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Elevated Atmospheric Carbon Dioxide in Agroecosystems Affects Groundwater Quality

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ABSTRACT

Increasing atmospheric carbon dioxide (CO_2) concentration has led to concerns about global changes to the environment. One area of global change that has not been addressed is the effect of elevated atmospheric CO_2 on groundwater quality below agroecosystems. Elevated CO_2 concentration alterations of plant growth and C/N ratios may modify C and N cycling in soil and affect nitrate (NO_3^-) leaching to groundwater. This study was conducted to examine the effects of a legume {soybean [*Glycine max* (L.) Merr.]} and a nonlegume {grain sorghum [*Sorghum bicolor* (L.) Moench]} CO_2-enriched agroecosystems on NO_3^- movement below the root zone in a Blanton loamy sand (loamy siliceous, thermic, Grossarenic Paleudults). The study was a split-plot design replicated three times with plant species (soybean and grain sorghum) as the main plots and CO_2 concentration (~ 360 and ~ 720 $\mu L\ L^{-1}$ CO_2) as subplots using open-top field chambers. Fertilizer application was made with ^{15}N-depleted NH_4NO_3 to act as a fertilizer tracer. Soil solution samples were collected weekly at 90-cm depth for a 2-yr period and monitored for NO_3^--N concentrations. Isotope analysis of soil solution indicated that the decomposition of organic matter was the primary source of NO_3^--N in soil solution below the root zone through most of the monitoring period. Significant differences were observed for NO_3^--N concentrations between soybean and grain sorghum, with soybean having the higher NO_3^--N concentrations. Elevated CO_2 increased total dry weight, total N content, and C/N ratio of residue returned to soil in both years. Elevated CO_2 significantly decreased NO_3^--N concentrations below the root zone in both soybean and grain sorghum. The results of this study indicate that retention of N in organic pools because of elevated atmospheric CO_2 could reduce the nitrate concentration in groundwater beneath agroecosystems as indicated by NO_3^- movement.

SCIENTISTS have realized that the combined impact of population increases, industrial expansion, and deforestation has resulted in changes to the global environment, including an increased atmospheric CO_2 concentration (Holland, 1978; Smil, 1985; Warneck, 1988), which is projected to double in the next century (Bolin, 1986). The implication of these changes to global warming and local climate shifts have been highly debated, but regardless of the eventual outcome of the climate issue, vegetation will be directly impacted by enrichment in atmospheric CO_2. Carbon dioxide is a prime chemical input to the metabolism of higher plants and has a major role in governing plant-water relations and water-use efficiency. These direct effects on vegetation could have important ramifications for agricultural production systems as crop plants respond to changes in global environment. This critical change within agroecosystems may affect groundwater quality.

In recent years, the amount of N fixed on a global basis has been greatly increased through cultivation of N-fixing plants and the use of fertilizers (Schlesinger, 1991). The fate of fertilizer N applied to agricultural soils is of growing concern because of the potential for groundwater contamination and health risks associated with high NO_3^- levels in groundwater (Spalding and Exner, 1993; Korom, 1992; Fedkiw, 1991). Changes in soil N dynamics can have a direct impact on the amount of NO_3^- that is susceptible to leaching. Most N transformations in soil are regulated by microbial activity and organic matter levels (Hart et al., 1993). For example, inorganic N levels are regulated by the balance between mineralization and immobilization of N in organic matter (Jansson and Persson, 1982; Van Miegroet et al., 1992). A potential effect of plant growth at elevated CO_2 may be an increased level of organic C in soil impacting N dynamics, including regulation of biological activity.

Changes in soil N dynamics also may be affected by CO_2-induced alterations of soil and plant residue C/N ratios. For example, changes in the composition of litter in a CO_2-rich environment may reduce decomposition rate and limit nutrient cycling in soil (Cotrufo et al., 1994; Couteaux et al., 1991). Goss et al. (1993) indicated that the most important factor (along with fertilizer N application) regulating N leaching was the mineralization of N from residues. The mineralization of organic matter over winter months is the dominant source of N even when fertilizer N is applied (Macdonald et al., 1989; Torbert and Reeves, 1995). Thus, the retention of N in these organic pools could reduce human impact on groundwater quality beneath agroecosystems. Recent work on plant decomposition indicated that even if decomposition rates of plant residue produced under CO_2 enrichment are not changed, the decomposition products of this residue may induce a considerable impact on soil N dynamics (Torbert et al., 1995).

