Available online at www.sciencedirect.com
SCIENCE DIRECT®
Agricultural and Forest Meteorology 118 (2003) 113–124
AGRICULTURAL AND FOREST METEOROLOGY
www.elsevier.com/locate/agrformet

An automated sampler for collection of atmospheric trace gas samples for stable isotope analyses

A.J. Schauer*, C.-T. Lai, D.R. Bowling, J.R. Ehleringer

Stable Isotope Ratio Facility for Environmental Research, Department of Biology, University of Utah, 257 S. 1400 E., Salt Lake City, UT 84112-0820, USA

Received 8 November 2002; received in revised form 4 March 2003; accepted 4 March 2003

Abstract

Research focused on the isotopic composition of CO_2 exchange between terrestrial ecosystems and the atmosphere has been historically constrained by the need for personnel to be present at remote field sites for sample collection. In practice, this has limited sampling frequency and duration, and potentially even biases sampling events to fair weather periods. We have developed an automated sampling system that can be installed and used for unattended collection of 100-ml air samples in remote areas. The sampler was designed with the primary goal of collecting samples for analysis of CO_2 concentration and its isotopic composition in ecosystem-atmosphere flux research, but several other potential applications are also discussed.

Laboratory tests examined potential artifacts associated with sampler components. These tests included evaluation of potential isotopic exchange between atmospheric CO_2 and sampler component materials and the effects of sample exposure to these materials for up to 5 days and under a wide range of temperatures (10–50 °C). Some of the rejected component materials influenced either CO_2 mole fraction or CO_2 isotopic content. Exposure of air at subambient CO_2 concentrations to all sampler components in an intact system for 5 days resulted in a [CO_2] value that was 0.9 μmol mol^{-1} higher than for an equivalent sample collected by the sampler but not stored. Associated exposure-induced errors in $\delta^{13}C$ of CO_2 were generally small, ranging between 0.03 and 0.17‰ for 0 day versus 5 days exposure, respectively. These error values were within the sampling precision associated with a PreCon continuous flow mass spectrometer analysis. A more substantial exposure-induced error was observed for $\delta^{18}O$ in CO_2 (0.29 and 0.88‰, respectively). The potential for isotopic exchange between CO_2 and sampler components increased under a combination of elevated temperature and multiple-day storage treatments. These errors were small and of similar magnitude between 10 and 40 °C, but unacceptably large at 50 °C. Finally, we compared Keeling plots created with samples collected by the sampler with those collected simultaneously by a manual method and found no detectable differences between the two approaches. Based on these results, we conclude that sampler induced isotopic exchange for air samples held up to 5 days between 10 and 40 °C is largely within the overall precision limits of a PreCon continuous flow mass spectrometer measurement.

Keywords: CO_2; Carbon dioxide; Stable isotopes; Isotopic air sampling; Isoflux; Instrumentation

1. Introduction

The release of CO_2 during respiration by plants, animals, and microorganisms increases atmospheric CO_2 concentration, whereas photosynthesis decreases

* Corresponding author. Tel.: +1-801-581-8917; fax: +1-801-581-4665.
E-mail address: schauer@biology.utah.edu (A.J. Schauer).

0168-1923/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0168-1923(03)00065-0

atmospheric CO_2 at local, regional, and latitudinal scales. During respiratory and photosynthetic activities, the carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope ratios of atmospheric CO_2 are also modified, because the isotope ratios of CO_2 in the troposphere tend to differ from those of the biological components influencing the atmosphere (Keeling, 1958; Francey and Tans, 1987; Trolier et al., 1996; Flanagan et al., 1996, 1997; Flanagan and Ehleringer, 1998; Bakwin et al., 1998a). The isotopic compositions of these biological CO_2 fluxes can reveal information about ecosystem processes such as photosynthesis and respiration, and also insights into plant water stress, caloric expenditures in animals, and water resources in both plants and animals (Nagy, 1980; Lin and Ehleringer, 1997; Farquhar et al., 1989; Ehleringer et al., 2000).

We can non-intrusively characterize some biological CO_2 sources by analyzing their impact on the isotopic composition of CO_2 in the atmosphere. This is most frequently done by collecting air samples within forests to understand ecosystem-scale carbon exchange (Flanagan et al., 1996, 1999; Buchmann et al., 1997; Bowling et al., 2002; Pataki et al., 2003), from chambers where individual plants (Evans et al., 1986; Flanagan et al., 1994) or animals (Ampulski and Boggs, 1977; Schoeller et al., 1984) are maintained, or by sampling the gas respired by soils or within the soil profile (Cerling et al., 1991; Flanagan et al., 1999; Miller et al., 1999). In most of these cases, a Keeling plot (Keeling, 1958) approach is used, in which the measured carbon or oxygen isotope ratios of CO_2 in air are regressed versus the inverse of CO_2 mole fractions in order to determine the flux-weighted isotopic ratio of respiratory CO_2 (Flanagan and Ehleringer, 1998; Pataki et al., 2003). Over the past decade, flask sampling at the ecosystem-scale has revealed vast differences in the isotopic composition of ecosystem respiration in forests, grasslands, and cultivated lands (Buchmann et al., 1997; Buchmann and Ehleringer, 1998; Pataki et al., 2003). Studies have also shown that the isotopic composition of both soil and ecosystem respiration are influenced by recent meteorological conditions (Ekblad and Högberg, 2001; Bowling et al., 2002; Ometto et al., 2002) and that stand age has an impact on the isotopic composition of respiration from entire forest ecosystems (Fessenden and Ehleringer, 2002). In each of these cases, the isotopic composition of ecosystem respiration has been mechanistically interpreted, which allowed a better understanding of the relationships between physiological-scale and ecosystem-scale processes (Farquhar et al., 1989; Ehleringer and Field, 1993).

The required frequency of air sample measurements is different for oceanic and terrestrial measurements. When assessing photosynthetic and respiratory activities at the global scale, typically a single 1–2 L flask is collected manually at weekly intervals at different marine sites along a latitudinal gradient (Conway et al., 1994; Trolier et al., 1996; Bakwin et al., 1998a). At oceanic sites, this sampling intensity may be sufficient because of more uniform fluxes from oceanic surfaces. Yet carbon-flux over terrestrial surfaces tends to be more dynamic. Additionally, at the continental scale, point sources and heterogeneous landscapes must be taken into consideration. Characterizing regional terrestrial surfaces requires a greater sampling frequency with sampling not just from a single height but instead from a vertical profile, since much of the local- and regional-scale information is contained in the lower portions of the convective boundary layer (Flanagan et al., 1996; Bakwin et al., 1998b). Therefore, ecosystem-scale measurements at the stand level require more than a single-flask observation. Typically 10–15 100-ml flasks are required to characterize ecosystem respiration for a single time period with sufficient statistical resolution (Pataki et al., 2003). However, to date these measurements have usually been collected manually, which has generally limited ecosystem-scale sampling to seasonal observation capacities.

