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RESEARCH ARTICLE

Effects of elevated atmospheric CO_2 and tropospheric O_3 on nutrient dynamics: decomposition of leaf litter in trembling aspen and paper birch communities

Lingli Liu · John S. King · Christian P. Giardina

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Abstract Atmospheric changes could strongly influence how terrestrial ecosystems function by altering nutrient cycling. We examined how the dynamics of nutrient release from leaf litter responded to two important atmospheric changes: rising atmospheric CO_2 and tropospheric O_3. We evaluated the independent and combined effects of these gases on foliar litter nutrient dynamics in aspen (*Populus tremuloides* Michx) and birch (*Betula papyrifera* Marsh)/aspen communities at the Aspen FACE Project in Rhinelander, WI. Naturally senesced leaf litter was incubated in litter bags in the field for 735 days. Decomposing litter was sampled six times during incubation and was analyzed for carbon, and both macro (N, P, K, S, Ca, and Mg) and micro (Mn, B, Zn and Cu) nutrient concentrations. Elevated CO_2 significantly decreased the initial litter concentrations of N (−10.7%) and B (−14.4%), and increased the concentrations of K (+23.7%) and P (+19.7%), with no change in the other elements. Elevated O_3 significantly decreased the initial litter concentrations of P (−11.2%), S (−8.1%), Ca (−12.1%), and Zn (−19.5%), with no change in the other elements. Pairing concentration data with litterfall data, we estimated that elevated CO_2 significantly increased the fluxes to soil of all nutrients: N (+12.5%), P (+61.0%), K (+67.1%), S (+28.0%), and Mg (+40.7%), Ca (+44.0%), Cu (+38.9%), Mn (+62.8%), and Zn (+33.1%). Elevated O_3 had the opposite effect: N (−22.4%), P (−25.4%), K (−27.2%), S (−23.6%), Ca (−27.6%), Mg (−21.7%), B (−16.2%), Cu (−20.8%), and Zn (−31.6%). The relative release rates of the nine elements during the incubation was: K≥P≥mass≥Mg≥B≥Ca≥S≥N≥Mn≥Cu≥Zn. Atmospheric changes had little effect on nutrient release rates, except for decreasing Ca and B release under elevated CO_2 and decreasing N and Ca release under elevated O_3. We conclude that elevated CO_2 and elevated O_3 will alter nutrient cycling more through effects on litter production, rather than litter nutrient concentrations or release rates.

Keywords Aspen FACE · Atmospheric change · Litter bag · Macro and micro nutrient · Nutrient cycling

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L. Liu (✉) · J. S. King
Department of Forestry and Environmental Resources,
North Carolina State University,
Campus Box 8002, Raleigh, NC 27695, USA
e-mail: lliu4@ncsu.edu

C. P. Giardina
Institute of Pacific Islands Forestry,
USDA Forest Service – PSW Research Station,
60 Nowelo Street, Hilo, HI 96720, USA

Introduction

Nutrient release from decomposing litter is important for sustaining ecosystem production (Chapin et al. 2002).

The atmospheric concentrations of CO_2 and tropospheric O_3 have increased substantially as a result of human activities (IPCC 2007). These atmospheric changes can have important impacts on litter chemistry. Elevated CO_2 caused a 37% increase in lignin concentration relative to control in oak leaves (Cotrufo et al. 1999), while concentration of total phenolics increased by 25% in Scots pine needles (Sallas et al. 2001). Elevated O_3 has been shown to increase acid soluble lignin concentration in birch leaves (Kasurinen et al. 2006) and decrease non-structural carbohydrate concentration in soybean leaf litter (Booker et al. 2005).

Changes in litter quality have the potential to alter nutrient dynamics by changing substrate availability for microbial metabolism (Zak et al. 1993). However, the response of mineral nutrient cycling to elevated CO_2 and O_3 is not well understood (Zak et al. 2000), and impacts on tissue chemistry are not universal (Liu et al. 2005). In particular, the effects of altered atmospheric chemistry on the release of nutrients from decomposing litter remain poorly quantified. Detailed studies are lacking that quantify both changes in tissue chemistry and subsequent changes in litter nutrient dynamics in response to elevated CO_2 and O_3, especially for forest species (Parsons et al. 2004). This severely constrains efforts to predict how biogeochemical process rates will respond to atmospheric change.

Increased atmospheric CO_2 is predicted to reduce nutrient concentrations of plant tissues (Strain and Bazzaz 1983). This has been attributed to either decreased nutrient uptake relative to C accumulation, or altered patterns of nutrient allocation under elevated CO_2 (Penuelas et al. 1997). However, published data for several species show no consistent response of foliar nutrient concentrations to elevated CO_2 (Table 1). The effects of CO_2 enrichment on nutrient concentrations are more complex than a simple dilution effect, and can depend on element, species, developmental stage, season, environmental stress, site variables, and management.

By comparison, far fewer studies have examined nutrient dynamics under elevated O_3. Ogner (1993) found O_3 increased K concentration of Norway spruce foliage. Barnes and Pfirrmann (1992) found O_3 increased the P and K concentration of radish root. Most studies, however, suggest that O_3 exposure does not modify nutrient concentrations of shoots or roots (Heagle et al. 1993; Fangmeier et al. 1997; Walin et al. 2002).

Litter decomposition is the key process influencing nutrient release from litter, controlling uptake by plants and microbes (Paul and Clark 1996). To date the consensus of research results seems to support the conclusion that elevated CO_2 and O_3 have little or no direct effect on specific rates of decomposition (Norby et al. 2001; Booker et al. 2005; Chapman et al. 2005; King et al. 2005a).

The objective of this study was to investigate the independent and combined effects of elevated CO_2 and

Table 1 Effect of elevated CO_2 on leaf nutrient concentrations: results of previous published studies

Source	N (%)	P	S	K	Ca	Mg	B	Cu	Mn	Zn
Picea abies[a]	n.s.	+14.9	n.s.	+5.3	n.s.	+15.3		n.s.	n.s.	n.s.
Erica arborea[b]	n.s.	+21.3		+42.0	n.s.	n.s.	−29.1	n.s.		n.s.
Juniperus communis[b]	n.s.	n.s.		+42.4	+10.0	+21.3	n.s.	n.s.		+43.4
Myrtus communis[b]	−17.7	−15.8		n.s.	n.s.	+28.7	+20.0	n.s.	+115	n.s.
Citrus aurantium[c]	−10.0	n.s.	−4.2	−3.3	−6.3	−2.6	9.8	0.6	−12.6	−0.9
Gossypium hirsutum[d]	−32.1	n.s.		−22.9	−32.0	−25.5	−18.5	n.s.	−22.6	−18.5
Trifolium repens[e]	−12.8	−13.1	−16.7	−13.7	n.s.	n.s.	−18.7	−15.3	+4.8	n.s.

Values represent the percentage change of nutrient concentrations at elevated CO_2. Data were selected according to two criteria (1) elevated CO_2 treatment was between 450 to 700 ppm; (2) concentrations of nutrient were reported on a mass basis.

− Decrease; + increase; *n.s.* no significant change

[a] Pfirrmann et al. (1996)

[b] Penuelas et al. (2001)

[c] Penuelas et al. (1997)

[d] Huluka et al. (1994)

[e] Heagle et al. (1993)

elevated O_3 on mineral nutrient cycling in aggrading aspen and birch-aspen stands of the Aspen FACE project in Rhinelander, WI. Elevated CO_2 increased total biomass production by 43% and elevated O_3 decreased it by 17% in this long-term experiment (King et al. 2005b). We therefore expect nutrient demand to increase under elevated CO_2 due to the higher productivity, and to decrease under elevated O_3 due to lower productivity. Total belowground C allocation (TBCA) was 15% higher under elevated CO_2 (Giardina et al. 2005), with much of the increase attributable to increased fine root production at this site. Several possible mechanisms that could be responsible for mitigating nutrient limitation under elevated CO_2, such as increasing the volume of soil exploited by increasing the production of fine roots (Giardina et al. 2005) and colonization of mycorrhizal fungus (Kubiske and Godbold 2001).