Elevated atmospheric CO_2 concentrations will not only alter C and N cycling in soil but may affect plant nutrition. With increased growth, plants presumably have larger demand for plant macronutrients and micronutrients (Kimball, 1985). On the other hand, increased root growth may result in increased plant efficiency for retrieval of nutrients from soil (Trabalka, 1985). Timlin et al. (1992) indicated that a major factor in solute transport mechanisms in soil is differential lateral root distribution. Changes in both root length density and root lateral distribution have been observed with plant growth under elevated CO_2 conditions (Rogers et al., 1992; Prior et al., 1994a, 1994b), which could affect plant N-use efficiency and uptake. Changes in levels of NO_3^- leaching during winter months were found to depend on residual NO_3^- levels in soil left by different maize (*Zea mays* L.)cultivars during the growing season, and the difference in cultivars was closely correlated to root length density (Wiesler and Horst, 1993). Campbell

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and Zentner (1993) observed a reduction in NO_3^- leaching with crop rotations that increased N-use efficiency.

To date, no research has measured the impact of elevated atmospheric CO_2 in agroecosystems on the potential for N movement to groundwater. The objective of this study was to measure agroecosystems exposed to ambient and elevated CO_2 levels for NO_3^- leaching below the rooting zone on two agronomically important crops.

MATERIALS AND METHODS

This study was conducted in an outdoor soil bin at the USDA-ARS National Soil Dynamics Laboratory in Auburn, AL. The bin was 2-m deep, 7-m wide, and 76-m long and was uniformly filled with surface soil of a Blanton loamy sand (loamy, siliceous, thermic Grossarenic Paleudult) that had been continuously fallow for over 25 yr (Batchelor, J.A., 1984. Properties of bin soils at the national tillage machinery laboratory. Natl. Soil Dynamics Lab.). The bottom of the bin (2-m depth) was covered with sand and gravel and was tile drained. Initial levels of P (8 kg ha^{-1}) and K (14 kg ha^{-1}) were in the 'very low' range. Cation-exchange capacity averaged 2.45 cmol$_c$ kg^{-1}, and soil pH averaged 4.7. The initial level of organic matter averaged 5.0 g kg^{-1} and total N was 0.06 g kg^{-1}. A more detailed description of the soil status prior to initiation of the study, fertilizer and lime amendments during the study, and subsequent soil analysis results have been reported previously (Reeves et al., 1994).

The study was a split-plot design replicated three times with main plots of two plant species, and three CO_2-exposure regimes as subplots. Soybean and grain sorghum were chosen as test crops to provide legume and nonlegume crop species, respectively, that are widely produced in agroecosystems. The CO_2 exposure regimes were two open top field chambers at ambient and twice ambient atmospheric CO_2 concentrations and an open plot (no chamber) under ambient atmospheric conditions.

The open top field chambers, 3-m in diameter and 2.4-m high, are described in detail by Rogers et al. (1983). Carbon dioxide concentrations were continuously monitored using a time-share manifold with samples drawn through solenoids to an infrared CO_2 analyzer (LI-COR 6252, LI-COR, Inc., Lincoln, NE). The atmospheric CO_2 concentration in the twice ambient chamber was continuously adjusted by injection of CO_2 into plenum boxes and air dispensed into each chamber through the bottom half of each chamber cover. The bottom half of the chamber cover was double-walled with the inside wall perforated with 2.5-cm diam. holes to serve as ducts to distribute air uniformly into the chamber. The average CO_2 concentrations were 357.5 ± 0.1 (SE) and 364.0 ± 0.2 µL L^{-1} for ambient chambers and 705.0 ± 0.3 and 731.7 ± 0.4 µL L^{-1} for twice ambient in 1992 and 1993, respectively.

An open plot (aluminum frame only with no chamber) provided a control to test the effect of the open-top PVC chambers per se vs. the effects of CO_2 on plant response. The average CO_2 concentrations in the open plots were 357.4 ± 0.1 (SE) and 364.0 ± 0.1 µL L^{-1} during the study in 1992 and 1993, respectively.

Soybean 'Stonewall' and grain sorghum 'Savannah 5' were planted in 76-cm rows oriented across the width of the soil bin on 2 June 1992 and 5 May 1993. Plants were thinned to a uniform density of 30 plants m^{-1} for soybean and 26 plants m^{-1} for grain sorghum.

