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Effects of CO_2 and nitrogen fertilization on soils planted with ponderosa pine

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Abstract

The effects of elevated CO_2 (ambient, 525, and 700 $\mu l\ l^{-1}$) and N fertilization (0, 10, and 20 g N m^{-2} yr^{-1}) on soil pCO_2, CO_2 efflux, soil solution chemistry, and soil C and nutrients in an open-top chamber study with *Pinus ponderosa* are described. Soil pCO_2 and CO_2 efflux were significantly greater with elevated CO_2, at first (second growing season) in the 525 $\mu l\ l^{-1}$ and later (fourth and fifth growing seasons) in the 700 $\mu l\ l^{-1}$ CO_2 treatments. Soil solution HCO_3^- concentrations were temporarily elevated in the 525 $\mu l\ l^{-1}$ CO_2 treatment during the second growing season, consistent with the elevated pCO_2. Nitrogen fertilization had no consistent effect on soil pCO_2 or CO_2 efflux, but did have the expected negative effect on exchangeable Ca^{2+}, K^+, and Mg^{2+}, presumed to be caused by increased nitrate leaching. Elevated CO_2 had no consistent effects on exchangeable Ca^{2+}, K^+, and Mg^{2+}, but did cause temporary reductions in soil NO_3- (second growing season). Statistically signficant negative effects of elevated CO_2 on soil extractable P were noted in the third and sixth growing seasons. However, these patterns in extractable P reflected pre-treatment differences, which, while not statistically significant, followed the same pattern. Statistically significant effects of elevated CO_2 on total C and N in soils were noted in the third and sixth growing seasons, but these effects were inconsistent among N treatments and years. The clearest effect of elevated CO_2 was in the case of C/N ratio in year 6, where there was a consistent, positive effect. The increases in C/N ratio with elevated CO_2 in year six were largely a result of reductions in soil N rather than increases in soil C. Future papers will assess whether this apparent reduction in soil N could have been accounted for by plant uptake.

Introduction

The long-term effects of elevated CO_2 on growth and carbon (C) sequestration are highly dependent upon the availability and cycling of nutrients. Many studies have addressed the effects of elevated CO_2 on N uptake and and soil C and N dynamics (Zak et al., 1993; McGuire et al., 1997; Johnson et al., 1997; Körner and Arnone, 1992; Bernsten and Bazazz, 1997; Cotrufo and Ineson, 1996; Diaz et al., 1993; Hirschel et al., 1997; O'Neill 1994; Randlett et al., 1996). However, few studies have addressed the effects of elevated CO_2 on soil nutrients other than C and N. Greenhouse studies on the effects of elevated CO_2 on soil nutrients have produced conflicting results. Norby et al (1986a) found an increase in soil extractable P with elevated CO_2 in a pot study with *Quercus alba* L. and speculated that elevated CO_2 increased phosphatase activity. On the other hand, Johnson et al (1996) found reduced soil extractable P levels with elevated CO_2 could be accounted for by increased plant P uptake by *Pinus ponderosa.* in a greenhouse study using a nutrient-poor soil. In another greenhouse study using a richer soil, Johnson et al. (1996) found no effects of elevated CO_2 on either plant P uptake or soil extractable P. Johnson et al. (1996) concluded from these two studies that the effects of elevated CO_2 on soil P "were inconsistent and no general conclusions can be drawn".

Elevated CO_2 could cause changes in soil exchangeable base cation pools via leaching and/or uptake. Körner and Arnone (1992) found that elevated CO_2 stimuled N mineralization in excess of what plants were able to take up in model tropical ecosystems, causing increased NO_3^- leaching. On the other hand, Torbert et al. (1996) found that elevated CO_2 caused reduced NO_3^- leaching in both soybean (*Glycine max* (L.) Murr.) and grain sorghum (*Sorghum bicolor* (L.) Moench) because of increased N uptake. The often-noted increase in soil respiration under elevated CO_2 (Johnson et al., 1994; Körner and Arnone, 1992; Liu et al., 1996; Vose et al., 1995) could cause increased carbonic acid production and bicarbonate – base cation leaching if soils are not extremely acidic (McColl and Cole, 1968; Johnson et al., 1977). This can be seen from the following equations describing the dissolution of CO_2 in solution and the dissociation of carbonic acid:

$$[H_2CO_3] = (Kh)(pCO_2) \qquad 1)$$

$$\frac{[HCO_3^-]\,[H^+]}{[H_2CO_3]} = K_1 \qquad 2)$$

where Kh = Henry's Law constant and K_1 = First dissociation constant for carbonic acid. Combining and solving for $[HCO_3^-]$ yields:

$$[HCO_3^-] = \frac{(K_1)(Kh)(pCO_2)}{[H^+]} \qquad 3)$$

Thus, bicarbonate concentration (and, therefore, cation leaching associated with bicarbonate) is a function of pCO_2 in the soil atmosphere and soil solution pH (Johnson et al 1977). McColl and Cole (1968) artificially increased pCO_2 in soil columns, and demonstrated increased carbonic acid leaching. Johnson et al., (1977) found that elevated pCO_2 due to greater biological activity in soils at a tropical site (La Selva, Costa Rica) caused greater carbonic acid leaching rates than in more northern forest soils with lower pCO_2 's.

The direct evidence for CO_2 effects on soil exchangeable cations is mixed, as in the case of N and P. Norby et al (1986a) found no effect of elevated CO_2 on exchangeable K^+, but a downward trend. Potassium leaching was lower with elevated than with ambient CO_2 in the study of Norby et al. (1986), and thus the reduced exchangeable K^+ was attributed to uptake. Johnson et al (1995b) found decreases in exchangeable K^+, Ca^{2+}, and Mg^{2+} with elevated CO_2 in two separate pot studies with ponderosa pine (*Pinus ponderosa.*) greater than could be accounted for by plant uptake and thus were attributed to increased leaching.

In this paper, we summarize the results of six years of investigation on the effects of CO_2 and N fertilization on soils from open-top chamber planted with ponderosa pine. In earlier papers summarizing results from years one through three of this study, we reported that elevated CO_2 caused: 1) elevated soil pCO_2, soil respiration, and increased rates of carbonic acid leaching; 2) reduced soil NO_3^- concentrations; and 3) declines in soil extractable P (Johnson et al., 1996, 1997; Vose et al., 1996). The reductions in soil NO_3^- concentration were attributed to increased inputs of labile C belowground (causing increased N immobilization, denitrification, or both). The only treatment effect at 3 years was the negative effect of elevated CO_2 on extractable P which appeared to be associated with increases in exchangeable Al^{3+}. Large reductions in C and N were also noted across all treatments and were attributed to the effects of disturbance (ploughing) prior to seedling establishment.

Sites and Methods

Site and Experimental Design

The open-top chamber site for the ponderosa pine research was located at the Institute of Forest Genetics in Placerville, California. The soil is Aiken clay loam, a Xeric Haplohumult derived from andesite. Soils were intensively sampled prior to chamber establishment, and were found to be very uniform. During February - April 1991, 24 hexagonal open-top chambers (3.6 m in diameter) were established on the site. The basic experimental design consisted of three levels of nitrogen (0, 10, and 20 g m^{-2} yr^{-1} of N as ammonium sulfate, applied in early spring), and four CO_2 treatments (ambient, no chamber; ambient, chambered; 525 $\mu l\ l^{-1}$ CO_2; and 700 $\mu l\ l^{-1}$ CO_2). Water was delivered to each plot via a timed stand pipe to a looped one inch diameter manifold, and low pressure spray heads. Each of the chambered treatments was replicated three times, and each of the unchambered treatments was replicated twice. Only the results from the chambered measurements will be reported here. Due to cost limitations, the 10 g m^{-2} yr^{-1} N, 525 $\mu l\ l^{-1}$ CO_2 treatment was excluded.

In May of 1991, Ponderosa pine (*Pinus ponderosa* Laws.) was planted in each chamber. Seedlings were grown from seed (21 planting locations per chamber) and seedlings (21 per chamber), the latter being a backup in the event of excessive mortality. Seed-grown seedling survival was very good, and the seedling-grown stock was removed in October 1991. In October 1991 (year 1), three trees from each chamber were harvested, including complete root systems. In October 1992 (year 2) and October 1993 (year 3), three trees from each chamber were harvested again, but only one complete root system per chamber was obtained because of the increased size of the seedlings and concern for excessive plot disturbance. The original plan was for a final harvest in October 1994, but additional funds became available for continuation of the project and this harvest was postponed until October 1996.

Sampling and Analysis Methods

Measurement and Calculation of Soil CO_2 Efflux

Between March, 1992 and August, 1996 soil pCO_2 concentrations were monitored from gas wells established at 15 and 30 cm depths in each chamber. The gas wells consisted of 4 mm tubing inserted ot the proper depth in the soil and fitted with a stoppered, female end of a plastic union at the surface. During gas collections, stoppers were removed and 15 ml of soil gas was withdrawn from each well (enough to completely evacuate the tubing and obtain soil gas) using a 50 ml sryinge fitted with tygon tubing and the male half of the plastic union. Samples for CO_2 analyses were obtained with Hamilton gas syringes from the section of Tygon tubing between the large syringe and the union. CO_2 analyses were performed on a LiCOR 6250 CO_2 gas analyzer using peak heights compared to a standard gas. Soil temperature and moisture were recorded at each soil gas sampling. Results from the period July 1992 through July 1993 were previously reported by Johnson et al. (1994).

Soil moisture was measured by various methods during the early part of the study. From July - August 1992 portable tensiometers (Soil Moisture Corp.) were used. In that soil moisture tension was normally kept well below 50 kPa by irrigation, there was little concern that tensiometers would become inoperable. The portable tensiometers provided adequate estimates of soil moisture content, as evidenced by comparisons with gravimetric analyses, but they were abandoned in October 1992 in favor of gravimetric samples because the time necessary to obtain tensiometer measurements was greater than that needed to take soil samples for gravimetric analyses. Between October 1992 and May 1993 gravimetric analyses were used for estimation of soil water content. After that time, gypsum blocks were calibrated and used for estimations of water content, because of concern over the repeated effects of destructive soil sampling.