In this paper, we describe an automated system designed for installation to collect air samples at remote locations. Laboratory tests were undertaken to evaluate potential components and to assess the integrity of air samples collected using the sampler under a variety of temporal and thermal conditions. We describe the sampler and associated tests, followed by a discussion of several potential applications for the sampler.

2. Description of sampler

The automated air-flask sampling system (sampler) is enclosed in a 66 cm × 81 cm × 36 cm weatherproof fiberglass electrical enclosure (N4X-FG-302412CH, AD Products Company, Cleveland, OH) potentially

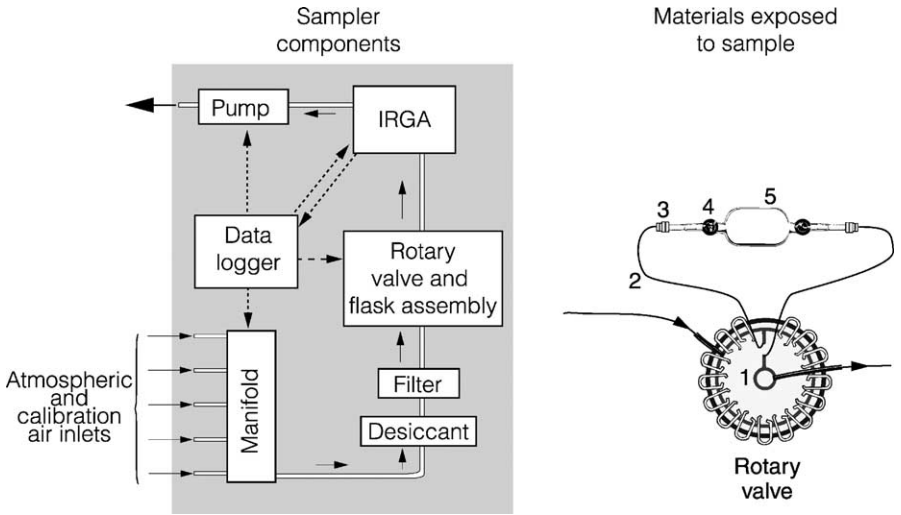

Fig. 1. During sample collection, the automated system routes air through the manifold, a desiccating magnesium perchlorate trap, a 7-μm filter, a 16-position rotary valve, 1 of 15 flasks, an IRGA, and a pump. Once a sample is collected it is exposed to the valve-rotor material (1), acetone-treated stainless steel tubing (2), Viton O-rings (3), Teflon stopcocks (4), and glass (5).

for permanent installation and weighs 23 kg. It can be powered by either AC or DC sources and requires 50 W. To comply with statistical requirements for characterizing ecosystem respiration, 15 flasks are used for each sampling session. During sampling, air is routed from a filtered inlet through tubing, a valve manifold to select among different inlet lines, 20 cm (640 cm^3) of magnesium perchlorate ($Mg(ClO_4)_2$) in a desiccating trap, a filter, a 16-position trapping flow path rotary valve, 1 of 15 glass flasks, an infrared gas analyzer (IRGA), and a pump (Fig. 1). All tubing external to the automated system is 0.64 cm O.D. high-density polyethylene (type 1300 Synflex, formerly known as Dekoron, Saint-Gobain Performance Plastics, Mantua, OH). Two-way, normally closed, manifold-mount solenoid valves (EV-2M-12, Clippard, Cincinnati, OH) are used to select among air inlets and are mounted to a six-valve manifold (15481-6, Clippard). Brass barb fittings and tubing (Bev-A-Line IV, Thermoplastic Processes Inc., Stirling, NJ) are used to interface between the Synflex tubing and the manifold. The solenoid valves, the 16-position trapping flow path rotary valve (EMTST16MWM, containing Valcon M type rotor material, Valco Instruments Company Inc., Houston, TX), the IRGA (Li-800 Gas Hound, Li-Cor Inc., Lincoln, NE), and the pump (UNMP50KNDC, KNF Neuberger Inc., Trenton, NJ) are controlled by a data logger (CR23X, Campbell Scientific, Logan, UT) (Fig. 1) via two six-channel relay drivers (A6REL-12, Campbell Scientific). Air is filtered to 1 μm on uptake (9967-008, Gelman Filter Assembly, Li Cor Inc.) and again to 7 μm (SS-2F-7, Swagelok Company, Cleveland, OH) downstream of the desiccant trap. Tubing downstream of the manifold is 0.32 cm O.D. chromatography-grade stainless steel (Type 304, Alltech Associates Inc., Deerfield, IL). The glass sample flasks are ∼100 ml and are equipped with Teflon stopcocks at two ends (34-5671, Custom Glass Shop at Kontes, Vineland, NJ). The glass flasks are connected to the stainless steel tubing using Ultra-Torr fittings (SS-6-UT-6-4, Swagelok Company, Cleveland, OH) that contain Viton FKM O-rings. Viton is a fluoroelastomer manufactured by DuPont-Dow and is commonly used in sealing applications. Convoluted stainless steel tubing (321-4-X-1, Swagelok) is used on one end of each flask to minimize chipping and breakage of glass tips while installing and removing sample flasks. The flow rate measured at the exhaust is 25 ml s^{-1}. The rotary valve is used to select a single flask from among the 15 flasks and seal the 14 other flask paths. One of the 16 valve positions is always open. Fifteen of the flask paths are routed through the sample flasks, while the 16th path is simply a bypass loop to allow the rotor

to seal all 15 flasks after sampling is complete. After a sample is collected, it is exposed to the valve rotor material, acetone-washed stainless steel tubing, Viton FKM O-rings, Teflon stopcocks, and glass (Fig. 1).

3. Laboratory testing

Several laboratory tests were performed to assess the potential influence of the sampler on the integrity of air samples. These tests evaluated potential isotopic fractionation associated with (1) individual components that are exposed to the air sample once collected and (2) the complete sampler using compressed gas standards of known isotopic composition and CO_2 mole fraction. A third test was conducted to compare automated and manual methods of air sample collection. The air used for testing was either from a compressed air cylinder ($\delta^{13}C = -9.96‰$, $\delta^{18}O = 29.88‰$, $[CO_2] = 252.8\,\mu mol\,mol^{-1}$) or mid-afternoon atmospheric air (typically $\delta^{13}C = -8‰$, $\delta^{18}O = 38‰$, $[CO_2] = 365\,\mu mol\,mol^{-1}$). Values of $\delta^{13}C$ and $\delta^{18}O$ are reported relative to V-PDB and V-SMOW scales, respectively, throughout this paper.

