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## Soil CO<sub>2</sub> Flux in Response to Elevated Atmospheric CO<sub>2</sub> and Nitrogen Fertilization: Patterns and Methods

J.M. Vose, K.J. Elliott, and D.W. Johnson

### I. Introduction

The evolution of carbon dioxide (CO<sub>2</sub>) from soils is due to the metabolic activity of roots, mycorrhizae, and soil micro- and macro-organisms. Although precise estimates of carbon (C) recycled to the atmosphere from belowground sources are unavailable, Musselman and Fox (1991) propose that the belowground contribution exceeds 100 Pg y<sup>-1</sup> globally. This represents a major component of C flux in the global C cycle. Belowground C cycling processes and subsequent soil CO<sub>2</sub> fluxes are equally important at ecosystem scales; however, we have limited knowledge of the magnitude of fluxes within and across ecosystems. Increased knowledge of the magnitude of C fluxes, as well as the factors which regulate these fluxes is critical for understanding ecosystem C cycling and potential responses to factors such as climatic change. In this study, we quantified soil CO<sub>2</sub> flux from soils growing ponderosa pine (*Pinus ponderosa* L.) under conditions of elevated atmospheric CO<sub>2</sub> and soil nitrogen (N).

Separating the contributing sources (i.e., roots vs. microbes) of soil surface CO<sub>2</sub> flux has proven difficult. The relative contribution of roots versus other soil components has been estimated to vary between 35 to 65% of the total CO<sub>2</sub> evolved (Edwards and Harris, 1977; Ewel et al. 1987). Factors influencing the rate of CO<sub>2</sub> evolution include soil temperature and moisture (through their influence on metabolic activity of both roots and microbes) (Schlentner and Van Cleve, 1985; Wiant, 1967), available soil carbon, and root biomass (Behera et al., 1990). Hence, changes in root biomass and/or activity related to elevated CO<sub>2</sub> should directly influence the total CO<sub>2</sub> evolution from forest soils. Indirect effects related to carbon source and amount (e.g., fine root turnover, exudates) should also influence CO<sub>2</sub> evolution by altering microbial activity. Finally, increased soil N availability could alter soil CO<sub>2</sub> flux by changing root (Ryan, 1991) and microbial activity and/or biomass, particularly if soil or litter C:N ratios are substantially altered.

Several techniques are available for measuring CO<sub>2</sub> evolution from soils. Static chamber methods include soda lime or bases (KOH or NaOH) which measure CO<sub>2</sub> "trapped" over the measurement interval (see Cropper et al., 1985). Static measures of CO<sub>2</sub> evolution may also be made by gas chromatograph analysis of air samples collected from sealed chambers on the soil surface (Raich et al. 1990). de Jong and Schappert (1972) describe a variation of the static method by using a chamberless technique based on CO<sub>2</sub> profiles (pCO<sub>2</sub>) in the soil. Dynamic chamber methods quantify CO<sub>2</sub> evolution by continuously monitoring CO<sub>2</sub> levels in chambers with either a closed or flow-through system and an infrared gas analyzer (IRGA). Studies comparing measurement techniques have found wide disparity between static chamber, static chamberless, and dynamic chamber methods (Edwards and Sollins, 1973; Cropper et al., 1985; Raich et al., 1990; Rochette et al., 1992; Norman et al., 1992). In general, static chamber techniques provide lower estimates of CO<sub>2</sub> evolution than dynamic chamber techniques, while pCO<sub>2</sub> techniques provide higher CO<sub>2</sub> evolution estimates than dynamic chamber techniques (de Jong et al., 1979). Although more difficult and expensive to conduct, dynamic, IRGA-based techniques are considered more reliable (Ewel et al., 1987) and they can be configured to quantify diurnal patterns.

The objectives of this study were: (1) to quantify diurnal patterns in soil CO<sub>2</sub> evolution using a dynamic, IRGA based measurement system, (2) to examine the impacts of elevated atmospheric CO<sub>2</sub> and nitrogen fertilization on soil CO<sub>2</sub> evolution, and (3) to compare estimates using the IRGA based system with pCO<sub>2</sub> measurements.