Cumulative soil respiration over the period March, 1992 through August, 1996 was estimated using the profile method (de Jong and Schappert 1972, 1974; Johnson et al 1994). In a comparison of static and profile methods for measuring soil respiration, Mattson (1995) concluded that the profile method "shows promise as a reliable means to measure CO_2 efflux" and this method was used in a previous paper for the Placerville site (Johnson et al 1994). De Jong et al. (1979) compared the profile method with the static chamber, dynamic chamber, and micrometerological methods of measuring CO_2 efflux for a grassland site in Saskatchewan. They found that the profile method gave the highest values, the dynamic chamber the lowest, and the micrometerological methods were intermediate. Kanemasu et al. (1974) found that very slight pressure within a dynamic chamber caused order of magnitude reductions in measured CO_2 efflux.

The profile method has the advantage of simplicity and ease of measurement, allowing multiple measurements in time and space, but it also involves assumptions and initial calibrations that need to be tested. In particular, the diffusion coefficient (D), which is a function of the diffusion of CO_2 in air adjusted for pore restrictions and tortuosity in soils, has proven to be a difficult parameter to obtain with accuracy. A recent paper by Moldrup et al (1996) offers promise for improvements in this regard using the Campbell soil water retention model, and this approach has shown some promise in initial work at the Florida site.

The profile method is based upon the assumption that CO_2 efflux is dominated by diffusion and therefore controlled by the partial pressure of CO_2 in the soil atmosphere (pCO_2):

$$q = D\frac{dC}{dz} \qquad 4)$$

Where $q = CO_2$ efflux ($g\ CO_2\text{-}C\ m^{-2}\ day^{-1}$), $C =$ soil CO_2 concentration ($g\ m^{-3}$), $z =$ depth (m), and $D =$ diffusion coefficient ($m^2\ day^{-1}$).

Because CO_2 diffusion through water is much lower than in air, D is strongly affected by soil water content. There are several formulations for D (Collin and Rasmuson 1988), all of which take soil moisture content into account. In a previous paper, we reported significant correlations between soil pCO_2, calculated soil CO_2 efflux, and CO_2 efflux measured with a continuous flow infrared gas analyzer (IRGA) system and the profile method (Vose et al., 1995). In that paper, we used the formulation for D given by Collin and Rasmuson (1988), which requires not only total porosity and soil water content but also a value for a coefficient which accounts for non-ideal pore shape and dead-end pores. For the Placerville soil, the value of this coefficient was determined from comparisons with measured CO_2 efflux using the IRGA system (Vose et al 1994). Since the publication of that paper, Moldrup et al. (1996) provided a more general empirical formulation for D which depends upon commonly-measured soil properites:

$$D = (Da)(E^{4/3})\left(\frac{Peff}{E}\right)^{(1.5 + 3/b)} \qquad 5)$$

Where D_a = diffusion coefficient of CO_2 in air ($cm^2\ sec^{-1}$), E = voids ratio, or total soil porosity, P_{eff} = effective porosity = total porosity (E) minus volumetric water content (V_w), $b = [(0.303 - 0.093(\ln BD)) - 0.0565(\ln(CL)) + 0.00003(FS^2)]^{-1}$, BD = bulk density ($g\ cm^{-3}$), CL = percent clay (<0.002 mm), and FS = percent fine sand (0.02 to 0.20 mm). This formulation for D was found to be an improvement over the previous model for D in the Placerville soil and was used to calculated soil CO_2 efflux in this paper.

Cumulative CO_2 flux was calculated by trapezoidal integration of respiration values (Cotrufo et al., 1994) over the period September, 1992 through August, 1996.

Soil Sampling and Analysis

Soils were sampled by horizon in March of 1991, March of 1993, and Sepember 1996 by punch auger. Soils from each sampling were analyzed for total C and N on the Perkin-Elmer, exchangeable Ca^{2+}, Mg^{2+}, K^+, and Al^{3+} (1 $\underline{M}$ NH_4Cl in 1991 and 1993; ammonium acetate in 1996); and extractable P (0.5 $\underline{M}$ HCl plus 1 $\underline{M}$ NH_4F; Olsen and Sommers, 1982). Soils from the 1991 and 1993 samplings were analyzed at the Desert

Research Institute and those from the 1996 sampling were analyzed at the Soil and Plant Analysis Laboratory, University of Missouri (because of lower analytical costs). Eleven subsamples from the 1991 and 1993 samplings were sent to the University of Missouri for quality assurance checks on laboratory bias. Unfortunately, significant bias was detected (University of Missouri results were lower) in the cases of all but exchangeable K, precluding analyses of changes over time for the 1993-1996 period. Because of lack of sensitivity of results for soil N for the University of Missouri analyses (a trace level of 0.1 was used), soils from 1996 were re-analyzed for C and N at DRI using a Perkin-Elmer 2400 CHNS Analyzer.

In addition to standard soil sampling, homogenized soil bags (David et al., 1992) were installed in the chambers in August, 1995 and retrieved in September 1996. Homogenized sampled from the Aiken Ap horizon were placed in 1 mm mesh bags, labelled and inserted in the Ap horizons of each chamber (3 per chamber). This technique was not designed to provide an estimate of actual rates of soil change (because the disturbance of homogenizing soils precludes this), but rather as a means of measuring relative treatment effects on soil properties. David et al. (1990) used this technique to detect very small changes in soil chemical properties in response to acidification treatments to a Spodosol in Maine. Due to budgetary constraints, only total C and N were analyzed on the buried soil bags.

Soil solution sampling and analysis

Ceramic cup, falling head lysimeters were installed in each of the unfertilized chambers in November, 1993 and collections were made on approximately a bi-monthly basis until April, 1995. All soil solution samples were analyzed for NH_4^+ and NO_3^- (automated colorimetric analysis), and selected samples were also analyzed for Ca^{2+}, K^+, Mg^{2+}, and Na^+ (atomic absorption), SO_4^{2-}, Cl^-, ortho-phosphate (automated colorimetric analysis), pH, and HCO_3^- (by titration to pH 4.5) at the Water Analysis Laboratory at the Desert Research Institute.

Statistical analyses

Statistical analyses for treatment effects on soils in any given year were performed using PROC GLM in Statistical Analysis System software.

Results

Soil pCO_2 and CO_2 Efflux

In previous papers, we reported a significant, positive effect of CO_2 treatment on soil pCO_2 and respiration (Johnson et al., 1994; Vose et al., 1995) during the period July 1992 – July 1993. This was apparently due to the greater root biomass with elevated CO_2, especially at the 525 µl l^{-1} level. These effects are evident in Figures 1 and 2, which summarize the pCO_2 data from March, 1992 through August, 1996 for the 15 and 30 cm depths, respectively. However, Figures 1 and 2 also reveal that the effects of CO_2 treatment faded during the summer of 1993, reappearing only sporadically and mostly in the high N treatment. In the summer of 1994, pCO_2 at the 15 cm depth was over two-fold greater in the 700 µl l^{-1}, high N treatment than in the 350 or 525 µl l^{-1}, high N CO_2 treatments. This transition from higher pCO_2 in the 525 to the 700 µl l^{-1} CO_2 matched the patterns observed in tree biomass between 1991 and 1993 and in tree diameter and heights between 1993 and 1996: the initially higher values for the 525 µl l^{-1} CO_2 treatments faded after year 2 and the µl l^{-1} 700 CO_2 treatment became dominant (Johnson et al., 1997 and J.T. Ball, unpubl. data). By the summer of 1996, however, the effects of the 700 µl l^{-1} CO_2 had also faded into insignificance, with the exception of the 700 µl l^{-1} CO_2 , high N treatment at the 30 cm depth (Figure 2).

Estimated cumulative soil CO_2 efflux between September, 1992 and August, 1996 and soil C contents in 1991 and 1996 are presented in Table 1. Cumulative soil CO_2 efflux was substantially greater in the high N, 700 µl l^{-1} CO_2 treatment than in all other treatments, primarily because of the high p CO_2 concentrations in the summers of 1994 and 1995 in this treatment (Figure 1). The cumulative CO_2 effluxes equalled approximately 50 to 100% of the standing soil C pools measured in either 1991 or 1996, and were many fold greater than any change in soil C which may have occurred. It is noteworthy that high CO_2 effluxes do not imply high net losses of soil C: the greatest apparent gain in soil C as well as the greatest cumulative CO_2 efflux were both in the 700 $\mu l\ l^{-1}$ CO_2, high N treatment.

Soil solution

As reported previously (Johnson et al., 1996), we found significantly greater soil solution HCO_3^- concentration with elevated CO_2 (unfertilized treatments) in one sampling (July, 1993 collection) (Figure 3). This was consistent with the greater pCO_2 concentrations observed at that time (Figures 1 and 2). There were no other statistically significant differences in soil solution base cation (Ca^{2+}, K^+, Mg^{2+}, or Na^+) or anion (SO_4^{2-}, $H_2PO_4^-$, Cl^-, NO_3^-) concentration among treatments on the July 1993 or on any other date, however (Figure 4). (There was a decided trend toward higher Cl^- and base cation concentrations on the July 1993 sampling date, but this was largely due to one replicate and the differences were not statistically significant.) Later samplings (November, 1993, October, 1994 and April 1995) revealed no significant differences in HCO_3^- concentration (or any other ion concentration) among CO_2 treatments, however (Figure 3). Again, this was consistent with the patterns in pCO_2 , which also showed no CO_2 treatment effects in the low N treatment after the summer of 1993.

Soil solution NO_3^- and NH_4^+ concentrations were generally very low with the exception of the first samplings (May, 1993) (Figure 5). The high values in these first sampling may have been due to disturbance associated with lysimeter installation. The only significant treatment effect was in the first sampling, where soil solution NO_3^- was lower with elevated CO_2 (Figure 5).

Soil Nutrient Changes

Figures 6 through 12 show C and nutrient concentrations in soils in years 1, 3, and 6 and Table 2 provides statistical analyses of CO_2 and N treatment effects by year.

