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Quantitative Comparison of *In Situ* Soil CO₂ Flux Measurement Methods

Jennifer D. Knoepp and James M. Vose

The Authors

Jennifer D. Knoepp, Research Soil Scientist, and
James M. Vose, Project Leader, U.S. Department of
Agriculture, Forest Service, Southern Research Station,
Coweeta Hydrologic Laboratory, 3160 Coweeta Lab Road,
Otto, NC 28763.

Chemical terms used in this paper

BaCl ₂	barium chloride
BaCO ₃	barium carbonate
C	carbon
CO ₂	carbon dioxide
HCl	hydrogen chloride
KOH	potassium hydroxide
<u>M</u>	molar
NaOH	sodium hydroxide
OH ⁻	hydroxide ion
μmol m ⁻² sec ⁻¹	micromole per meter square per second

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Southern Research Station
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Abstract

Development of reliable regional or global carbon budgets requires accurate measurement of soil CO₂ flux. We conducted laboratory and field studies to determine the accuracy and comparability of methods commonly used to measure *in situ* soil CO₂ fluxes. Methods compared included two static techniques, sodium hydroxide (NaOH) and soda lime as CO₂ traps; a multichamber open dynamic system (OC) with an infrared gas analyzer; and a headspace analysis system, with gas chromatograph with circulating fan (GCF) and gas chromatograph without circulating fan (GC), measuring changes in headspace CO₂ concentration using a gas chromatograph. In the laboratory, we compared NaOH, OC, GCF, and GC using sand-filled cylinders to simulate a soil system. Three concentrations of standard CO₂ gas (representing low, medium, and high soil-CO₂ flux rates) entered the cylinders through individually monitored flow meters. Flux rates measured using the OC method equaled the actual CO₂ flux at all three CO₂ concentrations. Flux rates determined with GC and GCF were < 55 percent of the actual flux rate. The percent of actual CO₂ flux measured increased with increasing CO₂ concentrations. At all concentrations, NaOH collected between 40 and 47 percent of CO₂ entering the system. A field study was conducted to verify laboratory results and allow comparison with the soda lime trap (SODA) method. In laboratory and field studies, all methods detected significant differences in flux rates among the standard CO₂ concentrations and field sites. Regression analyses showed good relationships between NaOH, SODA, and GC methods with flux rates measured using the OC methods ($r^2 \geq 0.78$). Slope values for these regression equations ranged from 0.34 for NaOH to 0.54 for GC and SODA. These results suggest that data collected using the other methods could be standardized to OC flux rates. However, because methodological differences significantly affect CO₂ flux measurements, care should be used in applying these relationships.

Keywords: CO₂ traps, flux rates, gas chromatograph, infrared gas analyzer, NaOH base trap, open dynamic chamber, soda lime trap, soil respiration.

Introduction

Carbon dioxide fluxes from soil and organic matter on the soil surface are a major component of the global terrestrial C cycle (Raich and Schlesinger 1992). To develop accurate C budgets for terrestrial ecosystems, accurate quantification of soil, humus, and leaf litter fluxes (termed "forest floor CO₂ flux") are required. Net forest floor CO₂ efflux reflects the combined contributions of respiration from organic matter decomposition, micro and macro soil organisms, and root growth and maintenance. This combination of contributing sources often results in large spatial and temporal variability in forest floor CO₂ flux. The significance of forest floor CO₂

flux in terrestrial C budgets and its spatial and temporal variability require accurate and precise techniques that are simple enough to allow multiple site measurements.

Several techniques are available for measuring forest floor CO₂ flux, including static chambers containing soda lime or alkali base, traps (Cropper and others 1985, Edwards 1982, Raich and others 1990), soil CO₂ concentration profiles (de Jong and Schappert 1972), open dynamic chamber methods (OC) (Edwards and Sollins 1973, Garret and Cox 1973, Hanson and others 1993, Vose and others 1995), and head space analysis via gas chromatography (GC), often used when additional trace gas fluxes are of interest (Castro and others 1994). Techniques have been compared since the early 1930s (Smith and Brown 1932), and more recent comparisons have often revealed wide disparity among measured fluxes (Cropper and others 1985, Edwards and Sollins 1973, Norman and others 1992, Raich and others 1990, Rochette and others 1992). For example, static chamber techniques generally provide lower (10 to 30 percent) CO₂ flux estimates than dynamic chamber methods (Ewel and others 1987, Rochette and others 1992), and soil CO₂ concentration profile approaches are generally higher than dynamic chamber techniques (de Jong and others 1979). Variations in CO₂ flux estimates among techniques have been attributed to differing protocols, the interaction of certain techniques with environmental conditions (Edwards 1982, Naganawa and others 1989), and the magnitude of CO₂ flux (Jensen and others 1996, Rochette and others 1992). For example, the effectiveness of NaOH as a trap for CO₂ varies with base normality (Minderman and Vulto 1973), incubation time (Kirita and Hozumi 1966), soil moisture (Edwards 1982), and soil temperature (Naganawa and others 1989). Soil CO₂ fluxes measured with a base trap and an open dynamic chamber method are similar at low flux rates but differ greatly at high fluxes (Jensen and others 1996).

While the results of previous comparisons demonstrate an often predictable disparity among techniques, few studies have evaluated the accuracy of the various approaches (Hiroki and Watanabe 1997, Nay and others 1994) under controlled conditions. Our objective was to test the accuracy and comparability of common methods of measuring CO₂ flux from soil. Method accuracy was examined using a simulated soil system in the laboratory.