## II. Methods

### A. Site Description

The study was conducted at the USDA Forest Service Institute of Forest Genetics in Placerville, CA (longitude = 121°W, latitude = 39°N). The elevation of the site is 843 m, receives an average of 1000 mm of annual precipitation, and has a mean annual temperature of 18 °C. The soil is Aiken clay loam (Xeric Haplohumult) derived from andesite. Extensive sampling prior to study establishment indicated uniform soil chemical and textural characteristics across the study area. Bulk density of the soil averaged 1.14 g cm<sup>-3</sup>, porosity was 54%, reaction was moderately acidic (pH<sub>CaCl</sub> = 5.1 in upper 18 cm), and base saturation (1 M NH<sub>4</sub>Cl extraction) was 50 to 60%.

### B. Experimental Design and Treatments

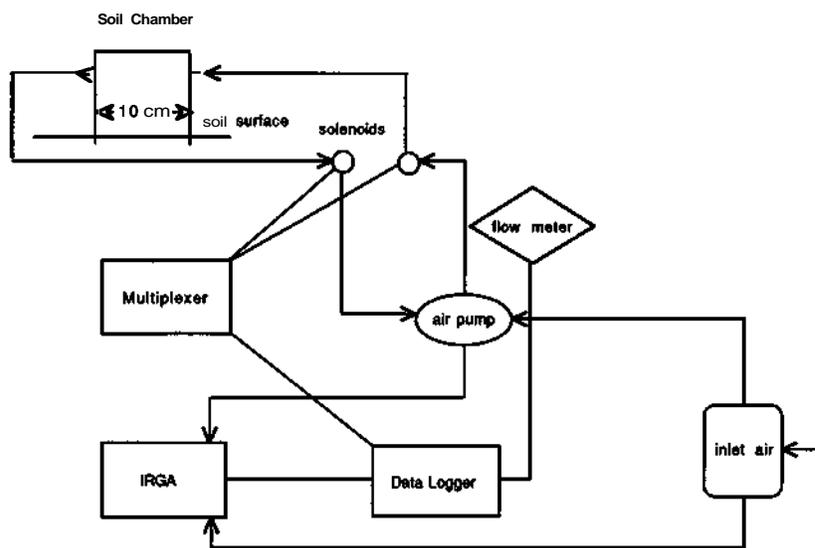
The experiment utilized open top chambers (3 m diameter; hexagonal shape) as a means of elevating CO<sub>2</sub> concentration (Ball et al. 1991). Air was delivered to the chambers at three air changes per minute and was distributed using 45 cm diameter plastic tubing perforated with 2.54 cm holes on 15 cm centers. The experimental design consisted of three levels of N (ambient, 10, and 20 g m<sup>-2</sup> yr<sup>-1</sup> of N as ammonium nitrate, applied in early spring), and four continuous CO<sub>2</sub> treatments (ambient, no chamber; ambient chamber; +175 ppm; and +350 ppm). Each of the chambered treatments was replicated three times, and the unchambered treatment was replicated twice. Due to cost limitations, the 10 g m<sup>-2</sup> yr<sup>-1</sup> N, +175 CO<sub>2</sub> treatment was excluded. Hence, there were a total of 11 treatments. Each chamber contained 21 ponderosa pine seedlings (grown from seed) equally spaced at about 0.3 m in all directions. At the time of sampling, seedlings had been grown in the chambers under treated conditions for two years. Soils were irrigated weekly with sufficient water to maintain soil water potential at > -0.07 MPa.

### C. CO<sub>2</sub> Sampling

#### 1. IRGA Measurements

We measured diurnal patterns of soil CO<sub>2</sub> flux using an automated, flow-through, IRGA based measurement system (Figure 1). The system measured flux sequentially from ten soil chambers (10 cm diameter, 10 cm height, 785 cm<sup>3</sup> volume) constructed of PVC pipe. Soil chamber edges were sharpened on the open end and driven approximately 2 cm into the soil surface with a rubber mallet. All tubing was 5 mm (i.d.) flexible PVC. Air was passed through the chambers via inlet and outlet fittings attached to the upper sides of the chamber. Air flow through the chambers was regulated with a dual-sided air pump (Spec-Trex Corp.) which balanced flow into and out of the chambers. Actual flow rate (ml min<sup>-1</sup>) was controlled by varying voltage (0-12 VDC) supplied to the pump and was measured and logged electronically with a flow meter and data logger (Campbell 21X). An air flow rate of 1000 to 1500 ml min<sup>-1</sup> provided stable readings within 7 to 8 minutes. Chamber sampling was controlled with a multiplexer, data logger, and solenoids which opened sequentially (chambers 1-10) at ten minute intervals. Carbon dioxide concentrations of air entering and exiting the chambers was measured and logged electronically with an IRGA (ADC LCA3) operating in differential mode and a data logger (Campbell 21X), respectively. Soil CO<sub>2</sub> flux (mg CO<sub>2</sub> m<sup>-2</sup> min<sup>-1</sup>) was calculated based on the difference in CO<sub>2</sub> entering and exiting the chamber, the soil area sampled beneath the chamber, and the flow rate. Only data from the last minute of sampling were used in flux calculations.

