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# Elevated $CO_2$ increases the long-term decomposition rate of *Quercus myrtifolia* leaf litter

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**Abstract**

**Decomposition of *Quercus myrtifolia* leaf litter in a Florida scrub oak community was followed for 3 years in two separate experiments. In the first experiment, we examined the effects $CO_2$ and herbivore damage on litter quality and subsequent decomposition. Undamaged, chewed and mined litter generated under ambient and elevated (ambient + 350 ppm V) $CO_2$ was allowed to decompose under ambient conditions for 3 years. Initial litter chemistry indicated that $CO_2$ levels had minor effects on litter quality. Litter damaged by leaf miners had higher initial concentrations of condensed tannins and nitrogen (N) and lower concentrations of hemicellulose and C : N ratios compared with undamaged and chewed litter. Despite variation in litter quality associated with $CO_2$, herbivory, and their interaction, there was no subsequent effect on rates of decomposition under ambient atmospheric conditions. In the second experiment, we examined the effects of source (ambient and elevated) of litter and decomposition site (ambient and elevated) on litter decomposition and N dynamics. Litter was not separated by damage type. The litter from both elevated and ambient $CO_2$ was then decomposed in both elevated and ambient $CO_2$ chambers. Initial litter chemistry indicated that concentrations of carbon (C), hemicellulose, and lignin were higher in litter from elevated than ambient $CO_2$ chambers. Despite differences in C and fiber concentrations, litter from ambient and elevated $CO_2$ decomposed at comparable rates. However, the atmosphere in which the decomposition took place resulted in significant differences in rates of decomposition. Litter decomposing under elevated $CO_2$ decomposed more rapidly than litter under ambient $CO_2$, and exhibited higher rates of mineral N accumulation. The results suggest that the atmospheric conditions during the decomposition process have a greater impact on rates of decomposition and N cycling than do the atmospheric conditions under which the foliage was produced.**

*Keywords:* ammonium, decomposition, elevated $CO_2$, herbivory, Kennedy space center, litter quality, mass loss, nitrate, *Quercus myrtifolia*

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## Introduction

Carbon dioxide ($CO_2$) concentrations in the atmosphere are currently increasing because of increased fossil fuel use and deforestation. These increases in $CO_2$ along with associated climate changes are expected to continue and to have significant impacts on terrestrial ecosystems (Houghton *et al*., 2001). There is abundant evidence that increased levels of $CO_2$ change the chemical composition of plant foliage (Curtis *et al*., 1989; Ceulemans & Mousseau, 1994; Koch & Mooney, 1996; Hall *et al*., 2005b). The most commonly reported changes in $CO_2$-grown plant foliage, increased C : N ratios and decreased nitrogen (N) concentrations, might be predicted to change the rate of decomposition and alter nutrient cycling because these variables are associated with decomposition in natural systems (Floate,

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1970; Berg & Ekbohm, 1983; Seastedt, 1988; Taylor *et al*., 1989). However, it remains to been seen whether changes in plant foliage induced under elevated $CO_2$ are retained in senesced leaves. Curtis *et al*. (1989) found that increased C : N ratios in the green foliage of the sedge, *Scirpus olneyi*, under enriched $CO_2$ were not maintained in the senesced foliage. Finzi *et al*. (2001) found no effect of elevated $CO_2$ on total nonstructural carbohydrates or N in green leaves or in leaf litter of five tree species. In our scrub oak ecosystem, previous work has shown that elevated $CO_2$ reduces foliar N concentrations and increases C : N ratios by an average of 6% and 7%, respectively, in green foliage across three oak species (Hall *et al*., 2005b). However, the senesced litter of these oaks does not exhibit lower N concentrations or higher C : N ratios. Rather, the strongest $CO_2$ effects are seen in the secondary metabolites, particularly condensed tannins (Hall *et al*., 2005a).

In other studies, chemical differences in senesced foliage between ambient and elevated $CO_2$ have been observed. Changes in N (Coüteaux *et al*., 1991; Kemp *et al*., 1994; Cotrufo *et al*., 1994, 1998; Robinson *et al*., 1997), C : N ratios (Cotrufo *et al*., 1994, 1998; Ball & Drake, 1997; Robinson *et al*., 1997; Lutze *et al*., 2000; Parsons *et al*., 2004) lignin : N ratios (Cotrufo *et al*., 1994, 1998, 1999; Parsons *et al*., 2004), condensed tannins (Cotrufo *et al*., 1999; Parsons *et al*., 2004), lignin (Cotrufo *et al*., 1994, 1999; Henry *et al*., 2005), and non-structural carbohydrates (Lutze *et al*., 2000) have been found in litter from enriched $CO_2$ plants compared with the controls.