Effects of elevated CO_2 on leaf chemistry at the Aspen FACE experiment have been intensively examined in the past decade (Lindroth et al. 2001; Kopper et al. 2002; Parsons et al. 2004; Mattson et al. 2005). Recently, Liu et al. (2005) examined the concentrations of sugar, hemicellulose, cellulose, tannins, phenolics and lignin in leaf litter, and found that elevated CO_2 had little effect on tissue chemistry. However, elevated O_3 increased condensed tannins (77.2%) and soluble phenolics (53.1%). These findings provide an important base for formulating hypotheses about how CO_2 and O_3 will impact nutrient dynamics in decomposing leaf litter. In the current study, our first hypothesis was that elevated CO_2 would have a small effect on nutrient concentrations because of adequate soil supply. All nutrient fluxes would increase due to higher litter production (Liu et al. 2005). Our second hypothesis was that elevated O_3 would have little effect on nutrient concentrations, but would decrease nutrient fluxes because of low biomass productivity. Our final hypothesis was that elevated CO_2 would have small effects on nutrient release, but elevated O_3 would decrease it due to increased concentrations of condensed tannins and soluble phenolics.

Materials and methods

Experimental design

The study was conducted at the Aspen FACE project in Rhinelander, Wisconsin (45°40.5′N, 89°37.5′E). The Aspen FACE project was established in 1997 and is the only open-air facility to study the response of whole forest communities to elevated CO_2 and elevated O_3 (Dickson et al. 2000). The experiment is divided into three blocks, each block consisting of four 30 m diameter circular plots. Two main effect treatments (CO_2 and O_3) with two levels each (ambient and elevated) were randomly assigned to the four plots in each block. One half of each plot was planted with five aspen (*Populus tremuloides* Michx) genotypes of differing O_3 sensitivity. One-quarter of each plot was planted with a single aspen clone and paper birch (*Betula papyrifera* Marsh), and the remaining quarter was planted with the same aspen clone and sugar maple (*Acer saccharum* Marsh). The trees were planted at 1×1 m spacing and have been exposed to the CO_2 and O_3 treatments since 1997. Fumigation is conducted only during daylight hours of the growing season from May to October. In the elevated CO_2 treatment, the target level of CO_2 was 560 ppm, which is about 200 ppm above ambient atmospheric CO_2. Elevated O_3 was applied at a level of 1.5 times the ambient ozone concentration, about 90–100 ppb on sunny days, 50–60 ppb on cloudy days, and no O_3 fumigation on cool (<15°C) or rainy days. The treatment gas concentrations are available at the Brookhaven National Laboratory web site http://oasd-ebi.das.bnl.gov/FACE_Graph_Images/). A complete description of the experimental design and operation of this FACE facility are provided by Dickson et al. (2000).

Litter collection and field incubation

Naturally senesced leaf litter samples were collected in plastic baskets of 43 cm diameter from aspen and birch-aspen communities every 2 weeks from June to October 2003 (Liu et al. 2005). After removing understory litter and other coarse woody material, leaf litter was composited across collection baskets and dates by community type for each plot, resulting in 24 samples used for analyses. Immediately after each bi-weekly collection, samples were air-dried at room temperature. From each of the 24 samples, about 2.5 g dry litter was put into 11×7 cm litter bags with 1 mm mesh size. For birch-aspen community, the 2.5 g leaf litter was composited according to the mass ratio of total annual aspen leaf litter to total annual birch leaf litter for that community within each plot.

Duplicate sets of litter bags were deployed on the soil surface in the respective treatment section from which the litter was collected. Field incubation was begun on November 6, 2003, and six collections occurred during the 2-year incubation (May 2004, July 2004, November 2004, May 2005, August 2005 and November 2005). Two litter bags were sampled from each treatment section at each collection. After freeze-drying, the recovered litter was analyzed for mass loss, and then ground in liquid N and stored at −20°C until nutrient analysis was performed.

Nutrient analysis

Total N and C were analyzed on a NC 2100 CHN auto-analyzer (CE Instruments Ltd., Hindley Green, Wigan, UK). Litter concentrations of other macro (P, K, S, Ca, Mg) and micro (Mn, B, Zn, Cu) nutrients were determined by wet digestion (Sah and Miller 1992). Briefly, a litter subsample (800 mg) was mixed with 10 ml concentrated HNO_3, reacted overnight at room temperature and then digested at 105°C for 2 h. After cooling for 30 min, the mixture was reacted with 2 ml high purity H_2O_2 at 200°C for 15–30 min, cooled, and then brought to volume (50 ml) with distilled deionized water. The digested sample was analyzed for macro and micro nutrients on an ICP-AES spectrophotometer (ICP-AES Liberty Series II, Varian, Palo Alto, CA, USA). Ash content was determined for each litterbag sample by combusting a subsample overnight in a muffle furnace at 500°C. This estimate of ash content was used to ash correct all estimates of chemical composition and decomposition.

Calculations and statistical analysis

Initial nutrient flux was defined as annual nutrient input from litter to the forest floor and was estimated by multiplying nutrient concentration of litter (g g^{-1}) by litter production (g m^{-2}) in 2003. Nutrient dynamics, defined as the release or accumulation of a nutrient during decomposition, was estimated by the change of the relative nutrient concentrations and the proportion of initial nutrient content remaining during the incubation. Here, the relative nutrient concentration was expressed as the ratio between nutrient concentration and carbon concentration ([nutrient]/[C]) in decomposing litter. The relative nutrient concentration revealed the release or accumulation of nutrient relative to C, which can elucidate the stoichiometric relationship between carbon and nutrients during decomposition (Moore et al. 2006). The proportion of initial nutrient content was defined as the ratio of remaining nutrient content in decomposing litter to the initial nutrient content.

Effects of CO_2 and O_3 on initial litter nutrient concentrations and fluxes were analyzed by ANOVA using a model developed by King et al. (2001) for Aspen FACE. To identify the potential factors affecting nutrient dynamics across treatments and communities, principle-component factor analysis with equimax rotation was used (Johnson and Wichern 2002). The factor analysis was computed based on a correlation matrix to eliminate the effect of different concentration ranges of macro and micro nutrients. The number of factors was determined using a screen plot and then identifying where the elbow in the curve occurs (Johnson and Wichern 2002). Differences in the remaining proportion of the nine elements at the end of incubation were determined by Tukey multiple comparisons ($P<0.05$). All statistical analyses were done using SAS® (Statistical Analysis System, Version 9, SAS Institute Inc., Cary, NC).

Results

Initial nutrient concentrations

Trace gas effects

Elevated CO_2 decreased leaf litter N (−10.7%) and B (−14.4%) concentrations and increased P (+19.7%) and K (+23.7%) concentrations relative to the control, but did not change other element concentrations (Table 2). Elevated O_3 decreased leaf litter concentrations of P (−11.2%), S (−8.1%), Ca (−12.1%), and Zn (−19.5%; Table 2). The negative effect of O_3 on Zn concentration was moderated by CO_2. Averaged across species, elevated CO_2 reduced Zn (−13%) concentration under ambient O_3, but increased Zn concentration (+19%) under elevated O_3, resulting in a significant interaction of $CO_2 \times O_3$ ($P=0.04$).