We tested the static base trap (NaOH), open dynamic chamber (OC), headspace analysis with gas chromatograph with a circulating fan (GCF) and without a circulating fan (GC). Field tests were conducted to verify results and included two static methods [NaOH and soda lime trap (SODA)] and two dynamic methods, OC and GC. Combining the laboratory results with field measurements allowed us to assess the comparability of methods.

Materials and Methods

We tested both static and dynamic methods of measuring soil CO₂ flux. First we mimicked a soil system and made laboratory comparisons of flux rates using sand-filled polyvinyl chloride (PVC) cylinders and a range of standard CO₂ gases. Second, we conducted field comparisons on a number of sites with a range of CO₂ flux rates. The laboratory comparisons, with known CO₂ flux rates, allowed us to test the accuracy of each method. The field comparisons allowed us both to verify the laboratory results and to compare the methods.

Open Dynamic Chamber

The OC method measures the difference in CO₂ concentration of inlet air (ambient) as it enters the chamber and outlet air as it leaves the chamber. The OC system consists of monitored air delivery and return systems and an ADC LCA4 infrared gas analyzer (IRGA). The OC system is automated, battery powered, and designed to measure soil CO₂ flux from 10 chambers, at 100-minute intervals, over a 24-hour period. Inlet air was delivered to the chamber from a 20-L bottle, which was located 20 m away from the sample collection site to prevent concentration fluctuations. Inlet air CO₂ concentration was measured (after drying with Drierite®) from the buffer using a second sample line connected to the IRGA. A perforated tube (diffuser) in the headspace of the chamber was used to mix inlet and headspace air (fig. 1A). Headspace air (outlet air) and inlet air were sampled simultaneously using a separate pump at a flow rate equal (+/- 5 percent) to inlet flow. Outlet air was dried and delivered to the IRGA for determination of CO₂ concentration. Inlet and outlet airflow rates resulted in at least one turnover of the chamber headspace per minute. Inlet and outlet CO₂ concentrations were measured for 10 minutes (differences between the inlet and outlet air stabilized after 6 to 7 minutes), and CO₂ flux rates were determined by the difference in inlet and outlet CO₂ concentration during the last minute of sampling [flux = (inlet CO₂ - outlet CO₂) x inlet flow rate].

Gas Chromatograph

The GC method measures change in headspace CO₂ concentration over time using a gas chromatograph. The area to be sampled was covered with a chamber top, and a gas-tight syringe was immediately inserted through a septum-covered access port to collect the initial gas sample. Successive samples were collected to determine change in chamber CO₂ concentration. Filling one 50-mL gas syringe with chamber air and rapidly expelling it into the chamber immediately before sample collection mixed headspace gases. Needles were sealed with septa until analysis. Five samples were collected from each chamber at 3- to 5-minute intervals, and exact times were recorded. Samples were analyzed for CO₂ concentration using a Varion 3700 GC. Flux rates were determined by calculating the slope of change in concentration over time using only the linear portion of the curve. The data were graphed to determine linearity, and linear regression analyses of the data were conducted ($r^2 \geq 0.95$). If nonlinearity was observed (i.e., an asymptote reached at the end of the measurement period), the nonlinear portion of the data was deleted and regression analysis conducted on the linear portion.

NaOH Base Trap

The base trap method (NaOH) is a static measurement method in which CO₂ entering the sample chamber is trapped by a chemical reaction with the base. NaOH (2.0 M) was put in an open jar and placed on or above the soil surface beneath a closed chamber. NaOH blanks (zero CO₂ flux) are necessary to calculate net CO₂ flux. In laboratory tests, NaOH in open jars was sealed in PVC cylinders at equilibrium with the standard test gas, and in field tests in 3.1-L cans at equilibrium with the atmosphere. NaOH traps were removed after 24 hours. Excess BaCl₂ was added to the NaOH to precipitate the carbonate as BaCO₃, and samples were titrated with standardized 1 M HCl to determine the amount of unreacted NaOH. Singh and Gupta (1977) found that the surface area of the NaOH solution in proportion to the total surface area covered by the chamber may affect the adsorption of CO₂. Anderson (1982) recommends that base solution surface area should be about 25 percent for the most efficient trapping of CO₂. Kirita and Hozumi (1966) found that the rate of CO₂ absorption was limited unless 80 percent of the base solution remained unreacted. The surface area of NaOH solution in our study was 4 percent in the field and 5 percent in the lab, suggesting that CO₂ flux measurements could be biased downward. We conducted a field test to calculate the effect of base trap surface area on CO₂ adsorption by 2.0 M NaOH. Base trap containers covering 5, 12, and 37 percent of the total collection area