In addition to changes induced by elevated $CO_2$, other factors can influence litter chemistry, one of which is the effects of insect herbivores. Insect herbivory can change the chemical composition of plant foliage, which may lead to changes in litter quality (Grace, 1986; Findlay *et al*., 1996; Chapman *et al*., 2003). Grace (1986) showed that gypsy moth defoliation resulted in increased N concentrations in Pennsylvania oak forest litter. Chapman *et al*. (2003) found that scale and moth herbivory increased litter N concentrations in pinyon pines and subsequently, C : N and lignin : N ratios decreased. Also scale herbivory increased annual needle litterfall. This herbivore-induced increase in litter quality translated into higher decomposition rates. Although there are a number of studies that have examined the effects of elevated $CO_2$ on insect herbivores (Lincoln & Couvet, 1986; Fajer *et al*., 1991; Roth & Lindroth, 1995; Stiling *et al*., 1999, 2002, 2003), we are not aware of any previous studies that have examined in detail the interactions among $CO_2$, insect herbivory, litter chemistry and decomposition.

In this study, we conducted two experiments to explore the links among elevated $CO_2$, herbivore damage, litter chemistry, decomposition, and N dynamics. Specifically, we investigated whether direct effects of $CO_2$ on foliage quality and litter dynamics matter more or less than indirect effects of $CO_2$ on litter dynamics mediated by other changes in the environment (Dukes & Hungate, 2002). In the first experiment, we tested the effects of $CO_2$ growth conditions and herbivore damage on the decomposition of *Quercus myrtifolia* leaf litter. In the second experiment we tested the effects of $CO_2$ growth conditions (source) and $CO_2$ decomposition conditions (site) on the decomposition of *Q. myrtifolia* litter without regard to herbivore damage.

## Methods

### *Study site*

Our study site lies within a 2 ha native scrub-oak community located at Kennedy Space Center, Florida. This woody ecosystem is controlled by a natural fire return cycle of 8–12 years and the mature canopy is 3–5 m high. The last burn was in 1996 before site set up. The ecosystem is subtropical with a mean annual temperature of 22.4 °C and an annual average precipitation of 131 cm. Sixteen 3.6 m diameter plots, each enclosed with a clear polyester film open-top chamber 3.4 m in height, were utilized to control $CO_2$ levels. Chambers were overlaid on an octagonal framework of PVC pipe with a removable access door and frustrum to reduce dilution of air within the chamber by outside wind. All regrowth was cut to ground level in May 1996 and, since that time, the vegetation in eight of the chambers has been exposed to almost twice ambient $CO_2$ (ambient + 350 ppm V), whereas the other eight chambers have been exposed to ambient levels of $CO_2$. The $CO_2$ is supplied 24 h a day. Monitoring and control of $CO_2$ injection into each chamber is carried out by infrared gas analysis in conjunction with manually adjusted needle valves. In ambient $CO_2$ chambers, the airflow is identical to that of the elevated $CO_2$ chambers but is not supplemented with $CO_2$. The study species, *Q. myrtifolia*, accounts for 76% by biomass of the species composition within this community.

*Experimental Design*. Rates of decomposition focused on litter from the most common tree in the system, *Quercus myrtifolia*. All vegetation within chambers had been exposed to either ambient or elevated $CO_2$ for 6 years before this study. Litter was collected and pooled (by chamber) from litter trays in all chambers during April–May of 2002, when litter was most plentiful. The litter was sorted into four categories: mined, chewed, undamaged and miscellaneous damage (more than one type of damage or damage other than chewers or

miners). This resulted in eight litter types (elevated $CO_2$ and ambient $CO_2 \times 4$ damage types). Litterbags consisted of 5 cm × 4 cm × 1.5 mm mesh and contained 0.1000–0.5000 g of uncut air-dried litter from each of the eight treatments depending on availability. Although litter bags exclude larger invertebrates from gaining access to litter (Hunter *et al*., 2003), microbial populations, protozoa, microarthropods, and nematodes have access. In the present study, our primary aim is to compare among treatment groups and we make the assumption that any changes in decomposition caused by litter bags are equivalent across treatments.

*Experiment I.* The undamaged, chewed and mined litter (UCM) was used to examine the effects of 'source' (ambient or elevated $CO_2$) and herbivore damage on litter decomposition. Litter bags were placed in six 3.6 m diameter open (unchambered) PVC rings adjacent to the $CO_2$ chambers, with three replicates of each treatment per ring ($n = 18$ per ring). Litter bags were covered by a one leaf thick layer of litter, available from the forest floor in each ring. One set (replicate) was collected from each ring annually for 3 years (four dates including time zero, May 2002). Time zero samples were analyzed for litter chemistry, and sample sizes were 16 undamaged (seven ambient, nine elevated), 20 chewed, 20 mined (ten from each $CO_2$ treatment) with sample sizes based on litter availability from pooled samples.

*Experiment II.* Each of the 16 chambers received six bags (one for each collection date) of the miscellaneous damaged (MD) litter from each of the ambient and elevated $CO_2$ treatments ($n = 12$ bags per chamber). PVC rings (12 cm diameter) were used to contain litter bags and prevent excessive movement of bags within the chambers under conditions of heavy rain. Three PVC rings were fixed into the bare soil of each chamber and the tops of the rings were approximately 0.25–0.50 cm above the soil surface. Two litter bags from ambient $CO_2$ and two litter bags from elevated $CO_2$ were placed in each PVC ring within chambers. Each ring was covered by a one leaf thick layer of litter, available from the forest floor in each chamber. One bag of each $CO_2$ treatment was removed from each chamber every 6 months for 3 years from time 6 months (November, 2002) to time 3 years (May 2005) (seven dates including time zero, May 2002). The total number of bags to be sampled was 36; however, some bags were not recoverable or had 100% mass loss and N analyses (below) could not be performed on all samples. Thus, sample sizes varied among collection dates. Actual sample sizes are noted on tables and figures. Time zero samples sizes were 10 ambient and 10 elevated from pooled samples. Our design allowed us to consider the effects of both 'source' (ambient and elevated $CO_2$) and 'site' (ambient and elevated) on the decomposition process. Owing to limited litter availability, herbivore damage effects were not included in this experiment.