Species effects

Birch-aspen leaf litter had higher concentrations of B (+12.6%), Mg (+15.7%) and Mn (+93.8%), and lower

Table 2 Mean±SE (n=3) and P values of nutrient concentrations of aspen and birch-aspen litter produced under the experimental treatments at the Aspen FACE project, Rhinelander, WI

Source		N (%)	P	S	K	Ca	Mg	B (ppm)	Cu	Mn	Zn
Aspen											
Ambient	Mean	1.53	0.21	0.14	0.39	2.04	0.34	24.12	8.62	332.55	226.04
	SE	0.19	0.03	0.02	0.08	0.21	0.07	1.02	1.35	144.46	38.33
$+CO_2$	Mean	1.31	0.24	0.14	0.46	2.38	0.35	21.34	8.78	173.29	208.08
	SE	0.12	0.03	0.00	0.10	0.28	0.09	4.45	1.80	11.84	10.91
$+O_3$	Mean	1.43	0.17	0.13	0.32	1.99	0.3	24.29	8.32	141.69	174.49
	SE	0.13	0.01	0.01	0.08	0.14	0.03	2.04	1.01	6.06	13.48
$+CO_2+O_3$	Mean	1.37	0.21	0.13	0.39	2.17	0.32	21.39	8.38	155.43	188.05
	SE	0.10	0.02	0.01	0.08	0.16	0.07	1.83	0.41	67.95	42.10
Birch-Aspen											
Ambient	Mean	1.53	0.22	0.13	0.37	1.97	0.35	28.93	7.49	276.97	233.26
	SE	0.11	0.02	0.01	0.06	0.28	0.03	3.18	0.61	79.08	45.62
$+CO_2$	Mean	1.25	0.23	0.11	0.51	1.83	0.41	22.93	7.10	476.63	194.25
	SE	0.05	0.03	0.02	0.11	0.30	0.03	3.62	1.14	80.42	41.03
$+O_3$	Mean	1.25	0.16	0.10	0.37	1.37	0.38	26.16	6.53	300.52	138.43
	SE	0.05	0.01	0.01	0.06	0.10	0.01	1.56	0.88	42.75	17.23
$+CO_2+O_3$	Mean	1.19	0.25	0.11	0.45	1.62	0.37	24.26	7.26	500.3	186.38
	SE	0.10	0.04	0.01	0.08	0.13	0.02	2.26	0.68	139.05	24.62
CO_2		**0.01**	**0.01**	0.06	0.07	0.20	0.35	**0.01**	0.94	0.15	0.91
O_3		0.07	**0.05**	**0.01**	0.23	**0.03**	0.21	0.96	0.57	0.34	**0.01**
$CO_2 \times O_3$		0.08	0.08	0.15	0.64	0.59	0.30	0.45	0.68	0.29	**0.04**
Com		**0.03**	0.63	**0.00**	0.29	**0.00**	**0.03**	**0.01**	**0.01**	**0.00**	0.34
$CO_2 \times$Com		0.70	0.38	0.87	0.56	0.27	0.97	0.53	0.92	**0.01**	0.74
$O_3 \times$Com		0.11	0.63	0.28	0.53	0.13	0.43	0.67	0.95	0.13	0.48
$CO_2 \times O_3 \times$Com		0.72	0.17	0.28	0.66	0.13	0.24	0.26	0.48	0.28	0.22

concentrations of Ca (−20.4%), Cu (−16.4%), N (−7.5%) and S (−16.2%), compared to aspen leaf litter (Table 2).

Litter nutrient fluxes

Trace gas effects

In 2003, elevated CO_2 increased litter biomass production by 34.5% averaged across aspen and birch-aspen communities (Liu et al. 2005). The increased litter production resulted in a significant increase in the fluxes of macro-nutrients to soil: N (+12.5%), P (+61.0%), S (+28.0%), K (+67.1%), Ca (+44.0%), and Mg (+40.7%; Table 3). Micro-nutrient fluxes also increased: Cu (+38.9%), Mn (+62.8%), and Zn (+33.1%). Because of decreased litter production, elevated O_3 significantly decreased the fluxes of N (−22.4%), P (−25.4), S (−23.6%), K (−27.2%), Ca (−27.6%), Mg (−21.7%), Cu (−20.8%), B (−16.2%) and Zn (−31.6%; Table 3).

Species effects

Averaged across the CO_2 and O_3 treatments, the birch-aspen community had lower fluxes of Ca (−23%), S (−19.9%) and Cu (−28.0%), and higher fluxes of Mn (+92.4%), compared to the aspen community.

Nutrient dynamics

Macro-nutrients

Trace gas effects. The relative nutrient concentrations and nutrient proportions exhibited diverse responses to the elevated CO_2 and O_3 treatments. Decomposing litter under the four treatments showed similar N

Table 3 Mean±SE (n=3) and P values for nutrient inputs (g m^{-2}) to soil through leaf litter produced in the experimental treatments at the Aspen FACE project (n=3)

Source		N	P	S	K	Ca	Mg	B	Cu	Mn	Zn
Aspen											
Ambient	Mean	3.42	0.49	0.32	0.90	4.69	0.78	5.57E-03	1.97E-03	7.61E-02	5.21E-02
	SE	0.52	0.09	0.05	0.17	0.55	0.15	1.53E-04	3.21E-04	3.15E-02	9.82E-03
$+CO_2$	Mean	3.90	0.73	0.41	1.41	7.14	1.04	6.40E-03	2.70E-03	5.25E-02	6.28E-02
	SE	0.65	0.14	0.06	0.42	0.64	0.28	1.32E-03	8.19E-04	8.95E-03	7.35E-03
$+O_3$	Mean	2.50	0.31	0.25	0.58	3.61	0.53	4.40E-03	1.53E-03	2.58E-02	3.20E-02
	SE	0.46	0.04	0.05	0.22	0.35	0.04	5.00E-04	3.79E-04	4.00E-03	6.49E-03
$+CO_2+O_3$	Mean	3.30	0.52	0.32	0.95	5.33	0.79	5.27E-03	2.07E-03	3.84E-02	4.64E-02
	SE	0.10	0.04	0.02	0.21	0.38	0.18	5.86E-04	1.53E-04	1.75E-02	1.13E-02
Birch-Aspen											
Ambient	Mean	3.11	0.46	0.27	0.77	4.18	0.74	6.00E-03	1.60E-03	5.68E-02	4.83E-02
	SE	0.48	0.03	0.05	0.06	1.12	0.12	1.00E-04	3.46E-04	1.12E-02	5.60E-03
$+CO_2$	Mean	3.51	0.66	0.33	1.46	5.28	1.17	6.63E-03	2.03E-03	1.38E-01	5.59E-02
	SE	0.37	0.08	0.02	0.17	1.04	0.21	1.34E-03	3.06E-04	3.42E-02	1.28E-02
$+O_3$	Mean	2.23	0.30	0.19	0.69	2.56	0.71	4.87E-03	1.20E-03	5.61E-02	2.59E-02
	SE	0.06	0.03	0.01	0.13	0.22	0.02	3.06E-04	1.73E-04	7.77E-03	4.25E-03
$+CO_2+O_3$	Mean	2.78	0.60	0.26	1.08	3.91	0.88	5.87E-03	1.77E-03	1.20E-01	4.49E-02
	SE	0.11	0.13	0.03	0.24	0.41	0.08	6.51E-04	2.52E-04	3.13E-02	6.04E-03
CO_2		**0.01**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	0.08	**0.01**	**0.01**	**0.00**
O_3		**0.01**	**0.00**	**0.00**	0.04	**0.00**	**0.02**	**0.04**	**0.05**	0.08	**0.00**
$CO_2 \times O_3$		0.41	0.61	0.88	0.38	0.60	0.34	0.68	0.64	0.64	0.22
Com		0.12	0.83	**0.01**	0.59	**0.00**	**0.02**	0.22	**0.01**	**0.00**	0.27
$CO_2 \times$Com		0.73	0.65	0.51	0.48	0.20	0.52	0.52	0.63	**0.00**	0.95
$O_3 \times$Com		0.93	0.28	0.74	0.27	0.95	0.21	1.00	0.63	0.23	0.88
$CO_2 \times O_3 \times$Com		0.84	0.36	0.68	0.59	0.45	0.07	0.52	0.63	0.17	0.62

dynamics over the 2-year incubation. In all cases N/C increased through time (Fig. 1a,b). A significant interaction of $O_3 \times$time (P<0.01) of N proportion suggests that elevated O_3 tended to decrease N mineralization during early decomposition, and caused accumulation of N at later stages (Fig. 2a,b). A rapid decrease of P/C was observed during the early days followed by a gradual increase until the end of the incubation (Fig. 1c,d). The initial P/C was higher under elevated CO_2 and lower under elevated O_3, but this difference disappeared by day 180, which resulted in significant $CO_2 \times$time (P<0.01) and $O_3 \times$ time interactions (P<0.01; Fig. 1c,d).