3.1. Individual component tests

Previous tests in our laboratory have shown that air samples stored in our 100-ml sample flasks showed no detectable change in CO_2 mole fraction or carbon or oxygen isotopic compositions over a time period of 90 days (Ehleringer and Cook, 1998; Schauer and Ehleringer, unpublished data). Therefore, selected individual materials that comprise the sampler were exposed to air samples after flasks had been filled. These included rotor materials in the rotary valve, stainless steel tubing, and Viton O-rings used in the Ultra-Torr fittings (Fig. 1). In all tests, air was dried with fresh $Mg(ClO_4)_2$ prior to introduction to the flasks, and control flasks were placed upstream of treatment flasks.

We evaluated potential isotopic exchange between CO_2 and two rotor sealants associated with valve switching and sample isolation. Rotor material shavings for the Valcon M and Valcon P type rotors were obtained from Valco Instruments Company Inc.; the Valcon M rotor material is a high-density polyethylene; the Valcon P rotor material is a polyphenolene sulfide with a carbon fiber and Teflon matrix (see VICI rotor material web page for more information, http://www.vici.com/ref/mat_rotr.htm#valm). Rotor material shavings were inserted into flasks equipped with septum ports and Teflon-lined silicone liners (98450, Alltech Associates Inc., Deerfield, IL), evacuated, flushed with mid-afternoon atmospheric air, and allowed to incubate for 6 days at temperatures that fluctuated diurnally between 25 and 50 °C ($n = 5$ sets). Approximately 0.25 g of material was placed into treatment flasks, which is several orders of magnitude greater than the exposed surface area in an intact sampler. Control flasks were identically equipped with septum ports and Teflon-lined silicone liners and subjected to identical conditions (in this and all subsequent tests).

Type 304 chromatography-grade stainless steel tubing was tested as delivered directly from the manufacturer (untreated), and after being flushed with HPLC grade acetone to remove any residual organic materials and heated to 70 °C while flushing with compressed N_2 for 12 h (treated). Both treated and untreated stainless steel tubing were cut into 1-cm pieces, inserted into flasks equipped with septum ports and Teflon-lined silicone liners, evacuated, flushed with mid-afternoon atmospheric air, and allowed to incubate for 5 days at 25 °C ($n = 10$).

Viton O-rings are known to influence the isotopic composition of CO_2 in very small flasks (Revesz and Coplen, 1991). The effect of Viton O-rings on sample air was tested by flushing three flasks connected in series using the Ultra-Torr fittings containing Viton O-rings with the compressed air; the stopcocks of the outside two flasks were closed, while the stopcocks of the inside (treatment) flask were left open, thus leaving the treatment flask exposed to the O-rings. This series of three flasks was incubated for 5 days at 25 °C ($n = 5$ sets). In contrast to the rotor material test, a representative O-ring surface area was exposed to the sample, rather than an excessive surface area.

3.2. Intact sampler tests

Two temporal tests of the intact sampler with all components were performed; we will refer to these as the “immediate” and “long-term” tests. Flasks were filled using a manual method commonly used in the field (e.g. Flanagan et al., 1996; Bowling et al., 2002;

Fessenden and Ehleringer, 2002; Ometto et al., 2002) which included a $Mg(ClO_4)_2$ trap, a 1 μm filter, a single flask, an IRGA, and a pump. In both, the compressed air source was used to maintain a buffer volume at slightly positive pressure. Air samples (and controls) were obtained from this buffer volume via a downstream pump for both methods. Flasks were isolated and removed either immediately after flushing (immediate test; $n = 6$ samplers and 59 flasks), or were allowed to incubate with the stopcocks open for 5 days at 25 °C (long-term test; $n = 7$ samplers and 99 flasks). During these tests, the intact sampler contained only materials that were accepted based on individual component tests (described below). The long-term sampler test was repeated at 10, 25, 40, and 50 °C. Flask stopcocks were left open for 5 days, leaving the rotary valve to isolate each air sample.

3.3. Automated versus manual tests

Our primary application for the sampler is collection of air samples to investigate ecosystem processes (e.g. Flanagan et al., 1996; Bowling et al., 2002; Fessenden and Ehleringer, 2002; Ometto et al., 2002). This approach involves establishment of an isotopic mixing line, where the carbon isotope ratios of CO_2 in flask samples are plotted against the inverse of measured $[CO_2]$ in the flask (commonly called a Keeling plot; Keeling, 1958). Air samples are collected at night as respiratory CO_2 builds within the nocturnal boundary layer. The *y*-intercept of this isotope—inverse concentration regression is the flux-weighted isotopic signature of total ecosystem respiration. We tested the sampler by comparing Keeling plots constructed with samples collected by (1) the sampler and (2) manual methods used in past studies (e.g. Flanagan et al., 1996; Bowling et al., 2002; Fessenden and Ehleringer, 2002; Ometto et al., 2002). Samples were collected simultaneously via the two approaches from the same inlet location on the roof of our laboratory as urban activities generated CO_2 during peak rush hour traffic.

3.4. Analytical and statistical methods

Air samples were analyzed for both carbon and oxygen isotope ratios using continuous flow isotope ratio mass spectrometery (Finnigan MAT 252 or DeltaS, Finnigan MAT, San Jose, CA) as described by Ehleringer and Cook (1998), and for CO_2 mole fraction as described by Bowling et al. (2001a). To evaluate treatment effects, results are presented as the root mean square (RMS) difference between treatment and control measurements. In an attempt to isolate effects associated with the sampler, an outlier test (Dixon, 1950) was conducted to remove potential human errors on manual and intact sampler tests using 1.645 S.D. (90% confidence interval) on treatment flasks. Data are presented before and after removing outliers. The RMS error was compared with overall measurement precision. The overall mass spectrometer measurement precision for a 400 μl atmospheric sample with a pre-concentrator (PreCon) operating in continuous flow mode was 0.12‰ ($\delta^{13}C$) and 0.16‰ ($\delta^{18}O$). The CO_2 mole fraction precision on a ~100 ml atmospheric sample was 0.2 μmol mol^{-1} as measured in the lab on a bellows/IRGA system (Bowling et al., 2001a). Following the tests of individual components, materials for the sampler were accepted or rejected based on their RMS error from controls.