On each collection date for both experiments, litter samples were weighed to determine mass loss. In addition during Experiment II, two N pools in the litter were followed over 3 years of decomposition: the mineral pool ($NH_4^+$ and $NO_3^-$) and dissolved organic nitrogen (DON) pool (See methods).

*Initial litter chemistry.* Subsamples of litter used in both experiments were retained for measures of initial litter chemistry. The litter was air dried then ground to a fine powder and stored at –80 °C before to analysis. Cellulose, hemicellulose, and lignin concentrations were determined by sequential neutral detergent/acid detergent digestion on an Ankom fiber analyzer (Abrahamson *et al*., 2003). Proanthocyanidins, an estimate of condensed tannin concentration, were assayed using *N*-butanol : HCl methods described in Rossiter *et al*. (1988). Total phenolics were estimated using the Folin–Denis assay (Swain, 1980), and gallotannins (hydrolysable tannins) were estimated using a potassium iodate technique developed by Bate-Smith (1977) and modified by Schultz & Baldwin (1982). The standards for tannin analyses were generated from bulk litter samples from our field site by multiple sequential washes of acetone extraction. Standards were not purified further. The percent dry weight N and carbon (C) were estimated using a Carlo-Erba NA1500 model C/N analyzer (Milan, Italy). (Carlo Erba, Milan, Italy)

*Decomposition.* Litter was air-dried before weighing and weights were used to determine mass loss. The air-dried litter was ground to a fine powder and stored at –80 °C before analysis for *N*-dynamics (Experiment II only).

Ground litter (0.05 g) was hydrated in 20 mL of distilled water and agitated overnight in a shaker at room temperature. The 'leachate' was then filtered through a 0.4 μL filter. The filtrate was analyzed for $NO_3^-$-N and $NH_4^+$-N using the automated cadmium reduction and phenate assays, respectively, on an Alpkem segmented-flow autoanalyzer (Alpkem RFA 300, Alpkem Corporation, Clackamas, OR, USA). Total dissolved nitrogen (TDN) of the filtrate was estimated following persulfate oxidation (Koroleff, 1983; Qualls, 1989) and DON was calculated as the difference between TDN and the sum of $NO_3^-$-N and $NH_4^+$-N.

The residue (anything that did not pass through the filter) was oven-dried at 60 °C for 24 h then used to estimate percent dry weight nitrogen (DWN) on a

Carlo-Erba NA1500 model C/N analyzer. Total N was calculated as DWN plus TDN.

*Data Analysis.* All data were tested for normality and log-transformed where appropriate. The initial litter chemistry was analyzed using ANOVA models generated by the GLM procedure of SAS 8.2 (SAS Institute, 1998). The UCM litter was analyzed using the repeated measures GLM (SAS Institute, 1998). The MD litter N was analyzed using the MIXED procedure of SAS 8.2 (SAS Institute, 1998). The Student–Neuman–Keuls (SNK) post hoc test ($\alpha = 0.05$) was used to distinguish among treatment means.

## Results

### *Experiment I – UCM litter*

*Litter chemistry.* The initial chemical composition of undamaged, chewed, and mined *Q. myrtifolia* litter derived from elevated and ambient $CO_2$ chambers is shown in Table 1. Litter from elevated $CO_2$ chambers had lower concentrations of cellulose ($F_{1,48} = 7.07$, $P < 0.01$), and hemicellulose ($F_{1,50} = 17.0$, $P < 0.01$) than litter from the ambient chambers. The litter from the two $CO_2$ treatments had similar N concentrations as well as similar C:N ratios. Similarly, lignin and phenolic concentrations, often used as indicators of litter quality, were unaffected by $CO_2$ levels (Table 1).

Herbivore damage was associated with variation in initial litter chemistry (Table 2). Condensed tannin concentrations were higher in mined litter than in undamaged or chewed litter ($F_{2,50} = 6.30$, $P < 0.01$) and N concentrations were also higher in mined litter than in undamaged litter ($F = 6.82_{2,50}$, $P < 0.01$). The C:N ratio was higher in undamaged litter than in mined litter ($F_{2,50} = 10.4$, $P < .01$) and hemicellulose was higher in undamaged litter than in either chewed or mined leaf litter ($F_{2,50} = 6.25$, $P < 0.01$; Table 2).