Sampling was conducted over a six day period in mid-October, 1992. On each day, two soil respiration chambers were randomly placed in each of five treatment-replication combinations, with the restriction that chambers could be no closer than 2.5 cm from a seedling. This restriction was imposed to ensure that



**Figure 1.** Schematic representation of automated sampling system. Only one of ten soil sampling chambers is shown in the diagram.

seedlings were not damaged in the course of installing the chambers. Soil CO<sub>2</sub> flux was measured for 20-22 hrs (i.e., a diurnal cycle) on each day. On each successive day, the chambers were moved to a new set of treatment-replication combinations and the diurnal measurements repeated until all treatments and replications were sampled. Using this sampling approach, we assumed that there would be minimal day to day variation in diurnal soil CO<sub>2</sub> flux. Because climatic conditions were generally constant (i.e., no rain, cloudless skies, and stable temperatures) throughout the six day measurement period, we are confident that this assumption is valid.

## 2. pCO<sub>2</sub> Measurements

Gas wells were established at 15 and 30 cm depths within each open top chamber. During the same week as the IRGA based sampling, gas wells were sampled during daytime hours with a syringe, and CO<sub>2</sub> concentration was determined with a LICOR 6262 analyzer. Soil CO<sub>2</sub> flux was estimated using a procedure based on the concentration gradient (pCO<sub>2</sub>) between the two depths and a CO<sub>2</sub> diffusion coefficient. This is described in the following formula:

$$q = -D(dc/dz),$$

where  $q$  = flux ( $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$ ),  $D$  = diffusion coefficient ( $\text{m}^2 \text{ min}^{-1}$ ),  $c$  = concentration ( $\text{mg CO}_2 \text{ m}^{-3}$ ), and  $z$  = depth (m) (from deJong and Schappert 1972). The diffusion coefficient,  $D$ , was calculated using the equation (Rolston 1986):

$$D = (P_{\text{eff}}^{10/3}/E^2),$$

where  $D$  = diffusion coefficient of CO<sub>2</sub> in soil ( $\text{m}^2 \text{ min}^{-1}$ ),  $P_{\text{eff}}$  = effective soil porosity (air-filled soil pores, a function of soil porosity and water content), and  $E$  = total porosity. Soil moisture release curves were constructed to determine the relationship between soil water tension and water content. The relationship between soil water tension and  $P_{\text{eff}}$  was determined by subtracting soil water content from total porosity across a range of soil water tensions. Hence, for each sample period soil water content was

determined gravimetrically and the corresponding soil water tension was determined from soil moisture release curves. Effective soil porosity at a given soil water content was then determined from the relationship between soil water tension and  $P_{\text{eff}}$ .

#### D. Soil Moisture and Temperature

Soil moisture (averaged over 15 cm depth) was measured within 10 cm of each soil  $\text{CO}_2$  flux chamber location using a "TRASE" time domain reflectometry measurement system (Soil Moisture Instruments, Inc.) with sample rods installed vertically in the soil. Soil moisture measurements were taken before and after the flux measurements were conducted. To characterize diurnal soil temperature variation, soil temperature at 10 cm depth was measured for one complete diurnal cycle at five locations within and outside open-top chambers. Measurements were made with Type-T thermocouples connected to a data logger (Campbell 21X) and multiplexer.