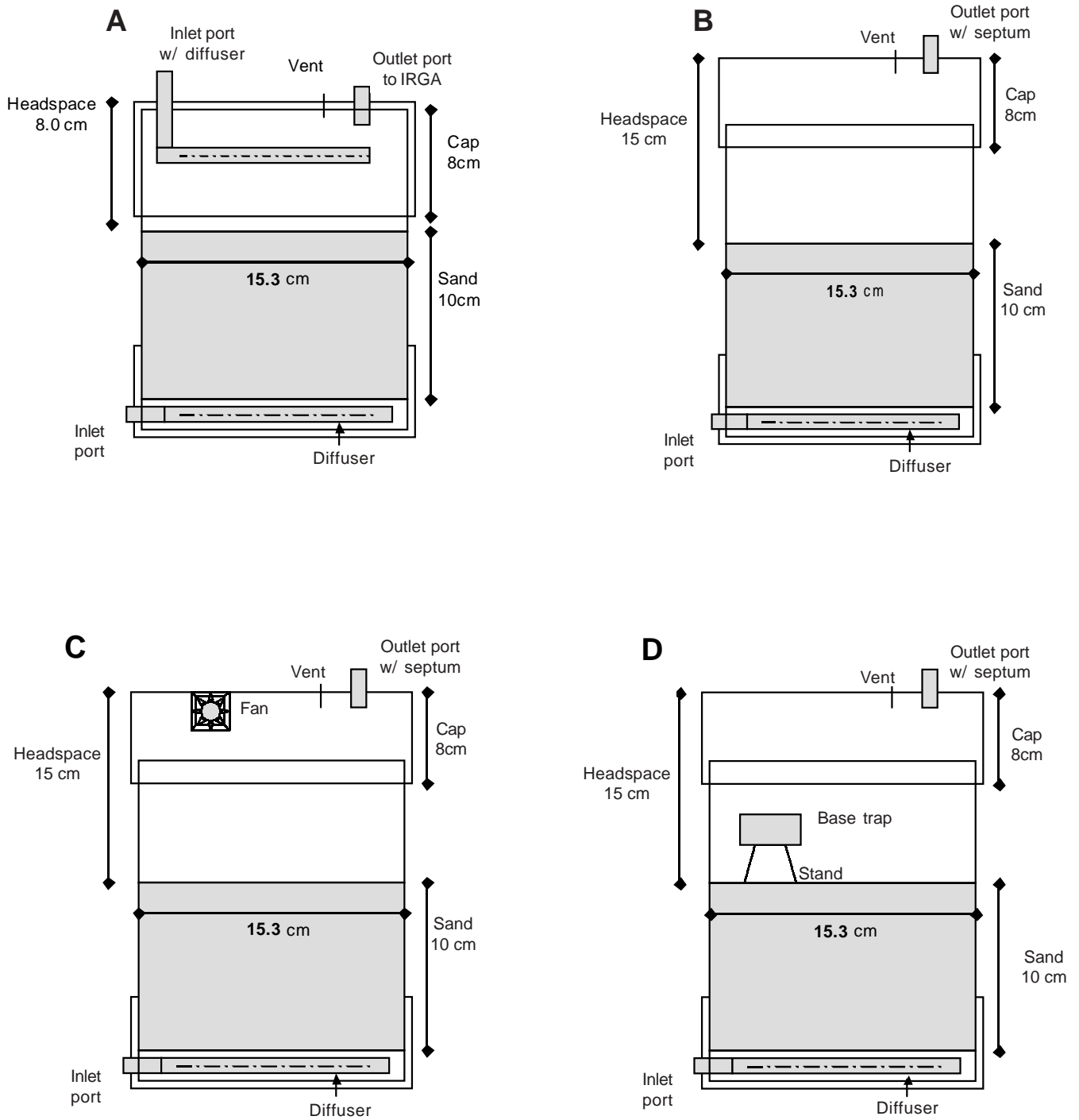


Figure 1— Diagram of cylinders used to simulate a soil system in the laboratory to compare in situ CO₂ flux methods. All cylinders contain 10 cm of Ottawa-density sand and an inlet port with diffuser in the base. Cylinders show modifications necessary for each method; (A) inlet port with diffuser in the cylinder headspace, no septum on outlet port (OC method); (B) no modification (GC method); (C) 4 cm circulating fan in cylinder headspace (GCF method); (D) stand and base trap container (NaOH method).

were used. There was no significant difference between CO₂ flux measured using the 5 and 12 percent trap size; however, the measured flux rate of the trap with a surface area 37 percent of the collection area was 15 percent greater than the other two sizes. Based on this finding, we corrected all NaOH measurements for base trap size prior to statistical analyses.

Soda Lime Trap

Another static measurement method used was the SODA method. In this method, soda lime is used to trap CO₂ entering the sample chamber. Oven-dried (105 °C) soda lime (1.5-2.0 mesh) was put in an open jar and placed on the soil surface beneath a closed chamber. Blanks necessary for CO₂ flux calculation were sealed in cylinders as described for the base trap method. Soda lime traps were removed after 24 hours, oven-dried, and reweighed to determine CO₂ absorbed.

Laboratory Comparisons

Laboratory comparisons were conducted using PVC cylinders to simulate a soil/gas system (fig. 1A-D) and generate known CO₂ fluxes. Within the cylinders, which were 15.3 cm inside diameter and 30 cm long, we placed a diffuser in the bottom chamber, 10 cm of Ottawa density sand, and PVC caps at the top and bottom with access ports. Standard CO₂ gases entered the PVC cylinders through the bottom access port. Headspace in the cylinders was 1470 cm³ for the OC measurements but 2756 cm³ for the other methods to allow space for any modifications. An airflow regulator maintained a constant pressure to a manifold that distributed the gas to each test cylinder at approximately 50 mL per minute. Flow meters linked to a data logger continuously monitored the actual flow rate of standard CO₂ into each cylinder. Before making any measurements, we flushed standardized gases through all cylinders until airflow in and airflow out reached equilibrium (about 2 hours). Blanks were set up for all methods tested. Blank cylinders also were equilibrated with the standard gases; then, gas flow was turned off and the bottom port of the cylinder was closed. We did not test the SODA method in the laboratory because dry CO₂ was delivered to the chambers, and soda lime requires the presence of water to react with CO₂.