Only condensed tannin concentrations showed an interaction between $CO_2$ and herbivore damage (Fig. 1). Mined litter was consistent in the concentrations of condensed tannins between $CO_2$ treatments. Undamaged litter from elevated $CO_2$ chambers had lower concentrations of condensed tannins than litter from elevated $CO_2$ chambers whereas chewed litter was the opposite with higher concentrations of condensed tannins in chewed litter from elevated $CO_2$ chambers ($F_{2,50} = 5.46$, $P < 0.01$; Fig. 1).

*Litter Decomposition.* Despite initial differences in litter chemistry associated with $CO_2$ treatment (Table 1) and

**Table 1** Initial chemical composition of undamaged, chewed, and mined *Quercus myrtifolia* litter from ambient and elevated $CO_2$ across damage categories

| Sample | Condensed Tannins (%) | Hydrolyzable Tannins (%) | Total Phenolics (%) | Nitrogen (%) | Carbon (%) | C:N | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|---|---|---|---|---|---|
| Elevated | 26.0 | 27.3 | 28.0 | 0.58 | 50.6 | 88.3 | 19.9 | 13.2 | 8.91 |
| | (1.25) | (0.95) | (1.77) | (0.01) | (0.98) | (2.04) | (0.32) | (0.27) | (0.34) |
| Ambient | 23.3 | 25.9 | 27.1 | 0.58 | 50.2 | 87.9 | 21.0 | 14.5 | 9.71 |
| | (1.67) | (0.97) | (1.07) | (0.01) | (0.11) | (1.97) | (0.16) | (0.22) | (0.19) |
| | NS | NS | NS | NS | NS | NS | $P = 0.003$ | $P < 0.001$ | NS |

Values are means, $n = 29$ for elevated and $n = 27$ for ambient, with SE in parentheses.

**Table 2** Initial chemical composition of undamaged, chewed, and mined *Quercus myrtifolia* litter by damage category across $CO_2$ treatments

| Sample | Condensed Tannins (%) | Hydrolyzable Tannins (%) | Total Phenolics (%) | Nitrogen (%) | Carbon (%) | C:N | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|---|---|---|---|---|---|
| Undamaged | 22.4 | 26.1 | 27.5 | 0.54 | 51.3 | 95.5 | 20.8 | 14.7 | 8.60 |
| | (1.29) | (1.51) | (1.77) | (0.018) | (1.76) | (2.09) | (0.32) | (0.31) | (0.40) |
| Chewed | 22.3 | 27.7 | 28.2 | 0.58 | 50.5 | 88.8 | 20.7 | 13.6 | 9.51 |
| | (1.74) | (1.24) | (1.37) | (0.02) | (0.14) | (2.19) | (0.23) | (0.35) | (0.31) |
| Mined | 28.9 | 26.0 | 27.1 | 0.62 | 49.6 | 81.6 | 19.9 | 13.4 | 9.64 |
| | (1.79) | (0.81) | (2.22) | (0.01) | (0.24) | (2.0) | (0.43) | (0.28) | (0.35) |
| | $P = 0.004$ | NS | NS | $P = 0.002$ | NS | $P < 0.001$ | NS | $P = 0.004$ | NS |

Values are means, $n = 16$ undamaged, $n = 20$ chewed, $n = 20$ mined, with SE in parentheses.

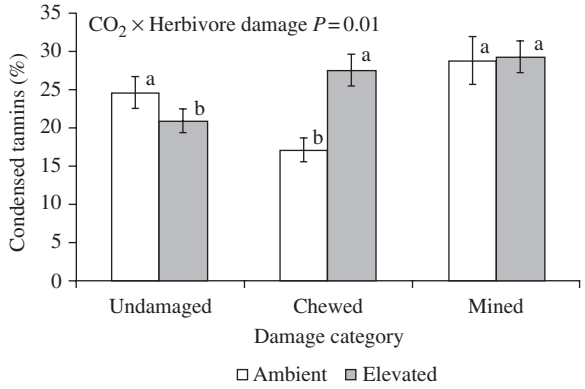


**Fig. 1** Effects of herbivore damage and $CO_2$ treatment on concentrations of condensed tannins in *Quercus myrtifolia* leaf litter. Data are the means of nine samples (undamaged ambient) seven samples (undamaged elevated) or ten samples (chewed or mined from ambient or elevated $CO_2$). Bars represent standard errors, and different letters denote significantly different means.

herbivore activity (Table 2, Fig. 1), neither $CO_2$ treatment ($F_{2,56} = 0.18$, $P = 0.83$; Fig. 2a) nor herbivore damage ($F_{2,56} = 0.38$, $P = 0.82$; Fig. 2b) influenced the rates of litter decomposition.

### *Experiment II – MD Litter*

*Initial Chemistry.* The initial chemical composition of miscellaneous damage litter is summarized in Table 3. Litter from elevated $CO_2$ chambers had higher concentrations of C, hemicellulose and lignin than did the litter from ambient chambers (C: $F_{1,17} = 15.9$ $P < 0.01$; hemicellulose: $F_{1,18} = 11.8$, $P < 0.01$; lignin: $F_{1,18} = 23.9$, $P < 0.01$).