To ensure adequate plant establishment, fertilizer N was broadcast applied at a rate of 34 kg N ha^{-1} to both the grain sorghum and the soybean shortly after planting (4 June 1992 and 6 May 1993). In the grain sorghum, an additional 67 kg N ha^{-1} was applied 30 d after planting (3 July 1992 and 7 June 1993). Fertilizer application was made as NH_4NO_3, with one-half of the chamber plot area receiving an application of ^{15}N-depleted NH_4NO_3 containing 0.01 atom % ^{15}N and the other half receiving nonlabeled NH_4NO_3 (0.3663 atom % ^{15}N). Application of the ^{15}N-depleted fertilizer was alternated to the other half of the chamber plot area in the second year of the study.

At physiological maturity, plants within the whole plot were harvested for determination of aboveground total dry weight production. Final harvest was made on 27 October for both crops in 1992, and on 1 October for grain sorghum and 5 October for soybean in 1993. Grain sorghum heads and soybean pods were removed from the plants and processed through a plot combine. Plant stalks were cut into approximately 15-cm lengths using hedge clippers and uniformly spread over the plots. Soybean pod hulls and grain sorghum chaff were added back to the plots. To simulate seed loss during combining, 10% (by weight) of the seed yield was returned to the plots. Bird netting (1.6 by 1.9 cm opening; Dalen Products Inc., Knoxville, TN) was placed over the entire soil bin to prevent movement of aboveground residue into or out of the plots.

Soil solution samplers were installed at 90-cm soil depth using porous cup suction lysimeters (no. 1900L4, Soil Moisture Corp., Santa Barbara, CA.). Monitoring of soil solution samples for NO_3^-–N concentrations was initiated on 1 July 1992 and continued weekly. The soil solution samples were broken into two monitoring periods, from 1 July 1992 to 5 May 1993 and from 12 May 1993 to 28 May 1994 corresponding to the two growing seasons. Nitrate–N in soil solution was determined using steam distillation techniques (Keeney and Nelson, 1982) during the first monitoring period, and was determined colorimetrically using a Technicon Autoanalyzer (Technicon Industrial Systems, 1973) during the second monitoring period. Because of environmental concern of fertilizer applications contributing to NO_3^- levels in groundwater, isotope-ratio analysis was also performed to determine the contribution of fertilizer-N to the NO_3^-–N concentrations of soil solution samples, when sufficient NO_3^-–N was collected in samples for analysis (30 µg N). Analysis for ^{15}N content for soybean only was conducted at several sampling dates because of limitations in NO_3^-–N content in grain sorghum.

Plant samples collected at physiological maturity were dried at 65°C (until weight loss was complete) and ground in a Wiley mill to pass a 0.44-mm screen. Total N contents of plant and soil samples were determined using a permanganate-reduced iron modification of a semimicro-Kjeldahl method (Bremner and Mulvaney, 1982). Distillates of plant, soil, and soil solution samples were concentrated for isotope-ratio analyses, which were performed as described by Mulvaney et al. (1990), using an automated mass spectrometer (Nuclide Model 3-60-RMS; Measurement and Analysis Systems, Bellefonte, PA).[1]

Statistical analysis of data was performed using ANOVA procedure and means were separated using contrast statements and least significant difference (LSD) at 10% probability level (SAS Institute, 1982). Soil solution NO_3^- concentration data was initially analyzed as a split-split-plot experimental design, with plant species as the main plot, CO_2 concentration as the first split, and sampling date as the final split. A significant interaction effect for sampling date with CO_2 concentration and crop species were observed in both monitoring periods,

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[1] Trade names and products are mentioned solely for information. No endorsement by the U.S. Dep. of Agric. is implied.

Table 1. Total dry weight, total N content, and C/N ratio of crop residue grown under ambient (360 µL L^{-1}) or elevated (720 µL L^{-1}) atmospheric CO_2 concentrations returned to soil after harvest in 1992 and 1993.†

	Total dry weight			Total N			C/N		
Crop	Ambient	Elevated	Mean	Ambient	Elevated	Mean	Ambient	Elevated	Mean
	Mg ha^{-1}								
					1992				
Grain sorghum	4.7	6.5	5.6 a	17.8	23.8	20.8 a	116.3	122.7	119.5 a
Soybean	4.3	6.2	5.2 b	89.5	104.2	96.1 b	21.7	26.8	24.2 b
Mean	4.5 a	6.3 b		53.7 a	64.0 b		69.0 a	74.8 b	
$LSD_{any\ two\ means}$	NS			14.4			NS		
					1993				
Grain sorghum	7.4	10.3	8.9 a	28.6	33.0	30.8 a	111.4	136.2	123.8 a
Soybean	8.1	12.3	10.2 b	189.7	251.7	220.7 b	18.9	12.1	20.0 b
Mean	7.8 a	10.2 b		109.1 a	142.4 b		65.1 a	78.6 a	
$LSD_{any\ two\ means}$	0.59			NS			NS		