Similar to N, sulfur showed alternate release and accumulation phases (Fig. 2e,f). Elevated CO_2 and elevated O_3 had no effects on S/C or S proportion (Figs. 1e,f and 2e,f). Litter from elevated CO_2 had lower initial K/C, but converged to a similar level as ambient CO_2 by day 180, which resulted in significant $CO_2 \times$time interaction (P=0.01; Fig. 3a,b). About 70% of the initial K was released from litter during the first 180 days. Thereafter the proportion of K remained unchanged in all treatments (Fig. 4a,b). Calcium release rates were significantly decreased by both elevated CO_2 (P<0.01) and elevated O_3 (P= 0.01; Fig. 4c,d). There were overall trends of increasing Ca/C and decrease Ca proportion with time. Elevated CO_2 and O_3 had no impact on Mg/C and Mg proportion.

Species effects. The relative nutrient concentrations and nutrient proportions also exhibited diverse responses to species. At the end of incubation, aspen litter showed 8% net increase in the total amount of N, while birch-aspen litter showed a 7% net loss of N, which resulted in a significant community×time interaction (P<0.01) of N proportion (Fig. 2a,b). Aspen litter had higher S/C than birch-aspen litter, and these differences were consistent throughout the decomposition process (P=0.03; Fig. 1e,f). The two communities showed different S release patterns, with a significant community×time interaction (P=0.01) of S proportion. By the end of the incubation, more S was retained in aspen litter (96%) than in birch-aspen litter (82%; Fig. 2e,f). Aspen litter had higher Ca/C

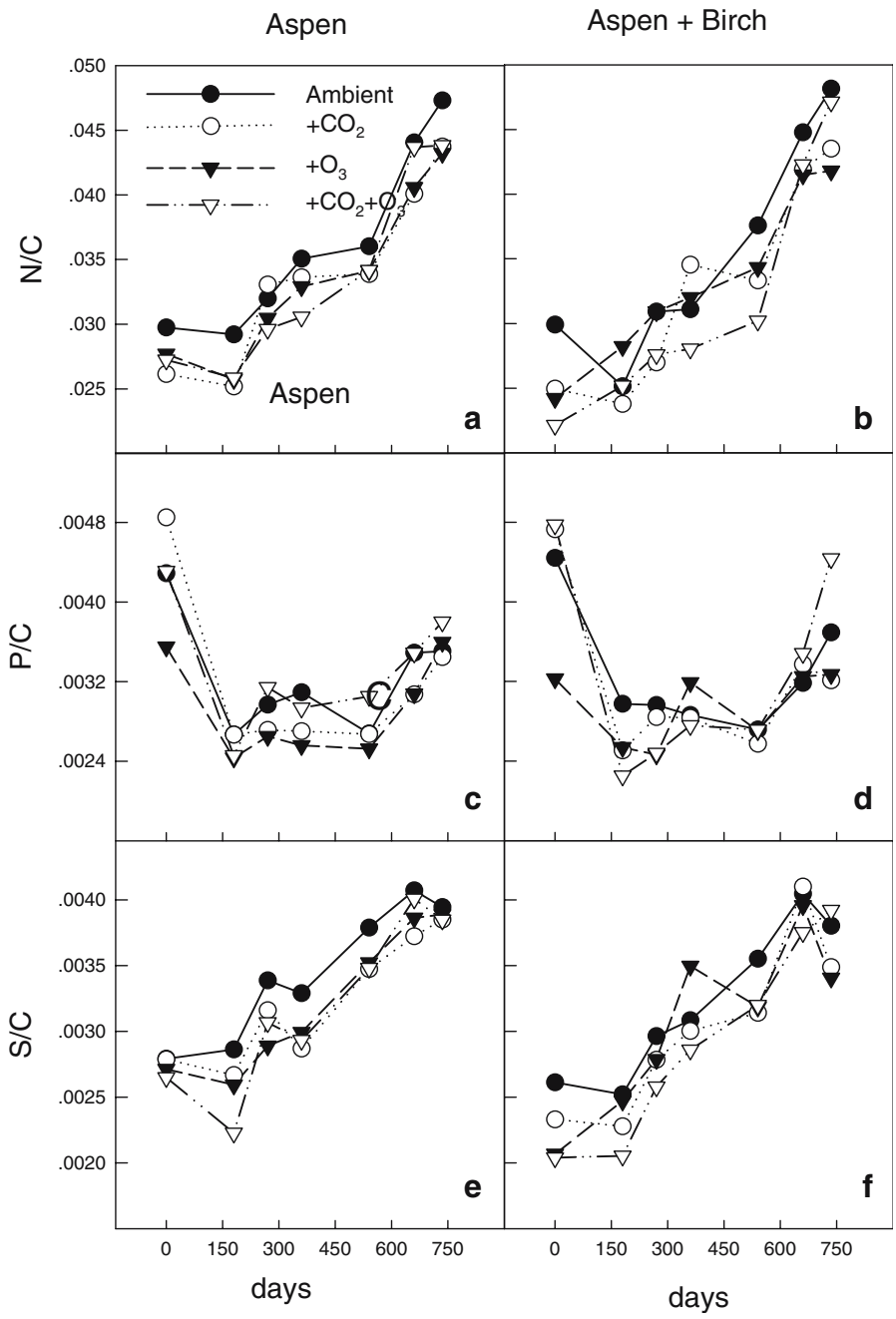

Fig. 1 Trends in N/C, (**a, b**) P/C (**c, d**) and S/C (**e, f**) levels in decomposing aspen and birch/aspen leaf litter samples from trees previously treated with elevated CO_2 and O_3 at the Aspen FACE site (n=3)

(P<0.01) and lower Mg/C (P<0.01) than birch-aspen litter across incubation period (Fig. 3c–f). After losing about 50% of the initial Mg, the proportion of Mg in aspen litter continued to increase to 67% by the end of the incubation, while the proportion of Mg in birch-aspen litter showed little change (Fig. 4e,f), which resulted in a significant community×time (P<0.01) interaction of Mg proportion.

Micro-nutrients

Trace gas effects. As with macro-nutrients, the relative nutrient concentrations and nutrient proportions of micro-nutrients showed diverse responses to the atmospheric treatments. Litter from elevated CO_2 had lower B/C early in the incubation. This difference disappeared by day 360 and resulted in a significant