Over about 2 months we measured CO₂ flux through the cylinders using each method. All measurements were compared with the actual CO₂ flux, which we calculated from recorded flow rates (approximately 50 mL per minute) and standard CO₂ concentrations. Standards used included 604

parts per million, 1,023 parts per million, and 3,039 parts per million CO₂, producing a range of CO₂ fluxes from 1.1 to 5.9 $\mu\text{mol m}^{-2} \text{s}^{-1}$, similar to those measured in most field studies.

We took lab measurements using four ports (three test cylinders, one blank) of the 10-port OC system (fig. 1A). Inlet and outlet airflow rates were approximately 1900 mL per minute allowing greater than one headspace turnover per minute. The balanced flow (inlet and outlet) and low-flow rates are shown to reduce or eliminate potential effects of pressure differences on flux estimates (Fang and Moncrieff 1996). Flux rates were calculated, and blank cylinder flux rates (no CO₂ flow) were subtracted.

We examined two variants of the GC method in the laboratory—the first using a standard PVC cap alone (fig 1B). In the second, we placed a 4-cm computer fan attached to a 9-V battery (GCF) inside the cylinder cap and used headspace analysis to determine the effect of air mixing on CO₂ flux measurements (fig. 1C). We collected five 20-mL gas samples for flux determination, at time zero and at 3-minute intervals. Actual sample collection times were recorded. We calculated flux rates and subtracted blank cylinder flux values.

For the NaOH method, we placed 20 mL of 2.0 M NaOH in a jar 3.6 cm in diameter on a stand on the sand surface and capped the PVC cylinder (fig. 1D). The NaOH traps and blank were removed after 24 hours, and total CO₂ absorbed determined. The blank-cylinder CO₂ value was subtracted from the measured flux rate.

Field Comparisons

Field measurements were conducted using NaOH, SODA, OC, and GC methods to determine soil CO₂ flux within 0.0625 m² aluminum bases inserted 2 cm into the soil. Plexiglass chamber tops (6.8-L volume) were used for measurements in three of the methods—NaOH, SODA, and GC. We located the bases in two groups of four about 30 m apart on three forest sites and in one fescue pasture (eight bases per site). Forest types included two aggrading mixed oak-hardwood communities with rhododendron in the understory and one aggrading cove hardwood community. Bases on the forested sites had been in place for 3 years as part of a separate study. The fescue pasture site was well maintained, fertilized, and limed regularly and harvested (hay) twice a year. Aluminum bases also were used on this site but were installed just before flux measurements. All sites were located on coarse or fine loamy-textured soils with high permeability in the Dystrochrepts or Hapludults great groups.

The four field sites were sampled between August 20 and October 2, 1997. Carbon dioxide flux measurements using all methods were made over a 30-hour period on each site. Weather patterns were stable at the time of measurement, and no precipitation events occurred during the flux-measurement period. The same measurement sequence was followed on all sites. First, NaOH and soda lime flux rates were measured coincidentally with two chambers of each group of four ($n = 4$ per site per method). Thirty-six mL of 2.0 M NaOH or 36 g of oven-dried soda lime were placed in a glass jar 5.5 cm in diameter. Jars were placed on the soil surface and covered with the chamber top for 24 hours. Blank values were obtained by placing identical jars of NaOH and soda lime in 3.1-L steel cans and sealing the lid for 24 hours.

Next, GC flux was measured after chamber tops were removed and bases left uncovered for 2 hours to allow soil gas flow to re-equilibrate. Measurements were made on the two sets of four bases sequentially ($n = 8$ per site). A time-zero gas sample (40 mL) was collected using a 50-mL gas-tight syringe after the plexiglass chamber tops were placed on bases and secured. Chambers were sampled again in the same order, approximately every 5 minutes, until five samples were collected from the headspace of each of the four chambers. Total time elapsed averaged 25 minutes. Sealed syringes were returned to the laboratory where samples were analyzed for CO₂ within 24 hours. Fluxes of CO₂ were calculated as previously described.

Finally, OC fluxes were measured after GC sample collection was complete. Chamber tops were removed and soil gas fluxes allowed to re-equilibrate for about 30 minutes (less time was necessary because chamber tops were in place for a shorter time for GC flux measurements than for static measurements). Measurements were made on the two sets of four bases sequentially ($n = 8$ per site). Four 1-L PVC chambers were placed in the center of the bases and pushed through the forest floor into the mineral soil to ensure that they were sealed from the atmosphere. Each chamber was sampled for 10 minutes to allow the CO₂ concentration within the chamber to equilibrate. Inlet and outlet airflow rates were 1000 mL per minute. These values were used to calculate CO₂ flux [flux = (outlet concentration - inlet concentration) x flow].

Statistical Analyses

Data were analyzed using the General Linear Models Procedure of SAS Institute Inc. (SAS 1985) and Tukey's mean separation test. For each method, accuracy was determined using laboratory data by calculating the difference between actual and measured CO₂ flux rates

through the PVC cylinder. Examining method differences among flux rates and sites for both laboratory and field measurements tested the comparability of methods. We determined method effectiveness by examining differences among sites for each method and conducted regression analyses using the mean value for each group of bases and each standard gas to establish the relationships among methods.