4. Results

The test results of individual components that could be used in the sampler are shown in Fig. 2. The Valcon P rotor material elicited the largest exchange effect on sample air relative to all other tested materials, with RMS errors of 0.81‰ ($\delta^{13}C$), 7.78‰ ($\delta^{18}O$), and 16.1 μmol mol^{-1} ($[CO_2]$). In contrast, the Valcon M rotor material influence on sample air was much less with RMS errors of 0.12‰ ($\delta^{13}C$), 0.78‰ ($\delta^{18}O$), and 0.4 μmol mol^{-1} ($[CO_2]$) (Fig. 2). Although the actual surface area exposed to sample air during use of the sampler is much smaller than in our tests, it is likely that some isotopic exchange could occur during sampling if Valcon P material were used. Therefore, we selected the Valcon M rotor material for the construction of the sampler.

Of the accepted materials, the stainless steel tubing contributed the greatest source of error on $\delta^{13}C$, $\delta^{18}O$, and $[CO_2]$ (Fig. 2). The untreated stainless steel tubing had a large exchange effect on sample air, with RMS errors of 0.28‰ ($\delta^{13}C$), 1.56‰ ($\delta^{18}O$), and 2.7 μmol mol^{-1} ($[CO_2]$). Treated stainless steel tubing had less potential for exchange with CO_2. To minimize the effects of oils and other compounds

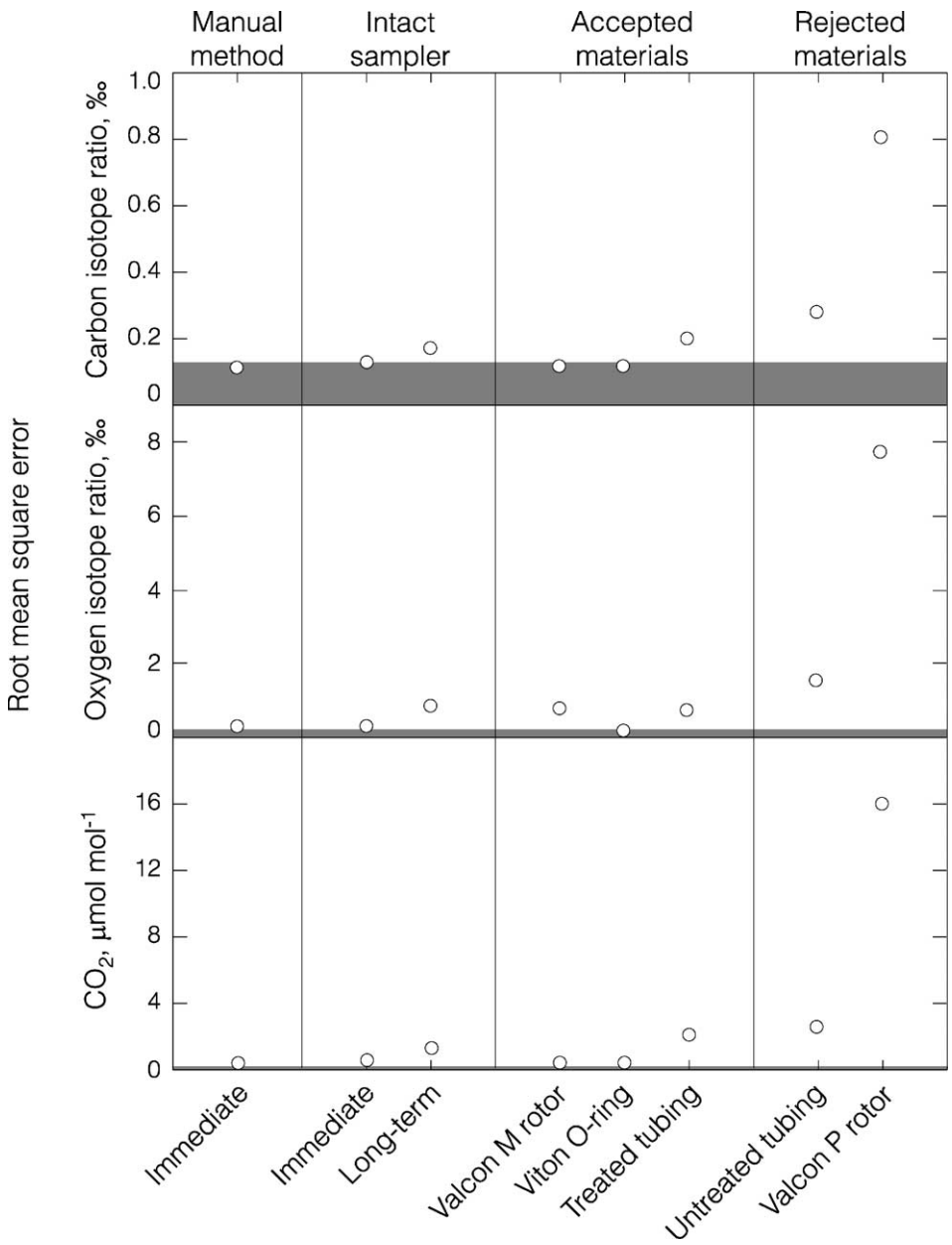

Fig. 2. Root mean square exposure-induced error of $\delta^{13}C$, $\delta^{18}O$, and $[CO_2]$ using control versus treatment flasks for a manual method commonly used to collect flasks (left panel), the intact automated system (second from left), and materials that are exposed to the sample upon collection (two right-most panels). All tests were conducted at 25 °C. The intact sampler contained accepted materials only. Shaded regions indicate mass spectrometer and CO_2 mole fraction precision ($\delta^{13}C = 0.12‰$ (V-PDB), $\delta^{18}O = 0.16‰$ (V-SMOW), and $[CO_2] = 0.2\,\mu mol\,mol^{-1}$).

used and produced during the production of the chromatography-grade stainless steel tubing used in the sampler, we treated all tubing prior to installation in the sampler.

The Viton O-rings did not significantly affect the value of sample air in our tests with RMS errors of 0.12‰ ($\delta^{13}C$), 0.10‰ ($\delta^{18}O$), and 0.1 μmol mol^{-1} ([CO_2]) (Fig. 2). While Revesz and Coplen (1991) cautioned against the use of Viton when analyzing $\delta^{18}O$ in CO_2 with small sample volumes, our sample volume was larger and exposure duration was reduced relative to that in Revesz and Coplen (1991) experiments.