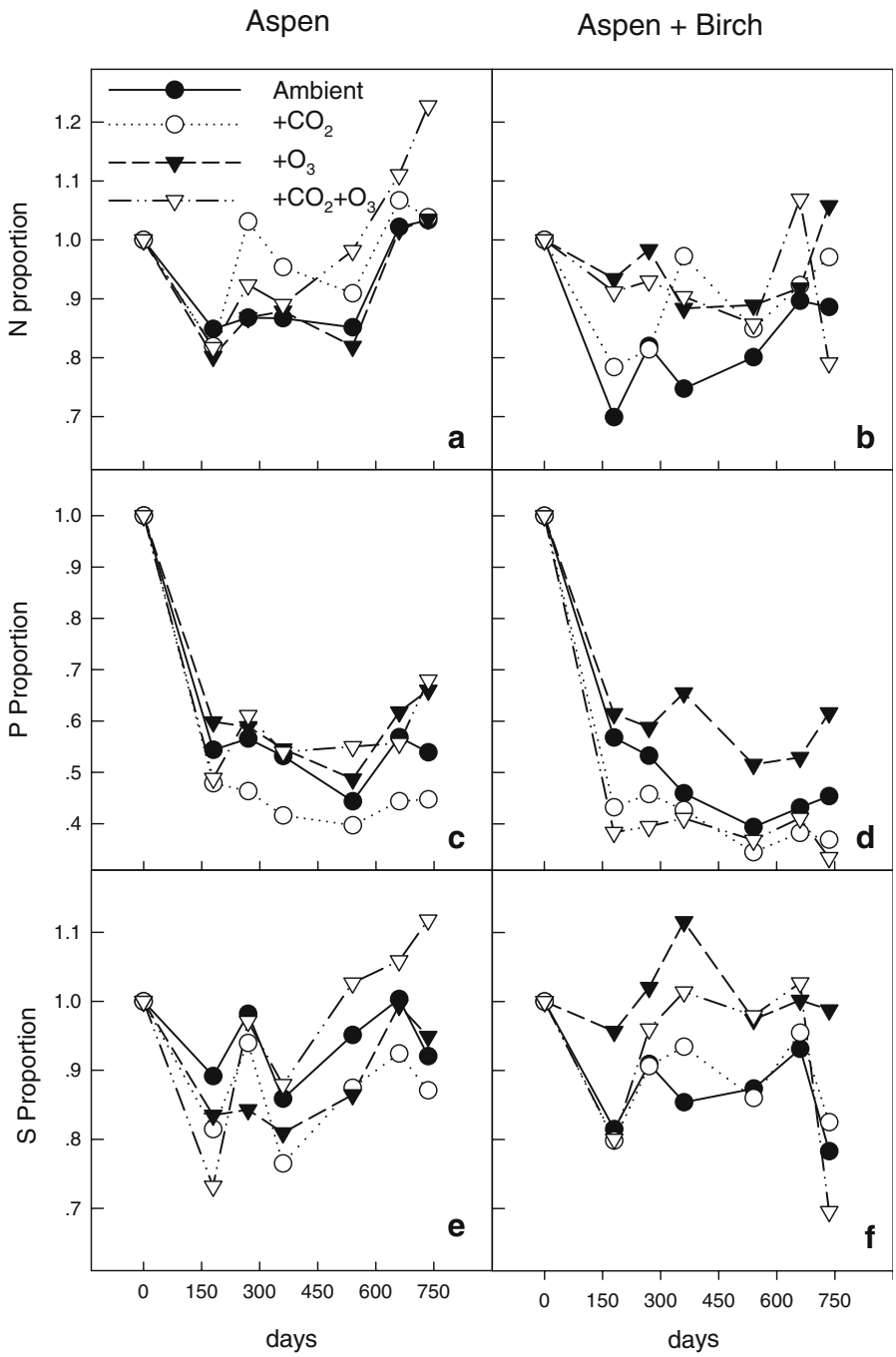

Fig. 2 Litter N, (**a, b**) P (**c, d**) and S (**e, f**) proportion dynamics over 735 days in decomposing aspen and birch/aspen litter under experimental treatments at the Aspen FACE project (n=3)

CO_2×time interaction (P=0.01; Fig. 5a,b). Elevated CO_2 significantly reduced the net release of B compared to the control (P=0.04; Fig. 6a,b). Elevated CO_2 and elevated O_3 had no significant impact on Cu dynamics. The proportion of Cu remained unchanged in the first 540 days, followed by a rapid increase throughout the rest of the incubation. The proportion of Cu increased by 70% by the end of incubation (Fig. 6c,d). There was a general trend of increasing Mn/C with time (Fig. 5e,f). The significant CO_2× community interaction (P=0.03) was due to the fact that elevated CO_2 tended to increase Mn/C of birch-aspen litter but had no impact in aspen litter. The relative Zn concentration (Zn/C) and proportion

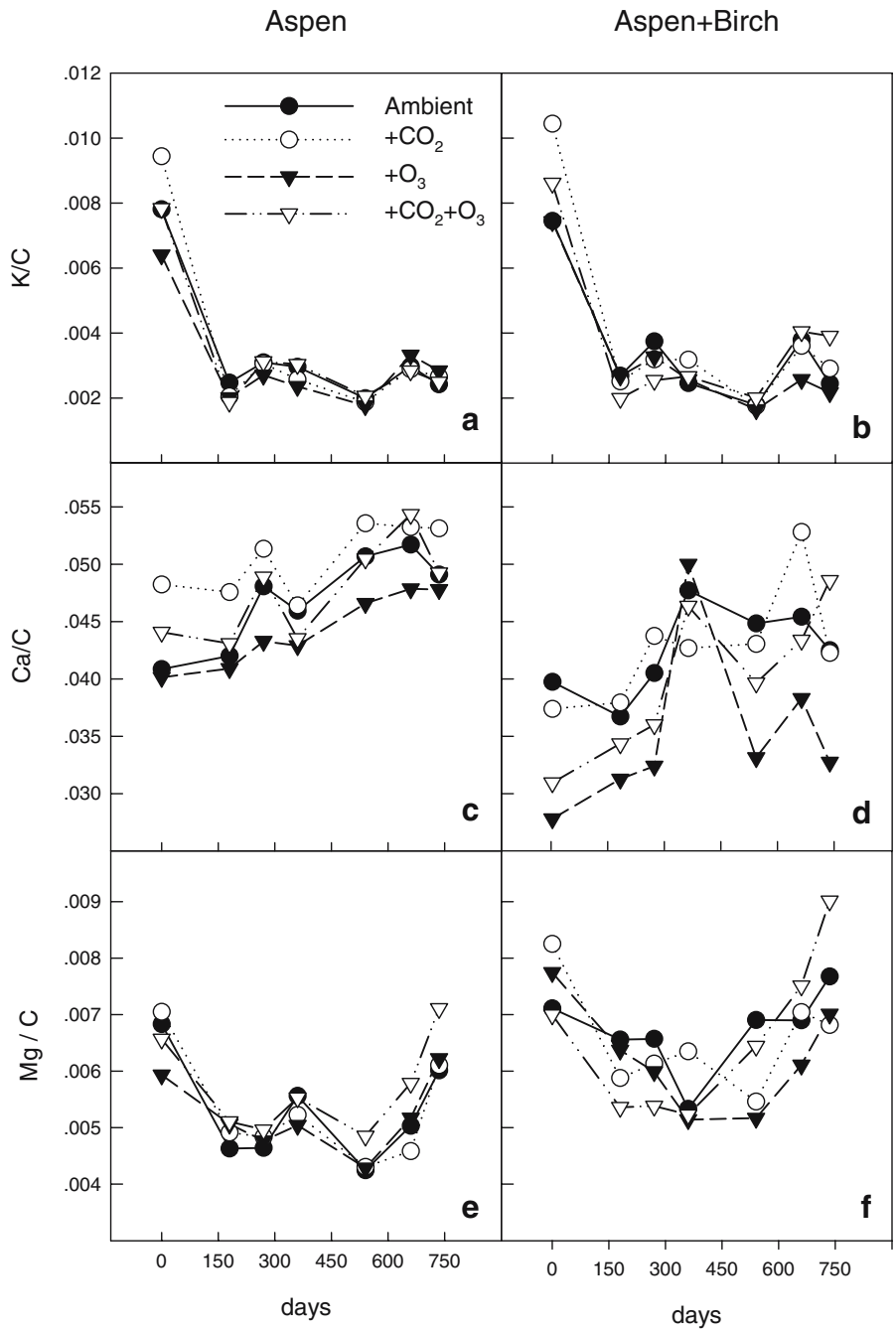

Fig. 3 Trends in K/C, (**a, b**) Ca/C (**c, d**) and Mg/C (**e, f**) levels in decomposing aspen and birch/aspen leaf litter samples from trees previously treated with elevated CO_2 and O_3 at the Aspen FACE project (n=3)

showed a rapid increase in the first year and then decreased. Elevated CO_2 tended to increase Zn release rate in birch-aspen litter under elevated O_3, but had no impact in aspen litter, which led to a significant CO_2× community×O_3 interaction of Zn proportion (P=0.01; Fig. 6g,h).

Species effects. For all micro-nutrients, aspen litter had lower B/C, Mn/C, Cu/C and Zn/C levels than birch-aspen litter during the decomposition period. Aspen litter showed a slower increase of B/C, Mn/C and Zn/C with time than that of birch-aspen during decomposition (Fig. 5a,b, e–h), which resulted in