Results and Discussion

Laboratory Measurements—Accuracy

The OC system was the most accurate method; measured flux rates did not differ significantly from the actual rates calculated for each standard CO₂ gas (fig. 2). In contrast, the other methods were less accurate, and their measured flux rates were lower than the actual. For some, the magnitude of these differences varied with the actual flux rate. NaOH consistently measured 40 to 47 percent of the actual flux rate, whereas GC measurement accuracy increased with increasing actual flux rate (fig. 2). At the lowest flux rate (1.1 $\mu\text{mol m}^{-2} \text{s}^{-1}$), GCF measured a negative rate, and GC measured 19 percent of actual. Both GCF and GC methods measured approximately 30 percent of the actual flux for the medium rate (2.0 $\mu\text{mol m}^{-2} \text{s}^{-1}$) and 42 to 54 percent of the high flux rate (5.9 $\mu\text{mol m}^{-2} \text{s}^{-1}$) (fig. 2).

To assess the precision of measurement techniques, we compared coefficients of variation (CV's). Actual flux rates had CV's < 6 percent, which were caused by variation in flow rates among replicate PVC cylinders and represent the experimental error (fig. 3). Hence, the CV's of the four measurement techniques reflected the methodological error plus the experimental error. Considerable variation in CV's was observed among measurement techniques and across actual flux rates (fig. 3). In general, the OC method had the lowest CV's (5 to 12 percent), followed by NaOH (8 to 21 percent), GC (10 to 24 percent), and GCF (8 to 70 percent). With the exception of the NaOH method, CV's for all methods were lowest at the medium rate and greatest at the low rate.

A major limitation in evaluating techniques for measuring soil CO₂ flux *in situ* is the lack of an actual flux rate. We are aware of only two other attempts to generate a known CO₂ flux rate in the laboratory. Nay and others (1994) diffused CO₂ beneath a foam column and used Fick's law of diffusion to calculate the actual CO₂ flux rate from the foam surface. They found good agreement between a closed flow-through dynamic chamber system

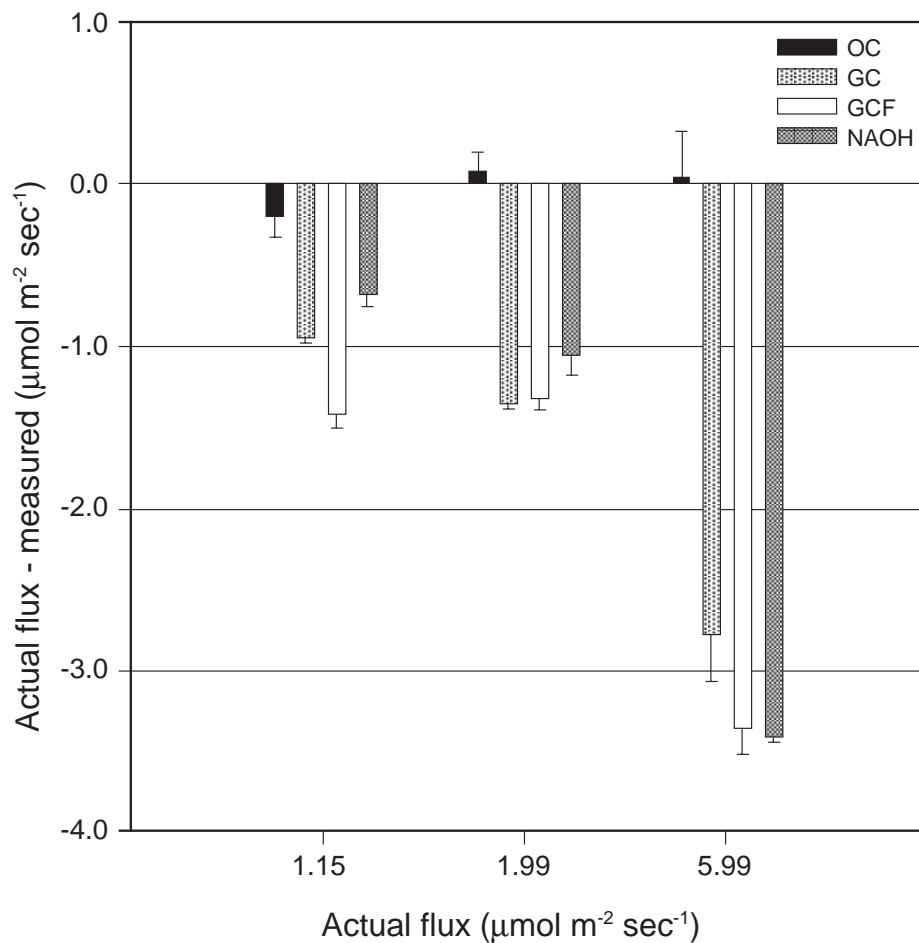


Figure 2—Results of laboratory experiment showing measured flux of CO₂ minus actual CO₂ flux (μmol m⁻² sec⁻¹). Solid bars represent mean values of three PVC cylinders used for each method and ⊥ represents standard errors.