Prior to conducting the outlier test, the manual method and the immediate and long-term sampler data are summarized along with post-outlier test data (Table 1). Using a 90% confidence interval as a threshold, we preserve 93.4% of the data points while significantly reducing the RMS error (Table 1). The data from the long-term test are presented as a histogram (Fig. 3) to explicitly describe the removal of outliers. Manual method and immediate and long-term data reported in Fig. 2 are filtered. The intact sampler did not alter the $\delta^{13}C$, $\delta^{18}O$, and [CO_2] of CO_2 in sample air immediately upon collection (Fig. 2). A 5-day incubation at 25 °C influenced the $\delta^{18}O$ and [CO_2] of CO_2 in sample air, yielding a RMS error of 0.88‰ and 1.5 μmol mol^{-1}, respectively. The RMS error for $\delta^{13}C$ was 0.17‰, which is similar to our measurement precision of 0.12‰. Increased incubation temperature led to increased exchange impact on $\delta^{13}C$, $\delta^{18}O$ and [CO_2] of CO_2 in sample air (Fig. 4). Based on our tests, it is suggested that samples remain exposed to the sampler materials for no more than 5 days and that the ambient temperature inside the sampler enclosure be continuously monitored and maintained below 40 °C once samples have been collected to ensure sample integrity.

The Keeling plots of manually and automatically collected samples were similar (Fig. 5). The larger

Table 1
The mean difference from control flasks (μ), standard deviation (σ), number of flasks (N), number of samplers or sets of flasks (sets), and root mean square error (RMS error) for $\delta^{18}O$ (‰), $\delta^{13}C$ (‰), and [CO_2] (μmol mol^{-1}) of the manual method of filling flasks (manual), immediate automated system treatment (immediate), and long-term automated system treatment (long-term)

Treatment	μ	σ	N	Sets	RMS error
$\delta^{18}O$					
Manual raw	−0.09	0.283	15	1	0.287
Manual filtered[a]	−0.09	0.217	13	1	0.226
Immediate raw	0.50	3.221	59	6	10.450
Immediate filtered[a]	−0.09	0.540	57	6	0.294
Long-term raw	−0.57	1.494	99	7	1.592
Long-term filtered[a]	−0.55	0.688	92	7	0.880
$\delta^{13}C$					
Manual raw	−0.05	0.140	15	1	0.142
Manual filtered[a]	−0.07	0.086	14	1	0.111
Immediate raw	−0.01	0.223	59	6	0.049
Immediate filtered[a]	0.01	0.168	55	6	0.028
Long-term raw	−0.10	0.176	99	7	0.202
Long-term filtered[a]	−0.10	0.132	90	7	0.166
[CO_2]					
Manual raw	−0.03	0.279	15	1	0.271
Manual filtered[a]	−0.09	0.114	14	1	0.144
Immediate raw	−0.72	0.622	59	6	0.903
Immediate filtered[a]	−0.69	0.405	57	6	0.639
Long-term raw	1.60	4.025	96	7	4.311
Long-term filtered[a]	0.77	1.320	90	7	1.522

Raw indicates no outlier tests. Filtered indicates the application of the Dixon outlier test using 1.645 S.D. (90% confidence interval) as the threshold. The RMS error is the S.D. of treatment flasks from control flasks.

[a] Indicates the RMS error is also presented in Fig. 2.

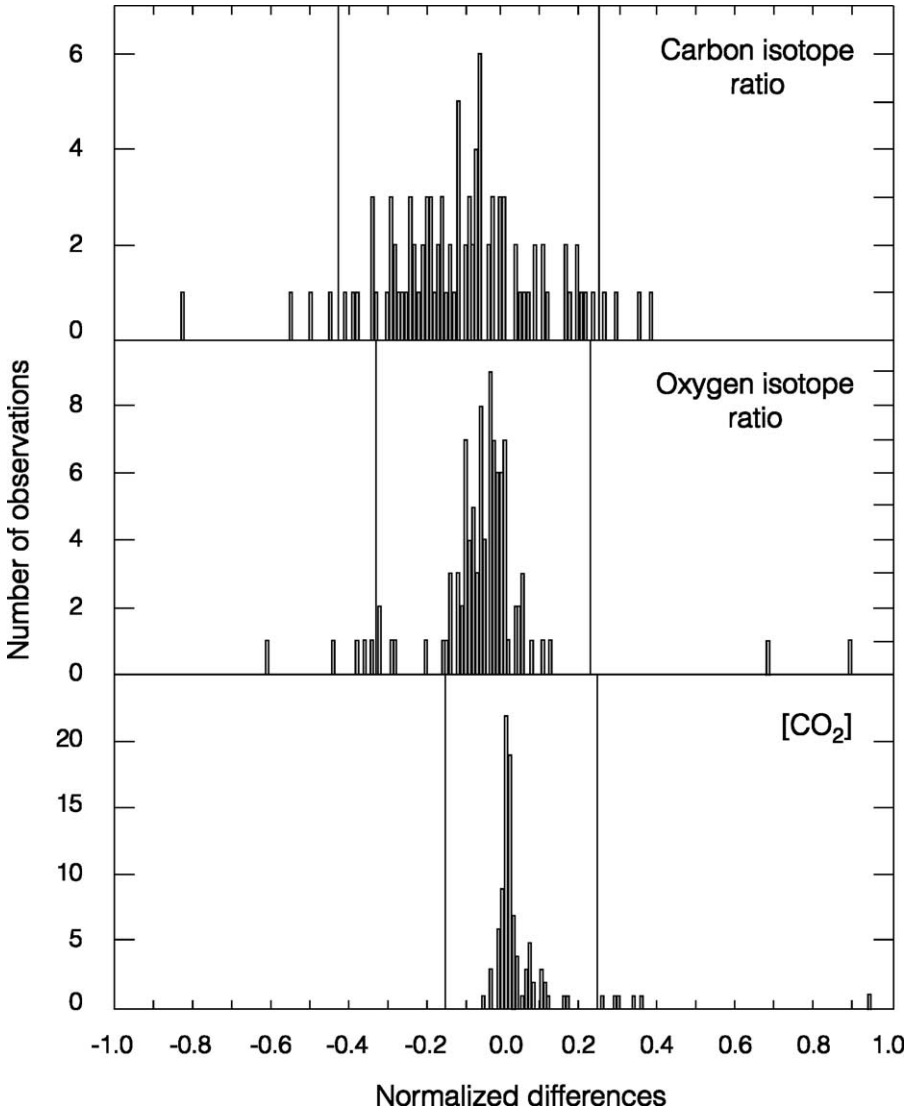

Fig. 3. Histograms of $\delta^{13}C$, $\delta^{18}O$, and [CO_2] data (flask minus control mean) from the long-term test of the sampler. The distributions were normalized from -1 to $+1$ for graphical purposes. Vertical lines ($\sigma \times 1.645$) indicate the boundaries for the outlier test.

standard error of the intercepts in the first test (0.7 and 1.3 $\mu mol\,mol^{-1}$ for the automated and manual tests, respectively) relative to the second test (0.8 and 0.3 $\mu mol\,mol^{-1}$ for the automated and manual tests, respectively) was associated with a smaller overall CO_2 range. Pataki et al. (2003) have shown that the standard deviations associated with calculated intercepts from Keeling plots are inversely proportional to the range in CO_2 concentrations. There was no indication that the automated system influenced air samples in any systematic manner and therefore the predicted isotope ratio of the respiratory source was similar between automated and manual collection methods.