† Values represent means of three replicates. Values within a row or within a column followed by the same letter do not differ significantly (0.10 level). Least significant differences (LSD) are shown for those means with significant crop species by CO_2 treatment interaction. NS = not significant.

therefore, a separate analysis was performed by sampling date. Differences in means for fertilizer N content of NO_3^--N were separated using contrast statements (SAS Institute, 1982). The term *trend* is used to designate appreciable, but nonsignificant, treatment effects with probability levels between 10 and 25%. In this manuscript, the term *fertilizer-N* is used to reflect N added to the plant-soil system through fertilizer application and the term *native soil N* is used to reflect N from sources other than fertilizer-N application.

RESULTS AND DISCUSSION

Carbon Dioxide Effect on Plants

For both species, significant differences were observed in the mass of plant residue returned to the plots (root biomass and aboveground biomass − seed) as a function of atmospheric CO_2 treatment during both years of the study (Table 1). A significant crop species by CO_2 treatment interaction was also observed in 1993, with the difference in total dry weight production between species being greater with elevated CO_2 compared to ambient.

Total N returned to the plots in residue was much greater in soybean compared to grain sorghum in both years (Table 1), because soybean is a legume with symbiotic N_2-fixation capabilities involving *Rhizobium japonicum*. Elevated CO_2 increased the N in residue in both the soybeans and the grain sorghum in both years. In 1992, there was also a significant interaction between CO_2 treatments and crop species, with the soybean having a greater response to elevated CO_2 compared to grain sorghum. The increased total N in grain sorghum residue due to elevated CO_2 indirectly indicates that a reduction in N losses may have occurred during the growing season (i.e., reduced NO_3^- leaching).

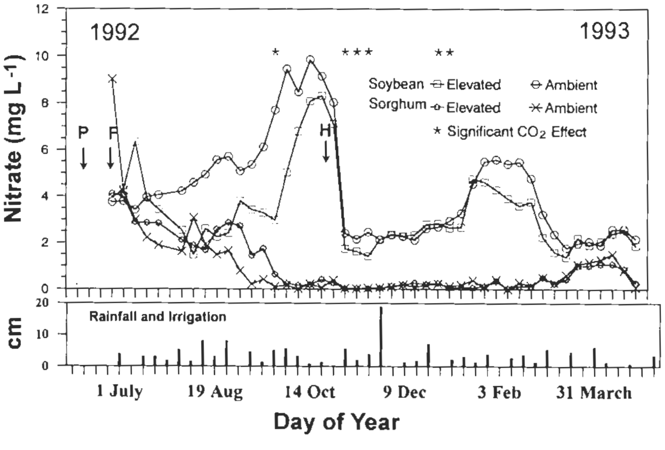

Fig. 1. Soil solution NO_3^--N sampled from a 90-cm depth for grain sorghum and soybean plants grown under ambient (357 µL L^{-1}) or elevated (705 µLL^{-1}) atmospheric CO_2 concentrations from 1 July 1992 to 5 May 1993. Means are for three replications and an asterisk denotes dates with significant CO_2 effect. Planting date (P), fertilizer application date (F), and final harvest date (H) are noted.

Differences were also observed in the C/N ratio of plant residues returned to soil after harvest (Table 1). A significant difference was observed for the C/N ratio between plant species in both years, with grain sorghum having higher C/N ratio than soybean (Table 1). In 1992, the C/N ratio was also affected by the atmospheric CO_2 treatment, with the ambient CO_2 having a lower C/N ratio than the elevated CO_2 treatment (Table 1). Although not significant in 1993, the C/N ratio tended ($P = 0.12$) to be higher with the elevated CO_2 treatment.

Soil Solution Nitrate

Significant differences between both crop species and CO_2 treatments were observed for NO_3^--N concentrations during the study (Fig. 1 and 2). Initially, NO_3^--N concentrations were relatively high compared to the remainder of the 2 yr of monitoring, with NO_3^--N only occasionally exceeding the 4.2 mg L^{-1} concentration initially measured. This corresponded to the seedling stage of grain sorghum when root systems were small and plant N was in low demand. Also, there were no significant differences between the grain sorghum and the soybean for NO_3^--N concentrations below the root zone, with approximately 4.2 mg L^{-1} NO_3^--N in soil solution. After approximately 10 wks from planting (29 July 1992), the NO_3^--N concentrations tended to increase under soybean and decrease under grain sorghum. On 30 Sept. 1992, a significant difference was observed for NO_3^--N between the grain sorghum and the soybean, and the differences remained significant for most of the two monitoring periods.