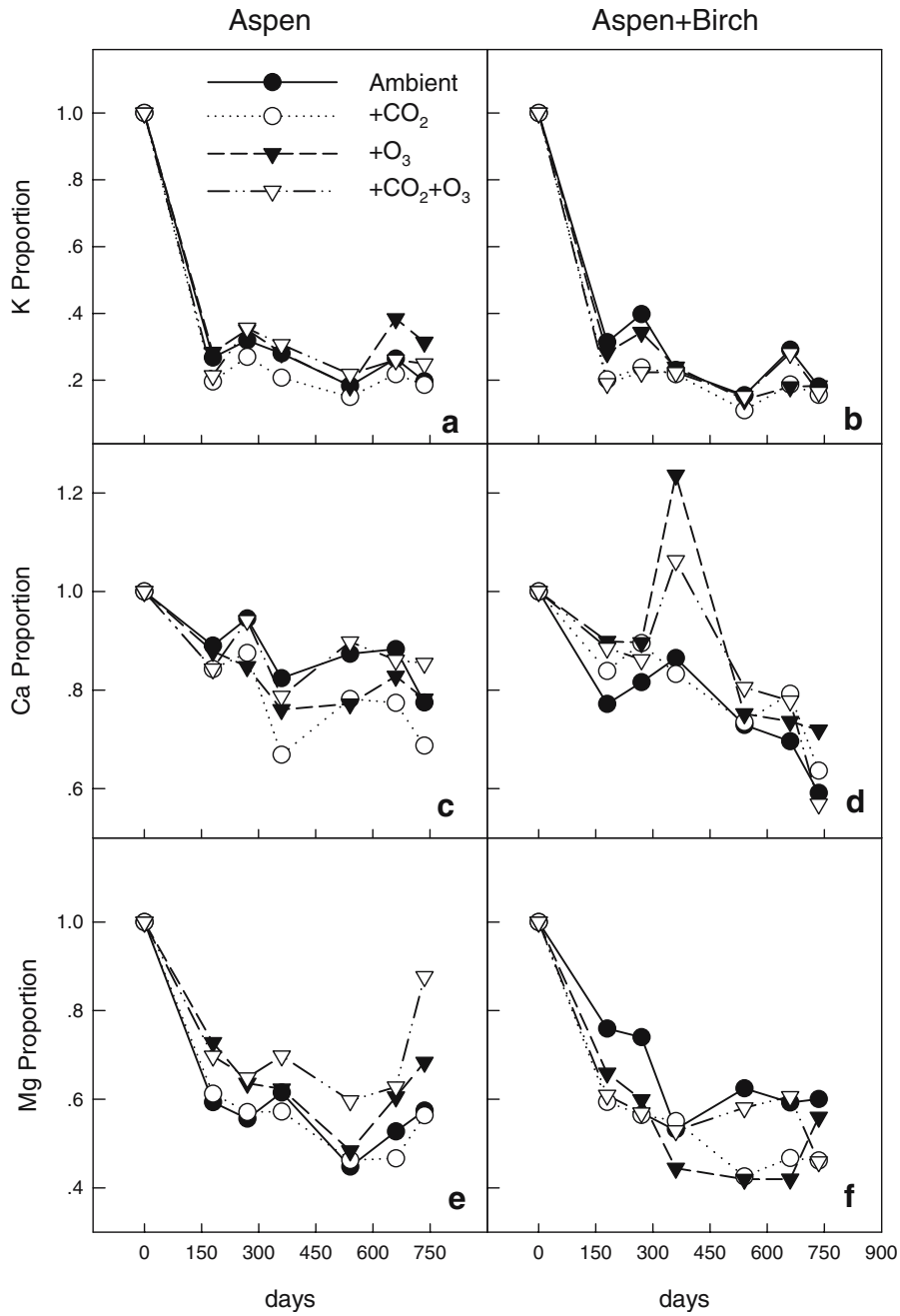

Fig. 4 Litter K, (**a, b**) Ca (**c, d**) and Mg (**e, f**) proportion dynamics over 735 days in decomposing aspen and birch/aspen litter under experimental treatments at the Aspen FACE project (n=3)

significant community×time interactions of B/C (P< 0.01), Mn/C (P<0.01) and Zn/C (P=0.01).

Factor analysis

Principle component factor analysis was used to group the original variables of relative nutrient concentration into fewer composite variables. The total variables of the relative nutrient concentration were allocated into three factors (Table 4). This three-factor model explained 98.5% of the variation in nutrient dynamics. Communalities estimate the variance in each variable explained by this model. The model explained about 70% of the variance for most macro-nutrients (N, P, S, K, and Ca) and 52% of the variance for Mg. The model performance for micro-

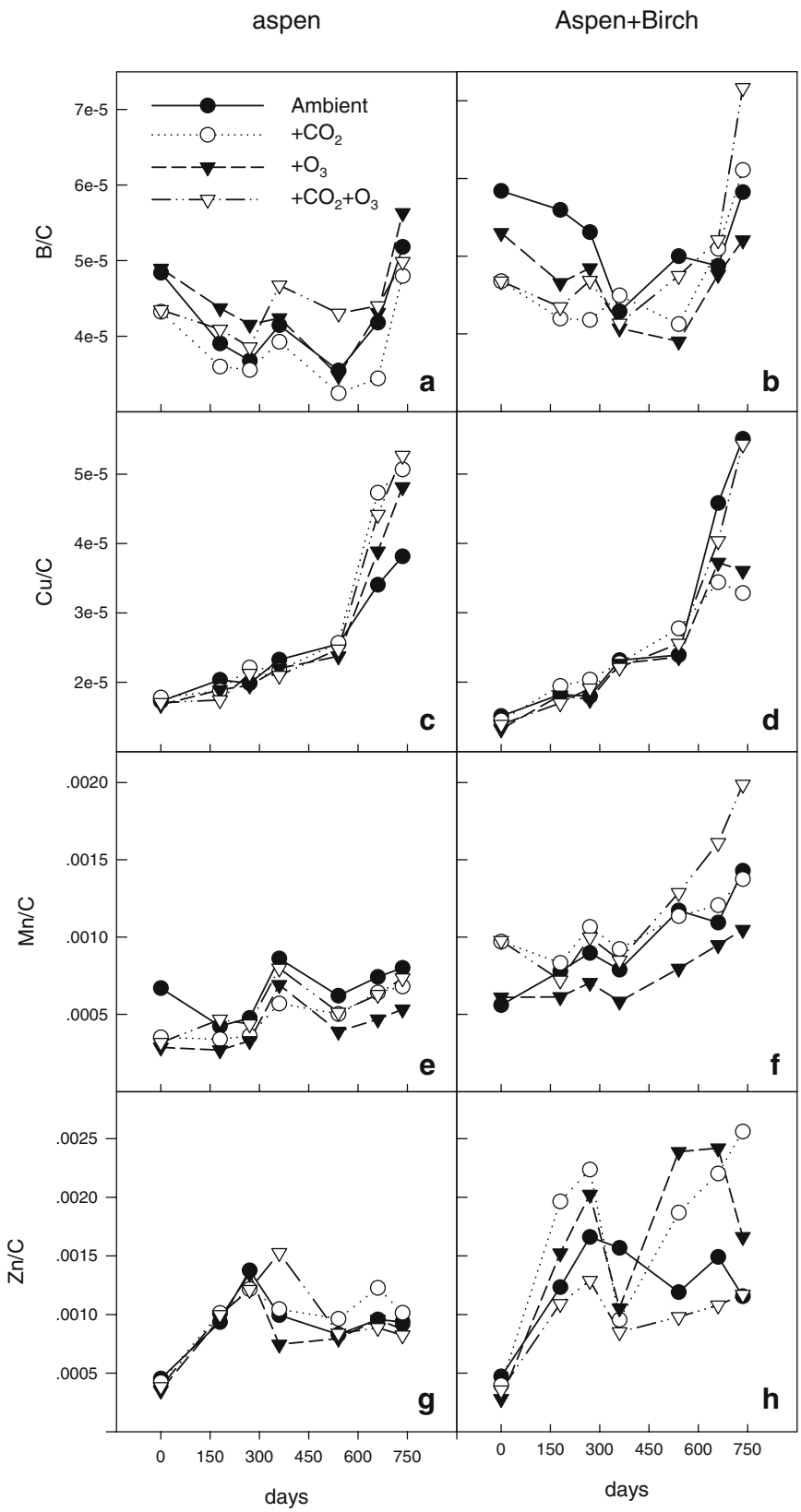

Fig. 5 Trends in B/C, (**a, b**) Cu/C, (**c, d**) Mn/C (**e, f**) and Zn/C (**g, h**) levels in decomposing aspen and birch/aspen leaf litter samples from trees previously treated with elevated CO_2 and O_3 at the Aspen FACE project (n=3)