5. Discussion

There are clear advantages and limits to using this sampler configuration for the isotope ratios of atmospheric CO_2. The overall carbon isotopic precision of

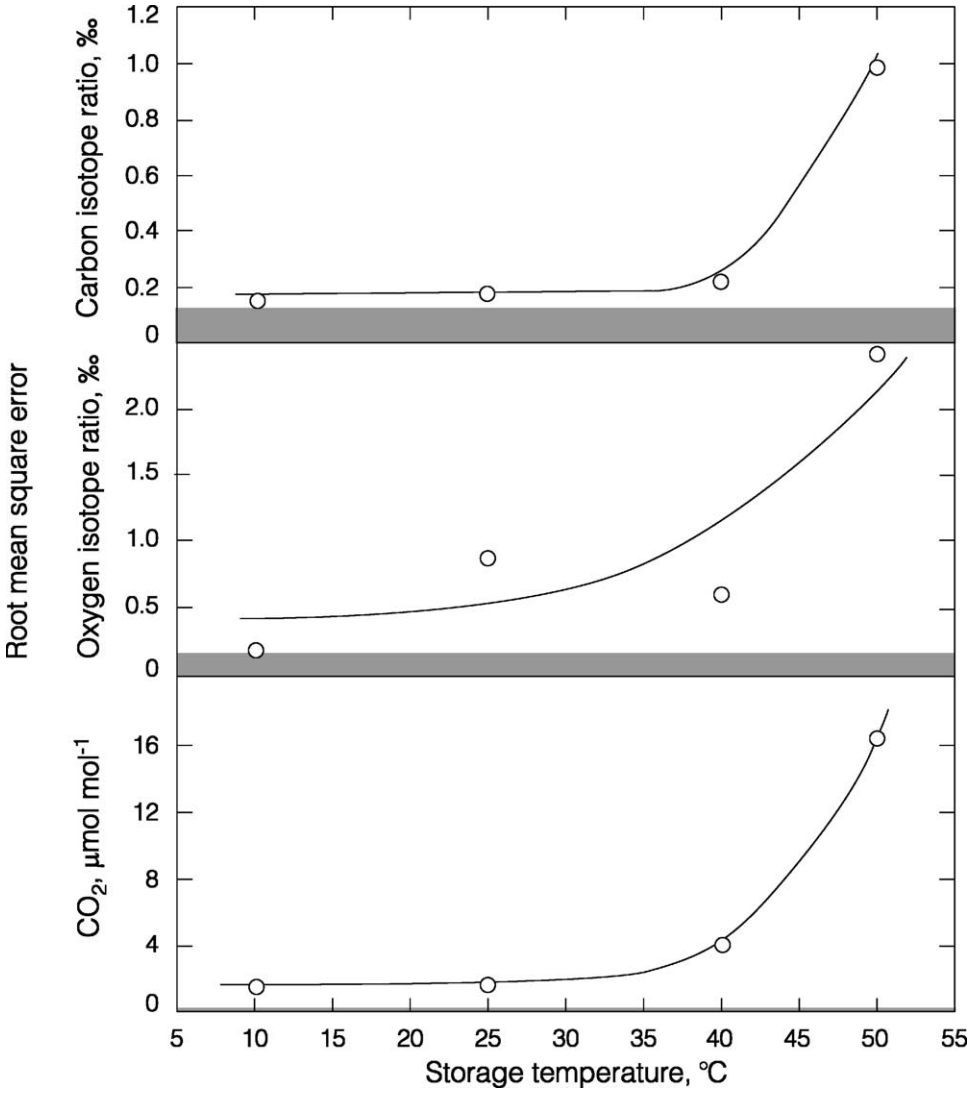

Fig. 4. The long-term intact autosampler test from Fig. 2 is shown here at four temperatures. Flask stopcocks were open for exposure to the materials described in Fig. 1, and temperature was held constant for 5 days. Shaded regions are as in Fig. 2.

the measurements using this sampler was similar to the continuous flow analysis method as described by Ehleringer and Cook (1998), suggesting that the precision limits were determined by the mass spectrometer approach used to measure isotope ratios rather than contaminants and exchanges with sampler materials. However, if an alternate mass spectrometer analytical technique were used with greater precision, such as that described by Ribas-Carbo et al. (2002), it is likely that the overall precision of the carbon isotope ratio measurements could improve to 0.02‰. This may not be the case with respect to oxygen isotope ratios of CO_2, where our results suggested that some isotopic exchange was occurring between sampler components and CO_2 over time. Since we know that there is no isotopic exchange occurring within the glass flask, then the small oxygen isotope ratio contamination was likely occurring as CO_2 interacted with organic components within the sampler. One possible improvement and solution to reduce the variance