#### E. Statistical Analysis

We used integrated values of diurnal measurements to estimate soil  $\text{CO}_2$  flux on a daily basis for each open-top chamber-treatment combination. These integrated values were used in analysis of variance (ANOVA) to test for treatment effects (General Linear Models Procedure, SAS Institute, 1987). A reduced error term {chamber(treatment)}, which accounted for the subsample of two soil  $\text{CO}_2$  flux chambers per open-top chamber, was used in the ANOVA to test for treatment effects. Because we had an unbalanced experimental design, contrast statements (Snedecor and Cochran, 1980) were constructed to determine the effects of  $\text{CO}_2$ , nitrogen, and  $\text{CO}_2 \times$  nitrogen interaction on soil  $\text{CO}_2$  flux.

### III. Results and Discussion

#### A. Diurnal Patterns

Across all treatments, soil  $\text{CO}_2$  flux varied by as much as seven-fold over a diurnal measurement period (Table 1). Maximum rates ranged from 7.78 to 17.00  $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$  and minimum rates ranged from 1.11 to 3.74  $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$ . These rates are comparable to those determined with other continuous techniques; e.g., in slash pine (*Pinus elliotii* Engelm.), Ewel et al. (1987) found average annual rates of 9  $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$ . Kucera and Kirkman (1971) found October rates in tall-grass prairie on the order of 7.5  $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$ . In a yellow poplar (*Liriodendron tulipifera* L.) forest, Edwards and Sollins (1973) found values ranging from 5 to 14  $\text{mg CO}_2 \text{ m}^{-2} \text{ min}^{-1}$  for spring and summer, respectively.

The diurnal patterns observed in our study were correlated with diurnal variation in soil temperature (Figure 2). Maximum rates of soil  $\text{CO}_2$  flux occurred in the late afternoon (= 1500 hr) when soils were warmest, and minimum rates occurred in the morning ( $\approx$ 0900 hr) when soils were coolest. The apparent temperature influence is not surprising. Temperature has a major impact on respiratory processes (Ryan 1991) and relationships between temperature and soil  $\text{CO}_2$  flux are well established (e.g., Schlentner and Van Cleve, 1985; Naganawa et al., 1989). However, there was a noticeable surge in soil  $\text{CO}_2$  flux between 2100 hr and 0100 hr and other periods when patterns in soil temperature and soil  $\text{CO}_2$  flux did not agree (e.g., 0900 hr). This indicates that other factors are also contributing to the diurnal patterns we observed. Soil moisture stayed consistent throughout the measurement cycle (Table 2) so the diurnal variation can not be attributed to moisture.

In contrast to our study, Edwards and Sollins (1973) found that forest floor  $\text{CO}_2$  flux rates were greatest at night and most of the nighttime increase came from the litter fraction. Two factors may explain the differences between our study and Edwards and Sollins (1973). First, they performed their experiments in a closed canopied forest which substantially dampened diurnal temperature variation. In fact, litter temperature in their study remained essentially constant. In contrast, conditions at our site (e.g., clear skies, no forest canopy) promoted large diurnal variations in soil temperature. Second, in our study there was no litter layer. Hence, any phenomena related to elevated night respiration from litter (e.g., increased moisture content due to dew formation) would not have been observed in our study.