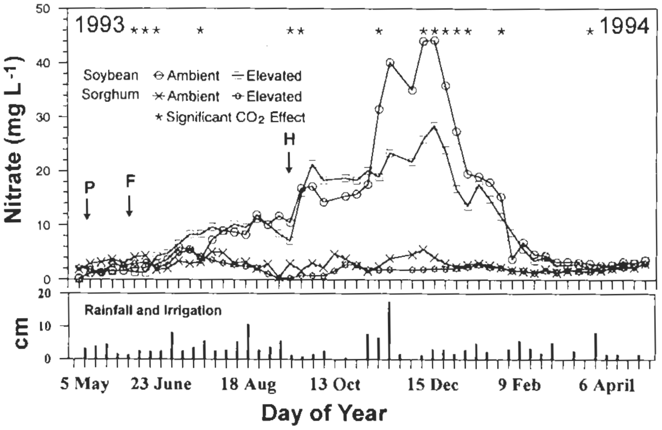

Fig. 2. Soil solution NO_3^--N sampled from a 90-cm depth for grain sorghum and soybean plants grown under ambient (364 μL L^{-1}) or elevated (731 μL L^{-1}) atmospheric CO_2 concentrations from 5 May 1993 to 28 Apr. 1994. Means are for three replications and an asterisk denotes dates with significant CO_2 effect. Planting date (P), fertilizer application date (F), and final harvest date (H) are noted.

At the initiation of the study, due to extensive fallow conditions (approximately 25 yr), the soil in the bin was extremely low in organic matter (Reeves et al., 1994) which was considered to be dominated by recalcitrant C fractions. These soil conditions combined with low plant N demand led to high potential NO_3^--N leaching and would explain the relatively high initial NO_3^--N concentrations observed in leachate. The ^{15}N analysis indicated that only a small portion of the solution NO_3^--N originated from fertilizer-N applied, with an average of 1.8 mg L^{-1} originating from fertilizer-N, which was an average of approximately 15% of total NO_3^--N in the first 9 wks of the study (Table 2).

Low levels of NO_3^--N derived from fertilizer-N compared to that from native soil N have been reported by others (Macdonald et al., 1989; Torbert and Reeves, 1995); Macdonald et al. (1989) concluded that NO_3^--N leaching would be dominated by N mineralization regardless of fertilizer N application. In our study, mineralization of native soil N was a dominant factor in NO_3^--N leaching despite the low soil organic matter content. A partial explanation of the low fertilizer-N content of soil solution would be mineralization-immobilization turnover (Jansson and Persson, 1982), where immobilization of fertilizer-N increased the proportion of fertilizer-N in organic form and, at the same time, mineralization of existing native soil organic N increased the proportion of nonlabelled N in soil solution. This also indicates very active mineralization and immobilization processes in this low and recalcitrant C soil.

Grain Sorghum

As the growing season progressed, NO_3^--N levels in soil solution below the rooting zone of grain sorghum tended to diminish slowly, until 30 Sept. 1992, when NO_3^--N concentrations of soil solution approached zero. This near zero concentrations of NO_3^--N continued through the remainder of the growing season and through the winter months. During the growing season, the low NO_3^--N concentration was most likely due to active root extraction of soil N for plant growth, since total soil N content was very low (0.06 g kg^{-1}) and soil N (either native soil N or fertilizer-N) must be in a plant-available form before leaching can occur. Following the growing season, N mineralization normally contributes to soil NO_3^--N leaching (Macdonald et al., 1989) but, in this case, we believe the high C/N ratio of grain sorghum residue (Table 1) would be expected to slow decomposition and limit N mineralization (Torbert et al., 1995; Ghidey and Alberts, 1993).

On approximately 31 Mar. 1993 and continuing into the second growing season, a slight increase in NO_3^--N concentrations was observed (Fig. 1 and 2). This was most likely because of warmer soil temperatures and increased microbial activity. Also, over time the C/N ratio of decomposing plant residue decreases with a corresponding increase in N release (Torbert et al., 1995). In addition, application of fertilizer-N after grain sorghum was planted may have contributed to an increase in soil N potentially available for leaching (Fig. 2). Isotope ^{15}N analysis of soil solution indicated that during this period of increased NO_3^--N concentrations (7 July–11 Aug. 1993), a substantial higher portion of NO_3^--N was fertilizer-N, with fertilizer N in NO_3^--N ranging from 15.3 to 34.4% of the total NO_3^--N (Table 2).