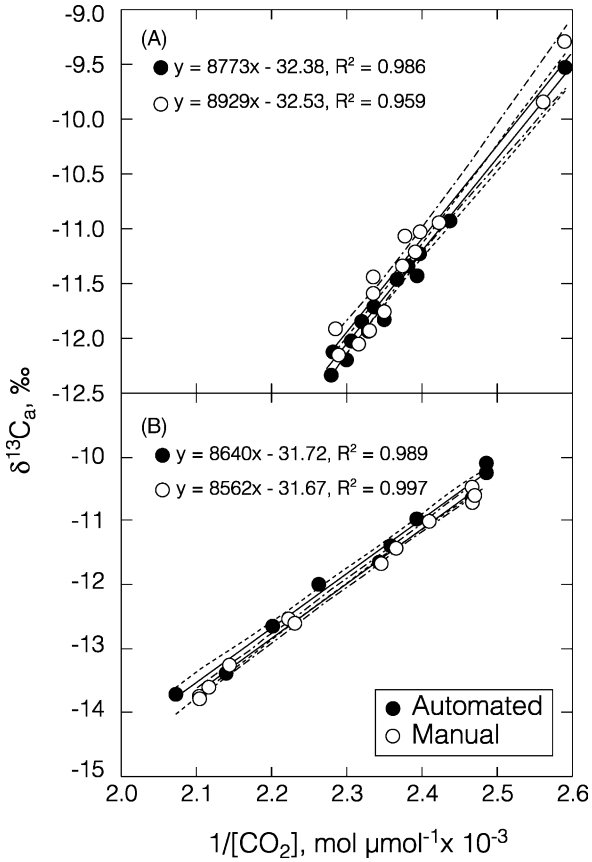

Fig. 5. Keeling plots constructed with air samples collected automatically (closed circles) and manually (open circles) from the same atmospheric inlet during the same time period. Panels A and B represent two separate tests. The intercepts (± standard error) for the automated and manual sets, respectively, were A -32.4 ± 0.7 and -32.5 ± 1.3‰, and B -31.7 ± 0.8 and -31.7 ± 0.3‰. Dashed and dash-dot-dashed lines indicate 95% confidence intervals for automated and manual treatments, respectively.

associated with oxygen isotope ratio sampling would be to introduce solenoids on either side of the flask to isolate the flask from the rest of the sampler system as has been done by Trolier et al. (1996). Overall though, a clear advantage to the sampler system described here is that any small variations in the absolute magnitude of an individual flask measurement did not affect the predicted Keeling plot intercept. However, using the sampler described here and an analytical measurement technique as described by Ribas-Carbo et al. (2002) would provide both absolute high precision measurements of individual air flask samples as well as that of the integrated Keeling plot intercept.

6. New field opportunities

The newly developed automated air sampling system described here provides a useful tool to sample isotopic compositions of atmospheric trace gases in the field with higher frequency. Such a sampling approach promises a greater capacity to improve our understanding of stable isotope patterns for various ecological studies, such as the interactions between the atmosphere and ecosystems (both natural and urban ecosystems) (e.g. Ometto et al., 2002), and the relationship between the metabolic activities of animals and diet (e.g. Ampulski and Boggs, 1977; Schoeller et al., 1984).

The use of this sampler makes it possible to more feasibly link eddy covariance and isoflux studies. To quantify the balance between carbon uptake, storage and losses within plant ecosystems for canopy carbon budget, one should consider simultaneous isotopic sampling with the eddy covariance measurements. The latter provides a useful means to measure the sum of the two one-way CO_2 fluxes as net ecosystem exchanges (NEE) during sufficient turbulent conditions. However, the eddy covariance technique fails when turbulent mixing is weak, often occurring during nighttime. While leaf-level photosynthesis processes are well understood and mechanistic photosynthesis models have been developed (Farquhar et al., 1980), the estimates of ecosystem respiration remain a challenge. Isotopic measurements of atmospheric CO_2 above and within plant canopies are very valuable in quantifying the production of different carbon sources. Bowling et al. (1999, 2001b) demonstrated that coupling of eddy covariance and carbon isotopic measurements could be used to partition the contribution of photosynthetic and respiratory fluxes. Yakir and Wang (1996) showed that such partitioning could be accomplished by simultaneous measurements of concentration and isotopic composition along a vertical profile above grassland ecosystems. Within forest ecosystems where the flux gradient method cannot be applied, Lagrangian inverse models (Lai et al., 2002) provided an alternative tool for estimating the nighttime ecosystem CO_2 fluxes and relative contributions

from different ecosystem components. Measurements of atmospheric CO_2 concentration and $\delta^{13}C$ at different canopy heights provide required model inputs for the inverse calculation (Raupach, 2001). What is needed most is more frequent $\delta^{13}C$ sampling of CO_2 within forest canopies. The automated air sampling system detailed here should suffice such demand even at remote locations.

Acknowledgements

This study was supported by the TCP Project # DE-FG03-00ER63012 from the US Department of Energy. The authors thank Diane Pataki for discussions on the statistical analyses, Craig Cook and Mike Lott for critical comments on design, and Meghann Hunter for graphical essentials. We also thank Valco Instruments Company Inc. for providing rotor material shavings for testing.

References

Ampulski, R.S., Boggs, R.W., 1977. A comparison between $^{14}CO_2$ and $^{13}CO_2$ measurements in the respired breath of rats fed sodium acetate. Biomed. Mass. Spectr. 4, 98–102.

Bakwin, P.S., Tans, P.P., White, J.W.C., Andres, R.J., 1998a. Determination of the isotopic ($^{13}C/^{12}C$) discrimination by terrestrial biology from a global network of observations. Global Biogeochem. Cycles 12, 555–562.

Bakwin, P.S., Tans, P.P., Hurst, D.F., Zhao, C.L., 1998b. Measurements of carbon dioxide on very tall towers: results of the NOAA/CMDL program. Tellus 50B, 401–415.

Bowling, D.R., Baldocchi, D.D., Monson, R.K., 1999. Dynamics of isotopic exchange of carbon dioxide in a Tennessee deciduous forest. Global Biogeochem. Cycles 13, 903–922.

Bowling, D.R., Cook, C.S., Ehleringer, J.R., 2001a. Technique to measuring CO_2 mixing ratio in small flasks with a bellows/IRGA system. Agric. For. Meteorol. 109, 61–65.

Bowling, D.R., Tans, P.P., Monson, R.K., 2001b. Partitioning net ecosystem carbon exchange with isotopic fluxes of CO_2. Global Change Biol. 7, 127–145.

Bowling, D.R., McDowell, N.G., Bond, B.V., Law, B.E., Ehleringer, J.R., 2002. ^{13}C content of ecosystem respiration is linked to precipitation and vapor pressure deficit. Oecologia 131, 113–124.

Buchmann, N., Ehleringer, J.R., 1998. CO_2 concentration profiles, and carbon and oxygen isotopes in C_3 and C_4 crop canopies. Agric. For. Meteorol. 89, 45–58.

Buchmann, N., Guehl, J.M., Barigah, T.S., Ehleringer, J.R., 1997. Interseasonal comparison of CO_2 concentrations, isotopic composition, and carbon dynamics in an Amazonian rainforest (French Guiana). Oecologia 110, 120–131.

Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On the isotopic composition of carbon in soil carbon dioxide. Geochim. Cosmochim. Acta 55, 3403–3405.

Conway, T.J., Tans, P.P., Waterman, L.S., Thoning, K.W., Kitzis, D.R., Masarie, K.A., Zhang, N., 1994. Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network. J. Geophys. Res. 99, 22831–22855.

