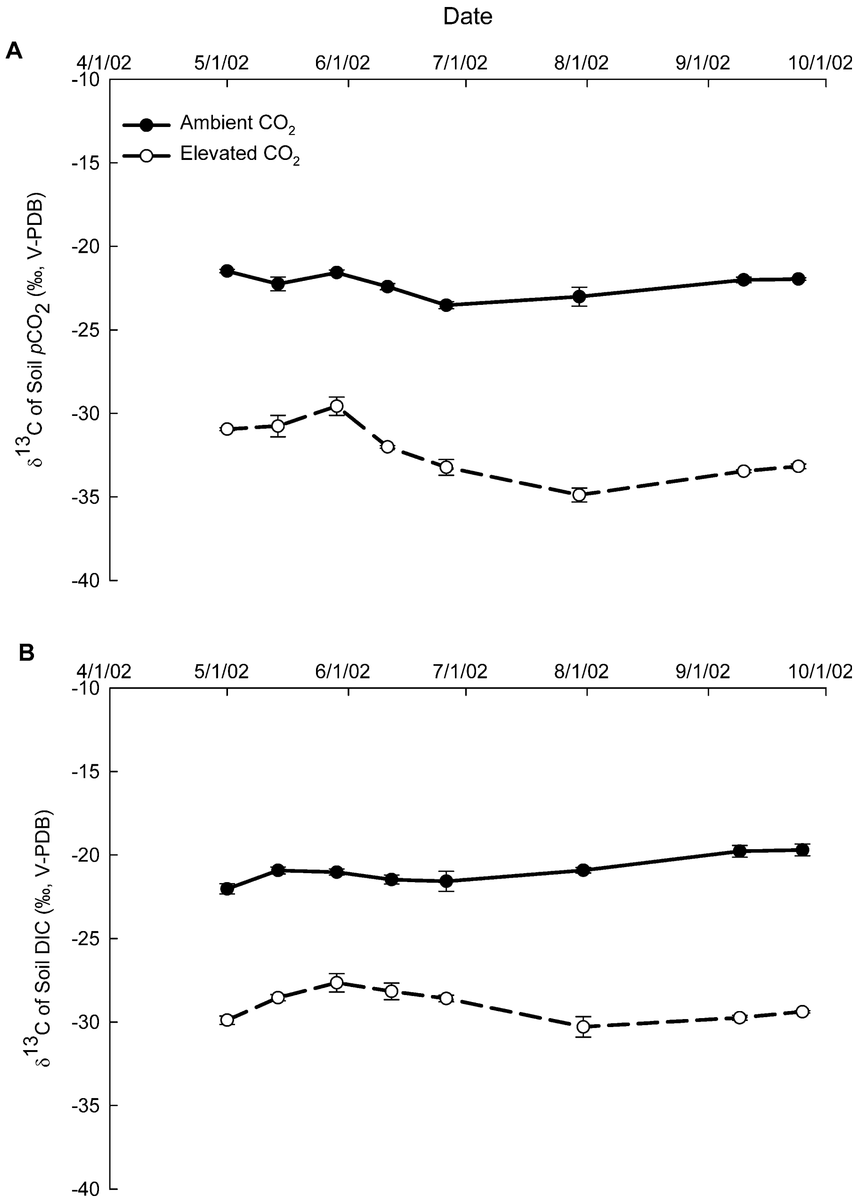

Fig. 2 Seasonal 2002 $\delta^{13}C$ of soil pCO_2 (**a**) and DIC (**b**) at the FACTS II Aspen FACE experiment. Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 μl l^{-1}, respectively; ambient and elevated O_3 levels were 33 and 49 ± 24 nl l^{-1}, respectively. For display purposes, the $+O_3$ and control treatments and the $+CO_2$ and $+CO_2 \times O_3$ treatments have been combined, respectively. Displayed values are plot means averaged across two species subplots, three depths, and $n = 6$ replicates; *bars* represent SEs. For abbreviations, see Fig. 1