Prior to treatment, there were no statistically significant differences in total C, total N, C/N ratio exchangeable K^+, or extractable P in any treatment or horizon, but there were significant differences in exchangeable Ca^{2+} and Mg^{2+} concentrations among the CO_2 treatments in both the Ap and Bw horizons when all treatments were combined for ANOVA (Table 2; Figures 6 through 12). When pre-treatment CO_2 effects were analyzed within N treatments, the only significant effect was in the case of extractable P in the Bw horizon of the low N treatment (Table 3).

Three years after the commencement of treatments, statistically significant effects of CO_2 treatment on total C, total N, extractable P, and exchangeable Mg^{2+} were found in the Ap horizon and significant effects of CO_2 treatment on extractable P and exchangeable Mg^{2+} were found in the Bw horizon when all treatments were combined for ANOVA. There were also significant (negative) effects of N treatment on exchangeable Mg^{2+} in the Ap horizon in year 3. When CO_2 treatment effects were anlyzed by N treatment, In the cases of C and N, the year 3 results followed a pattern of higher concentrations in the 525 $\mu l\ l^{-1}$ CO_2 treatments, consistent with the patterns in biomass over years 1 and 2 (Johnson et al., 1997). In the cases of P and Mg^{2+}, the year 3 results followed a patterns of lower extractable P with elevated CO_2 also present prior to treatment but not statistically significant until year 3 (Table 2 and Figures 9 and 12).

Six years after the commencement of treatments, the differences in total C were no longer significant in the Ap horizon, but there were significant effects of CO_2 treatment on total N, C/N ratio, and extractable P in the Ap horizon and significant effects of CO_2 treatment on total C, total N, C/N ratio, and extractable P in the Bw horizon. There were also significant effects of N treatment on exchangeable Ca^{2+}, K^+, and Mg^{2+} in the Ap horizon and significant effects of N treatment on exchangeable K^+, and Mg^{2+} in the Bw horizon.

The homogenized soil bags showed little change in C concentration after one year and no treatment effects on C (Figure 13). There were net gains in N in soil bags in all treatments, however, and significant ($p < 0.05$) treatment effects of N treatment on soil N and C/N ratio after one year.

Discussion

Carbon dioxide efflux is seldom estimated using the profile method, and thus comparisons of the values obtained here with those reported using active or passive chamber methods in the literature are of interest. When expressed on an annualized basis, the values for soil CO_2 efflux in this study (0.8 to 1.8 kg CO_2-C m^{-2} yr^{-1}) fall in the low end of the range of values summarized by Raich and Nadelhoffer (1989) from the literature (0.7 to 5.2 kg CO_2 -C m^{-2} yr^{-1}). This may be in part due to the lack of a well-established litter layer in these open-top chambers. Previous studies at this site suggested that root respiration accounted for more than 90% of total soil CO_2 efflux (Johnson et al., 1994); thus, soil respiration is not necessarily related to any change in soil C pools. Given that root respiration is the dominant source of soil CO_2 efflux, one would expect a trend of increased soil pCO_2 and soil CO_2 efflux over time as root biomass increased (Johnson et al., 1997).There were weak ($r^2 < 0.30$) upward trends in pCO_2 (Figures 1 and 2) and calculated soil CO_2 efflux (not shown), except in the low N, 525 $\mu l\ l^{-1}$ CO_2 treatment.

The temporary increases in soil pCO_2 in the 525 $\mu l\ l^{-1}$ CO_2 treatments caused increases in soil solution bicarbonate concentration, as expected, but these were very temporary and overshadowed by the effects of other anions on total cation leaching. Whatever effect elevated CO_2 might have had on cation leaching was small and temporary, however. In contrast to previous greenhouse studies (including one study on the same soil; Johnson et al., 1996), there were no consistent CO_2 treatment effects on soil exchangeable base cation concentrations over the six-year study period. The only significant CO_2 treatment effect on exchangeable base cations was in the case of Mg^{2+} in year 3, and this was clearly an artifact of pre-treatment bias which in fact disappeared in year 6. There was a decided increase in base cation uptake associated with increased biomass with elevated CO_2 (Johnson et al., 1997), but this apparently was insufficient to cause any detectable depletion of soil exchangeable base cation pools. The significant reductions in exchangeable Ca^{2+}, K^+, and Mg^{2+} with N fertilization were undoubtedly due to increased nitrate leaching in the fertilized treatments.

The effects of CO_2 treatment on extractable P, while stastistically significant, were rather inconsistent and reflective of pre-treatment patterns. There was certainly no pattern of signigicant soil P depletion or immobilzation with elevated CO_2. Extractable P, like exchangeable NH_4^+ and NO_3^-, is an ephemrral quantity which is known to vary on a seasonal basis (e.g., Johnson et al., 1988).

The strong CO_2 treatment effects on soil C/N ratio in year 6 were due largely to the significant negative effect of CO_2 treatment on soil N rather than to increases in C in the unfertilized treatment (Figures 6 though 8; Table 2). This pattern raises interesting questions regarding the source of N for tree uptake under elevated CO_2. As noted in a previous paper, N uptake rates were significantly greater with elevated CO_2, including in the unfertilized treatments (Johnson et al., 1997). This leads to the question of whether the additional N for uptake with elevated CO_2 came from 1) increased mineralilzation, 2) increased soil exploration, or 3) non-symbiotic N fixation (c.f., Bormann et al., 1992). Nitrogen mineralization rates during the course of this study were initially reduced (during year 1) and later unaffected (during year 4) by elevated CO_2 (Johnson et al., 1996 and uppublished). Thus, our conclusion at the end of year 3 was that the source of additional N uptake was either increases soil exploration or non-sybiotic N fixation. These results suggest that trees subjected to elevated CO_2 were able to "mine" soil N in the unfertilized N treatments, even though this was not detected by laboratory N mineralization tests or in the buried bag studies. This possibility will be explored in a future paper using ^{15}N analyses of plant tissues and soils.

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Table 1. Estimated cumulative CO_2-C flux from soils at the Placerville field site between March, 1992 and August, 1996.

N Treat.	CO_2 Treat.	Cumulative Flux	Soil C Pools	
			1991	1996
(g N m^{-2} yr^{-1})	(µl l^{-1})	kg C m^{-2}		
0	350	3.0±0.5	7.4±0.7	7.4±0.7
0	525	3.9±1.1	7.5±0.6	8.1±1.7
0	700	3.6±1.5	7.0±0.9	7.6±0.9
10	350	3.0±1.0	6.8±0.5	7.4±0.8
10	700	3.9±0.4	6.9±0.6	8.3±0.7
20	350	4.6±0.5	7.1±0.7	7.4±0.9
20	525	4.5±1.4	8.1±1.0	8.7±0.8
20	700	7.1±1.4	6.2±0.7	8.1±0.8

Table 2. Results of unbalanced ANOVA tests for effects of CO_2 and N treatments on soil chemical parameters between 1991 and 1996[†] .

Parameter	Before Treatment		Three Years		Six Years	
	N	CO_2	N	CO_2	N	CO_2
Ap Horizons						
C	NS	NS	NS	**	NS	NS
N	NS	NS	NS	*	NS	***
C/N	NS	NS	NS	NS	NS	***
P	NS	NS	NS	***	NS	*
Ca^{2+}	NS	*	NS	NS	***	NS
Mg^{2+}	NS	**	**	**	***	NS
K^+	NS	NS	NS	NS	***	NS
Bw Horizons						
C	NS	NS	NS	NS	NS	**
N	NS	NS	NS	NS	NS	***
C/N	NS	NS	NS	NS	NS	***
P	NS	NS	NS	**	NS	**
Ca^{2+}	NS	NS	NS	NS	NS	NS
Mg^{2+}	NS	**	NS	***	***	NS
K^+	NS	NS	NS	NS	***	NS

[†] *, **, and *** refer to 0.1, 0.05, and 0.01 levels of significance, respectively; NS = not significant.

Fig. 1. Soil pCO_2 at 15 cm depth in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (Low, Medium, and High N, corresponding to 0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 2. Soil pCO_2 at 30 cm depth in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (Low, Medium, and High N, corresponding to 0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 3. Soil solution anion concentrations in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (Low, Medium, and High N, corresponding to 0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 4. Soil solution cationconcentrations in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (Low, Medium, and High N, corresponding to 0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 5. Soil solution NO_3^- and NH_4^+ concentrations in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (Low, Medium, and High N, corresponding to 0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 6. Soil total carbon in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 7. Soil total nitrogen in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 8. Soil C/N ratio in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N $m^{-2}\ yr^{-1}$ as ammonium sulfate).

Fig. 9. Soil extractable P in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N m^{-2} yr^{-1} as ammonium sulfate).