*Litter Decomposition.* The rates of decomposition were comparable for litter originating from elevated and ambient $CO_2$ chambers ($F_{1,123} = 1.38$, $P = 0.24$; Fig. 3a), however the $CO_2$ level under which litter was decomposing did have an effect on mass loss. Litter decomposition was accelerated under elevated $CO_2$ ($F_{1,123} = 11.7$, $P < 0.01$; Fig. 3b). This effect of decomposition site was most pronounced from 18 to 36 months; before 18 months, decomposition rates under elevated and ambient $CO_2$ were comparable.

Ammonium accumulated to higher levels ($F_{1,121} = 12.7$, $P < 0.01$) in litter decomposing under elevated $CO_2$ than in litter decomposing under ambient $CO_2$ (Fig. 4a). Likewise, nitrate concentrations accumulated more rapidly in litter decomposing under elevated $CO_2$ ($F_{1,121} = 2.67$, $P = 0.03$; Fig. 4b). There were no effects of source chamber on the accumulation of mineral N in litter. Total litter N concentrations tended to increase

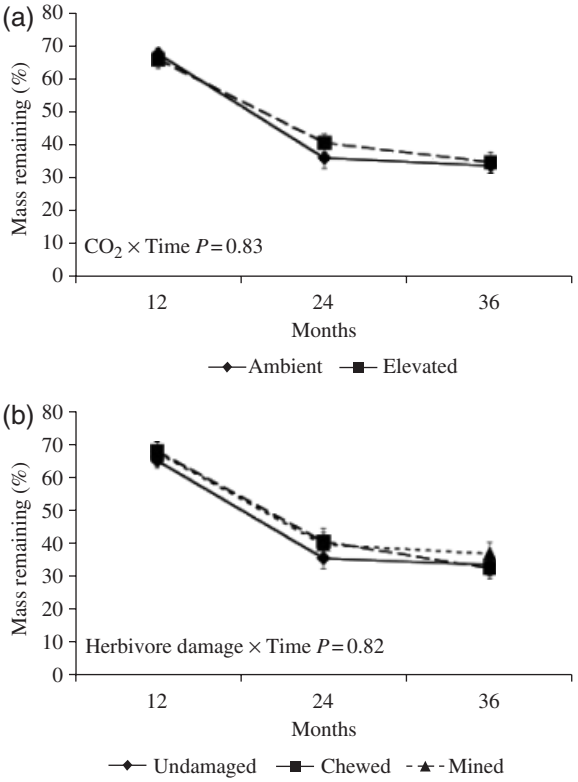


**Fig. 2** Decomposition rates for (a) UCM *Quercus myrtifolia* litter derived from ambient and elevated $CO_2$ and decomposing under ambient conditions for 3 years and (b) by herbivore damage category decomposing under ambient conditions for 3 years. Bars represent standard errors. Data are the means of 18 samples for ambient and elevated $CO_2$ treatments and 12 for undamaged, chewed and mined samples.

over time ($F_{5,118} = 41.4$, $P < 0.01$; Table 4). In general DON and mineral pools also increased during decomposition (Table 4) but these increases in concentration largely reflect the relative loss of C. The percent of initial litter C remaining on each sample date ($F_{5,118} = 22.58$, $P < 0.01$; Fig. 5a) declined faster in litter decomposing under elevated $CO_2$. The percent of initial litter N remaining on each sample date ($F_{5,118} = 0.79$, $P = 0.56$; Fig. 5b) did not differ between litter decomposing under ambient and elevated $CO_2$ and did not vary systematically over time.

## Discussion

Contrary to expectations, the source of leaf litter (ambient or elevated), its degree of damage, and its initial chemistry did not predict decomposition rates. Rather, litter decomposing under elevated $CO_2$ decomposed more rapidly than litter decomposing under ambient $CO_2$ (Fig. 3b). Coupled with the increase in decomposi-

**Table 3** Initial chemical composition of miscellaneous damaged *Quercus myrtifolia* litter

| Sample | Condensed tannins (%) | Hydrolyzable tannins (%) | Total phenolics (%) | Nitrogen (%) | Carbon (%) | C : N | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|---|---|---|---|---|---|
| Elevated | 24.1 | 28.9 | 31.9 | 0.62 | 50.8 | 82.6 | 20.4 | 14.5 | 10.5 |
| | (2.59) | (1.80) | (2.47) | (0.02) | (0.09) | (3.27) | (0.37) | (0.13) | (0.44) |
| Ambient | 23.6 | 25.8 | 29.9 | 0.63 | 49.5 | 80.7 | 20.7 | 13.4 | 8.07 |
| | (2.32) | (1.21) | (2.14) | (0.04) | (0.37) | (4.92) | (0.41) | (0.30) | (0.26) |
| | NS | NS | NS | NS | $P < 0.001$ | NS | NS | $P = 0.003$ | $P < 0.001$ |

Values are means, $n = 10$, with SE in parentheses.