$\delta^{13}C$ of soil pCO_2

The heavily depleted $\delta^{13}C$ signal of the fumigation gas led to significant ($P < 0.001$) differences in the isotopic ratio of soil pCO_2 between the ambient and elevated CO_2 treatments (Table 3). The average $\delta^{13}C$ of soil pCO_2 values in ambient CO_2 plots was measured at −21.5‰ in May, and became steadily more depleted to −23.5‰ in early July (Fig. 2a). Values then became steadily enriched into October. The $\delta^{13}C$ of soil pCO_2 followed a different pattern in the elevated CO_2 treatment. $\delta^{13}C$ values were measured at −30.0‰ in May, and became consistently depleted to values of −34.9‰ in late July. Values then became slightly enriched into October. Though values in the elevated atmospheric CO_2 treatments were already depleted by 9.0‰, they became increasingly depleted relative to ambient CO_2 treatments as the growing season progressed. These patterns gave rise to a significant seasonal time effect ($P < 0.001$) and $+CO_2 \times$Time effect ($P < 0.001$). A strong species effect was observed, with the $\delta^{13}C$ of soil pCO_2 becoming more depleted in aspen-birch subplots than in pure aspen subplots ($P = 0.0058$) (data not shown). A strong depth effect was also observed, with $\delta^{13}C$ values becoming more depleted with depth in the soil profile ($P = 0.0086$) (data not shown). The $\delta^{13}C$ of the fumigation gas was consistent throughout the growing season and did not explain the isotopic variation seen in the CO_2 fumigated plots.

$\delta^{13}C$ of DIC

The depleted $\delta^{13}C$ signal in the fumigation gas also led to significant differences in isotopic ratios between ambient and elevated CO_2 plots for DIC ($P < 0.001$),

Table 1 Inorganic C species concentrations at the FACTS II Aspen free air CO_2 and O_3 enrichment (FACE) experiment[a] located near Rhinelander, Wisconsin. Displayed values are plot means averaged across two species subplots, three depths, six sampling dates, and $n = 3$ replicates with the SE given *in parentheses*. *Different letters* following means represent significantly different values by treatment (repeated measures ANOVA, $\alpha = 0.05$). pCO_2 Partial pressure of CO_2, *DIC* dissolved inorganic carbonate, A_T Total alkalinity

Treatment	Soil pCO_2 ($\mu l\ l^{-1}$)[b]	DIC (μmol/kg)	$H_2CO_3^*$ (μmol/kg)	HCO_3^- (μmol/kg)	H^+ (nmol/kg)	CO_3^{2-} (pmol/kg)	OH^- (pmol/kg)	A_T (μmol/kg)[c]
Control	13,500 (890) a	0.84 (0.06) a	0.75 (0.05) a	0.09 (0.02) a	23.3 (4.61) a	2.66 (0.96) a	2.76 (0.37) a	0.07 (0.02) a
$+CO_2$	14,700 (800) b	0.98 (0.07) b	0.84 (0.06) b	0.14 (0.03) a	16.1 (6.05) a	7.00 (3.24) a	4.82 (0.92) a	0.13 (0.03) a
$+O_3$	13,100 (810) a	0.83 (0.05) a	0.73 (0.05) a	0.10 (0.03) a	216.8 (118.5) a	2.41 (0.38) a	3.57 (0.37) a	−0.11 (0.12) a
$+CO_2 \times O_3$	15,700 (900) b	1.06 (0.06) b	0.86 (0.05) b	0.20 (0.03) a	18.2 (3.79) a	12.98 (3.76) a	5.64 (1.00) a	0.18 (0.03) a

[a] Ambient and elevated CO_2 levels were 360 ± 16 and $542 \pm 81\ \mu l\ l^{-1}$, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1} [b] Soil pCO_2 was directly measured; DIC, A_T, and speciation were calculated from measured soil pCO_2, temperature, and pH according to carbonare equilibria reactions formulated by Garrels and Christ (1965)

though no differences were seen for elevated O_3. $\delta^{13}C$ of DIC in ambient CO_2 plots was measured at −22.0‰ in May, and became consistently enriched to values of −19.7‰ in October (Fig. 2b). $\delta^{13}C$ values followed a different pattern in the elevated CO_2 treatment, which also could not be explained by the seasonal $\delta^{13}C$ of the fumigation gas. $\delta^{13}C$ values were measured at −29.0‰ in early May, and became enriched to a value of −27.6‰ in late May (Fig. 2b). Values then became consistently depleted to −30.0‰ in October. This gave rise to a highly significant time effect ($P < 0.001$). While $\delta^{13}C$ values in elevated CO_2 treatments became more depleted relative to those in the ambient CO_2 plots, there were no significant time interactions to explain this tendency. No Species, Species×Time, Depth, or Species×Depth interactions were significant. As $\delta^{13}C$ of H_2CO_3 and HCO_3^- were calculated from $\delta^{13}C$ of soil pCO_2, these trends follow those of soil pCO_2 and thus *P*-values are not displayed, although annual means are displayed in Table 3.