[CDC-headspace air is recirculated to detect changes in CO₂ concentration (Norman and others 1992)] and actual flux, except at high actual flux rates (~5 μmol m⁻² s⁻¹) where measured flux was 20 percent lower than actual. Soda lime traps overestimated (25 percent) actual flux at low rates (~1 μmol m⁻² s⁻¹) and underestimated (57 percent) actual flux at high rates. Bekku and others (1997) measured glucose consumption and CO₂ flux by fungal respiration (maximum rates ~10 to 20 μmol m⁻² s⁻¹). They found good agreement (95 percent) among OC, CDC, and GC methods compared to calculated flux rates, whereas an alkali absorption method (1 M KOH) overestimated actual flux by 30 percent. Our laboratory results indicated that only the OC method provided accurate estimates of actual flux, whereas all other methods (GC, GCF, and NaOH) underestimated the CO₂ flux. Differences in these laboratory approaches to generating actual flux, the range of actual fluxes, and the choice of methods and protocols complicates any attempt to compare

them. Like previous laboratory studies (Bekku and others 1997, Nay and others 1994), our method for generating actual flux differed from natural processes. The efflux of CO₂ from soil occurs through the process of diffusion based on concentration gradients, whereas our technique used a continuous flow of CO₂ to generate actual flux. Hence, we also conducted field comparisons to determine if the patterns observed under controlled/artificial conditions were reproduced in the field.

Field Measurements—Comparability

All four methods—SODA, NaOH, OC, and GC—measured significant differences among the four study sites (tables 1, 2). In all methods, the pasture site had the greatest CO₂ flux rate (table 2). In general, field results were similar to those in the laboratory; CO₂ flux rates measured using the OC method were greater than those measured using all other

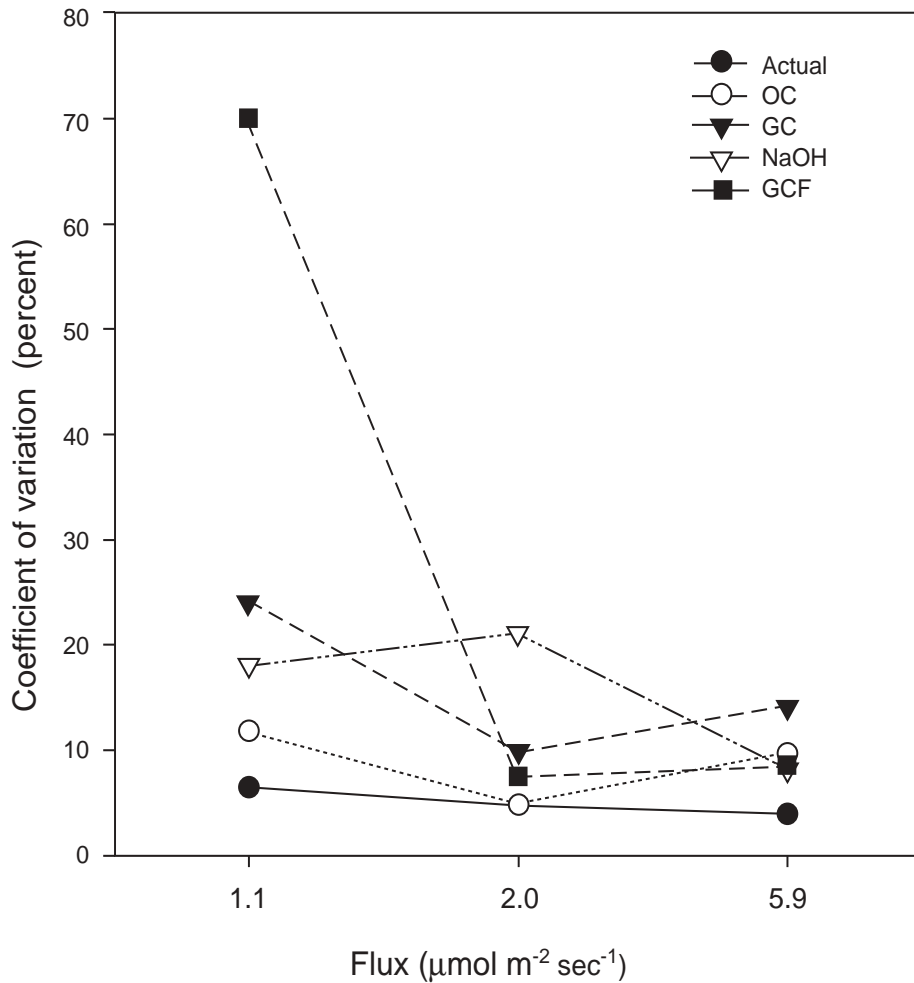


Figure 3—Coefficient of variation versus CO₂ flux rate ($\mu\text{mol m}^{-2} \text{sec}^{-1}$) in the laboratory showing the mean of all fluxes measured at low (1.1), mid (2.0), and high (5.9) flux rates. Values represent calculated actual fluxes (Actual, n = 12) and CV's for four methods tested (n = 3).

methods. The GC method measured 51 to 71 percent of the OC field flux rates, compared to 54 percent of OC at high CO₂ flux rates in the laboratory. Similarly, the NaOH field measurements were consistent with laboratory results, measuring 38 to 55 percent of the CO₂ flux measured by the OC. The SODA method gave inconsistent measurements when compared with OC. The percent of OC flux measured increased with increasing flux rates ranging from 11 to 40 percent.

Previous method comparisons have shown inconsistent responses using static trap methods, and results often vary with CO₂ flux rates (Cropper and others 1985, Edwards and Sollins 1973, Jensen and others 1996, Rochette and others 1992). Static chamber methods may overestimate or equal fluxes as determined with OC, CDC, or GC at low rates (e.g.,

Table 1—Results of analysis of variance examining the effect of site for each method

Method	df	F-value	Prob > F	CV
SODA	14	49.8	< 0.01	29
NaOH	15	7.0	< 0.01	33
OC	31	9.4	< 0.01	47
GC	31	6.2	< 0.01	44

df = degrees of freedom; Prob > F = probability of a value greater than F; CV = coefficient of variation; SODA = soda lime static trap; NaOH = 2.0 M NaOH static trap; OC = open dynamic chamber; and GC = gas chromatograph.