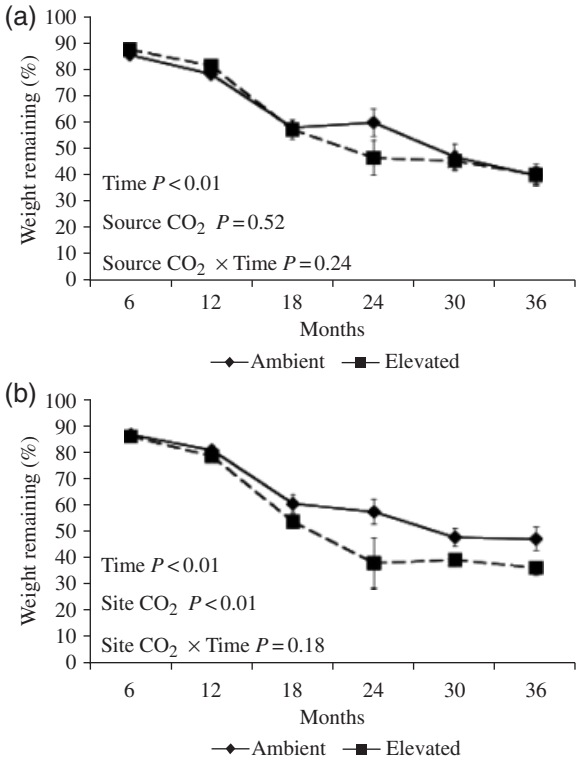


**Fig. 3** Decomposition rates for MD *Quercus myrtifolia* litter for (a) litter from ambient and elevated $CO_2$ treatments (source) and b) litter decomposing in ambient and elevated $CO_2$ treatments (site). Sample sizes vary by time and treatment and are as follows in order of time: Source–ambient = 16, 16, 15, 8, 5, 12; Source–elevated = 16, 16, 15, 12, 4, 12; Site–ambient = 16, 16, 16, 14, 7, 8; Site–elevated = 16, 16, 14, 6, 2, 16. Bars represent standard errors.

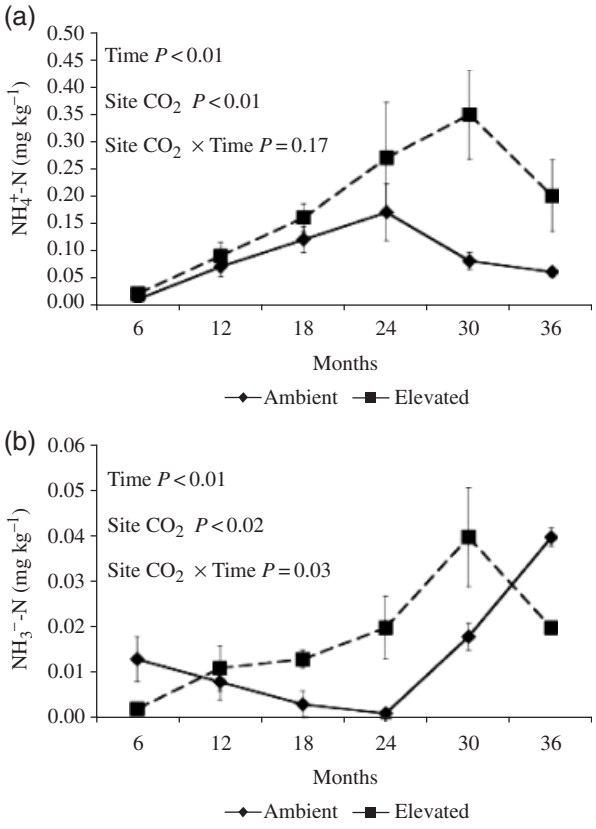


**Fig. 4** Ammonium concentrations (a) and nitrate concentrations (b) in litter decomposing under ambient and elevated $CO_2$ (site) for all collection dates of MD *Quercus myrtifolia* litter. Bars represent standard errors. Sample sizes varies by time and treatment and are as follows in order of time: ambient = 16, 16, 16, 13, 7, 7; elevated = 16, 16, 14, 5, 2, 16.

tion rate under elevated $CO_2$ was an increase in rate of mineral N accumulation in leaf litter (Fig. 4) and an increase in the rate of C loss (Fig. 5a). Litter C may, therefore, be driving the accumulation of mineral N. Given that overall levels of N varied little over the experiment (Fig. 5b), it is tempting to conclude that rates of N mineralization were higher under elevated than ambient $CO_2$. However, we cannot rule out the possibility that organic N export was balanced by mineral N import.

In this study (Experiment I), initial litter quality of UCM litter exhibited only minor differences between ambient and elevated $CO_2$ and none of the primary regulators (N, C : N ratio, lignin) of decomposition were affected by $CO_2$ concentrations. Rather, litter cellulose and hemicellulose concentrations were higher in litter