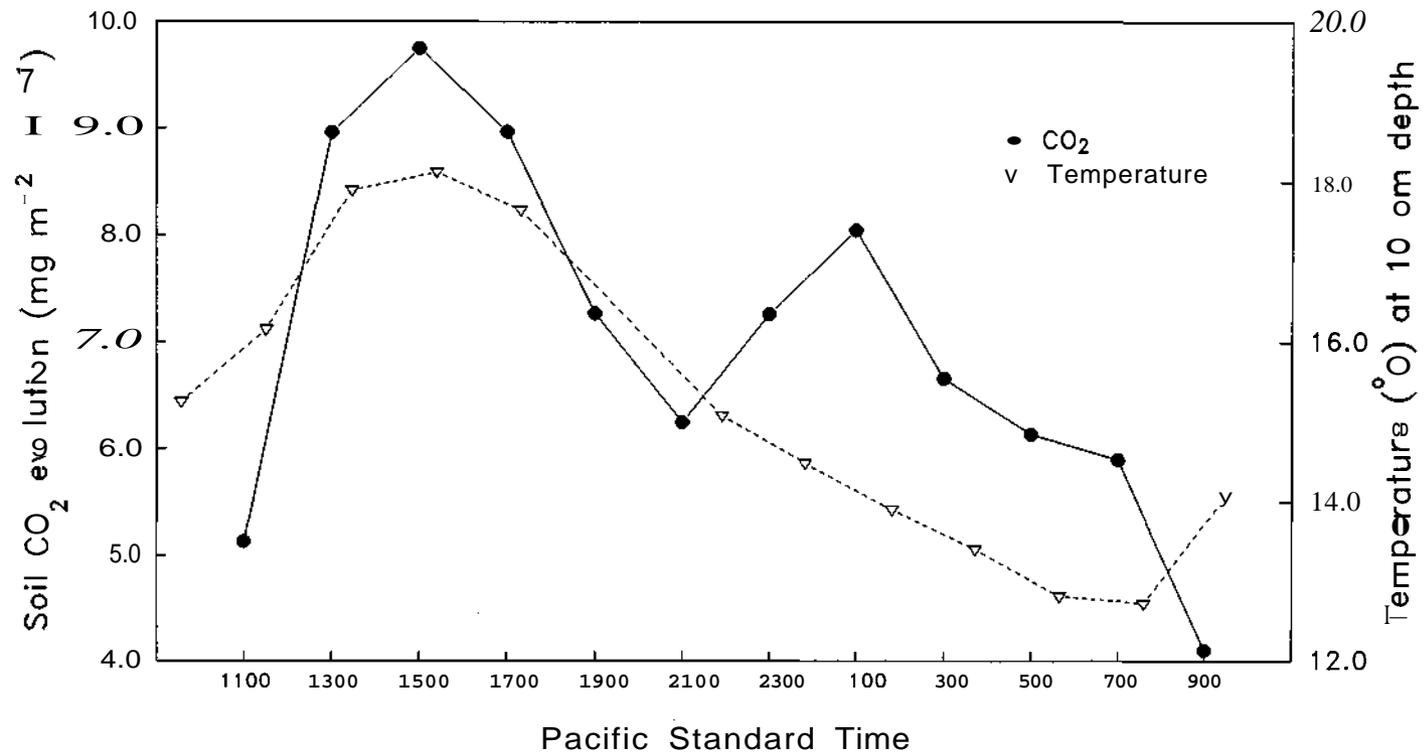
Table 1. Average, maximum, and minimum soil CO<sub>2</sub> evolution (mg m<sup>-2</sup> min<sup>-1</sup>) measured over a 24 hour period; values in parentheses are standard errors; n=2 for chamberless (OPEN) treatments and n=3 for all others

Treatment	24 hour average	Daily maximum	Daily minimum
350 CO <sub>2</sub> + ON	7.15 (2.54)	12.72 (5.90)	3.20 (0.77)
350 CO <sub>2</sub> + 10N	6.26 (2.82)	12.86 (7.63)	2.79 (0.94)
350 CO <sub>2</sub> + 20N	4.98 (1.01)	7.78 (1.73)	2.34 (0.35)
525 CO <sub>2</sub> + ON	10.18 (2.73)	17.00 (4.65)	2.52 (0.98)
525 CO <sub>2</sub> + 20N	8.20 (3.22)	13.87 (3.70)	2.06 (0.95)
700 CO <sub>2</sub> + ON	5.50 (0.85)	9.93 (1.57)	1.99 (0.91)
700 CO <sub>2</sub> + 10N	8.16 (1.73)	10.86 (2.45)	1.11 (0.58)
700 CO <sub>2</sub> + 20N	6.05 (1.71)	14.26 (3.57)	3.74 (0.74)
Open + ON	5.72 (0.03)	9.01 (3.08)	3.27 (0.44)
Open + 10N	6.88 (3.19)	11.04 (5.30)	2.89 (0.89)
Open + 20N	5.80 (0.47)	9.46 (0.81)	2.57 (0.22)