Discussion

Elevated atmospheric CO_2 has been hypothesized to increase soil pCO_2 through increased fine root production and turnover, and resulting increases in the respiration of autotrophs (R_A) and heterotrophs (R_H). Fine root production (measured in 1999) in the same stands of *P. tremuloides* increased 96% relative to the control under experimental atmospheric CO_2 enrichment (King et al. 2001). *P. tremuloides* fine root biomass was also shown to increase by 52% under elevated atmospheric CO_2 in an open top chamber study (Pregitzer et al. 2000). An increase in fine root biomass of 86% has also been reported for a similar forested FACE experiment of *Pinus taeda* (Matamala and Schlesinger 2000). While these increases in fine root standing stock represent increased levels of R_A, they also facilitate increases in R_H. For the 1999 data, King et al. (2001) reported a 139% increase in dead-root stock under elevated CO_2, and the authors have concluded that elevated atmospheric CO_2 increases fine root turnover (Kubiske et al. 1998; Pregitzer et al. 1995, 2000). As most microbial communities are C limited (Zak and Pregitzer 1998), this enhanced addition of organic matter through organic acids, root turnover, and increased microbial metabolism likely increased R_H as well (Zak et al. 2000).

Soil pCO_2 concentrations, averaged across soil depths and species subplots increased by 14% under elevated CO_2. Similar increases under elevated CO_2 have previously been reported (Andrews and Schlesinger 2001; King et al. 2001). With increasing concentrations of soil CO_2, Eq. 1 is driven to the right, increasing the production of DIC. The increase in DIC was calculated to be 22% under elevated CO_2. Though DIC concentrations were calculated with pH values that were corrected for tension lysimeter degassing, it is noted that DIC

Table 2 *P*-values for calculated carbonate chemistry speciation at the FACTS II Aspen FACE experiment[a]. Appropriate *F*-test error terms for a split-plot randomized design with a fixed block effect. Significant ($\alpha = 0.05$) values are shown as well as trends ($\alpha < 0.10$)

Source	$[H_2CO_3]$	$[HCO_3^-]$	$[H^+]$	$[CO_3^{2-}]$	$[OH^-]$	A_T
$+CO_2$	0.0281					
$+CO_2 \times O_3 \times$Species	0.0829					
Time	< 0.001	0.0026		0.0160	0.0796	0.0002
$+O_3 \times$Time	0.0957					
$+CO_2 \times$Species$\times$Time	0.0325					
$+O_3 \times$Species$\times$Time					0.0593	
Depth		0.0010	0.0029	0.0005	0.0006	0.0001
$+O_3 \times$Depth						0.0451

[a]Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 µl l^{-1}, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1}, respectively

Table 3 A comparison of $\delta^{13}C$ ratios from the FACTS II Aspen FACE experiment[a]. Displayed values are plot means averaged across two species subplots, three depths, eight sampling dates, and $n = 3$ replicates with the SE given *in parentheses*. *Different letters* following column means represent significantly different values by treatment (repeated measures ANOVA, $\alpha = 0.05$). For abbreviations, see Table 1

Treatment	$\delta^{13}pCO_2$ (‰)[b]	δ^{13} DIC (‰)[b]	δ^{13} H_2CO_3 (‰)[c]	δ^{13} HCO_3 (‰)[c]	pCO_2-C as DIC-C (‰)[d]
Control	−21.5 (0.29) a	−21.6 (0.12) a	−22.6 (0.30) a	−13.6 (0.30) a	100.0 (0.67)
$+CO_2$	−32.4 (0.31) b	−29.6 (0.26) b	−33.5 (0.31) b	−24.5 (0.31) b	92.3 (0.01)
$+O_3$	−20.7 (1.05) a	−20.5 (0.13) a	−21.8 (1.05) a	−12.8 (1.05) a	99.2 (3.70)
$+CO_2 \times O_3$	−32.3 (0.31) b	−28.8 (0.26) b	−33.4 (0.31) b	−24.4 (0.31) b	90.4 (0.06)