**Table 4** Total nitrogen and nitrogen pools in miscellaneous damaged litter of *Quercus myrtifolia* on each collection date from source and site of decomposition

| Source | Ambient | | | | Elevated | | | |
|---|---|---|---|---|---|---|---|---|
| Site | Ambient | | Elevated | | Ambient | | Elevated | |
| Total N | | | | | | | | |
| 6 | 0.41 | (0.05) 8 | 0.40 | (0.03) 8 | 0.38 | (0.07) 8 | 0.41 | (0.05) 8 |
| 12 | 0.46 | (0.03) 8 | 0.46 | (0.03) 8 | 0.37 | (0.03) 8 | 0.44 | (0.06) 8 |
| 18 | 0.75 | (0.05) 8 | 0.80 | (0.04) 7 | 0.71 | (0.03) 8 | 0.85 | (0.05) 7 |
| 24 | 0.72 | (0.03) 6 | 0.93 | (0.16) 2 | 0.56 | (0.04) 7 | 0.80 | (0.11) 3 |
| 30 | 1.04 | (0.08) 4 | 1.31 | (.) 1 | 0.73 | (0.04) 3 | 0.64 | (.) 1 |
| 36 | 0.76 | (0.12) 4 | 0.83 | (0.10) 8 | 0.78 | (0.08) 3 | 0.96 | (0.07) 8 |
| DON | | | | | | | | |
| 6 | 1.08 | (0.13) | 1.15 | (0.19) | 0.84 | (0.07) | 0.88 | (0.07) |
| 12 | 1.09 | (0.12) | 1.45 | (0.28) | 0.83 | (0.04) | 1.44 | (0.28) |
| 18 | 2.04 | (0.35) | 2.22 | (0.47) | 1.23 | (0.13) | 2.34 | (0.42) |
| 24 | 2.17 | (0.44) | 1.39 | (0.40) | 1.99 | (0.41) | 1.56 | (0.24) |
| 30 | 4.52 | (0.26) | 3.91 | (.) | 4.69 | (0.44) | 3.95 | (.) |
| 36 | 5.74 | (0.26) | 6.10 | (0.43) | 5.21 | (0.15) | 6.30 | (0.57) |
| $NO_3^-N$ | | | | | | | | |
| 6 | 0.024 | (0.010) | 0.004 | (0.003) | 0.002 | (0.002) | 0.0002 | (0.0003) |
| 12 | 0.003 | (0.002) | 0.020 | (0.009) | 0.014 | (0.007) | 0.004 | (0.001) |
| 18 | 0.016 | (0.003) | 0.014 | (0.004) | 0.016 | (0.005) | 0.011 | (0.003) |
| 24 | 0.012 | (0.001) | 0.026 | (0.019) | 0.014 | (0.002) | 0.016 | (0.002) |
| 30 | 0.021 | (0.005) | 0.051 | (.) | 0.015 | (0.005) | 0.028 | (.) |
| 36 | 0.020 | (0.002) | 0.022 | (0.001) | 0.013 | (0.0004) | 0.017 | (0.001) |
| $NH_4^+$-N | | | | | | | | |
| 6 | 0.005 | (0.005) | 0.016 | (0.014) | 0.015 | (0.008) | 0.009 | (0.007) |
| 12 | 0.070 | (0.021) | 0.090 | (0.038) | 0.061 | (0.034) | 0.085 | (0.033) |
| 18 | 0.157 | (0.036) | 0.142 | (0.043) | 0.093 | (0.032) | 0.177 | (0.031) |
| 24 | 0.177 | (0.079) | 0.276 | (0.276) | 0.160 | (0.076) | 0.266 | (0.096) |
| 30 | 0.092 | (0.016) | 0.272 | (.) | 0.067 | (0.034) | 0.435 | (.) |
| 36 | 0.594 | (0.009) | 0.211 | (0.125) | 0.062 | (0.015) | 0.187 | (0.053) |

Total nitrogen is given as mean percent. DON, $NO_3^-N$, and $NH_4^+$-N are given in mg kg. Standard errors are in parentheses unless sample size = 1. Sample size is given following SE for Total nitrogen and are consistent for all subsequent measures of nitrogen. Source is the $CO_2$ level (ambient or elevated) in which litter originated (grew) and site is the $CO_2$ level (ambient or elevated) in which litter decomposed.

from ambient $CO_2$. In line with other studies, which have documented little or no change in leaf litter quality (Finzi *et al*., 2001), there was no change in decomposition rates. Conversely, MD litter (Experiment II) had higher concentrations of C, hemicellulose and lignin in litter originating from elevated $CO_2$ chambers compared with that from ambient $CO_2$. Although lignin concentrations are often a good predictor of decomposition rates (Meetenmeyer, 1978), the origin of litter and, thus, litter quality did not affect decomposition rates in Experiment II. Overall, decomposition rates were unaffected by the source (ambient or elevated) of the litter regardless of whether or not litter quality was affected.

Although a number of studies have examined decomposition of litter from various $CO_2$ concentrations, few have examined the interactions between herbivory and $CO_2$ and their effects on nutrient cycling. Prior work on the three oak species in the scrub oak system found that herbivore-damaged litter was lower in soluble phenolic concentrations and higher in lignin concentrations and lignin : N ratios (Hall *et al*., 2005a). Whether these effects represented choice by herbivores or induction was not determined in the current or previous studies in the scrub oak system because herbivore densities could not be manipulated experimentally in the multiple-project chambers. Whether the result of induction or not, variation in litter quality associated with herbivore activity did not affect decomposition rates.