Dixon, W.J., 1950. Analysis of extreme values. Ann. Math. Stat. 21, 488–506.

Ehleringer, J.R., Buchmann, N., Flanagan, L.B., 2000. Carbon isotope ratios in belowground carbon cycle processes. Ecol. Appl. 10, 412–422.

Ehleringer, J.R., Cook, C.S., 1998. Carbon and oxygen isotope ratios of ecosystem respiration along an Oregon conifer transect: preliminary observations based upon small-flask sampling. Tree Physiol. 18, 513–519.

Ehleringer, J.R., Field, C.B. (Eds.), 1993. Scaling Physiological Processes: Leaf to Globe. Academic Press, San Diego, 388 pp.

Ekblad, A., Högberg, P., 2001. Natural abundance of ^{13}C in CO_2 respired from forest soils reveals speed of link between tree photosynthesis and root respiration. Oecologia 127, 305–308.

Evans, J.R., Sharkey, T.D., Berry, J.A., Farquhar, G.D., 1986. Carbon isotope discrimination measured concurrently with gas exchange to investigate CO_2 diffusion in leaves of higher plants. Aust. J. Plant Physiol. 13, 281–292.

Farquhar, G.D., Von Caemmerer, S., Berry, J.A., 1980. A biochemical model of photosynthetic CO_2 assimilation in leaves of C_3 species. Planta 149, 78–90.

Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination and photosynthesis. Annu. Rev. Plant Physiol. Plant Mol. Biol. 40, 503–537.

Fessenden, J.E., Ehleringer, J.R., 2002. Age-related variations in $\delta^{13}C$ of ecosystem respiration across a coniferous forest chronosequence in the Pacific Northwest. Tree Physiol. 22, 159–167.

Flanagan, L.B., Phillips, S.L., Ehleringer, J.R., Lloyd, J., Farquhar, G.D., 1994. Effect of changes in leaf water oxygen isotopic composition on discrimination against $C^{18}O^{16}O$ during photosynthetic gas exchange. Aust. J. Plant Physiol. 21, 221–234.

Flanagan, L.B., Brooks, J.R., Varney, G.T., Berry, S.C., Ehleringer, J.R., 1996. Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO_2 in boreal forest ecosystems. Global Biogeochem. Cycles 10, 629–640.

Flanagan, L.B., Brooks, J.R., Varney, G.T., Ehleringer, J.R., 1997. Discrimination against $C^{18}O^{16}O$ during photosynthesis and the oxygen isotope ratio of respired CO_2 in boreal forest ecosystems. Global Biogeochem. Cycles 11, 83–98.

Flanagan, L.B., Ehleringer, J.R., 1998. Ecosystem-atmosphere CO_2 exchange: interpreting signals of change using stable isotope ratios. TREE 13, 10–14.

Flanagan, L.B., Kubien, D.S., Ehleringer, J.R., 1999. Spatial and temporal variation in the carbon and oxygen stable isotope ratio of respired CO_2 in a boreal forest ecosystem. Tellus 51B, 367–384.

Francey, R.J., Tans, P.P., 1987. Latitudinal variation in ^{18}O of atmospheric CO_2. Nature 327, 495–497.

Keeling, C.D., 1958. The concentration and isotopic abundance of atmospheric carbon dioxide in rural areas. Geochim. Cosmochim. Acta 24, 277–298.

Lai, C.-T., Katul, G., Butnor, J., Ellsworth, D.S., Oren, R., 2002. Modeling night time ecosystem respiration by a constrained source optimization method. Global Change Biol. 8, 124–141.

Lin, G., Ehleringer, J.R., 1997. Carbon isotopic fractionation does not occur during dark respiration in C_3 and C_4 plants. Plant Physiol. 114, 391–394.

Miller, J.B., Yakir, D., White, J.W.C., Tans, P.P., 1999. Measurement of $^{18}O/^{16}O$ in the soil atmosphere CO_2 flux. Global Biogeochem. Cycles 13, 761–774.

Nagy, K.A., 1980. CO_2 production in animals: analysis of potential errors in the doubly labeled water method. Am. J. Physiol. 238, R466–R473.

Ometto, J.P.H.B., Flanagan, L.B., Martinelli, L.A., Moreira, M.Z., Higuchi, N., Ehleringer, J.R., 2002. Carbon isotope discrimination in forest and pasture ecosystems of the Amazon Basin, Brazil. Global Biogeochem. Cycles, 16, 1109, DOI: 10.1029/2001GB001462.

Pataki, D.E., Ehleringer, J.R., Flanagan, L.B., Yakir, D., Bowling, D.R., Still, C.J., Buchmann, N., Kaplan, J.O., Berry, J.A., 2003. The application and interpretation of Keeling plots in terrestrial carbon cycle research. Global Biogeochem. Cycles 17, 1022, DOI: 10.1029/2001BG001850.

Raupach, M.R., 2001. Inferring biogeochemical sources and sinks from atmospheric concentrations: general considerations and applications in vegetation canopies, In: Schulze, E.-D., Heimann, M., Harrison, S., Holland, E., Lloyd, J., Prentice, I.C., Schimel, D. (Eds.), Global Biogeochemical Cycles in The Climate System. Academic Press, San Diego, pp. 41–59.

Revesz, K., Coplen, T.B., 1991. Caution on the use of Viton® or FETFE® O-rings in carbon dioxide sample containers for $\delta^{18}O$ analysis. Chem. Geol. 86, 259–261.

Ribas-Carbo, M., Still, C., Berry, J.A., 2002. Automated system for simultaneous analysis of $\delta^{13}C$, $\delta^{18}O$, and CO_2 concentrations in small air samples. Rapid Commun. Mass Spectr. 16, 339–345.

Schoeller, D.A., Brown, C., Nakamura, K., Nakagawa, A., Mazzeo, R.S., Brooks, G.A., Budinger, T.F., 1984. Influence of metabolic fuel on the $^{13}C/^{12}C$ ratio of breath CO_2. Biomed. Mass Spectr. 11, 557–561.

Trolier, M., White, J.W.C., Tans, P.P., Masarie, K.A., Gemery, P.A., 1996. Monitoring the isotopic composition of atmospheric CO_2: measurements from the NOAA Global Air Sampling Network. J. Geophys. Res. 101, 25897–25916.

Yakir, D., Wang, X.-F., 1996. Fluxes of CO_2 and water between terrestrial vegetation and the atmosphere estimated from isotope measurements. Nature 380, 515–517.