[a]Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 µl l^{-1}, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1}, respectively

[b]$\delta^{13}pCO_2$ and δ^{13} rscript> DIC were directly measured

[c]δ^{13} H_2CO_3 and δ^{13} HCO_3 were calculated from measured $\delta^{13}pCO_2$ and fractionation measurements provided by Clark and Fritz (1997) and Zhang et al. (1994)

[d]The percentage of DIC-C derived from soil pCO_2 was calculated using a mixing model (see Materials and methods)

calculations utilizing uncorrected pH measurements may overstate DIC concentrations by up to 25%, since the concentration of DIC increases with pH (Fig. 3). The concentration of $H_2CO_3^*$ increased by 22% due to increased concentrations of soil CO_2, as governed by the Henry's law constant, K_H. However, while the concentration of $H_2CO_3^*$ increased under elevated CO_2, it made up a proportionately smaller percentage of DIC–C. The percentage of DIC–C existing as HCO_3^- increased from 11% under ambient CO_2 to 17% under elevated CO_2. This proportional increase in HCO_3^- under elevated CO_2 is accompanied by increases in the concentrations of carbonate (CO_3^{2-}), hydroxide (OH^-), and total alkalinity, as well as a decrease in the concentration of H^+.

Taken together these results support our first hypothesis that elevated atmospheric CO_2 can be shown to increase soil pCO_2 and concentrations of DIC. Trends in the data also suggest support for our hypothesis that elevated O_3 reduces soil pCO_2 and DIC. The effects of elevated O_3, however, are not statistically distinguishable from the other treatments. These data do not support our second hypothesis, that soil acidity will increase under elevated CO_2 due to increased concentrations of H^+ and $H_2CO_3^*$. The data instead show the opposite effect, that elevated atmospheric CO_2 increases soil alkalinity, and that soil pH is buffered by changes in soil inorganic carbonate chemistry under elevated CO_2. These observations are explained by an open system model of equilibrium carbonate chemistry (Fig. 3).

In the ambient CO_2 model, the open system equilibrium model is driven by the external soil pCO_2 concentration of 13,500 µl l^{-1}. Through carbonate equilibria equations and Henry's Law, the concentration of external soil pCO_2 then dictates $[H_2CO_3^*]$, which remains constant across the pH range. While $[H_2CO_3^*]$ remains constant, total DIC increases after pH 5.0 because of the increasing contribution of HCO_3^- until the species contribute an equal portion of C to DIC. Under elevated atmospheric CO_2, the system is driven by the external soil pCO_2 concentration of 14,500 µl l^{-1}. This greater concentration of external soil pCO_2 under elevated CO_2 then establishes a greater concentration of $H_2CO_3^*$. Figure 3 illustrates the result of these shifts in the open system equilibrium model. Under elevated soil pCO_2, the concentration of $H_2CO_3^*$ increases, as does the concentration of HCO_3^-. However, due to a small increase in pH the elevated CO_2 system equilibrium point moves to the right as well, explaining the greater proportion of HCO_3^- -derived C in DIC (Fig. 3).