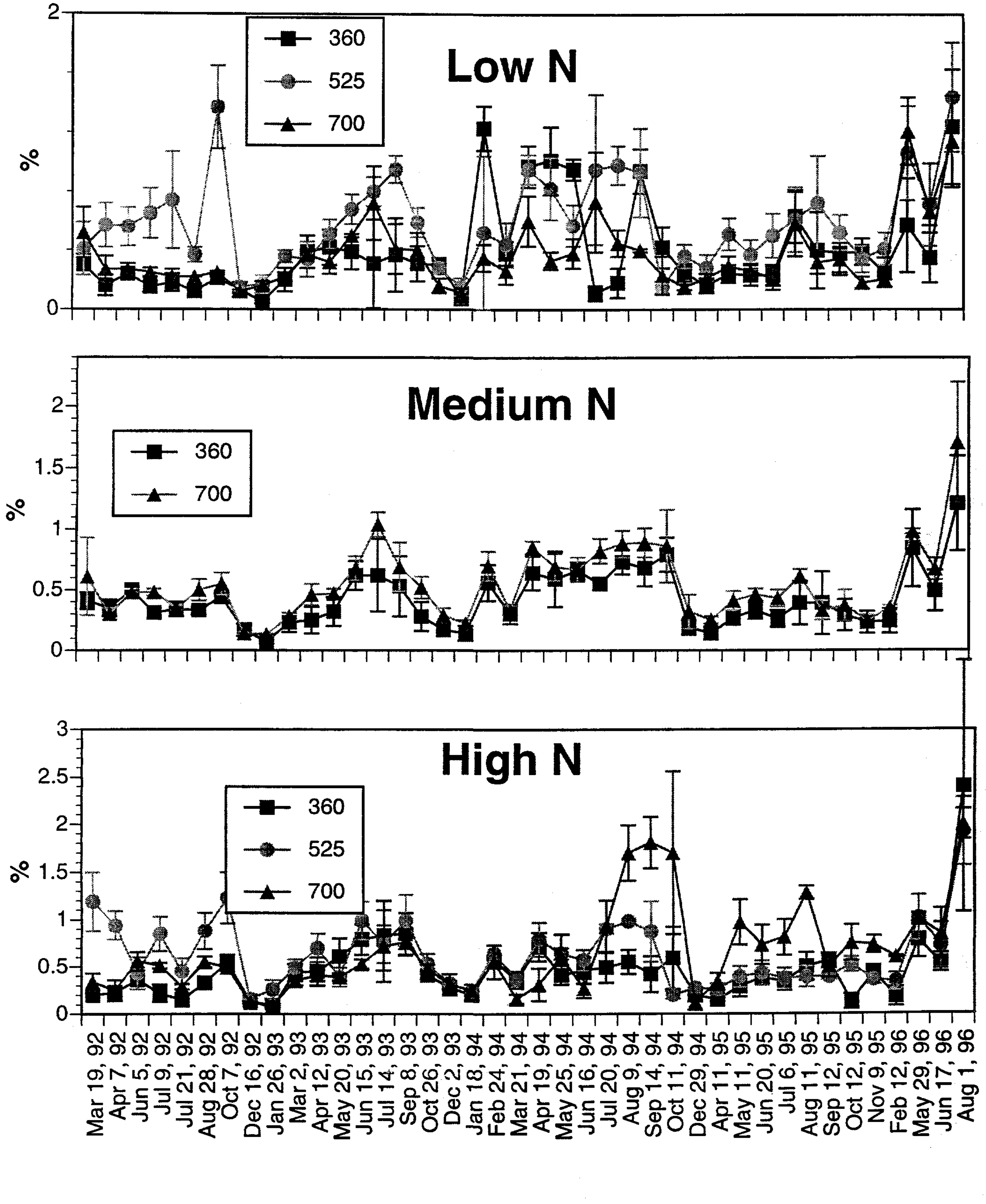
Fig. 10. Soil exchangeable Ca^{2+} in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N m^{-2} yr^{-1} as ammonium sulfate).

Fig. 11. Soil exchangeable K^+ in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N m^{-2} yr^{-1} as ammonium sulfate).

Fig.12. Soil exchangeable Mg^{2+} in 1991 (year 1), 1993 (year 3), and 1996 (year 6) of the study in chambers treated with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N m^{-2} yr^{-1} as ammonium sulfate).

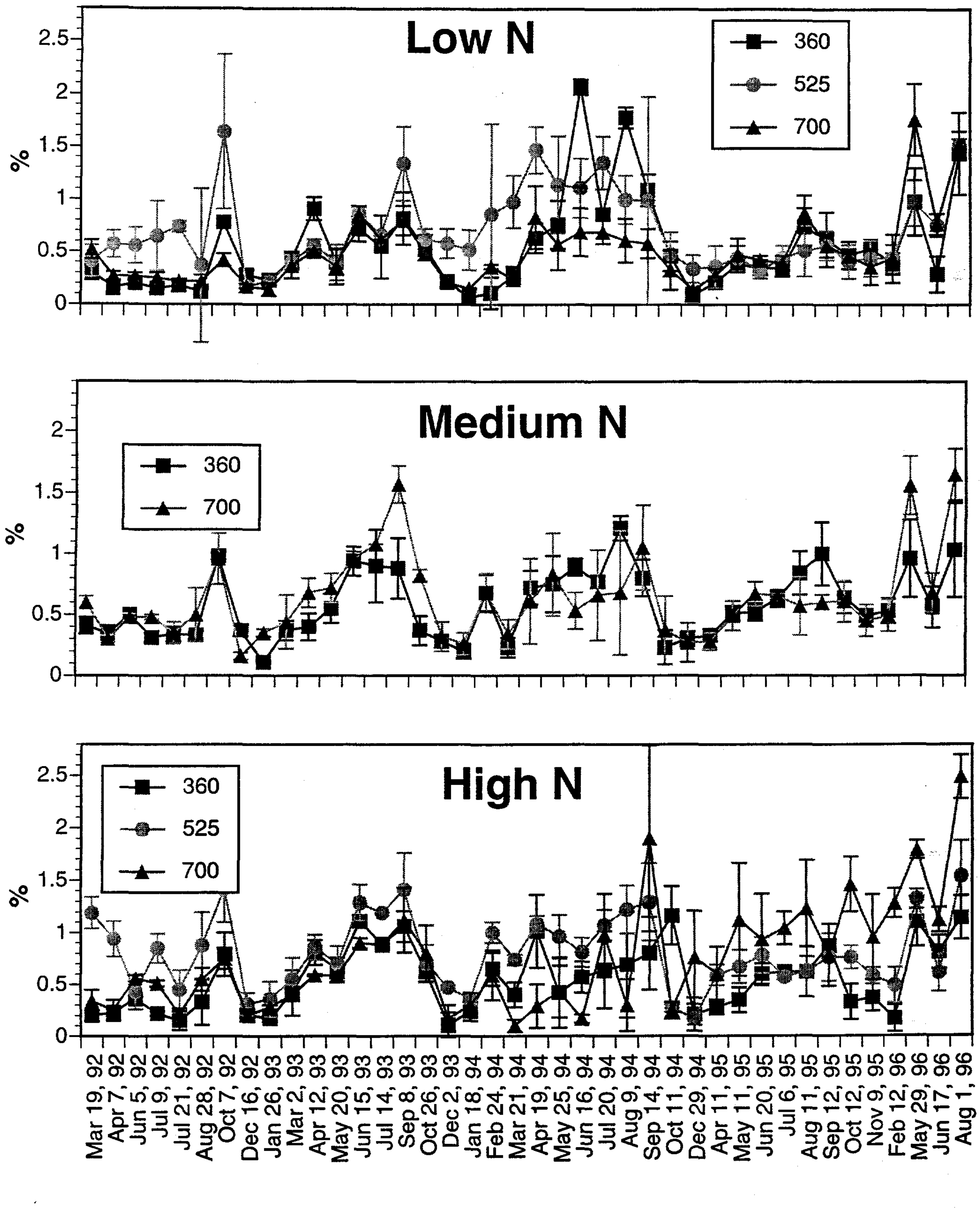
Fig. 13. Soil C and N in homogenized, buried bags prior to and 1.5 years after treatment with elevated CO_2 (ambient, or 350, 525, and 700 $\mu l\ l^{-1}$) and N (0, 10, and 20 g N m^{-2} yr^{-1} as ammonium sulfate).

pCO$_2$ at 15 cm

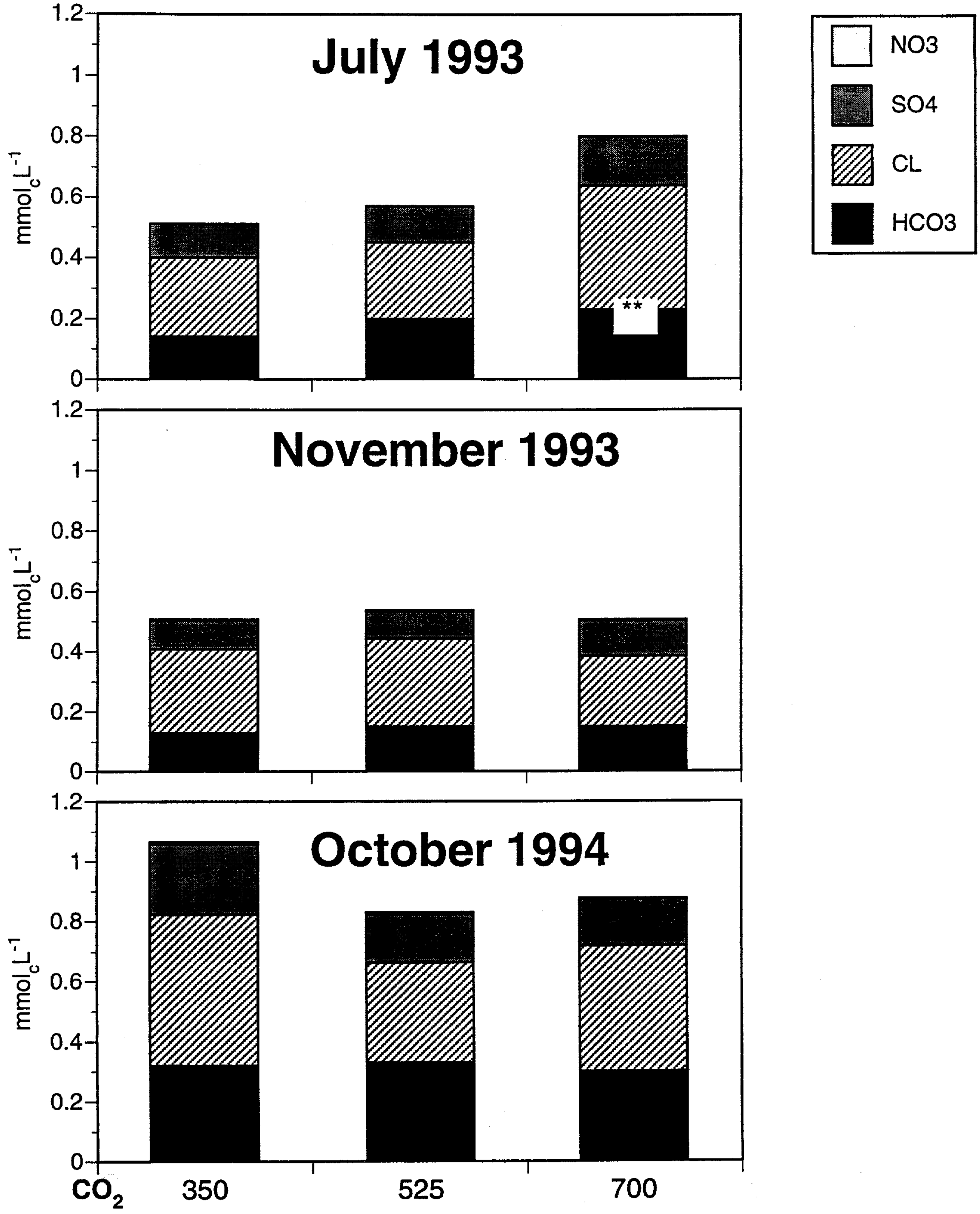


Low N
360
525
700
%
0
2
Medium N
360
700
%
0
0.5
1
1.5
2
High N
360
525
700
%
0
0.5
1
1.5
2
2.5
3
Mar 19, 92
Apr 7, 92
Jun 5, 92
Jul 9, 92
Jul 21, 92
Aug 28, 92
Oct 7, 92
Dec 16, 92
Jan 26, 93
Mar 2, 93
Apr 12, 93
May 20, 93
Jun 15, 93
Jul 14, 93
Sep 8, 93
Oct 26, 93
Dec 2, 93
Jan 18, 94
Feb 24, 94
Mar 21, 94
Apr 19, 94
May 25, 94
Jun 16, 94
Jul 20, 94
Aug 9, 94
Sep 14, 94
Oct 11, 94
Dec 29, 94
Apr 11, 95
May 11, 95
Jun 20, 95
Jul 6, 95
Aug 11, 95
Sep 12, 95
Oct 12, 95
Nov 9, 95
Feb 12, 96
May 29, 96
Jun 17, 96
Aug 1, 96