Similar to our study, Edwards and Sollins (1973) observed a noticeable surge in soil CO<sub>2</sub> flux between 2100 hr and 0100 hr and this phenomena has also been observed in other studies (e.g., **Witkamp**, 1969; **Witkamp** and Frank, 1969). Witkamp (1969) observed surges in soil CO<sub>2</sub> flux when the soil was warmer than the air, which he attributed to convective forces flushing soil CO<sub>2</sub> into the atmosphere. Convective processes may partially contribute to the diurnal patterns observed in our study because there was a rapid decline in air temperature in the early morning (0100 hr). The elevated soil CO<sub>2</sub> flux between 2100 hr and 0100 hr observed in our study and by Edwards and Sollins (1973) is surprising and difficult to explain. We are confident that these patterns are not artifacts of our sampling system because in recent studies we have included closed blank chambers which show no diurnal patterns (Vose and Elliott, unpublished data), while data from chambers on the soil surface show a distinct diurnal pattern. Edwards and Sollins (1973) hypothesized that physical/climatic factors, such as changes in vapor pressure, were responsible for the elevated late evening rates. Biological factors may also be important. For example, the contribution of root respiration could increase due to: (1) increased root activity following cessation of aboveground light driven processes, and/or (2) an increase in "apparent" root respiration due to decreased dissolution of respired CO<sub>2</sub> in the transpiration stream. We have no data on diurnal patterns in root respiration and know of no data from the literature. Hence, a complete understanding of factors driving the diurnal patterns we observed will require further study. It is clear from our results that soil CO<sub>2</sub> flux sampling techniques in ecosystems with highly variable diurnal soil temperature need to sample over the entire diurnal cycle. For example, sampling only during warm, afternoon hours will bias any extrapolations upward and sampling during cool, morning hours will bias extrapolations downward. Although less well understood, other physical and biological factors may also contribute to diurnal variability and increase the importance of diurnal sampling for accurate quantification of fluxes. Our automated system enabled us to sample over the entire diurnal cycle and integrate fluxes. While static techniques provide cumulative flux measurements over a 24-hr period, there can be substantial differences in flux estimates between static and dynamic methods (see Edwards and Sollins, 1973; Kucera and Kirkman, 1971; and Cropper et al., 1985; **Rochette et al.**, 1992).

## B. Treatment Effects

We tested the impacts of elevated CO<sub>2</sub> and N fertilization on daily flux rates (Table 3). The daily value integrated the shorter term data collected over the diurnal cycle. Differences in rates varied as much as two-fold (i.e., 7.1 vs. 15.5 g CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>); however, there was considerable variability which precluded detection of significant differences ( $p < 0.10$ ) among treatments (Table 4). While diurnal soil temperature variation was substantial (e.g., Figure 2), there was little variation in soil temperature among treatments (Vose and Elliott, unpublished data) and no correlation between mean soil CO<sub>2</sub> flux rates and soil moisture (Table 2). Although our system included only two-year-old seedlings, the range of soil CO<sub>2</sub> flux values observed in our study is at the upper end of values found in the literature for a variety of forests. The high soil CO<sub>2</sub> fluxes observed in our study may be due to favorable environmental conditions (i.e., warm and wet soils); however, some of these differences may be related to the method of measurement. For example,



**Figure 2.** Example of temporal variation in soil CO<sub>2</sub> flux and soil temperature at 10 cm depth. Soil CO<sub>2</sub> flux values are averaged across all treatments.

**Table 2.** Average percent soil moisture measured at 15 cm depth at the beginning and end of each 24-hour period for each treatment; values in parentheses are standard error

Treatment	Initial soil moisture (m <sup>3</sup> m <sup>-3</sup> )	Final soil moisture (m <sup>3</sup> m <sup>-3</sup> )
350 CO <sub>2</sub> + ON	26.25 (0.45)	25.08 (0.64)
350 CO <sub>2</sub> + 10N	27.58 (1.55)	26.43 (1.33)
350 CO <sub>2</sub> + 20N	<b>28.30 (1.64)</b>	<b>28.12 (1.92)</b>
525 CO <sub>2</sub> + ON	28.55 (1.63)	28.82 (1.56)
525 CO <sub>2</sub> + 20N	<b>29.65 (1.23)</b>	<b>28.17 (0.92)</b>
700 CO <sub>2</sub> + ON	24.48 (3.97)	23.52 (3.68)
700 CO <sub>2</sub> + 10N	23.47 (3.06)	21.73 (2.41)
700 CO <sub>2</sub> + 20N	23.63 (3.81)	23.00 (3.83)
Open + ON	26.88 (0.32)	26.45 (0.30)
Open + 10N	30.02 (0.52)	29.30 (1.00)
Open + 20N	23.58 (8.28)	23.28 (7.78)

OPEN = Chamberless

**Table 3.** Average integrated soil CO<sub>2</sub> evolution (g m<sup>-2</sup> day<sup>-1</sup>) per treatment measured in October 1992. Average values are least square means with standard errors in parentheses (n=3)