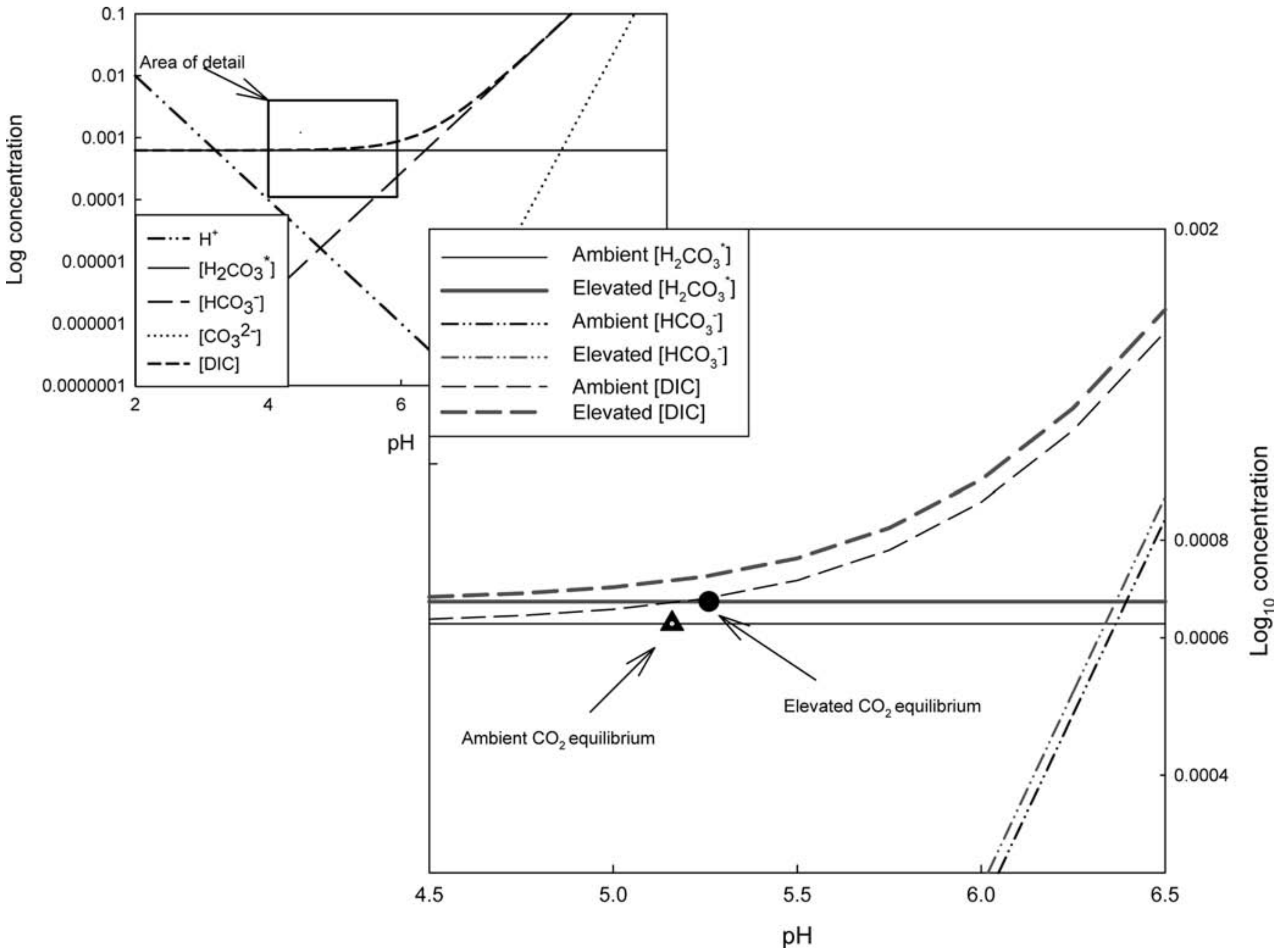

Fig. 3 Open system equilibrium diagram for ambient CO_2 FACE conditions of 16.3°C, pH of 5.16 and soil pCO_2 of $10^{-1.87}$ (13,500 μl l^{-1}). Ambient and elevated CO_2 levels were 360 ± 16 and 542 ± 81 μl l^{-1}, respectively; ambient and elevated O_3 levels were 33 ± 14 and 49 ± 24 nl l^{-1}, respectively. *Inset* illustrates equilibrium model shifts under the elevated CO_2 FACE system