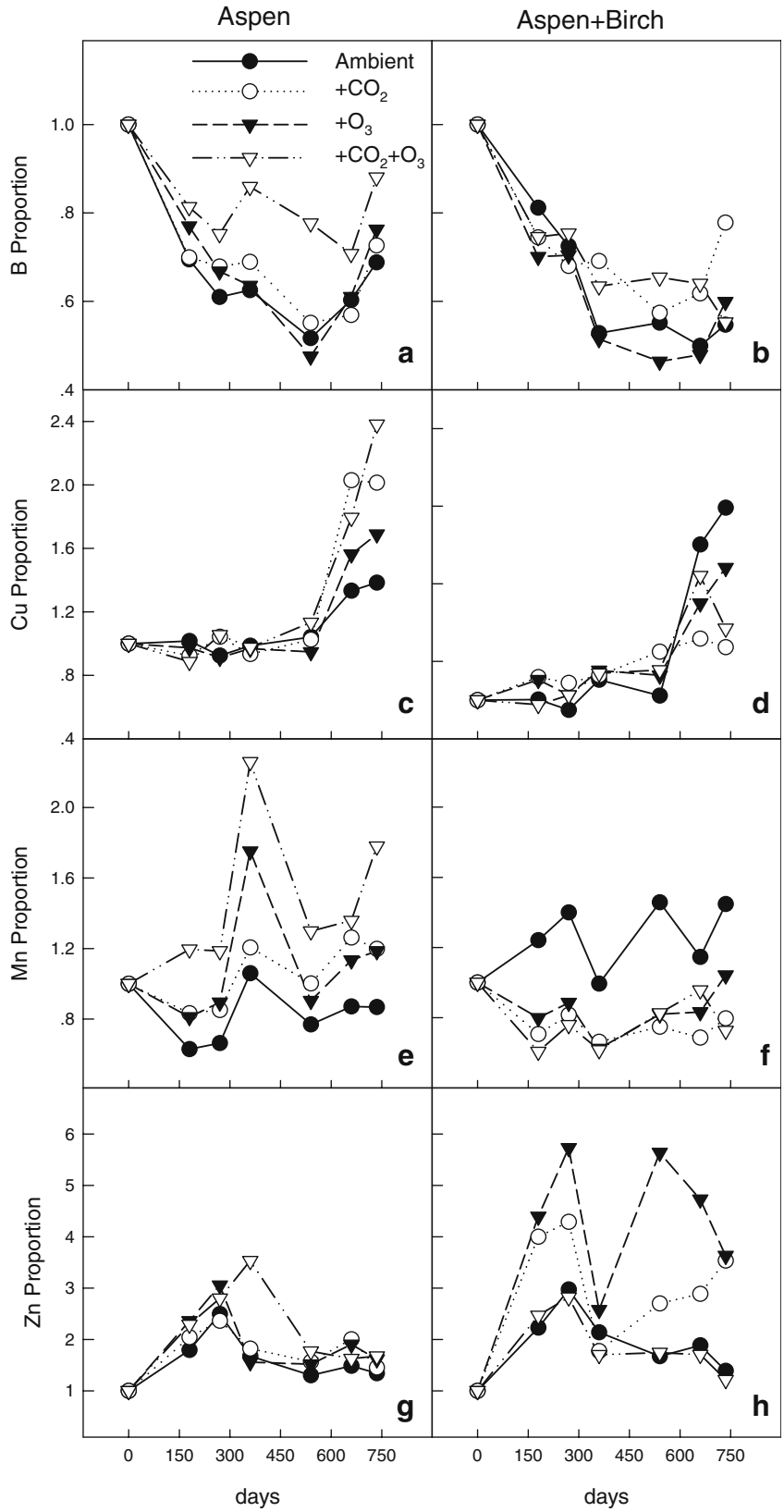

Fig. 6 Litter B, (**a, b**) Cu, (**c, d**) Mn (**e, f**) and Zn (**g, h**) proportion dynamics over 735 days in decomposing aspen and birch/aspen litter under experimental treatments at the Aspen FACE project (n=3)

Table 4 Results of principle components analysis (equimax rotated factor loadings and communalities) of the relative nutrient concentrations ([nutrient]/[C]) in decomposing leaf litter from Aspen FACE experiment, Rhinelander, WI

	Factor1 (64.4%)	Factor2 (31.1%)	Factor3 (3.0%)	Communalities
N/C	0.90	−0.09	0.42	1.00
S/C	0.86	0.00	0.02	0.74
P/C	0.37	0.75	0.20	0.75
K/C	−0.21	0.91	0.26	0.94
Ca/C	0.72	0.23	−0.66	1.00
Mg/C	0.06	0.49	0.53	0.52
Mn/C	0.15	0.05	0.48	0.25
B/C	0.19	0.29	0.42	0.30
Cu/C	0.60	−0.02	0.24	0.42
Zn/C	0.04	−0.28	0.02	0.08

nutrients was less satisfactory, explaining only seven to 42% of the variance depending on the element.

The first factor, which appears to be an accumulation/immobilization factor dominated by N, S and Ca, explained 64.4% of total variance. These nutrients were lost more slowly than C and were retained or even imported into the litter to meet the requirements of microorganisms. The second factor, which appears to be a release/mineralization factor dominated by P, K and Mg, explained 31.1% of total variance. These nutrients were lost faster than C, especially during the initial leaching phase. Finally, the third factor explained only 3.0% of the total variation, with high loadings from N, Mg, Mn and B. We limited interpretation of the third factor, which appears to be mixed effects of Factor 1 and Factor 2: release dominating the early incubation and accumulation dominating later in the incubation for those elements.

Comparing the proportion of the nine elements at the end of the incubation, a mobility series was suggested as follows (elements that did not differ significantly in their proportion are underlined together):

$$\underline{K \geq P} \geq \text{mass} \geq \underline{Mg \geq B \geq Ca} \geq \underline{S \geq N \geq Mn} \geq \underline{Cu \geq Zn}$$

Discussion

In the current study, we hypothesized that elevated CO_2 would have little effect on litter nutrient concentrations and that nutrient fluxes to soil would increase due to higher rates of litter production. Secondly, we hypothesized that elevated O_3 would also have little effect on nutrient concentrations, but would decrease nutrient fluxes to soil. Our final hypothesis was that elevated CO_2 would have little effect on nutrient release rate, but that elevated O_3 would decrease it due the effects of increased concentrations of condensed tannins and soluble phenolics on litter decomposition. On balance, our results support these hypotheses, although initial concentrations of several elements were affected by elevated CO_2 and O_3. Specific release rates of nutrients from decomposing litter, however, were little affected by the treatments, causing nutrient fluxes to soil to be dominated by productivity responses of the trees.

Initial litter nutrient content and fluxes

We found elevated CO_2 decreased N, S and B concentrations, increased K and P concentrations, and had no effect on the other six elements in aspen and birch leaf litter. The decrease in N concentration is commonly observed for leaves exposed to elevated CO_2 (Heagle et al. 1993; Fangmeier et al. 1997; Booker and Maier 2001; Norby et al. 2001; Kasurinen et al. 2006; Norby and Iversen 2006). Carbohydrate dilution did not explain N concentration change in the current study because no carbohydrate accumulation was observed in leaf litter (Liu et al. 2005). The lower N concentration under elevated CO_2 may be due to low nitrogen demand because the capacity of Rubisco to fix CO_2 is enhanced under elevated CO_2 (Nowak et al. 2004). Sulfur showed a nearly identical response to elevated CO_2 as N, with strong positive correlation between the two elements (R=0.74, P<0.01). The lower S concentration may be an indirect effect of decreased Rubisco and other proteins under elevated CO_2 (Wustman et al. 2001; Frehner et al. 1997; Akin et al. 1995). Concentrations of K and P increased and a possible factor contributing to this may have been that leaf surface properties changed under elevated CO_2. Percy et al. (2002) found cuticular wax production of aspen was stimulated by elevated CO_2 at this site, which could change leaf wettability and reduced cation leaching. This hypothesis is supported by the study of throughfall nutrient fluxes at Oak Ridge FACE site by Johnson et al. (2004), which