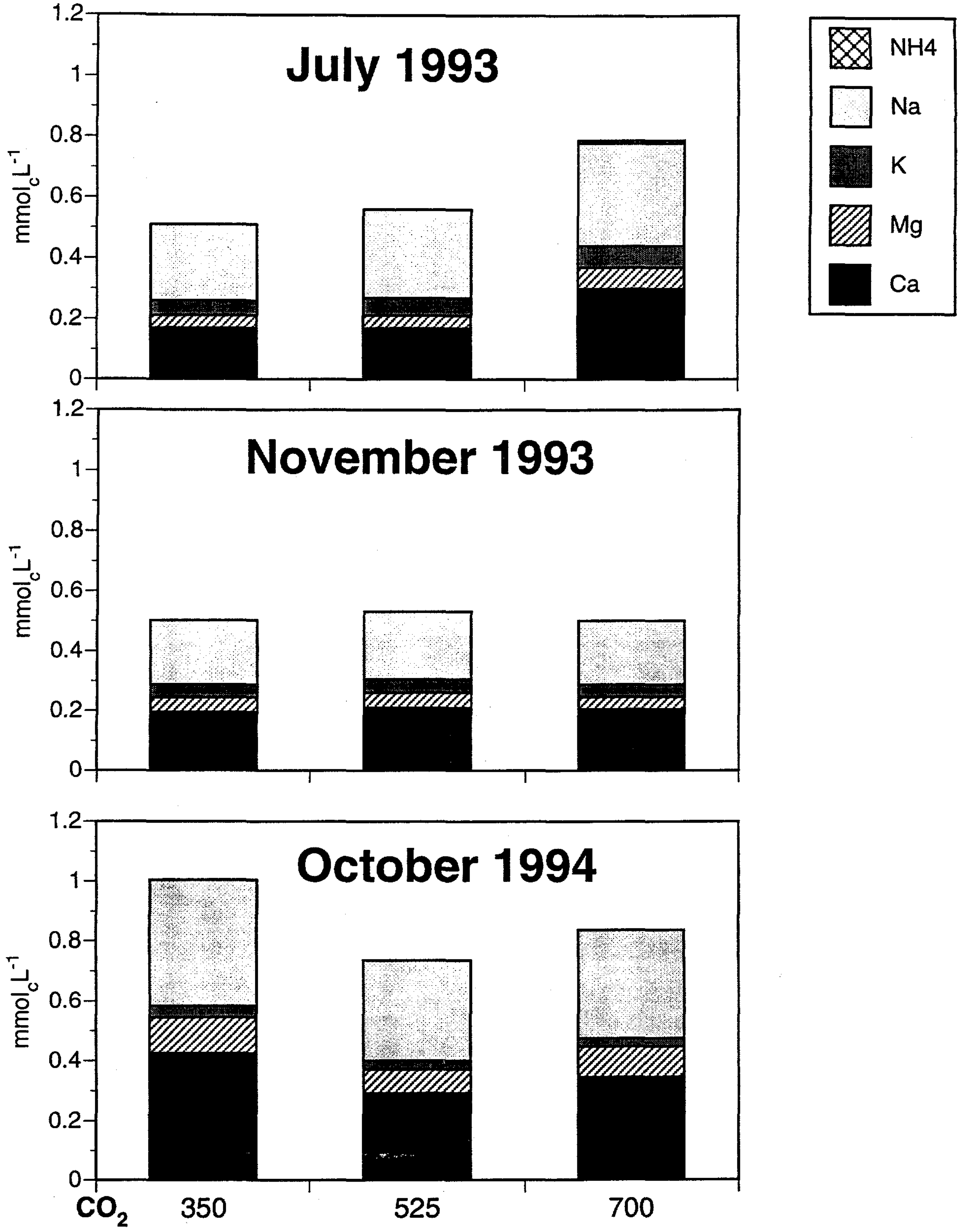
pCO$_2$ at 30 cm

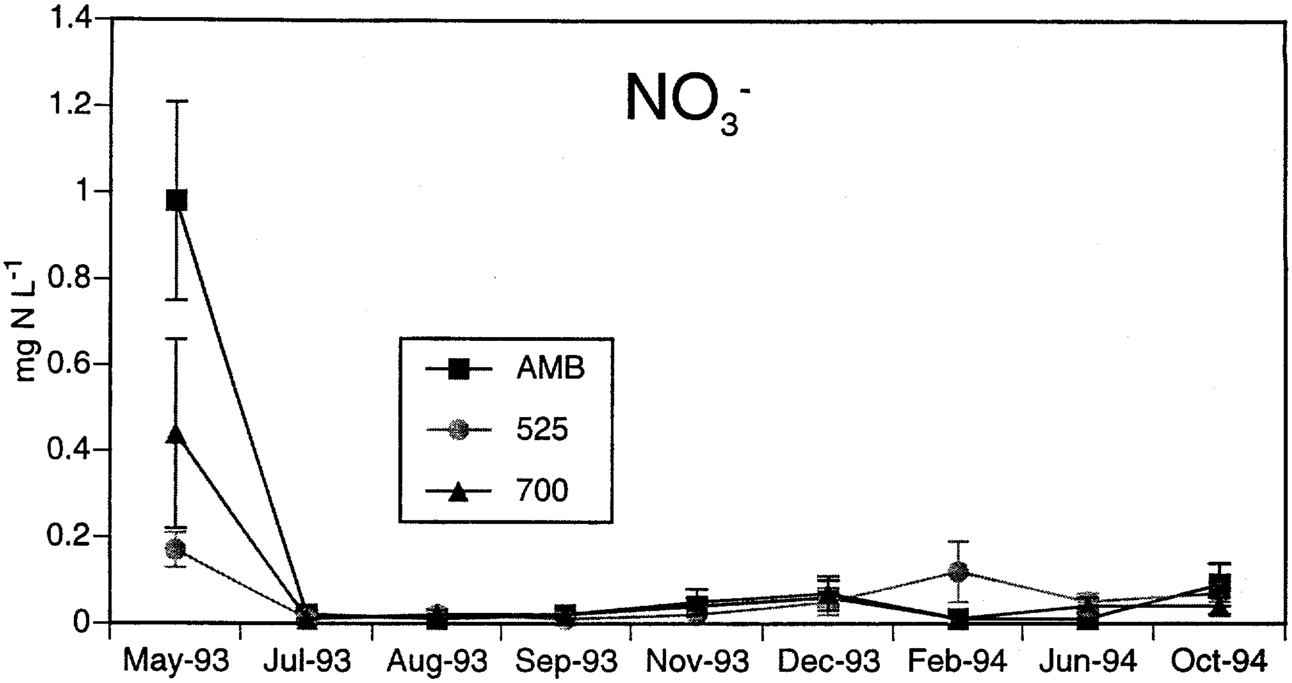

Low N
Medium N
High N
360
525
700
%
0
0.5
1
1.5
2
2.5
Mar 19, 92
Apr 7, 92
Jun 5, 92
Jul 9, 92
Jul 21, 92
Aug 28, 92
Oct 7, 92
Dec 16, 92
Jan 26, 93
Mar 2, 93
Apr 12, 93
May 20, 93
Jun 15, 93
Jul 14, 93
Sep 8, 93
Oct 26, 93
Dec 2, 93
Jan 18, 94
Feb 24, 94
Mar 21, 94
Apr 19, 94
May 25, 94
Jun 16, 94
Jul 20, 94
Aug 9, 94
Sep 14, 94
Oct 11, 94
Dec 29, 94
Apr 11, 95
May 11, 95
Jun 20, 95
Jul 6, 95
Aug 11, 95
Sep 12, 95
Oct 12, 95
Nov 9, 95
Feb 12, 96
May 29, 96
Jun 17, 96
Aug 1, 96