Treatment	Means
350CO <sub>2</sub> + 10N	9.84 (1.65)
350CO <sub>2</sub> + 20N	8.66 (1.90)
525CO <sub>2</sub> + ON	7.06 (2.13)
525CO <sub>2</sub> + 20N	15.52 (1.65)
700CO <sub>2</sub> + ON	15.52 (1.65)
700CO <sub>2</sub> + 10N	8.02 (1.90)
700CO <sub>2</sub> + 20N	8.69 (1.90)
OPEN + ON	11.73 (1.65)
OPEN + 10N	8.05 (2.02)
OPEN + 20N	10.52 (2.47)
	8.32 (2.02)

OPEN = Chamberless.

in aspen (*Populustremuloides* Michx.) stands, soil respiration rates in October ranged from about 4 to 6 g CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> using soda lime (Jurik et al., 1991; Weber, 1990). In jack pine (*Pinus banksiana* Lamb.) stands, Weber (1985) found November values of 4 g CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> using soda lime. Static techniques, such as soda lime or base traps, have been shown to underestimate soil CO<sub>2</sub> flux relative to IRGA systems (Ewel et al., 1987; Edwards and Sollins, 1973). In contrast, Edwards and Sollins (1973) found flux rates ranging from 3 to 26 g m<sup>-2</sup> day<sup>-1</sup> (mean = 16.7) in a yellow poplar (*Liriodendron tulipifera* L.) stand using a continuous IRGA system. Because there is no litter layer, the CO<sub>2</sub> evolved from the soil is exclusively from root and soil microbial respiration. Hence, some of the factors contributing to the flux variability observed among treatments may be related to variation in root biomass/activity and soil microbial populations among treatments. Several studies have shown increased root biomass in response to elevated CO<sub>2</sub> (e.g., Rogers et al., 1992; Norby et al., 1987) and plant respiration is positively correlated with tissue nitrogen (Ryan, 1991). In our study, there was a trend toward greater soil CO<sub>2</sub> evolution from the elevated CO<sub>2</sub> treatment (particularly the 525 CO<sub>2</sub> treatment) which coincides with greater root biomass on these treatments (determined from destructive sampling; R. Walker, unpublished data). As seedlings grow and continue to increase their belowground biomass, differences in soil CO<sub>2</sub> evolution among treatments may become more apparent.

**Table 4.** Analysis of variance table for test of treatments with contrasts for CO<sub>2</sub> and N comparisons (October 1992)

Source	df	SS	MS	F	p > F
Treatment	10	309.053	30.905	0.63	0.767
Contrast "Chamber"	1	1.135	1.135	0.02	0.880
Contrast "CO w/CC"	2	200.867	100.434	2.06	0.155
Contrast "N"	2	33.144	16.572	0.34	0.716
Contrast "N control vs N high"	1	18.301	18.301	0.38	0.547
Error Cham(Trt)	19	925.022	48.6854		