As in the first growing season, a decrease in NO_3^--N in the second growing season was observed in 1993 corresponding to increased plant N demand; however, unlike the first growing season,NO_3^--N concentrations did not decrease to near zero. This was most likely because of increased total soil organic matter along with increased soil N, creating soil conditions with lower plant N stress. Likewise, after harvest, the input of new plant residue into soil under less N-deficient conditions led to N mineralization of decomposing plant residue. This increase in NO_3^--N leaching from grain sorghum, however, was very small compared to the NO_3^--N lost under soybean during the same period.

After harvest, the proportion of fertilizer-N in soil solution averaged 20% of the total NO_3^--N from 13 Sept. 1993 to 28 Apr. 1994 (Table 2). This indicated that leached NO_3^--N was dominated by N mineralized from soil organic matter and not from residual fertilizer-N.

Soybean

As observed earlier, initial NO_3^--N concentrations was very similar between soybean and grain sorghum treatments, even though soybean did not receive an application of fertilizer-N shortly after monitoring began as did grain sorghum. This is further evidence that mineralized-N was the dominant source of NO_3^--N and was independent of fertilizer-N application. However, with soybean, the soil solution NO_3^--N concentrations slowly increased during the growing season (Fig. 1), most likely because the biological fixation of N_2 not only supplies plant N needs but also contributes to soil N (Jefferies et al., 1981; Van Kessel et al., 1994).

Shortly after harvest, NO_3^--N concentrations decreased in response to soybean residue deposition (11

Table 2. Fertilizer NO_3^--N and proportion of fertilizer NO_3^--N to total in soil solution measured at 90-cm soil depth for soybean and grain sorghum plants grown under ambient (360 µL L^{-1}) or elevated (720 µL L^{-1}) atmospheric CO_2 concentrations calculated from ^{15}N data, 1992 and 1993.†

	Soybean		Grain sorghum	
Date	Ambient	Elevated	Ambient	Elevated
	fertilizer NO_3^--N (mg L^{-1})			
		1st monitoring period		
1 July 1992	0.07 (1.8)	0.07 (1.9)	3.09 (24.6)	0.17 (4.1)
7	0.12 (3.1)	0.13 (3.0)	3.05 (21.6)	0.17 (4.5)
15	0.08 (2.4)	1.69 (16.9)	5.63 (28.9)	0.09 (3.7)
21	0.07 (1.8)	0.08 (2.0)	–	–
24	0.10 (2.5)	0.06 (1.9)	3.90 (21.3)	0.08 (2.8)
29	0.05 (1.2)	0.04 (1.6)	–	–
7 Oct.	1.32 (13.0)	0.37 (6.3)	–	–
21	2.04 (19.8)	1.19 (14.0)	–	–
28	2.01 (20.2)	1.20 (12.5)	–	–
4 Nov.	1.57 (17.7)	0.94 (11.9)	–	–
9 Dec.	0.13 (5.6)	0.14 (5.7)	–	–
13 Jan. 1993	0.20 (6.8)	0.17 (6.5)	–	–
20	0.23 (7.0)	0.18 (6.8)	–	–
27	0.33 (7.2)	0.34 (7.0)	–	–
3 Feb.	0.39 (7.1)	0.34 (7.3)	–	–
10	0.41 (7.2)	0.30 (7.0)	–	–
17	0.40 (7.0)	0.27 (6.7)	–	–
24	0.35 (6.5)	0.24 (6.6)	–	–
3 Mar.	0.33 (6.8)	0.24 (6.3)	–	–
31	0.11 (5.6)	0.13 (5.9)	–	–
28 Apr.	0.13 (5.0)	0.13 (5.2)	–	–
9 June	0.04 (1.4)	0.06 (1.5)	0.03 (1.9)	0.21 (8.3)
		2nd monitoring period		
7 July	0.16 (2.6)	0.47 (7.7)	0.58 (16.5)	1.88 (20.9)
14	0.11 (3.5)	0.43 (6.7)	0.76 (23.6)	2.34 (21.1)
21	0.13 (3.6)	0.23 (2.7)	0.88 (25.7)	1.63 (21.1)
29	0.38 (4.9)	0.86 (9.1)	1.99 (34.4)	1.17 (21.4)
4 Aug.	0.51 (5.1)	0.75 (9.3)	1.83 (34.1)	0.72 (20.4)
11	0.42 (4.5)	1.00 (9.7)	1.00 (31.6)	0.48 (15.3)
25	0.92 (7.1)	1.83 (15.2)	–	–
1 Sept.	1.15 (8.5)	1.34 (11.6)	–	–
9	1.20 (9.6)	1.76 (16.7)	–	–
15	1.26 (11.2)	1.36 (18.1)	–	–
6 Oct.	2.17 (15.3)	2.89 (15.1)	–	–
13	1.59 (7.7)	3.24 (15.6)	2.30 (27.5)	0.26 (12.0)
27	2.46 (14.3)	3.51 (18.2)	0.60 (22.8)	0.44 (12.2)
17 Nov.	14.04 (29.5)	5.87 (24.9)	0.85 (21.9)	1.16 (13.4)
15 Dec.	13.03 (26.7)	6.28 (19.4)	1.11 (22.1)	0.33 (15.5)
13 Jan. 1994	2.22 (11.9)	1.67 (9.9)	0.50 (17.0)	0.60 (21.6)
9 Feb.	0.61 (8.8)	0.51 (9.1)	0.25 (16.8)	0.33 (19.2)
17 Mar.	0.21 (6.7)	0.20 (6.9)	0.41 (20.2)	0.25 (15.8)
14 Apr.	0.17 (5.6)	0.21 (7.1)	0.51 (20.0)	0.34 (15.0)
28	0.17 (5.2)	0.27 (7.4)	0.45 (19.6)	0.50 (16.2)