The higher rates of decomposition and N cycling in elevated $CO_2$ chambers that we observed in this study could have been the result of differences in microclimate or biota. Elevated $CO_2$ chambers at this site have

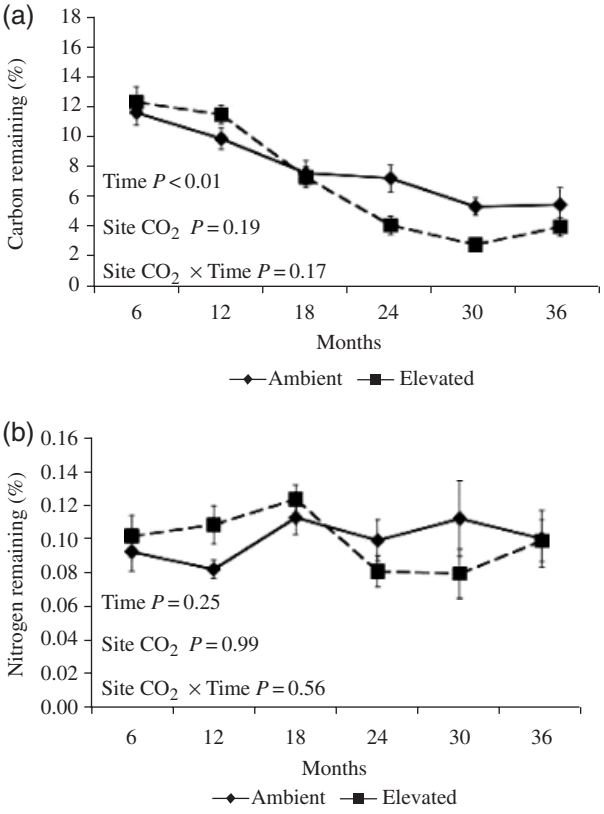


**Fig. 5** Dynamics of C (a) and N (b) concentration during decomposition of *Quercus myrtifolia* leaf litter decomposing under ambient and elevated $CO_2$ (site) for all collection dates of MD *Q. myrtifolia* litter. Bars represent standard errors. Sample sizes varies by time and treatment and are as follows in order of time: ambient = 16, 16, 16, 13, 7, 7; elevated = 16, 16, 14, 5, 2, 16.

greater productivity (Dijkstra *et al*., 2002) and litter cover on the chamber floors than do control chambers (Stiling *et al*., 2003), which may increase moisture levels above those in the ambient $CO_2$ chambers. As a radiative gas, $CO_2$ addition to chambers may have resulted in an increase in temperatures in elevated $CO_2$ chambers. If changes in the microclimate occurred, then activity rates of the biota may have been altered leading to increased decomposition and N accumulation. Unfortunately, no systematic comparisons of microclimate between ambient and elevated chambers have been made. Most reports of temperature differences related to open top chambers focus on interior and exterior temperature measurements (Drake *et al*., 1989; Whitehead *et al*., 1995). However, a review of open top chamber design and function by Leadley & Drake (1993) found no differences in long-term air temperature between elevated and ambient $CO_2$ chambers.

Changes in detritivore populations and activity levels other than those associated with microclimatic changes could also explain the acceleration of decomposition and N accumulation seen under elevated $CO_2$. Previous work in the scrub oak community at our site has demonstrated that fungal biomass in the soil is higher under elevated $CO_2$ than under ambient $CO_2$ (Klamer *et al*., 2002). In a different system, Moscatelli *et al*. (2005) have reported that microbial biomass increases by 16% in soils under elevated $CO_2$, with an apparent shift in enzyme activity towards fungal decomposition. How might such effects influence nutrient dynamics? There are two primary hypotheses concerning N availability under elevated $CO_2$. The first suggests that increased C availability under elevated $CO_2$ could boost microbial biomass and lead to increased immobilization of N (Diaz *et al*., 1993). Alternatively, Zak *et al*. (1993) suggested that increased C input would result in increased microbial activity leading to increased N availability. This latter suggestion is consistent with our results and some previous work (Cotrufo *et al*., 1999; Cotrufo *et al*., 2005). For example, under elevated $CO_2$, decomposing *Populus* leaves accumulate N in a manner similar to that in our experiments (Cotrufo *et al*., 2005). In the same study, the authors report that *Populus* litter decays more rapidly under elevated $CO_2$ than under ambient $CO_2$. However, they also found that *Populus* litter grown under elevated $CO_2$ decomposed more slowly than that grown under ambient $CO_2$, a 'source effect' that we did not find. It may be that there exists species-specific variation in decomposition depending on the source of litter (Cotrufo *et al*., 2005). Coüteaux *et al*. (1991) reported changes in litter quality including lower N concentrations and higher C : N ratios in chestnut litter grown under elevated $CO_2$. Litter from elevated $CO_2$ decomposed more slowly than did litter from ambient $CO_2$. However, when soil fauna complexity was increased, litter from elevated $CO_2$ plots displayed higher decomposition rates than did ambient $CO_2$ litter.

Our major finding is that the site of decomposition (ambient or elevated $CO_2$) has a greater impact on litter decomposition and N cycling than does variation in initial litter quality caused by elevated $CO_2$ or herbivore activity. As such, our results add to a growing body of work that suggests that increased concentrations of $CO_2$ may generate long-term shifts in decomposition processes and rates of nutrient cycling. Such shifts have the potential to change both ecosystem structure and function.

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