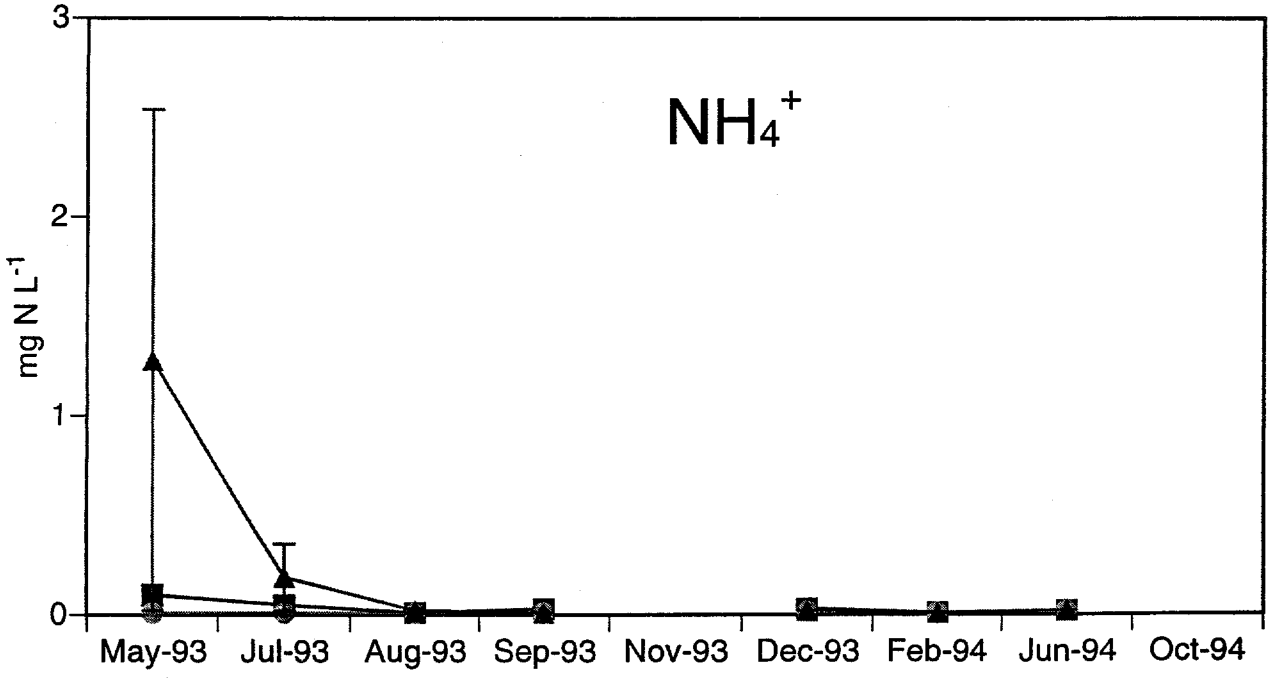
Soil Solution Anions
Low N Treatments



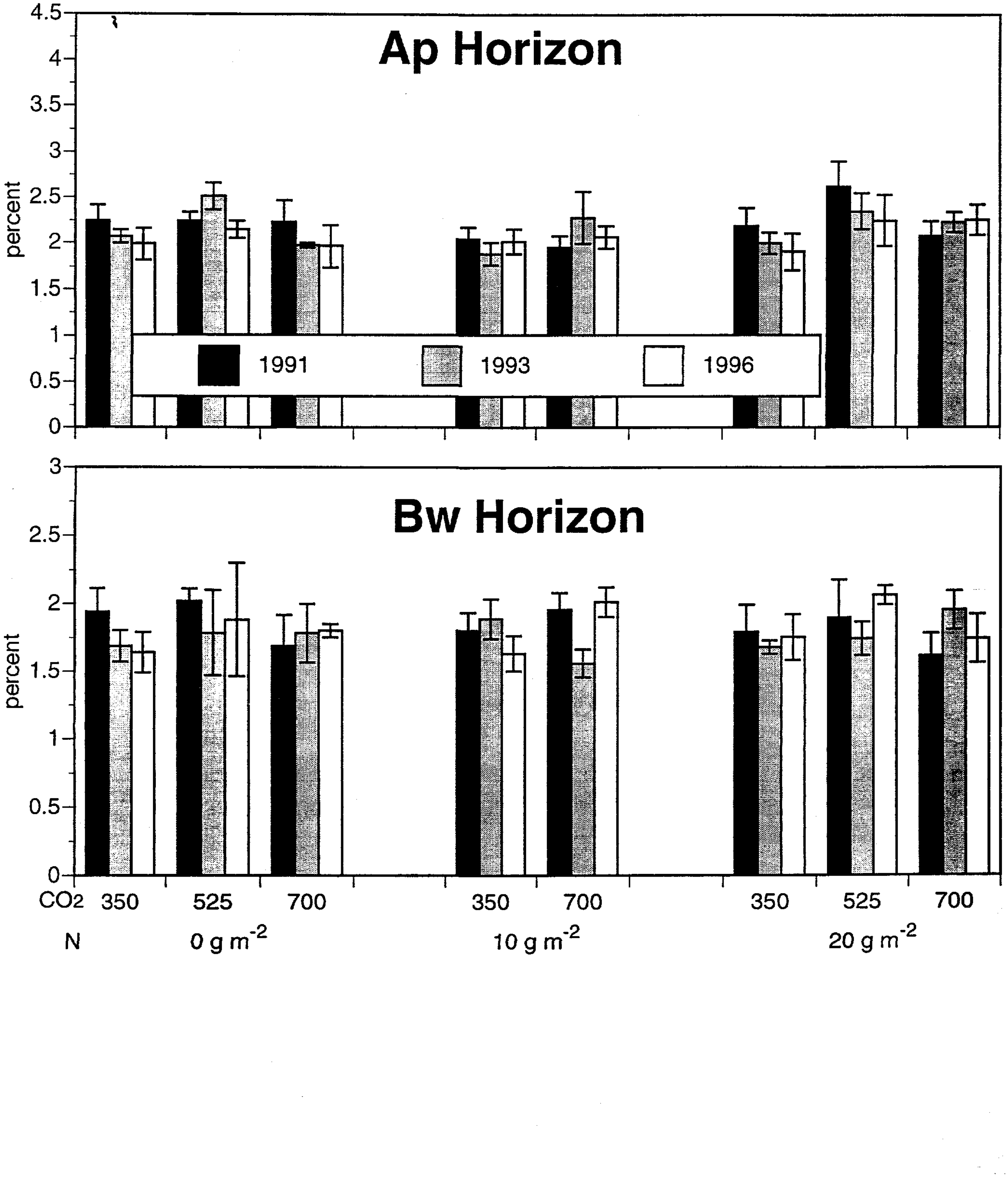
Soil Solution Cations
Low N Treatments



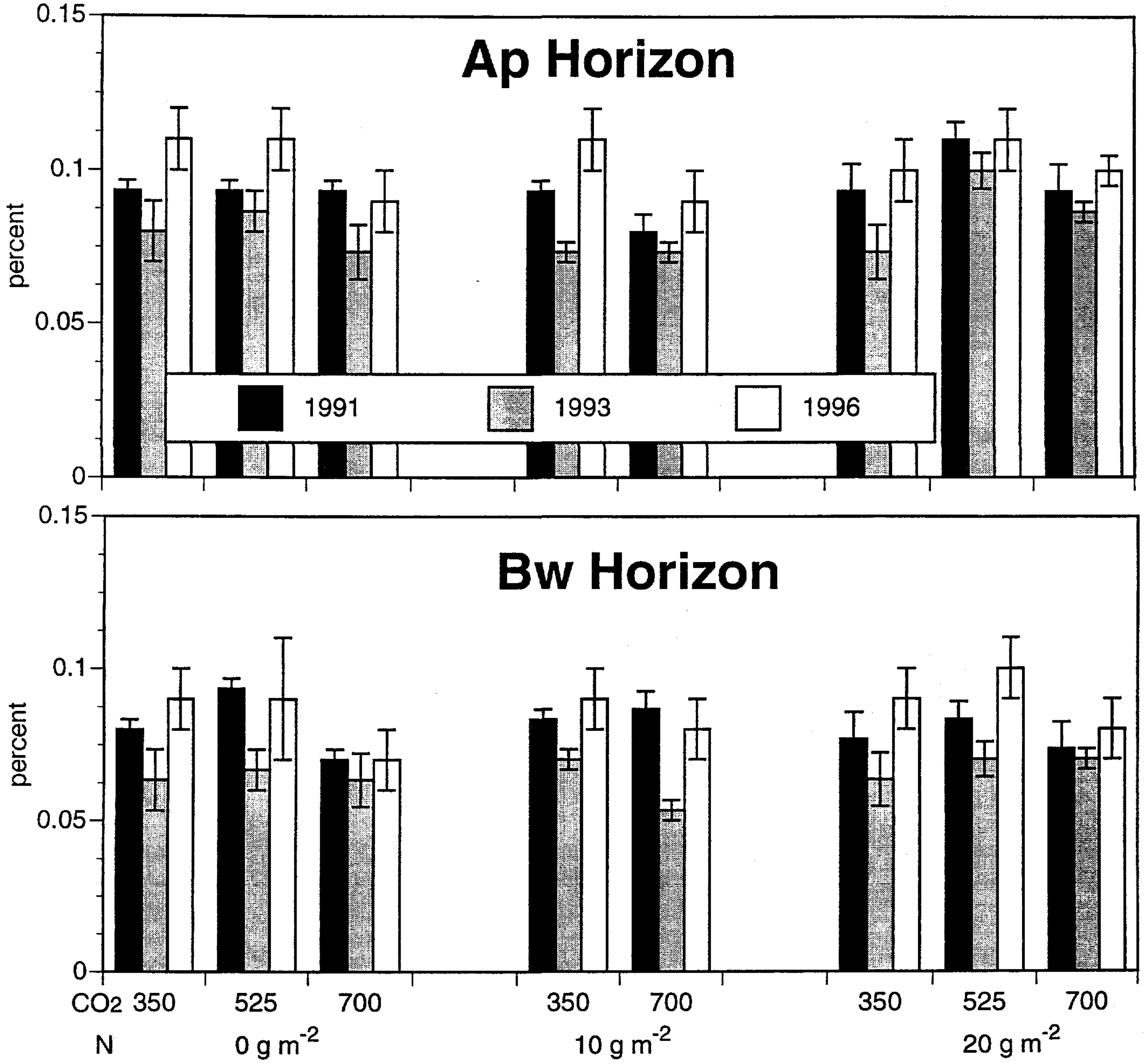

NO_3^-
mg N L^{-1}
1.4
1.2
1
0.8
0.6
0.4
0.2
0
AMB
525
700
May-93
Jul-93
Aug-93
Sep-93
Nov-93
Dec-93
Feb-94
Jun-94
Oct-94


NH_4^+
mg N L^{-1}
3
2
1
0
May-93
Jul-93
Aug-93
Sep-93
Nov-93
Dec-93
Feb-94
Jun-94
Oct-94