Table 2—Site means of *in situ* soil CO₂ flux (μmol m⁻² sec⁻¹) measurements for common methods

Method ^a	<i>In situ</i> soil CO ₂ flux (μmol m ⁻² sec ⁻¹) ^b							
	Forest 1		Forest 2		Forest 3		Pasture	
SODA(4)	0.68	(0.06)	0.22	(0.07)	0.24	(0.03)	2.13	(0.22)
NaOH (4)	1.06	(0.23)	0.75	(0.11)	1.23	(0.21)	2.04	(0.25)
OC (8)	2.66	(0.37)	1.96	(0.55)	2.24	(0.20)	5.32	(0.73)
GC(8)	1.90	(0.26)	1.26	(0.11)	1.28	(0.13)	2.74	(0.47)

SODA = soda lime static trap; NaOH = 2.0 M NaOH static trap; OC = open dynamic chamber; and GC = gas chromatograph.

^a Values in parentheses next to each method are the number of flux measurements in the mean.

^b Values in parentheses following each mean are standard errors of the mean.

when soils are cool), and underestimate fluxes when rates are high (Jensen and others 1996, Nakadai and others 1993, Nay and others 1994, Rochette and others 1997). In this study, both static methods yielded flux rates lower than the OC method in field and laboratory comparisons. Somewhat lower flux values in the static trap field measurements were expected due to the 24-hour sample period because this cumulative measure incorporates the diurnal variation in bulk soil CO₂ flux rates. We conducted the OC and GC measurements between 10 a.m. and 2 p.m., when CO₂ flux rates are increasing due to increasing soil temperature.¹ Diurnal measurements showed that midday flux rates range from 8 to 16 percent greater than the 24-hour mean. However, diurnal sampling does not appear to have affected the NaOH measurements, which were consistently 38 to 55 percent of the OC flux rate in both field and laboratory.

Some of the variation in results of NaOH method comparisons may be due to procedural differences. Minderman and Vulto (1973) found that measured CO₂ fluxes increase with increasing base trap molarity, with 2.0 M the maximum tested. Kirita and Hozumi (1966) found that when the amount of OH⁻ available for reaction falls below 80 percent, CO₂ absorption is limited. The lack of reactive base available may explain the decrease in measured CO₂ flux with increasing rates found in many studies. We used 2.0 M NaOH for our static trap method, assuring nonlimiting reactive base during the 24-hour measurement period, which could explain why we observed consistent measurements using NaOH across all flux rates in laboratory and field. The surface area of the base solution as a proportion of the collection chamber also affects the absorption of CO₂ (Singh and Gupta 1977). Studies have

shown that the surface area should be ≥ 6 percent of the soil surface covered by the chamber, and that maximum absorption may occur at about 25 percent coverage (Anderson 1982, Raich and Nadelhoffer 1989). The normality of bases used in previous methods comparisons ranges from 0.2 M to 1.0 M, and base trap surface areas covered between 16 and 25 percent of the total collection area (Cropper and others 1985, Edwards and Sollins 1973, Rochette and others 1992). Few studies have tested for the effect of collection solution surface area on flux rates with nonlimiting reactive base available, but our study indicates that for 2.0 M NaOH there was a 15-percent difference between 5 to 12 percent versus 37-percent base surface area.

The reliability of SODA as a CO₂ trap is dependent both on procedural differences, such as the amount and mesh size of the soda lime used (Minderman and Vulto 1973) and on environmental conditions during measurements. Because water is necessary for the adsorption of CO₂ by soda lime, the moisture content both of the soda lime and the soil air being sampled may affect adsorption (Edwards 1982). The variability in our results—11 to 40 percent when compared to OC—could result from site differences in soil moisture (cove versus midslope hardwood forest), a variable that was not noted in this study.

The few studies that compare OC and GC techniques indicate very good agreement between methods (Bekku and others 1995, Bekku and others 1997). In our study, the GC method considerably underestimated flux relative to the OC method, both in the laboratory and the field. One possible explanation for differences obtained in the field is the lack of a circulating fan in the GC chambers in the field comparison (6,670 cm³ volume). In laboratory tests, the circulating fan

¹ Knoepp, Jennifer D. 2001. Unpublished data on file with the author.

actually decreased measured CO₂ flux. However, the large chamber in the field test may require better mixing of gases in the headspace than was obtained by sample collection procedures.

Based on the similarity of field and laboratory results, we concluded that the artificial approach (i.e., continuous supply of CO₂ beneath a sand column) used in the laboratory to simulate actual soil CO₂ flux yielded valid flux rate measurements. Hence, we combined field and laboratory data for regression analyses between NaOH, SODA, and GC, and the OC method (table 3). All methods were significantly correlated with OC (*p*-values < 0.01). Slopes were ≤ 0.53, indicating that all methods underestimated CO₂ flux rates compared with the OC method (fig. 4). The strength of the relationships between all methods and the OC method suggests that these equations

Table 3—Results of regression analysis showing relationship between *in situ* soil CO₂ flux methods, soda lime trap static chamber, NaOH trap static chamber, closed dynamic chamber—gas chromatograph method, and the open dynamic chamber—IRGA system

Method	df	Intercept ^a	Slope ^a	r ²
SODA	7	-0.79 (0.30)	0.53 (0.09)	0.85
NaOH	10	0.22 (0.21)	0.34 (0.06)	0.78
GC	10	0.05 (0.25)	0.53 (0.07)	0.86

df = degrees of freedom; SODA = soda lime static trap; NaOH = NaOH static trap; and GC = gas chromatograph method.
^a Values in parentheses following each mean are standard errors of the mean.