Seasonal $\delta^{13}C$ data also support the assumptions of the open system equilibrium model. Distribution models show that system pH governs the distribution of carbonate species in water (Clark and Fritz 1997). In the FACTS II Aspen FACE experiment, $H_2CO_3^*$ is the dominant C-bearing species, with the importance of HCO_3^- increasing with pH. Fractionation models show that this pH-mediated speciation results in a temperature-dependent fractionation, with $\delta^{13}C$ values becoming depleted by approximately 1.1‰ from $CO_{2(g)}$ to $H_2CO_3^*$, and enriched 9.0‰ from $H_2CO_3^*$ to HCO_3^- (Zhang et al. 1994; Clark and Fritz 1997). Thus, with a $\delta^{13}C$ of soil pCO_2 of −21‰, DIC having a pure $H_2CO_3^*$ or HCO_3^- source would be −22.2 and −13.2‰, respectively. Under ambient CO_2, the $\delta^{13}C$ of DIC is very similar to soil pCO_2, suggesting very little influence of HCO_3^- on $\delta^{13}C$. However, under elevated CO_2, the measured $\delta^{13}C$ of DIC is enriched compared to soil pCO_2, suggesting a larger contribution of the enriched HCO_3^- to total DIC. It is unlikely that this pattern was complicated by contamination from local carbonate minerals with $\delta^{13}C$ ranges from −5.3 to 1.9‰ as reported by Middleton et al. (1990) for southern Ontario and Taylor and Sibley (1986) for the Michigan basin. Carbonates have already been weathered from the upper meter of this soil (D. R. Zak, personal communication), and laboratory tests for the presence of inorganic carbonate were negative (data not shown). Furthermore, seasonal $\delta^{13}C$ of soil pCO_2 and DIC showed no influence of enrichment that could be caused by rising water tables or hydraulic lift carrying carbonate-contaminated water from deeper soil to the near surface. Measured $\delta^{13}C$ of DIC and soil pCO_2 in the elevated CO_2 treatments agrees well with values calculated in the manner of Stumm and Morgan (1981) as displayed in Amiotte-Suchet et al. (1999) and values from another FACE system (Andrews and Schlesinger 2001). Values in the ambient CO_2 treatments also fall within the range of natural variation found in forest ecosystems (Kendall and McDonnel 1998).

Taken together, these data suggest to us that elevated atmospheric CO_2 alters ecosystem inorganic carbonate chemistry. A 50% increase in atmospheric CO_2 resulted in a 14% increase in soil pCO_2 concentrations. In the absence of carbonate, soil pCO_2 would account for all C present in DIC (Kendall and McDonnel 1998). With the use of a mixing model and assumed values of soil carbonate (see Materials and methods), 95–100% of DIC–C is attributable to biogenic pCO_2, establishing elevated atmospheric CO_2 as the direct cause of increased DIC concentration and altered speciation (Table 3). This finding also provides evidence that short-term terrestrial C cycling may be linked to the long-term silicate C weathering cycle through a time step shorter than may have been previously assumed. Soil pCO_2 increased by 14% under elevated CO_2 and $[H_2CO_3^*]$ increased by 14% also, as expected by K_H. However, calculated DIC concentrations increased by 22%, with a 78% increase in $[HCO_3^-]$, a 294% increase in $[CO_3^{2-}]$, and a 210% increase in A_T. The increases in [DIC] have likely contributed to the calculated increase in speciation and A_T. These increases may also be due in part to enhanced primary mineral weathering by increased production of $H_2CO_3^*$. It is possible that weathering of silicates (Eqs. 4, 5) increases alkalinity through the production of HCO_3^- and OH^-. Sufficient amounts of P- or S-bearing minerals could result in the weathering of sulfate and phosphate in concentrations high enough to neutralize H^+, explaining the pattern seen in $[H^+]$ under elevated CO_2 in Table 3. It is even possible that carbonate minerals such as calcite (Eq. 3) or dolomite could contribute excess inorganic carbonate, though this is unlikely without the presence of soil inorganic carbonate.

Conclusions

This study has shown that elevated atmospheric CO_2 increased soil pCO_2, [DIC], and $[H_2CO_3^*]$: the effects of elevated O_3 were transient or muted, and require further study. In addition to increasing concentrations of C in soil solution, the study has shown that elevated atmospheric CO_2 alters system inorganic carbonate chemistry by increasing alkalinity, with the potential to increase weathering rates of primary minerals. Given an estimated annual oceanic DIC input of 0.4×10^{15} g C year^{-1} (Schlesinger 1997), and extrapolating a 22% increase in soil solution DIC concentration as reported here to be consistent across soil types throughout the world, we calculate a potential 0.1×10^{15} g C year^{-1} increase in global DIC delivery to the ocean, a rate consistent with estimates cited in Houghton (2003). Though DIC is a minor global CO_2 flux compared to net primary production and respiration (60×10^{15} g C year^{-1}, Schimel 1995), it represents a potential long-lived sequestration reservoir in deep ocean sediments. This extrapolation is not intended to be a robust parameter for global C modeling: however, it illustrates that aggrading forest ecosystems may be used to capture and sequester atmospheric CO_2 through inorganic processes.

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