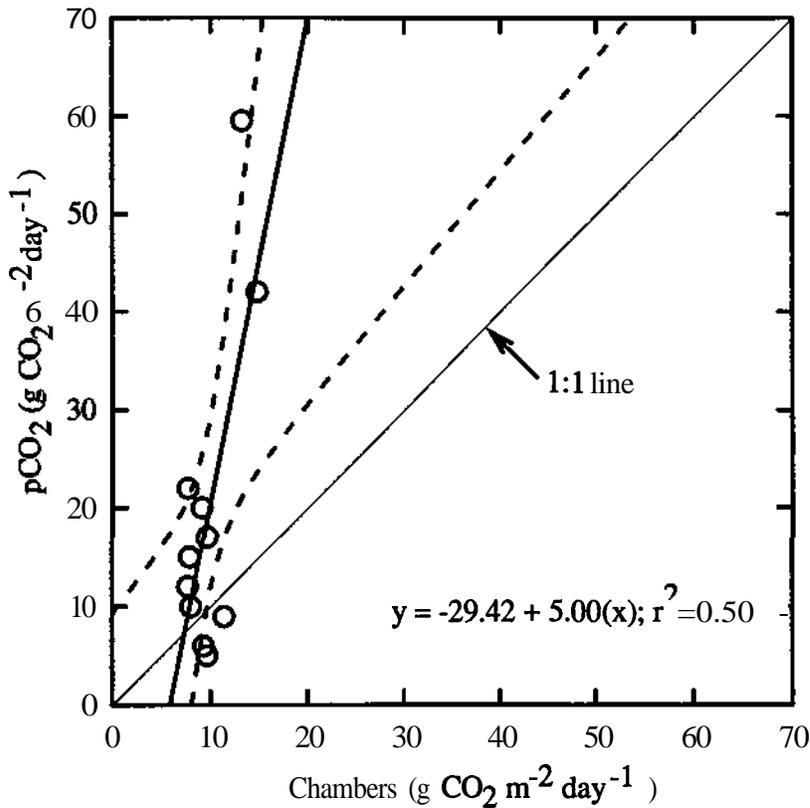
Note: **Contrast "Chamber"** tests for a difference between 350CO<sub>2</sub> and chamberless treatments across levels of N. Since there is no significant difference between 350CO<sub>2</sub> and chamberless treatments, then **Contrast "CO<sub>2</sub> w/CC"** tests for a difference between the average of 350CO<sub>2</sub> and chamberless treatments vs. the average of the 525CO<sub>2</sub> & 700CO<sub>2</sub> treatments across nitrogen level; +10N nitrogen level is ignored. **Contrast "N"** tests for a difference between +ON vs. average of the +10N and +20N treatments across CO<sub>2</sub> level; 525CO<sub>2</sub> level is ignored. **Contrast "N control vs N high"** test for a difference between +ON vs. +20N treatments across CO<sub>2</sub>; +10N is ignored because it doesn't occur in every possible level of CO<sub>2</sub>, i.e., no 525CO<sub>2</sub> + 10N treatment.

### C. pCO<sub>2</sub> vs. IRGA Measurements

Comparisons between soil CO<sub>2</sub> flux using the pCO<sub>2</sub> method versus the dynamic IRGA method are shown in Figure 3. In this comparison, only IRGA based fluxes from time periods and soil chambers corresponding with the time and location of pCO<sub>2</sub> measurements were used. Results of the two methods were significantly correlated ( $r^2 = 0.50$ ;  $p < 0.05$ ); however, there were substantial differences in the magnitude of the flux estimates. In addition, the relationship was strongly influenced by the two most extreme values. The pCO<sub>2</sub> estimates were two- to three-fold greater than the IRGA based measurements and substantially greater than values reported in the literature. deJong et al. (1979) also found consistently higher values in soil CO<sub>2</sub> flux using the pCO<sub>2</sub> method compared with a continuous IRGA system. They attributed the majority of those differences to pressurizing the soil chambers and clipping aboveground plant material in the IRGA measurements. Pressurized chambers and clipping of plant material were not relevant factors in our study. Instead, differences between the methods in our study may be related to errors in determining the CO<sub>2</sub> diffusion coefficient for the pCO<sub>2</sub> technique. Because the pCO<sub>2</sub> technique is substantially easier and less expensive to conduct than the IRGA based technique, we will continue to explore its utility by improving upon the diffusion estimates using laboratory studies.

## IV. Summary and Conclusions

We quantified significant diurnal patterns in soil CO<sub>2</sub> flux using an automated IRGA based system. Most of this variation corresponded to diurnal variation in soil temperature. From these patterns, it is clear that methods which sample only a portion of this diurnal period may produce misleading results, particularly if



**Figure 3.** Comparison of soil CO<sub>2</sub> flux predicted with the pCO<sub>2</sub> method versus the IRGA based method. Dashed lines represent 95% confidence intervals of the regression.

data are extrapolated temporally. Although there was substantial variation in average daily fluxes (e.g., flux rates varied from 7 to 15 g CO<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>), integrated values of soil CO<sub>2</sub> flux were not significantly different among treatments. Fluxes were greatest for the midlevel CO<sub>2</sub> treatment, which was the treatment with the greatest root biomass. Differences between treatments may be detectable in subsequent years assuming that differential root biomass patterns continue. Our fluxes were comparable to studies where continuous IRGA systems were used, but substantially greater than studies using static techniques. A major limitation in comparing flux rates among studies is the uncertainty of methods. For example, we found that pCO<sub>2</sub> flux estimates were two to three times greater than IRGA based estimates.

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