† Values within ( ) are the proportion of fertilizer NO_3^--N in total. Means followed by an * differ significantly (0.10 level). Fertlizer N application of 34 kg N ha^{-1} and 101 kg N ha^{-1} was made to soybean and grain sorghum, respectively.

Nov. 1992). While the C/N ratio of soybean was much lower than grain sorghum (Table 1), N immobilization could still occur in response to N limitations present in this soil (Torbert et al., 1995). However, soil NO_3^--N concentrations remained above that observed with grain sorghum throughout the study (Fig. 1 and 2).

In the second monitoring period, an increase in NO_3^--N concentrations was observed as the soybean growing season progressed (Fig. 2). During this period, as in the first, biological N_2 fixation contributed to soil-N content. However, in this year, a decrease in NO_3^--N concentrations after harvest was not observed. Instead, an upward trend continued for NO_3^--N concentrations through harvest and peaked near 15 Dec. 1993. This was most likely a result of the 2 yr of soybean residue in the soil system reducing soil N deficit conditions.

Following the NO_3^--N peak on 15 Dec. 1993, soil NO_3^--N decreased until 9 Mar. 1994. By planting of the 3rd year, the level of NO_3^--N concentrations had decreased to the level observed with grain sorghum. This might occur when the soil approached a C/N ratio equilibrium resulting in decreased N loss.

Carbon Dioxide Effect

Statistical analysis of NO_3^--N concentrations data indicated a significant effect for atmospheric CO_2 concentrations and a significant CO_2 treatment interaction with crop species. There were, however, no significant differences between CO_2 treatments for fertilizer-N content in soil solution (Table 2). With grain sorghum, no significant difference was observed between CO_2 treatments during the first monitoring period (Fig. 1). During this period, as discussed earlier, the extremely low soil N conditions limited NO_3^--N movement to groundwater.

During the second monitoring period (Fig. 2), elevated

CO_2 concentrations significantly reduced NO_3^--N concentrations, which averaged 3.3 and 2.3 mg L^{-1} for ambient CO_2 and elevated CO_2 treatments, respectively. Initially, a small increase in the NO_3^--N concentrations was observed for elevated CO_2, but these differences were very small and only significant on 9, 16, and 23 June 1993. After this period, NO_3^--N was greater for ambient CO_2 treatment compared to the elevated CO_2 treatment. The mean NO_3^--N concentrations was greater with the ambient CO_2 treatment from 29 July 1993 to 19 January 1994, with the greatest differences occurring after harvest (Fig. 2). During this period, NO_3^--N concentrations with elevated CO_2 remained relatively constant, with the observed differences in NO_3^--N occurring because of fluctuations in the ambient CO_2 treatment.