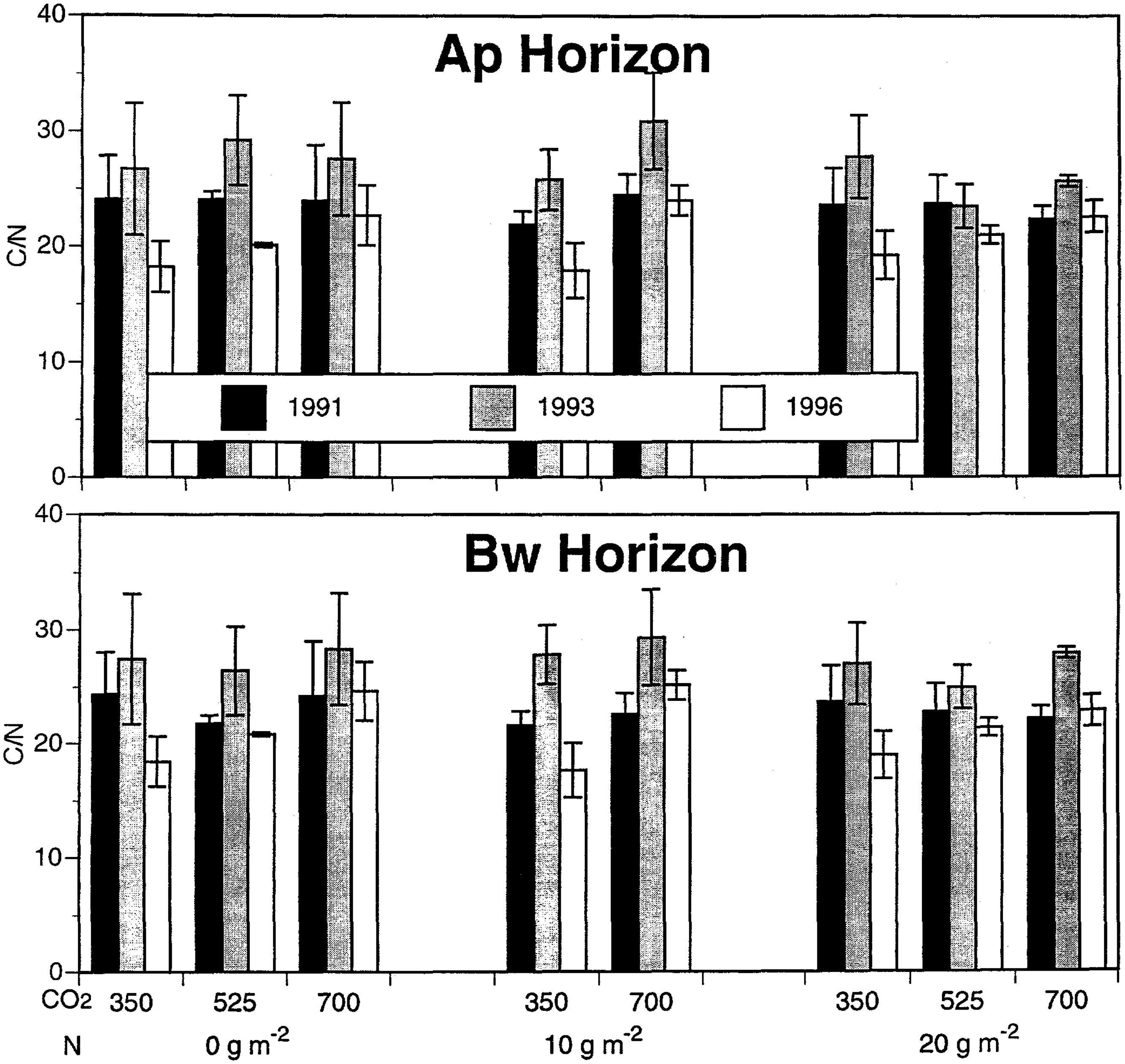
Total C


Ap Horizon
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
percent
1991
1993
1996
Bw Horizon
3
2.5
2
1.5
1
0.5
0
percent
CO2 350 525 700 350 700 350 525 700
N 0 g m-2 10 g m-2 20 g m-2