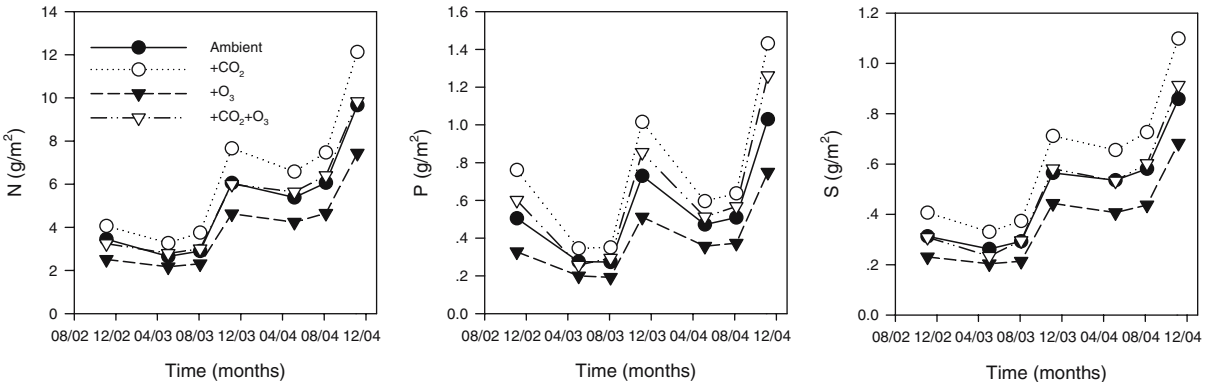

Fig. 7 Calculated nutrient inputs to soil (*N*, *P* and *S*) from 2002 to 2004 under the experimental treatments the Aspen FACE project

reported reduced N, P, Ca and Mg concentrations under elevated CO_2.

In this experiment, we found that O_3 tended to decrease litter nutrient concentrations (significant for S, P, Ca, and Zn, and marginally significant for N). This may have been caused by (1) lower root uptake; (2) increased translocation; (3) increased leaching; or (4) other related physiological processes. Rubisco concentration has been shown to decrease under elevated O_3 (Wustman et al. 2001), which could partly explain the decrease of N and S concentrations. Low carboxylation efficiency under O_3 (Karnosky et al. 2003) decreases inorganic P consumption for ATP synthesis and could result in lower P demand. Calcium transport is considered to be governed by transpiration (McLaughlin and Wimmer 1999). Elevated O_3 has been shown to decrease transpiration rates (Woo and Hinckley 2005; Moraes et al. 2004), which may have contributed to the decreased Ca accumulation in leaf litter reported here.

Nutrient input from 2002 to 2004 at Aspen FACE site

We estimated the nutrient pool (g/m^2) of decomposing litter by multiplying the remaining biomass (g/m^2) with corresponding nutrient concentration (g/g). Litter biomass was measured from 2002 to 2004 at Aspen FACE site (data not shown). Based on nutrient dynamics and biomass decomposition of the litter produced in 2003, nutrient pools of the litter produced in 2002 and 2004 were estimated, assuming litter produced in different years had the same initial nutrient concentrations and decomposition rates. Nutrient inputs from 2002 to 2004 were then calculated by summing litter nutrient pools of the 3 years. We found the accumulation of the nine elements in forest floor increased through time for all treatments in the order: $+CO_2$>$+CO_2+O_3$>control>$+O_3$ (Fig. 7).

Concentrations of most nutrients in plant tissue are constrained to relatively narrow ranges (Taiz and Zeiger 1998; Chapin et al. 2002). We observed small changes in litter nutrient concentrations under elevated CO_2 and O_3. However, the increase in litter biomass production under elevated CO_2 and the decrease under elevated O_3 resulted in significant changes in nutrient inputs to the forest floor. Our findings of reduced nutrient inputs under elevated O_3, and possibly decreased nutrient release rates associated with higher concentrations of carbon based secondary compounds (Liu et al. 2005), suggest that regional increases in tropospheric O_3 may slow rates of nutrient cycling in northern hardwood forests.

Nitrogen limitation

The hypothesis of progressive N limitation (PNL) of forest productivity in response to elevated CO_2 is currently an area of active investigation (Norby and Iversen 2006; Finzi et al. 2006; Luo et al. 2006; Johnson 2006). Luo et al. (2004) hypothesized that limitation by N is mostly due to N allocation to long lived biomass and soil organic carbon. Studies at the Aspen FACE project show that elevated CO_2 has had no impact on N concentration of wood and fine roots (Kaakinen et al. 2004; Chapman et al. 2005), and has caused a sustained increase in stand productivity (King et al. 2001, 2005b). These results suggest that the soil N supply is still sufficient to meet the increase

in productivity, even though more N is being immobilized in plant biomass. Litter decomposition from leaves and fine roots and soil N availability have not been significantly altered by elevated CO_2 (Chapman et al. 2005; Holmes et al. 2006; this study). Combined with increased N inputs from fine roots (Chapman et al. 2005; King et al. 2005b) and leaf litter (Liu et al. 2005), N incorporated into soil organic C would be expected increase at our site, in agreement with the PNL hypothesis. However, greater plant acquisition of N under elevated CO_2 may have resulted from greater soil exploration through increasing root biomass, surface area, and length (King et al. 1997, 2001, 2005b), or increased carbon allocation to roots and mycorrhizal fungi (Giardina et al. 2005). Thus we expect the potential for PNL to occur will be moderated by native soil N supply and plant and microbial responses to elevated CO_2. At more fertile sites, soil supply may be sufficient to sustain an increased demand for N under elevated CO_2 and PNL may be delayed or avoided altogether compared to less favorable sites.

Decomposition and nutrient dynamics

Although aspen and birch are both fast-growing, early-successional species, they showed different nutrient dynamics in the current study. This could be related to different litter decomposition rates of the two communities. During the 2 years of field incubation, aspen litter lost 34.5±1.5 (%) of the original biomass while birch/aspen litter lost 48±2.3 (%) of the original biomass (data not shown). Because of the faster biomass loss, birch/aspen litter retained less N, S, Ca, Mg and B than did aspen by the end of the incubation.

In terms of nutrient dynamics, the accumulation of N and S may have been controlled by microbial immobilization. The loss of K and Mg may have been related more to their chemical characteristics. These elements are relatively mobile in litter and the abiotic adsorption of humidified litter has low effect on them (Laskowski et al. 1995; Kraus et al. 2003). The proportion of P in litter decreased rapidly during the first 180 days, followed by a stable stage for the remainder of the incubation period. This pattern may be because P was recycled during litter decomposition processes, which hindered release to the soil solution (Wardle et al. 2004). Heavy metal elements, such as Cu and Zn, can chelate with humic matter and therefore accumulate in later decomposition stages (Laskowski et al. 1995). However, the accumulation may also be due to nutrient import from other sources, such as transport by soil microbes, leaching from overlying litter and canopy, and atmospheric deposition.

It should be kept in mind that our estimates of decomposition were based on a litterbag study, and interpretation of results is based on relative comparisons between the treatments at Aspen FACE. Decomposition of litter unconfined in bags may or may not have differed from that reported here. Litterbags with 1 mm mesh size were used in our study, which excluded macro and some meso-fauna from the litter. Macro fauna have strong effects on litter decomposition by fragmenting litter, mixing litter into the soil or grazing soil microorganisms (Chapin et al. 2002). Excluding macro fauna can reduce litter mass loss and nutrient release (Tian et al. 1992; Bradford et al. 2002; Koukoura et al. 2003; Schädler and Brandl 2005). Elevated CO_2 and O_3 can alter soil fauna abundance and composition (Loranger et al. 2004), also affecting litter consumption rates by soil fauna through changing litter chemistry (Kasurinen et al. 2007), thereby complicating litterbag-based efforts to evaluate the potential effects of macro fauna on nutrient dynamics. Additional research is clearly needed to better understand how soil fauna influence nutrient cycles under elevated CO_2 and O_3.

In conclusion, results from our study indicate that although leaf litter nutrient concentrations did not show consistent responses to elevated CO_2, all nutrient fluxes to soil, except B, were increased by elevated CO_2. Nutrient concentrations tended to be lower under elevated O_3. Combined with lower biomass production, all nutrient fluxes to soil, except Mn, were decreased by elevated O_3. Elevated CO_2 and O_3 also influenced nutrient release rates, but overall, microbial requirements and chemical properties of those elements had much more important effects on the patterns of nutrient dynamics. The forest floor in these aggrading stands acted as a nutrient sink for N, S, Mn, Cu and Zn, but as a source for K, P, Mg, Ca and B during the first 2 years of decomposition.

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