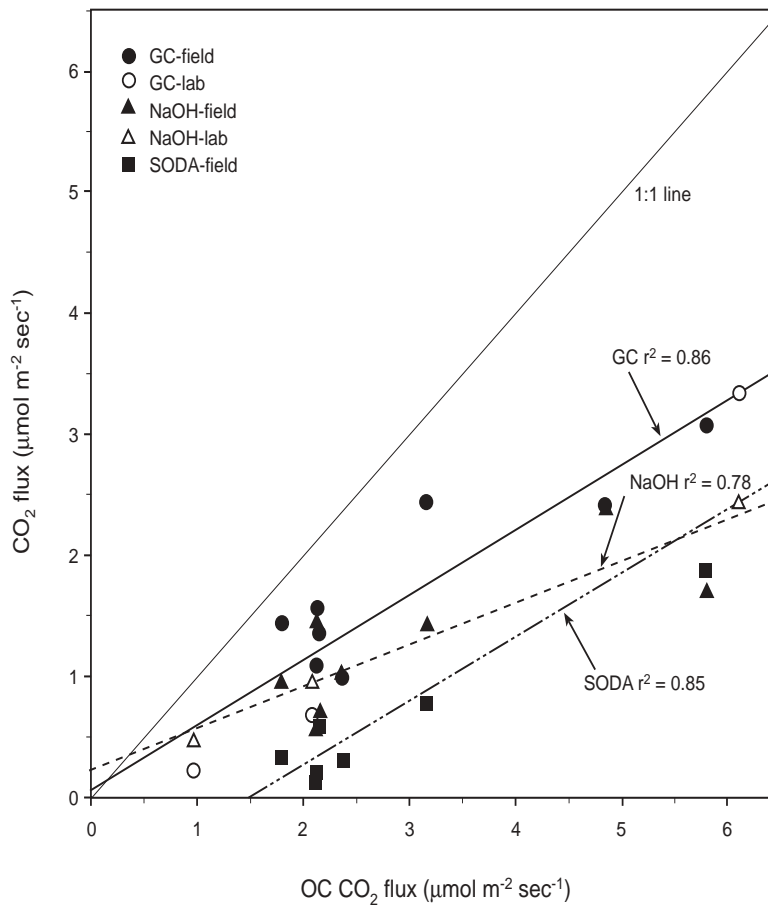


Figure 4—Regression of CO₂ flux measured with closed chamber system using gas chromatograph analysis of changes in headspace CO₂ concentration (GC), static 2.0 M NaOH base trap (NaOH), and static soda lime trap (SODA) with the open dynamic chamber infrared gas analyzer system (OC).

could be used to standardize flux measurements and allow comparisons of data in different studies. However, because method procedures may affect results, standardizing CO₂ flux rate measurements using different methods must be done carefully.

Laboratory studies showed that the OC system gave the most accurate CO₂ flux measurements. Field methods comparison showed that OC measurements yielded the greatest flux rates on all sampled sites. However, all methods tested—SODA, NaOH, GC, and OC—measured significant differences in flux rates among sites. This suggests that all four methods may be useful for detecting treatment effects and site differences, but only OC is suitable for estimating ecosystem carbon budgets.

Acknowledgments

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Development of reliable regional or global carbon budgets requires accurate measurement of soil CO₂ flux. We conducted laboratory and field studies to determine the accuracy and comparability of methods commonly used to measure *in situ* soil CO₂ fluxes. Methods compared included two static techniques, sodium hydroxide (NaOH) and soda lime as CO₂ traps; a multichamber open dynamic system (OC) with an infrared gas analyzer; and a headspace analysis system, with gas chromatograph with circulating fan (GCF) and gas chromatograph without circulating fan (GC), measuring changes in headspace CO₂ concentration using a gas chromatograph. In the laboratory, we compared NaOH, OC, GCF, and GC using sand-filled cylinders to simulate a soil system. Three concentrations of standard CO₂ gas (representing low, medium, and high soil-CO₂ flux rates) entered the cylinders through individually monitored flow meters. Flux rates measured using the OC method equaled the actual CO₂ flux at all three CO₂ concentrations. Flux rates determined with GC and GCF were < 55 percent of the actual flux rate. The percent of actual CO₂ flux measured increased with increasing CO₂ concentrations. At all concentrations, NaOH collected between 40 and 47 percent of CO₂ entering the system. A field study was conducted to verify laboratory results and allow comparison with the soda lime trap (SODA) method. In laboratory and field studies, all methods detected significant differences in flux rates among the standard CO₂ concentrations and field sites. Regression analyses showed good relationships between NaOH, SODA, and GC methods with flux rates measured using the OC methods ($r^2 \geq 0.78$). Slope values for these regression equations ranged from 0.34 for NaOH to 0.54 for GC and SODA. These results suggest that data collected using the other methods could be standardized to OC flux rates. However, because methodological differences significantly affect CO₂ flux measurements, care should be used in applying these relationships.

Keywords: CO₂ traps, flux rates, gas chromatograph, infrared gas analyzer, NaOH base trap, open dynamic chamber, soda lime trap, soil respiration.



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