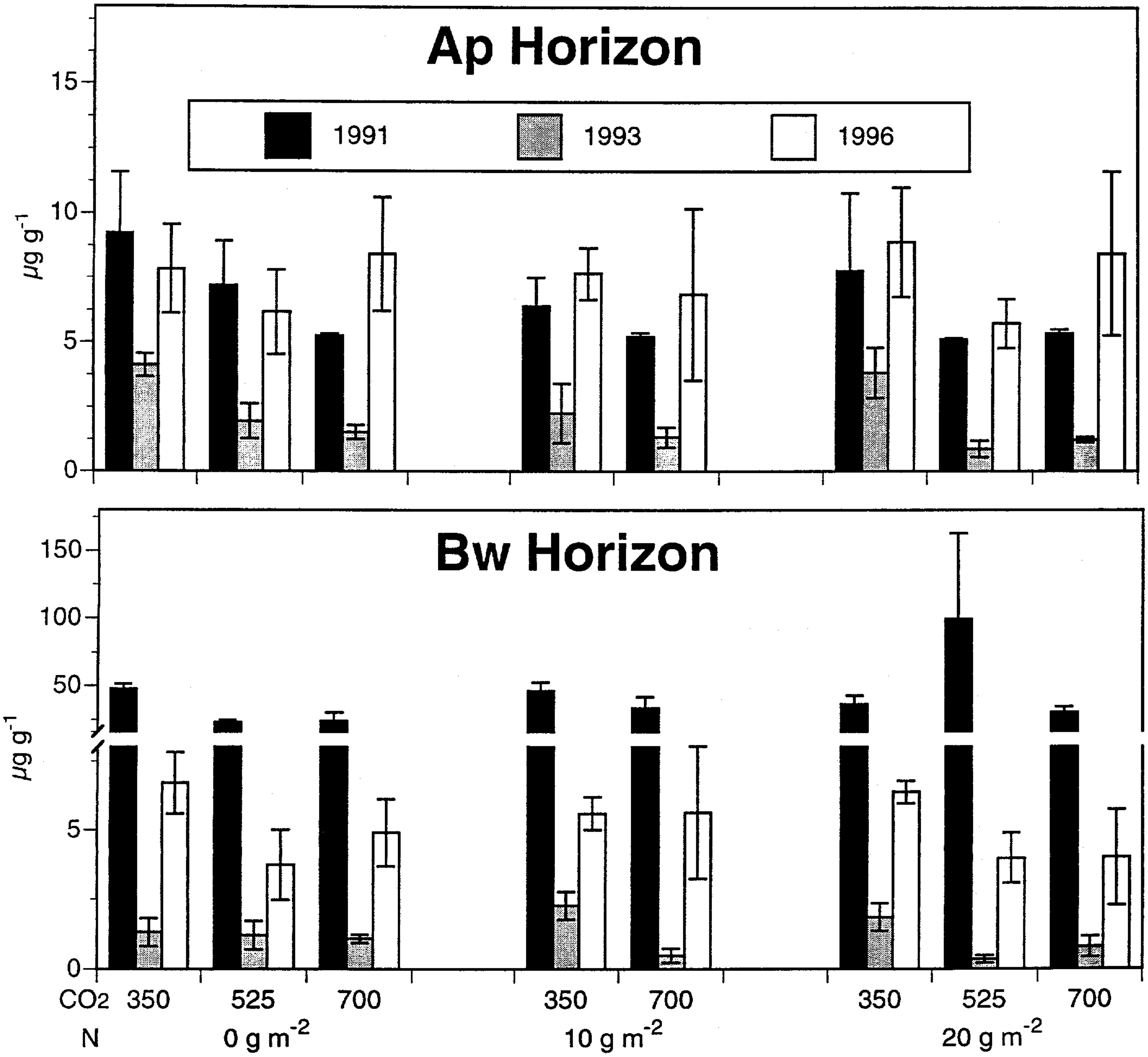
Total N

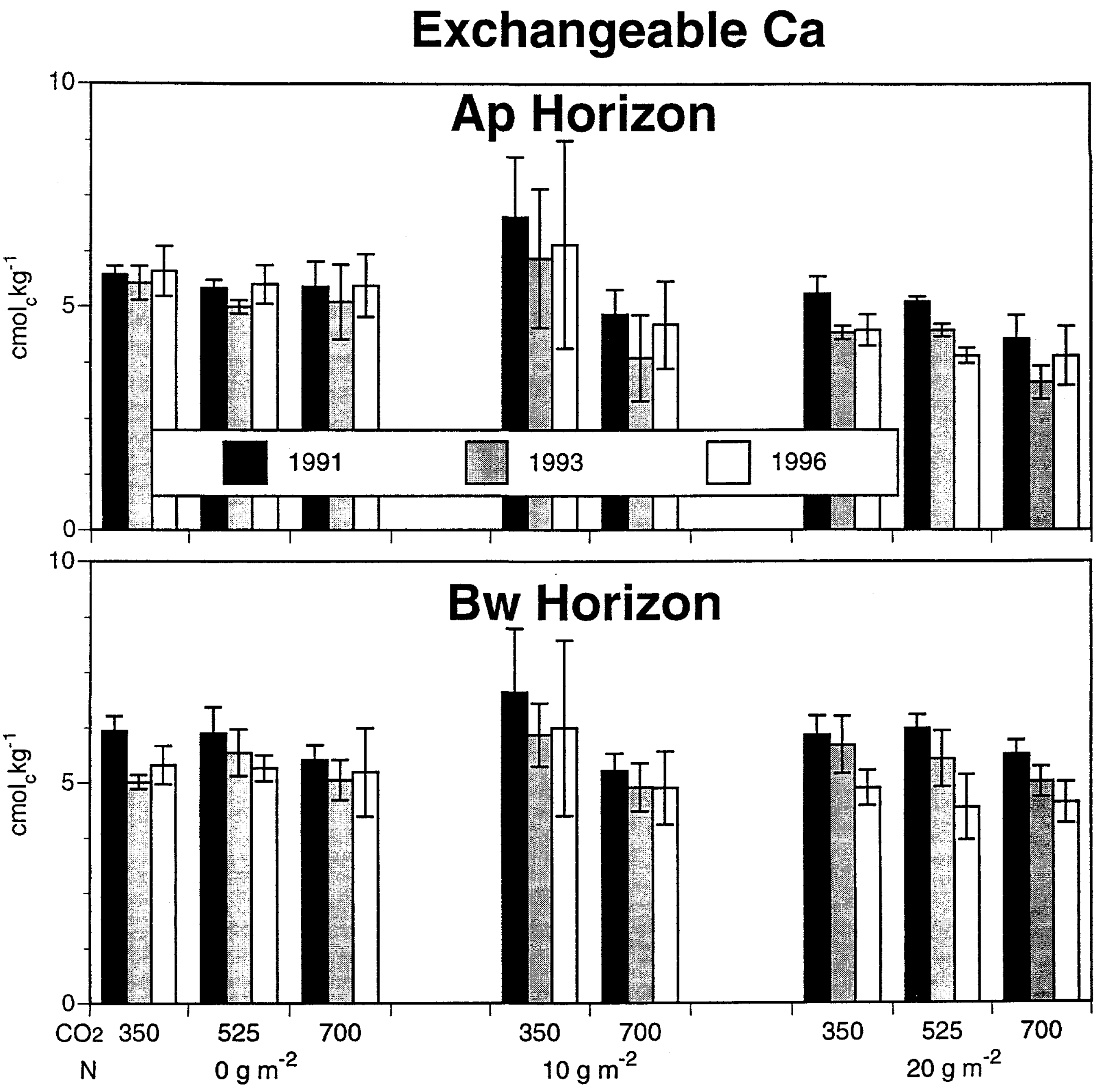

Ap Horizon
Bw Horizon
0.15
0.1
0.05
0
percent
1991
1993
1996
CO2 350
525
700
350
700
350
525
700
N
0 g m-2
10 g m-2
20 g m-2

C/N Ratio

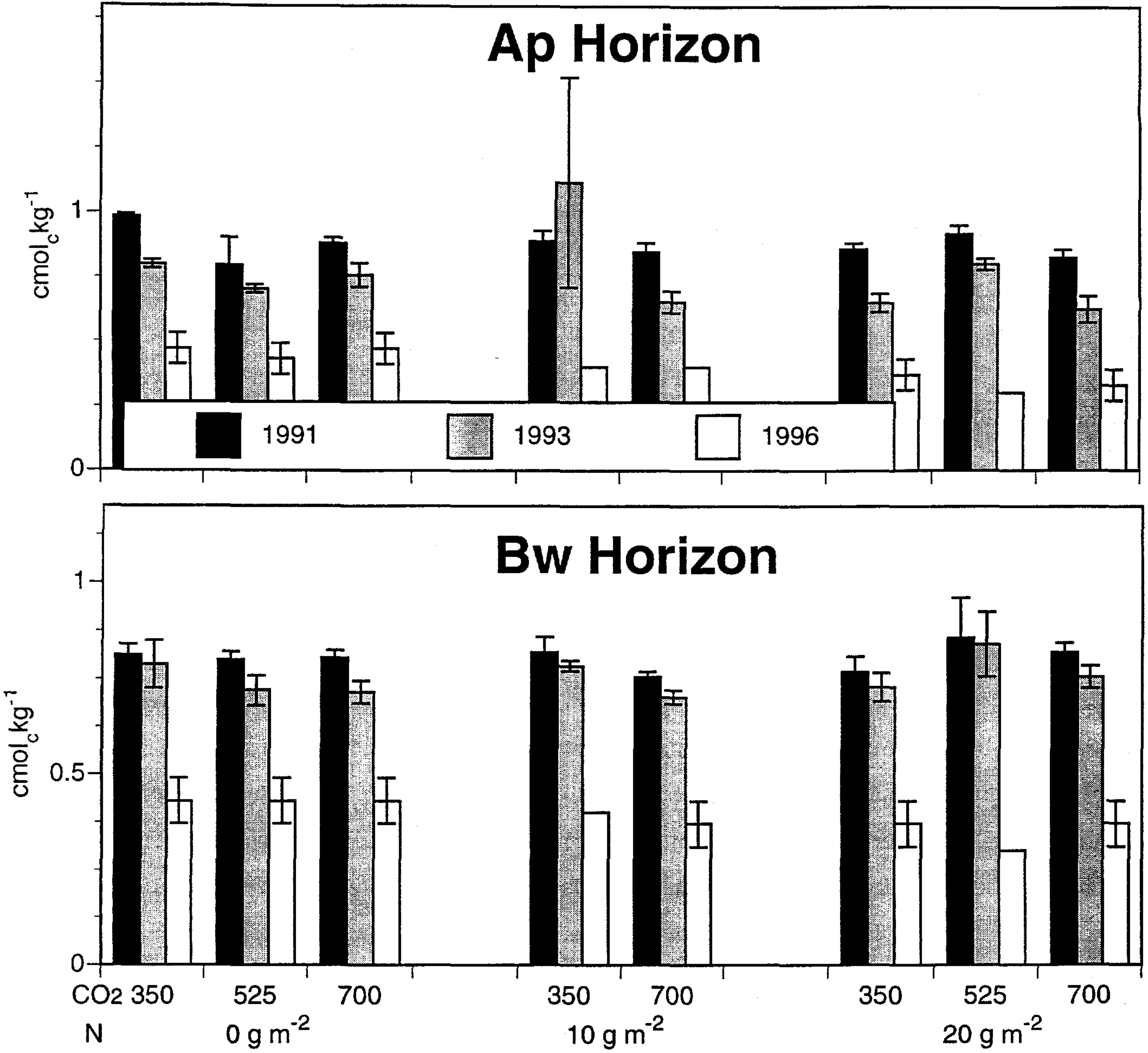

Ap Horizon
Bw Horizon
C/N
0
10
20
30
40
1991
1993
1996
CO2
350
525
700
350
700
350
525
700
N
0 g m^{-2}
10 g m^{-2}
20 g m^{-2}

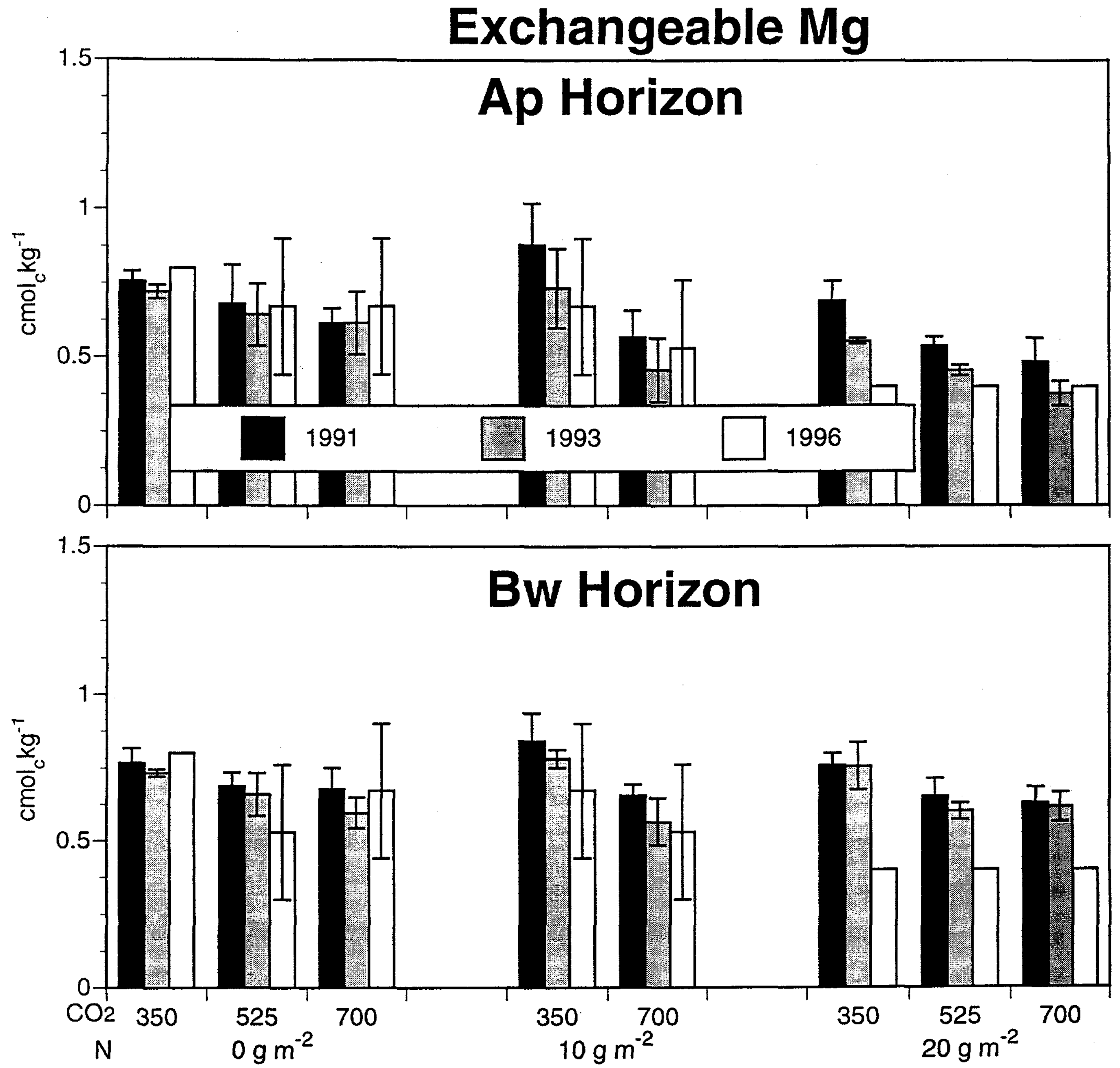
Extractable P




Exchangeable Ca
Ap Horizon
Bw Horizon
cmol$_c$kg^{-1}
10
5
0
1991
1993
1996
CO2
350
525
700
350
700
350
525
700
N
0 g m^{-2}
10 g m^{-2}
20 g m^{-2}

Exchangeable K




Exchangeable Mg
Ap Horizon
Bw Horizon
$cmol_c kg^{-1}$
0
0.5
1
1.5
1991
1993
1996
CO2
350
525
700
350
700
350
525
700
N
0 g m^{-2}
10 g m^{-2}
20 g m^{-2}

Buried Soil Bags