With soybean during the first monitoring period (Fig. 1), a significant increase was observed for NO_3^--N concentrations when averaged over sampling dates, with 4.1 and 3.4 mg L^{-1} NO_3^--N concentrations for ambient and elevated CO_2 treatments, respectively. The largest differences between the ambient and elevated CO_2 treatments were observed between 13 Aug. and 25 Nov. 1993, with the greatest differences between means occurring before harvest (Fig. 1). This would correspond to the period of greatest root growth and biological N_2 fixation.

During the second monitoring period, when averaged over sampling dates, there was no significant difference for the mean NO_3^--N concentrations between CO_2 treatments. However, a significant CO_2 × date interaction did occur and a significant CO_2 effect was observed at several sampling dates (Fig. 2). As in grain sorghum, a small increase in NO_3^--N concentrations was observed shortly after planting for elevated CO_2 compared to ambient CO_2 conditions (Fig. 2), but these differences were only significant on 9, 16, and 23 June 1993. Significant differences (or strong trends) were observed for CO_2 treatments between 18 Nov. 1993 and 20 Jan. 1994, which corresponded to the peak NO_3^--N concentrations observed with the soybean treatment (Fig. 2). During this period, NO_3^--N lost from the ambient CO_2 treatment was much higher compared to the elevated CO_2 treatment.

A partial explanation for differences in NO_3^--N concentrations could be the difference in water-use efficiency between CO_2 treatments. Elevated CO_2 has been shown to increase water-use efficiency that may decrease water use (Idso and Brazel, 1985). An increase in soil water could have resulted in a dilution of the measured NO_3^--N below the root zone. However, most of the significant differences observed between the CO_2 treatments occurred after plant harvest when difference in water-use efficiency would have no influence.

As discussed earlier, decomposition of plant residue and soil organic matter is the dominant process controlling NO_3^--N availability for leaching in this study. Analysis of plant residue indicated that the C/N ratio was significantly increased with elevated CO_2 (Table 1). This well-documented effect of elevated CO_2 may drastically change the decomposition of plant biomass (Bazzaz, 1990; Torbert et al., 1995). In a review, Bazzaz (1990) suggested that plant residue decomposition in elevated CO_2 would be slower than under ambient CO_2 conditions. Torbert et al. (1995) measured plant decomposition under controlled laboratory conditions and reported that, while no difference in microbial respiration rate was observed, there was a reduction in the amount of N released from decomposing plant parts. The reduction in NO_3^--N concentrations below the root zone observed in this study could have been caused by either a reduction in plant biomass decomposition or by a reduction in N released from decomposing plant biomass grown under elevated atmospheric CO_2 conditions. Regardless, the plant/soil environment exposed to elevated atmospheric CO_2 concentrations had reduced the NO_3^--N levels moving below the rooting zone and therefore would be expected to reduce the degradation of groundwater quality beneath agroecosystems.

Chamber Effect

Statistical analysis of the chamber effect on total dry weight, total N content, C/N ratio of plant residue, and NO_3^--N concentrations below the root zone were also performed. No significant differences because of the chambers (ambient CO_2 chambers vs. no chambers) were observed for total dry weight, total N content, or C/N ratio of plant residue in 1992 and 1993. Likewise, when averaged over sampling periods, no significant difference was observed for chamber effects on NO_3^--N concentrations in both years. However, as would be expected, results indicated a significant species effect between grain sorghum and soybean in both 1992 and 1993, with the differences closely following those discussed earlier (data not presented). Significant chamber effects were observed at some individual sampling dates during both monitoring periods but, in general, the patterns for NO_3^--N concentrations for ambient CO_2 without chamber treatment closely followed patterns observed for the ambient CO_2 with chamber treatment. The exception was from 8 Dec. 1993 to 9 Feb. 1994, when NO_3^--N concentrations for ambient CO_2 without chamber was much lower compared to ambient CO_2 with chamber for soybean, but reasons for these differences are unclear.

CONCLUSIONS

Results from this study indicate that both crop species and atmospheric CO_2 concentration will affect the NO_3^--N levels moving to groundwater. The concentration below the rooting zone of soybean were generally higher compared to grain sorghum, most likely as a result of higher N input into the soil system because of soybean symbiotic N_2 fixation. Analysis of soil solution NO_3^- for ^{15}N content indicated that most of the NO_3^- measured below the rooting zone originated from native soil N and not from N-fertilizer application. Elevated atmospheric CO_2 concentrations reduced the NO_3^--N levels below the rooting zone and therefore would be expected to reduce the degradation of groundwater quality beneath agroecosystems.

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